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Chapter 01

PERIODIC TABLE AND PERIODIC PROPERTIES

Student Learning Outcomes

After studying this chapter, students will be able to:

- Explain the arrangement of elements in the periodic table. **(Understanding)**
- Identify the positions of metals, non-metals and metalloids in the periodic table. **(Understanding)**
- Explain that the periodic table is arranged into four blocks associated with the four sublevels s, p, d, and f. **(Understanding)**
- Recognize that the period number (n) is the outer energy level that is occupied by electrons. **(Understanding)**
- Deduce the electronic configuration of an atom from the element's position on the periodic table, and vice versa (based on s, p, d and f subshells). **(Understanding)**
- State that the number of the principal energy level and the number of the valence electrons in an atom can be deduced from its position on the periodic table. **(Knowledge)**
- Deduce the nature, possible position in the Periodic Table and identity of unknown elements from given information about physical and chemical properties. **(Understanding)**
- Predict the characteristic properties of an element in a given group by using knowledge of chemical periodicity. **(Application)**
- Explain that vertical and horizontal trends in the periodic table exist for atomic radius, ionic radius, ionization energy, electron affinity and electronegativity. **(Understanding)**
- Explain the trends in the ionization energies and electron affinities of the **Group 1** and **Group 17** elements. **(Understanding)**
- Recognize that trends in metallic and non-metallic behaviour are due to the trends in valence electrons. **(Understanding)**
- Suggest the types of chemical bonding present in the chlorides and oxides from observations of their physical and chemical properties. **(Understanding)**
- Describe (including writing equations for) the reactions, if any, of the oxides (acidic and basic) with water (including the likely pHs of the solutions obtained). **(Understanding)**
- Explain with the help of equations for, the acid / base behaviour of the oxides and the hydroxides NaOH, $Mg(OH)_2$ including, where relevant, amphoteric behavior in reactions with acids and bases (sodium hydroxide only) **(Understanding)**
- Explain with equations for, the reactions of the chlorides with water including the likely pHs of the solutions obtained. **(Understanding)**
- Explain the variation in the oxidation number of the oxides and chlorides ($NaCl$; $MgCl_2$) in terms of their outer shell (valence shell) electrons. **(Understanding)**
- Write equations for the reactions of Na and Mg with oxygen, chlorine and water. **(Application)**
- Explain the variations and trends in terms of bonding and electronegativity. **(Understanding)**

Introduction

- The periodic table of elements is rightly referred as the "Symbol of Chemistry."
- It is a vital and thorough source of chemical knowledge and much more than just a simple chart.
- It would be difficult to explore and comprehend the enormous area of chemistry without its systematic categorization and arrangement of elements.
- One of the most important turning points in the history of science was the creation of the periodic table, which led to many important innovations.
- ***In modern periodic table, elements are arranged in tabular form in the current periodic table based on their atomic number, electrical configuration, and recurrent chemical characteristics.***
- Periodic table provides the foundation for comprehending **118** elements and their properties, making it a crucial tool in chemistry.
- The creation of the periodic table, provides a framework for researching the periodic behaviour.
- It is a significant accomplishment in scientific history.

HISTORICAL BACKGROUND

- Just three centuries ago only less than a dozen (12) elements were known to humanity.
- By 1700 A.D., only 12 elements-Gold, Silver, Copper, Iron, Lead, Tin, Mercury, Phosphorus, Sulphur, Carbon, Zinc, and Arsenic-were recognized.
- Over time, more elements were discovered, encouraging scientists to organize them systematically.

Rack Your Brain!

1. **Classification of elements in the modern periodic table is based on:**
   A) Law of Triads
   B) Law of Octaves
   C) Moseley's law
   D) Mendeleev's Periodic Law

(i) **Lavoisier:** Up to the end of 18th century, ***Antoine Lavoisier attempted to classify known elements as metals and nonmetals.***

(ii) **Döbereiner:** In 1829, ***Döbereiner grouped the elements into triads*** (a group of three) ***with similar properties*** in such a way that the atomic weight of the middle element was roughly the average of the other two. Examples of such triads include lithium, sodium, and potassium.

Element of Triads	Li	Na	K	Mean Value
Atomic masses of Triads	7	23	39	Atomic mass of Na = $\frac{7+39}{2} = 23$

(iii) **John Newlands:** English chemist John Newlands, in 1864, first time observed periodicity in the **62 known elements**, noticing that the properties of every eighth element were similar when arranged by the increasing order of their atomic masses.
He classified the elements into groups so that every eight elements resembled the first element in properties.



Dmitri Mendeleev arranged elements according to their atomic masses and his table was the first most notable effort in the classification of elements.

(iv) **Mendeleev:** In 1869, Russian chemist Dmitri Mendeleev is considered the **father of the Periodic Table.** He arranged **63 elements** into eight vertical columns by **increasing atomic mass**, aligning elements with similar properties into vertical groups.
The great success of Mendeleev's table was hidden in leaving gaps for undiscovered elements and predicting their atomic mass and properties, which proved accurate when these elements were practically found.

(v) **Luther Meyer:** In the same year 1869, Lother Meyer developed his famous curves by plotting a graph between the atomic weights and atomic volumes of elements. These curves also showed periodicity. These ***curves also showed periodic periodicity.***

Rack Your Brain!

2. What are the basis of arrangement of elements in Mendeleev's and Moseley's periodic tables?

(vi) **Moseley:** In 1913, Moseley ***determined the exact atomic numbers of known elements using X-ray emission.***

- He resolved flaws and discrepancies in Mendeleev's table by arranging the elements on the basis of atomic numbers instead of atomic masses.
- This significant breakthrough led Moseley to modify the Periodic Law.
- **Moseley or modern periodic law states that "the properties of elements are periodic functions of their atomic numbers".**

MODERN PERIODIC TABLE – MAIN FEATURES

The classification of elements in the modern periodic table helps in the easier understanding of their properties.

Main features of the modern periodic table:

(i) Presently, **118** elements are grouped in the table in ascending order of their respective atomic numbers.

(ii) There are seven **(07) horizontal rows called periods** and **eighteen (18) vertical columns called groups.** (In older versions of the table, there were eight (8) vertical groups were divided into two types of groups i.e., 08 A-Groups and 10 B-Groups.

(iii) In the periodic table, elements within the ***same group show similar chemical properties because they have the same number of valence electrons.*** However, they show a gradual change in physical properties from top to bottom in a group.

(iv) Elements in a period show a gradual change in properties moving from left to right in periods.

Note: Other than groups and periods in the periodic table, there are different ways of grouping the elements into various blocks, families and categories in order to enhance understanding.

METALS, NON-METALS AND METALLOIDS

- The elements can be broadly classified into:
  (i) Metals **(ii)** Nonmetals **(iii)** Metalloids
  (i) Metals: Elements which tend to lose electrons to form positive ions.
  Examples: Iron, copper, gold and silver etc.
  (ii) Non-metals: Elements which tend to gain electrons to form negative ions.
  Examples: Chlorine, Sulphur, phosphorous etc.
  (iii) Metalloids: Separates the metals and nonmetals on a periodic table. The metalloids exhibit some properties of metals and some of non-metals.
- Mostly periodic tables have a **"stair-step line"** on the table to help in identifying the elements. The line begins at boron (B) and extends down to polonium (Po) including Si, Ge, As, Sb and Te.

NOTE:

- *Elements to the left of the line are considered metals.*
- *Elements just to the right of the line exhibit properties of both metals and non-metals and are termed as metalloids or semimetals.*
- *Elements to the far right of the periodic table are non-metals. The exception is hydrogen, the first element on the periodic table.*

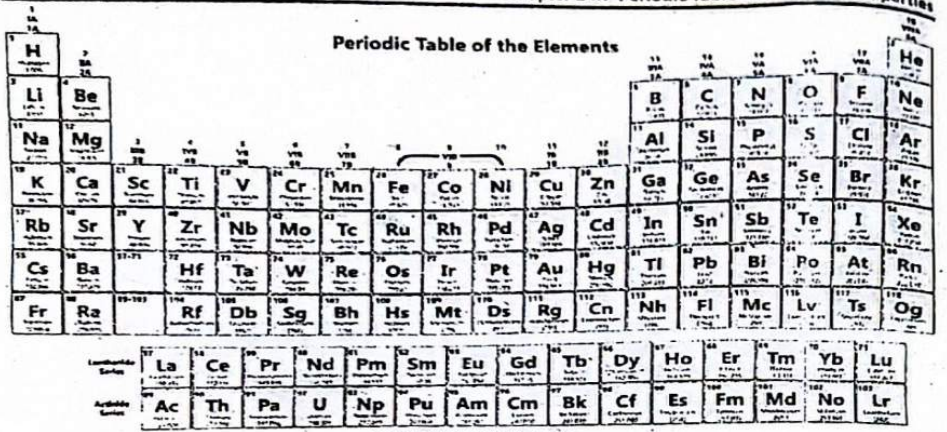


Fig: Modern periodic table

BLOCKS IN PERIODIC TABLE

- The elements in the periodic table can be classified into four blocks based on the subshells containing their valence electrons.
  - s-block
  - p-block
  - d-block
  - f-block

For example:

- The valence electrons of elements in the first two groups are in the "*s*" subshells, placing these elements in the s-block.

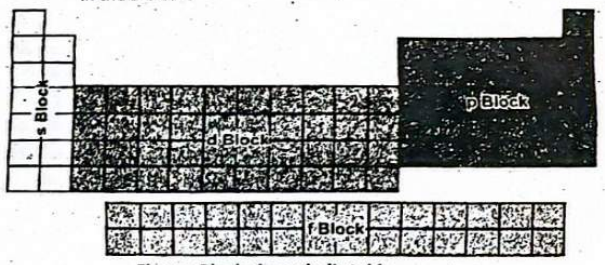


Figure: Blocks in periodic table

- In d-block elements, the last electrons enters in d-orbital of penultimate (inner to the outermost) shell i.e. it goes to (n –1) d orbital.
- In f-block elements, last electron enters in f-orbital of antipenultimate (inner to penultimate) shell.

- ***Transition elements belong to the d-block***, and the elements in the two series at the bottom of the table (known as ***Lanthanides and Actinides) are categorized as f-block elements.***
- The remaining elements in groups **13 to 18, including the inert gases in the last group (18),** belong to the **p-block.**

Note: Knowing the block to which an element belongs provides valuable information about its characteristics, chemical reactivity, oxidation states and other properties such as electronegativity and ionization energy, electron filling, etc.

So there are four blocks in the periodic table:

(i) *s*-block **(ii) p-block** **(iii) d-block** **(iv) f-block**

Rack Your Brain!

3. Non-metals are present in which block of periodic table?
   A) s-block B) p-block
   C) d-block D) f-block

FAMILIES IN PERIODIC TABLE

Elements may be categorized according to element families. An element family is a set of elements sharing common properties. There are **six famous families of elements in the periodic table:**

(i) Alkali metals (Li, Na, K, Rb, Cs, Fr) → **Group-IA**
(ii) Alkaline earth metals (Be,Mg,Ca,Ba,Ra) → **Group-IIA**
(iii) Transition metals (Sc,Ti,V,Cr,Mn,Fe,Co,Ni,Cu,Zn) → **3d-Series or 1st Transition Series**
(iv) Chalcogens (O, S, Se, Te, Po) → **Group-VIA**
(v) Halogens (F, Cl, Br, I, At, Ts) → **Group-VIIA**
(vi) Noble gases (He, Ne, Ar, Kr, Xe, Rn, Og) → **Group-VIIIA**

Rack Your Brain!

4. d and f-Block elements are called transition elements. Explain.

(i) Alkali Metals (ns^1)

The elements in the group 1 of the periodic table are known as alkali metals because they produce alkalis when they react with water.

- Sodium **(Na)** and potassium **(K)** are notable examples of these elements.
- Alkali metals are characterized by:
  - One valence electron
  - Low densities
  - Relatively low melting points
  - Low ionization energies
  - Most reactive metals.

(ii) Alkaline Earth Metals (ns^2)

The group 2 elements are metals primarily found in the earth and form alkalis that is why they are referred to as alkaline earth metals.

Examples: Magnesium (Mg), Beryllium (Be), Calcium (Ca) etc.

- These elements have two electrons in their valence shell, making them divalent.
- They are metallic solids that are harder and denser than alkali metals.
- They are easily oxidized, with high thermal and electrical conductivities.

iii) Transition Elements (d & f-block elements)

The transition metals make up the largest family of elements in the middle of periodic table. They include four series of d-block elements $(n-1)\,d^{1-10}\,ns^{1-2}$***, as well as the lanthanides and actinides (f-block elements)*** $(n-2)\,f^{1-14}\,(n-1)\,d^{0-1}\,ns^2$ ***found in the two rows below.***

- They exhibit high thermal and electrical conductivities, high melting points, high density, and variable oxidation states.
- They mostly from coloured compounds.

iv) Chalcogens ($ns^2\,np^4$)

- The group 16 elements are called **Chalcogens** (Ore Forming Compounds) because most ores of copper (Greek chalkos) are oxides or sulfides.
- In this group, oxygen & Sulphur are non-metals, **Se, Te, Po are metalloids and Rivernorium is a metal.**

v) Halogens ($ns^2\,np^5$)

Elements in group 17, known as halogens, are non-metallic. The term "halogen" means "salt-former" because these elements easily react with alkali metals and alkaline earth metals to form stable halide salts.

- Examples: Fluorine, Chlorine, Bromine and Iodine.
- HALOGENS are highly reactive non-metals with high electron affinities.
- Halogens can easily accept one electron to complete their outermost shell.

vi) Noble Gases ($ns^2\,np^6$)

The noble gases are a group of unreactive elements present at the extreme right of the periodic table in Group 18.

- **Examples:** Helium, Neon, Krypton, Argon etc.
- Due to their stable electron configuration (complete outermost shell), they are almost entirely unreactive under normal conditions and rarely form compounds with other elements.
- These elements are monoatomic in nature.

KEEP IN MIND: *Although, noble gases are unreactive, however they have some compounds e.g., compounds of xenon such as xenon hexafluoroplatinate ($XePtF_6$). Due to the formation of some compounds, the word inert gases was changed to noble gases.*

QUICK CHECK 1.1

a) Why are the elements in Groups 1 and 2 known as s-block elements?
Ans. As the valence electrons of group 1 and 2 are in the s-subshell so they are called s-block elements.
Group 1: ns^1 Group 2: ns^2
b) Name the elements in the chalcogen family. Give their two characteristics.
Ans. Members of Chalcogens:
O, S, Se, Te, Po, Lv (Livermorimum).
Two characteristics of Chalcogens:
(i) They are ore-forming elements because many metal ores contain them in the form of oxides or sulphides.
(ii) Chalcogens have six valence electrons and contain non-metals, metalloids and metals.

PERIODIC ARRANGEMENT AND ELECTRONIC CONFIGURATION

Understanding the periodic arrangement of elements in the periodic table gives valuable insight into their physical properties, such as their physical states and atomic radii, as well as their electronic structures and chemical reactivity.

- **Period Number:** ***The period number indicates the principal quantum number (n), representing the number of electron shells surrounding the nucleus.***
  For example, an element X in the 3rd period has three electron shells, with its valence electrons located in the 3rd shell. The specific subshell where the valence electrons are found, depends on the element's block (azimuthal quantum number). If an element X in the 3rd period is in the s-block, its valence electrons are in the 3 s subshell.
- **Group Number:** ***The group number indicates the number of valence electrons;***
  For instance, an element X in the 3rd period and group 2 has two valence electrons in its outermost shell. Thus, the element Z in the 3rd period and group 2 (s-block) has two valence electrons in the 3 s subshell, which means that X would be Magnesium (Mg).
- **Example to relate both period number and group number:** Example to relate period number and group number with electronic configuration and position of element in the period table.

X belongs to group 13 and period 3

In this example, the element X belongs to group 13 of periodic table so it has 3 valence electrons; and it is found in period 3 so it has three shells around its nucleus.
It means that the 3 valence electron are in the 3rd shell. The configuration will be:

$1s^2$ $2s^2 2p^6$ $3s^2 3p^1$
↓ ↓ ↓
1st shell 2nd shell 3rd shell

Understanding the periodic arrangement of elements provides an explanation of an element's electronic configuration, which is essential for understanding its chemical properties and behaviour.

QUICK CHECK 1.2

a) X belongs to group 14 and period 2
i. Write electronic configuration of the element X.
Ans. $6X_{(Ground\ State)} = 1s^2, 2s^2, 2p^2$ and period number 2, it is carbon.
ii. Identify block of the element. Identify this element from periodic table.
Ans. Group 14 (Carbon Group).
b) Predict the electronic configuration of an element that is in period 4 and group 17 without consulting the periodic table?
Ans. Group 17 (Halogens), Period 4, it means it is Bromine (Br)

PERIODICTY OF PROPERTIES

Modern Periodic Law:

- The Modern Periodic Law states: ***"The physical and chemical properties of elements are periodic functions of their atomic numbers."***
- The atomic number corresponds to the number of protons in an atom.
- This law is the "cornerstone" of the periodic table, indicating that elements with similar properties appear at certain intervals.
- For example, when elements are arranged by increasing atomic numbers, sodium, potassium, and cesium exhibit many physical and chemical characteristics similar to lithium, as they are all placed in the same group of the table.
- However, due to the gradual increase in the number of protons in the nucleus and the addition of new electron shells, the physical and chemical properties of elements vary systematically within a group and a period.

Atomic Radius

The atomic radius is a measure of the size of an atom. It is half of the distance between two identical atoms bonded together. The atomic radius can vary depending on the type of bond.

OR

It is half of the distance between nuclei of two identical atoms bonded together, whether by covalent, metallic or van der Waals force, depending on the state of the atom.

For example, the radius can be different in a covalent bond compared to an ionic bond.
The atomic radius is typically measured in picometers (pm) or Angstroms (Å).

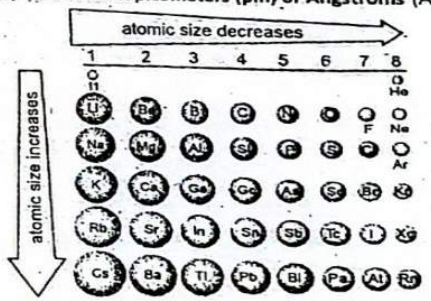


Fig: Variation in atomic radius across periods and down the groups

Periodic trends in atomic radius:

- The factors affecting the atomic radius are:
  (i) atomic number (ii) effective nuclear charge (iii) shielding effect of inner electrons
- **In a Period:** Generally, atomic radius decreases across a period (from left to right) in the periodic table due to increasing nuclear charge, which pulls the electron cloud closer.
- **Down the Group:** The atomic radius increases down a group (from top to bottom) because additional electron shells are added, so more shielding makes the atom larger despite the increase in nuclear charge (which is outweighed).

Rack Your Brain!
5. Which statement is correct?
A) Na atom is smaller than Na^+
B) Na atom is larger than K atom
C) F atom is smaller than F^-
D) F atom is larger than F^-

Ionic Radius

- The ionic radius is a measure of the size of an ion in a crystal lattice.
- It is typically defined as "the distance from the nucleus of an ion to the outermost electron shell"

- It is measured in picometers (pm) or angstroms (Å).
- When an atom loses one or more electrons to become a positive ion, it generally becomes smaller than the neutral atom. This is because the loss of electrons reduces electronic repulsion and allows the remaining electrons to be pulled closer to the nucleus.
- Contrarily when an atom gains one or more electrons to become an anion, it generally becomes larger than the neutral atom. This is because the addition of electrons increases electronic repulsion, as a result the nuclear pull on electrons decreases and the electron cloud expands.

Rack Your Brain!
6. Why the size of cation is always smaller than its parent atom?

In an isoelectronic ions, order of cationic radii.
$Na^+ > Mg^{2+} > Al^{3+}$

- **Along a Period:** As we move across a period from left to right, the ionic radius of cations decreases.
- **Reason:** It is due to the increasing nuclear charge which pulls the electrons closer. For anions, the ionic radius also decreases across a period because the increasing nuclear charge also pulls the electrons closer to the nucleus.
- **Down the Group:** Both cations and anions increase in size as we move down a group.
- **Reason:** As the principal quantum number (n) increases, there is an increase in the number of electron shells. As a result, the distance between the nucleus and the outermost electrons becomes larger, outweighing the effect of increased nuclear charge. The additional electron shells make the ions larger.

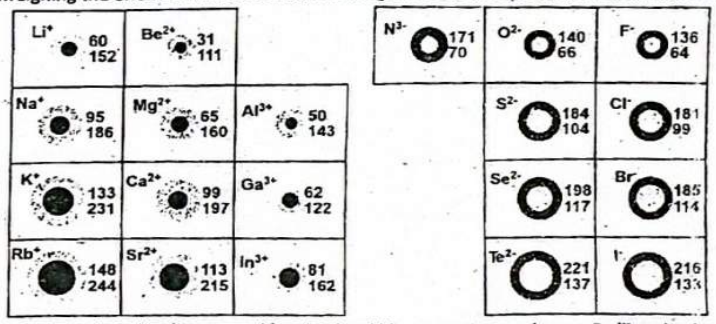


Fig.: Variation in Ionic Radius (Ions are coloured red and blue; parent atoms brown. Radii are in picometers)

QUICK CHECK 1.3

a) Which factors affect atomic and ionic radii?

Ans. Factors
(1) Atomic number (2) Effective nuclear change, shielding effect

b) Using your knowledge of Period 3 elements, predict and explain the relative sizes of:

i. the atomic radii of lithium and fluorine

Ans. Li > F: In a period (Li and F are in period number 2) atomic radii decrease from left to right i.e. from Li to F.

ii. a lithium atom and its ion, Li^+

Ans. Li > Li^+: After the loss of one electron from Li, now Li^+ has now 3 protons but 2 electrons so control of nucleus on remaining electron increases.

$$\underset{(152pm)}{Li} \longrightarrow \underset{(60pm)}{Li^+} + 1e^-$$

iii. an oxygen atom and its ion, O^{2-}

Ans. $O^{2-} > O$

The size of O^{2-} (oxide ions) is greater than its neutral atom.

$$O_{(g)} + 2e^- \longrightarrow O^{2-}$$
8P 8P
8e 10e (two extra electrons)

These extra electrons increase electron-electron repulsion in the atoms outer shell causing the electron cloud to expand. Moreover, the nuclear charge decreases.

iv. a nitride ion, N^{3-}, and a fluoride ion, F^-.

Ans. $N^{-3} > F^-$

N^{-3} and F^- have 10 electrons each and thus are iso-electronic.

Reasons:

(a) Lower Nuclear change of N^{-3}:
N^{-3} has 10 electrons and 7 protons so it has lower nuclear charge as compared to F^- having 9 protons and 10 electrons.

(b) More electron-electron repulsion in N^{-3}:
N^{-3} has gained three electrons thus the electron-electron repulsion increases causing electron cloud to expand more as compared to F^-.

Ionization Energy

➤ **1st ionization energy:**

"The energy needed to remove one electron from each atom in one mole of atoms of the element in the gaseous state to form one mole of gaseous 1^+ ions is known as 1st ionization energy (ΔH_{I_1})."

$$Na_{(g)} \longrightarrow Na^+_{(g)} + 1e^- \qquad \Delta H_{I_1} = +494 \text{ kJ mol}^{-1}$$

$$Ca_{(g)} \longrightarrow Ca^+_{(g)} + 1e^- \qquad \Delta H_{I_1} = +590 \text{ kJ mol}^{-1}$$

➤ **2nd Ionization energy:**

"The minimum amount of energy required to remove a second electron from the valence shell of a positive ion is called second ionization energy."

If a second electron is removed from each ion in a mole of gaseous 1+ ions, we call it the 2nd ionization energy, ΔH_{I_2}. Again, using calcium as an example:

$$Ca^+_{(g)} \longrightarrow Ca^{2+}_{(g)} + e^- \qquad \Delta H_{I_2} = +1150 \text{ kJ mol}^{-1}$$

➤ **3rd Ionization energy:**

"The minimum amount of energy required to remove third electron from the valence shell of a dipositive ion is called third ionization energy."

Removal of a third electron from each ion in a mole of gaseous 2 + ions is corresponding to the 3rd ionization energy. Again, using calcium as an example:

$$Ca^{2+}_{(g)} \longrightarrow Ca^{3+}_{(g)} + e^- \qquad \Delta H_{I_3} = +4940 \text{ kJ mol}^{-1}$$

An element can have several ionization energies; the exact number corresponds to its atomic number.

Exercise L.Q.6

Q. Describe the factors affecting and periodic trends of ionization energy.

➤ **Factors affecting the Ionization energy**

The magnitude of the ionization energy of an element depends upon the following factors:

i) Nuclear charge

Greater the effective nuclear charge, greater is the electrostatic force of attraction, more difficult is the removal of an electron from the atom. For this reason, ionization energy increases with an increase in the effective nuclear charge.

Effective nuclear charge is the net effect of nuclear force and screening of electrons and infact is responsible for controlling ionization energy.

ii) Size of the atom or Ion

In bigger atoms force of attraction between the nucleus and the outermost electrons is weaker. Therefore, the ionization energy decreases as the size of the atom increases and vice-versa.

iii) Electronic arrangement

It is observed half-filled and completely-filled orbitals are found to be more stable. Therefore, the ionization energy is higher when an electron is to be removed from a fulfilled or half-filled-shells.

(a) Noble gases have highest ionization energies in their respective periods. It is due to highly stable fully-filled shells (ns^2np^6).

(b) Exception: Ionization energy of N > O

Oxygen has lower ionization energy than nitrogen. The electronic configuration of oxygen and nitrogen are:

$_7N = 1s^2\ 2s^0\ 2p_x^1\ 2p_y^1\ 2p_z^1 \quad \Delta H_{i_1} = 1403\ kJ\ mol^{-1}$

$_8O = 1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1 \quad \Delta H_{i_1} = 1365\ kJ\ mol^{-1}$

Reason: Nitrogen has one unit less positive charge in its nucleus than oxygen, but due to the extra-stability of the half-filled sub-shell of nitrogen it is difficult to remove an electron from N atom.

iv) Shielding (Screening) Effect

Greater the shielding, easier it is to remove the valence electrons from an atom. Larger the number of inner electrons, greater is the screening effect, therefore, lower is the ionization energy.

v) Spin-Pair Repulsion

When electrons are spin-paired in the same orbital, the repulsion between them can lead to a slightly lower ionization energy compared to removing an unpaired electron. This is because the paired electrons experience increased repulsion, making it slightly easier to remove one of the paired electrons.

Oxygen (O) has two spin-paired electrons in its 2 p orbital. The ionization energy to remove one of these paired electrons is relatively lower due to the increased repulsion between the paired electrons. Nitrogen (N) has three unpaired electrons in its 2 p orbitals. Removing one of these unpaired electrons requires more energy due to the absence of spin pairing repulsion.

➢ **Periodic Trends in Ionization Energy**

- **Down the Group:** Going down in a group, the nuclear charge increases but as the size of the atom and the number of electrons causing the shielding effect also increases therefore ionization energy decreases from top to bottom.
- In Group I, the ionization energies decrease in the following order: Li > Na > K > Rb > Cs .
- For example, the 6s valence electron of Cs is farther from the nucleus and thus easier to remove compared to the 5s valence electron of Rb.

Rack Your Brain!

7. Ionization energy of calcium is lower than _____ element.
A) Strontium B) Magnesium
C) Barium D) Sodium

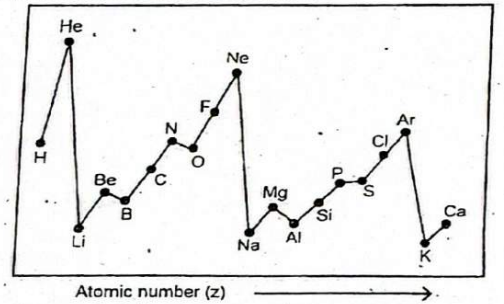


Figure: Variation in Ionization Energies across periods

Interesting Information!

Helium (He) has the highest first ionization energy among all elements in the periodic table.

- **Along a Period:** As we move from left to right across a period, no. of shells remains unchanged while the effective nuclear charge increases, making it more difficult to remove an electron. Although the number of electrons also increases across a period, the shielding effect within the same shell is same so not considered. Consequently, the ionization energy increases. So, the ionization energy increases.
- The trend of ionization energies of period (1-3) is shown in Figure. The figure shows reveals that noble gases have the highest values of ionization energy due to complete outermost shell in them, the removal of electron is extremely difficult, whereas alkali metals have lowest values of ionization energy.

QUICK CHECK 1.4

a) Explain with reasoning following facts about ionization energy:

i. 1st Ionization energy of Boron is lesser than Beryllium.

Ans. Electronic Configuration of

$_5B$: $1s^2, 2s^2, 2p^1$ (p-orbital is partially filled)

$_4Be$: $1s^2, 2s^2$ (s-orbital is complete)

I.E. of Be > B

Be has greater effective nuclear charge due to its stable $2s^2$ electronic configuration and smaller size making it harder to remove an electron. Boron has lesser ionization energy due to a single electron in 2p-orbital and removal of 2p electron is easier due to higher energy level and shielding effect.

ii. 1st ionization energy of Aluminum is lower than Magnesium.

Ans. Electronic configuration of

$_{12}Mg$: $1s^2, 2s^2, 2p^6, 3s^2$

$_{13}Al$: $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

I.E. of Al < Mg

Mg has a stable $3s^2$ electronic configuration making it harder to remove an electron. 3p electron in Al is shielded by the 3s electrons making it easier to remove.

b) What trend is observed in ionization energy as you go down group 3? Give reason.

Ans. Comparison of Electron Affinity of N and P:

Electron affinity of N = –7 kJ/mol.

Electron affinity of P = –72.0 kJ/mol

Nitrogen has half-filled 2p sub-shells ($2p^3$) and it is relatively more stable. Phosphorus has also half-filled 3p subshells ($3p^3$) but increased atomic size and shielding make it slightly easier for it to accept and electron than N. So electron affinity of P) N.

Electron Affinity (H°_{EA})

➢ **First Electron Affinity:**

- The first electron affinity, (ΔH°_{ea1}) is the enthalpy change involved when 1 mole of electrons is added to 1 mole of gaseous atoms to form 1 mole of gaseous uni-negative ions under standard conditions. Electron affinity of chlorine atom:

$$Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)} \qquad \Delta H^\circ_{EA1} = -348.8\ kJ\ mol^{-1}$$

Rack Your Brain!

8. Which Group 17 element has the most negative electron affinity?
A) Fluorine B) Chlorine
C) Bromine D) Iodine

- This is amount of energy released when 6.02×10^{23} atoms of chlorine in the gaseous state are converted into $Cl^-_{(g)}$ ions.
- Since, energy is released, so first electron affinity carries negative sign.

➢ **Second Electron Affinity:**

- The second electron affinity, ΔH°_{ea2} is the amount of energy required to add electrons to 1 mole of uni-negative gaseous ions to form 1 mole of gaseous 2-ions under standard conditions.
- **Example: 1st and 2nd Electron Affinities Oxygen:** when first electron is added to a neutral oxygen atom, 141 kJ mol^{-1} energy is released.

$$O_{(g)} + e^- \longrightarrow O^-_{(g)} \qquad \Delta H^\circ_{EA1} = -141\ kJ\ mol^{-1}$$

- But 798 kJ mol^{-1} of energy is absorbed on adding second electron to a uni-negative (O^-) ion.

$$O^-_{(g)} + e^- \longrightarrow O^{2-}_{(g)} \qquad \Delta H^\circ_{EA2} = +798\ kJ\ mol^{-1}$$

- The net enthalpy change for the formation of the oxide ion (O^{2-}) can be calculated by adding the first and second electron affinities.

$$O_{(g)} + 2e^- \longrightarrow O^{2-}_{(g)} \qquad \Delta H^\circ_{EA1} + \Delta H^\circ_{EA2} = (-141) + (+798) = +657\ kJ\ mol^{-1}$$

(Exercise Q.5)

Q. Describe the factors affecting and periodic trends of electron affinity.

➢ **Factors affecting electron affinity**

Important factors affecting the magnitude of electron affinity values of elements are as follows:

i) Size of atom

For small sized atoms the attraction of the nucleus for the incoming electron is stronger. Thus, smaller is the size of the atom, greater is its electron affinity.

ii) Nuclear charge

Greater the magnitude of nuclear charge of an element stronger is the attraction of its nucleus for the incoming electron. Thus, with the increase in the magnitude of nuclear charge, electron affinity also increases.

iii) Electronic configuration of atom

The electron affinity is low when the electron is added to a half filled sub-shell than that for partially filled one.

- **Half-filled p-subshells:** Electron affinity values of ' N ' and ' P ' group-15 (V-A), atoms are very low. This is because of the presence of half-filled 'np' orbitals in their valence shell $\left(N=2s^2 2p^3, P=3s^2 3p^3\right)$. These half-filled p-subshells, being very stable, have very little tendency to accept any extra electron to be added to them.
- **Noble gases:** Noble gases group-18 (VIII-A) have stable ns^2np^6 configuration and hence the atoms of these gases, do not accept any extra electron, this is evident from their positive 1st electron affinities.

➢ **Periodic trends in electron affinity**

- **Down the Group:** As the atomic size increases down the group, the larger electron cloud causes the incoming electron to experience less attraction from the nucleus. Consequently, electron affinity generally decreases down the group. This trend is observed in the halogens ($At < I < Br < F < C\ell$).
- **Along a Period:** Generally, electron affinities become more negative as we move from left to right period. This is firstly due to increase in the nuclear charge, which attracts additional electrons more strongly and secondly due to decreasing atomic radius.

Table: Electron Affinities (KJ/Mol) for Group 1 and Group 17

ELEMENT	ELECTRON AFFINITY (kJ/Mol)	ELEMENT	ELECTRON AFFINITY (kJ/Mol)
Fluorine	–328.0	Lithium	–60.0
Chlorine	–349.0	Sodium	–53.0
Bromine	–324.0	Potassium	–48.0
Iodine	–295.0	Rubidium	–47.0
Astatine	–270.1	Cesium	–46.0

QUICK CHECK 1.5

Explain with reasoning following facts about electron affinity:

a) 1st electron affinity of Oxygen is –141KJ / mol but 2nd electron affinity is +844.0KJ / mol.

Ans. Usually the electronegative elements release energy when first electron is added into them. But when a second electron is added in a uni-negative ion, the incoming electron is repelled by the already present – ive ion (charge). In order to overcome this repulsion, energy is absorbed during the process. Thus the formation of a di-negative ion is an endothermic process and its E.A. is shown with positive sign.

$$O_{(g)} + e^- \longrightarrow O^{-1}_{(g)} \qquad E.A_1 = -141 \text{ kJ mol}^{-1}$$

$$O^{-1}_{(g)} + e^- \longrightarrow O^{-2}_{(g)} \qquad E.A_2 = +780 \text{ kJ mol}^{-1}$$

b) Which of nitrogen and phosphorus has the higher electron affinity? Justify with reason.

Ans. The electron affinities of both Nitrogen and Phosphorus are low with value –7 kJ/mol (or zero E.A.) and – 72 kJ/mol respectively. So, phosphorus has a more negative electron affinity or in other words greater tendency to accept electrons.

c) F has lower electron affinity than Cℓ although its size is smaller. Explain why?

Ans. Electron affinity of

$$\underset{-322\ KJmol^{-1}}{F} > \underset{-349\ KJmol^{-1}}{C\ell}$$

Explanation:

Fluorine has unexpectedly lower electron affinity than Chlorine. It may be due to small size of Fluorine atom and its thick electronic cloud. The addition of an extra electron produces high electron density which increases strong electron-electron repulsion. The repulsive forces between electrons result in low electron affinity.

d) Why noble gases (group–18) have positive 1st electron affinities? Explain in terms of electronic configuration.

Ans. **Noble gases** have positive electron affinity because their outermost shells are completely filled (e.g., Ne: $1s^2\ 2s^2\ 2p^6$) Adding an extra electron forces it into a higher energy level (new shell), which is unfavorable. This process requires energy, so electron affinity is positive (endothermic), unlike most elements where it is negative.

Electronegativity

Electronegativity is the power of an atom to attract shared pair of electrons toward itself in a molecule Linus Pauling, an American chemist, developed a scale of dimensionless electronegativity values, which range from just below one for alkali metals to a maximum of four for fluorine. Higher electronegativity values signify a stronger attraction for electrons compared to lower values.

Did You Know?

Linus Pauling is the only person to have received two unshared Nobel Prizes, one for chemistry in 1954 for his work on the nature of chemical bond and one for peace in 1962 for his opposition to weapons of mass destruction.

Rack Your Mind!

9. Which element shows the most non-metallic behavior? (Understanding)
A) Lithium B) Magnesium
C) Sulfur D) Fluorine

➢ **Factors Affecting Electronegativity**

i) Atomic size

A larger atomic size will result in a lower value of electronegativity. This is because electrons being far away from the nucleus will experience a weaker force of attraction. For example, the electronegativities of halogens in group 17 are in the order:

$$F > C\ell > Br > I$$

ii) Effective nuclear Charge

A higher value of the effective nuclear charge will result in a greater value of electronegativity, because an increase in nuclear charge causes greater attraction to the bonded electrons. This is why the electronegativity in a period increases from left to right. The electronegativity of Li in period 2 is 1.0 and F has a value of 4.0.

➢ **Periodic Trends in Electronegativity**

When we move from left to right along the period, the electronegativity increases this is due to increasing nuclear charge and decreeing size. In the groups, it decreases from top to bottom this is due to the increase in size due to the addition of shells and increasing shielding effect. For example, in the halogen group, the electronegativity value decreases from fluorine (4.0) to iodine (2.5) (as shown in a part of the periodic table in Fig).

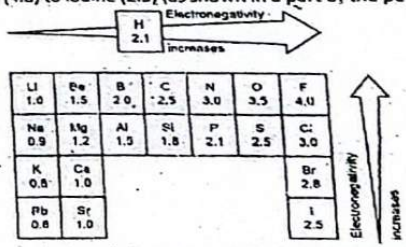


Figure: Variation of electronegativity in groups and periods

Generally, metals being on the left side of the periodic table, possess lower electronegativity values than those of non-metals. Hence, metals are electropositive and non-metals are electronegative, relatively. Figure provides a summary of all the variation trends in various physical properties of elements in the periodic table.

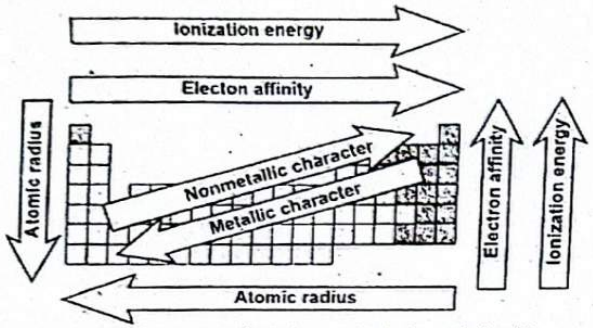


Figure: Trends in various physical properties in the periodic table

➢ Variation in Metallic Character

- The ***metallic character of elements is typically their tendency to lose electrons.***
- It is observed that the elements on the left side of the periodic table have a greater tendency to lose their outermost electrons to achieve noble gas configuration.
- In contrast, elements on the right side of the table tend to gain electrons.
- Thus, elements on the left side of the periodic table are metals that form positive ions. while elements on the right side, particularly in the right corner, are nonmetals that form negative ions.
- Thus the metallic character of an element largely depends on its valence shell electronic configuration.

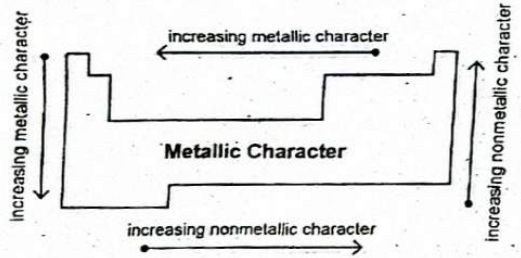


Figure: General trends for the metallic character of elements

- As a result, the metallic character of the elements decreases.
- In other words, the increase in nuclear charge pulls the electron cloud closer to the nucleus, making it more difficult for the atom to lose electrons and thereby decreasing across the period, the nuclear charge increases while the at size decreases, which results in stronger attraction to the valence electrons making its difficult. Therefore, metallic character (m.c) decreases from left to right. Its metallic character. Thus, metallic character decreases across a period from left to right.
- On the other hand, metallic character increases as one moves down in a group of the periodic table. This is due to the increases in at size and the shielding effect which reduce the nuclear attraction on the valence electrons. The increase in metallic character (ease of losing electron) makes the element more reactive.
- **Example:** Cesium is far more reactive and electropositive than sodium or lithium.

☑ QUICK CHECK 1.6

a) Illustrate how does the metallic character vary in group 14.

Ans. In Group 14 (Carbon group) of the periodic table, metallic character increases, down the group.

C = Non-metal
Si = Metalloid
Ge = Metalloid
Sn = Metal
Pb = Metal

Reason: As the atomic size increases and ionization energy decreases, making to easier for atoms to lose electrons. Tendency to lose electrons is one of the key trait of metallic character.

b) Identify semi metals in groups 14, 15 and 16. Why they are semi metals?

Ans. Group 14 = Si and Ge
Group 15 = As and Sb
Group 16 = Te and Po
Semi-metals (Metalloids) have intermediate properties between metals and non-metals.

REACTIONS OF Na AND Mg WITH WATER, OXYGEN AND CHLORINE

Exercise 1.Q.3

Q. Write equations for the reactions of Na and Mg with oxygen, chlorine, and water. Compare the reactivity of both elements with these in terms of metallic character.

➲ With water

Sodium is more reactive than magnesium towards water. Na reacts vigorously with water to form sodium hydroxide and hydrogen while Mg reacts more slowly in forming magnesium hydroxide and hydrogen. However magnesium reacts with steam more vigorously to make magnesium oxide and hydrogen gas.

$$2Na_{(s)} + 2H_2O_{(\ell)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$

$$Mg_{(s)} + 2H_2O_{(\ell)} \longrightarrow Mg(OH)_{2(aq)} + H_{2(g)}$$

$$Mg_{(s)} + 2H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}$$



Magnesium powder burns very rapidly with an intense white flame. This has led to its use in fireworks and S.O.S. flares

➲ With Oxygen

Sodium burns in oxygen with a golden yellow flame to produce a white solid mixture of sodium oxide and sodium peroxide. Sodium is kept under kerosene oil to prevent its reaction with air. It reacts vigorously with oxygen in open air to form peroxide.

$$2Na_{(s)} + O_{2(g)} \xrightarrow[\text{Supplies of Oxygen}]{\text{Abundant}} \underset{\text{(Pale Yellow)}}{Na_2O_{2(s)}}$$

Under special conditions like limited O_2 or high temperature, sodium oxide is formed.

$$4Na_{(s)} + O_{2(g)} \longrightarrow 2Na_2O_{(s)}$$

Magnesium burns in oxygen with an intense white flame to give white solid magnesium oxide.

$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$$

With Chlorine

Chlorine reacts with both metals to give soluble salts. It reacts exothermically with sodium, golden yellow flame is seen and white solid, sodium chloride is formed. Magnesium also reacts with chlorine to give white solid, magnesium chloride.

$$2Na_{(s)} + C\ell_{2(g)} \longrightarrow 2NaC\ell_{(s)}$$

Rock Your Brain!
10. Write down the Reactions of Na with water, oxygen and chlorine.

Magnesium also reacts with chlorine to give white solid, magnesium chloride.

$$Mg_{(s)} + C\ell_{2(g)} \longrightarrow MgC\ell_{2(s)}$$

QUICK CHECK 1.7

(a) What is the nature of oxides and hydroxides of Na and Mg?

Ans. The oxides and hydroxide of sodium (Na) and Magnesium (Mg) are basic in water.

Sodium (Group IA-Alkali metal)

- **Oxide: Na_2O**

$$Na_2O + H_2O \longrightarrow 2NaOH$$

Na_2O reacts strongly with water to form basic oxide.

- **Hydroxide: NaOH**

NaOH is strong base and it completely dissociates as follows:

$$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

pH of solution when dissolved in water = 13 – 14

Magnesium (Group IIA-Alkaline Earth Metal)

- **Oxide: MgO**

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

MgO is basic.

$$Mg(OH)_2 \longrightarrow MgO + H_2O$$

$Mg(OH)_2$ is sparingly soluble in water pH of solution when dissolved in water = 10

(b) What could you predict about the reactivity of Ca, a group 2 element, when reacted with water and oxygen?

Ans. Reaction of Ca with Water: $CaO + H_2O \longrightarrow Ca(OH)_2$

Calcium reacts relatively slowly with water to produce calcium hydroxide and hydrogen gas and a white precipitate of calcium hydroxide is formed.

Reaction of Ca with Oxygen: $2Ca + O_2 \longrightarrow 2CaO$

Calcium reacts with oxygen to form calcium oxide.

TRENDS IN BONDING IN OXIDES AND CHLORIDES OF PERIOD 3

- Oxides of group 1, 2 & 3 (e.g., Na_2O) have more ionic character. These oxides exist as giant ionic lattices with strong electrostatic forces between oppositely charged ions.
- Oxides of group 4, 5, 6 & 7 (e.g., SO_2) are more covalent These oxides exist as covalent molecules with weak intermolecular forces. This transition is a result of the increasing electronegativity and decreasing ionic character.
- Chlorides of group 1, 2 and 3 (e.g., $NaC\ell$) are predominately ionic.
- Chlorides of elements from group 4, 5, 6 and 7 (e.g., $PC\ell_5$) are covalent. The covalent character in chlorides increases due to decrease in difference of electronegativity between the halogen and the other atom.

Acidic Strength
$SO_3 > SO_2$
$N_2O > NO > N_2O_3$
$N_2O_4 > N_2O_5$
Increase in oxidation state increases acidic strength.

Exercise Q.4

Q. Explain with the help of equations acidic and basic behaviour of oxides and chlorides.

Classification of Oxides

i) Oxides

Oxides are binary compounds formed by the reaction of oxygen with other elements. Oxides are classified into neutral, amphoteric and basic or acidic based on their characteristics.

ii) Basic Oxides

A basic oxide is an oxide that when combined with water gives off an alkali. Metals react with oxygen to give basic oxides. These oxides are usually ionic in nature. The elements of group 1 and 2 form basic oxides when react with oxygen.

Examples: Na_2O, CaO, BaO.

Group 2 hydroxides solubility increases down the group so alkalinity also increases down the group.

$$Na_2O_{(s)} + H_2O_{(\ell)} \longrightarrow 2NaOH_{(aq)}$$

$$CaO_{(s)} + H_2O_{(\ell)} \longrightarrow Ca(OH)_{2(aq)}$$

iii) Amphoteric Oxides

Amphoteric oxides are oxides that can react with both acids and bases. So they have the ability to behave as either an acid or a base, depending on the conditions. Aluminum oxide ($A\ell_2O_3$) is insoluble in water but reacts with hydrochloric acid to form aluminium chloride and water, and with sodium hydroxide to form sodium aluminate and water.

Rock Your Brain!
11. BeO is amphoteric oxide. Justify it by giving reactions.

$$A\ell_2O_{3(s)} + 6HC\ell_{(aq)} \longrightarrow 2A\ell C\ell_{3(s)} + 3H_2O_{(\ell)}$$

$$A\ell_2O_{3(s)} + 2NaOH_{(aq)} \longrightarrow Na_2A\ell_2O_{4(s)} + H_2O_{(\ell)}$$

Examples of Amphoteric Oxides: BeO, ZnO, B_2O_3 etc.

iv) Acidic Oxides:

An acidic oxide is an oxide that when combined with water gives off an acid. Non-metals react with oxygen to form acidic oxides which are held together by covalent bonds. Silicon dioxide is acidic oxide as it can react with bases.

Examples: Acidic oxides in period 3 = $P_2O_3, P_2O_5, SO_3, SO_2$

$$P_2O_{3(s)} + H_2O_{(\ell)} \longrightarrow H_3PO_{3(aq)}$$

$$SO_{2(g)} + H_2O_{(\ell)} \longrightarrow H_2SO_{3(aq)}$$

Reactions of theses oxides with bases are given below:

$$SiO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SiO_{3(aq)} + H_2O_{(\ell)}$$

$$P_2O_{3(s)} + 6NaOH_{(aq)} \longrightarrow 2Na_3PO_{3(aq)} + 3H_2O_{(\ell)}$$

$$SO_{2(g)} + 2NaOH_{(aq)} \longrightarrow Na_2SO_{3(aq)} + H_2O_{(\ell)}$$

Classification of Chlorides

Chlorine forms compounds with other elements known as chlorides. These chlorides show characteristic behaviour when we add them into water, resulting in solutions that can be acidic or neutral.

i) Neutral Chlorides

Neutral chlorides are salts that, when dissolved in water, produce a neutral solution with a pH close to 7. At the start of period 3, chloride sodium and magnesium do not react with water. The solutions formed contain the positive metal ions and negative chloride ions surrounded by water molecules. These ions are now known as hydrated ions and this process is known as **hydration**. For example,

$$NaC\ell_{(s)} \longrightarrow Na^+_{(aq)} + C\ell^-_{(aq)} \quad (pH = 7)$$

$$MgC\ell_{2(s)} \longrightarrow Mg^{+2}_{(aq)} + 2C\ell^-_{(aq)} \quad (pH = 6.5)$$

Group 1 and group 2 chlorides are also neutral with few exceptions.

ii) Acidic Chlorides:

If we move in period 3, from Aluminium to Sulphur, all chlorides react with water to make acidic solution with pH less than 7. This process is called hydrolysis, when $AlCl_3$ is added to water, aluminium and chloride ions in solution. Al^{3+} ion is hydrated and causes a water molecule to lose an H^+ ion, this process is hydrolysis. This turns the solution acidic. The following reaction occurs:

$$AlCl_{3(s)} + 3H_2O_{(\ell)} \longrightarrow Al(OH)_{3(s)} + 3HCl_{(aq)}$$

Other examples of acidic chlorides are given below.

$$SiCl_{4(\ell)} + 2H_2O_{(\ell)} \longrightarrow SiO_{2(s)} + 4HCl_{(aq)}$$

$$PCl_{3(\ell)} + 3H_2O_{(\ell)} \longrightarrow H_3PO_{3(s)} + 3HCl_{(aq)}$$

QUICK CHECK 1.8

(a) ZnO reacts with HCl to give $ZnCl_2$ and with NaOH to give Na_2ZnO_2. Give equations and also predict the type of this oxide?

Ans. ZnO is amphoteric in nature. It is explained by following two reactions.

When ZnO reacts with an acid:

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O \text{ (Basic character)}$$

When ZnO reacts with a base:

$$ZnO + 2NaOH + H_2O \longrightarrow Na_2[Zn(OH)_4] \text{ (Acidic character)}$$

(Sodium Zincate)

b) Why $AlCl_3$ is an acidic halide, but NaCl not?

Ans. when $AlCl_3$ is added to water, aluminium and chloride ions in solution. Al^{3+} ion is hydrated and causes a water molecule to lose an H^+ ion, this process is hydrolysis.

$$AlCl_{3(s)} + 3H_2O_{(\ell)} \longrightarrow Al(OH)_{3(s)} + 3HCl_{(aq)}$$

NaCl is a neutral salt with pH about 7.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

Strong acid and base react here to form neutral salt and water.

c) Predict whether the chlorides PCl_5, NCl_3 would be acidic or basic, give reason.

Ans.

$$PCl_{3(\ell)} + 3H_2O_{(\ell)} \longrightarrow H_3PO_{3(s)} + 3HCl_{(aq)}$$

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$$

$$HClO \rightleftharpoons H^+ + ClO^-$$

Both PCl_3 and NCl_3 in water show acidic in nature.

d) Would SO_2 and P_2O_5 react with HCl and H_2SO_4 or with NaOH?

Ans. SO_2 and P_2O_5 will react with NaOH.

$$SO_{2(g)} + 2NaOH_{(aq)} \longrightarrow Na_2SO_{3(aq)} + H_2O_{(\ell)}$$

$$P_2O_5 + 6NaOH \longrightarrow 2Na_3PO_4 + 3H_2O$$

VARIATION IN OXIDATION NUMBER IN OXIDES AND CHLORIDES

Oxidation Number:

"The oxidation number of an atom is the formal charge on that atom in a molecule or ion".

- The oxidation number is also referred to as the oxidation state.
- In ionic compounds the oxidation number of an atom is defined as the charge which appears on the, ions.

Let's examine the oxidation numbers in oxides and chlorides of the third period.

- The oxidation number of an element of 3rd Period in its oxide or chloride corresponds to the number of electrons used for bonding and is always positive because oxygen and chlorine are more electronegative than any of these elements.
- The oxidation number matches the group number, reflecting the total number of valence electrons. Consider the following table for oxidation states of various elements of the periodic table.
- In the oxides, the oxidation number increases from +1 in Na to +6 in S. In chlorides, the oxidation number increases from +1 in Na to +5 in P.
- Phosphorus and sulphur show several oxidation numbers because they can expand their octet by exciting electrons into empty 3d orbitals. For instance, in SO_2, sulphur has an oxidation number of +4 because only four electrons are used for bonding, while in SO_3, sulphur has an oxidation number of +6 because all six electrons are used for bonding.

Table: Oxidation Numbers in Oxides and Chlorides of 3rd Period elements

Oxide	Oxidation Number	Chloride	Oxidation Number
Na in Na_2O	+1	Na in NaCl	+1
Mg in MgO	+2	Mg in $MgCl_2$	+2
Al in Al_2O_3	+3	Al in $AlCl_3$	+3
Si in SiO_2	+4	Si in $SiCl_4$	+4
P in P_4O_{10} / P in P_4O_6	+5/+3	P in PCl_5	+5
S in SO_3	+6	P in PCl_3	+3
S in SO_2	+4	S in SCl_2	-2

QUICK CHECK 1.9

(a) Calculate the oxidation number of sulphur in SO_2 and SO_3.

Ans. SO_2

(Oxidation Number of S) + 2(Oxidation number of O) = 0

$S + 2(-2) = 0$

$S - 4 = 0$

$S = +4$

SO_3

(Oxidation Number of S) + 3(Oxidation number of O) = 0

$S + 3(-2) = 0$

$S - 6 = 0$

$S = +6$

b) Why some p block elements show variable oxidation state?

Ans. Some p-block elements with higher atomic number show variable valence due to inert pair effect in p-block elements.

- Group IIIA: $ns^2\ np^1$
- Group IIIA: $ns^2\ np^1$
- Sn and Pb shows +2 and +4 oxidation states.

Solution File — Rock Your Brain!

Sr. #	Option	Explanation
1.	C	Classification of elements in the modern periodic table is based on Moseley's law
2.	S.Q	Mendeleev's periodic table was arranged on the basis of increasing atomic mass. Moseley's periodic table was arranged on the basis of increasing atomic number.
3.	B	Non–metals are present on the right side of periodic table in p–block.
4.	S.Q	The d-block and the f-block elements are called transition elements because they are placed between the s and p-block elements and their properties are in transition between the metallic elements of the s-block and non-metallic elements of the p-block.
5.	C	F atom is smaller than F^-
6.	S.Q	A cation is formed by the loss of one or more electrons from a neutral atom. The size of cation is always smaller than its parent atom. **Reasons:** (i) There is imbalance of electron-proton ratio (No. of Protons are greater than no. of electrons). (ii) Nucleus holds the remaining electrons with a stronger force. (iii) Usually loss of shell occurs during removal of electron/s. **Examples:** $Li \longrightarrow Li^+ + e^-$ (123 pm → 60 pm); $Na \longrightarrow Na^+ + e^-$ (186 pm → 95pm)
7.	B	The 1st ionization energy of Mg = 738 kJ/mol, while Calcium = 590 kJ/mol approx.
8.	B	$Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)} \quad \Delta H^\circ_{eal} = -348.8\ kJ\ mol^{-1}$
9.	D	Fluorine is highly electronegative with strong non-metallic character.
10.	S.Q	$2Na_{(s)} + 2H_2O_{(\ell)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$ $2Na_{(s)} + O_{2(g)} \xrightarrow[\text{Supplies of Oxygen}]{\text{Abundant}} Na_2O_{2(s)}$ (Pale Yellow) $2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$
11.	S.Q	**BeO – An Amphoteric Oxide:** "An oxide which acts as a base when reacts with strong acid and as an acid when reacts with strong base is called an amphoteric oxide." BeO is an amphoteric oxide. • **With acids,** BeO behaves as a base and gives salt and water. $BeO + H_2SO_4 \longrightarrow BeSO_4 + H_2O$ • **With bases,** BeO just like acids. $BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. Which scientist first time observed the periodicity in the elements?
a) J. Newlands b) L. Meyer c) J.W. Döbereiner d) D. I. Mendeleev

II. Recognize the element if it has 3 electron shells, belongs to "s" block and has 2 electrons in its outer most shell.
a) Calcium b) Sodium c) Magnesium d) Potassium

III. Which one do you think is correct about metallic character?
a) It decreases from top to bottom in a group. b) It increases from top to bottom in a group.
c) It remains constant from left to right in a period. d) It increases from left to right in a period.

IV. Which property increases as you go down a group in the periodic table?
a) Atomic radius b) Electron Affinity c) Electronegativity d) Ionization energy

V. Which set of the following conditions results in higher ionization energy?
a) Smaller atom and greater nuclear charge. b) Smaller atom and smaller nuclear charge
c) larger atom and greater nuclear charge d) larger atom and the smaller nuclear charge

VI. Which of the following atoms show more than one (variable) oxidation states?
a) Sodium b) Magnesium c) Aluminum d) Phosphorous

VII. Which is the correct general trend in the variation of electron affinity in a group?
a) It becomes less negative from top to bottom.
b) It becomes more negative from top to bottom.
c) It remains the same.
d) It has no definite trend and changes irregularly.

VIII. What is the oxidation state of sulphur in the sulfate ion (SO_4^{2-}).
a) +4 b) +2 c) +6 d) 0

IX. Which is the correct trend in variation of electronegativity along a period of the periodic table?
a) It decreases from left to right across a period. b) It increases from left to right across a period.
c) It remains constant. d) It has no definite trend.

X. The atomic radius generally .....across a period in the periodic table.
a) Increases b) Decreases c) Remains constant d) First increases then decreases

XI. Which one of the following elements has the highest ionization energy?
a) Sodium (Na) b) Magnesium (Mg) c) Aluminium (Al) d) Argon (Ar)

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	a	J. Newlands	• John Newlands proposed the Law of Octaves (1864), noting periodicity in properties every 8th element. • Mendeleev later formalized the periodic table (1869).
II.	a	Magnesium	• 3 electron shells (n = 3) + 2 outer electrons (s^2) → Group 2 (alkaline earth metals). • Calcium: [Ar] $4s^2$ (n = 4) Magnesium [Ne] $3s^2$). The correct answer is (c) Magnesium (n = 3, 2 valence electrons).

III.	b	It increases from top to bottom in a group	• Metallic character increases down a group as atomic size grows, reducing ionization energy.
IV.	a	Atomic radius	• Down a group, atomic radius increases due to additional electron shells.
V.	a	Smaller atom and greater nuclear charge	• Ionization energy increases with smaller size (stronger attraction) and higher nuclear charge.
VI.	d	Phosphorous	• P shows variable oxidation states (−3, +3, +5) due to vacant d-orbitals. • Na/Mg/Al have fixed states (+1, +2, +3).
VII.	a	It becomes less negative from top to bottom	• Electron affinity decreases (less negative) down a group as atomic size increases, reducing attraction for added electrons.
VIII.	c	+6	• SO_4^{2-}: Let oxidation state of S = x • x + 4(−2) = −2 → x = +6
IX.	b	It increases from left to right across a period	• Electronegativity increases left to right due to higher nuclear charge and smaller atomic size.
X.	b	Decreases	• Across a period, atomic radius decreases due to increasing nuclear charge pulling electrons closer.
XI.	d	Argon (Ar)	• Noble gases (e.g., Ar) have the highest ionization energy in a period due to stable full valence shells.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. What is 1st ionization energy? Give an example.

Ans. 1st ionization energy:

"The energy needed to remove one electron from each atom in one mole of atoms of the element in the gaseous state to form one mole of gaseous 1^+ ions is known as 1st ionization energy (ΔH_{i_1})."

$$Na_{(g)} \longrightarrow Na^+_{(g)} + 1e^- \quad \Delta H_{i_1} = 494 \text{ kJ mol}^{-1}$$

b. Explain why sulphur has a lower first ionization energy than phosphorus.

Ans. Sulphur has a lower first ionization energy than phosphorus due to electron-electron repulsion in its 3p orbitals, which makes it easier to remove an electron.

Electronic Configuration:

- Phosphorus: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
- Sulphur: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

Half-filled stability (Phosphorus):

- Phosphorus has a half-filled 3p subshell ($3p^3$), which is relatively stable due to symmetrical distribution and minimized electron repulsion.
- This stability makes it harder to remove one of its electrons.

Increased electron repulsion in Sulphur:

- Sulphur has one more electron than phosphorus, giving it a $3p^4$ configuration.
- In this case, one of the 3p orbitals contains a pair of electrons, which experience increased repulsion.
- This repulsion makes it easier to remove one of the paired electrons, hence lowering the ionization energy.

c. Why the elements in Group 13 to 17 are called p-block elements?

Ans. In Group 13 to 17 elements, the last electron enters in p-orbital of their respective shells. That is why they are called p-block elements e.g., B, C, N, O, F.

d. What are the factors that affect electronegativity?

Ans. Factors Affecting Electronegativity

i) Atomic size

A larger atomic size will result in a lower value of electronegativity. This is because electrons being far away from the nucleus will experience a weaker force of attraction. For example, the electronegativities of halogens in group 17 are in the order:

F > Cl > Br > I

ii) Effective nuclear Charge

A higher value of the effective nuclear charge will result in a greater value of electronegativity, because an increase in nuclear charge causes greater attraction to the bonded electrons. This is why the electronegativity in a period increases from left to right. The electronegativity of Li in period 2 is 1.0 and F has a value of 4.0.

e. What factors are responsible for the increasing reactivity of alkali metals as you move down the group?

Ans. Down the group (in alkali metals), Atomic size increases and ionization energy decreases. It results in greater tendency to form positive ions and they react more readily.

f. Why some of the elements show variable oxidation numbers while others do not?

Ans. The variability in oxidation numbers among elements is primarily due to differences in electronic configurations, atomic structure, and position in the periodic table. Here's a breakdown of why some elements show variable oxidation states while others do not:

1. **Transition Metals and Variable Oxidation States**
   - Transition metals (like iron, copper, manganese) show variable oxidation states because they have partially filled d-orbitals.
   - Their outer electron configuration typically ends in $(n-1)d^{1-10}ns^{0-2}$, so both s- and d-electrons can be involved in bonding.
   - **Example:** Iron (Fe) can lose 2 electrons to become Fe^{2+} or 3 electrons to become Fe^{3+}.
2. **Relativistic and Inert Pair Effects (in heavier elements)**
   - Heavier p-block elements (like Sn, Pb) show variable oxidation states due to the inert pair effect, where the s-electrons are less available for bonding due to relativistic stabilization.
   - **Example:** Lead (Pb) shows both +2 and +4 oxidation states.
3. **Main Group Elements and Fixed Oxidation States**
   - Group 1 and Group 2 metals (like Na, Mg) almost always show a fixed oxidation number (+1 and +2 respectively) because they lose their valence s-electrons easily, and further loss would require breaking into a stable inner shell, which is energetically unfavorable.
   - Similarly, nonmetals like fluorine always have an oxidation number of −1 because it is the most electronegative element and can only gain one electron to complete its octet.
4. **Stability of Electron Configurations**
   - Some elements achieve stable noble gas configurations after gaining or losing a specific number of electrons. Once this stability is reached, further changes are energetically unfavorable.
   - For example, oxygen typically forms −2 oxidation state to complete its octet.

g. Identify the element which is in period 5 and group 15?

Ans. Antimony (Sb)

h. Why oxides of sodium and magnesium are more ionic than the oxides of nitrogen and phosphorous?

Ans. Oxides of sodium (Na) and magnesium (Mg) are more ionic than the oxides of nitrogen (N) and phosphorus (P) due to differences in electronegativity, metallic character, and bonding tendencies of these elements.

1. **Nature of Elements (Metals and Non-metals)**
   - Sodium and magnesium are metals (from Groups 1 and 2). Metals tend to lose electrons easily and form cations.

- Nitrogen and phosphorus are non-metals (Group 15). Non-metals prefer to share electrons rather than form ions, leading to covalent bonding.

2. **Electronegativity Difference**
   - Ionic character is stronger when there is a large electronegativity difference between the metal and oxygen.
   - Sodium (0.93) and magnesium (1.31) have much lower electronegativities than oxygen (3.44), resulting in highly polar/ionic bonds.
   - Nitrogen (3.04) and phosphorus (2.19) have closer electronegativity values to oxygen, leading to covalent bonds.
3. **Bond Formation Tendencies**
   - Na_2O and MgO form ionic lattices, with strong electrostatic attraction between ions (e.g., Na^+ and O^{2-}).
   - N_2O_5 and P_4O_{10}, oxides of nitrogen and phosphorus, exist as molecular compounds with covalent bonds (electron sharing).

i. Give reason for the different chemical reactivities of Na and Mg toward oxygen and chlorine.

Ans. With Oxygen

Sodium burns in oxygen with a golden yellow flame to produce a white solid mixture of sodium oxide and sodium peroxide. Sodium is kept under kerosene oil to prevent its reaction with air. It reacts vigorously with oxygen in open air to form sodium peroxide.

$$2Na_{(s)} + O_{2(g)} \longrightarrow \underset{\text{(Pale Yellow)}}{Na_2O_{2(s)}}$$

Under special conditions like limited O_2 or high temperature, sodium oxide is formed.

$$4Na_{(s)} + O_{2(g)} \longrightarrow 2Na_2O_{(s)}$$

Magnesium burns in oxygen with an intense white flame to give white solid magnesium oxide.

$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$$

With Chlorine

Chlorine reacts with both metals to give soluble salts. It reacts exothermically with sodium, golden yellow flame is seen and white solid, sodium chloride is formed. Magnesium also reacts with chlorine to give white solid, magnesium chloride.

$$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$$

$$Mg_{(s)} + Cl_{2(g)} \longrightarrow MgCl_{2(s)}$$

j. Why the ionization energy of lithium is much lower than that of helium despite the fact that the nuclear charge of lithium is +3 and that of helium is +2.

Ans. The ionization energy of lithium is much lower than that of helium because of the following key factors:

1. **Electron Configuration and Shell Structure**
   Helium has the electron configuration: $1s^2$
   Both electrons are in the first energy level, very close to the nucleus and strongly held.
   Lithium has the electron configuration: $1s^2\ 2s^1$
   The outermost electron (2s) is in the second energy level, which is farther from the nucleus and shielded by the inner 1s electrons.
2. **Electron Shielding Effect**
   In lithium, the two inner 1s electrons shield the outer 2s electron from the full +3 nuclear charge.
   As a result, the effective nuclear charge felt by the 2s electron is significantly less than +3, it is roughly around +1.
   In helium, there's no shielding, both electrons are strongly attracted to the nucleus.
3. **Distance from the Nucleus**
   The 2s electron in lithium is farther from the nucleus compared to helium's 1s electrons.
   Greater distance = weaker attraction = easier to remove = lower ionization energy.

k. The ionization energy of Be (atomic no. 4) is higher than that of B (atomic no. 5), despite the fact that the nuclear charge of Be is +4 and that of B is +5.

Ans. Beryllium (Be) has a higher ionization energy than boron (B) despite having a lower nuclear charge.
Beryllium (Be): Atomic number = 4, Electronic configuration: $1s^2\ 2s^2$
Boron (B): Atomic number = 5, Electronic configuration: $1s^2\ 2s^2\ 2p^1$

- In Be, the electron is removed from a 2s orbital, which is lower in energy, more penetrating, and closer to the nucleus.
- In B, the electron is removed from a 2p orbital, which is Higher in energy, farther from the nucleus, less penetrating and more shielded by the inner 1s and 2s electronsSo, even though B has a higher nuclear charge (+5 vs. +4), the 2p electron is easier to remove than the 2s electron in Be.
- So, 2p orbitals are less tightly bound than 2s orbitals, despite being in the same principal energy level (n = 2). This makes the first ionization energy of B lower, because you're removing an electron that's already less stable.

l. What is common in Na^+, Mg^{2+}, Al^{3+}, Ne^0 and F^-? Arrange them in increasing order of sizes.

Ans. $Al^{3+} < Mg^{2+} < Na^+ < Ne < F^-$

They all have 10 electrons each so they are iso-electronic species.
As the nuclear charge increases (with constant number of electrons), the electron cloud is pulled in tighter, and the radius decreases.
Al^{3+}: Highest nuclear charge with 10 electrons → most tightly held → smallest
F^-: Lowest nuclear charge with 10 electrons → weakest pull on electrons → largest

m. Consider the chlorides of sodium, magnesium, and phosphorus (v): $NaCl$, $MgCl_2$, and PCl_5
(i) Classify each of these chlorides as acidic, basic, or neutral.
(ii) For each chloride, briefly explain the reason for your classification, referring to their behaviour when dissolved in water.

Ans.

(i) Neutral = $NaCl$, Basic = $MgCl_2$, Acidic = PCl_5

(ii) $NaCl_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$ (pH=7)

$MgCl_{2(s)} \longrightarrow Mg^{+2}_{(aq)} + 2Cl^-_{(aq)}$ (pH=6.5)

- Neutral chlorides are salts that, when dissolved in water, produce a neutral solution with a pH close to 7.

$$PCl_{5(s)} + 4H_2O_{(l)} \longrightarrow H_3PO_{4(aq)} + 5HCl_{(aq)}$$

- PCl_5 reacts with water to produce phosphoric acid and hydrochloric acid i.e. produces acidic solution.

DESCRIPTIVE QUESTIONS

Q.3 Write equations for the reactions of Na and Mg with oxygen, chlorine, and water. Compare the reactivity of both elements with these in terms of metallic character.

Ans. See Page No. (15)

Q.4 Explain with the help of equations acidic and basic behaviour of oxides and chlorides.

Ans. See Page No. (17)

Q.5 Describe the factors affecting and periodic trends of electron affinity.

Ans. See Page No. (12)

Q.6 Define Ionization energy. Discuss the factors affecting and periodic trends of ionization energy.

Ans. See Page No. (09)

ADDITIONAL SLOs BASED MCQs

1. Elements in the same group have:
   A) Same number of protons B) Similar mass
   C) Same number of valence electrons D) Same number of neutrons
2. The period number of an element shows:
   A) Group number B) Number of valence electrons
   C) Type of block D) Number of occupied shells
3. Which of the following has the configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$?
   A) Na B) Mg C) Aℓ D) Si
4. The element in group 2 and period 4 has which configuration?
   A) [Ar] $3d^2$ B) [Ar] $4s^2$ C) [Ar] $4s^1$ D) [Ne] $3s^2$
5. An unknown gas forms a -1 ion and is highly reactive. It likely belongs to:
   A) Group 1 B) Group 14 C) Group 17 D) Group 18
6. An element reacts with water to form a strong base and hydrogen gas. It is likely:
   A) A noble gas B) An alkali metal C) A halogen D) A metalloid
7. Which property increases down Group 1 elements?
   A) Electronegativity B) Reactivity C) Ionization energy D) Non-metallic character
8. Why do Group 1 elements have low ionization energy?
   A) Small size B) High nuclear charge C) Large atomic radius D) High shielding
9. Which factor mainly determines an element's metallic character?
   A) Number of neutrons B) Atomic mass C) Valence electrons D) Density
10. Which oxide forms a basic solution in water?
    A) SO_3 B) CO_2 C) MgO D) P_2O_5
11. Which of the following oxides is acidic in nature?
    A) CaO B) Na_2O C) SO_3 D) MgO
12. Which hydroxide is slightly soluble and weakly basic?
    A) NaOH B) $Mg(OH)_2$ C) $Ca(OH)_2$ D) KOH
13. Which chloride forms an acidic solution in water due to hydrolysis?
    A) NaCℓ B) $AlCℓ_3$ C) KCℓ D) $MgCℓ_2$
14. Which equation correctly shows magnesium reacting with chlorine?
    A) $Mg + Cℓ \rightarrow MgCℓ$ B) $Mg + Cℓ_2 \rightarrow MgCℓ_2$ C) $Mg + 2Cℓ \rightarrow MgCℓ_2$ D) $Mg + 2Cℓ_2 \rightarrow MgCℓ_4$
15. Why is MgO more ionic than $Aℓ_2O_3$?
    A) Aℓ is more reactive B) Mg has fewer electrons
    C) Mg is less electronegative than Aℓ D) Aℓ has more orbitals

Answer Key with Explanations

Sr No.	Option	Explanations
1.	C	Group elements have same number of outer electrons.
2.	D	Period number equals the number of electron shells.
3.	C	Aluminum has 13 electrons; the configuration matches.
4.	B	Group 2 elements end with s^2; $4s^2$ indicates period 4.
5.	C	Group 17 elements (halogens) form -1 ions and are reactive.
6.	B	Group 1 metals react with water to form strong bases and H_2.
7.	B	Alkali metals become more reactive down the group.
8.	C	Larger atoms with shielding make electron removal easier.
9.	C	Fewer valence electrons = more metallic behavior.
10.	C	$MgO + H_2O \rightarrow Mg(OH)_2$, a basic solution.

11.	C	SO_3 is an acidic oxide that forms H_2SO_4 in water.
12.	B	$Mg(OH)_2$ is sparingly soluble and weakly basic.
13.	B	Al^{3+} causes hydrolysis, lowering pH of solution.
14.	B	Magnesium forms $MgCl_2$ with Cl_2 gas.
15.	C	Greater difference in electronegativity makes MgO more ionic.

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 How are elements arranged in the modern periodic table?

Ans. Elements in the modern periodic table are arranged in order of increasing atomic number. Elements with similar chemical properties are placed in the same group, and the pattern of properties repeats periodically.

Q.2 What do the s, p, d, and f blocks in the periodic table represent?

Ans. These blocks (s, p, d, and f) represent the type of atomic orbital being filled by the valence electrons. The s-block includes Groups 1 and 2, the p-block includes Groups 13 to 18, the d-block contains transition metals, and the f-block includes lanthanides and actinides.

Q.3 What does the period number of an element indicate?

Ans. The period number indicates the number of occupied electron shells in an atom of the element. For example, an element in Period 3 has electrons in three energy levels.

Q.4 We determine the electron configuration of an element using its position on the periodic table. How?

Ans. The element of the period number represents the highest principal energy level, and the block shows the type of orbital. The group number of the element helps to determine the number of electrons in the outermost shell.

Q.5 How can we identify an unknown element based on its physical and chemical properties?

Ans. We can identify an unknown element based on its physical and chemical properties by comparing the properties of an elements such as reactivity, ion formation, and bonding behavior with known trends in the periodic table, we can estimate its possible group and period and identify it.

Q.6 How can we predict the properties of elements in the same group?

Ans. Elements in the same group have the same number of valence electrons, so they exhibit similar chemical properties and reactions. For example, Group 1 elements all react with water to form hydroxides and release hydrogen gas.

Q.7 How do atomic radius and ionization energy change across a period and down a group?

Ans. **Across a period:** The atomic radius decreases and ionization energy increases across a period due to greater nuclear attraction on the valence shell electrons.
Down a group: The atomic radius increases and ionization energy down the group decreases due to added electron shells and increased shielding. So nuclear attractions decreases.

Q.8 How does the number of valence electrons affect metallic and nonmetallic character?

Ans. An elements with fewer valence electrons (like 1 to 3) tend to lose them easily and show metallic character, on the other hand, those elements with more valence electrons (like 5 to 7) gain electrons and show nonmetallic character.

Q.9 How do oxides of metals and non-metals behave in water?

Ans. The metal oxides usually react with water to form basic solutions, on the other hand, non-metal oxides form acidic solutions. For example, Na_2O forms NaOH, and SO_3 forms H_2SO_4.

$$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$$

$$SO_{2(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3(aq)}$$

Q.10 How does the reactivity of Group 1 and Group 17 elements change down the group?

Ans. In Group 1, reactivity of elements increases down the group because the outermost electron is more easily lost. In Group 17, reactivity of elements decreases down the group as gaining an electron becomes harder.

Q.11 How do transition metals differ from s-block elements?

Ans. The transition metals differ from s block elements because of following aspects

- Transition metals can form multiple oxidation states
- They often form colored compounds
- They act as catalysts
- They involve the filling of d-orbitals.

Q.12 Why do non-metals tend to gain electrons while metals tend to lose them?

Ans. The non-metals have high electronegativity and nearly full valence shells, so that is why, they tend to gain electrons. On the other hand, metals have low ionization energy and few valence electrons, that is why, they lose them easily.

SELF-ASSESSMENT Chapter # 01

Total Mark: 30

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) **Which of the following elements is not a member of the chalcogen family?**
(A) Oxygen (O) (B) Sulfur (S) (C) Selenium (Se) (D) Bromine (Br)

(ii) **Non-metals are present in which block of periodic table?**
(A) s-block (B) p-block (C) d-block (D) f-block

(iii) **Which of the following has the highest electron affinity?**
(A) Fluorine (B) Chlorine (C) Bromine (D) Iodine

(iv) **Among the following members of group 14 which is a non-metal?**
(A) C (B) Si (C) Ge (D) Sn

(v) **The oxides of electropositive elements are:**
(A) Acidic (B) Basic (C) Amphoteric (D) Neutral

(vi) **Oxidation number of Al in Al_2O_3 is:**
(A) +2 (B) +3 (C) +4 (D) +5

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) Why are the elements in groups 1 and 2 known as s-block elements?
(ii) How does electron affinity varies in a group of the periodic table?
(iii) Using your knowledge of Period 3 elements, predict and explain the relative sizes of the atomic radii of lithium and fluorine.
(iv) Explain with reasoning following facts about ionization energy 1st ionization energy of Boron is lesser than Beryllium
(v) What is the nature of oxides and hydroxides of Na and Mg?
(vi) ZnO reacts with HCl to give $ZnCl_2$ and with NaOH to give Na_2ZnO_2. Give equations and also predict the type of this oxide?
(vii) Discu. any two factors affecting electronegativity.
(viii) What is the role of Shielding Effect on Ionization Energy?

Q.3 Extensive Questions. (2 × 4 = 8)

(a) Define 1st, 2nd and 2nd Ionization Energy with one example each. Also discuss periodic trends in ionization energy.
(b) Write down the reactions of Na and Mg with water, Oxygen and Chlorine (equations only).

Chapter 02

ATOMIC STRUCTURE

Student Learning Outcomes

After studying this chapter, students will be able to:

- Describe protons, neutrons, and electrons in terms of their relative charge and relative masses. **(Understanding)**
- Recognize that the terms atomic and proton number represent the same concept. **(Understanding)**
- Recognize that the terms mass and nucleon nuclear represent the same concept. **(Understanding)**
- Explain the change in atomic and ionic radius across a period and down a group **(Understanding)**
- Describe the behaviour of beams of protons, neutrons and electrons moving at the same velocity in an electric field. **(Understanding)**
- Determine the number of protons, neutrons, and electrons present in both atoms and ions given atomic or proton number, mass/or nucleon number and charge. **(Knowledge)**
- Relate Quantum Numbers to electronic distribution of elements. **(Understanding)**
- Account for the variation in successive ionization energies of an element. **(Understanding)**
- Define terms related to electronic configuration (some examples include: shells, subshells, orbitals, principal quantum number (n), ground state). **(Knowledge)**
- Describe the order of increasing energy of the sub-shells (s, p, d, and f). **(Understanding)**
- Describe that, each atomic shell and sub-shell are further divided into degenerate orbitals having the same energy. **(Understanding)**
- Apply Aufbau principle, Pauli's exclusion principle and Hund's rule to write the electronic configuration of elements. **(Application)**
- Describe the number of orbitals making up s, p, d, and f sub-shells, and the number of electrons that can fill s, p, d, and f sub-shells. **(Understanding)**
- Describe the shapes of s, p, and d orbitals. **(Understanding)**
- Determine the electronic configuration of elements and their ions with proton numbers. **(Knowledge)**
- Some examples include:
  a. simple configuration e.g., 2,8
  b. Sub-shells e.g., $1s^2, 2s^2, 2p^6, 3s^1$
  c. students should be able to determine both of these from periodic table and are not required to memorize these.
  d. Students should understand that chemical properties of an atom are governed by valence electrons.
- Explain the electronic configurations to include the number of electrons in each shell, subshell and orbitals. **(Understanding)**
- Explain the electronic configurations in terms of energy of the electrons and inter-electron repulsion. **(Understanding)**
- (Determine the electronic configuration of atoms and ions given the proton or electron number and charge. **(Understanding)**

- Describe free radical as a species with one or more unpaired electrons. **(Understanding)**
- Illustrate the importance of electronic configurations and development of new materials for electronic devices. (For example, semiconductors such as silicon has a specific electronic configuration that makes them ideal for their use in electronic devices) **(Understanding)**
- Deduce the electronic configurations of elements using successive ionization energy data. **(Application)**
- Deduce the position of an element in the periodic table using successive ionization energy data. **(Application)**
- Explain that ionization energies are due to the attraction between the nucleus and the outer electrons. **(Understanding)**
- Explain how ionization energy helps account for the trends across the period and down a group of the periodic table. **(Understanding)**
- Explain the factors influencing the ionization energies of elements in terms of nuclear charge, atomic/ionic radius, shielding by inner shells and sub-shells and spin pair repulsion. **(Understanding)**

ATOMIC NUMBER, PROTON NUMBER AND NUCLEON NUMBER; IDENTITY OF AN ELEMENT

Atomic Number (Z)

"Atomic number is the number of proton in the nucleus of an atom".

In 1913, Moseley observed that when different elements were bombarded with cathode rays, the X-rays of some characteristic frequencies were produced. It was found that the **"the square root of the frequency of the X-rays was directly proportional to the atomic number of an element Z".**

$$\sqrt{\text{frequency}}\,(\nu) \propto Z$$

- Moseley concluded that this number, i.e. the atomic number Z was a fundamental property of an element.
- It is also called proton number.

Nucleon Number

"The number of protons and neutrons in the nucleus of an atom is collectively called its nucleon number (A), also called mass number".

Atomic number is related to the mass number by the following equation

$$A = Z + N$$

Example: An atom of an element X having atomic number Z and mass number A is described as ${}^{A}_{Z}X$, e.g. ${}^{27}_{13}A\ell$. Number of neutrons in an atom can be calculated as

$$N = A - Z$$

For example, ${}^{27}_{13}A\ell$

Atomic number/proton number $(Z) = 13$

Mass number/nucleon number $(A) = 27$

$$N = 27 - 13 = 14$$

Similarly, the number of electrons, protons, and neutrons can be justified for an ion as in the following example:

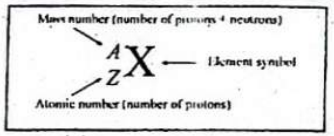
${}^{27}_{13}A\ell$ atom loses three electrons to form $A\ell^{3+}$ then, For $A\ell^{3+}$

- No. of protons = 13
- No. of neutrons = 14
- No of electrons = 13 − 3 = 10

Similarly, ${}^{35}_{17}C\ell$ gains an electron to form $C\ell^{-}$ ion, then, For $C\ell^{-}$

Rock Your Brain!

1. The total number of fundamental particles in an atom of Carbon – 14 is:
(A) 6 (B) 8
(C) 14 (D) 20



- No. of protons = 17
- No. of neutrons = 18
- No of electrons = 17 + 1 = 18

In the cases where electron gain happens by the neutral atoms, say ${}^{16}_{8}O$ to ${}_{8}O^{2-}$, ${}^{31}_{15}P$ to ${}_{15}P^{3-}$ and ${}^{32}_{16}S$ to ${}_{16}S^{2-}$, the number of neutrons, protons and electrons are as follows:

Table: Number of protons, electrons and neutrons in different ions

Species	Neutrons	Protons	Electrons
O^{2-}	8	8	10
S^{2-}	16	16	18
P^{3-}	16	15	18

Thus the atomic number and proton number represent the same concept.

EFFECT OF ELECTRIC FIELD ON FUNDAMENTAL PARTICLES

The behaviour of particles in an electric field depends upon their mass and charge. If we allow the beams of electrons, protons and neutrons to pass one by one at the same speed through an electric field, they show their behaviour as follows.

1. Neutrons being neutral are not deflected but travel in a straight path perpendicular to the direction of electric field.
2. Protons being positively charged are deflected towards the negative plate.
3. Electrons being negatively charged are deflected towards the positive plate, to greater extent since they are $\frac{1}{1836}$ times lighter than protons.

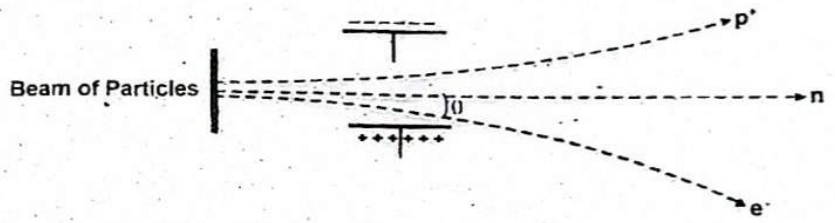


Figure: Behaviour of proton, electron and neutron in the electric field

The amount of deviation from its original direction of movement is measured in two ways.

(i) Angle of deflection $\propto \frac{\text{charge}}{\text{mass}}$

(ii) Radius of deflection $\propto \frac{\text{mass}}{\text{charge}}$

This is possible if we imagine that after deflection, the particle moves in a circular path. Hence, ***the factors affecting the radius of deflection are reciprocal to that for the angle of deflection.***

Rock Your Brain!

2. Cathode rays are negatively charged. Why?

Properties of Fundamental Particles

The Table shows the properties of three fundamental particles electron, proton and neutron present in an atom.

Table: Properties of three fundamental particles

Particle	Charge (coulomb)	Relative charge	Mass (kg)	Mass (amu)
Proton	$+1.6022\times10^{-19}$	+1	1.6726×10^{-27}	1.0073
Neutron	0	0	1.6750×10^{-27}	1.0087
Electron	-1.6022×10^{-19}	-1	9.1095×10^{-31}	5.4858×10^{-4}

QUICK CHECK 2.1

a) Calculate the number of neutrons in the following elements.

(i) $^{39}_{19}K$ (ii) $^{35}_{17}Cl$ (iii) $^{40}_{18}Ar$

Ans.

Number of Neutrons in:		
(i) $^{39}_{19}K$	(ii) $^{35}_{17}Cl$	(iii) $^{40}_{18}Ar$
Mass number = A = 39	Mass number = A = 35	Mass number = A = 40
Number of Protons = Z = 13	Number of Protons = Z = 17	Number of protons = Z = 18
Number of Neutrons = N = A – Z	Number of Neutrons = N = A – Z	Number of Neutron = N = A – Z
= 39 – 13	= 35 – 17	= 40 – 18
= 26	= 18	= 22

b) Which of electron, proton and neutron is deflected the most in the magnetic field?

Ans. Electron is deflected the most because it is charged and has a very small mass.
Proton is deflected less because it is charged but much heavier.
Neutron is not deflected at all because it has no charge.

EXPERIMENTAL EVIDENCES FOR THE ELECTRONIC CONFIGURATION

The modern theory of electronic structure takes its origin from the Bohr Model of atom. *Evidence for this and later models of the atoms derives principally from two sources; atomic spectra and ionization energies.*

➲ Atomic Spectra

➢ **Atomic Emission Spectrum:**

"When an element in its gaseous state is heated to high temperatures or subjected to electrical discharge, radiation of certain wavelengths is emitted. The spectrum of this radiation contains coloured lines and is called atomic emission spectrum".

The atomic emission spectrum of hydrogen is shown in Figure (a).

➢ **Atomic Absorption Spectrum:**

"When a beam of white light is passed through a gaseous sample of an element in cold state, certain wavelengths are absorbed. The wavelengths of the white light that has been absorbed by the atoms show up as dark lines on the spectrum. The spectrum of this radiation is called an atomic absorption spectrum".

The atomic absorption spectrum of hydrogen is shown in Figure (b).

NOTE: The wavelengths of the dark lines in the absorption spectrum are exactly the same as those of coloured lines in the emission spectrum.

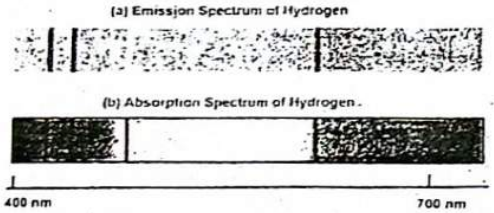


Figure: (a) atomic emission spectrum of hydrogen (b) atomic absorption spectrum of hydrogen

- Each element has a unique arrangement of electrons and thus a unique range of fixed energy levels.
- It follows that the wavelengths and frequencies of the radiation absorbed or emitted when electrons jump from one energy level to another must also be unique.
- This uniqueness convinces us to conclude that every element has its own characteristic spectrum. Therefore, every element is identified by its characteristic spectrum.
- The atomic spectra are the finger prints of the elements. Figure shows the emission spectra of some elements.

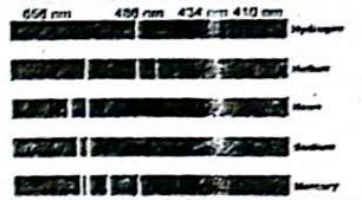


Figure: Spectral series of various elements as plotted by a spectrometer

Exercise Q 6

a. **What do you mean by successive ionization energies? How the electronic shell structure of magnesium (Mg) is derived from the successive ionization energies?**

➲ Ionization Energy and Energy Levels (Electronic Shells)

A major difference between electrons in different types of shells is their energy. We can investigate the electronic configuration of the atoms by measuring experimentally the energies of the electrons within them. This can be done by measuring ionization energies.

Ionization energies are used to investigate the electronic configurations of elements in two ways.

i. Successive ionization energies of the same element
ii. First ionization energies for different elements

I) Successive Ionization Energies of the Same Element

We can look at an atom of a particular element and measure the energy required to remove each of its electrons, one by one.

$$X \longrightarrow X^+ + e^- \quad \Delta Hi_1$$
$$X^+ \longrightarrow X^{2+} + e^- \quad \Delta Hi_2$$
$$X^{2+} \longrightarrow X^{3+} + e^- \quad \Delta Hi_3$$

We can continue to remove electrons from an atom until only the nucleus is left. We call this sequence of ionization energies, successive ionization energies. The successive ionization energies show clearly the arrangement of electrons in shells around the nucleus.

Example: If we take the magnesium atom as an example, and measure the energy required to remove successively the first electron, the second, the third, and so on. We obtain a graph when the ionization energies values are plotted against number of electrons as in Figure.

$$Mg_{(g)} \longrightarrow Mg^+_{(g)} + e^- \quad \Delta H_{i_1} = +738 kJ\ mol^{-1}$$
$$Mg_{(g)} \longrightarrow Mg^{2+}_{(g)} + e^- \quad \Delta H_{i_2} = +1450 kJ\ mol^{-1}$$
$$Mg^{2+}_{(g)} \longrightarrow Mg^{3+} + e^- \quad \Delta H_{i_3} = +7730 kJ\ mol^{-1}$$

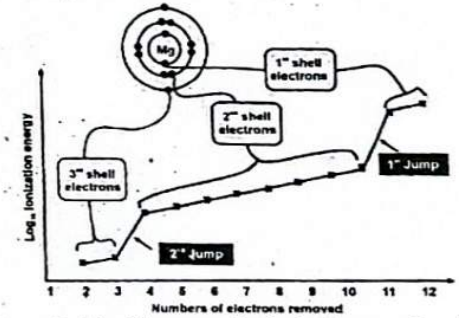


Figure: A plot of the successive ionization energies of Mg

➢ **Graph Depicting Successive Ionization Energies:**

- This plot shows that ***successive ionization energies increase when we move from the valence shell to the inner shells.***
- First two electrons are removed from the outermost shell and require lower energy for their removal.
- A very large increase occurs when the third electron is removed. This is because when two electrons of the outer shell have been removed, the next has to be removed from the shell that is very much closer to the nucleus. The next seven electrons are removed successively from the second shell and a gradual increase in ionization energy is observed.
- A similar but much more enormous jump occurs when the eleventh and twelfth electrons are removed.
- These electrons are removed from the first, innermost shell, right next to the nucleus. Hence, over all, we observe two large jumps in the successive ionization energies. These two large jumps in the series of successive ionization energies are very good evidence that the electron in the magnesium atoms exist in three different shells.

ii) First Ionization Energies of Different Elements

The second way in which ionization energies show us the details of electronic configuration is to look at how the first ionization energies of elements vary with atomic numbers. The following figure shows a plot for the first 88 elements.

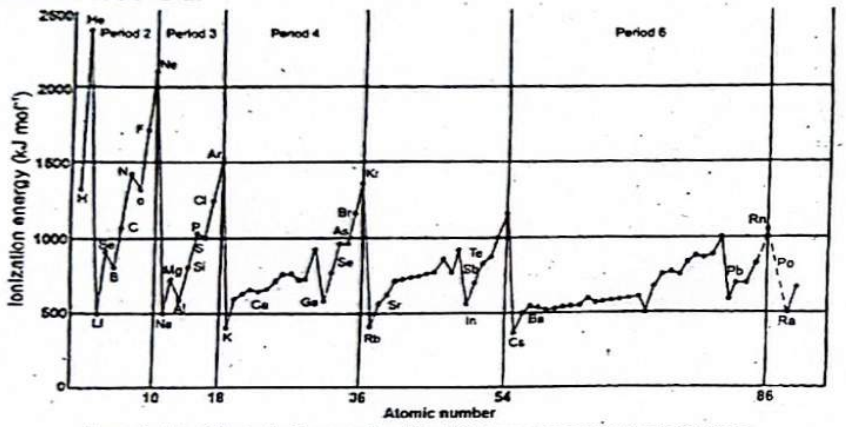


Figure: A plot of the ionization energies of first 88 elements against atomic number

This graph tells us the following:

- ***All ionization energies are strongly endothermic;*** it takes energy to separate an electron from an atom.
- **Down the Group:** As we go down a particular group, **e.g.,** from Helium to Neon to argon, or from Lithium to Sodium to potassium, ionization energies decrease. The larger the atom, the easier is to separate an electron from it. ***Actually, down the group, number of shells increases, hold of nucleus on the valence electrons decreases, hence removal of electrons becomes easier.***

  Along a Period: ***The ionization energies generally increase on going across a period.*** The group 1 elements, the alkali metals, have the lowest ionization energy within each period, and the noble gases have the highest. It is due to the reason that across the period shell number remains same. As the proton number increases, electrons are added in the same shell. Therefore, nucleus attracts the valence electrons more strongly. As a result, ionization energy increases across the period.

QUICK CHECK 2.2

a) Write equations that describe:

i. 1st ionization energy of calcium

Ans. $Ca_{(g)} \longrightarrow Ca^{+}$ ΔH_{i_1} = kJ/mol

ii. 3rd ionization energy of potassium

Ans. $K^{2+}_{(g)} \longrightarrow K^{3+} + 1e$ ΔH_{i_3} = kJ/mol

iii. 2nd ionization energy of lithium

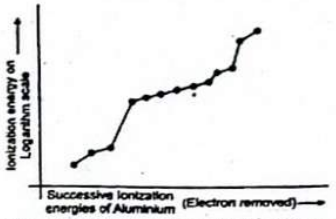
Ans. $Li^{+1}_{(g)} \longrightarrow Li^{+} + 1e^{-}$ ΔH_{i_2} = kJ/mol

iv. 5th ionization energy of sulphur.

Ans. The 5th ionization energy of Sulphur is 7004.3 kJ/mol.

b) For the element aluminium (Z = 13), draw a sketch graph between the log 10 of the successive ionization energies (y-axis) against the number of electrons removed (x-axis).

Ans.



c) The first ΔH_{i_1} and the second ΔH_{i_2} ionization energies (kJ/mol) of a few elements are given in table.

Element	ΔH_{i_1}	ΔH_{i_2}
I	2372	5251
II	520	7300
III	900	1760
IV	1680	3380

Which of the above element is likely to be:

i. a reactive metal,

Ans.

Element	ΔH_{i_1}	ΔH_{i_2}
II	520	7300

ii. a reactive non-metal,

Ans.

Element	ΔH_{i_1}	ΔH_{i_2}
IV	1680	3380

iii. a noble gas

Ans.

Element	ΔH_{i_1}	ΔH_{i_2}
I	2372	5251

iv. a metal that forms a stable binary halide of the formula AX_2 (X = halogen).

Ans.

Element	ΔH_{i_1}	ΔH_{i_2}
III	900	1760

QUANTUM NUMBERS

(Exercise L Q 3)

Q. What are quantum numbers? Describe briefly principal and spin quantum numbers.

- The Bohr model was a one-dimensional model that used one quantum number to describe the distribution of electrons in the atom.
- ***The only important information was the size and energy of the orbit,*** which was described by the n-quantum number. Since Schrodinger's model allowed the electron to occupy three-dimensional space, therefore, it required three coordinates, or three quantum numbers, to describe the orbitals in which electrons can be found.
- ***The three quantum numbers that come from Schrödinger's wave equations are the principal (n), angular (ℓ), and magnetic (m) quantum numbers.***
- ***These quantum numbers describe the size, shape, and orientation in space of the orbitals in an atom.***

Rack Your Brain!

3. Quantum number values for '3d' orbital will be:
(A) n = 3, ℓ = 0 (B) n = 3, ℓ = 1
(C) n = 3, ℓ = 2 (D) n = 3, ℓ = 3

➲ Principal Quantum Number (n)

- The principal quantum number, n, can have positive integral values 1,2,3,4... designated by K, L, M, N..., and it corresponds the quantum number (number of orbit) in Bohr's model of the hydrogen atom.
- ***This quantum number, n, describes the size and energy of the orbital.***
- The collection of orbitals with the same values of n is called an electron shell.
- The larger 'n' is, the greater the average distance of an electron in the orbital from the nucleus and therefore the larger the orbital.
- ***An increase in 'n' also means that the electron has a higher energy and is therefore less tightly bound to the nucleus.***
- The principal Quantum number, n, can also be used to calculate the maximum number of electrons in a shell by the formula $2n^2$.
- Therefore shells K, L, M and N can accommodate maximum electrons. 2, 8, 18, 32 respectively.

Rack Your Brain!

4. Quantum number value for 2s orbitals are:
(A) n = 2, ℓ = 1 (B) n = 1, ℓ = 2
(C) n = 1, ℓ = 0 (D) n = 2, ℓ = 0

Rack Your Brain!

5. What is the value of (n + ℓ) for the 3d sub-shell?
(A) 3 (B) 4
(C) 5 (D) 6

Rack Your Brain!

6. (n + ℓ) value for 5s orbital will be:
(A) 3 (B) 5
(C) 7 (D) 9

(Exercise L Q 4)

Q. Draw the shapes of s, p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

➲ Azimuthal Quantum Number (ℓ)

- Azimuthal a.nl also called Angular Momentum Quantum Number, ℓ, can have integral values 0 to (n – 1) for each value of n.
- ***This quantum number describes the shape of the orbital.***
- The values of 'ℓ' are integers that depend on the value of the principal quantum number.
  - If n = 1, there is only one possible value of 'ℓ', i.e., ℓ = 0 (n – 1, where n = 1).
  - If n = 2, there are two values of 'ℓ' i.e. 0 and 1.
  - If n = 3 there are, three values of 'ℓ' i.e. 0,1 and 2.
  - If n = 4, there are four values of 'ℓ', i.e. 0,1,2, and 3.

Rack Your Brain!

7. For azimuthal quantum number ℓ = 3, calculate the total values of magnetic quantum number (m).

- ***The values of 'ℓ' are designated by the letters s,p,d, and f, with which stand for sharp, principal, diffused and fundamental, respectively.*** These are the spectral terms used to describe certain features of spectral lines.
- **Subshell:** The set of orbitals that have the same n and ℓ values is called a subshell. The number of electrons in a subshell can be calculated by the formula $2(2\ell + 1)$ as given in the Table.

Table: Shapes of orbital

Value of ℓ	0	1	2	3
Orbital designation	s	p	d	f
shape of orbital	spherical	polar (dumb bell)	cloverleaf (double dumb bell)	complicated
No. of electrons in a subshell, $2(2\ell+1)$	2	6	10	14

- The number of subshells in a shell is equal to its shell number. For example 1st, 2nd, 3rd, and 4th shells have one, two, three and four subshells respectively.

Table: Relationship between n, ℓ and subshells

Shell	Principal Quantum number n	(Azimuthal) Quantum Number (ℓ)	Subshells	No. of subshells in a shell
K	1	0	1s	1
L	2	0	2s	2
		1	2p	
M	3	0	3s	3
		1	3p	
		2	3d	
N	4	0	4s	4
		1	4p	
		2	4d	
		3	4f	

➲ Magnetic Quantum Number (m)

- **The magnetic quantum number 'm' describes the orientation of an orbital in space.**
- Within a subshell, the value of m depends on the value of ℓ. For a certain value of ℓ there are (2ℓ + 1) integral values of m as follows:

$$-\ell \ldots\ldots 0 \ldots\ldots +\ell$$

- The values of m indicate the number of orbitals in a subshell.
- If ℓ = 0, (s-subshell) there is only one possible value of m, i.e. 0: It means s-subshell has only 1 orbital.
- If ℓ = 1, (p-subshells) there are three values of m; –1, 0 and +1. It means p-subshells has three orbitals.
- If ℓ = 2, (d-subshell), there are five values of m, namely, –2, –1, 0, +1 and +2. It means d-subshells have 5 orbitals.
- If ℓ = 3, (f-subshell) there are seven values of m: i.e. –3, –2, –1, 0, +1, +2, +3. It means f-subshells have 7 orbitals.

Did You Know?

Splitting of small fine lines in the presence of magnetic field and there three dimensional orientation in space indicate the presence of orbitals in subshells.

- **Degenerate Orbitals:** ***Orbitals of the same subshell have same energy and are called degenerate orbitals.*** These degenerate orbitals are differentiated from each other in the presences of magnetic field, hence the name of this quantum number, i.e. magnetic quantum number. The relationship between the magnetic quantum numbers is provided in Table.

Table: Relationship between ℓ and m

Subshell	Azimuthal / angular Quantum number (ℓ)	Magnetic Quantum number (m) $-\ell$ .....0..... $+\ell$	Number of degenerate orbitals ($2\ell+1$)
s	0	0	One orbital
p	1	−1 0 +1	Three degenerate p-orbitals
d	2	+2 +1 −1 −2	Five degenerate d-orbitals
f	3	+3 +2 +1 0 −1 −2 −3	Seven degenerate f-orbitals

➲ Spin Quantum Number (s)

- *Electrons are thought of spinning around their own axes (as the Earth does).*
- According to electromagnetic theory, a spinning charge generates a magnetic field.
- It is this motion that causes an electron to behave like a magnet. Figure shows the two possible spinning motions of an electron. One is clockwise and the other is anticlockwise.
- To take the electron spin into account, it is necessary to introduce a fourth quantum number called the electron spin quantum number (s).
- Its values are $+\frac{1}{2}$ and $-\frac{1}{2}$.
- The anti-clockwise spin is represented by an arrow (↑) pointing upwards, while the clockwise spin is represented by an arrow (↓) pointing downwards.
- Each orbital can accommodate at the most two electrons provided the two electrons have opposite spins.
- Thus it takes three quantum numbers to describe an orbital but forth quantum number to differentiate between the two electrons that can occupy an orbital.



Figure: (a) clockwise (b) counterclockwise spins of an electron.

Did You Know?

In the nth principal quantum number, there are n subshells consisting of n^2 orbitals with a maximum number of $2n^2$ electrons.

QUICK CHECK 2.3

a) What information about an electron in an atom can be obtained from:

I. Principal Quantum Number(n)

- The different energy levels in Bohr's atom are represented by 'n'. This is called principal quantum number by Schrodinger.
- Its value is non-zero, positive integers upto infinity.

  n = 1, 2, 3, 4, ... (n ≠ 0, −ve, fractional)
- The value of 'n' represents the shell or energy level in which the electron revolves around the nucleus.

n	1	2	3	4
Shell	K	L	M	N

- These value of 'n' tells us about the radius of orbit.

II. Azimuthal Quantum Number (ℓ)

- The presence of several fine lines in an individual line spectrum can be explained in term of Azimuthal quantum number. Azimuthal quantum number is also known as angular momentum or secondary or subsidiary quantum number.
- It is represented by 'ℓ'.
- Its values are $\ell = 0, 1, 2, 3, \ldots (n-1)$
- Its value depends upon the value of n.

III. Magnetic Quantum Number (m)

To explain one of the defects of Bohr's model i.e. Zeeman effect (splitting of spectral lines due to strong magnetic field) a third quantum number called magnetic quantum number (m) has been proposed.

- This quantum no. is represented by 'm'.
- Where m = 0, ±1, ±2, ±3

IV. Spin Quantum Number (s)

- The doublet line structure of line spectrum can be explained by spin Quantum number.
- Alkali metals have one electron in their outermost shell. We can record their emission spectra, when the outermost electron jumps from an excited state to a ground state. When the spectra are observed by means of high resolving power spectrometer, each line in the spectrum is found to consist of pair of lines, this is called doublet line structure.

b) For an electron(s):

I. If n = 2 and $\ell = 1$, how many orientations in space are possible?

Ans. 2p has 3 orientations i.e. p_x, p_y, p_z

II. If n = 3 and $\ell = 2$, which shell and subshell does the electron belong to?

Ans. 3d
Shell number 3 (M-shell)
Subshell = d

III. If $\ell = 2$, find all possible values of m and maximum number of electrons for m.

Ans. d subshell
It has five orientation m = +2, +1, 0, −1, −2.

SHAPES OF ATOMIC ORBITALS

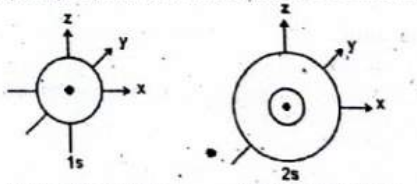
Atomic Orbital

An atomic orbital is defined as the three dimensional region in space around the nucleus in which the probability of finding the electron is maximum.

Let us discuss the different orbitals one by one.

➲ s-orbital

- The shape of an 's' orbital is spherical.
- The electronic density around the nucleus in an s orbital is uniformly distributed in all directions.
- With the increase in the principal quantum number, the size of s orbital also becomes larger.



(a) n = 1, ℓ = 0, m = 0 (b) n = 2, ℓ = 0, m = 0

Figure: The boundary surface for, (a) 1s (b) 2 s

➲ p-orbitals

- The distribution of electron density for a 2p orbital is shown in Figure.

- The electron density is not distributed in a spherically symmetric fashion as in an *s* orbital. Rather, a 'p' orbital has two lobes on any of the axis.
- The p orbitals are named as p_x, p_y and p_z, accordingly to their axes.

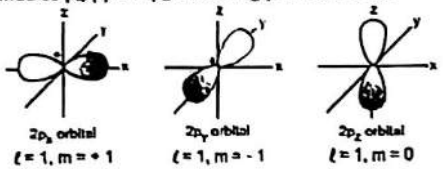


Figure: The 2p orbitals shapes of 2P orbitals

➲ d and f orbitals

- In a given shell, 'd' orbitals have different shapes and orientations in space.
- The d_{xy}, d_{xz}, and d_{yz} lie in the xy, xz and yz planes, respectively.
- The lobes of the $d_{x^2-y^2}$ lie along the x and y axes. The d_z^2 orbital has two lobes along the z -axis and a "doughnut" in the xy plane.
- The shapes for the five d orbitals ($\ell = 2$) are shown in Figure.

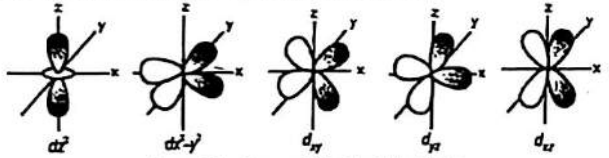


Figure: The shapes of the five 3d orbitals

An *f* subshell has seven orientations in space, i.e. there are seven *f* orbitals. However, the shapes of *f* orbitals are very complicated.

☑ QUICK CHECK 2.4

a) What does an orbital represent according to the wave mechanical model of atom?

Ans. According to the wave mechanical model of atom, an orbital represents a region of space around the nucleus where there is high probability of finding an electron. It is a 3-D wave function that describes the electrons state and energy.

b) There are three orientations of p-orbital due to three values of magnetic quantum number. Justify it.

Ans. For p-orbital value of $\ell = 0, m = 0, +1, -1$
So there are three orientations of p-orbital.

ELECTRONIC CONFIGURATION

"Electronic configuration is the distribution of electrons among available shells, subshells, or orbitals of an atom or ion".

- In case of subshells, the electronic configuration is described by a notation that lists the subshell symbols, one after the other.
- Each symbol has a superscript on the right. This gives the number of electrons in the subshell. For example, the configuration of $^{9}_{4}Be$ atom with two electrons in the ' 1s ' subshell and two electrons in the ' 2s ' subshell is written $1s^2 2s^2$.
- Each group of orbitals in a subshell is labeled by its subshell notation.
- An electron in an orbital is shown by an arrow. The arrow points upward, when $s = +1/2$ and downward when $s = -1/2$. The orbital diagram of boron ($^{11}_{5}B$) is as follows

$$^{11}_{5}B = 1s^2, 2s^2, 2px^1, 2py^0, 2pz^0$$

➲ Distribution of Electrons in Shells

Rack Your Brain!

8. Calculate the number of electrons in s, p, d and f sub shells from the formula and write separately.

- The electronic configuration of an atom describes the distribution of electrons in its atomic shells.
- The shells, denoted as K, L, M, N, and so on, correspond to the principal quantum number (n) of the orbitals.
- Shell capacities each shell has a specific capacity for electrons:
  - K shell (n=1): 2 electrons maximum (1 s orbital)
  - L shell (n=2): 8 electrons maximum (2 s and 2 p orbitals)
  - M shell (n=3): 18 electrons maximum (3s, 3p, and 3d orbitals)
  - N shell (n=4): 32 electrons maximum (4s, 4p, 4d, and 4 f orbitals)

For example:

- **Hydrogen (H): $1s^1$ (K shell)**
- **Helium (He): $1s^2$ (K shell)**
- **Sodium (Na): $1s^2 2s^2 2p^6 3s^1$ (K, L, and M shells)**

➲ Distribution of Electrons in Subshells

Following rules are applied to fill the orbitals of multi-electron atoms.

Aufbau Principle

Aufbau principle is also known as the building up principle. This principle says ***that the subshells in an atom are filled with electrons in an increasing order of their energy values.***

Arrangement of the subshells energy wise:

The energy of a subshell in the absence of any magnetic field, depends upon the principal quantum number (n) and the azimuthal quantum number (ℓ).

Thus the order of filling subshells with electrons may be obtained from the summation $(n + \ell)$. $(n + \ell)$ values are given in Table.

Table: $(n + \ell)$ values of various sub-shells.

Principal quantum no. (n)	Azimuthal quantum no. (ℓ)	Subshell	$(n+\ell)$ Value
1	0	1s	(1 + 0) = 1
2	0 1	2s 2p	(2 + 0) = 2 (2 + 1) = 3
3	0 1 2	3s 3p 3d	(3 + 0) = 3 (3 + 1) = 4 (3 + 2) = 5
4	0 1 2 3	4s 4p 4d 4f	(4 + 0) = 4 (4 + 1) = 5 (4 + 2) = 6 (4 + 3) = 7

a) The subshell having lower $(n + \ell)$ value has lower energy and is filled first.
For example, 4 s orbital has $(n + \ell) = 4 + 0 = 4$ and 3d orbital has $(n + \ell) = 3 + 2 = 5$. Since $(n + \ell)$ value of 4s orbital is lower than that of 3d, hence 4 s subshell has lower energy than 3d and 4s will be filled first.

b) In case there are two subshells are having equal $(n + \ell)$ values, then the subshell with lower 'n' value will be filled first.
For example, both 4p and 3d subshells have n + 1 value equal to 5(4p = 4 + 1 = 5) and (3d = 3 + 2 = 5); 3d subshell will be preferred to be filled because of its low n value.
According to this rule the energy wise arrangement of orbitals should be.

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s$$

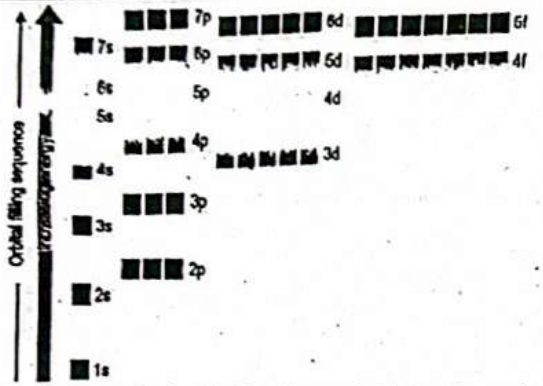


Fig: The diagram shows the energy of each subshell. Each box on the diagram represents an atomic orbital.

So, the order of filling of various subshells with electrons obtained by this rule is given below Figure.

Pauli's Exclusion Principle

According to this principle:

"No two electrons in an atom can have the same values for all the four quantum numbers"

Or

"Two electrons in an orbital will always have opposite spins".

➢ **Explanation:**

In the first shell of helium (He) atom, there are two electrons. They are present in 1 s orbital. According to the concept of quantum numbers and Pauli's exclusion principal, the values of their quantum numbers are:

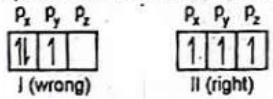
Table values of quantum numbers of two electrons in the same orbital

Electron	n	ℓ	m	s
Electron 1	1	0	0	$+\frac{1}{2}$ (clockwise)
Electron 2	1	0	0	$-\frac{1}{2}$ (anticlockwise)

The two electrons having the same values of 'n', 'ℓ' and 'm' can have different values of 's'. It means that their spins are in the opposite directions.

Hund's Rule

This rule gives an idea for filling electrons into the orbitals having equal energies. For example, three p-orbtials, i.e., p_x, p_y and p_z have equal energy. To understand it, let us take an example in which three electrons are to be filled into three p-orbitals. There are two different ways to do this as shown below:



I (wrong) II (right)

The structure II is correct. Hund's rule, states that,

When degenerate orbitals are available and more than two electrons are to be placed in them, they should be placed in separate orbitals with the same spin rather than in the same orbital with opposite spins.

- According to the Hund's rule, the correct way of filling three electrons in three p orbitals is that in which each orbital is singly occupied.

Filling the Orbitals

A useful way of representing electronic configurations is a diagram that places electrons in boxes Figure.

- Each box represents an atomic orbital.
- The boxes (orbitals) can be arranged in order of increasing energy from bottom to top.

- An electron is represented by an arrow.
- The direction of the arrow represents the 'spin' of the electron.
- When there are two electrons in an orbital, the 'spins' of the electrons are opposite, so the two arrows in this box point in opposite direction.
- Electrons in the same region of space repel each other because they have the same charge.
- So wherever possible, electrons will occupy separate orbitals in the same subshell to minimize this repulsion. These electrons have the same 'spins' in different orbitals.
- Electrons are only paired when there are no more empty orbitals available within a subshell.

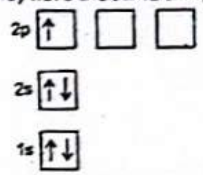


Figure: The electronic configuration of boron

Figure: shows the electronic structures of carbon, nitrogen and oxygen to illustrate these points

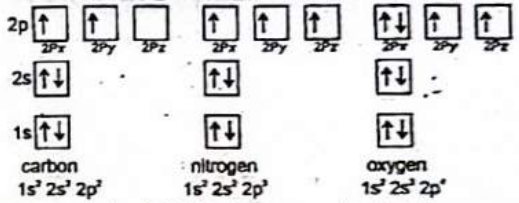


Figure: When adding electrons to a particular subshell, the electrons are only paired when no more empty orbitals are available.

The electron configurations of some elements of the periodic table in the light of the abovementioned principles are given in Table.

Table: Electronic configuration of ground states of elements Z = 1–36.

Z	Element	Configuration	Z	Element	Configuration
1.	H	$1s^1$	19.	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
2.	He	$1s^2$	20.	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
3.	Li	$1s^2 2s^1$	21.	Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
4.	Be	$1s^2 2s^2$	22.	Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
5.	B	$1s^2 2s^2 2p^1$	23.	V	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
6.	C	$1s^2 2s^2 2p^2$	24.	Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
7.	N	$1s^2 2s^2 2p^3$	25.	Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
8.	O	$1s^2 2s^2 2p^4$	26.	Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
9.	F	$1s^2 2s^2 2p^5$	27.	Co	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
10.	Ne	$1s^2 2s^2 2p^6$	28.	Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
11.	Na	$1s^2 2s^2 2p^6 3s^1$	29.	Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
12.	Mg	$1s^2 2s^2 2p^6 3s^2$	30.	Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$
13.	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	31.	Ga	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$
14.	Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	32.	Ge	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
15.	P	$1s^2 2s^2 2p^6 3s^2 3p^3$	33.	As	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$
16.	S	$1s^2 2s^2 2p^6 3s^2 3p^4$	34.	Se	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$
17.	Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$	35.	Br	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
18.	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$	36.	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

ELECTRONIC CONFIGURATION AND THE PERIODIC TABLE

- We have seen that the electron configurations of elements are related to their position in the periodic table. The periodic table is structured so that elements with the same pattern of outer-shell (valence) electron configuration are arranged in same groups.
- We can easily write the electron configuration of an element based on its location in the periodic table. The pattern is summarized in Figure. Notice that the elements can be grouped in terms of the type of orbital into which the electrons are placed.

Rack Your Brain!

9. Write electronic configuration of Cu_{29} and I_{53}.

- ***On the left are two columns of elements. These elements, known as the alkali metals and alkaline earth metals (groups 1 and 2), are those in which the outer-shell s orbitals are being filled.***
- We see that the group 1 and 2 elements all have ns^1 and ns^2 outer configurations respectively.
- When we jump to group 13 elements, we find that they have ns^2np^1 configuration.
- ***On the right is a block of six columns. These are the elements in which the outermost 'p' orbitals are being filled.***
- ***In the middle of the table is a block of ten columns that contain the transition metals. In these, the d orbitals are being filled.***

Rack Your Brain!

10. Distribute electrons in the orbitals of: (A) Ca_{20} (B) Cs_{55}

- Below the main portion of the table are two rows that contain fourteen columns. These elements are often referred to as the f-block elements. These are the ones in which the '*f*' orbitals are being filled. Recall that the numbers 2, 6, 10, and 14 are precisely the number of electrons that can fill the s, p, d, and f subshells, respectively.

QUICK CHECK 2.5

a) With the help of periodic table, write the electronic configurations for the following elements by giving the appropriate noble-gas inner core plus the electrons beyond it (i) $_{48}Cd$; (ii) $_{57}La$.

Ans. (i) $_{48}Cd = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}$
$= [Kr]4d^{10}5s^2$

(ii) $_{57}La = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 5d^1$
$= [Xe]5d^16s^2$

b) Write the complete electron configuration for antimony (Sb) with atomic number 51.

Ans. $_{51}Sb = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 4d^{10}, 5s^2, 5p^3$
$= [Kr]4d^{10}5s^25p^3$

c) How many unpaired electrons are there in each atom of $_{51}Sb$?

Ans. Number of unpaired electrons in $_{51}Sb$ = 03 (three)
$5px^1, 5py^1, 5pz^1$

d) Write down the electronic configuration of valence shell of the following in terms of orbitals:
i) $_{13}Al$ ii) $_{14}Si$ $_{28}Ni$

Ans. The valence shell electronic configurations in terms of orbitals for the given elements:
i) Aluminium ($_{13}Al$): $3s^2\,3p^1$ ii) Silicon ($_{14}Si$): $3s^2\,3p^2$ iii) Nickel ($_{28}Ni$): $3d^8\,4s^2$

Valence Electrons

The electrons in an atom in the outermost shell are called valence electrons. These are such electrons that are primarily involved in chemical reactions.

The similarities among the configurations of valence electrons account for similarities of the chemical properties among groups of elements.

Figure shows a periodic table which include the valence shell configurations included. Note the similarity in electron configuration within any group (column) of elements.

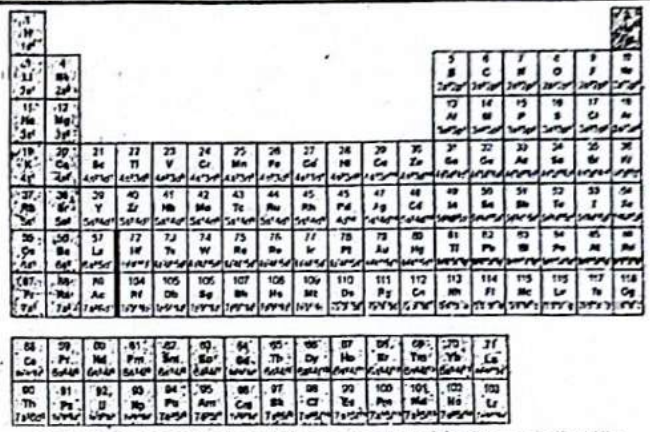


Figure: The electronic distribution of elements of modern periodic table

Classification of Elements of Periodic Table

The main-group or representative elements all have valence-shell configurations ns^anp^b. They have some choice of 'a' and 'b'. In other words, the outer 's' or 'p' subshell is being filled. Similarly, in the d-block transition elements, a 'd' subshell is being filled. In the *f*-block transition elements or inner-transition elements, an '*f*' subshell is being filled.

There is a definite pattern to the order of filling of the subshells as we go through the elements in the periodic table. From this we can write down the building-up order. The overall sketch of periodic table is given in Figure. This shows the blocks of elements.

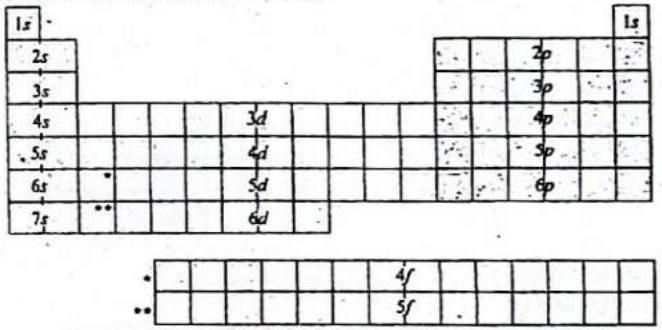


Figure: Modern periodic table showing s, p, d and f-block elements.

Figure shows a periodic table indicating this pattern. For example, in the blue colored area, an 'ns' subshell is being filled. In the green colored area, an np subshell is being filled. In the yellow area, an (n – 1)d subshell is being filled. In the light golden area and (n – 2)*f* subshell is being filled.

We start building-up order by starting with the first period, in which the '1s' subshell is being filled. In the second period, we have '2s'; then staying in the same period but jumping across, we have '2p'. In the third period, we have '3s' and '3p'; in the fourth period, '4s', '3d' and then '4p'. This pattern should become clear enough to visualize with a periodic table.

- The classification of elements of periodic table has been done into metals, non-metals, representative, transition elements, periods, groups and blocks (s, p, d, f). This division is done on the basis of electronic configuration and their valence electrons. The chemical properties of various categories of elements discussed above can be easily assessed.

QUICK CHECK 2.6

a) An element has the electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$

i. Which block in the Periodic Table does this element belong to?

Ans. p-block

ii. Which group does it belong to?

Ans. Halogens

iii. Which period does it belong to?

Ans. 5

iv. Identify this element.

Ans. Iodine

b) Which block in the periodic table does the element with the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ belong to? Name it.

Ans. d-block and the element is Chromium (Cr).

ELECTRONIC CONFIGURATION OF IONS AND FREE RADICALS

Ions

Positive Ions: ***Positive ions are formed when electrons are removed from atoms.***

The sodium ion, Na^+ (proton number = 11), has 10 electrons. So, its electronic configuration is $1s^2 2s^2 2p^6$. Note that this is the same as the electronic configuration of neon, the element with 10 electrons in each atom.

Negative Ions: ***Negative ions are formed when atoms gain electrons.***

The sulfide ion, S^{2-} (proton number = 16), has 18 electrons. Its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6$, which is the same as argon, the element with 18 electrons in each atom.

Note that, in general, electrons in the outer subshell are removed when metal atoms form the positive ions. However, the d-block elements behave slightly differently. Reading across the Periodic Table from potassium to zinc, the 4 s subshell fills before the 3 d subshell. But when atoms of a d-block element lose electrons to form ions, the 4 s electrons are lost first.

For example:

- Ti atom: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
- Ti^{2+} ion: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$
- Cr atom: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
- Cr^{3+} ion: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

Free Radicals

"A free radical is a species that has one or more unpaired electrons".

For example: Free chlorine atom:

$Cl^\bullet$: The electron configuration of this radical is $1s^2 2s^2 2p^6 3s^2 3p^5$. In the 2p subshell, two orbitals have paired electrons whereas, the third one contains a single unpaired electron. The unpaired electron is shown by a single dot as in $Cl^\bullet$. Apart from single atoms, groups of atoms can also be free radicals. For example, $OH^\bullet$, $CH_3^\bullet$, etc.

QUICK CHECK 2.7

Write electronic configurations for the following ions and free radicals:

i. $Al(Z=13)$ — Ans. $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

ii. $O^{2-}(Z=8)$ — Ans. $1s^2, 2s^2, 2p^6$

iii. $Fe^{3+}(Z=26)$ — Ans. $1s^2, 2s^2, 2p^6, 3s^2, 2p^6, 3d^5$

iv. $Cu^{2+}(Z=29)$ — Ans. $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^9$

v. $Cu(Z=29)$ — Ans. $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$

ELECTRONIC CONFIGURATION AND THE FORMATION OF SEMICONDUCTORS

Semi-Conductors

"The materials whose electrical conductivity lies in between that of conductors and insulators are called semiconductors".

According to number of elements, these are classification into two classes:

(i) Elemental Semiconductors (ii) Compound Semiconductors

Semiconductors are materials that can conduct electricity under some conditions. They are used in many electronic devices, including smartphones, laptops, and cars.

Examples: Silicon, germanium and arsenic etc. The formation of semiconductors is possible because of a unique electronic configuration of these elements.

Silicon as Semiconductor:

Consider the example of Si and explore how it can be converted into a p-type and n-type semiconductors.

The electron configuration of $_{14}Si = 2,8,4$; meaning that it has 4 electrons in its valence shell. In the pure crystalline form, each Si atom is bonded to four other Si atoms. In this form, there is no possibility of electronic conduction through the Si crystal.

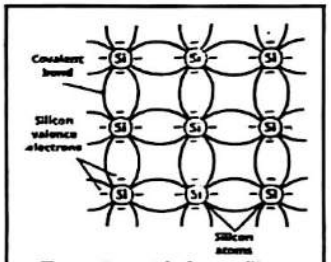


Figure: A crystal of pure silicon

P-type and N-type semiconductors are formed by "doping" a pure semiconductor material with impurity atoms, where adding trivalent impurities (like boron or aluminum) creates a P-type semiconductor, while adding pentavalent impurities (like phosphorus or arsenic) creates an N-type semiconductor.

The difference lies in whether the added impurity creates "holes" (positive charge carriers) in the lattice, leading to P-type, or extra electrons (negative charge carriers) leading to N -type.

P-type Semiconductor Formation

- Impurity atoms with three valence electrons (like Al) are added to the pure semiconductor.
- Some of the trivalent atoms take place of the Si atoms in the crystals.
- The silicon atoms cannot make four bonds due to the lack of electrons.
- For this reason, there are created holes in the crystal lattice, which act as positive charge carriers as shown in Figure.
- This process creates a positive-type semiconductor or N-type semiconductor.
- Electrons from an external current source can move through the semiconductor and it can act as a conductor.

N-type Semiconductor Formation

- When impurity atoms with five valence electrons (like phosphorus) are added to the pure semiconductor, some of Si atoms are replaced with the pentavalent phosphorus atoms.
  The Si atoms in the vicinity of these atoms can make four bonds and the fifth electron is an extra electron.
- These impurity atoms contribute extra electrons to the crystal lattice, which become free to move and act as negative charge carriers as in Figure.
- The result is an N-type semiconductor that can conduct electricity when connected to an external source.

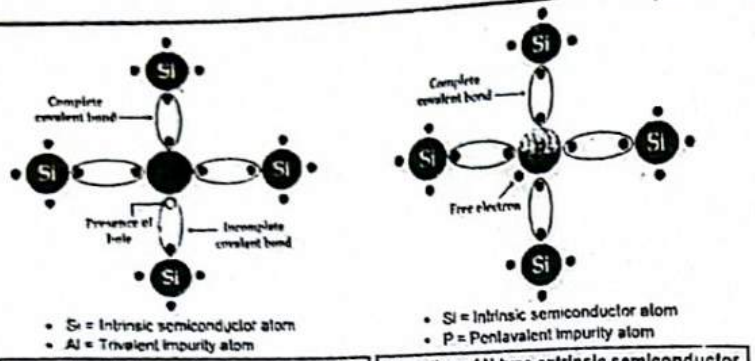


Figure: Doping and the formation of P-type and N-type semiconductor

Solution File — Rock Your Brain!

Sr. #	Option	Explanation
1.	D	P = 6, n = 8, e = 6, ⇒ total = 20 fundamental particles.
2.	S.Q	In the absence of any electric or magnetic field, cathode rays move in straight line perpendicular to the surface of cathode. In 1895, J. Perrin showed that when cathode rays are passed between the poles of the magnet, the cathode rays was deflected which showed that they have charge. In 1897, Sir J.J. Thomson established their electric charge by the application of electric field. The cathode rays deflected towards positive plate showing their negative nature.
3.	C	Quantum number values for '3d' orbital will be n = 3 , $\ell = 2$
4.	D	Quantum number value for 2s orbitals are n = 2, $\ell = 0$
5.	C	The value of $(n + \ell)$ for the 3d sub-shell = 3 + 2 = 5.
6.	B	The value of $(n + \ell)$ for the 5s sub-shell = 5 + 0 = 5.
7.	S.Q	For $\ell = 3$ as $\ell = 3$ and subshell is 'f'. This shows that f-subshell has 7 different ways of orientation in space because it has 7 values of magnetic quantum number When $\ell = 3$, then m = 0, ±1, ±2, ±3 =7 values i. f_{z^3} ii. f_{y^3} iii. f_{x^3} iv. f_{xyz} v. $f_{x^3-y^3}$ vi. $f_{y^2-z^2}$ vii. $f_{x^2-z^2}$
8.	S.Q	The formula for calculating electrons is $2(2\ell + 1)$. When ℓ = 0s-subshell total electrons = 2 ℓ = 1 p-subshell total electrons = 6 ℓ = 2 d-subshell total electrons = 10 ℓ = 3 f-subshell total electrons = 14
9.	S.Q	Element — Electronic Configuration Copper 29(Cu) — $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1\,3d^{10}$ Iodine 53(I) — $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,5p^5$
10.	S.Q	Element — Electronic Configuration Calcium 20(Ca) — $1s^2\,2s^2\,2p^6\,3p^2\,3p^6\,4s^2$ Ceslum 55(Cs) — $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,4d^{10}\,5s^2\,5p^6\,6s^1$

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. The quantum number ' m ' of a free gaseous atom is associated with:
a) the effective volume of the orbital
b) the shape of the orbital
c) the spatial orientation of the orbital
d) the energy of the orbital in the absence of a magnetic field

II. When 3d subshell is completely filled, the next entering electron goes into:
a) 4f b) 4s c) 4p d) 4d

III. Quantum number values for 2p orbitals are:
a) $n=2, \ell=1$ b) $n=1, \ell=2$ c) $n=1, \ell=0$ d) $n=2, \ell=0$

IV. An electron having the set of values: $n=4, \ell=0, m=0$ and $s=+1/2$ lies in:
a) 2s b) 3s c) 4s d) 5s

V. The quantum number values for the fourth electron of $^{9}_{4}Be$ atom are:
a) 1, 0, 0 b) 2, 0, 0 c) 2, 1, 0 d) 1, 1, 1

VI. The correct order of first ionization energies is:
a) F>He>Mg>N>O b) He>F>N>O>Mg c) He>O>F>N>Mg d) N>F>He>O>Mg

VII. A p orbital has a characteristic shape with how many lobes?
a) 1 b) 2 c) 3 d) 4

VIII. The three p orbitals in a given energy level are oriented:
a) Along the same axis.
b) At 45° to each other.
c) Mutually perpendicular to each other along the x, y, and z axes.
d) In a complex tetrahedral arrangement.

IX. How many d orbitals are there in a given energy level?
a) 1 b) 3 c) 5 d) 7

X. What information does the principal quantum number (n) give us about orbitals?
a) Size b) Shape c) Size and shape d) Spin

XI. How many unpaired electrons are present in an atom of cobalt?
a) Two b) Three c) Four d) Five

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	c	the spatial orientation of the orbital	• The magnetic quantum number (m) determines the orientation of an orbital in space (e.g., p_x, p_y, p_z).
II.	c	4p	• After filling 3d, the next electron enters 4p (Aufbau order: 3d → 4p).
III.	a	n = 2, ℓ = 1	• For 2p orbitals: o Principal quantum number (n) = 2. o Azimuthal quantum number (ℓ) = 1 (for p-subshell).
IV.	c	4s	• Quantum numbers n=4, ℓ=0 indicate a 4s orbital (ℓ=0 for s-orbitals).

V.	b	2, 0, 0	• Beryllium (Be, Z = 4): Electron configuration = $1s^2\ 2s^2$. • The 4th electron is in 2s: n=2, ℓ=0, m=0.
VI.	b	He > F > N > O > Mg	• Ionization energy trend: Noble gases (He) > halogens (F) > N > O > metals (Mg). • N > O due to half-filled 2p subshell stability.
VII.	b	2	• A p orbital has two lobes (dumbbell shape) with a nodal plane at the nucleus.
VIII.	c	Mutually perpendicular to each other along the x, y, and z axes	• The three p orbitals (p_x, p_y, p_z) are oriented 90° apart along Cartesian axes.
IX.	c	5	• Each energy level has 5d orbitals (dxy, dxz, dyz, dx^2-y^2, dz^2).
X.	a	Size	The principal quantum number (n) determines the size of an orbital. As the value of n increases, the size of the orbital also increases. The principal quantum number (n) does not determine the shape of an orbital; that's determined by the azimuthal quantum number (l). Spin of orbital is determined by Magnetic quantum number.
XI.	b	Three	Cobalt's atomic number is 27. Its electronic configuration is [Ar] $3d^7\ 4s^2$. According to Hund's rule, the 3d electrons occupy the orbitals with maximum spin multiplicity, resulting in 3 unpaired electrons.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. There are three orientations of p-orbital due to three values of magnetic quantum number. Justify it.

Ans. It is correct. **There are three orientations of the p-orbital due to the three values of the magnetic quantum number (m_l).** Here's the justification in simple scientific terms:

Quantum Numbers:

Each electron in an atom is described by four quantum numbers:

1. **Principal quantum number (n)** – energy level
2. **Azimuthal/angular quantum number (ℓ)** – shape of orbital
3. **Magnetic quantum number (m_l)** – orientation of orbital
4. **Spin quantum number (m_s)** – spin direction of electron

For a p-orbital:

- The azimuthal quantum number (ℓ) = 1
- (Because p-orbitals correspond to ℓ = 1)
- The magnetic quantum number (m_l) can have three values:

$$m\ell = -1, 0, +1 m\ell = -1, 0, +1 m\ell = -1, 0, +1$$

b. 'I_3' of Mg is much bigger than its 'I_2'. Justify.

Ans. The third ionization energy (I_3) of magnesium (Mg) is much bigger than its second ionization energy (I_2). Here's the scientific justification:

- **Ionization energy** is the energy needed to remove one electron from an atom or ion.
- **I_1:** Remove 1st electron
- **I_2:** Remove 2nd electron
- **I_3:** Remove 3rd electron

Electronic Configuration of Magnesium:

Neutral Mg atom:

Mg (Z = 12) = $1s^2\ 2s^2\ 2p^6\ 3s^2$

- **First ionization (I_1)** removes one electron from $3s^2$ → becomes Mg^+
- **Second ionization (I_2)** removes second 3s electron → becomes Mg^{2+}
- **Third ionization (I_3)** would now try to remove an electron from the $2p^6$ (inner, noble gas core)

After removing two outermost 3s electrons, Mg^{2+} has the stable configuration of Neon (Ne):

$$Mg^{2+} = 1s^2\ 2s^2\ 2p^6$$

Now, the third electron to be removed is from a completely filled inner shell (2p), which:

- Is very stable (noble gas configuration)
- Is closer to the nucleus
- Is more strongly attracted by nuclear charge

Hence, much more energy is needed to remove this tightly bound electron.

c. Among the elements Li, K, Ca, S and Kr which one has the lowest first ionization energy? Which has the highest first ionization.

Ans. Ionization Energy Trend Recap:

- **Increases across a period** (left → right) due to increasing nuclear charge.
- **Decreases down a group** (top → bottom) as outer electrons are farther from the nucleus and more shielded.

Element	Group	Period	Electron Configuration	Notes
Li (Lithium)	1	2	$1s^2\ 2s^1$	Alkali metal (low IE)
K (Potassium)	1	4	[Ar] $4s^1$	Lower IE than Li (further down)
Ca (Calcium)	2	4	[Ar] $4s^2$	Slightly higher IE than K
S (Sulphur)	16	3	[Ne] $3s^2\ 3p^4$	Nonmetal (higher IE)
Kr (Krypton)	18	4	[Ar] $3d^{10}\ 4s^2\ 4p^6$	Noble gas (very high IE)

- **Lowest first ionization energy = Potassium (K)**
- **Reason:** It's a Group 1 element in Period 4 → outermost electron is loosely held and easily removed.
- **Highest first ionization energy = Krypton (Kr)**
- **Reason:** Noble gas with a full outer shell → very stable → requires lots of energy to remove an electron.

d. Consider the electronic configuration of the potassium atom (atomic number 19).

Ans. Element: Potassium (K)

Atomic Number: 19

So it has 19 electrons.

Electronic Configuration:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

(i) Write the full electronic configuration of potassium using the s, p, d, f notation.

Ans. Element: Potassium (K)

Atomic Number: 19

So it has 19 electrons.

Electronic Configuration:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

(ii) Explain why the 4s subshell is filled before the 3d subshell in potassium, even though the principal quantum number of the 3d subshell is lower.

Ans. Even though:

- 3d has a lower principal quantum number (n = 3)
- 4s has a higher principal quantum number (n = 4)

The 4s subshell has *lower energy* than 3d at the time potassium's electrons are being placed.

Key Principles:

1. **Aufbau Principle**
   Electrons fill orbitals in order of increasing energy, not just by n value. According to the Aufbau (building-up) principle:
   $$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p$$
   As you can see, **4s comes before 3d**.
2. **Energy Level Overlap**
   - 4s orbital is farther from the nucleus but has less electron-electron repulsion, making it lower in energy than 3d.
   - So, the first 19 electrons (in potassium) go into the 4s before starting to fill 3d.

Potassium (Z = 19):

- **Configuration:** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
- The 3d subshell remains empty in potassium because it's higher in energy at this point.

Conclusion:

The 4s subshell is filled before 3d in potassium because, despite having a higher principal quantum number, it is lower in energy at the point when electrons are added, following the Aufbau principle.

e.(i) An atom of element X has an atomic number of 17 and a mass number of 35. Determine the number of protons, neutrons, and electrons in this atom.

Ans. Number of Protons = Atomic Number
Protons = 17
Number of Neutrons = Mass Number – Atomic Number
Neutrons = 18
Number of Electrons = Number of Protons (in a neutral atom)
Electrons = 17

(ii) If this element forms an ion with a charge of –1, how many protons, neutrons, and electrons will be present in the ion?

Ans. X element has:

- Atomic number = 17
- Mass number = 35

We previously identified it as chlorine (Cl).
Now, let's consider the Cl^- ion (chloride ion), which has a -1 charge.

Protons

- The number of protons never changes, even when forming ions.

Protons = 17

Neutrons

- Mass number = 35, Atomic number = 17

Neutrons = 18

Electrons (for Cl^- ion)

- Neutral chlorine atom has 17 electrons
- A –1 charge means it has gained one extra electron

Electrons = 17+1 = 18

f. In the ground state of mercury $_{80}Hg$:

Ans. In the **ground state of mercury (Hg)**, which has an atomic number of 80, we can determine several important features of the atom, such as its **electron configuration**, and the number of **protons, neutrons, and electrons.**

Basic Information for Mercury (Hg):

- **Symbol:** Hg
- **Atomic number (Z):** 80 → Protons = 80, Electrons = 80 (in a neutral atom)
- **Mass number** (most common isotope): 200 → So, Neutrons = 200 – 80 = 120

Ground-State Electron Configuration:

Mercury is a **transition metal**, and its full electron configuration is:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}$$

In noble gas short hand:

$$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2$$

i. How many electrons occupy atomic orbitals with n = 3?

Ans. Electrons can occupy atomic orbitals where the **principal quantum number n = 3n = 3n = 3.**

For **n = 3n = 3n = 3**, the possible **subshells** (values of ℓ) are:

- $\ell = 0$\ell = 0 ℓ=0 → 3s
- $\ell = 1$\ell = 1 ℓ=1 → 3p
- $\ell = 2$\ell = 2 ℓ=2 → 3d

Each subshell has a certain number of **orbitals**, and each orbital holds **2 electrons**:

Subshell	Orbitals	Electrons
3s	1	2
3p	3	6
3d	5	10

Total electrons when n = 3n = 3n = 3:

2 (3s) + 6 (3p) + 10 (3d) = 18 electrons

So, **18 electrons** can occupy atomic orbitals with **principal quantum number n = 3n = 3n = 3.**

ii. How many electrons occupy 4d atomic orbitals?

Ans. The 4d atomic orbitals can hold a maximum of 10 electrons. This is because the 4d subshell consists of 5 orbitals (each orbital can hold a maximum of 2 electrons), so 5 orbitals × 2 electrons = 10 electrons in total.

iii. How many electrons occupy $4p_z$ atomic orbital?

Ans. The 4pz atomic orbital can hold a maximum of 2 electrons. Each atomic orbital, including the 4pz orbital, can accommodate up to 2 electrons, with each electron having opposite spins.

iv. How many electrons in the valence shell have spin "up" ($s = -\frac{1}{2}$)?

Ans. In an atomic orbital, each electron can have one of two possible spins: "up" (denoted as $s = +\frac{1}{2}$) or "down" (denoted as $s = -\frac{1}{2}$).

If you are asking how many electrons have a spin of $s = -\frac{1}{2}$ in a particular orbital, it depends on how many electrons are present in that orbital. For example:

- In a single atomic orbital (such as the 4pz orbital), a maximum of 2 electrons can occupy it, one with spin $+\frac{1}{2}$ and one with spin $-\frac{1}{2}$.
- If there are multiple orbitals (such as in a subshell like the 4d or 4p), the electrons will fill the orbitals according to the Pauli exclusion principle, with one electron having spin $+\frac{1}{2}$ $+\frac{1}{2}$ $+\frac{1}{2}$ and the other having spin $-\frac{1}{2}$ in each orbital.

So, in general, half of the electrons in any set of orbitals would have spin $s = -\frac{1}{2}$, assuming the electrons are paired and fill orbitals according to Hund's rule and the Pauli exclusion principle.

Conclusion: 80 electrons in total and thus 40 orbitals in Hg.

g. The successive ionization energies for an unknown element are

$I_1 = 896$ kJ / mol $I_2 = 1752$ kJ / mol

$I_3 = 14,807$ kJ / mol $I_4 = 17,948$ kJ / mol

To which family in the periodic table, does the unknown element most likely belong?

Ans. As there is greatest difference between 2nd and 3rd ionization energies, it means this element belongs to group 2A (Alkaline Earth's metal).

i. Consider the following ionization energies for aluminum:

$Al_{(g)} \longrightarrow Al^{+}_{(g)} + e^{-}$ $I_1 = 580$ kJ / mol

$Al^{+}_{(g)} \longrightarrow Al^{2+}_{(g)} + e^{-}$ $I_2 = 1815$ kJ / mol

$Al^{2+}_{(g)} \longrightarrow Al^{3+}_{(g)} + e^{-}$ $I_3 = 2740$ kJ / mol

$Al^{3+}_{(g)} \longrightarrow Al^{4+}_{(g)} + e^{-}$ $I_4 = 11,600$ kJ / mol

(i) Account for the trend in the values of the ionization energies.

(ii) Explain the large increase between I_3 and I_4.

(iii) List the four aluminum ions given in order of increasing size, and explain your ordering.

Ans.

(i) $I_4 > I_3 > I_2 > I_1$

(ii) As there is greatest difference between 3rd and 4th ionization energies, it means this element belongs to group 3A (Boron family).

(iii) After loosing 3rd electron, Aluminium gets stable electronic configuration of noble gas.

$$\underset{2,8,3}{Al} \longrightarrow \underset{2,8}{Al^{3+}} + 3e^{-}$$

$$\underset{13p\ 9e^{-}}{Al^{4+}}\ (\underset{13p\ 10e^{-}}{Al^{3+}}\ (\underset{13p\ 11e^{-}}{Al^{2+}}\ (\underset{13p\ 12e^{-}}{Al^{1+}}$$

In Al^{+1} there are 13 protons and 12 electrons so, control of nucleus is lesser on outer electrons so its size is greatest among above.

In Al^{+4} there are 13 protons and 9 electrons, there is more imbalance between proton to electron ratio so, control of nucleus is greatest and its size is the least among above.

h. (i) State the general order of filling orbitals up to the 4p subshell.

(ii) Explain why the 4s subshell is filled before the 3d subshell, according to the Aufbau principle.

Ans. (i) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$

(ii) The 4s subshell is filled before the 3d subshell according to the Aufbau principle because the 4s orbital is lower in energy than the 3d orbital when these orbitals are empty or partially filled in neutral atoms.

1. **Energy Considerations:**
   - Even though 4s has a higher principal quantum number (n = 4) than 3d (n = 3), the energy of an orbital depends on both the principal quantum number n and the azimuthal quantum number ℓ.
   - *For 4s:* $n = 4$, $\ell = 0$, so $n + \ell = 4$
   - *For 3d:* $n = 3$, $\ell = 2$, so $n + \ell = 5$

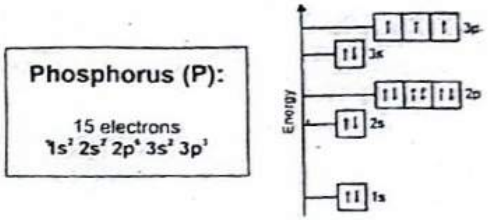
- According to the $(n + \ell)$ rule (used in the Aufbau principle), orbitals with a lower $n + \ell$ value are filled first.

2. **Electron Shielding and Penetration:**
   - The 4s orbital penetrates closer to the nucleus and experiences less shielding than the 3d orbital.
   - As a result, electrons in the 4s orbital are more tightly held and thus occupy a lower energy level initially.

However, once electrons are added to the 3d subshell, the energy levels shift slightly. In ions of transition metals, for example, the 4s electrons are usually lost before the 3d electrons, because the 4s orbital becomes higher in energy after the 3d subshell is filled or partially filled.

i. Draw the orbital box diagram for the valence electrons of a phosphorus atom (atomic number 15), ensuring that your diagram adheres to Hund's rule and the Pauli Exclusion Principle.

Ans.



DESCRIPTIVE QUESTIONS

Q.3 What are quantum numbers? Describe briefly principal and spin quantum numbers.

Ans. See Page No. (36)

Q.4 Draw the shapes of s, p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

Ans. See Page No. (36)

Q.5 What do you mean by successive ionization energies? How the electronic shell structure of magnesium (Mg) is derived from the successive ionization energies?

Ans. See Page No. (33)

ADDITIONAL SLOs BASED MCQs

1. **What does the electron configuration $1S^2 2S^2 2P^6$ represent?**
   A. Carbon (C) B. Oxygen (O) C. Neon (Ne) D. Helium (He)
2. **Which subshell can hold a maximum of 10 electrons?**
   A. s B. p C. d D. f
3. **How many unpaired electrons are there in the electron configuration d^5?**
   A. 0 B. 1 C. 2 D. 5
4. **Which element has the electron configuration $s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$?**
   A. Iron (Fe) B. Zinc (Zn) C. Nickel (Ni) D. Copper (Cu)
5. **What is the electron configuration of a chlorine ion (Cl^-)?**
   A. $1s^2 2s^2 2p^6 3s^2 3p^6$ B. $1s^2 2s^2 2p^6 3s^2 3p^5$ C. $1s^2 2s^2 2p^6 3s^2 3p^7$ D. $1s^2 2s^2 2p^6 3s^2 3p^8$
6. **As we move away from nucleus the distance between the adjacent orbits goes on:**
   A. Increasing B. Decreasing
   C. Remains same D. May increase or decrease

7. Which of the following has the same number of electrons as that of α-particles:
A. Li^+ B. H^+ C. He^+ D. Be^{+2}

8. Which of the following orders with respect to relative energy is incorrect:
A. 2s < 2p B. 2p < 3p C. 3p < 3d D. 4d < 3s

9. After filling the 4s orbital the entering electron goes into:
A. 4p B. 3s C. 3d D. 4f

10. Which of the following particles contains 20 neutrons, 19 protons and 18-electrons?
A. $^{39}_{19}K^+$ B. $^{39}_{19}K$ C. $^{40}_{18}Ar$ D. $^{37}_{20}Ca$

11. Which of the following has maximum number of unpaired electrons?
A. Fe^{+3} B. Zn^{+2} C. Ni^{+2} D. Cu^+

12. According to (n + l) rule. Which one of the following has the highest energy?
A. 2s B. 3s C. 3p D. 2p

13. How many unpaired electrons are in the 3d sub-shells of an element with an Z = 24?
A. 2 B. 3 C. 4 D. 5

14. With increase in the value of principal quantum number 'n' the shapes of the s-orbital remain same although their sizes.
A. Increase B. Decrease
C. Remain the same D. May or may remain the same

15. The correct order of sub-shells, within a shell w.r.t decreasing energy is:
A. f > d > s > p B. f > d > p > s C. s > p > d > f D. p > s > f > d

Answer Key with Explanations

Sr.No.	Option	Explanations
1.	C	The electron configuration $1s^2\ 2s^2\ 2p^6$ corresponds to a total of 10 electrons, which is the electron configuration of Neon (Ne), a noble gas.
2.	C	The d subshell can hold a maximum of 10 electrons, as it has five orbitals, with each orbital capable of holding two electrons.
3.	D	The electron configuration $3d^5$ indicates five electrons in the d subshell. According to Hund's rule, each of these five electrons will occupy a separate orbital in the d subshell, resulting in five unpaired electrons.
4.	C	The electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$ corresponds to Nickel (Ni). The total 28 number of electrons, which shows the atomic number of Nickel.
5.	A	A chlorine ion (Cl^-) has gained one extra electron compared to the neutral chlorine atom, resulting in a full p orbital. The electron configuration of Cl^- thus becomes $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.
6.	A	Distance between shell can be calculated by $0.529n^2A°$ $r_1 = 0.529A°$ $r_1 = 2.11A°$ so Distance $r_3 = 4.761A°$ b/w consectutive $r_4 = 8.4A°$ shell is increasing continenusely $r_2 - r_1 < r_3 - r_2 < r_4 - r_3$
7.	B	α-particle similarly H^+ also having no $\bar{e}$.
8.	D	According to $n + \ell$ rule 4d < 3s 4 + 2 < 3 + 0 6 < 3 Incorrect order
9.	C	According to $n + \ell$ rule after $4s \Rightarrow 4 + 0 = 4$ Entering $\bar{e}$ goes into $3d \Rightarrow 3 + 2 = 5$
10.	A	Among the following potassium contain 20 neutrons, 19 protons and 18-electrons.

11.	A	$Fe^{+3} = 1s^2, 2s^2, 2P^6, 3s^2, 3P^6, 3d^5, 4s^0$ – 5 unpaired $\bar{e}$ in 3d $Ni^{+2} = 1s^2, 2s^2, 2P^6, 3s^2, 3P^6, 3d^8, 4s^0$ – 2 unpaired $\bar{e}$ in 3d $Cu^{+1} = 1s^2, 2s^2, 2P^6, 3s^2, 3P^6, 3d^{10}, 4s^0$ – no unpaired $\bar{e}$ in 3d $Zn^{+2} = 1s^2, 2s^2, 2P^6, 3s^2, 3P^6, 3d^{10}, 4s^0$ – no unpaired $\bar{e}$ in 3d
12.	C	2s = 2 + 0 = 2 3s = 3 + 0 = 3 3p = 3 + 1 = 4 2p = 2 + 1 = 3 Highest $(n + \ell)$ value is for 3P
13.	D	Z = 24 is Cr, $Cr_{24} = 1s^2, 2s^2, 2P^6, 3s^2, 3P^6, 3d^5, 4s^1$
14.	A	With the increase n value (principal quantum number), the size of s-orbital increases where as the shape remains the same. e.g. the size of 2s-orbital is greater than 1s-orbital. 1s 2s
15.	B.	The correct order of sub-shells, within a shell w.r.t decreasing energy is f > d > p > s.

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 According to Moseley, the atomic number Z was a fundamental property of an element. How?

Ans. In 1913, Moseley v observed that when different elements were bombarded with cathode rays, the X-rays of some characteristic frequencies were produced. It was found that the square root of the frequency of the X-rays was directly proportional to the atomic number of an element Z.

$\sqrt{\text{frequency}}$ (v) α Z

He concluded that this number, i.e. the atomic number Z was a fundamental property of an element.

Q.2 What is effect of electric field on the fundamental particles?

Ans. The behaviour of particles in an electric field depends upon their mass and charge. They show their behaviour as follows.

- Neutrons being neutral are not deflected but travel in a straight path perpendicular to the direction of electric field.
- Protons being positively charged are deflected towards the negative plate.
- Electrons being negatively charged are deflected towards the positive plate.

Q.3 Differentiate between atomic spectra and atomic absorption spectrum.

Ans.

Atomic emission spectrum	Atomic absorption spectrum
When an element in its gaseous state is heated to high temperatures or subjected to electrical discharge, radiation of certain wavelengths is emitted. The spectrum of this radiation contains coloured lines and is called atomic emission spectrum.	When a beam of white light is passed through a gaseous sample of an element in cold state, certain wavelengths are absorbed. The wavelengths of the white light that has been absorbed by the atoms show up as dark lines on the spectrum. The spectrum of this radiation is called an atomic absorption spectrum.

Q.4 What is the trend of Ionization energy in the periodic table?

Ans.

- As we go down a particular group, ionization energies decrease. The larger the atom, the easier is to separate an electron from it. Actually, down the group, number of shells increases, hold of nucleus on the valence electrons decreases, hence removal of electrons becomes easier.

- The ionization energies generally increase on going across a period. It is due to the reason that across the period shell number remains same. As the proton number increases, electrons are added in the same shell. Therefore, nucleus attracts the valence electrons more strongly. As a result, ionization energy increases across the period.

Q.5 Differentiate between shell and subshell.

Ans.

Shell	Subshell
• The collection of orbitals with the same values of n is called an electron shell • It is denoted by n.	• The set of orbitals that have the same n and ℓ values is called a **subshell.** • They are denoted by s,p,d and f.

Q.6 Define electronic configuration and give example.

Ans. Electronic configuration is the distribution of electrons among available shells, subshells, or orbitals of an atom or ion.
Example: the electronic configuration beryllium is given below,
$_5B = 1s^2, 2s^2, 2px^1, 2py^0, 2pz^0$

Q.7 State Hund's rule and Puali's exclusion principle.

Ans. **Hund's rule:** When degenerate orbitals are available and more than two electrons are to be placed in them, they should be placed in separate orbitals with the same spin rather than in the same orbital with opposite spins.
Puali's exclusion principle: According to this principle. No two electrons in an atom can have the same values for all the four quantum numbers or, "Two electrons in an orbital will always have opposite spins".

Q.8 Write the classification of the periodic table on the basis of electronic configuration.

Ans. The classification of elements of periodic table has been done into metals, non-metals, representative, transition elements, periods, groups and blocks (s, p, d, f). This division is done on the basis of electronic configuration and their valence electrons. The chemical properties of various categories of elements discussed above can be easily assessed.

Q.9 Write the electronic configuration of ions with examples.

Ans. **Positive ions** are formed when electrons are removed from atoms. The sodium ion, Na^+ (proton number = 11), has 10 electrons. So, its electronic configuration is $1s^2\ 2s^2\ 2p^6$.
Negative ions are formed when atoms gain electrons. The sulfide ion, S^{2-} (proton number = 16), has 18 electrons. Its electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$, which is the same as argon, the element with 18 electrons in each atom.

Q.10 What is the trend of ionization energy in the periodic table?

Ans. "A free radical is a species that has one or more unpaired electrons".
An example of a simple free radical is free chlorine atom $:\dot{C}l:$. The electron configuration of this radical is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$. In the 2p subshell, two orbitals have paired electrons whereas, the third one contains a single unpaired electron. The unpaired electron is shown by a single dot as in Cl.

Q.11 What is the trend of ionization energy in the periodic table?

Ans.

Property	p-type Semiconductor	n-type Semiconductor
Doping Element	Trivalent (like, Boron, Aluminium).	Pentavalent (like, Phosphorus, Arsenic).
Charge Carriers	Holes	Electrons
Type of Conduction	Mainly due to holes.	Mainly due to electrons.
Electrons in Conduction Band	Few	Many
Effect of Doping	It creates more holes.	Increases free electrons
Example	Positive side of a diode (anode).	Negative side of a diode (cathode).

SELF-ASSESSMENT Chapter # 02

Total Mark: 30

Q.1 Encircle the correct option. **(1 × 6 = 6)**

(i) When 3d subshell is completely filled, the next entering electron goes into:
A. 4f B. 4s C. 4p D. 4d

(ii) What is the shape of a p-orbital?
A. Spherical B. Dumbbell C. Circular D. Vertical

(iii) Quantum number values for 2p orbitals are:
A. $n = 2, \ell = 1$ B. $n = 1, \ell = 2$ C. $n = 1, \ell = 0$ D. $n = 2, \ell = 0$

(iv) Which principle states that electrons fill the lowest energy orbitals first?
A. Pauli's exclusion principle B. Hund's rule
C. Aufbau principle D. Heisenberg principle

(v) Which of the following species has a zero bond order according to MOT?
A. H_2^{1+} B. He_2^{1+} C. He_2^{2+} D. He_2

(vi) The number of protons, electrons, and neutrons in Na^+ are:
A. 11p, 11e, 12n B. 11p, 10e, 12n C. 11p, 12e, 11n D. 10p, 11e, 12n

Q.2 Write short answers of the following questions. **(2 × 8 = 16)**

(i) Size of Mg is bigger than Al, but ionization energy of Mg is more than that of Al. Why?
(ii) Define atomic number and how is it related to proton number?
(iii) How does ionic radius change compared to atomic radius in metals and nonmetals?
(iv) Define principal quantum number and orbital.
(v) Write the electronic configuration of Mg (Z = 12) using sub-shell notation.
(vi) Define degenerate orbitals.
(vii) Apply Hund's rule to explain why nitrogen has three unpaired electrons.
(viii) Write the behavior of protons and electrons in an electric field.

Q.3 Extensive Questions. **(2 × 4 = 8)**

(a) What are quantum numbers? Describe briefly principal and spin quantum numbers.
(b) Draw the shapes of s, p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

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Chapter 03

CHEMICAL BONDING

Student Learning Outcomes

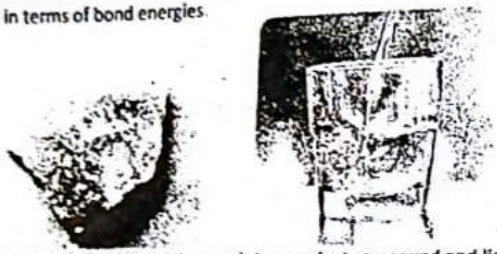
After studying this chapter, students will be able to:

- Analyze the formation of dative bond in CO, ozone and H_3O^+ ion (resonance structures are not required). **(Understanding)**
- Recognize that molecular ions/polyatomic ions can have expanded octets e.g., sulphate and nitrate. **(Understanding)**
- Use the differences in Pauling electronegativity values to predict the formation of ionic and covalent bonds. **(Application)**
- Use the concept of electronegativity to explain **bond polarity and dipole moments** of molecules. **(Understanding)**
- Explain the importance of **VSEPR theory in the field** of drug design by discussing how the shape and bond angles of the molecules help chemist predict their interactions in the body. **(Understanding)**
- Describe the shapes and bond angles in molecules using VSEPR theory (including describing sketching). **(Understanding)**
- Explain valence bond theory. **(Understanding)**
- Predict the shapes, and bond angles in molecules and ions. **(Understanding)**
- Describe covalent bonding in molecules using the concept of hybridization to describe sp, sp^2, and sp^3 orbitals. **(Understanding)**
- Explain hybridization and types of **hybridization**. **(Understanding)**
- Explain the salient features of molecular orbital theory (MOT). **(Understanding)**
- Explain the paramagnetic nature of oxygen molecule in the light of MOT. **(Understanding)**
- Calculate bond order of N_2, O_2, F_2, and He_2. **(Understanding)**
- Describe the types of van der Waals forces. **(Understanding)**
- Describe hydrogen bonding limited to molecules including ammonia and water. **(Understanding)**
- Use the concept of hydrogen bonding to explain the anomalous properties of water. **(Understanding)**
- Use bond energy values and the concept of bond length to compare the reactivity of covalent molecules. **(Application)**
- State that, in general, ionic, covalent, and metallic bonding are stronger than intermolecular forces. **(Understanding)**
- Define electronegativity as the power of an atom to attract electrons to itself. **(Knowledge)**
- Explain the factors influencing the electronegativities of elements in terms of nuclear charge, shielding by inner shells and subshells. **(Understanding)**
- Explain the trends in electronegativity across a period and down a group of the periodic table. **(Understanding)**

Chemical Bond

"A chemical bond is the force that holds together two or more atoms, molecules or ions"

- The properties of a substance depend on the type of the chemical bond between its atoms.
- The term chemical bond includes ionic, covalent, dative, metallic bonds, as well as intermolecular forces, i.e. van der Waals forces. However, being weak enough, van der Waals forces are usually not termed as pure chemical bonds.
- We shall discuss the types of bonds in the light of electronegativity and its effect on the nature of bonding, dipole moment, and polarity. Then, the modern bonding theories such as VSEPR, VBT, Hybridization, and MOT will be discussed in detail. The intermolecular forces, i.e. van der Waals forces will also be taken into account. Finally, a comparison of the chemical bonds and intermolecular forces will be presented in terms of bond energies.



NaCℓ has ionic bond and is solid, but water is a covalent compound and liquid

TYPES OF BONDING

Lewis concept of bonding gives a simple explanation of the formation of all types of bonds. According to this theory, atoms make bonds to complete their outermost shells to have noble gas-like configuration. This is mostly attained through the formation of an octet in the valence shell.

Ionic Bond

According to the Lewis theory, the ***ionic bond is formed by the complete transfer of electrons from an atom with low ionization energy to another atom with high electron affinity.***

- The Na atom ($_{11}$Na=2,8,1) tends to lose the outermost electron to form Na^+(2,8) ion, which has the electronic configuration of $_{10}$Ne, a noble gas nearest to it. Chlorine atom Cℓ(2,8,7) gains one electron to form the chloride ion, $Cℓ^-$(2,8,8), also gaining the next noble gas electron arrangement. The oppositely charged Na^+ and $Cℓ^-$ ions are held together by strong ionic bond in the crystal of NaCℓ.
- A similar type of bond is expected between group land 2 metals and groups 16 and 17 elements.

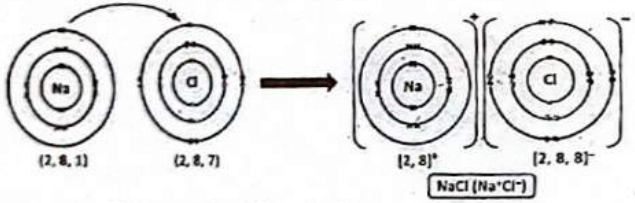


Figure: Ionic bond formation between Na and Cℓ

Covalent Bond (Electron Pair Bond)

- ***A covalent bond is formed by the mutual sharing of electrons between two atoms.***
- While sharing electrons, each atom completes its valence shell and attains the nearest noble gas configuration. The bond formation between two Cℓ atoms is shown below (Fig.).

- A covalent bond may be:
  (i) Non-polar in character (ii) Polar in character.
- The bond between two Cℓ atoms is purely covalent and non-polar. The electronegativity of the two atoms is exactly the same, due to which, the bonded atoms remain electrically neutral and there is no charge on either atom. The other such molecules are H_2, F_2, Br_2 and I_2.
- **Examples of polar covalent bonds:** H–Cℓ, H–Br, H_2O, etc.

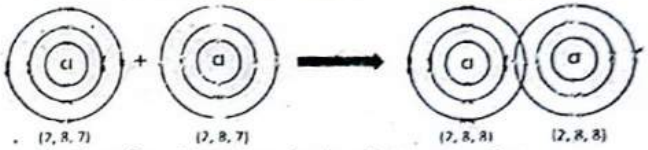


Figure: formation of a covalent bond between two Cℓ atoms

Rock Your Brain!

1. The bond which is formed by mutual sharing of electrons is called:
   (A) Ionic bond
   (B) Covalent bond
   (C) Metallic bond
   (D) Coordinate Covalent bond

Dative bond (Coordinate Covalent Bond)

Definition:

"A dative bond is formed between two atoms when the shared pair of electrons is donated by one of the bonding atoms".

Examples:

Rock Your Brain!

2. Justify that Covalent Bonds is directional in nature.

(a) Hydronium Ion

Let us consider the example of bond formation between H_2O and a proton (H^+).

- H_2O has two covalent bonds and there are two lone pairs of electrons on the oxygen atom.
- On the other hand, the proton is deficient in electrons. Therefore, the oxygen atom can donate its lone pair of electrons to the acceptor H^+, and this results in the formation of a dative bond as in the following diagram Figure (a).

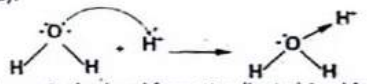
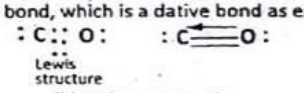


Figure : Dative bond formation (hydronium) ion.

(b) Carbon Monoxide

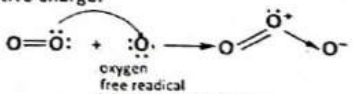
- Carbon monoxide also contains a dative bond between oxygen and carbon atoms.
- Oxygen shares its two valence shell electrons with the carbon atom to make normal double covalent bond. However, the valency of carbon is not satisfied with these bonds.
- It needs one more pair of electrons to complete its octet. Oxygen atom donates one of its lone pairs for the formation of a covalent bond, which is a dative bond as exhibited in Figure (b).



(b) Carbon monoxide

(c) Ozone Molecule

- The structure of ozone molecule is presented in Figure (c).
- It is formed by a reaction between the oxygen molecule with an oxygen atom (a free radical (O)).
- One of the oxygen atoms in the molecule donates a pair of electrons to make a coordinate covalent bond with this free radical.
- Therefore, the central atom has total three bonds including a double covalent bond on one side and a coordinate covalent bond on the other. It carries a positive charge, while the oxygen atom that accepts the lone pair carries a negative charge.



(c) ozone molecule

QUICK CHECK 3.1

a) Draw the Lewis structures of N_2 and CS_2 molecules?

Ans. N_2: :N≡N:

CS_2: :S: :C: :S:

b) How many electrons are there in the valence shell of B in BF_3? Does it have the ability to accept a lone pair of electrons?

Ans. In BF_3, the boron (B) atom has:

- 3 valence electrons (Group 13 element).
- Forms 3 bonds with fluorine (F), using all valence electrons (no lone pairs).

Ability to Accept Lone Pair:

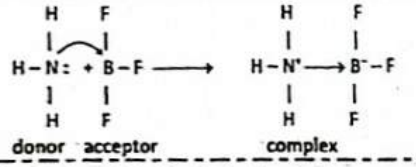
- Boron's valence shell has only 6 electrons (incomplete octet).
- Yes, it can act as a Lewis acid by accepting a lone pair (e.g., forming BF_4^- with F^-).

In short:

- Valence electrons in BF_3: 3 (all bonded).
- Electron-deficient, accepts lone pairs to complete octet.

c) Show the formation of a dative bond between NH_3 and BF_3.

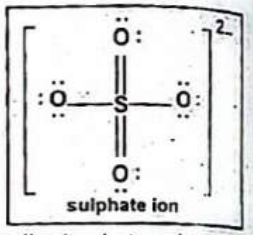
Ans.



Expanded Octet in Polyatomic Ions

Polyatomic ions are the ions composed of more than one type of atoms.

- There formal charge is the net charge on them which is calculated based on the number of electrons in their valence shells after the formation of bonds.
- With the exception of ammonium ion (NH_4^+), these ions mostly carry a negative charge, for example the carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), and nitrate (NO_3^-) ions.

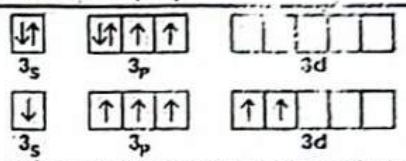


- In some polyatomic ions, the central atom violates the octet rule by expanding its electron density to the higher orbitals. These are said to have expanded octets.
- Examples: SO_4^{2-}, ClO_4^-, PO_4^{3-}.

Octet Rule:
The tendency of atoms to attain a maximum of eight electrons in the valence shell is known as the octet rule.

Sulphate SO_4^{2-}:

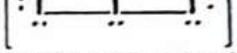
- From the Lewis structures of SO_4^{2-}, we can calculate the number of electrons around the central S atom.
- The number of electrons in the valence shell of S atom can be calculated as:
- No. of valence electrons= 2 × (double bond electrons) + 2 × (single bond electrons)
  = 2(4) + 2(2) = 12
- Thus, S has 12 electrons in its valence shell and it exceeds the octet by 4 electrons.
- The expansion of octet is caused by the involvement of the d orbital in bonding, which can accommodate the extra electrons. The following electronic configuration of native S(0) atom shows that it has two unpaired electrons in the p orbitals. The presence of d-orbital allows this configuration to extend to 4 unpaired electrons by the transfer of one electron from the 3 p pair. It explains not only the variable oxidation states of S, but also the possibility of accepting extra electrons in its d orbital.



Rack Your Brain!

3. Octet rule is not followed in:
(A) CH_4 (B) CF_4
(C) CCl_4 (D) PCl_5

In the same way, we can calculate the number of valence electrons around the central iodine atom in the tri-iodide ion. The Lewis structure of the tri-iodide ion (I_3^-) is given by:



The number of valence electrons of the central atom can be calculated as follows:

No. of valence electrons = 2 × (no. of single bond electrons) + 2 × (no. of lone pairs)
= 2(2) + 2(3)
= 10

The central iodine atom in tri-iodide ion (I_3^-) has 10 electrons in the valence shell and the octet expands by two electrons.

QUICK CHECK 3.2

a) Can the elements of period 2 of the periodic table have expanded octet? Explain why or why not?

Ans. No, elements of Period 2 cannot have expanded octets because they lack the necessary orbitals to accommodate more than 8 electrons in their valence shell.

Detailed Explanation:

What is an "Expanded Octet"?

- An expanded octet refers to a situation where an atom has **more than 8 electrons in its valence shell**
- This is possible only if the atom has access to empty d orbitals, which can be used to hold extra electrons beyond the typical s and p orbitals.

Electron Configuration of Period 2 Elements

Period 2 elements include:

Lithium (Li), Beryllium (Be), Boron (B), Carbon (C), Nitrogen (N), Oxygen (O), Fluorine (F), Neon (Ne)

- These elements have valence electrons in the second energy level (n = 2).
- The second energy level has the following orbitals:
  2s (1 orbital)
  2p (3 orbitals)
- Total: 4 orbitals → can hold a maximum of 8 electrons (4 × 2 electrons)

No d orbitals in Period 2

- d orbitals first appear in the 3rd period (n = 3).
- Since Period 2 elements don't have 3d orbitals, they are limited to the 2s and 2p orbitals only.
- Therefore, they cannot accommodate more than 8 electrons in their outer shell.

Examples:

Element	Normal Valency	Can it Expand Octet?	Why/Why Not?
Carbon (C)	4	No	$2s^2\ 2p^2$ → Max 8e⁻
Nitrogen (N)	3	No	$2s^2\ 2p^3$ → No d orbitals
Oxygen (O)	2	No	$2s^2\ 2p^4$ → Octet only
Fluorine (F)	1	No	$2s^2\ 2p^5$ → Can't exceed octet

Contrast with Period 3 and Beyond

- Starting from Period 3, elements like phosphorus (P), sulfur (S), chlorine (Cl) have access to 3d orbitals.
- This allows them to have expanded octets.

Examples:

- **Phosphorus pentachloride (PCl_5):** P has 10 electrons in its valence shell.
- **Sulfur hexafluoride (SF_6):** S has 12 electrons in its valence shell.

Summary:

Feature	Period 2 Elements
Valence shell	n = 2
Available orbitals	2s, 2p (no d orbitals)
Maximum valence electrons	8
Expanded octet possible?	No

Conclusion:

Elements of **Period 2** (like **C, N, O, and F**) **cannot have expanded octets** because:

- They **lack low-energy d orbitals** in their valence shell.
- They are limited to **the s and p orbitals only**, which hold **a maximum of 8 electrons.**
- Therefore, they follow the **octet rule strictly**, unlike elements in Period 3 and beyond.

b) Predict and explain the expanded octets in the following ions: ClO_3^-, PO_4^{3-}.

Ans. Great! Let's analyze the possibility of **expanded octets** in the following polyatomic ions:

- **ClO_3^-** (chlorate ion)
- **PO_4^{3-}** (phosphate ion)

We'll determine **whether the central atom uses an expanded octet and why.**

1. ClO_3^- (Chlorate Ion)

Step 1: Total Valence Electrons

- Cl: 7 valence electrons
- O: 3 × 6 = 18
- Charge: −1 → add 1 electron

Total = 7 + 18 + 1 = 26 electrons

Step 2: Skeleton Structure

- Central atom: **Cl**
- 3 oxygens around **Cl**
- Single bonds to each O (initially)

Step 3: Expanded Octet?

- If Cl only used 8 electrons (octet), it couldn't form stable structures with enough resonance. But:
- **To account for resonance and formal charges**, it's often shown with **one double bond** to one O and two single bonds to the other O's.
- This means chlorine has **10 electrons** around it (2 double-bond electrons + 2 × 2 single-bond electrons = 6 bonding pairs = 12 e^-).

Yes, chlorine can have an **expanded octet.**

Why Expanded Octet is Possible:

- **Chlorine is in Period 3 → has access to 3d orbitals**
- Can accommodate more than 8 electrons in valence shell

Conclusion:

Cl in ClO_3^- exhibits an expanded octet to minimize formal charges and form resonance-stabilized structures.

2. PO_4^{3-} (Phosphate Ion)

Step 1: Total Valence Electrons

- P: 5 valence electrons
- O: 4 × 6 = 24
- Charge: −3 → add 3 electrons

Total = 5 + 24 + 3 = 32 electrons

Step 2: Skeleton Structure

- Central atom: P
- 4 single bonds to O atoms
- Remaining electrons go on the oxygens as lone pairs

Step 3: Expanded Octet?

- In basic Lewis structures, phosphorus forms 4 single bonds to oxygen (8 bonding electrons).
- However, more resonance-stabilized forms can be drawn where one P=O double bond exists, leading to 10 electrons around phosphorus.

Yes, phosphorus can also expand its octet.

Why Expanded Octet is Possible:

- **Phosphorus is in Period 3**
- Can utilize 3d orbitals to accommodate more than 8 electrons

Conclusion:

Phosphorus in PO_4^{3-} can have an expanded octet, especially in resonance forms with one or more P=O double bonds.

Summary:

Ion	Central Atom	Period	Expanded Octet?	Why
ClO_3^-	Cl	3	Yes	Access to 3d orbitals
PO_4^{3-}	P	3	Yes	Access to 3d orbitals

ELECTRONEGATIVITY AND THE TYPE OF BOND

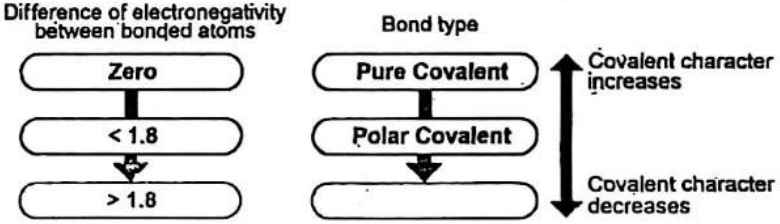
➢ **The effect of electronegativity on the type of bonding:**

The difference in electronegativity of two bonded atoms provides an approximate measure of the bond polarity and an indication of the type of bond.

- When this difference is very small or zero, the bond is covalent and nonpolar.
- When it is large, the bond is polar covalent or ionic.

➢ **Change in the nature of bond with electronegativity difference:**

- The following figure graphically depicts the change in the nature of bond with electronegativity difference.
- Two atoms having electronegativity difference less than 0.4 are said to make a pure covalent bond (or non-polar covalent bond).
- An electronegativity difference between 0.4 and 1.8 corresponds to a **polar covalent bond,** whereas, above this value the bond between two atoms will be ionic in nature.
- The electronegativity differences between the atoms in the bonds such as H—H, H—Cl, and NaCl are 0 (non-polar), 0.9 (polar covalent), and 2.1 (ionic), respectively. This is why H—H bond is purely non-polar, H—Cl a polar covalent bond, whereas NaCl is an ionic compound.



QUICK CHECK 3.3

a) **Predict with the help of electronegativity values whether the bonds in these compounds would be non-polar covalent, polar covalent, or ionic.**

i) HF ii) KI iii) CaF_2 iv) ICl v) Br_2

Ans.

Compounds	Type of Bond
i) HF	Polar covalent
ii) KI	Ionic bond
iii) CaF_2	Ionic bond
iv) ICl	Polar covalent
v) Br_2	Non-polar covalent

Dipole Moment and Polarity of Molecules

Definition:

"The product of electric charge (q) and the distance between the positive and negative centers (r) is called dipole moment".

$$\mu = q \times r$$

Units:

The dipole moment is measured in:

(i) Debye (D) unit

(ii) Coulomb meter (Cm) – SI unit

- In compounds such as HF, where the bonded atoms are from different elements, the electronic distribution between the atoms is uneven. Due to this reason, one atom carries causes partial positive and the other negative charge. A molecule with δ^+ charge on one part and δ^- charge on the other part is called a dipole and such a molecule is said to have a **dipole moment.**
- It is a quantitative measurement of the polarity of a bond or a molecule. The dipole moments of diatomic molecules like HF, HCl, HBr, HI, NO, etc. are directed from the positive ends (δ^+) to negative ends (δ^-) as in Fig. Higher dipole moment indicates high polarity in a molecule. Dipole moment is measured in Debye unit (D).

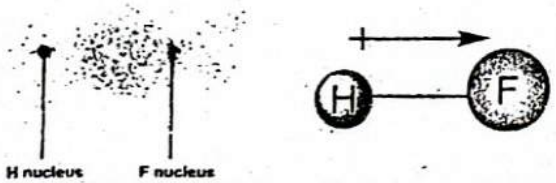


Figure: Electron density in HF is higher near the F atom and the dipole moment is directed from H to F

(a) Dipole Moment and Molecular Structure

For compounds having more than two atoms, the dipole moment depends on the structure of the molecule.

(i) Water

- The dipole moment of water is 1.85 D which is directed from the end having two hydrogen atoms to the end with the oxygen atom as in the structure shown in Fig. A linear H_2O molecule (H-O-H) would have zero dipole moment.
- The non-zero dipole moment value shows that water is a non-linear molecule.
- Experiments reveal that the water molecule has a v-shaped structure.

Rack Your Brain!

4. Which of the following molecules has zero dipole moment?
(A) NH_3 (B) $CHCl_3$
(C) H_2O (D) BF_3

(ii) SO_2

- SO_2 has a dipole moment of 1.61 D and in opposite direction to that in water.

(iii) H_2S

- H_2S is also a non-linear molecule as the individual bonds are polar, but they don't cancel each other's dipole moment and the overall molecule has some dipole moment.

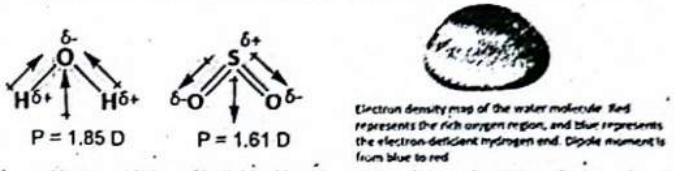


Figure: Vector addition of individual bond moments in angular H_2O and SO_2 molecules

(b) Zero Net Dipole Moment

Some molecules have zero dipole moments as the symmetry in their structures causes the cancellation of the individual bond moments.

(i) $BeCl_2$

- $BeCl_2$ is a linear molecule having two similar Cl atoms on both sides of the central atom at 180°. The individual Be–Cl bond moments are cancelled out as they are opposite in direction and equal in amount.

(ii) CCl_4

- CCl_4 has four C–Cl bonds which are expected to have high polarity due to a large electronegativity difference between C and Cl atoms. The bond moments associated to the four C–Cl bonds are directed in such a way that they cancel each other. The net dipole moment of the CCl_4 molecule is zero making it a non-polar molecule. The CCl_4 molecule is perfectly tetrahedral.

(iii) BF_3

- BF_3 has a trigonal planar symmetrical structure and its dipole moment is also zero. As a rule, the molecules that have same ligands (atoms or groups of atoms with the central atom) in a regular geometry, the individual dipole moments may not be zero, but overall molecule has zero dipole moment. Such a molecule is said to be non-polar.

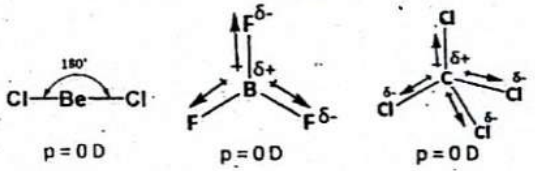


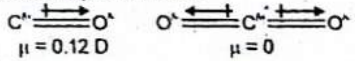
Figure: The individual bond moments in symmetrical molecules; $BeCl_2$, BF_3 and CCl_4 are cancelled out to give zero net dipole moment.

QUICK CHECK 3.4

a) **Can you explain why CO has a dipole moment but CO_2 does not have any?**

Ans. CO has a dipole moment while CO_2 does not have any.

Reason: CO_2 has a linear structure, because the dipoles being equal and opposite, cancel out each other's effect. Similarly CS_2 has zero dipole moment.



b) **Do you think that individual bonds CCl_4 are polar? Explain in terms of the electronegativity difference. What about the polarity of overall CCl_4 molecule?**

Ans. Electronegativity of C = 2.5

Electronegativity of Cℓ = 3.2
Individual C – Cℓ bonds in CCl_4 are polar due to electronegativity difference with partial position charge on C and partial negative charge on Cℓ. So each C – Cℓ bond in polar with a dipole moment. However, due to symmetrical tetrahedral shape of CCl_4. The overall molecule is non-polar because the individual bond dipoles cancel each other.

c) Are these molecules polar or non-polar? Briefly give reasons. HF, CH_2Cl_2, O_2, H_2S

Ans.

Molecules	Polar/Non-polar
HF	Polar
CH_2Cl_2	Polar
O_2	Non-polar
H_2S	Polar

INTERMOLECULAR FORCES

Intermolecular forces are also the binding forces just like chemical bonds. However, the attraction between the molecules is much weaker than the chemical bonds. These forces are believed to exist between all kinds of atoms and molecules when they are sufficiently close to each other. Such intermolecular forces are called van der Waals forces. These intermolecular forces bring the molecules close together and give particular physical properties to the substances in gaseous, liquid, and solid states.

Three types of such forces are mentioned here:

i) Instantaneous dipole-induced dipole forces or London dispersion forces.
ii) Permanent dipole-permanent dipole forces
iii) Hydrogen Bonding
(For the detailed discussion on these forces, see the chapter "states and phases of matter").

BOND ENERGY AND BOND LENGTH

"The bond energy is the average amount of energy required to break all bonds of a particular type in one mole of a substance."

- It is determined experimentally by measuring the heat involved in a chemical reaction and its unit is kJ mol^{-1}.
- Bond energy is a measure of the strength of a bond and its reactivity.
- The strength of a bond depends upon the following factors.

➢ **Factors Affecting Bond Energy:**

(i) Electronegativity difference of bonded atoms
(ii) Size of atoms.

The bond energies/enthalpies of some bonds are presented in Table.

Table: Average bond energies of some selected bonds in kJ mol^{-1}

Single bonds						Multiple bonds	
H – H	432	C – I	240	F–F	154	C = C	614
H – F	565	C – Cℓ	339	Cℓ – Cℓ	239	C ≡ C	839
H – Cℓ	427	C – N	305	Br – Br	193	O = O	495
H – Br	363	C – O	358	I – I	149	C = O	745
H – I	295	N – H	391	S – S	266	N ≡ N	941
C – H	413	N – O	201	Si – Si	340	C ≡ N	615
C – C	347	O – H	467	Si – O	452	N = O	607

Let us consider the role played by electronegativity difference. Look at the bond energies of H-X type of compounds, where X=F, Cℓ, Br, I. The data show that the bond energy of a bond rises with the increasing electronegativity difference between the bonded atoms. As the difference in electronegativity increases, the bond polarity also becomes greater and this gives rise to additional attractive force for binding the atoms.

This is why the bond energy for HF is higher (565 kJ mol^{-1}) than for HI (295 kJ mol^{-1}). It may be noted that energies of multiple bonds are greater than those of single bonds.

C ≡ C > C = C > C - C

➢ **Bond Length:**

- **Definition:** "Bond length is the distance between the nuclei of two atoms forming a covalent bond".
- **Measurement:** The bond lengths are experimentally determined by physical techniques, such as electron diffraction, X-ray diffraction, or spectral studies.
- **Factors Affecting Bond Length:** The bond length of a bond is governed by many factors including electronegativity (electronegativity difference), size, and the nature of the covalent bond (single, double, or triple).
- **Explanation:** With an increase in size of the atoms, the covalent bond length also increases. The C – Cℓ bond length is about 180 pm, whereas the C – F bond length is 135. This is because the Cℓ atom is much larger. With the rise in electronegativity difference between the bonded atoms, the bond becomes shortened. For example, Si–F bond length in SiF_4 is found to be near 155 pm, whereas the calculation of Si–F bond from the covalent radii of Si and F(Si=117pm and F=64pm) is 181 pm. The electronegativity difference causes an ionic character in the covalent bond. The ionic character results in shortening of the bond length due to the additional attraction between the bonded atoms.
- Some selected bond lengths are given in Table.

Table: Bond lengths of some selected bonds

Bond	Bond length (pm)	Bond	Bond length (pm)
H – H	74	Si – F	155
H – Br	144	C – F	135
C – C	154	C – Cℓ	180
C = C	133	C – Br	196
C ≡ C	120	C – I	214
C = O	122	B – F	130
Si – H	146	B – Cℓ	175

☑ QUICK CHECK 3.5

(a) **HI is a stronger acid and a robust reducing agent, whereas HF is a weaker acid. Explain.**

Ans. The difference in acid strength and reducing ability between HI (hydroiodic acid) and HF (hydrofluoric acid) is rooted in bond strength, electronegativity, and ion stability.

Reasons:

1. **Acid Strength: HI > HF**
Acid strength depends on how easily a molecule donates a proton (H^+).
Bond strength (H–X bond):
- **H–F bond is very strong (565 kJ/mol) due to the small size of fluorine and strong overlap with hydrogen.**
- **H–I bond is much weaker (297 kJ/mol) because iodine is large and the overlap with hydrogen's orbital is poor.**

Weaker H–I bond breaks more easily, releasing H^+ more readily → stronger acid.
Anion stability (F^- and I^-):
- **F^- is small and highly charged (high charge density) → strongly attracts protons, so it holds onto H^+ tightly → reverses the dissociation.**
- **I^- is large, more polarizable, and better stabilizes the negative charge → doesn't recombine as easily with H^+ → acid remains dissociated.**

I^- is more stable in solution than F^- → favors complete dissociation → stronger acid.

2. **Reducing Strength: HI > HF**
A reducing agent donates electrons (i.e., gets oxidized itself).
- In redox terms:

$I^- \rightarrow I_2 + 2e^-$ (gets oxidized)
$F^- \rightarrow F_2 + 2e^-$

Ease of oxidation:

- **I^- is much easier to oxidize than F^- because:**
  - **Iodine has a lower electronegativity (2.5) than fluorine (4.0)**
  - **Fluoride ion (F^-) is very stable and resists giving up electrons**
  - **I^- can be oxidized to I_2 more readily → good reducing agent**

HI is a stronger reducing agent because I^- is more easily oxidized than F^-.

Property	HI	HF
H–X Bond Strength	Weak (easily broken)	Strong (hard to break)
Acid Strength	Strong acid	Weak acid
X^- Anion Stability	I^- stable (large, polarizable)	F^- less stable (small, high charge density)
Reducing Power	Strong reducing agent	Weak reducing agent

(b) Acetylene (HC ≡ CH) is more stable than ethene ($H_2C = CH_2$). Can you explain why?

Ans. Actually, acetylene (C_2H_2) is less stable than ethene (C_2H_4) in terms of enthalpy or thermodynamic stability — not more stable.

Explanation:

Structures

- **Acetylene (C_2H_2):**
  Linear molecule with a **triple bond** between the carbon atoms: H–C ≡ C–H
- **Ethene (C_2H_4):** Planar molecule with a **double bond** between the carbon atoms: $H_2C = CH_2$

Thermodynamic Stability (Bond Energies)

Let's look at the **total bond energy** (approximate values):

Molecule	C–C Bond Type	C–H Bonds	Total Bond Energy (kJ/mol)
Acetylene	1 triple (839 kJ/mol)	2 × C–H (2 × 412) = 824	1663
Ethene	1 double (614 kJ/mol)	4 × C–H (4 × 412) = 1648	2262

Ethene has more total bond energy → more stable (lower energy).

Higher total bond energy = more stable molecule

Heat of Formation (ΔH_f°)

- **Acetylene (C_2H_2): +226 kJ/mol (positive → less stable)**
- **Ethene (C_2H_4): +52 kJ/mol (less positive → more stable)**

Ethene has a lower heat of formation → more thermodynamically stable.

Acetylene can seem "stronger" or "tougher" because of the triple bond, which is short and strong. But this doesn't mean it's more thermodynamically stable overall. In fact, acetylene contains more energy (more reactive), which is why it's used as a fuel (e.g. in oxy-acetylene torches).

Property	Acetylene (C_2H_2)	Ethene (C_2H_4)
C–C Bond Type	Triple	Double
Heat of Formation (ΔH_f°)	+226 kJ/mol	+52 kJ/mol
Thermodynamic Stability	Lower	Higher
Reactivity	Higher (more reactive)	Lower

A COMPARISON AMONG IONIC, COVALENT, METALLIC BONDS AND INTERMOLECULAR FORCES

Chemical bonds (ionic, covalent, and metallic bond) are usually termed as true chemical bonds because they affect the chemical properties of a substance.

Distinction between chemical bonds and intermolecular forces:

(i) Chemical bonds result in the formation of new species through transfer and sharing of electrons. Whereas, intermolecular forces act to bring molecules closer and influence the physical properties. (However, such a clear distinction between the chemical bonds and intermolecular forces is not possible).

(ii) Bond Strength: The distinctive feature of the chemical bonds and intermolecular forces is the bond strength. The strength of a force is measured by the bond energy. Table provides a comparison among different chemical bonds and intermolecular forces.

Table: Relative strengths of chemical bonds and intermolecular forces

Bond Type	Bond Energy ($kJ\ mol^{-1}$)
Ionic bond in NaCl	760
O–H bond in water	464
Hydrogen bonding	20–50
Permanent dipole- Permanent dipole force	5–20
Van der Waals forces	1–20

The bond energy of ionic bond (sodium chloride, 760 kJ mol^{-1}) is highest, followed by covalent bond (O–H = 464 kJ mol^{-1}) and average hydrogen bond energy (20–25 kJ mol^{-1}). It shows that the ionic bond is the strongest form of chemical bonding. It also reveals that chemical bonds are generally much stronger than intermolecular forces. The permanent dipole-dipole forces (5–20 kJ mol^{-1}) and London dispersion forces (1–20 kJ mol^{-1}) are even weaker as indicated by their low bond energies.

The metallic bond is mostly elaborated in terms of electrostatic forces, although some theories suggest that it may be of covalent nature. In any case, the metallic bond is weaker than both the ionic and covalent bonds. The average bond energy of the metallic bond is 100–150 kJ mol^{-1}. A satisfactory argument for the low strength of metallic bond is extensive delocalization of electrons within the metallic crystal.

VALENCE BOND THEORY (VBT)

Exercise LO-2

Q. How the bonding in the following molecules can be explained with respect to valence bond theory?
(i) $C\ell_2$ (ii) O_2 (iii) N_2 (iv) HF (v) H_2S

The VSEPR model predicts and explains the shapes of molecules but does not give reasons for the formation of bonds.

➢ **Introduction of VBT:**

VBT is concerned with both the formation of bonds and the shapes of molecules. This method of describing a covalent bond considers a molecule as a combination of atoms

➢ **Postulates of VBT:**

The postulates of VBT are given below:

- A covalent bond is formed when half-filled orbitals in the valence shells of two atoms with similar energy overlap.
- A greater overlap of the orbitals results in a stronger bond.
- Covalent bonds are directional. The direction of the bond is determined by the shape and mode of the overlapping orbitals.

⊃ Formation of Sigma Bond

A sigma bond is formed by the linear overlap of two half-filled atomic orbitals on adjacent atoms. The orbitals approach each other on the nuclear axis. Both s and p orbitals can overlap head-on to form sigma bonds.

Rack Your Brain!

5. How sigma bonds are formed?

➢ **s-s Overlap (H – H Molecule)**

The 's' orbital of one atom overlaps with the s-orbital of the other to give a bond orbital. This type of overlap occurs during the formation of the H_2 molecule, where each hydrogen atom has a half-filled 's' orbital.

After the bond formation, the electrons are paired up and the electron density in this molecule is symmetrical around the two nuclei as in Figure.

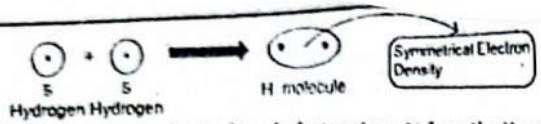


Figure: Overlap between s orbitals of two hydrogen atoms to form the H_2 molecule

➢ **s-p Overlap (H – Cℓ Molecule)**

The s orbital of one atom can overlap with the p orbital of the other to form a covalent bond (σ). For example, in HCℓ molecule, a half-filled s orbital of hydrogen overlaps with a halffilled p orbital of chlorine as shown in Figure. The electron density is higher close to the Cℓ atom due to its higher electronegativity value. This is why HCℓ is a polar molecule.

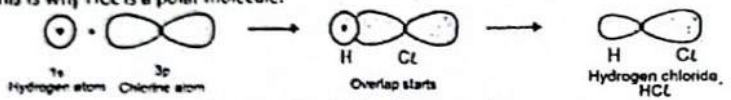


Fig.: Formation of σ bond by s-p overlap

➢ **p-p Overlap (Cℓ – Cℓ Molecule)**

An example of this type of overlap is the formation of the $Cℓ_2$ molecule where ' p ' orbitals of two chlorine atoms overlap on the nuclear axis. The electron density is symmetrical around the nuclei of the two Cℓ atoms because both have same value of electronegativity.

Interesting Information!
The bond angle in H_2O is 104.5°, whereas in H_2S, it is 92°. This is because the orbitals of S are larger and the lone pair exerts a stronger repulsion.

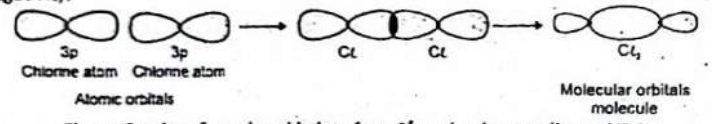


Figure: Overlap of p and p orbitals to form $Cℓ_2$ molecule according to VBT

➢ **H_2S Molecule**

The H_2S molecule is a non-linear molecule which is formed by the combination of one Sulphur and two hydrogen atoms. The two 3p (say $3p_y$ and $3p_z$) orbitals of Sulphur containing one electron each can overlap with the 1s orbitals of two hydrogen atoms. A v-shaped molecule is thus formed having a bond angle of 92° as in Fig.

Rack Your Brain!
6. How pi (π) bonds are formed?

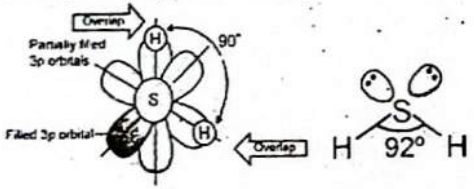


Fig.: The formation of H_2S molecule by H and S orbitals overlap

➲ Formation of π bond

➢ **Formation of Double bond in O = O**

Consider the formation of a double covalent bond between oxygen atoms (O = O). There are two unpaired electrons on each atom in perpendicular p orbitals (say P_x and P_y). The p_x orbitals on the two oxygen atoms are oriented in such a way that they overlap end-to-end linearly. The linear overlap of the p_x orbitals gives a σ bond. However, the p_y orbitals on both atoms are aligned parallel to each other. They overlap in a parallel way so that the two p lobes overlap above the plane of the nuclei and the other two lobes below the plane as shown in Figure. This results in the formation of π bond. The oxygen atoms are doubly bonded through σ and π bonds.

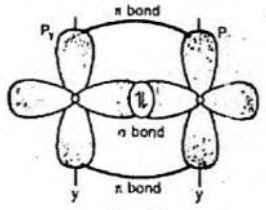


Figure: Formation of double bond (σ and π) between oxygen atoms

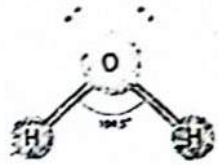
QUICK CHECK 3.6

a) Draw the orbital structures of H_2O and N_2 molecules.

Ans. Water (H_2O)

Lewis Structure:

- Oxygen (O): 6 valence electrons
- Hydrogen (H): 1 each × 2 = 2
- Total = 8 electrons
- Oxygen forms **2 single bonds** with hydrogen and retains **2 lone pairs**



Electron Geometry:

- **4 electron regions** (2 bonding pairs + 2 lone pairs)
- **Electron geometry:** Tetrahedral
- **Molecular shape: Bent (V-shaped)** due to lone pair repulsion
- **Bond angle:** 104.5°

2. Nitrogen Molecule (N_2)

Lewis Structure:

- Each nitrogen atom has 5 valence electrons
- They share **three pairs of electrons to form a triple bond**
- Each N has a lone pair remaining

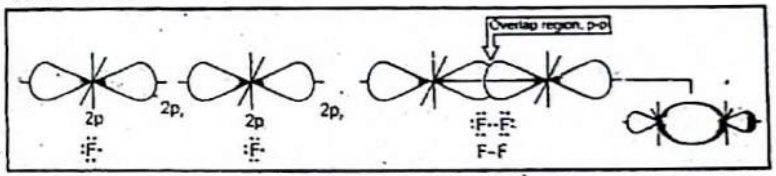
Electron Geometry:

- Only 2 atoms, so it is **linear**
- **Bond type: Triple bond**
- **Molecular shape: Linear**
- **Bond angle:** 180°

:N≡N:

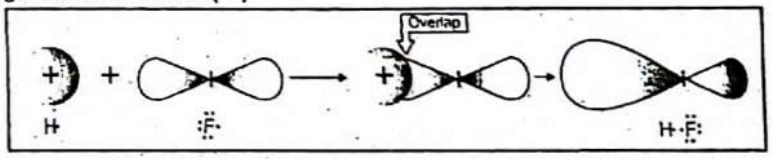
b) Draw the orbital overlap to show the formation of F_2 and HF molecules.

Ans. Fluorine molecule (F_2)



The formation of the fluorine molecule

Hydrogen Fluoride Molecule (HF)



The formation of the hydrogen fluoride molecule

ATOMIC ORBITAL HYBRIDIZATION

Exercise Q.5

Q. Explain the orbital hybridization for CH_4, NH_3, BF_3, and $BeCl_2$.

Hybridization:

A process in which atomic orbitals of slightly different energies and shapes are mixed together to form a new set of equivalent orbitals of same energy and same shape is called hybridization.

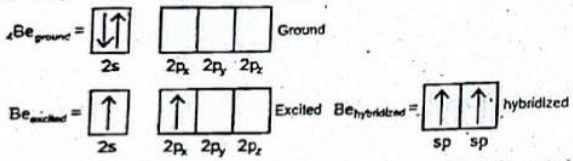
KEEP IN MIND

- Hybridization is a process of mixing of orbitals in a single atom (or ion).
- Only orbitals of comparable (relatively close) energies can be mixed to form hybrid orbitals.
- The number of mixing orbitals is always equal to the number of the resulting hybrid orbitals.

Types of Hybridization

sp Hybridization

- In sp hybridization, ones (low energy and spherical) and one p orbital (high energy and dumb-bell shaped), intermix to give a new set of two orbitals of same energy and same shape called sp hybrid orbitals. These sp hybrid orbitals are arranged in linear geometry and oriented at 180°.
- **Beryllium Chloride ($BeCl_2$):** The electronic configuration of the outermost shell of Be is as follows:



- The two sp hybrid orbitals lie linearly as in the following diagram Fig. The sp hybridization explains the geometry of linear molecules such as beryllium chloride, $BeCl_2$. It is formed when two sp hybrid orbitals of Be atom overlap with the half-filled p-orbitals of chlorine atoms.

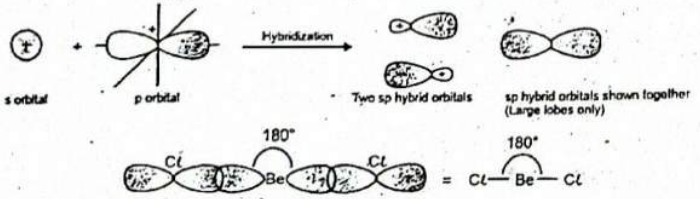


Figure: Mixing of s and p orbitals to give two hybrid sp orbitals and the formation of $BeCl_2$

sp^2 Hybridization

- In sp^2 hybridization, one s and two p atomic orbitals of an atom intermix to form three orbitals called **sp^2 hybrid orbitals.**
- The three half-filled sp^2 hybrid orbitals are arranged in a trigonal planar geometry with bond angles of 120°

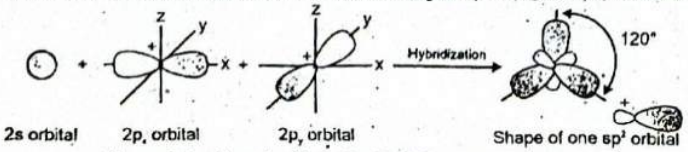
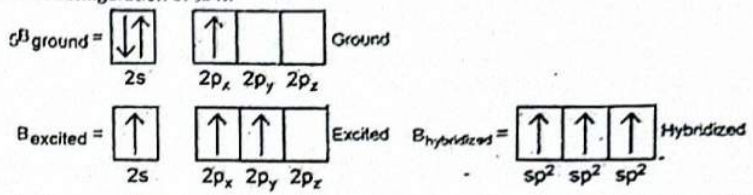


Figure: Formation of sp^2 hybrid orbitals from atomic orbitals

- **Boron Trifluoride (BF_3):** The sp^2 hybridization explains the geometry of planar molecules such as BF_3. Electronic configuration of $_5B$ is:



- The three outermost orbitals of B mix together to give three sp^2 hybrid orbitals. On the other hand, one of the p orbitals of fluorine is half filled (e.g. $2p_z$). BF_3 is formed by the overlap of three half-filled sp^2 hybrid orbitals of boron with $2p_z$ orbitals of three fluorine atoms. The structure is triangular planer with bond angles equal to 120°, each as in Figure.

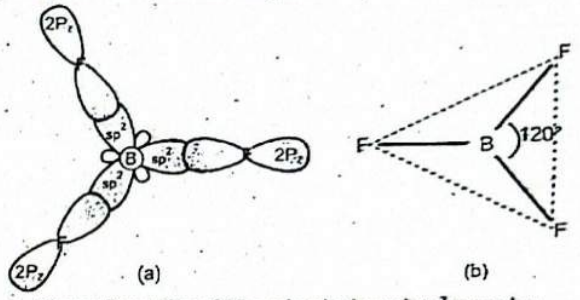
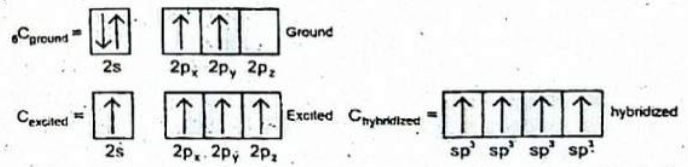


Figure: Formation of BF_3 molecule through sp^2-p overlap

sp^3 Hybridization

- In sp^3 hybridization, one s-orbital (low energy and spherical) and three p-orbitals (high energy and dumbbell shaped), intermix to give a new set of four orbitals of same energy and same shape. Each of these hybrid orbitals is a sp^3 hybrid orbital.
- **Methane (CH_4):** These hybrid orbitals are arranged in the tetrahedral geometry as shown in the example of CH_4 as in Fig.
- The electronic configurations of valence shell of $_6C$ in its excited and hybridized states are given as follows:



- The energies of hybrid orbitals are lower than unhybrid orbitals. Figure shows the outermost four atomic orbitals of carbon mix up to give four hybrid orbitals of same energy and same shape.

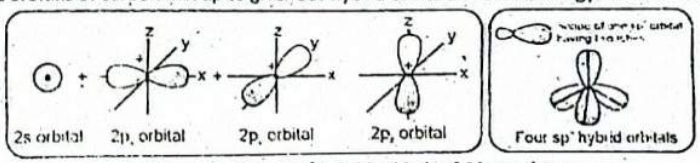


Figure: Formation of sp^3 hybrid orbitals of C in methane

- The four new hybrid orbitals of equal energy have a tetrahedral geometry with carbon nucleus at the center. The methane molecule is formed by the overlap of sp^3 hybrid orbitals of carbon with 1s orbitals of four hydrogen atoms separately to form four sigma bonds. The four C–H bonds, which result from sp^3-s overlaps, are directed towards the corners of a regular tetrahedron.

Did You Know?

Each sp^3 hybrid orbital consists of two lobes, one larger and the other smaller. For the sake of simplicity, the smaller lobe is usually not shown while representing sp^3 hybrid orbitals together.

VALENCE SHELL ELECTRON PAIR REPULSION MODEL (VSEPR)

(Exercise L.O.4)

Q. What are the postulates of VSEPR model? Discuss the structures of the following species with reference to this theory.

(i) CH_4 (ii) NH_3 (iii) H_3O^+ (iv) PCl_5 (v) SO_2 (vi) SF_6

The VSEPR model describes the shapes of molecules based on the electron pairs that surround the central atom. This model was presented by Sidgwick and Powell in 1940. It is based on the assumption that a molecule will take a shape such that the electronic repulsions among the valence electrons of that atom are minimum. In order to have the minimal repulsions, the electron pairs arrange themselves at farthest possible distances. This arrangement of the electron pairs determines the geometry of the resulting molecule.

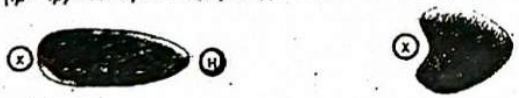
Postulates:

i. Both the lone pairs (non-bonded) as well as the bond pairs participate in determining the geometries of molecules.

ii. The electron pairs are arranged around the central atom so as to remain at maximum distance apart to avoid repulsions.

iii. The electrons of lone pairs occupy more space than the bond pairs. As a result, the non- bonding electron pairs exert greater repulsive forces on bonding electron pairs and, thus, tend to compress the bond pairs. The magnitude of repulsions between the electron pairs in a given molecule decreases in the following order:

Lone pair-lone pair (lp – lp) > lone pair-bond pair (lp – bp) > bond pair (pm) bond pair (bp – bp)



An electron pair shared by two nuclei occupies less space than a lone pair bound by a single nucleus

iv. The two electron pairs of a double bond and three electron pairs of a triple bond, contain a higher electronic charge density, but they are regarded as single pairs.

v. The presence of highly electronegative atoms with the central atom results in decreased electronic repulsions between the bond pairs, but stronger repulsion by the lone pair.

Rack Your Brain!

7. Why does lone pair of electrons occupy more space as compared to bond pair?

⊃ Predicting the Shapes of Molecules

In order to illustrate this model, the central atom is named ' A '. The electron pairs around ' A ' are designated as ' B '. There may be different number of electron pairs around the central atom depending upon its valency. It gives rise to various types of molecules, such as AB_2, AB_3, AB_4, etc. The electron pair geometry of a molecule is determined by the total number of electron pairs around ' A ' whereas, the actual shape of the molecule is determined by the atoms excluding the lone pairs. Following Table gives the possible shapes of different types of molecules having varying numbers of bond and lone pairs.

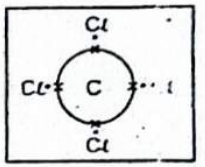
Table: Geometries and shapes of different systems of covalently bonded compounds

No. of electron pairs around central atom	No. of lone pairs	Electron pair geometry	Shape with respect to atoms	Angular separation of atoms	Examples
2	0	linear	linear	180°	CO_2, $BeCl_2$
3	0	trigonal	trigonal	120°	BCl_3, SO_3
3	1	trigonal	Angular, v- shaped	Less than 120°	SO_2, $SnCl_2$
4	0	tetrahedral	tetrahedral	109.5°	CH_4, CCl_4
4	1	tetrahedral	pyramidal	Less than 109.5°	NH_3, H_3O^+
4	2	tetrahedral	Angular, v-shaped	Less than 109.5°	H_2O, Cl_2
5	0	Trigonal	Trigonal bipyramidal	120°, 90°	PCl_5
6	0	octahedral	octahedral	90°	SF_6, XeF_4

⊃ Steps to Determine the Shapes of Molecules

The following steps are followed to predict the shape of a molecule.

i. The least electronegative atom or the element with the least number of atoms is mostly selected as the central atom. For example, in CCl_4, the carbon atom is the central atom.



ii. The total number of electron pairs around the central atom are counted (including bond pairs and lone pairs). For example in CCl_4, the total number of bond pairs around the C atom are 4 and it has no lone pair.

iii. The total number of electron pairs determines the electron pair geometry (as in the above table) of the molecule. For example, CCl_4 has total four electron pairs and its geometry is tetrahedral.

iv. Finally, the actual shape of the molecule is determined excluding the lone pairs (if any).

KEEP IN MIND

Number of electron pairs around the central atom are calculated as in the following example:

- Valence electrons in N = 5
- Electrons shared by 3H = 3 × 1 = 3
- Total number of electrons = 5 + 3 = 8
- Total number of electron pairs = $\frac{8}{2} = 4$

Calculation for lone pairs on N
No. of lone pairs on N = Total no. of pairs – no. of bond pairs
No. of lone pairs on N = 4 – 3 = 1
Thus, N has 1 lone pair in NH_3

⊃ AB_2 type Molecules (Linear geometry)

In such molecules, two electrons pairs around the central atom are arranged at an angle of 180° to minimize repulsions between them. Thus, they form a linear geometry as shown in Figure. $BeCl_2$ molecule is of AB_2 type with Be as the central atom and two bond pairs around it, but no lone pair.

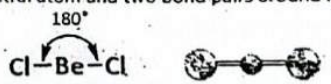


Figure: Linear shape of the $BeCl_2$ molecule

Molecule	Electron pairs			Type	Arrangement of pairs	Molecular geometry	Shape
	Total	Bonding	Lone				
$BeCl_2$	2	2	0	AB_2	Linear	Linear	180° Cl–Be–Cl
$MgCl_2$	2	2	0	AB_2	Linear	Linear	180° Cl–Mg–Cl

Other Examples: $MgCl_2$, $CaCl_2$, $CdCl_2$, $SrCl_2$, $HgCl_2$

➲ AB_3 type (Trigonal planar geometry)

➢ **AB_3 type with bond pairs and no lone pair:**

In AB_3 type molecules, the central atom is surrounded by three electron pairs, which are arranged at maximum distance apart at an angle of 120° giving a trigonal geometry.

Example BF_3 Molecule: BF_3 molecule has a trigonal planar shape with each F-B-F bond angle of 120° Figure. The similar geometries are expected in the hydrides of group 3 (III-A), i.e. AlH_3, GaH_3, BH_3, etc

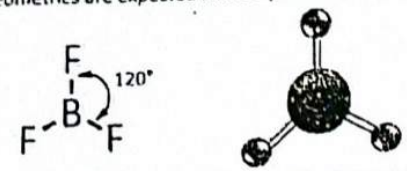
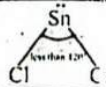


Figure: BF_3 is an AB_3 system having triangular planar geometry

➢ **AB_3 type with one lone pair and two bond pairs:**

In $SnCl_2$, the Sn atom has 4 electrons in its outermost shell. It makes two bonds with two Cl atoms and the remaining two electrons exist as a lone pair (Figure below). One of the corners of the triangle is occupied by this lone pair, giving rise to a distorted trigonal electron pair geometry (in vapour phase). The actual shape of $SnCl_2$ is v -shaped and bond angle less than 120° due to the presence of a lone pair on Sn atom.

Molecule	Electron pairs			Type	Arrangement	Geometry	Shape
	Total	B	L				
$SnCl_2$ [Stannous chloride]	3	2	1	AB_3	Triangular planar	Bent or angular	

➲ AB_3 Type with Multiple Bonds

The molecule of SO_3 has all the three regions occupied by S = O bonds. The structure of SO_3 is perfectly trigonal with each angle equal to 120°. On the other hand, in SO_2, one corner of the triangle is occupied by a lone pair and the other two corners each by a double bond (S = O). Thus, it makes an angular or v -shaped structure just as $SnCl_2$ does as in Fig.

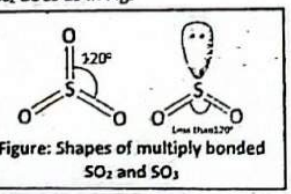
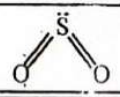
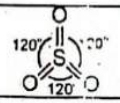


Figure: Shapes of multiply bonded SO_2 and SO_3

Rack Your Brain!

8. Geometry of SO_2 molecule is:
(A) Linear (B) Angular
(C) Tetrahedral (D) Trigonal pyramidal

Molecule	Electron pairs			Type	Arrangement	Geometry	Shape
	Total	B	L				
SO_2 [Sulphur dioxide]	3	2	1	AB_3 with multiple bonds	Triangular planar	Bent or angular	

Molecule	Electron pairs			Type	Arrangement	Geometry	Shape
	Total	B	L				
SO_3 [Sulphur trioxide]	3	3	0	AB_3 with multiple bond	Triangular planar	Triangular planar	

➲ AB_4 Type (Tetrahedral geometry)

➢ **AB_4 type with four bond pairs and no lone pair:**

In this type of molecules, the charge clouds due to four electron pairs avoid their electrostatic repulsions by being farthest apart to form the shape of a regular tetrahedron. Each of the bond angles is of 109.5°. Each of the four valence electrons of carbon pair up with the sole (one) electron of a hydrogen atom in methane. The four bonded electron pairs are directed from the center towards the corners of a regular tetrahedron, (as shown in Fig) with each corner representing a hydrogen nucleus. This arrangement permits a non-planar geometry of electron pairs: Each H–C–H bond angle is perfectly 109.5°.

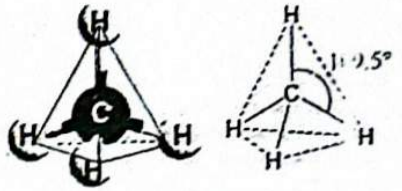
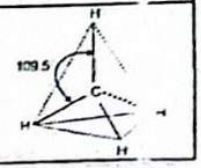


Figure: Regular tetrahedral shape of the CH_4 molecule

Examples: On the same grounds, SiH_4, GeH_4, CCl_4 possess the similar shape.

Molecule	Electron pairs			Type	Arrangement of pairs	Geometry	Shape
	T	B	L				
CH_4	4	4	0	AB_4	Tetrahedral	Tetrahedral	

Extend Your Knowledge

The tetrahedral shape has four corners, four faces, six edges and six bond angles. Ideally it has bond angles of 109.5° each.

➢ **AB_4 type with three bond pairs and one lone pair:**

(i) NH_3

- In the ammonia molecule (NH_3), there are three atoms attached to the nitrogen atom having one lone pair.
- Due to a lone pair, the ideal angle 109.5° is reduce to 107° as in Figure. This effect compels ammonia to assume a triangular pyramidal shape with reduced bond angles, instead of a tetrahedral.
- The substitution of hydrogen in NH_3 with electronegative atoms like F or Cl further reduces the bond angles.

(ii) NF_3

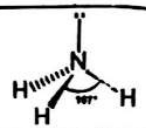
- Take the example of NH_3, which contains three highly electronegative F atoms bonded to the N atom. The bond angles are further compressed to 102.5°.

➢ **Reasons:**

The first reason being the strong polarity of N–F bond, due to which N atom pulls the lone pair closer to its nucleus. This, in turn, exerts a stronger repulsion over bonding electrons. Moreover, the bond pairs (N -F bonds) are closer to F atoms than N atom. The increased distances in these bond pairs make their repulsions weaker and allow the bonds to come closer.

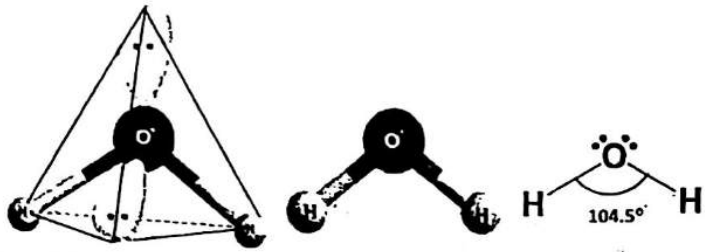


Figure: Distorted geometry and pyramidal shape of the NH_3 molecule

Molecules	Electron pairs			Type	Arrangement of pairs	Geometry	Shape
	Total	B	L				
NH_3 Ammonia	4	3	1	AB_4	Tetrahedral	Trigonal Pyramidal	

(iii) H_2O

Experiments show that the water molecule (H_2O) is angular or v -shaped, although it has four electron pairs around the central atom. Two of the corners of the tetrahedron are occupied by two lone pairs and the remaining two by bond pairs. But, due to the greater repulsions of the lone pairs, the bond angle is reduced to 104.5° as in Fig.



Tetrahedral geometry including lone pairs Angular shape of water molecule excluding lone pairs

Figure: Water molecule has two lone pairs and is v-shaped with suppressed bond angle

Molecule	Electron pairs			Type	Arrangement of pairs	Geometry	Shape
	Total	B	L				
H_2O	4	2	2	AB_4	Tetrahedral	Bent or angular	

(iv) Hydronium Ion

The VSEPR model also explains the shapes of ions. The hydronium ion $[H_3O]^+$ is formed when a water molecule captures a proton. The hydronium ion belongs to AB_4 type with one lone pair and possesses a trigonal pyramidal shape just like the ammonia molecule.

(v) Amide Ion

The amide ion $[NH_2]^-$ is also AB_4 type as it is surrounded by two lone pairs and two bond pairs. Its geometry is tetrahedral, but it has a bent shape (v-shape) similar to the water molecule (Figure).

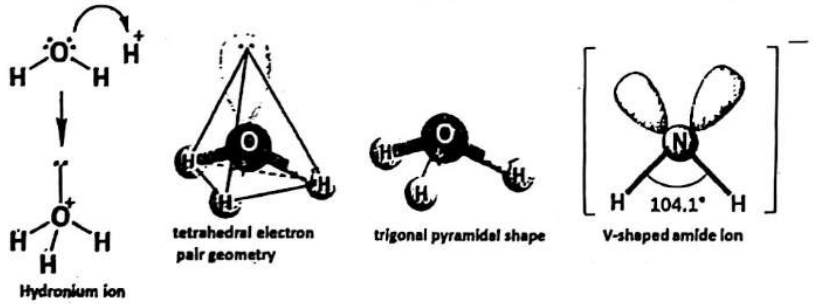


Figure: Shapes of hydronium (H_3O^+) and amide ions (NH_2^-)

QUICK CHECK 3.7

a) Calculate the number of lone pairs on the central atoms in the following: H_2O, ICl_3, I_3^-

Ans. H_2O (Water):

- **Central atom: Oxygen (O)**
- **Valence electrons of O: 6**
- **Hydrogen atoms: 2 × 1 = 2 electrons shared**
- **Total electron pairs around O: (6 + 2)/2 = 4 pairs**
- **Bonding pairs: 2 (from two O – H bonds)**
- **Lone pairs on O: 4 – 2 = 2 lone pairs**

ICl_3 (Iodine Trichloride)

- **Central atom: Iodine (I)**
- **Valence electrons of I: 7**
- **Chlorine atoms: 3 × 1 bond = 3 bonding pairs**
- **Total valence electrons involved: 7(I) + 3 (shared with Cl) = 10 electrons = 5 pairs**
- **Bonding pairs: 3**
- **Lone pairs on I: 5 – 3 = 2 lone pairs**

I_3^- (Triiodide Ion)

- **Central atom: Iodine (middle I)**
- **Total Valence electrons:**
  - **3 Iodine atoms = 3 × 7 = 21**
  - **Extra 1 electron (due to –1 charge) = 22 electrons**
- **Total electron pairs: 22 ÷ 2 = 11 pairs**
- **Bonding pairs: 2 (I – I bonds)**
- **Non–bonding pairs on central I: Remaining 9 pairs – 6 on outer I atoms = 3 on central I**
- **Lone pairs on central I: 3 lone pairs**

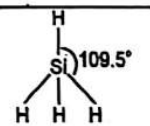
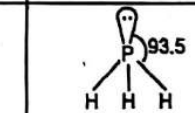
b) Calculate the number of bond pairs and lone pairs in SiH_4, H_2Se, and PH_3.

Ans.

Compound	Bond Pairs	Lone pairs
SiH_4	4	0
H_2Se	2	2
PH_3	3	1

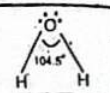
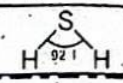
c) Predict the shapes and angles in SiH_4, H_2Se, and PH_3.

Ans.

	SiH_4	H_2Se	PH_3
Type of molecule	AB_4	AB_4	AB_4
No. of bond pairs	4	2	3
No. of lone pairs	0	2	1
Bond angle	109.5°	91°	93.5°
Shape of molecule	 Tetrahedral	Bent or V-shaped	 Trigonal Pyramidal

d) Predict how the bond angle in H_2S would be different from that in H_2O.

Ans.

Molecule	Electron pairs			Type	Arrangement of pairs	Geometry	Shape
	Total	B	L				
H_2O	4	2	2	AB_4	Tetrahedral	Bent or angular	
H_2S	4	2	2	AB_4	Tetrahedral	Bent or angular	

⊃ AB_5 type (Trigonal Bipyramid Geometry)

➢ **AB_5 type with five bond pairs and no lone pairs:**

PCl_5:

- In AB_5 type molecules, repulsions between the five electron pairs can be minimized by an even distribution of electrons among the corners of a trigonal bipyramid.
- In a trigonal bipyramid, three positions lie along the corners of the planar triangle, whereas, the other two positions lie along an axis perpendicular to the plane.
- This is evident from the geometry of the PCl_5 molecule given in Figure. The angles within the plane are 120° and that between the axial atom and a planar atom is 90°.

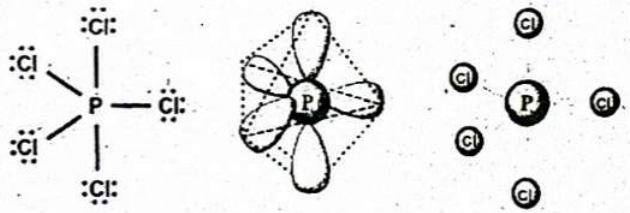


Figure Lewis structure and shape of PCl_5 molecule

Note: Just as in the AB_3 and AB_4 types, the presence of lone pairs in AB_5 system also changes the shape and the angles, but the change in this case is more dramatic.

Example: Tri-iodide ion $[I_3]^-$:

Tri-iodide ion $[I_3]^-$ is linear, although it is an AB_5 system. The central atom in this ion is the iodine atom. There are five electron pairs around the iodine atom including two bond pairs and three lone pairs. Therefore, it is an AB_5 type molecule with three lone pairs and possesses trigonal bipyramidal geometry. The lone pairs occupy the corners of the trigonal region and the iodine atoms occur on the apices, one being above and the second below the plane. However, excluding the three lone pairs, the actual shape of the tri-iodide ion is linear and the iodine atoms are farthest apart at an angle of 180° as in Figure.

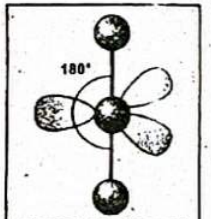


Figure 3.18: Shape of triiodide ion (I_3^-)

⊃ AB_6 Type Molecules (Octahedral Geometry)

➢ **AB_6 type with six bond pairs and no lone pair:**

AB_6 type molecules have 6 electron pairs around the central atom. The repulsions between the electron pairs can be minimized by assuming an octahedral geometry. In this geometry, four electron pairs are at the corners of a planar square and the other two lie along an axis perpendicular to the square. All the ABA angles in this type of geometry are of 90°.

Example:

The Lewis structure of SF_6 is given in Figure, it shows that this is an, AB_6 type molecule.

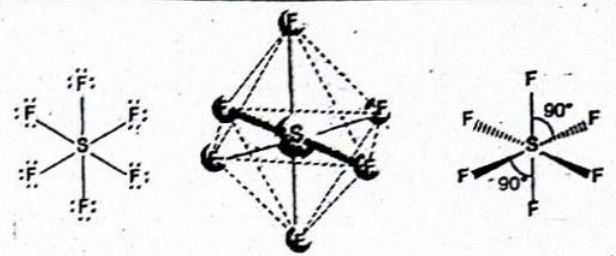


Figure: Lewis structure and octahedral shape of SF_6 with each angle of 90°

XeF_4 is an AB_6 type molecule with four bond pairs and two lone pairs. The two lone pairs remain at farthest distance at angle of 180°. Excluding the lone pairs, the actual shape of XeF_4 is square planar with all F–P–F angles equal to 90°.

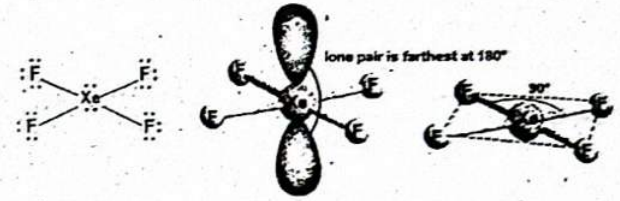


Figure: Lewis structure and square planar shape of XeF_4

☑ QUICK CHECK 3.8

Q. Draw the Lewis structures for IF_3 and IF_5 and predict their geometry with reference to the VSEPR model.

Ans. **Number of Valence electrons:**

- **Iodine (I):** 7 valence electrons
- Fluorine (F): 3 × 7 = 21
- Total = 7 (I) + 21 (F) = 28 electrons

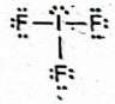
Bonding:

- 3 bonds between I and F use 6 electrons → 28 – 6 = 22 electrons left.
- Distribute remaining electrons to satisfy octets on the fluorine atoms → 6 electrons per F × 3 = 18 electrons → 22 – 18 = 4 electrons left.
- 4 electrons = 2 lone pairs on iodine.
- **Electron regions around iodine:** 3 bonding pairs + 2 lone pairs = 5 regions

VSEPR Geometry:

- 5 regions → trigonal bipyramidal electron geometry
- 2 lone pairs go in equatorial positions to minimize repulsion.
- Molecular shape = **T-shaped**

Structure: IF_3 Lewis Structure



IF_5 (Iodine Pentafluoride)

Valence electrons:

- **Iodine (I):** 7 valence electrons
- **Fluorine (F):** 5 × 7 = 35
- Total = 7 (I) + 35 (F) = 42 electrons

Bonding:

- 5 I–F bonds use 10 electrons → 42 – 10 = 32 electrons left

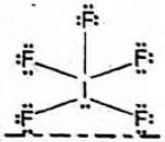
- 6 electrons per F × 5 = 30 electrons → 32 − 30 = 2 electrons left
- 2 electrons = 1 lone pair on iodine

Electron regions around iodine: 5 bonding pairs + 1 lone pair = 6 regions

VSEPR Geometry:

- 6 regions → **octahedral electron geometry**
- 1 lone pair → **square pyramidal molecular geometry**

Structure: IF_5 Lewis Structure

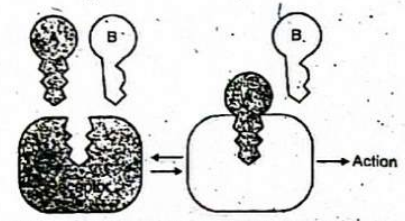


Applications of VSEPR Model in Drug Designing

Drugs are chemical substances that prevent, diagnose, or treat a disease. Drugs interact with human body at specific points, or with specific processes called targets or substrates, through their bioactive molecules called ligands. A receptor is mostly a protein that receives and responds to a ligand through binding. The examples of targets in the body are receptors, such as enzymes, proteins, nucleic acids, and cellular pathways. Each drug interacts with a specific target in the body to a different degree, this feature is called specificity of a drug or a ligand.

Molecular shape is an important feature that determines how a drug interacts with a biological target. Only the ligands with suitable shape can fit in the active sites of a biological target as a specific key fits in a specific lock. VSEPR model is successfully applied in determining the shapes of various biological systems, such as substrate recognition, ligand specificity or selectivity, and antibody recognition. For example, Aspirin is an analgesic drug (painkiller) used for relief from pain as a primary medicine. It interacts with an enzyme COX (cyclooxygenase) by binding to its active site through the acetyl group ($-OCCH_3$).

The shape of COX active site and that of acetyl group on Aspirin are compatible with each other as in fig. Therefore, the binding is successful to block COX, which is a cause of the pain in the body.



Drug A binds to receptor Drug B cannot bind to receptor

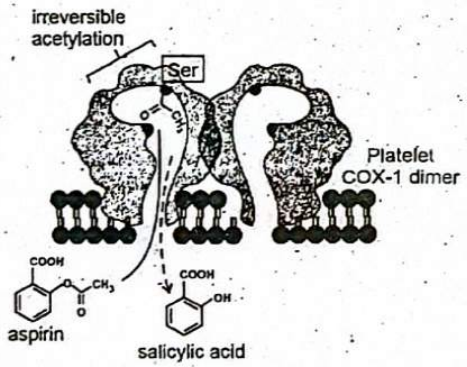


Figure: An interaction of Aspirin with COX (Published after permission from Tulane University Press)

MOLECULAR ORBITAL THEORY (MOT)

The molecular orbital approach explains the results of quantum mechanical calculations for covalent bonding. The postulates of this theory are:

- During the formation of a molecule, the atomic orbitals of the combining atoms overlap to form new orbitals called 'molecular orbitals', which are characteristic of the whole molecule.

Rack Your Brain!

9. Why is MOT superior to VBT?

- The atomic orbitals overlap with the lobe having suitable sign of the wave function of the orbital. For example, one lobe of a p orbital is given the '+' sign and the other is marked with '-' sign.
- Two atomic orbitals overlap to form two molecular orbitals. When same sign orbitals overlap, the **bonding molecular orbital** (σ or π) is formed that has lower energy than the parent atomic orbital, while with opposite signs, high energy **anti-bonding molecular orbital** (σ^* or π^*) is formed, that has higher energy than the parent atomic orbitals.
- The number of bonds formed between two atoms after the atomic orbitals overlap, is called the bond order and is taken as half of the difference between the number of bonding electrons (say a) and anti-bonding electrons (say b).

$$\text{Bond order} = \frac{a-b}{2}$$

s-s Overlap

In the formation of H_2 molecule, two s orbitals of H atoms combine to give two molecular orbitals. The bonding molecular orbital is symmetrical about the axis joining the nuclei of the bonded atoms (nuclear axis), while the anti-bonding molecular orbital has the electron density away from the nuclei of the overlapping atoms as in Fig

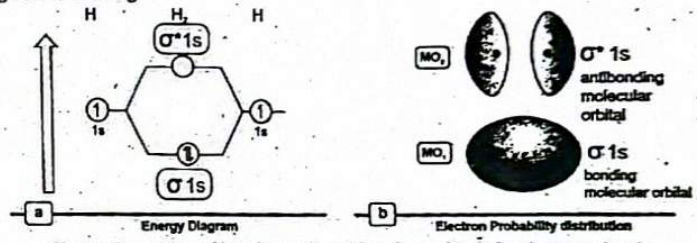


Figure: Formation of bonding and anti-bonding orbitals for the H_2 molecule

The p orbitals of an atom can combine to give:

a) Head on approach

Here, the p-orbitals of the two atoms approach along the same axis (say x-axis) as shown in Figure. This combination of atomic orbitals gives rise to $\sigma(2p_x)$ bonding and $\sigma^*(2p_x)$ antibonding molecular orbitals.

b) Sideways Approach

When the axes of two p -orbitals (i.e. p_y or p_z orbitals) are parallel to each other, they interact to form π molecular orbitals as shown in the diagram Figure. The bonding molecular orbitals $\pi(2p_y)$ or $\pi(2p_z)$ have zero electron density on the nuclear axis (called the nodal plane). On the other hand, anti-bonding molecular orbitals $\pi^*(2p_y)$ and $\pi^*(2p_z)$ have the least electron density in the inter-nuclear region.

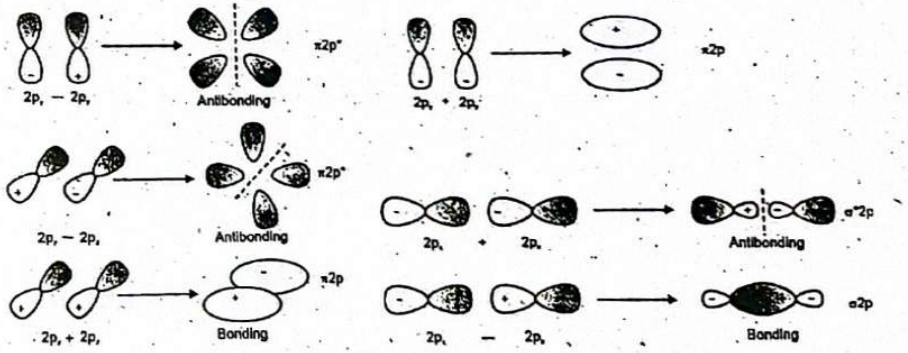


Figure: Formation of δ and π MOs from p_x, p_y and p_z orbitals

Exercise L.O.A.

Q. Draw the molecular orbital diagrams of the following molecules. Calculate their bond orders?
(i) H_2 (ii) He_2 (iii) N_2 (iv) O_2

Molecular Orbital Diagrams of some Diatomic Molecules and their Bond Orders

i) Helium

The electron configuration of He is $1s^2$. For a successful formation of He_2 molecule, 1s orbitals of two He atoms must combine to form bonding ($\delta 1s$) and anti-bonding ($\delta^* 1s$) orbitals as shown in Figure. Out of four electrons, two enter the bonding molecular orbital $\delta(1s)$ and the remaining two occupy the antibonding $\delta^*(1s)$ molecular orbital. But on calculation we discover that the bond order for He_2 is zero. Hence, He_2 molecule is not formed.

Bond order of H_2:
The number of bonds formed between H-atoms in Hydrogen molecule may be calculated as follows:
Number of electron in bonding molecular orbital = 2
Number of electron in anti-bonding molecular orbital = 0
Bond order = $\frac{2-0}{2} = 1$

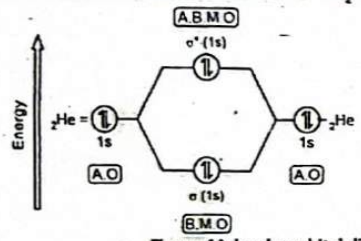


Figure: Molecular orbital diagram of He_2 molecule

Rack Your Brain!
10. What bond order? Give an example.

$$\text{Bond order of } He_2 = \frac{2-2}{2} = 0$$

ii) Nitrogen (N_2)

Electronic configuration of N is,

$$_7N: 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$$

The molecular orbital diagram of N_2 based on this electron configuration is shown in the figure below (Figure). The valence shell 2 s on both N atoms give σ2 s and $\sigma^* 2s$ orbitals; whereas, 2p orbitals give six molecular orbitals which are arranged in the increasing order of energy as:

$$\sigma 2s < \sigma^* 2s < \pi 2p_y = \pi 2p_z < \sigma 2p_x < \pi^* 2p_y = \pi^* 2p_z < \sigma^* 2sP_x$$

The bond order for N_2 can be calculated from its orbital diagram as:

$$\text{Bond order of } N_2 = \frac{6-0}{2} = 3$$

Therefore, there are three covalent bonds between the nitrogen atoms in this molecule. One of these is a σ bond while the other two are π bonds. Nitrogen molecule has a triple bond between its atoms.

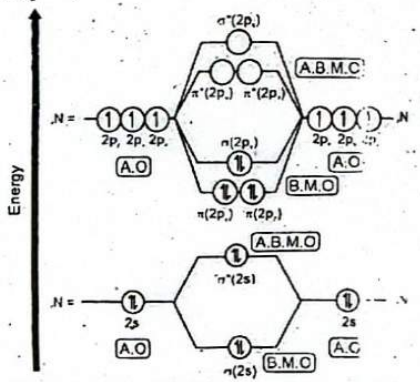


Fig: Molecular orbital diagram of N_2 molecule

iii) Oxygen, O_2

The formation of molecular orbitals in oxygen molecule is shown as follows in figure 36.

The bond energy of the MOs can be arranged as

$$\sigma 2s < \sigma^* 2s < \sigma 2p_x < \pi 2p_y = \pi 2p_z < \pi^* 2p_y = \pi^* 2p_z < \sigma^* 2P_x$$

The bond order of oxygen is $2\left(\frac{6-2}{2}\right)$, which shows the presence of one σ and one π bond between the oxygen atoms, i.e. they are linked by a double bond (O=O). Oxygen molecule is paramagnetic in nature, which means it is attracted by a magnetic field. Paramagnetic substances have one or more unpaired electrons in them. A substance with large number of unpaired electrons is strongly paramagnetic. MOT successfully explains the paramagnetic behavior of oxygen molecule.

Rack Your Brain!
11. Bond order of O_2 according to MOT is
(A) 1 (B) 2
(C) 3 (D) 5

The MO diagram of oxygen shows the presence of two unpaired electrons, one in $\pi^*(2p_y)$ and $\pi^*(2p_z)$ each. Due to the presence of these unpaired electrons, oxygen molecule has a net magnetic field, which interacts with the external magnetic field.

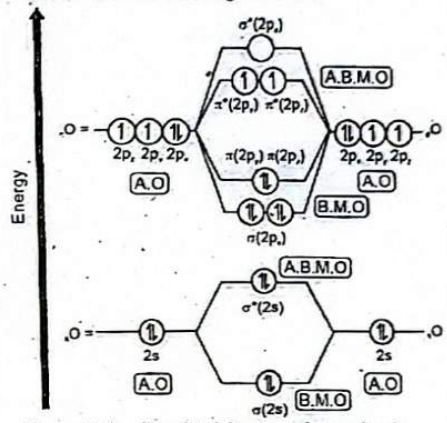
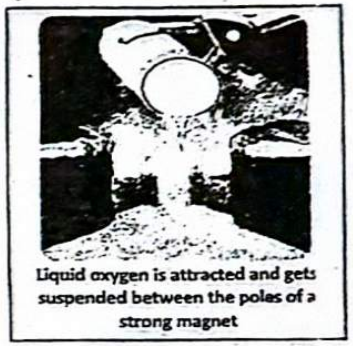


Figure: Molecular orbital diagram of O_2 molecule

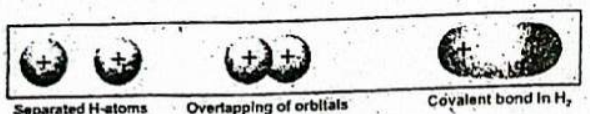


Liquid oxygen is attracted and gets suspended between the poles of a strong magnet

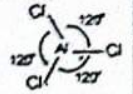
Difference between Bonding Molecular Orbital (BMO) and Anti-Bonding Molecular Orbital (ABMO)

Bonding Molecular Orbital (BMO)	Anti-Bonding Molecular Orbital (ABMO)
• It is formed by the addition overlapping (constructive interference of electron waves) of atomic orbitals	• It is formed by the subtraction overlapping (destructive interference of electron waves) of atomic orbitals.
• The wave function (ψ) of a BMO is given by $\psi_{BMO} = \psi_A + \psi_B$	• The wave function (ψ) of an ABMO is given by $\psi_{ABMO} = \psi_A - \psi_B$
• Its formation takes place when the lobes of atomic orbital have same sign.	• Its formation takes place when the lobes of atomic orbital have different sign.
• The energy of BMO is lesser than that of parent atomic orbitals. Thus stability of the molecule increases.	• The energy in A.B.M.O is higher than that of parent atomic orbitals. Thus stability of the molecule decreases.
• The electron density increase in the region between the nuclei of the bonded atom.	• The electron density decrease in the region between the nuclei of the bonded atom.
• Every electron in BMO contributes toward the attractive forces.	• Every electron in A.B.M.O. contributes toward the repulsive forces
• e.g. Sigma (σ) and Pi(π) in BMO.	• e.g. Sigma (σ^*) and Pi(π^*) in A.B.M.O.

Solution File — Rack Your Brain!

Sr. #	Option	Explanation
1.	B	Atoms share electrons to form a covalent bond, resulting in a stable molecule.
2.	S.Q	Covalently bonded atoms have specific orientations in space with respect to each other. The shared electron pairs are localized between two atoms which are formed by the overlap of half-filled orbitals which have definite directions. Thus covalent bonds are directional.
3.	D	$PC\ell_5$ has 5 + 5 = 10 electrons (Expansion of octet)
4.	D	BF_3 is a regular trigonal planar molecule, when dipoles cancel each other.
5.	S.Q	**Sigma (σ) Bond:** Sigma bond is formed by linear or head to head overlapping of partially filled orbitals. ⊃ **Example: Hydrogen (H_2) Molecule** $H = 1s^1$  Separated H-atoms; Overlapping of orbitals; Covalent bond in H_2 **s and s orbital overlap in H_2** As the two hydrogen atoms approach each other, their 1s orbitals overlap to form H-H bond. The electron density becomes concentrated between the two nuclei. The bond is called σ bond (sigma bond). A single bond is formed when two partially filled atomic orbital overlap in such away that the probability of finding the electron is maximum around the line joining the two nuclei.
6.	S.Q	**Pi (π) Bond:** Pi (π) bond is formed by parallel overlap of half-filled atomic orbitals. In π bond electronic charge density lies above and below the inter-nuclear axis and is weakly attracted by nuclei. e.g., $H_2C = CH_2$ (Ethene) has one Pi (π) bond.
7.	S.Q	**MOT superior to VBT:**
8.	B	Geometry of SO_2 is angular because it is an example of AB3 with one lone pair.

Valence Bond Theory	Molecular Orbital Theory
• According to this theory only valence electrons are involved in bond formation	• According to this theory, all the electrons of interacting atoms are involved in bond formation
• In VBT the two concerned atoms do not lose their individual identity	• In MOT, the two atoms lose their individual identity
• It does not explain the paramagnetic behaviour of molecules like O_2.	• It explains the paramagnetic behaviour of molecules like O_2.
• It does not give idea about the bond order	• It give idea about bond order by which we can determine that whether the bond is single, double or triple
• It does not explain the non- existence of He_2 molecule	• It explains the non-existence of He_2 molecule

9.	S.Q	A bonding electron pair is attracted by both nuclei of atoms while non-bonding by only one nucleus. Because a lone pair experiences less nuclear attraction, its electronic charge is spread out more in space than that for bonding pair. As a result, the non-bonding electron pairs exert greater repulsive forces on bonding electron pairs and thus tend to compress the bond pairs. That is why the electron pairs of lone pairs occupy more space than the bond pairs. 
10.	S.Q	**Bond Order:** "Half of the difference between the number of bonding electrons and anti-bonding electrons is called the bond order." $\text{Bond Order} = \frac{\text{Number of electrons in B.M.O} - \text{Number of electrons in A.B.M.O}}{2}$ **Example: Bond Order of N_2** Number of electrons in bonding molecular orbital = 6 Number of electrons in antibonding molecular orbital = 0 $\text{Bond order} = \frac{6-0}{2} = 3$
11.	.B	Bond order of O_2 according to MOT is 2.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. **Chemical bond formation takes place when:**
a) Force of attraction are equal to the force or repulsion
b) Force of repulsion is greater than force of attraction
c) Force of attraction overcomes force of repulsion
d) None of these

II. **An ionic compound A^+B^- is most likely to be formed when:**
a) Ionization energy of A is high and electron affinity of B is low.
b) Ionization energy of A is low and electron affinity of B is high.
c) Both the ionization energy of A and electron affinity of B are high.
d) Both the ionization energy of A and electron affinity of B are low.

III. **Which of the following molecules has zero dipole moment?**
a) NH_3 b) $CHC\ell_3$ c) H_2O d) BF_3

IV. **The numbers of σ and π bonds in the N_2 molecule are:**
a) one σ and one π bonds b) one σ and two π bonds
c) three σ bonds only d) two σ and one π

V. **Which of the following species has unpaired electrons in antibonding molecular orbitals?**
a) O_2^{2+} b) N_2^{2-} c) B d) F_2

VI. **The shape of $IC\ell_5$ according to the VSEPR model is:**
a) Tetrahedral b) Trigonal planar c) Trigonal bipyramidal d) Square pyramidal

VII. **Which of the following molecules has a net dipole moment?**
a) CO_2 b) CS_2 c) SO_2 d) $CC\ell_4$

VIII. How many electrons are present in the valence shell of P in PO_4^{3-} ?
a) 8 b) 10 c) 12 d) 14

IX. How many extra electrons than a normal octet are there in the valence shell of I in ICl_5 ?
a) 2 b) 3 c) 4 d) 5

X. What is the type and shape of $[ICl_4]^-$ according to the VSEPR model?
a) AB_4, tetrahedral b) AB_4, pyramidal c) AB_5, trigonal bipyramidal d) AB_6, square planar

XI. Which of the following molecules has a central atom with sp3 hybridization and a tetrahedral electron pair geometry?
(a) BF_3 b) SO_2 (c) CCl_4 d) PCl_5

XII. Which of the following species contains a dative bond?
a) CH_4 b) NaCl c) NH_4^+ d) O_2

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	c	force of attraction overcomes force of repulsion	• Chemical bonds form when attractive forces (e.g., nucleus-electron) overcome repulsive forces (e.g., electron-electron).
II.	b	the ionization energy of A is low and electron affinity of B is high	• Ionic bonds require: ▪ Low ionization energy (A loses electrons easily). ▪ High electron affinity (B gains electrons readily).
III.	d	BF_3	• BF_3 is trigonal planar with symmetric charge distribution ⇒ zero dipole moment. • NH_3 (pyramidal), $CHCl_3$ (polar), and H_2O (bent) have dipole moments.
IV.	b	one σ and two π bonds	➢ N ≡ N has: ▪ 1 σ bond (head-on p-orbital overlap). ▪ 2 π bonds (sideways p-orbital overlaps).
V.	a	O_2^{2+}	➢ O_2^{2+} has unpaired electrons in antibonding π orbitals* (MOT diagram).
VI.	d	Square pyramidal	➢ ICl_5 has 5 bonding pairs and 1 lone pairs electrons. ➢ Leading to a configuration with a square base formed by the chlorine atoms and the iodine atom above the centre of the square, giving it pyramidal appearance.
VII.	c	SO_2	• SO_2 is bent (V-shaped) ⇒ net dipole moment. ➢ CO_2/CS_2 (linear) and CCl_4 (tetrahedral) are nonpolar.
VIII.	c	12	• PO_4^{3-}: P forms 4 bonds (8 electrons) + 1 lone pair (2 electrons) ⇒ 10 total. • **Correction:** The correct answer is (b) 10 (P expands its octet via d-orbitals).
IX.	a	2	• ICl_5: I has 5 bonds + 1 lone pair ⇒ 12 electrons (4 extra beyond octet). • **Correction:** The correct answer is (a) 2 (ICl_5 has 5 bonds ⇒ 10 electrons, 2 extra).
X.	a	AB_4, square planar	• $[ICl_4]^-$ has 4 bonds + 2 lone pairs ⇒ square planar (AX_4E_2).
XI.	c	CCl_4	• CCl_4 has sp^3 hybridization and tetrahedral geometry (4 bond pairs).
XII.	c	NH_4^+	• NH_4^+ has a dative bond (N → H) where N donates both electrons.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Define the following:
(i) Dipole (ii) Bond order
(iii) Permanent dipole- permanent dipole force (iv) London dispersion force

Ans. (i) Dipole:
A dipole is a pair of equal and opposite electric charges separated by a small distance, creating a partial positive and partial negative region in a molecule.

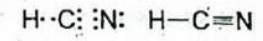
(ii) Bond Order:
Bond order is the number of chemical bonds between a pair of atoms; it indicates bond strength and stability.

(iii) Permanent dipole-permanent dipole force:
Permanent dipole–permanent dipole force is an intermolecular force that occurs between molecules that have permanent dipoles. These forces arise from the electrostatic attraction between the positive end of one polar molecule and the negative end of another.

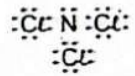
(iv) London dispersion force:
London dispersion forces are weak intermolecular forces caused by temporary fluctuations in the electron distribution of atoms or molecules, which create temporary dipoles that induce dipoles in neighboring particles.

b. Draw the Lewis (electron dot) structures for the following species:
(i) HCN (ii) NCl_3 (iii) CO (iv) O_3 (v) NO_2

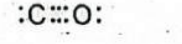
Ans. (i) HCN



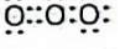
(ii) NCl_3



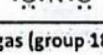
(iii) CO



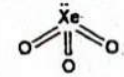
(iv) O_3



(v) NO_2

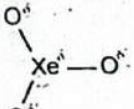


c. Xenon is a noble gas (group 18); xenon trioxide has the following structure:



i. By counting electron pairs around the central atom, explain why xenon trioxide has this shape.
ii. Draw a structure of xenon trioxide showing partial charges on the atoms and the direction of the dipole in the molecule.

Ans. (i) Xenon trioxide (XeO_3) has a **trigonal pyramidal** shape because the central xenon atom has **3 bonding pairs and 1 lone pair** of electrons (total of 4 electron pairs), which adopt a tetrahedral arrangement. The lone pair repulsion distorts the structure into a pyramid with Xe at the apex.



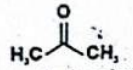
(ii) XeO_3 has a **trigonal pyramidal** geometry with polar bonds. The dipole arises from the electronegativity difference (O > Xe), creating a net dipole toward the O atoms.

d. Explain the difference between the formation of σ and π bonds in terms of VBT.

Ans.

Feature	Sigma (σ) Bond	Pi (π) Bond
Formation	Sigma (σ) bond is Formed by end-to-end (axial) overlap of orbitals.	Pi (π) bond is Formed by side-to-side (lateral) overlap of orbitals.
Orbital Overlap	s-s, s-p, or p-p orbitals along the axis.	Only p-p orbitals (unhybridized) overlapping sideways.
First or Additional	Always the first bond between two atoms.	Forms after a sigma bond in double or triple bonds.
Bond Strength	Generally stronger due to greater overlap.	Weaker than sigma due to less effective overlap.
Electron Density	Concentrated along the bond axis.	Concentrated above and below the bond axis.
Free Rotation	Allows free rotation around the bond.	Restricts rotation due to the fixed overlap orientation.

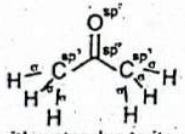
e. The structure of propanone (acetone) is:



i. Show how the central carbon atom forms σ and π bonds through hybridization.

ii. Can propanone make a hydrogen bond with water when both are intermixed?

Ans. (i)



(ii) Yes, acetone can form hydrogen bonds with water due to its polar carbonyl (C=O) group.

1. **Acetone's Structure:** The oxygen (O) in the C=O group is highly electronegative, creating a partial negative charge (δ^-), while the carbon carries a partial positive charge (δ^+).
2. **Hydrogen Bonding:** Water (H_2O) acts as a hydrogen bond donor ($H^{\delta+}$), and acetone's $O^{\delta-}$ acts as an acceptor, forming:

$$H-O-H\cdots O=C$$

3. **No H-Bond Donation from Acetone:** Acetone lacks H bonded directly to O/N/F (unlike alcohols), so it cannot donate H-bonds, only accept them.

f. Predict the shapes of sulfate ($[SO_4]^{2-}$), borate ($[BH_4]^-$) and tri-iodide ions ($[I_3]^-$) according to the VSEPR model.

Ans. VSEPR (Valence Shell Electron Pair Repulsion) model:

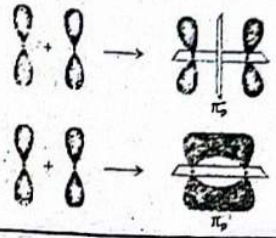
1. **Sulphate ion $[SO_4]^{2-}$**
   - **Central atom:** Sulphur (S)
   - **Valence electrons:** 6 (from S) + 4 × 6 (from O) + 2 (charge) = 32 electrons
   - **Electron pairs around S:** 4 bonding pairs (no lone pairs on S)
   - **Electron geometry:** Tetrahedral
   - **Molecular shape:** Tetrahedral
   - **Bond angles:** 109.5°
2. **Borohydride ion $[BH_4]^-$**
   - **Central atom:** Boron (B)
   - **Valence electrons:** 3 (from B) + 4 × 1 (from H) + 1 (charge) = 8 electrons
   - **Electron pairs around B:** 4 bonding pairs (no lone pairs)
   - **Electron geometry:** Tetrahedral
   - **Molecular shape:** Tetrahedral
   - **Bond angles:** 109.5°

3. **Triiodide ion $[I_3]^-$**
   - **Central atom:** Iodine (I)
   - **Valence electrons:** 3 × 7 = 21 + 1 (charge) = 22 electrons
   - **Electron pairs on central I:** 2 bonding pairs (with outer I atoms), 3 lone pairs
   - **Electron geometry:** Trigonal bipyramidal (based on 5 regions of electron density)
   - **Molecular shape:** Linear (3 lone pairs occupy equatorial positions)
   - **Bond angle:** 180°

Ion	Electron Geometry	Molecular Shape	Bond Angle
$[SO_4]^{2-}$	Tetrahedral	Tetrahedral	109.5°
$[BH_4]^-$	Tetrahedral	Tetrahedral	109.5°
$[I_3]^-$	Trigonal bipyramidal	Linear	180°

g. Sketch the molecular orbital pictures of π(2p) and π*(2p).

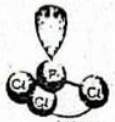
Ans.



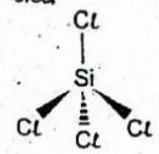
h. Sketch the hybrid orbitals and bond formation in PCl_3, $SiCl_4$ and NH_4^+.

Ans. PCl_3

Formula: PCl_3
Hybridization: sp^3
Bond angle: 109.5°
Geometry: Tetrahedral
Shape: Trigonal pyramidal

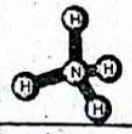


$SiCl_4$

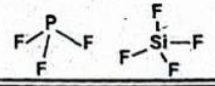


NH_4^+

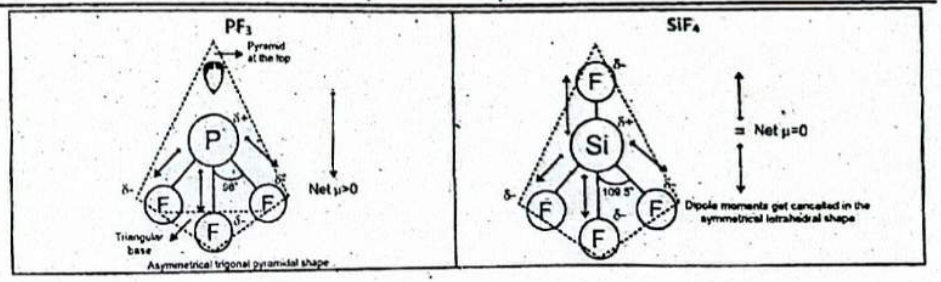
Formula: NH_4^+
Hybridization: sp^3
Bond angle: 109.5°
Geometry: Tetrahedral
Shape: Tetrahedral



i. The structures of PF_3 and SiF_4 are given below. Redraw these with partial charges and state which is polar and which is non-polar.

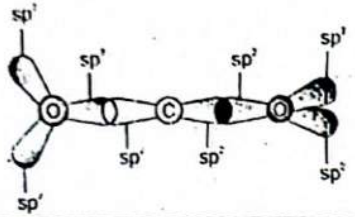


Ans.



j. Draw the orbital structures of the CO_2 molecule in terms of VBT.

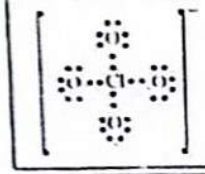
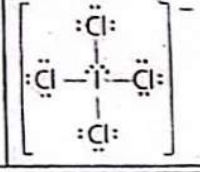
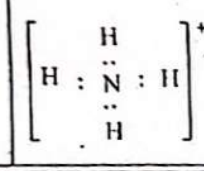
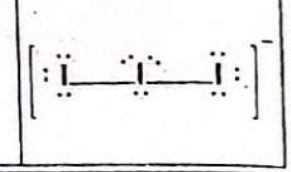
Ans.



k. Draw the Lewis structures and tell whether these ions involve expanded octets?

i) $C\ell O_4^-$ ii) $IC\ell_4^-$ iii) NH_4^+ iv) I_3^-

Ans.

$C\ell O_4^-$	$IC\ell_4^-$	NH_4^+	I_3^-
			

l. The bond between K and $C\ell$ is ionic but that between Si and $C\ell$ is polar covalent. Explain why?

Ans. The difference in bonding between K-$C\ell$ (ionic bond) and Si-$C\ell$ (polar covalent bond) can be explained based on the electronegativity difference between the atoms involved and their positions in the periodic table.

1. **K-$C\ell$ (Ionic Bond):**
   - Potassium (K) is a metal in Group 1 of the periodic table, and it has a low electronegativity (0.82).
   - Chlorine ($C\ell$) is a non-metal in Group 17 and has a high electronegativity (3.16).
   - Electronegativity difference: 3.16 – 0.82 = 2.34
   - When the electronegativity difference is large (usually greater than 1.7), one atom (in this case, K) will lose an electron to become a positively charged ion (K^+), while the other atom ($C\ell$) will gain the electron to become a negatively charged ion ($C\ell^-$). This creates an ionic bond where the electrostatic attraction between the oppositely charged ions holds them together.
2. **Si-$C\ell$ (Polar Covalent Bond):**
   - Silicon (Si) is a metalloid with an electronegativity of 1.90.
   - Chlorine ($C\ell$), has an electronegativity of 3.16.
   - Electronegativity difference: 3.16 – 1.90 = 1.26
   - When the electronegativity difference is moderate (between 0.4 and 1.7), the electrons are not completely transferred as in ionic bonds, but instead, they are shared unequally between the two atoms.
   - In this case, chlorine attracts the shared electron pair more strongly than silicon, creating a polar covalent bond. The $C\ell$ atom becomes partially negative (δ^-), and the Si atom becomes partially positive (δ^+). The bond is polar because of the unequal sharing of electrons.

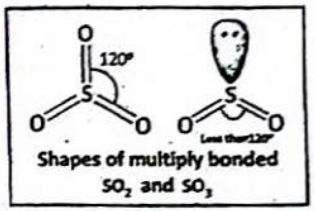
In short

- **K-$C\ell$:** Large electronegativity difference → Ionic bond (electron transfer).
- **Si-$C\ell$:** Moderate electronegativity difference → Polar covalent bond (unequal electron sharing).

m. SO_2 is a polar molecule but SO_3 not. Justify.

Ans. The difference in polarity between SO_2 (Sulphur dioxide) and SO_3 (Sulphur trioxide) can be explained by the molecular geometry and symmetry of the molecules.

1. **SO_2 (Sulphur Dioxide) – Polar:**
   - **Electron Geometry:** Bent or V-shaped (due to sp^2 hybridization of the central Sulphur atom).
   - **Bond Angles:** The bond angle between the oxygen atoms is approximately 120°.
   - **Lone Pairs on Sulphur:** The Sulphur atom has one lone pair in SO_2, which influences the shape and causes a bent molecular geometry.
   - **Electronegativity Difference:** Oxygen is more electronegative than Sulphur, creating a dipole moment pointing towards the oxygen atoms.
   - **Asymmetry:** Due to the bent shape, the individual bond dipoles do not cancel each other out, resulting in a net dipole moment, making SO_2 a polar molecule.
2. **SO_3 (Sulphur Trioxide) – Nonpolar:**
   - **Electron Geometry:** Trigonal planar (due to sp^2 hybridization of the central Sulphur atom).
   - **Bond Angles:** The bond angles between the oxygen atoms are exactly 120°, forming a flat, symmetric structure.
   - **No Lone Pairs on Sulphur:** The Sulphur atom in SO_3 has no lone pairs.
   - **Symmetry:** The molecule is highly symmetric, with the three oxygen atoms arranged symmetrically around the central Sulphur atom, and the bond dipoles in each C=O bond cancel each other out. This results in no net dipole moment, making SO_3 a nonpolar molecule.



Shapes of multiply bonded SO_2 and SO_3

n. Which of O_2^{2+}, and O_2^{2-} would be paramagnetic? Give reason in the light of MOT.

Ans. O_2^{2+}

Electron configuration for O_2^{2+}:

- O_2^{2+} has 2 fewer electrons than O_2.
- Starting with O_2's configuration (16 electrons), remove 2 electrons:
- From the π orbitals* (since these are the highest energy orbitals).
- The electron configuration for O_2^{2+} is:
  $\sigma(2s)^2, \sigma(2s)^2, \sigma(2p_z)^1, \pi(2p_x)^2, \pi(2p_y)^2, \pi(2p_x)^1, \pi^*(2p_y)^{1**}$
- Since both $\pi(2p_x)^*$ and $\pi(2p_y)^*$ are fully paired, there are no unpaired electrons in O_2^{2+}.
- Therefore, O_2^{2+} is diamagnetic (no unpaired electrons).

O_2^{2-}

Electron configuration for O_2^{2-}:

- O_2^{2-} has 2 more electrons than O_2.
- Starting with O_2's configuration (16 electrons), add 2 electrons:
- These electrons will fill the *π orbitals**.
- The electron configuration for O_2^{2-} is:
  $\sigma(2s)^2, \sigma(2s)^2, \sigma(2p_z)^2, \pi(2p_x)^2, \pi(2p_y)^2, \pi(2p_x)^2, \pi^*(2p_y)^{2**}$
- Since all electrons are paired in O_2^{2-} (even in the antibonding *π orbitals**), there are no unpaired electrons in O_2^{2-}.
- Therefore, O_2^{2-} is also diamagnetic (no unpaired electrons).

Conclusion:

- Both O_2^{2+} and O_2^{2-} are diamagnetic, not paramagnetic, because they both have no unpaired electrons when analyzed using the Molecular Orbital Theory (MOT).

o. Which of the following bonds would be most polar?
i) C – Cℓ ii) Si – F iii) Se – F

Ans.

(i) C – Cℓ

- The C-Cℓ bond:
  - Carbon (C) has an electronegativity of 2.55.
  - Chlorine (Cℓ) has an electronegativity of 3.16.
  - The electronegativity difference is: 3.16 – 2.55 = 0.61
- A polar covalent bond is formed when the electronegativity difference is between 0.4 and 1.7. Since the difference between C and Cℓ is 0.61, the bond is polar covalent.

(ii) Si – F

- The Si–F (silicon–fluorine) bond is highly polar due to the large difference in electronegativity between the two atoms:
  - Electronegativity of Si (Silicon) ≈ 1.90
  - Electronegativity of F (Fluorine) ≈ 3.98
  - Difference = 3.98 – 1.90 = 2.08
- Reason: A greater electronegativity difference between two bonded atoms means that the bonding electrons are more strongly attracted to the more electronegative atom (in this case, fluorine), resulting in a highly polarized bond.
- This large difference gives the Si–F bond a significant dipole moment, with fluorine becoming partially negative (δ^-) and silicon partially positive (δ^+).
- Conclusion: Si–F is a highly polar bond, and if compared with most common bonds, it would indeed be one of the most polar due to the extreme electronegativity of fluorine.

(iii) Se – F

- To determine whether the Se–F bond is polar, and how polar it is, we look at the electronegativity difference between the two atoms:
- Electronegativity values:
  - Se (Selenium) ≈ 2.55
  - F (Fluorine) = 3.98
- Electronegativity difference: $\Delta EN = 3.98 - 2.55 = 1.43$
- Conclusion: Since the electronegativity difference is significant (1.43), the Se–F bond is polar covalent.
- In short: Among all these bonds Si – F bond is most polar covalent.

p. Compare the bond energies of single, double, and triple bonds between the same two atoms. (e.g., H–H, O = O, N ≡ N). Explain the trend in terms of the number of shared electrons.

Ans. Bond energy of H – H = 432 kJ/mol (No. of shared electron: 1 each)
Bond energy of O = O = 459 kJ/mol (No. of shared electron: 2 each)
There is no stable triple bond between two oxygen atoms (O≡O) under normal conditions.
However, (Bond energy of C ≡ C = 839 kJ/mol (No. of shared electron: 3 each))

DESCRIPTIVE QUESTIONS

Q.3 How the bonding in the following molecules can be explained with respect to valence bond theory?
(i) $C\ell_2$ (ii) O_2 (iii) N_2 (iv) HF (v) H_2S

Ans. See Page No. (73)

Q.4 What are the postulates of VSEPR model? Discuss the structures of the following species with reference to this theory.
(i) CH_4 (ii) NH_3 (iii) H_3O^+ (iv) $PC\ell_5$ (v) SO_2 (vi) SF_6

Ans. See Page No. (78)

Q.5 Explain the orbital hybridization for CH_4, NH_3, BF_3, and $BeC\ell_2$.

Ans. See Page No. (76)

Q.6 Draw the molecular orbital diagrams of the following molecules. Calculate their bond orders?
(i) H_2 (ii) He_2 (iii) N_2 (iv) O_2

Ans. See Page No. (88)

Q.7 Discuss the formation of F_2 molecule in the light of Lewis concept, VBT, and MOT.

Ans. F_2 in the light of Lewis concept:

Fluorine molecule (F_2) according to VBT:

The bond in the fluorine molecule (F_2) is formed by the overlap of half-filled 2p, orbital on each fluorine atom.

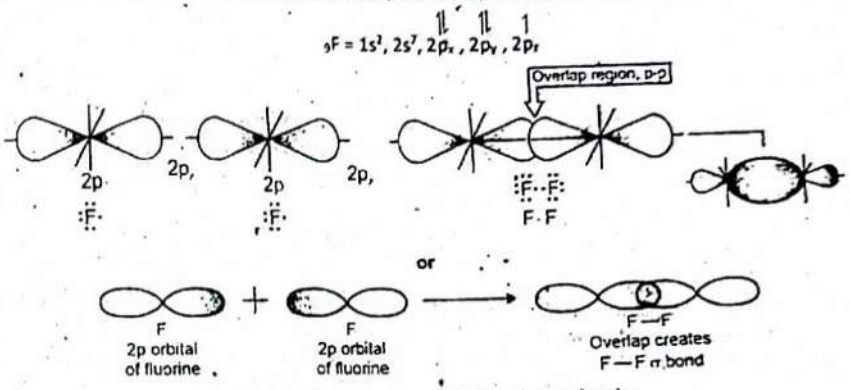
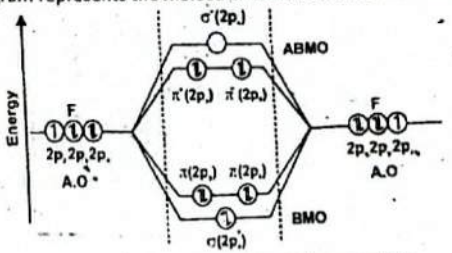


Figure: The formation of the fluorine molecule

Fluorine molecule (F_2) w.r.t MOT:

- Electronic configuration of Fluorine = $1s^2, 2s^2, 2px^2, 2py^2, 2pz^1$
- The following diagram represents the molecular orbitals of fluorine molecule.



Molecular orbitals energy level diagram of F_2

$$F_2 = (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2 = (\pi(2p_x)^2(\pi^* 2p_y)^2 = (\pi^* 2p_z)^2$$

$$\text{Bond order} = \frac{10-8}{2} = 1$$

ADDITIONAL SLOs BASED MCQs

1. Which atom donates a lone pair in the formation of a dative bond in H_3O^+?
   A) One of the hydrogen atoms B) The oxygen atom
   C) A proton D) Water molecule
2. Which ion has an expanded octet around the central atom?
   A) NH_4^+ B) NO_3^- C) SO_4^{2-} D) OH^-
3. Which of the following pairs will form a covalent bond?
   A) Na and Cl B) K and F C) H and Cl D) Mg and O
4. Which statement about dipole moments is true?
   A) They depend only on bond length
   B) They depend only on molecular mass
   C) They result from equal sharing of electrons
   D) They arise from bond polarity and molecular shape
5. The bond angle in a trigonal planar molecule is:
   A) 90° B) 104.5° C) 109.5° D) 120°
6. Valence bond theory explains:
   A) Ionic bond formation B) Molecular shapes
   C) Bond formation through orbital overlap D) Electron transfer
7. What is the shape of the ammonium ion (NH_4^+)?
   A) Linear B) Trigonal pyramidal C) Tetrahedral D) Bent
8. Which hybridization is present in methane (CH_4)?
   A) sp B) sp^2 C) sp^3 D) sp^3d
9. In ethene (C_2H_4), the carbon atoms are:
   A) sp hybridized B) sp^2 hybridized C) sp^3 hybridized D) Unhybridized
10. What is the bond angle in a molecule with sp^3 hybridization?
    A) 120° B) 109.5° C) 180° D) 90°
11. Which of the following supports paramagnetism in oxygen (O_2)?
    A) Bond length B) Lone pairs
    C) Unpaired electrons in antibonding orbitals D) Resonance
12. Which orbital in O_2 contains unpaired electrons?
    A) $\sigma(2s)$ B) $\sigma(2pz)$ C) $\pi^*(2px)$ and $\pi^*(2py)$ D) $\pi(2py)$
13. Electronegativity values are useful to predict:
    A) Number of protons B) Bond lengths C) Bond polarity D) Boiling point
14. Which factor increases the electronegativity of an element?
    A) Increased atomic size B) Greater shielding effect
    C) Higher nuclear charge D) More electron shells
15. Which element has lower electronegativity due to shielding?
    A) F B) O C) Li D) Cs

Answer Key with Explanations

Sr.No.	Option	Explanations
1.	B	Oxygen donates a lone pair to a proton (H^+) in H_3O^+.
2.	C	Sulphur in SO_4^{2-} exceeds the octet due to available d orbitals.
3.	C	H and Cl have a small electronegativity difference → covalent bond.
4.	D	Both electronegativity difference and molecular geometry affect dipole moments.
5.	D	Trigonal planar molecules have bond angles of 120°.
6.	C	Valence bond theory describes covalent bonding as orbital overlap.
7.	C	NH_4^+ has 4 bonding pairs → tetrahedral shape.
8.	C	CH_4 has four sigma bonds → sp^3 hybridization.
9.	B	Each carbon in ethene forms 3 sigma bonds → sp^2 hybridization.
10.	B	sp^3 hybridization leads to a tetrahedral geometry with 109.5° angles.
11.	C	MOT explains O_2's Paramagnetism due to unpaired electrons in π^* orbitals.
12.	C	$\pi^*(2px)$ and $\pi^*(2py)$ each have one unpaired electron in O_2.
13.	C	The difference in electronegativity between atoms determines bond polarity.
14.	C	Higher nuclear charge attracts bonding electrons more strongly.
15.	D	Cesium has many inner shells, causing high shielding and low electronegativity.

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Define ionic bond with example.

Ans. Ionic Bond or Electrovalent Bond:
"The electrostatic force of attraction between oppositely charged ions i.e. cation and anion is called ionic bond or electrovalent bond."

IA group form ionic bond with VIIA

IA	VIIA
Li^+	F^{-1}
Na^+	Cl^{-1}
K^+	Br^{-1}
Rb^+	I^{-1}

Q.2 Define bond energy. What are factors influencing bond energy?

Ans. Bond Energy:
"The average amount of energy required to break all bonds of a particular type in one mole of the substance is called the bond energy."

Factors Affecting Bond Energy:
Bond energy is a measure of the strength of a bond. The strength of a bond depends upon the following factors:

i. **Electronegativity Difference of Bonded Atoms:** Greater the electronegativity difference of bonded atom, more will be the polarity of bond and higher will be its bond energy.

ii. **Sizes of the Atoms:** Bond energy decreases with increase in the atomic radii.

Bond	Bond Energy ($kJmol^{-1}$)
H – F	567
H – Cl	431
H – Br	366
H – I	299

iii. **Bond Length:** The bonds with higher bond energy values have shorter bond lengths. The bond energies of C to C bonds being in the order C ≡ C > C = C > C – C. Their bond lengths are in the reverse order i.e. C – C > C = C > C ≡ C.

iv. **Bond Polarity:** Generally, a polar covalent bond is stronger than a non-polar covalent bond.

Q.3 How do you compare the bond strengths of polar and non-polar molecules?

Ans. Polar and Non-Polar Molecules and Their Strength:

In polarity bonded atoms in molecules have partial positive and partial negative centres because of difference of electronegativity. Additional attractive force is created between bonded atoms due to dipole formation. As a result bond is stronger than it is expected.

Example: Bond energy (Calculated) for H–Cℓ = 336 kJ/mol^{-1}
Bond energy (observed) for H–Cℓ = 432 kJ/mol^{-1}

Difference in Bond energy = Bond energy (observed) – Bond energy (calculated)

Difference in Bond energy = 432 – 336 = 96 kJ mol^{-1}

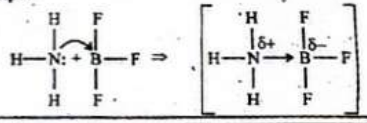
Difference in Bond energy is created due to extra strength of polar bond/ionic character of molecule.

On the other hand, no dipole formation occurs in non-polar molecule, so bond is comparatively weaker e.g., bond energy of Cℓ–Cℓ = 242 kJ mol^{-1}.

Hence, we conclude that **a polar bond is stronger than non-polar bond due to ionic character present in it.**

Q.4 Differentiate between co-ordinate covalent bond and covalent bond.

Ans. Differences between Co-ordinate Covalent Bond and Covalent Bond:

Covalent Bond	Coordinate Covalent Bond
(i) The bond which is formed by the mutual sharing of electrons between two atoms is called as covalent bond.	(i) A coordinate covalent bond is formed between two atoms when the shared pair of electrons is donated by one of the bonded atoms.
(ii) Single covalent bond is represented by a single line, double covalent bond by two lines and triple covalent bond by tree lines.	(ii) Coordinate covalent bond is represented by an arrow pointing from the donor atom to the acceptor atom.
Example: $H^{\bullet} \times H \rightarrow H-H$ $:\ddot{C}\ell^{\bullet} \times \rightarrow C\ell-C\ell$	**Example:** 

Q.5 What is basic assumption of VSEPR theory?

Ans. The Basic Assumption of VSEPR Theory:

The valence electron pairs (lone pairs and the bond pairs) are arranged around the central atom to remain at a maximum distance apart to keep repulsions at a minimum.

(Note: This way of arrangement of electron pairs gives minimum energy and maximum stability to the molecules).

Q.6 Why are the bond angles of H_2O and NH_3 not equal to 109.5° like that of CH_4 although oxygen and nitrogen atoms are Sp^3 hybridized?

Ans. According to VSEPR theory, the shape of a molecule is decided on the basis of repulsions between of lone pairs and bond pairs around the central atom. Although N and O are sp^3 hybridized yet they differ in bonding from C compounds with sp^3 hybridization according to VSEPR theory.

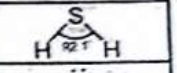
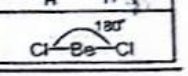
The description of these molecules is as follows:

Properties	CH_4	NH_3	H_2O
Type of molecule	AB_4	AB_4	AB_4
No. of bond pairs	4	3	2
No. of lone pairs	0	1	2
Shape of molecule	Tetrahedral	Pyramidal	Angular
Bond angle	109.5°	107.5°	104

Properties	CH_4	NH_3	H_2O
Reason of difference	Structure is regular due to only bond pair-bond pair repulsions.	Structure is distorted due to lone pair as Lone pair-Bond pair repulsion effects more than Bond pair-Bond pair repulsions so bond angle is reduced.	Here due to two lone pairs, Lone pair-Lone pair has a greater effect so angle is further reduced to 104°.

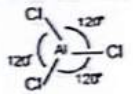
Q.7 Predict the shapes of following molecules according to VSEPR theory
(i) H_2S (ii) H_2O (iii) $BeCl_2$

Ans.

Molecule	Electron Pairs			Type	Arrangement of Pairs	Geometry	Shape
	T	B	L				
H_2S	4	2	2	AB_4	Tetrahedral	Bent or angular	
H_2O	4	2	2	AB_4	Tetrahedral	Bent or angular	
$BeCl_2$	2	2	0	AB_2	Linear	Linear	

Q.8 Why does lone pair of electrons occupy more space as compared to bond pair?

Ans. A bonding electron pair is attracted by both nuclei of atoms while non-bonding by only one nucleus. Because a lone pair experiences less nuclear attraction, its electronic charge is spread out more in space than that for bonding pair. As a result, the non-bonding electron pairs exert greater repulsive forces on bonding electron pairs and thus tend to compress the bond pairs. That is why the electron pairs of lone pairs occupy more space than the bond pairs.

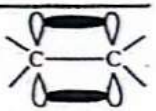


Q.9 Write two points of Valence Bond theory.

Ans. Points of Valence Bond Theory

(i) A bond between two atoms is formed by the overlap of half-filled orbitals of two atoms. The two overlapping atomic orbitals retain their identities.

(ii) The two overlapping orbitals must have electrons of opposite spin.



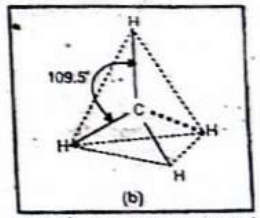
Q.10 Explain the structure of CH_4 on the basis of sp^3 hybridization.

Ans. Hybridization:

"The process of mixing of atomic orbitals having different shapes and energies to form hybrid orbitals with same shape and almost same energy is called Hybridization".

Types: 1. sp^3 – hybridization
2. sp^2 – hybridization
3. sp – hybridization

Structure of CH_4: Methane molecule is formed by the overlap of sp^3 hybrid orbitals of carbon with 1s orbitals of four hydrogen atoms separately to form four sigma bonds. The molecule thus formed, possesses a **tetrahedral** geometry. The four C-H bonds which result from **sp^3-s overlaps** are directed towards the corners of a regular tetrahedron. The tetrahedral structure of CH_4 has four faces, four corners, six edges and six bond angles of 109.5°.

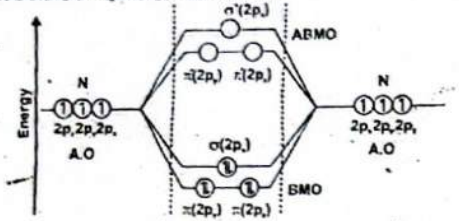


Four sp^3-s overlaps in tetrahedral structure of CH_4 molecule

Q.11 Draw molecular orbital picture of N_2 molecule and also calculate its bond order.

Ans. Molecular Orbital Picture of N_2 Molecule:

The molecular orbital structure of N_2 molecules is shown



Molecular orbitals energy level diagram of N_2

Since no unpaired electron is present in MOs so N_2 molecule shows diamagnetic behaviour.

Bond Order:

$$\text{Bond order} = \frac{\text{No. of electrons in BMO} - \text{No. of electrons in ABMO}}{2} = \frac{6-0}{2} = 3$$

So, the bond order of nitrogen is 3.

Q.12 Differentiate between Bonding and Antibonding Molecular Orbitals.

Ans. Differences between Bonding and Antibonding Molecular Orbitals:

Bonding Molecular Orbital (BMO)	Anti-Bonding Molecular Orbital (ABMO)
It is formed by the addition overlapping (constructive interference) of atomic orbitals.	It is formed by the subtraction overlapping (destructive interference) of atomic orbitals.
The wave function (ψ) of a BMO is given by $\psi_{BMO} = \psi_A + \psi_B$	The wave function (ψ) of an ABMO is given by $\psi_{ABMO} = \psi_A - \psi_B$
Its formation takes place when the lobes of atomic orbital have same sign.	Its formation takes place when the lobes of atomic orbital have different sign.
The energy of BMO is lesser than that of parent atomic orbitals.	The energy in A.B.M.O is higher than that of parent atomic orbitals.
The electron density is high in the region between the nuclei of the bonded atom.	The electron density is lower in the region between the nuclei of the bonded atom.
Every electron in BMO contributes toward the attractive forces.	Every electron in A.B.M.O. contributes toward the repulsive forces
e.g., Sigma (σ) and Pi (π) in BMO.	e.g., Sigma (σ^*) and Pi (π^*) in A.B.M.O.

Q.13 Differentiate between a Sigma and Pi bond.

Ans. Differences between a Sigma and Pi Bond:

Sr. #	Sigma bond (σ)	Pi bond (π)
(i)	Sigma bond is formed by linear or head to head overlapping of partially filled orbitals.	Pi bond is formed by parallel or side to side overlap of atomic orbitals.
(ii)	Representation of sigma bond is 'σ'.	Representation of Pi bonds is π.
(iii)	Electronic charge density is present on bond axis between the two nuclei.	Electronic charge density is present above and below bond axis of two nuclei.
(iv)	Charge density of σ-bond is comparatively less diffused than π and due to stronger nuclear attraction.	Charge density of π bond is more diffused due to lesser nuclear attraction.
(v)	Sigma bond is stronger.	π bond is weaker.
(vi)	σ-bond is comparatively inert.	π bond is comparatively reactive.
(vii)	Bonded atoms always form σ-bond firstly and then π-bond if necessary.	π-bond formation is preceded by σ-bond formation.
(viii)	**Examples:** H–H σ-bond	$O \overset{\sigma}{\underset{\pi}{=}} O$

Q.14 Define dipole moment and write the units of dipole moment.

Ans. The product of electric charge (q) and the distance between the positive and negative centers (r) is called dipole moment.

$$\mu = \vec{q} \times \vec{r}$$

Units:

(I) The common unit of dipole moment is Debye (D).

(II) In S.I. the units of dipole moment are mC.

Relationship between Debye (D) and mC: $1D = 3.336 \times 10^{-30}$ mC

Q.15 Define bond length. Give two factors affecting bond length.

Ans. Bond Length: "The distance between the nuclei of two atoms forming a covalent bond is called the bond length."

Factors Affecting Bond Length

i **Electronegativity Difference:** With an increase in electronegativity difference between the bonded atoms, the bond becomes shortened.

Case – II: e.g. Si-F bond length in SiF_4 is found to be 154-159 pm, whereas the addition of their covalent radii (Si = 117pm and F = 64 pm) give Si-F bond length to be equal to 181 pm. The calculated values are almost always higher due to electronegativity differences. The ionic character results in shortening of the bond length due to force of attraction between the polar ends.

ii. **Hybridization:** Hybridization scheme involved, also explains the shortening of bonds due to the predominant participation of s-orbitals. Since the **2s-orbital of carbon has smaller mean radius than the 2p-orbitals,** it would be expected that greater the s character in the hybrid orbitals used, the shorter will be the bond distance.

Example: C-C bond lengths are 154,133 and 120 pm for ethane, ethene and ethyne, respectively where s-orbital contribution increases from sp^3 to sp.

◈◈◈◈◈

SELF-ASSESSMENT Chapter # 03

Total Mark: 30

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) The shape of ammonia (NH_3) molecule according to VSEPR theory is:
A. Linear B. Tetrahedral C. Trigonal pyramidal D. Bent

(ii) The numbers of σ and π bonds in the N_2 molecule are:
A. one σ and one π bonds B. one σ and two π bonds
C. three σ bonds only D. two σ and one π

(iii) Which of the following molecules has zero dipole moment?
A. NH_3 B. $CHCl_3$ C. H_2O D. BF_3

(iv) Which of the following species contains a dative bond?
A. CH_4 B. NaCl C. NH_4^+ D. O_2

(v) Which of the following molecules shows hydrogen bonding?
A. CH_4 B. NH_3 C. CO_2 D. CF_4

(vi) Which type of hybridization of C occurs in CO_2?
A. sp^3 B. sp^2 C. sp D. dsp^3

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) Explain the difference between the formation of σ and π bonds.
(ii) What are necessary conditions for the hydrogen bond to form?
(iii) Why does bond polarity lead to the development of dipole moments?
(iv) State the shape and bond angle of BF_3 using VSEPR theory.
(v) Draw the orbital structures of the CO_2 molecule in terms of VBT.
(vi) Write the hybridization of carbon in ethyne (C_2H_2).
(vii) Calculate the bond order of O_2 using molecular orbital theory.
(viii) SO_2 is a polar molecule but SO_3 not. Justify.

Q.3 Extensive Questions. (2 × 4 = 8)

(a) Draw the molecular orbital diagrams of the following molecules. Calculate their bond orders? (i) N_2 (ii) O_2
(b) What are the postulates of VSEPR model? Discuss the structures of the following species with reference to this theory.
(i) H_3O^+ (ii) PCl_5 (iii) SO_2 (iv) SF_6

Chapter 04

STOICHIOMETRY

Student Learning Outcomes

After studying this chapter, students will be able to:

- Derive measurements of mass, volume, and number of particles using moles. **(Application)**
- State the volume of one mole of a gas at STP. **(Knowledge)**
- Use the volume of one mole of gas at STP to solve mole-volume problems. **(Knowledge)**
- Calculate the gram molecular mass of a gas from density measurements at STP. **(Application)**
- Express balanced chemical equations in terms of moles, representative particles, masses, and volumes of gases at STP. **(Application)**
- Explain the concept of limiting reagents. **(Understanding)**
- Calculate the maximum amount of product and amount of any unreacted excess reagent. **(Application)**
- Calculate theoretical yield, actual yield, and percentage yield when given appropriate information. **(Application)**
- Calculate the quantities of reactants and products involved in a chemical reaction using stoichiometric principles. (Some examples include calculations involving reacting masses, volumes of gases, volumes, and concentrations of solutions, limiting reagent and excess reagent, percentage yield calculations). **(Application)**
- Explain with examples, the importance of stoichiometry in the production and dosage of medicine. **(Understanding)**

Introduction

Stoichiometry is derived from Greek words ***stoicheion*** means **element** and ***metron*** means **measure**. Collectively, stoichiometry means quantitative measure of reactants and products.

Stoichiometry

Stoichiometry (pronounced as stoy-key-om.eh-tree) is the branch of chemistry in which the relationship between the amounts of reactants and products in a balanced chemical equation is studied.

- The balanced chemical equation has the same number of atoms of each type on both sides of equation.
- It has definite ratios of reactants and products just as compounds have definite ratios of elements. Such ratios are used to calculate the mass or mole of other substances.

Laws in Stoichiometry:

Stoichiometric calculations obey **law of conservation of mass** and **law of definite proportions.**

1. According to the **law of conservation of mass, "matter (mass) can neither be created nor destroyed".** It states in terms of stoichiometry that the total mass of reactants is equal to the total mass of products in a balanced equation.
2. According to the law of definite proportions, **a pure compound always contains the same element combined in the same ratio by mass.**

CONCEPT OF MOLE

➤ **Definition**

The mole is the amount of a substance which contains as many elementary entities as there are atoms in 0.012 kg(12 g) of carbon-12.

- The elementary entities may be atoms, molecules, ions, electrons, and other particles.
- It is represented by 'n'.
- The number of entities present in one mole of a substance is a constant number named **Avogadro's Number**, i.e. 6.02×10^{23}. It is represented by N_A.
- This value is attributed to an Italian scientist **Amedo Avogadro (1776-1856).**

Did You Know?

The word 'mole' was introduced in 1896 by Wilhelm Ostwald who derived the term from Latin word moles meaning a 'heap' or 'pile'.

Did You Know?

Avogadro's number is a physical constant representing the molar number of entities. The exact value of it is 6.02214179×10^{23} mol^{-1}. In calculations we use the rounded off value 6.02×10^{23}.

➤ **Examples are Given Below:**

- 1 mole of ^{12}C contains 6.02×10^{23} atoms of ^{12}C.
- 1 mole of H_2O contains 6.02×10^{23} molecules of H_2O.
- 1 mole of $NaC\ell$ contains 6.02×10^{23} formula units of $NaC\ell$.
- 1 mole of Na^+ contains 6.02×10^{23} ions of Na^+.

➲ Molar Mass

- **Definition:** "The mass of one mole of a substance expressed in grams is called molar mass".
- **Unit:** The unit of molar mass is g / mol.
- **Example:** The molar mass is the sum of the masses of the component atoms.

Rack Your Mind!

1. Which of the following quantities represents one mole of oxygen molecules (O_2)?
   A) 16.0 g of O_2
   B) 6.02×10^{23} atoms of oxygen
   C) 32.0 g of O_2
   D) 22.4 cm^3 of O_2 at STP

The mass of one mole of $CC\ell_4$ can be found by adding the masses of carbon and chlorine present.

Molar mass of $CC\ell_4$ = Molar mass of one C + Molar mass of $C\ell\times4$

Molar mass of $CC\ell_4 = 12.0\times1 + 35.5\times4$

Molar mass of $CC\ell_4 = 12.0 + 142.0 = 154.0$ g

The chemists use the mole as the SI unit to weigh and count atoms, molecules, formula units or ions.

The mass of one mole of a substance (element, compound or ionic species) is equal to the atomic mass, molecular mass, formula mass or ionic mass of a substance when expressed in grams and is known as molar mass, represented by M.

➤ **Other Examples**

- 1 mole of carbon atoms is 12.0 g.
- 1 mole of CO_2 molecule is 44.0 g.
- 1 mole of CaO formula units is 56.1 g.
- 1 mole of CO_3^{2-} ions is 60.0 g.

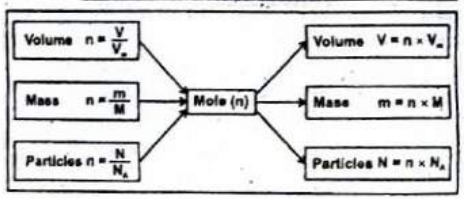
Rack Your Mind!

2. One mole of H_2O has two moles of bonds, three moles of atoms, ten moles of electrons and 28 moles of total fundamental particles. Explain.

The number of moles of a substance can be calculated by dividing mass in grams by molar mass. The formula for number of moles is:

$$\text{Number of moles} = \frac{\text{Given mass}}{\text{Molar mass}}$$

$$n = \frac{m}{M}$$



Sample Problem 4.1

Calculate the number of moles present in 20 g of NaOH.

Solution:

$$\text{Number of moles} = \frac{\text{Given mass}}{\text{Molar mass}}$$

$$n = \frac{20}{40} = 0.5 \text{ mol}$$

Sample Problem 4.2

Calculate the mass of 0.5 moles of $HC\ell$.

Solution:

$$\text{Mass of } HC\ell = \text{Number of moles} \times \text{Molar mass}$$
$$= 0.5\times36.5 = 18.3 \text{ g}$$

Sample Problem 4.3

Calculate the mass of 10^{-3} mol of $MgSO_4$.

Solution:

Molar mass of $MgSO_4 = 24 + 96 = 120$ g mol^{-1}

Number of moles of $MgSO_4 = 10^{-3}$

Mass of $MgSO_4 = 10^{-3}$ mol $\times 120$ g $mol^{-1} = 120\times10^{-3} = 0.12$ g

QUICK CHECK 4.1

a. **Calculate the molar mass of $KMnO_4$.**

Ans. $KMnO_4 = 39 + 55 + 16(4)$
$= 39 + 55 + 64$
$= 274$ gram/mol

b. **Calculate the number of moles in 0.23 g of sodium.**

Given: mass of sodium = m = 0.23 g
Molar mass of sodium = M = 23 g

To Find: Number of moles = n = ?

Solution: $n = \frac{m}{M} = \frac{0.23g}{23g}$

$n = 0.01$ moles

c. **Calculate the mass of 1.5 moles of $Ca(OH)_2$.**

Ans. Molecular mass of 1 mole of $Ca(OH)_2 = 40 + 2(16 + 1) = 84$ g
Molecular mass of 1.5 mole of $Ca(OH)_2 = 84\times1.5 = 126$ g

d. **The given mass of $KC\ell O_3$ is 24.5 g. Calculate the number of moles of potassium chlorate.**

Given: Mass of $KC\ell O_3 = 24.5$ g

To Find:
Number of moles of $KC\ell O_3$ = ?
Number of formula units of $KC\ell O_3$ = ?

Solution:

$$\text{Number of moles of } KC\ell O_3 = \frac{\text{Mass of } KC\ell O_3}{\text{Molar mass of } KC\ell O_3} \quad \boxed{n = \frac{m}{M}}$$

Molar Mass of $KC\ell O_3 = 22.5$ g mol^{-1}

$$\text{Number of moles of } KC\ell O_3 = \frac{100}{122.5} = 0.816 \text{ moles}$$

1 mole of $KC\ell O_3$ contains formula units $= 6.02\times10^{23}$

0.816 moles of $KC\ell O_3$ contain formula units $= 0.816\times6.02\times10^{23}$
$= 4.91\times10^{23}$ formula units

e. How many molecules are present in 1.75 g of H_2O_2?

Given: Mass of H_2O_2 = m = 1.75 g

Molar mass of H_2O_2 = M = 2 + (16×2) = 34 g

To Find: Number of molecules N = ?

Solution:

$$\text{Number of molecules } H_2O_2 = N = \frac{m}{M} \times N_A$$

$$= \frac{1.75\,g}{34\,g} \times 6.02\times10^{23} = 0.31 \times 10^{23}$$

$$= 3.1 \times 10^{22}$$

f. How many atoms are present in 15 g of gold ring?

Given: mass of Gold (Au) = m = 15.0 g

Molar mass of Gold = M =

To Find: Number of atoms = N = ?

$$N = \frac{m}{M} \times N_A$$

$$= \frac{15\,g}{g} \times 6.02\times10^{23}$$

$$= 4.58\times10^{22} \text{ atoms}$$

RELATIONSHIP BETWEEN MOLE, MOLAR MASS AND AVOGADRO'S NUMBER

A sample of 12.0 grams of natural carbon contains the same number of atoms as 4.0 grams of natural helium.

Both samples contain 1 mole of atoms i.e., *Note that different masses of elements have the same number of atoms.*

- 1.0 g of hydrogen = 1 mol of hydrogen = 6.02×10^{23} atoms of H
- 23.0 g of sodium = 1 mol of Na = 6.02×10^{23} atoms of Na
- 238.0 g of uranium = 1 mol of U = 6.02×10^{23} atoms of U

An atom of sodium is 23 times heavier than an atom of hydrogen. In order to have equal number of atoms, sodium should be taken 23 times greater in mass than hydrogen.

- 18.0 g of H_2O = 1 mol of water = 6.02×10^{23} molecules of water

180.0 g of glucose = 1 mol of glucose = 6.02×10^{23} molecules of glucose

Hence, one mole of different compounds has different masses but the same number of molecules.

Similarly, *the number of ions in one mole of different ionic species is always the same, i.e., Avogadro's number.*

- 96.1 g of SO_4^{2-} = 1 mole of SO_4^{2-} = 6.02×10^{23} ions of SO_4^{2-}
- 62.0 g of NO_3^{1-} = 1 mole of NO_3^{1-} = 6.02×10^{23} ions of NO_3^{1-}

One can calculate the number of moles by dividing the number of particles by Avogadro's number.

$$\text{Number of moles} = \frac{\text{No. of particles of a substance}}{\text{Avogadro's Number}}$$

The relationship between amounts of substances in terms of their moles and the number of particles (atoms, molecules, ions, electrons or particles) is given below:

$$\text{Number of particles} = \frac{\text{Mass of subtance} \times N_A}{\text{Molar Mass}}$$



Q Justify the following statements:

(i) 23 g of sodium and 238 g of Uranium have equal number of atoms in them.

(ii) 180 g of glucose and 342 g of sucrose have same number of molecules but different number of atoms present in them.

Sample Problem 4.4

A sample of glucose, contains 3.76×10^{24} molecules of glucose. What is the number of moles in this quantity?

Solution:

$$\text{No. of moles of glucose} = \frac{3.76\times10^{24} \text{ molecules}}{6.02\times10^{23} \text{ molecules mol}^{-1}} = 6.24 \text{ moles}$$

Sample Problem 4.5

How many atoms are there in a sodium metal that contains 2.3 g?

Solution:

$$\text{Number of moles of sodium} = \frac{2.3}{23.0} = 0.1 \text{ mol}$$

$$\text{Number of atoms of sodium} = \text{Number of moles of sodium} \times N_A$$

$$= 0.1\times6.02\times10^{23}$$

$$= 0.602\times10^{23} \text{ atoms}$$

$$= 6.022\times10^{22} \text{ g}$$

Sample Problem 4.6

Juglone, is a dye and is produced from the husks of black walnuts. The formula for juglone is $C_{10}H_6O_3$.

a) Calculate the molar mass of juglone.

b) Calculate number of moles in 0.87 g of a sample of juglone extracted from black walnut husks.

Interesting Information!

Juglone, is a natural herbicide (weed killer). It kills off competitive plants around the black walnut tree but does not affect grass and other noncompetitive plants.

Solution:

a) $C_{10}H_6O_3$

$$10\times A_r(C) + 6\times1.0\,A_r(H) + 3\times A_r(O) (10\times12.0) + (6\times1.0) + (3\times16.0) 120 + 6 + 48 = 174 \text{ g/mol}$$

Mass of 1 mol of $C_{10}H_6O_3 = 174\,g\,mol^{-1}$

b) $$\text{Moles of juglone} = \frac{\text{Mass}}{\text{Molar Mass}} = \frac{0.87\,g}{174\,g\,mol^{-1}} = 0.005 \text{ mol}$$

QUICK CHECK 4.2

a) A copper wire contains 27.10×10^{25} atoms of copper. Calculate the number of moles of copper.

Solution: $$\text{Number of moles of Copper} = \frac{27.10\times10^{25} \text{ atoms}}{6.02\times10^{23} \text{ atoms mol}^{-1}} = 4.50\times10^{2} \text{ mol}$$

b) Calculate the molecules of 1×10^{-6} g of isopentyl acetate, $C_7H_{14}O_2$ which are released in a typical bee sting. How many atoms of carbon, hydrogen and oxygen are present in it?

Solution: mass of isopentyl acetate = m = 1×10^{-6} g

Molecular mass of isopentyl acetate = M = $C_7H_{14}O_2$

$$= (12\times7) + (14\times1) + (16\times2)$$

$$= 84 + 14 + 32$$

$$= 130 \text{ g/mol}$$

$$N = \frac{m}{M} \times N_A = \frac{1\times10^{-6}}{130} \times 6.02\times10^{23}$$

$$= 46.29\times10^{14} = 4.629\times10^{15}$$

Number of C-atoms = $4.629\times10^{15}\times7 = 3.2382\times10^{16}$

Number of H-atoms = $4.629\times10^{15}\times14 = 6.4764\times10^{16}$

Number of O-atoms = $4.629\times10^{15}\times2 = 9.252\times10^{15}$

Interesting Information!

Isopentyl acetate ($C_7H_{14}O_2$) is the compound responsible for the scent of bananas. Interestingly, bees release about $1\mu g (1\times10^{-6}\ g)$ of this compound when they sting. The resulting scent attracts other bees to join the attack.

MOLAR VOLUME (V_m)

"The volume of one mole of an ideal gas at STP (Standard temperature and pressure) is called molar volume".

- Its value is equal to 22.414 dm^3.
- The value of molar volume is commonly rounded to 22.4 dm^3.
- It is denoted by V_m. By using molar volume relationship, mass or mole of a gas at STP can be converted into volume, and vice versa.

Rack Your Mind!

3. The volume of one mole of an ideal gas at STP is equal to:
A) 1 dm^3 B) 22.4 dm^3
C) 273 dm^3 D) 6.02×10^{23} dm^3

According to Avogadro's law,

"Equal volumes of all ideal gases at the same temperature and pressure contain equal numbers of molecules".

This statement is indirectly the same when we say that one mole of an ideal gas at 273.16 K and one atm pressure has a volume of 22.414 dm^3. Since one mole of a gas has Avogadro's number of particles, so 22.414 dm^3 of various ideal gases at STP will have Avogadro's number of molecules i.e., 6.02×10^{23}. **22.4 dm^3 of a gas at STP = Molar mass of a gas = 6.02×10^{23} particles of a gas = 1 mole of a gas**

Smart Thinking

Interesting Facts:
The molar volume of gas is 24 dm^3 at RTP (Room temperature and pressure)

- 22.4 dm^3 of CO_2 at STP = 44.0 g of CO_2 = 6.02×10^{23} molecules of CO_2 = 1 mole of CO_2
- 22.4 dm^3 of any gas at STP = molar mass in grams = 6.02×10^{23} molecules = 1 mole
- 22.4 dm^3 of H_2 gas at STP = 2 g = 6.02×10^{23} molecules = 1 mole
- 22.4 dm^3 of NH_3 gas at STP = 17 g = 6.02×10^{23} molecules = 1 mole

If the number of moles of a gas is known, one can calculate the volume of a gas by multiplying number of moles of the gas by molar volume:

$$\text{Volume of a gas} = \text{Number of moles} \times \text{Molar volume}$$
$$V = n \times V_m$$

Sample Problem 4.7

Determine the volume of 2.5 moles of chlorine molecules at STP.

Solution:

The formula for volume determination at STP

$$V = n \times V_m$$

2.5 mole of $C\ell_2$ occupy a volume = 22.4 $dm^3 \times 2.5 = 56.0\ dm^3$

Rack Your Mind!

4. 2 g of H_2, 16 g of CH_4 and 44 g of CO_2 occupy separately the volumes of 22.414 dm^3, although the sizes and masses of three gases are very different from each other.

Sample Problem 4.8

What is the volume in dm^3 of 4.75 mol of methane (CH_4) gas at STP?

Solution:

The formula for volume determination at STP

$$V = n \times V_m$$

Volume of methane in dm^3 at STP = $4.75\times22.4 = 106.4\ dm^3$

MOLAR MASS AND DENSITY OF GASES

Density is defined as the mass per unit volume of a substance.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$
$$d = \frac{m}{V}$$

As molar mass of all the gases occupies same volume at STP, therefore, density of a gas depends on its molar mass. A gas having higher molar mass will have higher density and vice versa. If the density of gas at STP is determined, its molar mass can be calculated.

Rack Your Mind!

5. How is the density of a gas related to its molar mass at STP?

Sample Problem 4.9

Calculate the molar mass of a gas which has density of 1.97 g / dm^3 at STP.

Solution

$$m = d \times V$$
$$\text{Mass of gas at STP} = 1.97\times22.4 = 44.1\ g\ mol^{-1}$$

QUICK CHECK 4.3

Q. Calculate the molar mass of a gas which has density of 1.34 g / dm^3 at STP.

Ans. $m = d \times V$

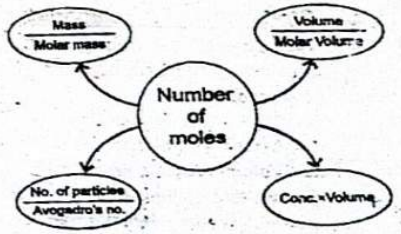
$m = 1.34 \times 22.4 = 30.016\ g\ mol^{-1}$

MOLAR CONCENTRATION

Molar concentration of solutions is given as mol / dm^3, which is the number of moles of a substance (reactant or product) dissolved per volume of a solution in dm^3.

The relationship between number of moles and molar concentration is given by

$$n = C \times V$$
$$C = \frac{n}{V}$$



where C is the molar concentration and V is the volume of the solution.

$$\text{Molar Concentration (C)} = \frac{\text{Number of moles (n)}}{\text{Volume in } dm^3 \text{ (V)}}$$

Example: If n = 0.2 mol and volume of solution = V = 1 dm^3 then,

$$C = \frac{0.2\ mol}{1\ dm^3} = 0.2\ mol\ dm^{-3}$$

Sample Problem 4.10

Calculate the molar concentration of a substance containing 27.64 g of K_2CO_3 dissolved in 1 dm^3 of the given solution.

Solution:

Mass of K_2CO_3 = 27.64 g

Molar mass of K_2CO_3 = 138.2 g mol^{-1}

$$\text{Number of moles} = \frac{\text{Given mass}}{\text{Molar mass}}$$
$$n = \frac{m}{M}$$

$$n = \frac{27.64}{138.2} = 0.2 \text{ mol}$$

Volume of Solution = $1 dm^3$

$$\text{Molar Concentration} = \frac{\text{Number of moles}}{\text{Volume in } dm^3}$$

$$C = \frac{0.2 \text{ mol}}{1 dm^3} = 0.2 \text{ mol} dm^{-3}$$

QUICK CHECK 4.4

Calculate the molar concentration of a solution containing 7.9 g of $KMnO_4$ dissolved in $1 dm^3$ of the given solution. The molar mass of $KMnO_4$ is $158 g mol^{-1}$.

Solution:

No. of moles of $KMnO_4 = \frac{7.9 g}{158 g mol^{-1}} = \frac{1}{20}$ mol

$n = 0.05$ mol

Now, $C = \frac{n}{V} = \frac{0.05 mol}{1 dm^3}$

$C = 0.05 \text{ mol } dm^{-3}$

Alternate Method:

$$C = \frac{m}{M_r} \times \frac{1}{V(dm^3)}$$

$$= \frac{7.9}{158} \times \frac{1}{1}$$

$$= 0.05 mol dm^{-3}$$

STOICHIOMETRIC RELATIONSHIPS

Stoichiometry is a branch of chemistry which tells us the quantitative relationship between reactants and products in a balanced chemical equation.

With the knowledge of mole, Avogadro's number, molar mass, molar volume, and molar concentration, we can establish quantitative relationships between reactants and products using the balanced chemical equations.

Stoichiometric Relationships

The following types of relationship can be studied with the help of a balanced chemical equation involving quantities of reactant(s) and product(s).

i. Mole-Mole Relationship
ii. Mass-mass relationship
iii. Volume-Volume Relationship
iv. Mole-Mass Relationship
v. Mole-Volume Relationship
vi. Mass-Volume Relationship

Explanation:

Formation of Ammonia

To understand these relationships, we need to interpret information hidden in a balanced chemical equation which is used to make stoichiometric calculations. For example:

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

This equation can be described in three different ways;

I. 1 mole of N_2 reacts with 3 moles of H_2 to form 2 moles of NH_3.

II. $22.4 dm^3$ of N_2 reacts with $67.2 dm^3$ of H_2 to form $44.8 dm^3$ of NH_3.

III. 28.0 g of N_2 react with 6 g of H_2 to form 34.0 g of NH_3.

Rack Your Mind!

6. What is stoichiometry?
A) Study of chemical reactions
B) Study of chemical bonding
C) Quantitative relationship between reactants and products
D) Study of chemical kinetics

Rack Your Mind!

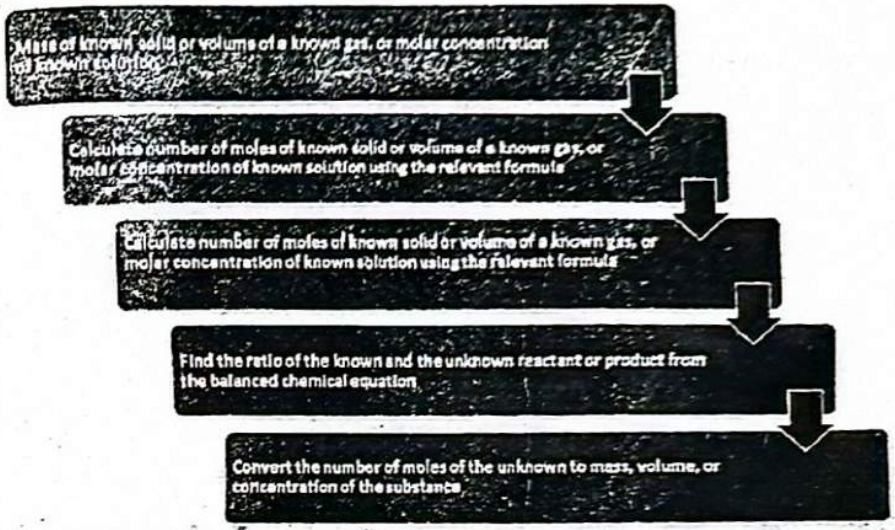
7. Which of the following is not a type of stoichiometric relationship?
A) Mole-mole relationship
B) Mass-mass relationship
C) Time-mass relationship
D) Volume-volume relationship

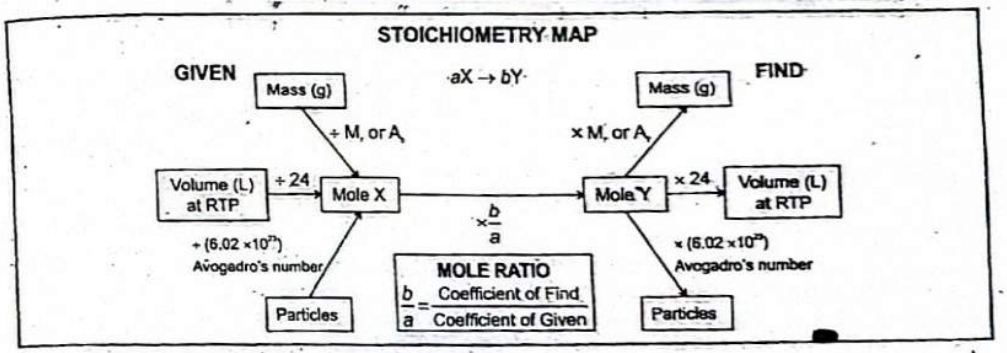
KEEP IN MIND

Important Assumptions of Stoichiometry

The following assumptions must be made while performing stoichiometric calculations:
1. All the reactants are completely converted into the products.
2. Law of conservation of mass and law of definite proportions are obeyed. No side reaction occurs.

Approach to do Stoichiometric Calculations





Sample Problem 4.11 (Mole-Mole Conversion)

When 3.3 moles of nitrogen reacts with hydrogen to form ammonia, how many moles of hydrogen are consumed in the process? The equation for this reaction is

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

Solution:

Number of moles of $N_2 = 3.3$ mol

Number of moles of $H_2 = ?$

1 mole of N_2 needs H_2 to produce $NH_3 = 3$ mol

3.3 moles of N_2 needs H_2 to produce $NH_3 = 3 \times 3.3 = 9.9$ mol

☑ QUICK CHECK 4.5

How many moles of carbon dioxide are produced when 2.25 moles of glucose are used by a person? The oxygen is in excess. The equation for the reaction is:

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(\ell)}$$

Solution:

1 mole of $C_6H_{12}O_6$ produces CO_2 = 6 moles

2.25 moles of $C_6H_{12}O_6$ produces CO_2 = $2.25 \times 6 = 13.5$ moles

Sample Problem 4.12 (Mass-Mass Conversion)

Calculate the mass of Al needed to react completely with 32.0 g of iron (III) oxide according to the equation given below:

$$2A\ell_{(s)} + Fe_2O_{3(s)} \longrightarrow A\ell_2O_{3(s)} + 2Fe_{(s)}$$

Solution:

Molar mass of Fe_2O_3, M = 160 g mol^{-1}

$$\text{Number of moles of } Fe_2O_3 \text{ (n)} = \frac{m}{M} = \frac{32.0\text{ g}}{160\text{ g mol}^{-1}} = 0.2 \text{ mole}$$

From the balanced equation, 1 mol of Fe_2O_3 reacts with 2 moles of Aℓ, therefore, number of moles of Aℓ that reacts with 0.02 mole of $Fe_2O_3 = 2 \times 0.2 = 0.4$ mol

Mass of Aℓ = n × M

= 0.4 mol × 27 g mol^{-1} = 10.8 g

☑ QUICK CHECK 4.6

Fe_2O_3, an ore of iron is called Hematite. CO can reduce it to get free Fe as below:

$$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

How much Fe can be produced from 160 g of Fe_2O_3?

Given Data: Molar mass of Fe_2O_3 = (56 × 2) + (16 × 3)

= 160 g/mol

mass of Fe_2O_3 = 160 g

To Find: Mass of Fe produced = ?

Equation:

$$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

Mole of Fe_2O_3 produces moles of Fe = 2

Mass of Fe produced = 2 × 56

Mass of Fe produced = **112 g**

Sample Problem 4.13 (Volume-Volume)

Calculate volume of ammonia that can be produced by the reaction of 100 dm^3 of hydrogen with excess of nitrogen at STP? The balanced chemical equation for the reaction is:

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

Solution: Volume of hydrogen = 100 dm^3

Volume of ammonia = ?

67.2dm^3 (3 mol) of H_2 produce ammonia = 44.8 dm^3 (2 mol)

$$1\text{ dm}^3 \text{ of } H_2 \text{ produce ammonia} = \frac{44.8}{67.2} = \frac{2}{3}$$

$$100\text{ dm}^3 \text{ of } H_2 \text{ produce ammonia} = \frac{2}{3} \times 100 = 66.7\text{ dm}^3$$

So, the volume of ammonia produced by the reaction of 100 dm^3 of H_2 with excess nitrogen is 66.7dm^3.

☑ QUICK CHECK 4.7

Calculate the volume of carbon dioxide produced at STP when 4.5dm^3 of methane is burnt by a person. The oxygen is in excess. The equation for the reaction is:

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$$

Solution:

22.44 dm^3 of CH_4 produces = 22.414 dm^3 of CO_2

For gaseous reaction mole ratio is equal to volume. Ratio.

One mole CH_4 produce one mole CO_2. SO, 4.5 dm^3 will produce 4.5 dm^3 of CO_2.

Sample Problem 4.14 Mole-Mass Calculations

Solid lithium hydroxide LiOH is used in space vehicles. It is employed to remove exhaled carbon dioxide from the living environment by forming solid lithium carbonate and liquid water. Calculate the mass of Li_2CO_3 that can be produced by 20.0 mol of LiOH.

$$2LiOH_{(s)} + CO_{2(g)} \longrightarrow Li_2CO_{3(s)} + H_2O_{(\ell)}$$

Solution:

According to the given balanced chemical equation,

2 moles of LiOH produces = 1 mole Li_2CO_3

$$20.0 \text{ moles of LiOH produces} = \frac{1}{2} \times 20.0 = 10.0 \text{ mol } Li_2CO_3$$

Mass of Li_2CO_3 produced = Number of mole × Molar mass

Mass of Li_2CO_3 produced = 10.0 mol × 73.9 g mol^{-1} = 739.0 g

Thus, 739.0 g Li_2CO_3 will be produced from 20.0 moles of LiOH.

☑ QUICK CHECK 4.8

Calculate the mass of sodium hypochlorite (NaOCℓ), a household bleach, produced by the reaction of 2.25 moles of chlorine with excess sodium hydroxide. The balanced equation is

$$2NaOH_{(aq)} + C\ell_{2(g)} \longrightarrow NaOC\ell_{(aq)} + NaC\ell_{(aq)} + H_2O_{(\ell)}$$

Solution:

Because NaOH is in excess so $C\ell_2$ is limiting reactant. One mole $C\ell_2$ produce one mole of NaOCℓ. So, 2.25 mole of $C\ell_2$ will produce 2.25 mole of NaOCℓ.

Molar mass of NaOCℓ = 23 + 16 + 35.5 = 74.5 g

Mass of NaOCℓ = 2.25 × 74.5 = 167.625 g

Sample Problem 4.15 (Mass-mole calculations)

Baking soda ($NaHCO_3$) acts as an antacid. It can neutralize excess hydrochloric acid (HCℓ) secreted by the stomach according to equation.

$$NaHCO_{3(s)} + HC\ell_{(aq)} \longrightarrow NaC\ell_{(aq)} + H_2O_{(\ell)} + CO_{2(aq)}$$

How many moles of HCℓ will be neutralized by 2.1 g of baking soda?

Solution:

Molar mass of $NaHCO_3$ = 84.0 g mol^{-1}

$$\text{Moles of } NaHCO_3 = \frac{2.1\text{ g}}{84.0\text{ g mol}^{-1}} = 0.025 \text{ mol}$$

Stoichiometrically, the mole ratio of HCℓ and $NaHCO_3$ is 1:1.

Hence moles of HCℓ used = 0.025 mol

Thus 2.1 g of $NaHCO_3$ will neutralize 0.025 moles of HCℓ.

Rack Your Mind!

8. Why is it important to convert between mass and moles in stoichiometric calculations?

Sample Problem 4.16 (Mass-Volume Conversion)

What volume of hydrogen at STP will be produced when 7.0 g of iron are reacted with an excess of sulphuric acid?

$$Fe_{(s)} + H_2SO_{4(aq)} \longrightarrow FeSO_{4(aq)} + H_{2(g)}$$

Solution:

Molar mass of Fe (M) = 55.8 g/mol

Number of moles of iron (n) $= \frac{m}{M}$

$$= \frac{7.0\ g}{55.8\ g\,mol^{-1}}$$

$$= 0.125\ mol$$

From the balanced equation, 1 mol of iron produces 1 mole of hydrogen.

So, number of moles of H_2 = 0.125 mol

Volume of H_2 in dm^3 = molar volume x moles of H_2

$$= 22.4\ dm^3\,mol^{-1} \times 0.125\ mol$$

$$= 2.8\ dm^3$$

LIMITING AND EXCESS REACTANT

Exercise L.Q.3

Q. Differentiate limiting and non-limiting reactants. How a limiting reactant is determined from a balanced chemical equation and given data?

In many chemical processes, the quantities of the reactants are usually not present in the proportions indicated by the balanced chemical equation. Frequently, a large amount of inexpensive reactant is supplied because of the following reasons:

a. ***To ensure that whole of the mass of the expensive reactant is completely converted to the desired product.***
b. ***To produce maximum amount of product.***
c. ***To increase the rate of reaction.***

We know that a large quantity of oxygen in a chemical reaction makes things burn more rapidly. In this way, excess of oxygen is left behind at the end of reaction and the other reactant, i.e. fuel, is consumed earlier.

Definition 1:

"This reactant which is consumed earlier is called the limiting reactant". In this way, the amount of product that forms is limited by the reactant that is completely used. Once this reactant is consumed, the reaction stops and no additional product is formed.

Definition 2:

"The reactant which controls the amounts of products formed in a chemical reaction and is consumed earlier is called the limiting reactant or reagent".

The maximum amount of the product formed depends upon the amount of limiting reactant in the reaction mixture.

Properties of Limiting Reactant:

i. Limiting reactant controls the amount of product formed.
ii. Limiting reactant is taken in lesser amount.
iii. Limiting reactant is consumed earlier.
iv. Limiting reactant produces least amount of product.

Rack Your Mind!

9. Why does a chemical reaction stop even when one reactant is still present?

Did You Know?

Fire is a combustion reaction in which fuel and oxygen, O_2, combine, usually at high temperatures, to form water and carbon dioxide. Once the fire has started, it is self-supporting. An effective way to quench a fire is smothering, which reduces the amount of available oxygen below the level needed to support combustion. In other words, smothering decreases the amount of the excess reactant. Foams, inert gas, and CO_2 are effective substances for smothering.

➲ Strategy for the Identification of Limiting Reactant

To identify a limiting reactant, the following three steps are performed.

i. Calculate the number of moles from the given amounts of reactants.
ii. Find out the number of moles of product with the help of a balanced chemical equation.
iii. Identify the reactant which produces the least amount of product as limiting reactant and the other as an excess reactant.

Limiting Reactant	Non-Limiting (Excess) Reactant
1. The reactant used up first in a chemical reaction is called limiting reactant.	1. The reactant which left unreacted after completion of a chemical reaction is called excess reactant.
2. It controls the amount of product.	2. It does not control the amount of product.
3. It is not present at the end of reaction.	3. Some amount is present at the end of reaction.
4. It limits the amount of product formed from chemical reaction.	4. It has no effect on product formed from reaction.

Following numerical problem will make the idea clear.

Sample Problem 17 (Limiting Reactant)

Calculate the mass of N_2 produced from 18.1 g of NH_3 (molar mass = 17.0 g mol^{-1}) and 90.4 g of CuO (molar mass = 79.5 g mol^{-1}) according to following balanced equation:

$$2NH_{3(g)} + 3CuO_{(s)} \longrightarrow N_{2(g)} + 3Cu_{(s)} + 3H_2O_{(g)}$$

Solution:

Moles of NH_3 = 18.1 g of NH_3 / 17.0 g mol^{-1} = 1.06 mol

Moles of CuO = 90.4 g of CuO / 79.5 g mol^{-1} = 1.14 mol

In balanced equation,

CuO : N_2
3 : 1
1.14 : $\frac{1}{3} \times 1.14 = 0.38$ mol

NH_3 : N_2
2 : 1
1 : $\frac{1}{2}$
1.06 : $\frac{1}{2} \times 1.06 = 0.53$ mol

Thus, CuO is the limiting reactant and the number of moles of N_2 produced will be 0.38 mol.

Hence, mass of N_2 produced = n × M
= 0.38 × 28
mass of N_2 produced = 10.64 g

Rack Your Mind!

10. For the reaction: $N_2 + 3H_2 \rightarrow 2NH_3$, if 2 moles of N_2 react with 4 moles of H_2, how many moles of NH_3 are produced?
A) 2 moles
C) 2.67 moles

Sample Problem 4.18 (Limiting Reactant)

When aqueous solutions of Na_2SO_4 and $Pb(NO_3)_2$ are mixed, $PbSO_4$ precipitates down. Calculate the mass of $PbSO_4$ formed when 1.25 dm^3 of 0.05 mol dm^{-3} $Pb(NO_3)_2$ and 2.00 dm^3 of 0.025 mol dm^{-3} Na_2SO_4 are mixed.

$$Na_2SO_{4(aq)} + Pb(NO_3)_{2(aq)} \longrightarrow PbSO_{4(s)} + NaNO_{3(aq)}$$

Solution:

The net ionic equation is

$$Pb^{+2}_{(aq)} + SO^{-2}_{4(aq)} \longrightarrow PbSO_{4(s)}$$

Since 0.05 mol dm^{-3} $Pb(NO_3)_2$ contains 0.05 mol dm^{-3} Pb^{2+} ions.

The formula: No. of moles = Concentration (mol dm^{-3}) × (Volume dm^3)

$n = CV$

moles of Pb^{2+} ions = 0.05 mol dm^{-3} × 1.25 dm^3 = 0.0625 mol

Thus, 0.025 mol dm^{-3} Na_2SO_4 solution contains 0.025 mol dm^{-3} SO_4^{-2} ions.

moles of SO_4^{-2} ions = 0.025 mol dm^{-3} × 2.00 dm^3 = 0.05 mol

As Pb^{2+} and SO_4^{-2} react in a 1:1 ratio, here, SO_4^{2-} (0.05 mol) will be consumed earlier than Pb^{2+} (0.0625 mol). The amount of SO_4^{-2} will be limiting. The reason is that 0.05 mole of SO_4^{-2} is less than 0.0625 mole of Pb^{2+}. Since the Pb^{2+} ions are present in excess, only 0.05 mole of solid $PbSO_4$ will be formed. The mass of $PbSO_4$ formed can be calculated using the molar mass of $PbSO_4$ (303.3 g mol^{-1}):

Mass of $PbSO_4$ = 0.05 mol × 303.3 g mol^{-1} = 15.2 g

➲ Maximum Amount of Product and Amount of Any Unreacted Excess Reagent

➢ **Excess Reactant:**

"The reactants which are in larger amounts (according to stoichiometry of reaction) and remain unreacted at the end of the reaction are called "excess reagents" (or excess reactants)".

OR

"The reactant that is left unreacted after the completion of reaction is called non-limiting or excess reactant".

Consider the reaction between hydrogen and oxygen to form water.

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(\ell)}$$

- When we take 2 moles of hydrogen (4 g) and allow it to react with 2 moles of oxygen (64 g), then we will get only 2 moles (36 g) of water.
- **Reason:** It is because 2 moles (4 g) of hydrogen react with 1 mole (32 g) of oxygen according to the balanced equation. Since less hydrogen is present as compared to oxygen, so **hydrogen is a limiting reactant.**
- When 1 mole of O_2 and 1 mole of H_2 are mixed, all the H_2 will react completely and O_2 will be left unreacted because for 1 mole of H_2, $\frac{1}{2}$ mole of O_2 is required. The remaining $\frac{1}{2}$ mole of O_2 will be excess and H_2 is a limiting reactant.

Sample Problem 4.19 (Excess Reactant)

Natural gas consists primarily of methane (CH_4). The complete combustion of methane (CH_4) gives carbon dioxide (CO_2) and water.

$$CH_{4(g)} + 2O_{2(g)} \xrightarrow{\text{Ignition}} CO_{2(g)} + 2H_2O_{(g)}$$

a) How many grams of CO_2 can be produced when 30 g of CH_4 and 50 g of O_2 are allowed to combine?

b) How many grams of excess reagent are left unreacted after the completion of reaction?

Solution (a):

Step 1: Write balanced chemical equation.

Step 2: Convert the given mass of both the reactants into their moles.

$$\text{Moles of } CH_4 = \frac{\text{given mass of } CH_4}{\text{molar mass of } CH_4} = \frac{30\text{ g}}{16\text{ g mol}^{-1}} = 1.875\text{ mol}$$

$$\text{Moles of } O_2 = \frac{\text{given mass of } O_2}{\text{molar mass of } O_2} = \frac{50\text{ g}}{32\text{ g mol}^{-1}} = 1.563\text{ mol}$$

Step 3: Calculate the number of moles of product from each reactant.

Compare the number of moles of CH_4 with those of CO_2. From the balanced chemical equation.

1 mole of methane produces CO_2 = 1 mol

1.875 mole of methane produces CO_2 = 1 × 1.875 mol = 1.875 mol of CO_2

Compare the number of moles of O_2 with those of CO_2. From the balanced chemical equation, we know:

2 moles of oxygen produces CO_2 = 1 mol

1.563 moles of oxygen produce CO_2 = 0.5 × 1.563 mol = 0.7815 moles of CO_2

From the above calculation, it is clear that the limiting reactant is O_2 because it produces lesser amount (moles) of product CO_2 than CH_4.

Step 4: Convert the moles of the product into mass.

Mass of CO_2 in grams = Moles of CO_2 × Molar mass of CO_2

= 0.7815 moles × 44 g mol^{-1} = 34.39 g

Step 5: The quantity of limiting reactant can also be used to calculate the quantity of excess reactant used:

2 moles of O_2 reacts with moles of CH_4 = 1 mol

1.563 moles of O_2 reacts with moles of $CH_4 = \frac{1}{2} \times 1.563\text{ mol} = 0.7815\text{ mol}$

Step 6: The mass of methane (excess reagent) is equal to the starting quantity minus the amount used during the reaction.

Number of moles of CH_4 = Quantity taken − Quantity used

= 1.875 mol − 0.7815 mol = 1.0935 mol

Mass of CH_4 (excess reagent) = 1.0935 × 16.0 = 17.5 g

☑ QUICK CHECK 4.9

Which of the following reaction mixtures could produce the greatest amount of product when they combine according to the reaction given below?

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

a) 1 mole of N_2 and 3 moles of H_2

Ans. 2 moles of NH_3

b) 2 moles of N_2 and 3 moles of H_2

Ans. 2 moles of NH_3

c) 1 mole of N_2 and 5 moles of H_2

Ans. 2 moles of NH_3

d) 3 moles of N_2 and 3 moles of H_2

Ans. 2 moles of NH_3

e) Each produces the same amount of product.

Ans. Yes, This is the correct answer.

THEORETICAL YIELD AND ACTUAL YIELD

Exercise LO 4

Q. Differentiate actual and theoretical yields. Why the theoretical yield is always greater than actual yield?

Actual Yield:

"The amount of the products obtained in a chemical reaction is called the actual yield of that reaction".

Theoretical Yield:

"The amount of the products calculated from the balanced chemical equation represents the theoretical yield". The theoretical yield is the maximum amount of the product that can be produced by a given amount of a reactant, according to balanced chemical equation.

NOTE: In most chemical reactions the ***amount of the product obtained is less than the theoretical yield.***

➲ Theoretical Yield is always Greater than Actual Yield

Reasons:

There are following reasons for that:

- The processes like filtration, separation by distillation, separation by a separating funnel, washing, drying and crystallization, if not properly carried out, decrease the actual yield.
- Some of the reactants might take part in a competing side reaction and reduce the amount of the desired product. So, in most of the reactions the actual yield is less than the theoretical yield.
- A reaction may be reversible. Therefore, the amount of the product will be reduced by the backward reaction.

A chemist is usually interested in the efficiency of a reaction. The efficiency of a reaction is expressed by comparing the actual and theoretical yields in the form of percentage (%) yield.

$$\% \text{ Yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Percentage Yield & Efficiency of the Reaction:

Greater the % age yield, higher will be the efficiency of reaction and vice versa.

Differentiate Between Theoretical and Actual Yield

Theoretical Yield	Actual Yield
1. The amount of product calculated from a balanced chemical equation is called theoretical yield.	1. The amount of product obtained while performing a chemical reaction is called actual yield.
2. It is also called expected yield or calculated yield.	2. It is also called experimental yield.
3. Theoretical yield is always greater than actual yield.	3. Actual yield is always lesser than theoretical yield.
4. There is no need to perform experiment. It is easily calculated from balanced chemical equation.	4. In order to get actual yield experiment has to be performed.

Sample Problem 4.20 (% age Yield)

Aspirin ($C_9H_8O_4$) is prepared by heating salicylic acid, $C_7H_6O_3$ (molar mass 138.12 g mol^{-1}) and acetic anhydride, $C_4H_6O_3$ (molar mass 163.93 g mol^{-1}).

$$C_7H_6O_3 + C_4H_6O_3 \longrightarrow C_9H_8O_4 + CH_3COOH$$

Calculate the theoretical yield of aspirin, (molar mass = 180.16 g mol^{-1}) when 3.00 g of salicylic acid is heated with 6.00 g of $(CH_3CO)_2O$. What is % yield when actual yield is 3.15 g?

Solution:

$$\underset{\text{Salicylic acid}}{C_7H_6O_3} + \underset{\text{Acetic anhydride}}{C_4H_6O_3} \longrightarrow \underset{\text{Aspirin}}{C_9H_8O_4} + CH_3COOH$$

1 mol 138.12 g | 1 mol 163.93 g | 1 mol 180.16 g

1 mole of Salicylic acid produces aspirin = 1 mol

Mass of Salicylic acid = 3.00 g

Number of moles of Salicylic acid = 3.00 g / 138.12 g mol^{-1} = 0.022 mol

Mass of Salicylic acid = 6.00 g

Number of moles of Salicylic acid = 6.00 g / 163.93 g mol^{-1} = 0.037 mol

Here, salicylic acid is limiting reactant while acetic anhydride is an excess reactant. The amount of salicylic controls the yield of product i.e., aspirin.

0.022 mole of Salicylic acid produces aspirin = 0.22 mol

Number of moles of Salicylic acid = Mass of Salicylic acid/ Molar mass of Salicylic acid

$$= \frac{3.00}{138.12} = 0.022 \text{ mol}$$

0.022 mol Salicylic acid produces Aspirin = 0.022 mol

Mass of Aspirin = 0.022 mol × 180.16 g mol^{-1} = 3.96 g

Theoretical yield = 3.96

Actual yield = 2.85

$$\% \text{ age yield} = \frac{2.85}{3.96} \times 100$$

$$= \boxed{71.97\%}$$

QUICK CHECK 4.10

When limestone ($CaCO_3$) is roasted, quicklime (CaO) is produced according to the following equation.

$$CaCO_3 \longrightarrow CaO_{(s)} + CO_{2(g)}$$

The actual yield of CaO is 2.5 kg, when 4.5 kg of limestone is roasted. What is the percentage yield of this reaction?

Given Data:

Mass of limestone roasted = 4.5 kg = 4.5 × 1000 = 4500 g

Mass of quick lime (actual yield) = 2.5 kg = 2.5 × 1000 = 2500 g

Molar Mass of $CaCO_3$ = 40 + 12 + 16 × 3

= 40 + 12 + 48 = 100 g mol^{-1}

Molar mass of CaO = 40 + 16 = 56 g mol^{-1}

Required: Percentage yield of CaO = ?

Solution:

Equation: $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$

According to balanced chemical equation

100g of $CaCO_3$ give CaO = 56g

1g of $CaCO_3$ gives CaO = $\frac{56}{100}$ g

4500g of $CaCO_3$ give CaO = $\frac{56}{100} \times 4500$

Theoretical yield of CaO = 2520g

Actual yield of CaO = 2500g

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100 = \frac{2500}{2520} \times 100$$

% yield of CaO = 99.2%

IMPORTANCE OF STOICHIOMETRY IN PRODUCTION AND DOSAGE OF MEDICINE

While preparing required dose of a medicine, the optimum amount of the active ingredient in a medicine is essential to produce desired effects in the patient. Stoichiometry ensures the accuracy of drug synthesis. Any deviation can result in incomplete reaction or contamination with un-reacted reactants or by-products. Stoichiometry allows chemists to precisely control chemical reactions to produce drugs, to ensure its efficiency, effectiveness and safe use.

Significance of Stoichiometry in Medicine

Stoichiometry is very important in the field of medicine and is used to:

1. In the preparation of antibiotics, the stoichiometry ensures that each dose matches the active ingredient and target bacteria.
2. To determine the cholesterol level in the blood of patients. Cholesterol is a form of fat that is not all bad. However, cholesterol can have harmful effects.
3. To determine the glucose level in the blood of diabetic patient. Use of insulin relies on the stoichiometry to precise control of blood sugar levels.
4. To determine the steroid and other stimulants in the urine of athletes. Athletes use steroids and other stimulants to enhance performance and increase strength.
5. To determine the concentration of viral antigens in the preparation of vaccine for effective results.
6. To determine the amount and number of drugs to give a dosage to a patient. The medicine has no effect when given in small amounts and can cause toxic state or death when given in large amounts.

Example: Paracetamol is used as a pain killer and to decrease fever. An overdose may result a blood thinning, organ damage and severe liver damage.

Solution File — Rack Your Brain!

Sr.#	Option	Explanation
1.	C	O_2 gas = 32 grams = 1 mole of O_2 gas = 6.02×10^{23} molecule of O_2
2.	S.Q	Water (H–O–H) molecule has two bonds. So two moles of bonds are present in water. H_2O contains two moles of H-atoms and one mole of O-atoms so total 3 moles of atoms. H_2 = 2e, O = 8e. So H_2O contains 10 moles of electrons. H_2 = 2p, 2e = 4; O = 8p, 8e, 8n = 24; Total = 28. So, 1 mole of H_2O has 28 moles of fundamental particles.
3.	B	Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.
4.	S.Q	2g of H_2 = 1 mol H_2 = 6.02×10^{23} molecule = 22.414 dm^3; 16 g of CH_4 = 1 mol CH_4 = 6.02×10^{23} molecules = 22.414 dm^3; 44 g of CO_2 = 1 mol CO_2 = 6.02×10^{23} molecules = 22.414 dm^3. According to Avogadro's law, equal moles of gases at same temperature and pressure (STP) occupy same volume. One mole of any gas can occupy 22.414 dm^3 at STP. So 2g of H_2, 16g of CH_4 and 44g of CO_2 occupy 22.414 dm^3. Volume occupied by a gas does not depend on size and mass of gas molecule. It only depends on number of molecules. Reason is that at STP, distance between gas molecules is 300 times greater than their own diameters.
5.	S.Q	At STP, gases with higher molar masses have higher densities because all gases occupy the same volume per mole (22.4 dm^3). **NOTE: Formula to calculate molar mass from density at STP:** Molar Mass = Density × 22.4 dm^3
6.	C	Stoichiometry is study of quantitative relationship between reactants and products.
7.	C	Time –mass is not a stoichiometric relationship.
8.	S.Q	The purpose is to convert between mass and moles allows us to use the mole ratio from the balanced equation to calculate quantities.
9.	S.Q	The reaction stops when the limiting reactant is completely used up. Even if another reactant remains, no more product can form without the limiting reactant.
10.	C	4 moles of H_2 will produce 8/3 (2.66) moles of NH_3 according to the stoichiometry of $N_2 + 3H_2 \rightarrow 2NH_3$, where H_2 is the limiting reagent.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. Which one of the following statements is incorrect?
a) One mole of nitrogen gas contains Avogadro's number of molecules
b) One mole of ozone gas contains Avogadro's number of molecules
c) One mole of ozone contains Avogadro's number of O atoms
d) One mole of hydrogen gas contains Avogadro's number of molecules

II. Which one of the following has greatest mass?
a) 0.5 mol of N_2 b) 0.5 mol of NH_3 c) 0.5 mole of He d) 0.5 mol of CO_2

III. Which one of the following gases will have greatest volume at STP?
a) 22 g of CO_2 b) 88 g of N_2O c) 28 g of CO d) 28 g of N_2

IV. Which of the following contains same number of particles as present in 12 g of carbon?
a) 28 g of iron (Atomic mass of Fe = 56) b) 48 g of magnesium (Atomic mass of Mg = 24)
c) 32 g of S_8 molecules (Atomic mass S = 32) d) 40 g of carbon monoxide (molar mass of CO = 28)

V. Volume at S.T.P. of 22 g of CO_2 is same as that of:
a) 2 g of hydrogen b) 8.5 g of NH_3 c) 64 g of gaseous SO_2 d) 7 g of CO

VI. 4.0 g of NaOH (molar mass 40 g mol^{-1}) contains same number of sodium ions as are present in:
a) 10.6 g of Na_2CO_3, (molar mass 106) b) 58.5 g of NaCℓ (molar mass 58.5)
c) 76 g Na_2SO_4 (formula mass 142) d) 85 g of $NaNO_3$ (molar mass 85)

VII. A container holds 0.5 moles of an ideal gas at STP. What is the volume of the gas in dm^3?
a) 11.2 dm^3 b) 22.4 dm^3 c) 44.8 dm^3 d) 12.2 dm^3

VIII. A solution contains 4.0 g of sodium hydroxide (NaOH, molar mass = 40.0 g mol^{-1}) in 250 cm^3 of solution. What is the molar concentration of this solution?
a) 0.10 mol dm^{-3} b) 0.20 mol dm^{-3} c) 0.40 mol dm^{-3} d) 0.80 mol dm^{-3}

IX. A solution contains 10.0 g of an unknown solute in 250 cm^3 of solution. If the molar concentration of the solution is 0.20 mol dm^{-3}, what is the molar mass of the solute?
a) 50 g mol^{-1} b) 100 g mol^{-1} c) 200 g mol^{-1} d) 400 g mol^{-1}

X. A sample of nitrogen gas (N_2, molar mass = 28.0 g mol^{-1}) has a mass of 14.0 g. How many nitrogen atoms are present in this sample?
a) 3.01×10^{23} atoms b) 6.02×10^{23} atoms c) 1.20×10^{24} atoms d) 2.40×10^{24} atoms

XI. A gas has a density of 1.43 g dm^{-3} at STP. What is the molar mass of the gas? (Molar volume at STP = 22.4 dm^3 mol^{-1})
a) 14.3 g mol^{-1} (b) 22.4 g mol^{-1} c) 32.0 g mol^{-1} (d) 64.0 g mol^{-1}

XII. A gas has a density of 1.96 g dm^{-3} at STP (0°C and 1.00 atm). What is its molecular mass? (Molar volume at STP = 22.4 dm^3 mol^{-1})
a) 11.2 g mol^{-1} b) 22.4 g mol^{-1} c) 44.0 g mol^{-1} d) 88.0 g mol^{-1}

Answer Key with Explanations

Q. No.	Option	Answer	Explanation
I.	c	One mole of ozone contains Avogadro's number of O atoms	• 1 mole of O_3 contains Avogadro's number of O_3 molecules, not O atoms (which would be 3 × Avogadro's number).
II.	d	0.5 mol of CO_2	• Mass = moles × molar mass: ○ N_2: 0.5 × 28 = 14 g ○ NH_3: 0.5 × 17 = 8.5 g, He: 0.5 × 4 = 2 g, CO_2: 0.5 × 44 = 22 g (Highest)
III.	d	28 g of N_2	• At STP, volume ∝ moles: ○ 28 g N_2 = 1 mol (22.4 dm^3). ○ 22 g CO_2 = 0.5 mol (11.2 dm^3), 88 g N_2O = 2 mol (44.8 dm^3), 28 g CO = 1 mol (22.4 dm^3). • **Correction:** (b) 88 g of N_2O has maximum volume (2 mol = 44.8 dm^3).
IV.	d	28 g of carbon monoxide	• 12 g C = 1 mol C = 6.02×10^{23} atoms. • 28 g CO = 1 mol CO = 6.02×10^{23} molecules (each with 2 atoms ⇒ 1.2×10^{24} atoms). • **Correction:** (b) 48 g Mg = 2 mol Mg = 1.2×10^{24} atoms (matches C).
V.	b	8.5 g of NH_3	• 22 g CO_2 = 0.5 mol ⇒ 11.2 dm^3 at STP. • 8.5 g NH_3 = 0.5 mol ⇒ same volume.
VI.	a	10.6 g of Na_2CO_3	• 4 g NaOH = 0.1 mol ⇒ 0.1 mol Na^+ ions. • 10.6 g Na_2CO_3 = 0.1 mol ⇒ 0.2 mol Na^+ ions. • **Correction:** (b) 58.5 g NaCℓ = 1 mol ⇒ 1 mol Na^+ ions. • **Actual answer:** (a) 10.6 g Na_2CO_3 has 0.2 mol Na^+, but none match exactly.
VII.	a	11.2 dm^3	• At STP, 1 mol = 22.4 dm^3 ⇒ 0.5 mol = 11.2 dm^3.
VIII.	c	0.40 mol dm^{-3}	• Molarity = moles/volume = (4 g / 40 g/mol) / 0.25 dm^3 Molarity = 0.40 mol dm^{-3}
IX.	c	200 g mol^{-1}	• Moles = M × V = 0.2 × 0.25 = 0.05 mol. • Molar mass = mass/moles = 10 g / 0.05 mol = 200 g mol^{-1}.
X.	b	6.02×10^{23} atoms	• 14 g N_2 = 0.5 mol ⇒ 0.5 × 6.02×10^{23} molecules = 6.02×10^{23} N atoms (each N_2 has 2 atoms).
XI.	c	32.0 g mol^{-1}	• Molar mass = density × molar volume Molar mass = 1.43 g/dm^3 × 22.4 dm^3/mol = 32.0 g mol^{-1}.
XII.	c	44.0 g mol^{-1}	• Molar mass = 1.96 g/dm^3 × 22.4 dm^3/mol Molar mass = 44.0 g mol^{-1} (matches CO_2)

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. How is the concept of mole derived from Avogadro's number?

Ans. Amedeo Avogadro proposed that:

"Equal volumes of gases, at the same temperature and pressure, contain equal numbers of molecules."

$N_A = 6.02214076 \times 10^{23}$ particles per mole

The mole (mol) was then defined as:

"The amount of substance containing exactly N_A elementary entities (atoms, molecules, ions, etc.)."

This means:

1 mol = N_A particles = 6.022×10^{23} particles

Derivation of Molar Mass

- The atomic mass unit (u) is defined based on ^{12}C (12 u = mass of one ^{12}C atom).
- Since N_A atoms of ^{12}C weigh 12 grams, the molar mass (mass per mole) is numerically equal to the atomic/molecular mass in u:

Molar mass of ^{12}C = 12 g/mol

We can calculate the number of moles by dividing the number of particles by Avogadro's number.

b. Define the following terms with one example in each case.
(a) Molar mass (b) Molar volume (c) Molar concentration

Ans. (a) Molar Mass

The mass of one mole of a substance expressed in grams is called molar mass.

Molar mass of $CC\ell_4$ = Molar mass of one C + Molar mass of $C\ell \times 4$
Molar mass of $CC\ell_4 = 12.0 \times 1 + 35.5 \times 4$
Molar mass of $CC\ell_4 = 12.0 + 142.0 = 154.0$ g

(b) Molar VOLUME

The volume of one mole of an ideal gas at STP (Standard temperature and pressure) is called molar volume. Its value is equal to 22.414 dm^3. The value of molar volume is commonly rounded to 22.4 dm^3. It is denoted by V_m. By using molar volume relationship, mass or mole of a gas at STP can be converted into volume, and vice versa.

(c) Molar Concentration

Molar concentration of solutions is given as mol/dm^3, which is the number of moles of a substance (reactant or product) dissolved per volume of a solution in dm^3. The relationship between number of moles and molar concentration is given by

$$n = C \times V$$

$$C = \frac{n}{V}$$

where C is the molar concentration and V is the volume of the solution.

$$\text{Molar Concentration (C)} = \frac{\text{Number of moles (n)}}{\text{Volume in } dm^3 \text{ (V)}}$$

c. What do you mean by molar volume of a gas? How Avogadro's number is related with molar volume?

Ans. Molar Volume of a Gas:

The (molar volume) of a gas is the volume occupied by one mole of any ideal gas at standard temperature and pressure (STP).

- At STP (0°C or 273.15 K and 1 atm pressure),
- 1 mole of any ideal gas occupies 22.414 dm^3 (or liters).

Relation with Avogadro's Number:

Avogadro's number (6.022×10^{23} particles/mol) tells us that 1 mole of gas contains this many molecules.
Therefore, 22.414 dm^3 of any ideal gas at STP contains exactly 6.022×10^{23} molecules.

Conclusion:

- Molar volume links the physical volume of a gas to the number of particles (via Avogadro's number) under standard conditions.

d. 39 g of potassium and 56 g of iron have equal number of atoms in them. Justify.

Ans. Molar mass of K (potassium) = 39 g/mol
Molar mass of Fe (iron) = 56 g/mol
It means Moles of K = 39 g/mol; 39 g = 1 mol
Moles of Fe = 56 g/mol 56; g = 1 mol
We know that 1 mole of any element contains Avogadro's number of atoms = 6.022×10^{23} atoms
Thus, 39 g of K = 1 mol = 6.022×10^{23}
56 g of Fe = 1 mol = 6.022×10^{23}

In sheet, 39 g of potassium and 56 g of iron contain an equal number of atoms, because both represent 1 mole of their respective elements.

e. 4 g of He, 17 g of NH_3 and 64 g of SO_2 occupy separately the volumes of 22.414 dm^3 although the sizes and masses of molecules of three gases are very different from each other. Explain.

Ans. Molar Masses: He (helium) 4 g/mol, NH_3 (ammonia) 17 g/mol, SO_2 (sulfur dioxide) 64 g/mol

At STP (Standard Temperature and Pressure), 1 mole of any ideal gas occupies:

22.414 dm^3

Even though the masses and sizes of individual He, NH_3, and SO_2 molecules differ:

The number of molecules in each case is the same:

1 mol = 6.022×10^{23} molecules

The volume a gas occupies depends mainly on:

- Number of particles (moles)
- Temperature
- Pressure

It does not depend on mass or size of individual molecules (according to ideal gas behaviour).

Although He, NH_3, and SO_2 differ in molecular mass:

If you take 1 mole of each, they will all occupy 22.414 dm^3 at STP.

Because the volume of a gas is determined by number of moles, not the mass of molecules.

f. Do you think that 1 mole of H_2 and 1 mole of NH_3 at 0 °C and 1 atm will have Avogadro's number of particles?

Ans. According to Avogadro's Law:

Equal volumes of all gases at the same temperature and pressure contain an equal number of molecules.

1 mole of H_2 (hydrogen gas) and 1 mole of NH_3 (ammonia gas) at 0°C and 1 atm will each contain Avogadro's number of particles, i.e.: 6.022×10^{23} molecules

1 mole of H_2 gas = 6.022×10^{23} H_2 molecules,

1 mole of NH_3 gas = 6.022×10^{23} NH_3 molecules

g. What is stoichiometry? Give the basic assumptions of stoichiometric calculations.

Ans. Stoichiometry

Stoichiometry is a branch of chemistry which tells us the quantitative relationship between reactants and products in a balanced chemical equation.

Assumptions of Stoichiometry:

The following assumptions must be made while performing stoichiometric calculations:

- All the reactants are completely converted into the products.
- Law of conservation of mass and law of definite proportions are obeyed.
- No side reaction occurs.

h. What is a limiting reactant? How does it control the quantity of the product formed?

Ans. The limiting reactant (or limiting reagent) is the reactant that is completely consumed first during a chemical reaction. Once it is used up, the reaction stops, and no more product can form, even if other reactants are still available.

Chemical reactions require specific mole ratios between reactants.

If one reactant runs out, the remaining reactants can't react further — they become excess.

The amount of product is directly determined by how much of the limiting reactant was present at the start.

Example:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Suppose we have:

1 mole of N_2 and 2 moles of H_2. According to the equation, we need 3 moles of H_2 for every 1 mole of N_2. But we only have 2 moles of H_2. Thus H_2 is the limiting reactant.

i. Differentiate theoretical and actual yields. How is the percentage yield of a reaction calculated?

Ans. Differentiate Between Theoretical and Actual Yield

Theoretical Yield	Actual Yield
1. The amount of product calculated from a balanced chemical equation is called theoretical yield.	1. The amount of product obtained while performing a chemical reaction is called actual yield.
2. It is also called expected yield or calculated yield.	2. It is also called experimental yield.
3. Theoretical yield is always greater than actual yield.	3. Actual yield is always lesser than theoretical yield.
4. There is no need to perform experiment. It is easily calculated from balanced chemical equation.	4. In order to get actual yield experiment has to be performed.

We can calculate the percentage yield of a chemical reaction with the help of actual yield and theoretical yield of the reaction. The efficiency of a reaction is also expressed in the form of percentage yield.

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Greater the percentage yield, more amount of reactants will convert into product and high will be the efficiency of the reaction i.e. % age yield $\propto$ Efficiency of the reaction.

j. What are the factors which are mostly responsible for the low yield of the products in chemical reactions?

Ans. Actual yield of a chemical reaction is usually lesser than theoretical yield due to many reasons. They are:

i. Practically inexperienced worker has many shortcomings and cannot get expected yield.
ii. Mechanical loss during experimentation e.g., filtration, separation by distillation or by a separating funnel, washing, drying and crystallization if not properly carried out, decrease the yield.
iii. Some of the reactants might take part in a competing side reaction.
iv. The reaction might be reversible.
v. The reactants might be impure.
vi. Sometimes the reaction conditions are not suitably maintained.

DESCRIPTIVE QUESTIONS

Q.3 Differentiate limiting and non-limiting reactants. How a limiting reactant is determined from a balanced chemical equation and given data?

Ans. **See Page No. (118)**

Q.4 Differentiate actual and theoretical yields. Why the theoretical yield is always greater than actual yield?

Ans. **See Page No. (121)**

NUMERICAL PROBLEMS

Q.5 A solution of sodium hydroxide (NaOH) is prepared by dissolving 2.00 g of solid sodium hydroxide in water to make a final volume of 250 cm^3.

a) Calculate the number of moles of sodium hydroxide used.
b) Determine the molar mass of sodium hydroxide.
c) Calculate the concentration of the sodium hydroxide solution in mol dm^{-3}.
d) If more water is added to the above solution to raise the volume of solution to cm^3, what would be the concentration now?

(a) Number of moles of sodium hydroxide used

Formula:

$$\text{Number of moles (n)} = \frac{\text{Mass of solute (g)}}{\text{Molar mass (g/mol)}}$$

We'll calculate molar mass in part (b), but we need it here, so let's move to part (b) first.

(b) Molar mass of sodium hydroxide (NaOH)

Sodium hydroxide (NaOH) is composed of:

- Na (Sodium) = 23 g/mol
- O (Oxygen) = 16 g/mol
- H (Hydrogen) = 1 g/mol

Molar mass of NaOH = 23 + 16 + 1 = 40 g/mol

Back to Part (a):

Now use this molar mass in the formula:

$$\text{Number of moles} = \frac{2.00}{40} = 0.050 \text{ mol}$$

(c) Concentration of NaOH solution in mol dm^{-3}

Formula:

$$\text{Concentration (C)} = \frac{\text{Number of moles}(n)}{\text{Volume of solution in dm}^3}$$

Step 1: Convert cm^3 to dm^3

$$1 \text{ dm}^3 = 1000 \text{ cm}^3 \Rightarrow 250 \text{ cm}^3 = \frac{250}{1000} = 0.250 \text{ dm}^3$$

Step 2: Use formula

$$\text{Concentration} = \frac{0.050}{0.250} = 0.20 \text{ mol/dm}^3$$

(d) New concentration if volume is increased to 500 cm^3

Important Concept:

When more water is added, the number of moles remains the same (no new NaOH is added), but the volume increases.

Convert 500 cm^3 to dm^3

$$500 \text{ cm}^3 = \frac{500}{1000} = 0.500 \text{ dm}^3$$

Use concentration formula again

$$\text{New Concentration} = \frac{\text{Same moles}(0.050)}{\text{New volume}(0.500 \text{dm}^3)} = 0.10 \text{ mol/dm}^3$$

Q.6 Ammonia gas (NH_3) reacts with oxygen gas (O_2) according to the following balanced equation:

$$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$$

In an experiment, 34.0 g of ammonia is reacted with 80.0 g of oxygen.

a) Determine the limiting reactant.

b) Calculate the maximum mass of nitrogen monoxide (NO) that can be formed.

c) Calculate the mass of the excess reactant remaining after the reaction is complete. (Relative atomic masses: H = 1.0, N = 14.0, O = 16.0)

Ans. Reaction Given: $4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(g)}$

Given Data:

Mass of NH_3 = 34.0 g

Mass of O_2 = 80.0 g

Atomic Masses: H = 1.0 N = 14.0 O = 16.0

Step 1: Calculate Molar Masses

NH_3: Molar mass = 14 + (3 × 1) = 17 g/mol

O_2: Molar mass = 2 × 16 = 32 g/mol

Step 2: Calculate Number of Moles of Reactants

Moles of NH_3: $n = \frac{\text{mass}}{\text{molar mass}} = \frac{34.0}{17} = 2.00 \text{ mol}$

Moles of O_2: $n = \frac{80.0}{32} = 2.50 \text{ mol}$

Step 3: Determine the Limiting Reactant

We now compare the mole ratio required by the equation with the mole ratio available.

According to the equation:

2 mol NH_3 reacts with 5 mol $\Rightarrow \frac{4}{5} = 0.80$

Mole ratio from given moles:

$$\frac{2.00 \text{ mol } NH_3}{2.50 \text{ mol } O_2} = 0.80$$

This means they are in the exact stoichiometric ratio, so both will be completely used up, and no reactant is in excess.

But according to more careful comparison with actual mole needs:

2.00 mol NH_3 would require

$$\frac{5}{4} \times 2.00 = 2.50 \text{ mol } O_2$$

We have exactly 2.50 mol O_2, so both are used up → No excess, no limiting reactant (but usually in exam terms, either one may be stated as "used up").

Step 4: Calculate Maximum Mass of NO Formed

From balanced equation:

$$4 \text{ mol } NH_3 \longrightarrow 4 \text{ mol NO}$$

So, 2.00 mol NH_3 will produce 2.00 mol NO

Molar Mass of NO: 14 + 16 = 30 g/mol

Mass of NO: Mass = n × M = 2.00 × 30 = 60.0 g of NO

Step 5: Calculate Mass of Excess Reactant Remaining

As discussed, both NH_3 and O are completely consumed, so:

Excess reactant remaining = 0 g

Q.7 When iron (III) oxide (Fe_2O_3) reacts with carbon monoxide (CO) in a blast furnace, iron metal (Fe) is produced according to the following equation:

$$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

If 1000 kg of iron (III) oxide is reacted with excess carbon monoxide, and 650 g of iron is obtained, what is the percentage yield of iron? (A$_r$ of O = 16.0, Fe = 55.8)

Ans. Chemical Equation:

$$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

Given Data:

Mass of Fe_2O_3 used = 1.00 kg = 1000 g

Mass of Fe actually obtained = 650 g

Atomic Masses: Fe = 55.8 O = 16.0

Step 1: Calculate Molar Mass of Fe_2O_3

$$Fe_2O_3 \Rightarrow (2 \times 55.8) + (3 \times 16.0) = 111.6 + 48.0 = 159.6 \text{ g/mol}$$

Step 2: Calculate Moles of Fe_2O_3 Used

$$n = \frac{\text{mass}}{\text{molar mass}} = \frac{1000}{159.6} \approx 6.265 \text{ mol } Fe_2O_3$$

Step 3: Use Stoichiometry to Find Theoretical Mass of Fe

From the equation:

$$1 \text{ mol } Fe_2O_3 \longrightarrow 2 \text{ mol Fe}$$

So,

$$6.265 \text{ mol } Fe_2O_3 \longrightarrow 6.265 \times 2 = 12.530 \text{ mol Fe}$$

Now, calculate mass of 12.530 mol Fe:

$$\text{Mass} = n \times M = 12.530 \times 55.8 \approx 699.2 \text{ gFe (theoretical)}$$

Step 4: Use Percentage Yield Formula

$$\text{Percentage Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100$$

$$= \frac{\text{[illegible]}}{699.2} \times 100 \approx 92.96\%$$

Final Answer:

Percentage Yield of Fe = 92.96%

Q.8 1.5g of C_2H_6 is burnt in excess of O_2 to produce CO_2 and H_2O. What volume of CO_2 is produced at STP.

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$

Also calculate:

a) No. of molecules of solid CO_2 produced.
b) No. of O_2 molecules reacted.
c) No. of CH bond of C_2H_6 are broken in this reaction.

Given Data:

Mas of C_2H_6 = 1.5g

Reaction: $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

STP condition

Molar mass of $C_2H_6 = (2 \times 12) + (6 \times 1) = 30$ g/mol

$$\text{No. of moles of } C_2H_6 = \frac{1.5g}{30g/mol} = 0.05mol$$

(a) From the balanced equation, 2 moles of C_2H_6 produce 4 moles of CO_2.

$$\text{No. of moles of } CO_2 = \frac{4}{2} \times 0.05mol = 0.1mol$$

At STP, 1 mole of any gas occupies 22.4 dm^3.

Volume of CO_2 = 0.1 mol × 22.4 dm^3/mol = 2.24 dm^3

Avogadro's number = 6.022×10^{23} molecules/mol

No. of CO_2 molecules = 0.1 mol × 6.022×10^{23} molecules/ mol = 6.022×10^{22}

(b) From the balanced equation, 2 moles of C_2H_6 react with 7 moles of O_2.

$$\text{Moles of } O_2 = \frac{7}{2} \times 0.05mol = 0.175mol$$

No. of O_2 molecules = 0.175 mol × 6.022×10^{23} molecules/mol = 10.54×10^{22}

(c) Each C_2H_6 molecules has 6 C – H bonds.

No. of C_2H_6 molecules = 0.05 mol × 6.022×10^{23} molecules/mol = 3.011×10^{22}

Total C – H bonds broken = 3.011×10^{22} molecules × 6 bonds/molecule = 1.806×10^{23}

ADDITIONAL SLOs BASED MCQs

1. How many molecules are there in one mole of H_2O?
   A. 6.023×10^{19} B. 6.023×10^{23} C. 1.084×10^{18} D. None of these
2. A flask contains 500 cm^3 of SO_2 at STP. The flask contains
   A. 40 g B. 100 g C. 50 g D. 1.427g
3. A necklace has 6 g of diamond in it. What are the numbers of atoms in it?
   A. 6.02×10^{23} B. 12.04×10^{23} C. 1.003×10^{23} D. 3.01×10^{23}
4. What is the mass of aluminium in 204 g of the aluminium oxide, Al_2O_3?
   A. 26 g B. 27 g C. 54 g D. 108 g
5. The reactant which is consumed earlier and gives least quantity of product is called.
   A. Reactant in excess B. Stoichiometry C. Limiting reactant D. Stoichiometric amount

6. Which one of the following compounds contains the highest percentage by mass of nitrogen?
   A. NH_3 B. N_2H_4 C. NO D. NH_4OH
7. Vitamin-A has a molecular formula $C_{20}H_{30}O$. The number of vitamin-A molecules in 500 mg of its capsule will be:
   A. 6.02×10^{23} B. 1.05×10^{21} C. 3.01×10^{22} D. 3.01×10^{23}
8. When one mole of each of the following is completely burnt in oxygen, which will give the largest mass of CO_2?
   A. Carbon Monoxide B. Diamond C. Ethane D. Methane
9. One mole of ethanol and one mole of ethane have an equal:
   A. Mass B. Number of Atoms C. Number of electrons D. Number of molecules
10. Methane reacts with steam to form H_2 and CO as shown below.

$$CH_{4(g)} + H_2O_{(g)} \longrightarrow CO_{(g)} + 3H_{2(g)}$$

What volume of H_2 can be obtained from 100 cm^3 of methane at the standard temperature and pressure?
   A. 300 cm^3 B. 200 cm^3 C. 150 cm^3 D. 100 cm^3
11. The Avogadro's constant is the number of:
   A. Atoms in 1g of Helium B. Molecules in 35.5g of Chlorine
   C. Electrons needed to deposit 24g of Mg D. Atoms in 24g of Mg
12. How many moles of oxygen are needed for the complete combustion of two moles of butane?
   A. 2 B. 8 C. 10 D. 13
13. If four moles of SO_2 are oxidized to SO_3, how many moles of oxygen molecules are required?
   A. 0.5 B. 1.0 C. 1.5 D. 2.0
14. Which of the following statements is incorrect?
   A. 12 g of Carbon gas contains one mole of atoms
   B. 28 g of Nitrogen gas contains one mole of molecules of N_2
   C. 1 dm^3 of 1.0 mole dm^{-3} solution of NaCl contains one mole of Chloride ions
   D. None of above
15. What volume of SO_2 at room temperature and pressure is produced on heating 9.7g of Zinc Sulphide (ZnS) if reaction takes place as follows;

$$2ZnS_{(s)} + 3O_{2(g)} \longrightarrow 2ZnO_{(s)} + 2SO_{2(g)}$$

   A. 1.2 dm^3 B. 2.4 dm^3 C. 3.6 dm^3 D. 4.8 dm^3

Answer Key with Explanations

Sr.No.	Option	Explanations
1.	B	Water is a molecular substance. One mole of a molecular substance contains Avogadro's number (6.023×10^{23}) molecules.
2.	D	1 mol of a gas at STP = 22.414 dm^3 = 22414 cm^3 1 mol of SO_2 = 64g 22414 cm^3 of SO_2 at STP has mass = 64g 500 cm^3 of SO_2 at STP has mass = $\frac{64}{22414} \times 500 = 1.427g$
3.	D	Diamond is an allotrope of carbon. 12g carbon (Diamond) = 1 mol = 6.023×10^{23} atoms 6g carbon (Diamond) = 0.5 mol = 3.011×10^{23} atoms

4.	D	Molar mass of $Al_2O_3 = 27(2) + 16(3) = 102 g\ mol^{-1}$ 102g Al_2O_3 contains $Al = 54g$ 204g Al_2O_3 contains $Al = \frac{54}{102} \times 204 = 108g$
5.	C	A reactant which is used or consumed earlier due to its lesser amount and controls the amount of product formed in a chemical reaction is called limiting reactant.
6.	B	NH_3: % of N $= \frac{14}{17} \times 100 = 82.3\%$; N_2H_4: % of N $= \frac{28}{32} \times 100 = 87.5\%$ NO: % of N $= \frac{14}{30} \times 100 = 46.6\%$; NH_4OH: % of N $= \frac{14}{35} \times 100 = 40\%$
7.	B	Number of molecules of a compound $= \frac{\text{Mass of compound}}{\text{Molecular mass}} \times N_A$ Molecular mass of vitamin-A ($C_{20}H_{30}O$) = 276g Number of molecules of vitamin-A $= \frac{0.5}{276} \times 6.023 \times 10^{23} = 1.05 \times 10^{21}$
8.	C	$CO + \frac{1}{2}O_2 \longrightarrow CO_2$ $C + O_2 \longrightarrow CO_2$ $C_2H_6 + 3\frac{1}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$ $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$
9.	D	Both ethanol and ethane are molecular substances. So 1 mole of each ethanol and ethane contains Avogadro's number (6.023×10^{23}) molecules.
10.	A	$CH_{4(g)} + H_2O_{(g)} \longrightarrow CO_{(g)} + 3H_{2(g)}$ The above equation shows that 1 mole of methane (CH_4) produces 3 moles of hydrogen (H_2). So 100 cm^3 of CH_4 will produce 300 cm^3 of H_2.
11.	D	24g of Mg = 1 mol of Mg = 6.023×10^{23} atoms (Avogadro's constant)
12.	D	According to balance chemical equation; $2C_4H_{10} + 13O_2 \longrightarrow 8CO_2 + 10H_2O$
13.	D	$2SO_2 + O_2 \longrightarrow 2SO_3$ $4SO_2 + 2O_2 \longrightarrow 4SO_3$
14.	D	(a), (b) and (c) are correct statements because in each statement the number of stated particles are Avogadro's number.
15.	B	$2ZnS_{(s)} + 3O_{2(g)} \longrightarrow 2ZnO_{(s)} + 2SO_{2(g)}$ $n_{ZnS} = \frac{9.7}{97} = 0.1$ mol ZnS : SO_2 2mol : 2mol 0.1 mol : 0.1 mol 1 mole of SO_2 = 22.414 dm^3 at STP 0.1 mole of SO_2 = 2.4 dm^3 at STP

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Define Avogadro's number and molar volume.

Ans. Avogadro's Number:

"The number of particles (atoms, molecules, formula units or ions) which are present in one mole of a chemical substance is called Avogadro's number."

Equal volumes of all the ideal gases at same temperature and pressure contain equal number of molecules.

- It is represented by N_A
- Its unit is mol^{-1}
- Its value is 6.022×10^{23}

Example:

16g CH_4 = 1 mole of CH_4 = 22.414 dm^3 of CH_4 = 6.02×10^{23} molecules of CH_4.

Molar Volume:

"The volume occupied by one mole of an ideal gas at standard temperature and pressure (STP) i.e. 0°C and 1 atm is called molar volume."

Value: Its value is 22.414 dm^3 (0.022414 m^3 or 22414 cm^3)

Examples:

(i) 2g of H_2 = 1 mole of H_2 = 22.414 dm^3

(ii) 16g of CH_4 = 1 mole of CH_4 = 22.414 dm^3

(iii) 44g CO_2 = 1 mole of CO_2 = 22.414 dm^3

From above examples it is clear that 1 mole of different gases e.g., 2g H_2, 16g CH_4, 44g CO_2 have same number of molecules and same volume (22.414 dm^3) at STP but different masses.

Q.2 Define mole with two examples.

Ans. Mole: "The amount of a substance which contains Avogadro's number of particles (atoms, molecules, formula units, or ions) is called mole."

Examples:

1 mole of Na = 23 g

1 mole of H_2O = 18 g

1 mole of NaCl = 58.5 g

1 mole of HCO_3^{-1} = 61 g

Formula: $\text{Mole} = \frac{\text{Given mass of the substance}}{\text{Molar mass}}$

Q.3 Why 180 g of glucose and 342 g of sucrose have same number of molecules but different number of atoms?

Ans. Molar mass of glucose ($C_6H_{12}O_6$) = 180 g mol^{-1}

Molar mass of sucrose ($C_{12}H_{22}O_{11}$) = 342 g mol^{-1}

Both glucose and sucrose are molecular species. Therefore one mole contains same number of molecules i.e., Avogadro's number (6.02×10^{23}).

180 g of glucose = 1 mol = 6.02×10^{23} Molecules of glucose

342 g of sucrose = 1 mol = 6.02×10^{23} Molecules of sucrose

One molecule of glucose has different number of atoms than one molecule of sucrose so one mole of each molecule contains different number of atoms in them.

As 1 molecule of glucose (contains) = 24 atoms

So, 1 mole glucose molecules (contains) = $24 \times 6.02 \times 10^{23}$ atoms

Similarly,

As 1 molecule of sucrose (contains) = 45 atoms

So, 1 mole of sucrose molecules (contains) = $45 \times 6.02 \times 10^{23}$ atoms

Q.4 Calculate the number of oxygen atoms in 10.037g of $CuSO_4.5H_2O$ (Atomic mass of Cu = 63, H = 1, O = 16).

Given Data: Mass of $CuSO_4.5H_2O$ = 10.037 g

Required: Number of O atoms = ?

Solution:

$$\text{Number of moles of } CuSO_4.5H_2O = \frac{\text{Mass of } CuSO_4.5H_2O}{\text{Molar mass of } CuSO_4.5H_2O}$$

Molar Mass of $CuSO_4.5H_2O = 63.5 + 32 + (4 \times 16) + (5 \times 18) = 249.5\ g\ mol^{-1}$

Number of moles of $CuSO_4.5H_2O = \frac{10.037}{249.5} = 0.04$ moles

1 mole of $CuSO_4.5H_2O$ have moles of O = 9 moles

0.04 moles of $CuSO_4.5H_2O$ have moles of O = $9 \times 0.04 = 0.36$ moles

Number of Oxygen atoms = Number of moles of oxygen atoms $\times N_A$

$= 0.36 \times 6.02 \times 10^{23}$

Number of Oxygen atoms = 2.167×10^{23} atoms

Q.5 Calculate mass in Kg of 2.6×10^{20} molecules of SO_2.

Given Data: Number of SO_2 molecules = 2.6×10^{20} molecules

Required: Mass in kg of SO_2 molecules = ?

Solution: $\text{Number of } SO_2 \text{ molecules} = \frac{\text{Mass of } SO_2 \text{ molecules}}{\text{Molar mass of } SO_2} \times N_A$

Molar Mass of $SO_2 = 32 + (16 \times 2) = 64\ g\ mol^{-1}$

$2.6 \times 10^{20} = \frac{\text{Mass of } SO_2 \text{ molecules}}{64} \times 6.02 \times 10^{23}$

$\frac{2.6 \times 10^{20} \times 64}{6.02 \times 10^{23}} = \text{Mass of } SO_2 \text{ molecules}$

$27.641 \times 10^{-3} g = \frac{27.641 \times 10^{-3}}{1000}$

$= 2.764 \times 10^{-5}$ kg = Mass of SO_2 molecules

Q.6 Calculate the number of water molecules in 10 g of ice.

Given Data: Mass of ice (water) = 10.0 gm

Molar mass of water = $18\ gmol^{-1}$

To Find: Number of molecules of water = ?

Solution:

$$\text{Number of molecules of water} = \frac{\text{Mass of water in gm}}{\text{Molar mass of water in } gmol^{-1}} \times \text{Avogadro's number}$$

$$= \frac{10}{18 gmol^{-1}} \times 6.02 \times 10^{23}$$

$$= 0.55 \times 6.02 \times 10^{23} = 3.31 \times 10^{23}$$

Q.7 Write down only steps to determine Limiting Reactant.

Ans. Limiting Reactant:

"A reactant which is used or consumed earlier due to its lesser amount and controls the amount of product formed in a chemical reaction is called limiting reactant."

A limiting reactant is that which

(i) controls the amount of product formed (ii) is taken in lesser amount

(iii) is consumed earlier (iv) produces least amount of product.

Identification of Limiting Reactant:

The following three steps should be followed to find out the limiting reactant:

(i) Calculate the number of moles from the given amount of reactant.

(ii) Find out the number of moles of product with the help of a balanced chemical equation.

(iii) Identify the reactant which produces the least amount of product as limiting reactant.

Q.8 Many reactions taking place in our surrounding involve limiting reactant. Justify with examples.

Ans. "The reactant which is consumed earlier and controls the amount of product in a chemical reaction is called a limiting reactant."

Mostly combustion reactions taking place in our surroundings involve the limiting reactant.

For example:

- $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$
- $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

In above examples, O_2 gas is present in excess while CH_4 and C are the reactants which are consumed earlier so they are limiting reactants.

Q.9 Law of conservation of mass has to be obeyed during stoichiometric calculations. Justify it.

Ans. According to law of conservation of mass.

"Mass can neither be created nor destroyed during a chemical reaction but it changes its form from one form to another."

In stoichiometric calculations, we use balanced chemical equation where total mass of reactants is equal to the total mass of products.

For Example:

- $2H_2 + O_2 \longrightarrow 2H_2O$
- $4g + 32g \longrightarrow 36g$

So while doing stoichiometric calculations law of conservation of mass has to be obeyed.

Q.10 What is stoichiometry? Which laws are obeyed during stoichiometric calculation?

Ans. Stoichiometry:

"The branch of chemistry which deals with the study of quantitative relationship between reactants and products in a balanced chemical equation is called stoichiometry."

Assumptions:

When stoichiometric calculations are performed, we have to assume the following **Conditions:**

(i) All the reactants are completely converted into products.

(ii) No side reaction occurs.

During stoichiometric calculations, law of conservation of mass and law of definite proportions are obeyed.

Q.11 Why theoretical yield of a chemical reaction is greater than the actual yield?

Ans. Actual yield of a chemical reaction is usually lesser than theoretical yield due to many reasons. They are:

(i) **Practically inexperienced** worker has many shortcomings and cannot get expected yield.

(ii) **Mechanical loss** during experimentation **e.g.,** filtration, separation by distillation or by a separating funnel, washing, drying and crystallization if not properly carried out, decrease the yield.

(iii) Some of the reactants might take part in a **competing side reaction.**

(iv) The reaction might be **reversible.**

(v) The reactants might be **impure.**

(vi) Sometimes the **reaction conditions** are not suitably maintained.

Q.12 Differentiate between Theoretical and Experimental yield.

Ans.

Theoretical Yield	Actual Yield
1) The amount of product calculated from a balanced chemical equation is called **theoretical yield.**	1) The amount of product obtained while performing a chemical reaction is called **actual yield.**
2) It is also called expected yield or calculated yield.	2) It is also called experimental yield.
3) Theoretical yield is always greater than actual yield.	3) Actual yield is always lesser than theoretical yield.
4) No need to perform experiment. Just to calculate from balanced chemical equation.	4) In order to get actual yield experiment has to be performed.

Q.13 How many moles of CO_2 can be produced from burning one mole of octane (mass of octane is 114)?

Ans. $2C_8H_{18} + 25O_2 \longrightarrow 16CO_2 + 18H_2O$

Number of moles of octane = 2 moles

Number of moles of CO_2 = ?

2 mole of octane gives CO_2 = 16 moles

1 mole of octane gives CO_2 = 8 moles

SELF-ASSESSMENT Chapter # 04

Total Mark: 30

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) **Which one of the following has maximum mass?**
A. 0.5 mol of N_2 B. 0.5 mol of NH_3 C. 0.5 mole of He D. 0.5 mol of CO

(ii) **Which of the following represents Avogadro's number?**
A. 6.022×10^{23} mol^{-1} B. 6.022×10^{-23} mol^{-1} C. 3.011×10^{23} mol^{-1} D. 1.008×10^{24} mol^{-1}

(iii) **If 2 moles of H_2 react with 1 mole of O_2, what is the limiting reagent?**
A. H_2 B. O_2 C. H_2O D. None

(iv) **A sample of nitrogen gas (N_2, molar mass = 28.0 g mol^{-1}) has a mass of 14.0 g. How many nitrogen atoms are present in this sample?**
A. 3.01×10^{23} atoms B. 6.02×10^{23} atoms C. 1.20×10^{24} atoms D. 2.40×10^{24} atoms

(v) **If a gas has a density of 1.43 g/L at STP, what is its molar mass?**
A. 14.3 g/mol B. 22.4 g/mol C. 32.0 g/mol D. 28.6 g/mol

(vi) **The number of molecules in 2 moles of CO_2 is:**
A. 3.01×10^{23} B. 1.20×10^{24} C. 6.02×10^{23} D. 2.00×10^{23}

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) Calculate the number of molecules in 0.5 mol of O_2.
(ii) Do you think that 1 mole of H_2 and 1 mole of NH_3 at 0 °C and 1 atm will have Avogadro's number of particles?
(iii) Calculate the molar mass of CO_2 from its density (1.96 g/L) at STP.
(iv) Define stoichiometry. Give the basic assumptions of stoichiometric calculations.
(v) Differentiate theoretical and actual yields. How is the percentage yield of a reaction calculated?
(vi) Calculate the theoretical yield of water when 4 g of H_2 reacts with excess O_2.
(vii) The reaction produced 9 g of product when the theoretical yield was 10 g. Calculate percentage yield.
(viii) How is stoichiometry important in medicine dosage?

Q.3 Extensive Questions. (2 × 4 = 8)

(a) When iron(III) oxide (Fe_2O_3) reacts with carbon monoxide (CO) in a blast furnace, iron metal (Fe) is produced according to the following equation:

$$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

(b) If 1.00 kg of iron(III) oxide is reacted with excess carbon monoxide, and 650 g of iron is obtained, what is the percentage yield of iron? (A_r of O = 16.0, Fe = 55.8)

Chapter 05

STATES AND PHASES OF MATTER

Student Learning Outcomes

After studying this chapter, students will be able to:

- Describe the physical properties of gases (including compressibility, expandability, and pressure exerted by gases). **(Understanding)**
- Origin of pressure in terms of collisions between molecules and the walls of container, Understand that ideal gas have zero partial volume, State and use the ideal gas equation PV = nRT in Calculations including determination of Mr. **(Understanding)**
- Describe simple properties of liquids e.g., diffusion, compression, expansion, motion of molecules, spaces between them, intermolecular forces and kinetic energy based on kinetic molecular theory. **(Understanding)**
- Describe types of intermolecular forces. **(Understanding)**
- Explain the strength and applications of dipole-dipole forces, hydrogen bonding and London forces. **(Understanding)**
- Describe physical properties of liquids such as evaporation, vapour pressure, boiling point, viscosity and surface tension. **(Understanding)**
- Apply the concept of hydrogen bonding to explain the properties of water (specifically high surface tension, high specific heat, low vapour pressure, high heat of vapourization, and high boiling point). **(Application)**
- Define molar heat of fusion and molar heat of vapourization. **(Knowledge)**
- Describe how heat of fusion and heat of vapourization affect the particles that make up matter. **(Understanding)**
- Outline the importance of heat of fusion in the study of glaciers and ice sheets (particularly while studying polar ice caps). **(Understanding)**
- Describe liquid crystals and give their uses in daily life. **(Understanding)**
- Differentiate liquid crystals from pure liquids and crystalline solids. **(Understanding)**
- Describe simple properties of solids e.g., compression, expansion, motion of molecules inter-particle space, intermolecular forces and kinetic energy based on kinetic molecular theory. **(Understanding)**
- Differentiate between amorphous and crystalline solids. **(Knowledge)**
- Describe properties of crystalline solids like geometrical shape, melting point, habit of a crystal, cleavage, and crystal growth. **(Understanding)**

➢ **Matter exists in four states:**

(i) solid (ii) liquid (iii) gas (iv) plasma

- Gaseous State is the simplest form of matter.
- Most of matter around us is in the solid state. Liquids are less common than solids, gases and plasmas. The reason is that the liquid state of any substance can exist only within a relatively narrow range of temperature and pressure.

Let us study at the general properties of gases, liquids, and solids. Kinetic molecular theory of gases can help us to understand their properties.

PROPERTIES OF GASES

i. Gases do not have a definite shape and volume. The volume of an ideal gas is the volume of the container.
ii. Ideal gases have zero particle volume.
iii. The molecules of gases are widely separated from one another and most of the volume of the gas is empty space (nearly 99.9%). That is why gases can be compressed easily. When sudden expansion of gases occurs cooling takes place. It is called Joule Thomson effect.
iv. Pressure of a gas is due to the collisions of gas molecules with the walls of the container.
v. There are no intermolecular forces in ideal gases.

Rack Your Mind!

1. Gases can be compressed more easily than solids or liquids because:
A) Gases have stronger intermolecular forces
B) Gas molecules are close together
C) Most of the volume of a gas is empty space
D) Gas molecules have fixed positions

IDEAL GAS EQUATION

It is a matter of common observation that when external conditions of temperature and pressure are changed, the volume of a given quantity of a gas is affected. The gas laws describe the relationships between volume of a given amount of gas and the prevailing conditions of temperature and pressure.

While describing Boyle's and Charles' laws, some of the variables are held constant during the changes produced in the gases.

Rack Your Mind!

2. Which equation represents the ideal gas law?
A) $V \propto 1/P$ B) $V \propto T$
C) $V \propto n$ D) $PV = nRT$

According to Boyle's law

$$V \propto \frac{1}{P} \text{ (when 'n' and 'T' are held constant)} \quad \text{_____ (1)}$$

According to Charles' law

$$V \propto T \text{ (when 'n' and 'P' are held constant)} \quad \text{_____ (2)}$$

According to Avogadro's law volume of the given gas at constant temperature and pressure is directly proportional to the number of moles.

$$V \propto n \text{ (when P and T are held constant)} \quad \text{_____ (3)}$$

If we think for a moment that none of the variables are to be kept constant, then all the above three relationships can be joined together as:

$$V \propto \frac{nT}{P}$$

$$V = \text{constant}\frac{nT}{P}$$

The constant suggested is 'R' which is called ideal gas constant. Its value is 0.0821 atm $dm^3 K^{-1}$ mol^{-1}.

Hence,

$$V = R\frac{nT}{P}$$

$$PV = nRT \quad \text{_____ (4)}$$

The equation (4) is called the ideal gas equation.

Calculation of Relative Molecular Mass (M_r) of a Gas

Equation (4) can be employed to calculate the relative molecular mass of a gas whose P, T, V and mass in grams are known. This is achieved by rearranging equation (4).

Putting $n = m/M$ in equation (4)

Where m = mass in g and M = molar mass of the gas:

$$PV = \frac{mRT}{M} \quad \text{_____ (5)}$$

Now rearranging equation (5)

$$M = \frac{mRT}{PV} \quad \text{_____ (6)}$$

At molecular level, the molar mass becomes relative molecular mass of a compound, therefore, we can write

$$M_r = \frac{mRT}{PV} \quad \text{_____ (7)}$$

Sample Problem 5.1

The volume of 134 g of a gas at −73°C under 10 atm pressure is 5 dm^3. Determine the relative molecular mass of the gas.

Solution: The molecular mass of the gas can be calculated by using the formula:

$$M = \frac{mRT}{PV}$$

$$M = \frac{(134\text{ g})(0.0821\text{ atm dm}^3\text{ mol}^{-1}\text{ K}^{-1})(200\text{ K})}{(10\text{ atm})(5\text{dm}^3)}$$

$$M = 44\text{ g mol}^{-1}$$

Therefore, the relative molecular mass of the gas is 44 g mol^{-1}.

QUICK CHECK 5.1

a) Explain why gases can be compressed easily?

Ans. Gases can easily be compressed because the molecules in a gas are very widely separated. Moreover, there are weak intermolecular forces present in it.
This large space between molecules allows them to be pushed together when pressure is applied and thus reduces the volume of gas significantly.

b) What is Joule-Thomson effect

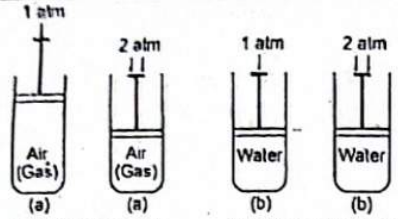
Ans. **Joule-Thomson Effect:**
When sudden expansion of gases occurs cooling takes place, it is called Joule Thomson effect.

c) The volume of 84g a gas is 8 dm^3 at −90°C under 7 atm pressure. Calculate the relative molecular mass of the gas.

Ans. $M = \frac{(84\text{ g})(0.0821\text{ atm dm}^3\text{ mol}^{-1}\text{ k}^{-1})(363\text{k})}{(7\text{ atm})(8\text{dm}^3)} = \frac{2,503.3932}{56} = 44.703\text{ g/mol}$

PROPERTIES OF LIQUIDS

i. Liquids also diffuse like gases, however the rate of diffusion in liquids is much lower than that in gases.
ii. There are little spaces among liquid molecules because of relatively stronger intermolecular forces.
iii. Liquids are 10^5 times less compressible than gases, but about 10 times more compressible than solids.
iv. The molecules of a liquid are in constant random motion, but their speed of movement is lower than gases. Diffusion among the miscible liquids is an evidence for the free motion of liquid molecules. Similarly, liquids can flow because of the free movement of their molecules.



(a) Volume of gas is reduced to half when pressure is doubled

(b) Volume of a liquid changes by about 0.0045% when pressure is doubled

Figure: Effect of pressure on the volumes of gases and liquids.

v. Liquids expands when their temperature is increased. However, this expansion is negligible compare to that in gases.

vi. According to kinetic molecular theory, molecules of a liquid are in constant motion, therefore they possess a certain amount of kinetic energy at any temperature. The kinetic energies of the molecules may increase or decrease by the rise or fall in temperature respectively. For example, a liquid is converted into a solid by decreasing its kinetic energy (on cooling) and converted into vapour by increasing kinetic energy (on heating).

INTERMOLECULAR FORCES

(Exercise L.Q.3)

Q. What are London dispersion forces? Give examples, and discuss the factors affecting these forces.

The intermolecular forces among the molecules of a liquid are reasonably stronger. Three types of such forces are mentioned here.

i. Instantaneous dipole-induced dipole forces (id-id) (London dispersion forces)
ii. Permanent dipole- permanent dipole forces
iii. Hydrogen bonding

Rack Your Mind!

3. Why does iodine have a higher boiling point than fluorine?

➲ Instantaneous Dipole-Induced Dipole forces (id-id)

The momentary force of attraction between an instantaneous dipole and an induced dipole is called instantaneous dipole-induced dipole force.

These are only forces that exist among the molecules of non-polar compounds. The strength of these forces depend upon the following factors

i. Molecular Mass and Size:

When the molecular mass (M_r) of a compound is greater, the id-id forces are stronger and vice versa. This is because in a larger atom or molecule the dispersion of electronic cloud and polarization is relatively easier.

Examples:

This factor operates in the halogen and noble gas families.

Physical States of Halogens:

The physical state changes in the halogen family from top to bottom due to the increase in size and polarizability. The first two members in the halogen family (F_2 and $C\ell_2$) are gases, but bromine is a liquid and iodine a solid (b.p. = 458K). The boiling points of noble gases in group 18 also increase from helium (He) to xenon (Xe) as in Table.

Table: Molar masses and boiling points of group 17 and 18 of periodic table.

17 (VII-A)	Molecular Mass	Boiling points (K)	18 VIII	Molecular mass	Boiling points (K)
F_2	38	85	He	4.003	4.22
$C\ell_2$	71	239	Ne	20.18	27.1
Br_2	159	333	Ar	39.95	87.3
I_2	253.8	458	Kr	83.8	120
			Xe	131.3	165

ii. Surface Area (shape of molecule)

A molecule with larger surface area has more number of contacts for a nearby molecule. Thus the forces among the molecules of a compound having larger surface area are stronger.

Saturated Hydrocarbons: Consider saturated hydrocarbons. These have chains of carbon atoms linked with hydrogen atoms.

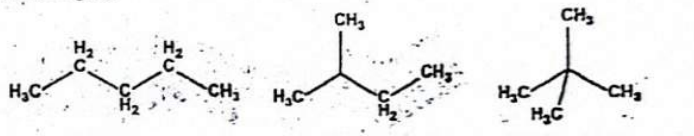
Comparison of Ethane and Hexane:

Compare the length of the chains in C_2H_6 and C_6H_{14}. They have the boiling points –88.6°C and 68.7°C, respectively. It is evident that the molecules with larger chain length experiences stronger attractive forces. The reason is that longer molecules have more places along the length where they can be attracted to other molecules. Boiling points of some hydrocarbons are given in Table.

Table: Boiling points and physical states of some hydrocarbons

Name	B.Pt. °C (1 atm)	Physical state at S.T.P.	Name	B.Pt. °C (1 atm)	Physical state at S.T.P
Methane (CH_4)	–164	Gas	Pentane (C_5H_{12})	36.1	Liquid
Ethane (C_2H_6)	–88.6	Gas	Hexane (C_6H_{14})	68.7	Liquid
Propane (C_3H_8)	–42.1	Gas	Decane ($C_{10}H_{22}$)	174.1	Liquid
Butane (C_4H_{10})	–0.5	Gas	Isodecane ($C_{20}H_{42}$)	327	Solid

Three isomers of pentane have the same relative molecular mass (M_r), however, they differ in their surface areas. Straight chain pentane has largest surface area and so is its boiling point among the three isomers of pentane. 2-Methylbutane (Isopentane) has smaller surface area than n-pentane but larger than 2, 2-Dimethylpropane (Neopentane). Therefore, the forces among 2-Methylbutane molecules are intermediate and the least strong forces occur in 2,2-Dimethylpropane. The isomers of pentane alone with their boiling points are given in Figure.



pentane (n-pentane) 36.2 °C

2-Methylbutane (iso-pentane) 28 °C

2,2-Dimethylpropane (neo-pentane) 9.5 °C

Figure: The three isomers of pentane have different structures, surface areas and intermolecular forces

➲ Permanent Dipole-Permanent Dipole Forces (pd-pd)

The force of attraction between the positive end of a polar molecule and the negative end of a nearby polar molecule is called permanent dipole forces in $HC\ell$ and chloroform dipole-permanent dipole force.

Rack Your Mind!

4. Permanent Dipole-Permanent Dipole Forces (pd-pd) are present among:
A) Molecules of Iodine
B) Atoms of Neon in gaseous state
C) Chloroform molecules
D) CCl_4

Example 1:

$HC\ell$ Molecules: Whenever the $HC\ell$ molecules are close to each other (as in liquid state), they tend to line up (as in Figure).

Example 2:

Chloroform Molecules: pd-pd forces are present among the molecules of chloroform ($CHC\ell_3$).

The molecule of chloroform has a positive center at the H atom and the negative center on the end with $C\ell$ atoms.

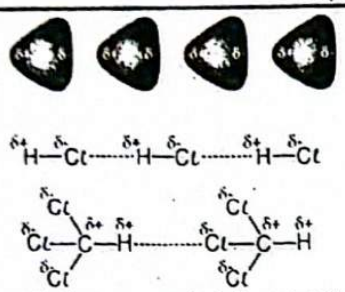


Figure: Permanent dipole-permanent dipole forces in HCℓ and chloroform

QUICK CHECK 5.2

a) To improve the quality of gasoline (petrol), straight chain hydrocarbons in the gasoline fraction of petroleum are converted to branched chain ones? What could be the possible reason?

Ans. The conversion of straight-chain hydrocarbons to branched-chain hydrocarbons in gasoline is done to improve its quality, particularly to improve its octane number.

Straight-chain alkanes (like n-heptane) have low octane numbers and tend to knock.

Branched alkanes (like iso-octane) have high octane numbers, meaning they burn more efficiently (smoothly) and are less prone to knocking in internal combustion engines than straight-chain hydrocarbons.

b) Which forces are present among the molecules of the following substances? $CC\ell_4$, SiF_4

Ans. **$CC\ell_4$ (Carbon Tetrachloride):**

- **Polarity:** Non-polar (symmetrical shape cancels dipoles)
- **Forces present:** London dispersion forces (only)

SiF_4 (Silicon Tetrafluoride):

- **Polarity:** Non-polar (symmetric, dipoles cancel)

Although the Si–F bonds are **polar**, the molecule as a whole is **non-polar** despite having polar bonds because the dipole moments cancel out due to its symmetry.

- **Forces present:** London dispersion forces (only)

c) Differentiate id-id and pd-pd forces with examples.

Ans.

Feature	id-id Forces (London Dispersion)	pd-pd Forces (Dipole–Dipole)
Molecular Polarity	Present in non-polar molecules	Present in polar molecules
Cause	Temporary fluctuations in electron clouds	Electrostatic attraction between permanent dipoles
Strength	Weak (but can be significant in large molecules)	Stronger than id-id forces
Universality	Found in all molecules, even polar ones	Found only in polar molecules
Effect of Molecular Size	Increases with molecular size and surface area	Mostly influenced by dipole strength
Examples	$CC\ell_4$, CH_4, I_2	$HC\ell$, $CH_3C\ell$, SO_2

Exercise L.Q.4

Q. Hydrogen bonding is present in H_2O, NH_3, HF, $(CH_3)_2CO$ and $CHC\ell_3$ molecules. Sketch structures and discuss briefly.

Hydrogen Bonding

- Hydrogen bond is a special type of dipole-dipole force.
- It is the strongest force among intermolecular forces, but is weaker than all the major types of bond, i.e. ionic, metallic, and covalent bonds.
- **Formation of Hydrogen Bond:** A hydrogen bond is formed when the following conditions are fulfilled:

i. The hydrogen atom is connected to a highly electronegative atom, such as F, O, or N.
ii. The electronegative atom must have a lone pair of electrons on it.

The covalent bond between a highly electronegative atom and hydrogen is highly polarized. It means the hydrogen atom carries a sufficient δ+charge and the electronegative atom δ-charge. The presence of lone pair on the electronegative allows the partial positively charged hydrogen atom to make a bond with F, O, or N called a hydrogen bond. This bond is represented by a dotted line (...) and its strength is one tenth of an ordinary covalent bond. The number of hydrogen bonds a molecule can form on average depends on:

- The number hydrogen atoms bonded to the electronegative atom.
- The number of lone pairs present on F, O, or N.

L.Q Why HF is a weaker acid than HCℓ, HBr and HI?

Examples:

(i) Water

- A water molecule contains two hydrogen atoms and two lone pairs on oxygen atom.
- Water can form two hydrogen bonds per molecule on average.
- This is why water molecules are extensively hydrogen bonded with one another.
- This unique feature of water is responsible for its characteristic properties, e.g., high boiling point of water (100 °C). The water molecules in liquid form are arranged three dimensionally (as shown in Fig.).
- This bonding acts as a bridge between two electronegative oxygen atoms.

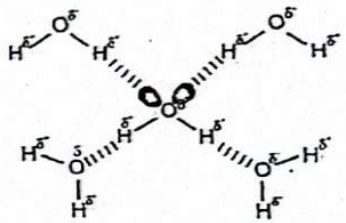


Figure: Hydrogen bonding in water

(ii) Ammonia

- Ammonia can form only one hydrogen bond per molecule although it has three hydrogen atoms.
- **Reason:** This is due to the availability of only one lone pair on the N atom as shown in Figure. The hydrogen bonding in liquid ammonia is much weaker than water. This is why its boiling point is much lower (–33°C).

(iii) HF

- HF is even more distinct than water and ammonia.
- It has three lone pairs on the F atom which allows it to form three H-bonds.
- However, it has only one H atom and due to this reason, it is restricted to form only one bond again.
- In HF, hydrogen bond is strong enough compared to NH_3, which owes to its high electronegativity.
- Thus, its B.Pt. (19.9°C) is much higher than ammonia (–33.5°C).
- The molecules of HF join with one other in a zig-zag manner in liquid state due to the presence of the hydrogen bonds.

Lowest Acidic strength of HF among hydrogen halides:

The exceptional low acidic strength of HF molecule as compared to HCℓ, HBr and HI is attributed to this strong hydrogen bonding, because the partial positively charged hydrogen is entrapped between two highly electronegative atoms (Figure).

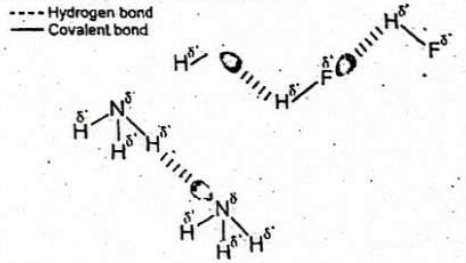
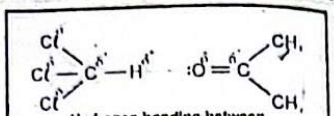


Figure: Hydrogen bonding in NH_3 and HF

L.Q What is hydrogen bonding? Discuss the structure and low density of ice.

(iv) Acetone and Chloroform:

- Chloroform has three chlorine atoms are responsible for H-bonding with other molecules.
- These atoms deprive the carbon atom of its electrons and the partial positively charged hydrogen can form a strong hydrogen bond with oxygen atom of acetone (propanone).



Hydrogen bonding between chloroform and acetone

(Exercise L.Q.5)

Q. Discuss the structural changes when water turns into ice. Justify the empty spaces in its crystals as compared to H_2O at 4°C and lower density of ice.

Influence of Hydrogen Bonding on the Properties of Water

i. Structure and Low Density of Ice

- The molecules of water have tetrahedral structure.
- Two lone pairs of electrons on oxygen atom occupy two corners of the tetrahedron.
- When the temperature of water is decreased and ice is formed, the molecules become more regular and this regularity extends throughout the whole structure.
- Empty spaces are created in the extensively hydrogen bonded structure as shown in the following diagram (Figure). This is why, when water freezes, **it (ice) occupies 9% more space** and its density decreases. For this reason, ice floats on water. Due to this so called anomalous behaviour of ice, the fish and other living creatures survive under the frozen lakes and oceans. The ice blanket covers the water surface due to its low density and the water beneath is insulated from the environment.

Rack Your Mind!

5. Discuss anomalous behaviour of water saves aquatic life.

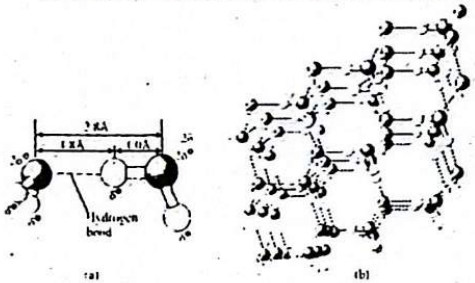
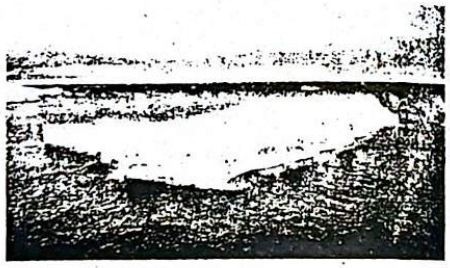


Figure: Extensive hydrogen bonding in ice and spaces among molecules



This part of a glacier is floating on the surface due to low density of ice

ii. High Heat Capacity

Water has a high specific heat capacity. This is due to its unique molecular structure which allows strong hydrogen bonds.

iii. Anomalous Heat of Vaporization and Boiling Point

The general trend of enthalpy change of vaporization of group 16 hydrides is a regular increase from H_2S to H_2Po (Figure). This is because the molecules of these compounds are bound by weak London dispersion forces.

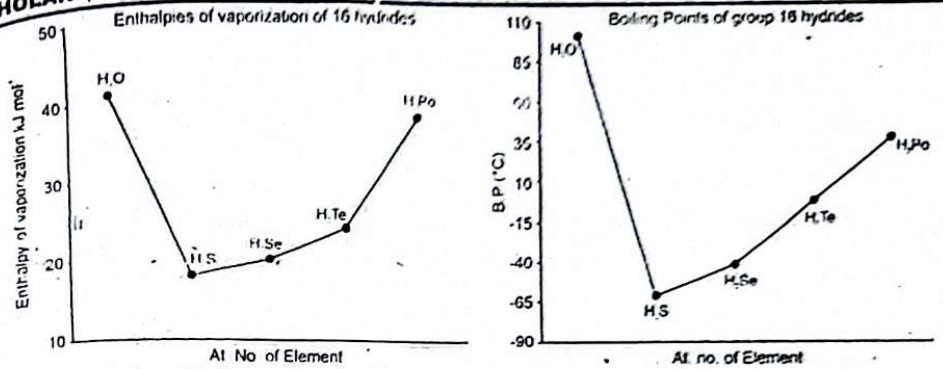


Figure: A graphical expression of variation in enthalpy of vaporization and B.Ps of group 16 hydrides

With the increasing atomic size down the group, from S to Po, the van der Waals forces also become stronger. If water had followed this trend, the heat of vaporization of water would be the lowest among the group members.

S/Q. Water has highest boiling point and highest enthalpy change of vaporation. Explain

Ans. Water has the highest enthalpy change of vaporization (41 kJ mol⁻¹) in the group. This is because water is exceptionally hydrogen bonded, which makes it difficult to break forces among water molecules and vaporize it. The boiling point of water is also remarkably higher than the rest of group 16 hydrides. Simply, the energy required to break the water molecules apart is very high due to extensive hydrogen bonding in it. It needs high temperatures to provide so much energy as to boil water into its vapour.

iv. Surface Tension and Viscosity

The surface tension and viscosity of water are also very high. Surface tension is a downward pull of water molecules at the surface, making the water surface stretched and strained. This downward pull is due to the attraction of inner molecules through hydrogen bonds.

- **Viscosity is the resistance by a liquid to its flow.** Water has higher viscosity than many of liquids including lower hydrocarbons and alcohols (e.g., hexane and ethanol. The high viscosity of water is also due strong hydrogen bonds among the molecules. Alcohols can make hydrogen bonds, but the strength and extent of hydrogen bonding is far less than that in water. Hydrocarbons lack the ability to make the hydrogen bond.
- **Order of Viscosity in Water, Hydrocarbons and Alochols:**

Water ⟩ Alcohols ⟩ Lower Hydrocarbons

QUICK CHECK 5.3

a) Can the CHF_3 molecule make a hydrogen bond? Explain why or why not?

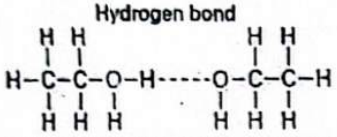
Ans. No, CHF_3 (trifluoromethane) cannot form hydrogen bonds with itself.

Explanation:

- Hydrogen bonding typically occurs when a hydrogen atom is covalently bonded to a highly electronegative atom (like F, O, or N) and this hydrogen has a partial positive charge that can interact with a lone pair on another electronegative atom.
- **In CHF_3:**
  - The hydrogen is bonded to carbon, not to fluorine.
  - While fluorine is very electronegative, the H atom is not directly bonded to it, so the necessary strong dipole (H–F) does not exist.
- Therefore, CHF_3 does not meet the criteria for hydrogen bonding, although it does have dipole–dipole interactions and London dispersion forces.
- In short, CHF_3 cannot hydrogen bond because the hydrogen is not bonded directly to fluorine, oxygen, or nitrogen.

b) Show a hydrogen bond between two molecules of ethanol (CH_3CH_2OH).

Ans.



c) Describe which forces are present in the following and arrange them in increasing order of boiling point.

i. $CH_3CH_2CH_3$ ii. CH_3CH_2OH iii. CH_3CH_2Cl

Ans. The intermolecular forces present in each compound and then arrange them in increasing order of boiling point:

i. $CH_3CH_2CH_3$ (Propane)

- **Forces present:** Only London dispersion forces (induced dipole-induced dipole)
- **Polarity:** Nonpolar
- **Boiling point:** Lowest among the three due to weak intermolecular forces.

ii. CH_3CH_2OH (Ethanol)

- **Forces present:**
  - **Hydrogen bonding** (due to –OH group)
  - Dipole–dipole forces
  - London dispersion forces
- **Polarity:** Polar
- **Boiling point:** Highest due to strong hydrogen bonding.

iii. CH_3CH_2Cl (Chloroethane)

- **Forces present:**
  - Dipole–dipole forces (due to C–Cl bond)
  - London dispersion forces
- **Polarity:** Polar
- **Boiling point:** Intermediate

d) The boiling point difference in each of the following pairs is given

i. CH_3CH_3 (–89°C) and CH_3OH(65°C), difference = 154°C

ii. $CH_3CH_2CH_2CH_4$ 0°C and $CH_3CH_2CH_2OH$(97°C), difference = 97°C

Explain why the difference decreases as the size of the molecules increase.

Ans.

(i) The large boiling point difference (154 °C) between ethane (CH_3CH_3, –89 °C) and methanol (CH_3OH, 65 °C) is primarily due to hydrogen bonding in methanol, while ethane only has weak London dispersion forces.

A. Intermolecular Forces in Ethane (CH_3CH_3):

- Only London dispersion forces (van der Waals) are present.
- Weak, temporary dipoles due to electron motion.
- Low molecular weight (30 g/mol) → very weak attractions → boiling point = –89 °C.

B. Intermolecular Forces in Methanol (CH_3OH):

- Hydrogen bonding (strong dipole-dipole interaction):
- The H bonded to O (δ^+) attracts the lone pairs on O (δ^-) of another methanol molecule.

In short, The 154 °C difference arises because methanol forms strong H-bonds, while ethane relies solely on weak London forces. Hydrogen bonding drastically increases the energy needed to separate molecules.

(ii) Let us compare the boiling points of two substances, butane ($CH_3CH_2CH_2CH_3$) and ethanol ($CH_3CH_2CH_2OH$).

- **Butane ($CH_3CH_2CH_2CH_3$) has a boiling point of 0°C.**
- **Ethanol ($CH_3CH_2CH_2OH$) has a boiling point of 97°C.**

The difference in their boiling points is:

97°C – 0°C = 97°C

This difference is due to the different types of intermolecular forces. Ethanol, which has hydrogen bonding due to its -OH group, has a much higher boiling point than butane, which only has van der Waals forces between molecules.

Explain why the difference decreases as the size of the molecules increases.

As the size of molecules increases, the boiling point differences between polar (hydrogen-bonding) and nonpolar molecules tend to decrease. Here's why:

Reasons:

I. **Increasing London Dispersion Forces:** Larger nonpolar molecules exhibit stronger London dispersion forces, which narrows the boiling point gap with polar molecules.

II. **Hydrogen Bonding Remains Strong:** Polar molecules continue to exhibit strong hydrogen bonding, but the relative impact on boiling point decreases as London dispersion forces become more significant.

Effect:

Convergence of Boiling Points: As molecular size increases, boiling points of polar and nonpolar molecules converge, reducing the difference.

This trend is observed when comparing smaller molecules (like methanol and ethane) to larger ones (like longer-chain alcohols and alkanes).

e) Molecules of ethanoic acid (acetic acid) exist in the form of dimers in pure form but not in aqueous solution. How hydrogen bond can explain this?

Ans. Hydrogen Bonding in Acetic Acid:

Dimer Formation: In pure acetic acid, molecules form dimers through hydrogen bonding between the carbonyl oxygen and hydroxyl hydrogen. This stabilizes the dimer structure.

In Aqueous Solution:

i. **Competition with Water:** Water molecules form hydrogen bonds with acetic acid molecules, disrupting the dimer structure.

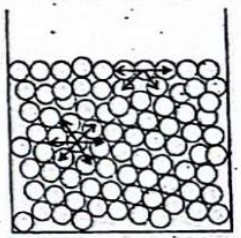
ii. **Solvent Effect:** The polar aqueous environment favours solvation of individual acetic acid molecules over dimer formation.

Conclusion:

Hydrogen bonding with water molecules in aqueous solution competes with and disrupts the intermolecular hydrogen bonds between acetic acid molecules, preventing dimer formation.

SURFACE TENSION OF LIQUIDS

- **Surface tension is a property of liquids** that describes the force acting along the surface of a liquid, causing it to behave like an elastic sheet. This force arises due to the intermolecular forces between the molecules at the surface.
- Molecules at the surface experience a net force inward due to intermolecular forces, leading to a "skin" on the surface. Liquids tend to minimize their surface area due to surface tension, which explains why droplets form spheres.
- Surface tension influences various phenomena, such as:
  - capillary action
  - wetting of surfaces
  - formation of droplets and bubbles



Did You Know?

Q. Which of the following best explains why a small insect can walk on the surface of water?

(A) Water has high density
(B) Water has strong cohesive forces due to surface tension
(C) The insect repels water molecules
(D) Water has high viscosity

Factors Affecting Surface Tension

I) **Temperature:** Surface tension typically decreases with increasing temperature.

$$\text{Surface tension} \propto \frac{1}{\text{Temperature}}$$

ii) **Intermolecular forces:** Stronger intermolecular forces lead to higher surface tension.

Surface tension ∝ Intermolecular forces



Mosquitos can float on surface on water due to high surface tension

Rock Your Mind!

6. Which property allows insects to walk on water?
A) Viscosity B) Surface tension
C) Capillarity D) Adhesion

Table: Surface tension of some liquids at 20°C in Nm^{-1}

Sr. No.	Liquid	$\gamma(10^{-3}Nm^{-1})$	Sr. No.	Liquid	$\gamma(10^{-3}Nm^{-1})$
1	Water H_2O	72.75	4	Acetone $(CH_3)_2CO$	23.70
2	Ethyl alcohol CH_3CH_2OH	22.75	5	Benzene C_6H_6	28.85
3	Methyl alcohol CH_3OH	22.61	6	Carbon tetrachloride $CC\ell_4$	26.95

'γ' are values multiple of $10^{-3} = 1/1000$. It means 'γ' value of the water (H_2O) at 20°C = $72.75 \times 10^{-3} Nm^{-1}$ or 72.75 dynes cm^{-1}.

VISCOSITY OF LIQUIDS

Explanation

Example:

Take water in a beaker. It is stirred with a glass rod, and left undisturbed for some time. Its swirling motion subsides after a while.

It is observed that the liquid layer adjacent to the walls of the beaker comes to rest first and layer near the centre stops last. It can be inferred that stationary layer of walls of beaker slows down the motion of layer touching it immediately. This slowed layer in touch with container also slows the next inner layer, but to less extent. This means that a slow moving layer of a liquid tends to slow down the fast moving layer adjacent to it. This is a frictional force operating between adjacent layers.

- **Viscosity Definition:** "This resistance to the flow of a liquid is termed as viscosity".
- **Units:** In international system (SI), unit of viscosity is in $kgm^{-1}\ s^{-1}$.
- In CGS system, the unit of viscosity is poise (P).

Factors Affecting Viscosity

The factors affecting viscosity are as follows:

i. **Temperature:** An increase of temperature increases the average kinetic energy of molecules. This allows the molecules to overcome the attractive forces. This lowers the viscosity.

ii. **Intermolecular Forces:** The stronger the intermolecular forces, the greater the viscosity of liquids because liquid molecules cannot move around each other freely, so the resistance to flow increases.

QUICK CHECK 5.4

a) **Arrange the following liquids is increasing order of surface tension, give reason: Acetone (CH_3COCH_3), ethanol (C_2H_5OH), methoxy methane (dimethyl ether, CH_3OCH_3)**

Ans.

1. **Ethanol (C_2H_5OH):**
   - **Hydrogen bonding:** Ethanol has a hydroxyl (–OH) group, which can form hydrogen bonds with other ethanol molecules. This results in a relatively high surface tension because hydrogen bonds are strong forces that resist the disruption of the surface.
   - **Surface tension:** High compared to acetone and methoxy methane.

2. **Methoxy methane (dimethyl ether, CH_3OCH_3):**
   - **Dipole-dipole interactions:** Methoxy methane has an ether group (–O–), which has some polarity, but it cannot form hydrogen bonds like ethanol. This results in weaker intermolecular forces compared to ethanol.
   - **Surface tension:** Lower than ethanol, but higher than acetone, due to dipole-dipole interactions.
3. **Acetone (CH_3COCH_3):**
   - **Dipole-dipole interactions:** Acetone has a carbonyl group (C=O), which is polar, but it does not have hydrogen bonding capability because it lacks –OH or –NH groups. Therefore, it only experiences dipole-dipole interactions and weaker van der Waals forces compared to ethanol and methoxy methane.
   - **Surface tension:** Lowest of the three due to weaker intermolecular forces.
   - **Increasing order of surface tension:**

Acetone < Methoxy methane < Ethanol

b) **Why do you think tetracholromethane (carbon tetrachloride, $CC\ell_4$) has higher viscosity than chloroform ($CHC\ell_3$) but less than ethanol (C_2H_5OH)?**

Ans. $CC\ell_4$ has higher viscosity than $CHC\ell_3$ because it is a larger, more symmetrical molecule with stronger London dispersion forces, increasing resistance to flow.

However, ethanol (C_2H_5OH) has even stronger hydrogen bonding, which greatly increases intermolecular attraction, making its viscosity higher than $CC\ell_4$.

Viscosity trend: $CHC\ell_3 < CC\ell_4 < C_2H_5OH$

Reason: Increasing strength of intermolecular forces — dispersion < dipole < hydrogen bonding.

c) **The viscosity of honey is higher than water, explain why.**

Ans. Honey has higher viscosity than water because it contains large amounts of sugars (like glucose and fructose), which form extensive hydrogen bonds with water and each other. This creates a dense, structured network that resists flow, unlike water's smaller, more mobile molecules.

Higher viscosity slows down molecular motion and oxygen diffusion, thereby reducing the rate of oxidation.

d) **Which of the following is more viscous: glycerine ($CH_2OHCH_2OHCH_2OH$) or hexane (C_6H_6)? Why?**

Ans. Glycerine ($CH_2OHCH_2OHCH_2OH$) is more viscous than hexane (C_6H_{14}) because:

- Glycerine has three –OH (hydroxyl) groups, enabling extensive hydrogen bonding, which strongly resists flow.
- Hexane is a nonpolar hydrocarbon with only weak van der Waals forces, offering minimal resistance to flow.
- In short, Glycerine > Hexane in viscosity due to strong hydrogen bonding.

EVAPORATION

Definition:

"Evaporation is the spontaneous conversion of a liquid into vapour at any temperature".

- When high energy molecules leave the liquid and low energy molecules are left behind, the temperature of the liquid falls.
- The heat moves from the surrounding to the liquid and then the temperature of the surrounding also falls. This phenomenon helps to understand that evaporation causes cooling.

Rock Your Mind!

7. Water in earthenware pots stay cool due to:
A) boiling B) condensation
C) evaporation D) insulation

A person after bath feels a sense of cooling due to evaporation of water from his body when exposed to air. The molecules of H_2O take away the energy of body. Earthenware vessels keep water cooler under the same phenomenon. Earthenware vessels are porous.

The water molecules having sufficient K.E to overcome inter molecular forces come out of these pores and evaporate. This process of evaporation keeps on taking place and energy required for this process comes from the liquid. Thus, the average K.E of remaining water molecules decreases which results in decrease in temperature of the liquid. Hens, earthenware vessels keep water cool.

Rock Your Mind!

8. Earthenware vessels keep water cool. Explain with reason.

Q. Evaporation causes cooling. Explain.

Ans. The molecules of a liquid are not motionless. The energy of molecules is not equally distributed. Evaporation causes cooling, because when high energy molecules leave the liquid and low energy molecules are left behind, the temperature of liquid falls and heat moves from the surrounding to the liquid and then the temperature of the surrounding also falls. That is why, evaporation causes a cooling effect.

VAPOUR PRESSURE

The molecules of a liquid which leave the open surface are mixed up with air above the liquid. If the vessel is open these molecules go on leaving the surface of liquid. But if we close the system the molecules of liquid start gathering above the surface. These molecules collide with the walls of the container, and also with the surface of the liquid as well. There are chances that these molecules are recaptured by the surface of liquid. This process is called condensation. The two processes, i.e., evaporation and condensation continue till a stage reaches when the rate of evaporation becomes equal to the rate of condensation Fig.

➢ **Definition:**

"The pressure exerted by the liquid vapour in equilibrium with its liquid at a given temperature is called vapour pressure".

$$\text{Liquid} \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}} \text{Vapour}$$

The magnitude of vapour pressure does not depend upon the amount of liquid in the container or the volume of container.

➲ **Surface Area of a liquid:**

- **Reason:** The larger surface area presents a larger target for returning the molecules, so the rate of condensation also increases.

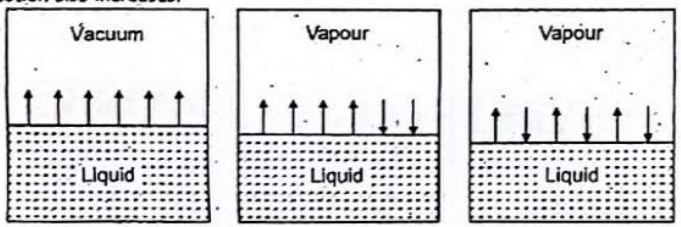


Figure: Attainment of equilibrium when the evaporation of liquid is carried out in an evacuated closed vessel. (a) Initial state, with evacuated space above the liquid, (b) intermediate state, and (c) equilibrium state, when the rate of evaporation is equal to the rate of condensation.

QUICK CHECK 5.5

a) Which of the liquids in each of the following pairs has a higher vapour pressure?
i) Alcohol, glycerine ii) Petrol, kerosene, iii) Mercury, water?

Ans.

(i) **Alcohol, Glycerine:** Alcohol has a higher vapour pressure than glycerine. Glycerine, with three -OH groups, forms strong hydrogen bonds, making it less volatile and giving it a lower vapour pressure.

(ii) **Petrol, Kerosene:** Petrol has a higher vapour pressure than kerosene. Petrol consists of smaller, more volatile hydrocarbons with weaker intermolecular forces, allowing more molecules to escape into the vapour phase. Kerosene has larger, heavier molecules with stronger intermolecular forces, resulting in lower vapour pressure.

(iii) **Mercury, Water:** Water has a higher vapour pressure than mercury. Water has weaker intermolecular forces (hydrogen bonding) compared to mercury, which has strong metallic bonding. As a result, water molecules escape into the vapour phase more easily, leading to a higher vapour pressure.

b) i) Which one in each of the following pairs is more viscous: Glycerine or kerosene?

Ans. Glycerine is more viscous than kerosene.

Glycerine has 3-OH groups, allowing strong hydrogen bonding between molecules, which greatly increases resistance to flow. Kerosene, a mixture of hydrocarbons, has weak van der Waals forces and lacks hydrogen bonding, so it flows more easily.

In short, Viscosity of glycerine is greater than Kerosene due to stronger intermolecular (hydrogen) bonding present in glycerine.

c) Separate portions of acetone and water at the same temperature are poured on your hands. The acetone feels colder. Account for this in terms of attractive forces.

Ans. Acetone feels colder than water because it evaporates more quickly, absorbing more heat from your skin.

Reason: Acetone has weaker intermolecular forces (dipole-dipole) compared to water's strong hydrogen bonds. Weaker forces mean acetone molecules escape into the air more easily, causing faster evaporation and greater cooling (evaporative cooling).

d) Why evaporation gets faster at higher temperatures?

Ans. Evaporation gets faster at higher temperatures because more molecules gain enough kinetic energy to overcome intermolecular forces and escape into the vapour phase.

In short, Higher the temperature, higher kinetic energy, faster evaporation.

e) Why do we feel cool near the bank of a river?

Ans. We feel cool near the bank of a river because the water evaporates, and evaporation is a cooling process. Also, water has a high specific heat capacity, so it absorbs heat from the surroundings, keeping the area cooler.

BOILING POINT

- When a liquid is heated, its vapour pressure goes on increasing. A stage reaches when the vapour pressure of the liquid becomes equal to the atmospheric or external pressure.
- At this temperature the liquid starts boiling. The reason for this is that the bubbles of vapour which are formed in the interior of the liquid have greater internal pressure than atmospheric pressure on the surface of liquid. This makes the bubbles to come out of the liquid and burst at the surface. A constant stream of bubbles comes out at the boiling point of the liquid.
- **Temperature and B.Pt:** When a liquid is heated, the kinetic energy of its molecules increases. This causes the increase of the temperature. At the boiling point, the kinetic energy of the molecules becomes maximum. Any further heating at this stage will not increase the temperature. This further heating is utilized to break the intermolecular forces and convert the liquid into its vapour. The boiling points of some commonly available liquids at 1 atmospheric pressure are shown in the Table.

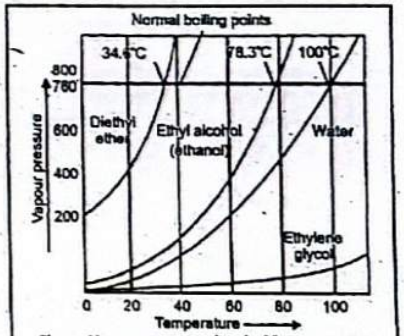


Figure: Vapour pressures (torr) of four common liquids shown as a function of temperature.

- **Graphical Evidence:** The figure shows the variation of vapour pressure of water, ethyl alcohol ethylene glycol and diethyl ether with temperature. The graphs show that the liquids reach upto their boiling points when their vapour pressures are equal to 760 torr at sea level.

Factors Affecting Boiling Points of Liquids

The boiling point of a liquid is affected by the factors given below.

1) Strength of Intermolecular Forces ∝ B.Pt

Stronger the intermolecular forces, lower will be the vapour pressure and higher will be the boiling point. Higher boiling point of H_2O indicates stronger intermolecular forces than that of ethanol and methanol, Table.

Table: Boiling points of some common liquids at 760 torr (1 atm)

Liquids	Formula	B.P °C	Liquids	Formula	B.P °C
Acetic acid	CH_3COOH	118.50	Carbon tetrachloride	CCl_4	76.50
Acetone	CH_3COCH_3	56.00	Ethanol	C_2H_5OH	78.30
Benzene	C_6H_6	80.15	Naphthalene	$C_{10}H_8$	218.00
Carbon disulphide	CS_2	46.30	Water	H_2O	100.00

2) External Pressure ∝ B.Pt

When vapour pressure of a liquid becomes equal to the external pressure then the liquid boils. It means that when external pressure is changed, its boiling point will also change. When the external pressure is high the liquid requires greater amount of heat to equalize its vapour pressure to external pressure. In this way boiling point is raised. Similarly, at a lower external pressure a liquid absorbs less amount of heat and it boils at a lower temperature.

e.g., Application of B.Pt. Vacuum Distillation etc.

Temperature – Vapour Pressure Graph

External pressure (torr)	Boiling point (°C)
1489 torr	120°C
760 torr (at sea level)	100°C
700 torr (at Murree Hills)	98°C
323 torr (at Mount Everest)	69°C
23.7 torr	25°C

Boiling points of water at various external pressure

Pressure Cooker:

- We can increase the external pressure artificially on the surface of boiling water by using a pressure cooker. Pressure cooker is a closed container.
- The vapour of water formed is not allowed to escape.
- In this way, it exerts they develop more pressure on the water surface in the cooker and the boiling temperature increases.
- As more heat is absorbed in water, so food is cooked quickly under increased pressure.

☑ QUICK CHECK 5.6

a) Why food cooking is difficult in the areas with high altitudes?

Ans. At high altitudes, atmospheric pressure is lower, so water boils at a lower temperature, producing less heat for cooking. This makes food take longer to cook.

b) The food cooks faster in the pressure cooker, explain.

Ans. Food cooks faster in a pressure cooker because it traps steam, increasing the pressure inside. This raises the boiling point of water (above 100 °C), allowing food to cook at a higher temperature. The higher heat speeds up chemical reactions, reducing cooking time.

- Normally, water boils at 100°C (212°F) at 1 atm (sea level pressure).
- In a pressure cooker, pressure rises to ~1.5–2 atm, raising the boiling point to 110–120°C (230–250°F)

Factor	Open Pot (1 atm)	Pressure Cooker (~2 atm)
Boiling Point	100°C (212°F)	120°C (248°F)
Cooking Speed	Slow	3–10 × faster
Energy Use	More (longer time)	Less (shorter time)

In short, Higher the pressure, higher boiling point, faster cooking.

c) Why the boiling point of water (100°C) is higher than that of ethanol (78°C), although both have hydrogen bonds?

Ans. The boiling point of water (100°C) is higher than that of ethanol (78°C) because water forms stronger and more extensive hydrogen bonds due to its molecular structure, whereas ethanol's hydrogen bonding is partially hindered by its nonpolar ethyl group.

Property	Water (H_2O)	Ethanol (CH_3CH_2OH)
H–bond donors	2 (two H atoms)	1 (only –OH H)
H–bond acceptors	2 (two lone pairs on O)	1 (one lone pair on O)
Effect on boiling point	Stronger, more extensive network, higher energy needed to break bonds	Weaker, limited network, easier to vaporize

In short, While both substances have hydrogen bonds, water's smaller size, higher polarity, and ability to form twice as many H-bonds per molecule make its intermolecular forces significantly stronger, leading to a higher boiling point than ethanol.

ENERGETIC OF PHASE CHANGES

Whenever, matter undergoes a physical change, it is always accompanied by an energy change. This change in energy is the quantitative measurement of the difference in the strength of intermolecular forces.

Molar Heat of Fusion (ΔH_f)

The amount of heat absorbed by one mole of a solid to melt it into the liquid at its melting point at 1 atmospheric pressure is called molar heat of fusion.

Example:

$$H_2O_{(s)} \longrightarrow H_2O_{(\ell)} \qquad \Delta H_f = 4.6 \text{ kJ mol}^{-1}$$

Molar Heat of Vaporization (ΔH_v)

The amount of heat absorbed by one mole of a liquid to convert it into one mole of vapour at its boiling point at 1 atmospheric pressure is called molar heat of vapourization.

The molar heats of vaportization depends upon the strength of intermolecular forces. When one mole H_2O is converted to vapour at 100°C, then heat absorbed is 40.6 kJ mol^{-1}.

$$H_2O_{(\ell)} \longrightarrow H_2O_{(g)} \qquad \Delta H_v = 40.6 \text{ kJ mol}^{-1}$$

NH_3 and $HC\ell$ only need 21.7 and 15.6 kJ mol^{-1} respectively to become vapour at their boiling points. This difference is due to the stronger intermolecular forces in water.

Effect of Molar Heat of Vapourization and Fusion on Matter Particles

The molar heat of fusion and vapourization affect the particles that make up matter by providing them with enough energy. Due to this, the particles move away from one another and change the state of the substances from solids to liquids and liquids to gases respectively. Particles gain more freedom to move and rotate in the liquid and gas phase.

SOLIDS

Solids are those substances which are rigid, hard, have definite shape and definite volume. The atoms, ions and molecules that make up a solid are closely packed. They are held together by strong cohesive forces. The constituent atoms, ions or molecules of solids cannot move at random.

General Properties of Solids

i) Compression of Solids

The atoms, molecules or ions of a solid substance are closely packed. The particles of solids cannot move closer to each other unlike gases. It is true for metallic solids that their atoms are spherically symmetrical. So, when such particles are arranged, they can give birth to hexagonal and cubic close-packed structures. Here outer boundaries of constituent particles touch each other but due to their spherical shapes, they cannot occupy more than 74% space. It means the compression of solids is not possible.

ii) Expansion of Solids

The expansion is the property in which spaces between constituent particles are increased. In case of solids the forces of attractions are so strong that increase of temperature hardly affects their relative positions. The particles in a solid have vibrational motions about their mean positions. Increase in temperature of solids hardly increases their volume. No doubt, there are parameters like coefficient of linear and cubic expansions of various solids, but these are negligible as compared to liquids and gases.

iii) Motion of Particles in Solids

The constituent particles of a solid do not undergo translatory motion, and neither rotational ones. They only vibrate about their mean positions. These vibrations become more intense at higher temperature.

iv) Inter-particle Space in Solids

The interpaticle spaces in solids are far less than liquids. This is due to the stronger forces among their particles. Due to closely packed atoms, molecules, and ions, solids are mostly hard, have high melting points and high stability.

v) Inter-particle Forces in Solids

In solids, the particles (atoms, ions, molecules) are held together by ionic, covalent, metallic or van der Waals forces. These forces are strong enough to fix the particles at their places thus allowing these particles to just vibrate about their mean positions.

vi) Kinetic Energy Based on KMT

Kinetic energy is due to the motion of constituent particles of a solid. Solid particles have only vibratory motion and they do not have translational or rotational motion. Therefore, the only kinetic energy that solids possess is vibrational kinetic energy.

TYPES OF SOLIDS

There are two types of solids on the basis of the way their particles are arranged;

i. Crystalline solids ii. amorphous solids

➲ Crystalline Solids

➢ **Crystal Lattice**

The regular arrangement of ions, atoms, or molecules in three dimensional space is called the crystal lattice. The solids which have definite regular and three dimensional geometric shapes are called crystalline solids. For example, diamond, sodium chloride, ice, etc.

(Exercise Q.7)

Q. Describe the following properties of crystalline solids.
i) Geometrical shape ii) Melting point iii) Cleavage plane iv) Habit of a crystal

➢ **Properties of Crystalline Solids**

i. Geometrical Shape

- All the crystalline solids have a definite, distinctive geometrical shape due to definite and orderly arrangement of atoms, ions or molecules in three-dimensional space.
- For a given crystal, the interfacial angles, at which the surfaces intersect, are always the same no matter in which shape they are grown.
- The faces and angles remain characteristic even when the material is ground to a fine powder.

Rack Your Mind!
9. Why the ionic crystalline solids have high melting points?

ii. Melting Points

- Crystalline solids have sharp melting points.
- They can be identified from their definite melting points. e.g., Melting point of NaCℓ = 801°C

Rack Your Mind!
10. Cleavage of the crystals is itself anisotropic behaviour.

iii. Cleavage Planes

- Whenever the crystalline solids are broken they do so along definite planes.

- These planes are called the cleavage planes and they are inclined to one another at a particular angle for a given crystalline solid.
- The value of this angle varies from one solid to another solid.

iv. Growing of a Crystal

- When we have a saturated or super saturated solution of a crystalline material in a suitable solvent, it can give us same types of crystals by arranging atoms, ions or molecules.
- This happens through the process called growth of crystals.
- This can be done by slow evaporation of the solvent or by **Seeding process** from saturated solution.

Seeding Process:
Seeding involves introducing a small "seed crystal" into a supersaturated solution or melt to initiate and guide the growth of larger, well-formed

- **Example:** The solubility of sodium thiosulphate $Na_2S_2O_3$ in water at 100°C is 231 g / 100 cm^3. At room temperature, solubility is 50 g / 100 cm^3. If we have saturated solution of $Na_2S_2O_3$ at 100°C, on cooling slowly no growth of crystal happens. It means that super saturated solution is not in equilibrium with solid substance. Now, if small crystal of $Na_2S_2O_3$ is added to super saturated solution, the crystallization happens rapidly.

v. Habit of a Crystal

- The shape of a crystal in which it usually grows is called habit of a crystal.
- If the conditions for growing a crystal are maintained, then the shape of the crystal always remains the same.
- If the conditions are changed the shape of the crystal may change.
- For example, a cubic crystal of NaCℓ becomes needle like when 10% urea is present in its solution as an impurity.

➲ Amorphous Solids: (Prefix 'A' = without, morph: Shape ⇒ Shapeless)

Definition:

"Amorphous substances are those whose constituent atoms, ions or molecules do not possess a regular orderly arrangement".

Amorphous solids, contrary to the crystalline solids, do not possess regular three dimensional geometrical shapes.

Examples of Amorphous Solids: Glass, wood, amorphous sulphur (plastic sulphur), charcoal, coal, coke, etc.

➢ **Properties of Amorphous Solids:**

i. The amorphous solids can have small regions where orderly arrangement of particles is found, but they do not have long range of regularity. The regions where orderly arrangement of particles is present are known as crystallites.
ii. Amorphous solids like glass melts over a wide temperature range.
iii. They can be molded and blown to form different shapes.
iv. Amorphous solids do not have definite value of heat of fusion.

Table: Comparison of crystalline and amorphous solids.

Property	Crystalline solids	Amorphous solids
1. Geometry of solid	Crystalline solids show characteristic geometrical shapes.	Amorphous solids generally appear in lump or in a fine powder form.
2. Melting of solid	Crystalline solids melt sharply at their melting points.	Amorphous solids do not have sharp melting points and they melt over a range of temperature.
3. Directional character of the properties	Crystalline solids are anisotropic in nature. It means that their properties depend upon the direction along which the measurements are made.	Amorphous solids are isotropic. Their properties do not depend upon the direction of measurement.
4. Order of particles in solid	Crystalline solids have long-range order.	In amorphous solids, long-range order is absent.
5. Examples:	NaCℓ, Diamond etc.	Glass, Glue etc.

QUICK CHECK 5.7

a) Why solids have very low compressibility and expansion?

Ans. Solids have very low compressibility (resistance to volume reduction under pressure) and low thermal expansion due to their rigid, closely packed atomic/molecular structure. The reasons are:

1. **Low Compressibility:**
   - **Strong Intermolecular Forces:** Particles (atoms/ions/molecules) in solids are held tightly by strong bonds (e.g., covalent, ionic, or metallic) or van der Waals forces (in molecular solids).
   - **Minimal Empty Space:** Particles are densely packed, leaving almost no gaps to compress further.
   - **Electron Repulsion:** When forced closer, electrons in adjacent atoms repel strongly, resisting compression.
2. **Low Thermal Expansion:**
   - **Vibrational Motion Only:** When heated, particles vibrate more but cannot move freely (unlike liquids/gases). This limits expansion.

b) What is meant by habit of a crystal?

Ans. See (Properties of Crystalline solids) Above Point_v. Habit of a crystal.

c) Why solids do not undergo translatory motion?

Ans. Solids do not undergo translatory motion (free movement of molecules from one position to another) because of their rigid, fixed molecular structure and strong intermolecular forces.

Reasons:

1. **Strong Intermolecular Forces:**
   - Solids have strong bonds (ionic, covalent, metallic) or dense van der Waals forces that hold particles in fixed positions.
   - **Example:** In a salt crystal ($NaCl$), ions are locked in place by electrostatic forces.
2. **Fixed Lattice Structure:**
   - Particles in solids are arranged in a rigid, ordered lattice (crystalline) or a tightly packed disordered structure (amorphous).
   - Unlike liquids/gases, they cannot flow because their molecules lack freedom to move past one another.
3. **Only Vibrational Motion:**
   - When heated, particles vibrate around fixed positions but do not translate.
   - **Example:** Atoms in a diamond vibrate but stay locked in a covalent network.

LIQUID CRYSTALS

(Exercise L Q 6)

Q. How liquid crystals resemble liquids and solids? Give their uses in daily life.

Introduction

We know that the distinction between liquids and solids is clear-cut. Moreover, the phase transition between them is always sharply defined. However, at certain temperature, many substances exist in a phase that is neither fully liquid nor fully solid. The molecules in these substances can move around, as in viscous liquids, but have a restricted range of motion, as in solids. These substances are called liquid crystals.

Crystalline solid ⟶ Cloudy liquid (liquid crystal) ⟶ Clear liquid

In most liquid crystals, the molecules have a rigid, rod-like shape with a length four to eight times greater than their diameter. When packed together, the molecules tend to orient with their long axes roughly parallel, like logs in a stack of firewood. Individual molecules can migrate through the fluid. They can spin around their long axis, but they can't rotate end over end.

"The turbid liquid phase of a solid that exists in between the melting and clearing temperature is called liquid crystal."

Crystal ⟹ Liquid Crystal ⟹ Liquid

Rack Your Mind!

9. **Which of the following best describes liquid crystals?**
   A) Solid substances
   B) Amorphous solids
   C) Substances with properties between liquids and solids
   D) Completely gaseous substances

General Properties of Liquid Crystals

Liquid Crystals

The general properties of liquid crystals are as follows:

i. They have parallel ordered arrangement.
ii. They are elongated, rod-like and linear.
iii. They flow like liquids.
iv. They show viscosity like liquids.
v. They show optical properties like crystals.
vi. They are somewhat rigid.
vii. They are always anisotropic.

Discovery of Liquid Crystals

- First of all, in 1888, Frederick Reinitzer, an Austrian botanist discovered the liquid crystals
- He was studying an organic compound Cholesteryl benzoate.
- This compound turns milky liquid at 145°C and becomes a clear liquid at 179°C.
- When the substance is cooled, the reverse process occurs
- This turbid liquid phase was called liquid crystal.

Uses of Liquid Crystals in Daily Life

The main application area of liquid crystals is in electro-optic devices. These are electrically controlled devices that modulate light in a desired way. Liquid crystals have many uses in daily life.

i) **In Diagnostics**
   - Special liquid crystal devices can be used to diagnose the tumors and infections in the human body.
   - This is because often physical problems, such as tumors, have a different temperature than the surrounding tissue.
   - When cholesteric liquid crystals are applied to the breast, a tumor is located because of being warmer than the other parts. This technique is successfully applied to diagnose breast cancer in the early stage.

ii) **Characteristic Higher Temperature Determination**
   - Liquid crystal temperature sensors can also be used to find faulty connections on a circuit board by detecting the characteristic higher temperature.
   - As temperature sensors, they are be used in thermometers.

iii) **Liquid Crystal Displays (LCDs)**
   - The most common application of liquid crystal technology is liquid crystal displays (LCDs.).
   - Examples of liquid crystal screens are oscillograph and TV, laptops, cell phone displays. Liquid crystals are used in TV displays, computer screens, calculators and watches, etc.
   - **Note:** As new properties and types of liquid crystals are investigated and researched, these materials are sure to gain increasing importance in industrial and scientific applications.

QUICK CHECK 5.8

a) Name the properties of liquid crystals in which they resemble solids.

Ans. Liquid crystals (LCs) share several key properties with solids, despite their fluid-like behaviour. Here are the solid-like characteristics they exhibit:

i. **Long-Range Orientational Order**
   - Like solids, LCs have molecules aligned in a preferred direction (e.g., nematic phase) or in layers (smectic phase).
   - **Solid-like Example:** Crystals have fixed atomic positions; LCs maintain directional order while allowing some mobility.

ii. **Optical Anisotropy**
   - LCs split light into two polarized rays, just as crystalline solids do, due to their ordered structure.
   - **Application:** LCD screens exploit this property to control pixels.

iii. **Elastic Response to Deformation**
   - LCs resist distortions (e.g., bending, twisting) and recover their alignment when disturbed, similar to elastic solids.

b) Mention the properties of liquid crystals in which they resemble liquids.

Ans. Liquid crystals (LCs) exhibit several **liquid-like properties** while maintaining some degree of molecular order. Here are the key ways they resemble liquids:

i. **Fluid-like Flow and Viscosity**
   - LCs can flow and take the shape of their container, just like ordinary liquids (e.g., isotropic liquids).
   - **Example:** Nematic LCs pour like oils but retain directional order.

ii. **No Fixed Positional Order (Short-Range Mobility)**
- Unlike solids, LC molecules do not occupy fixed lattice positions—they can slide past one another while maintaining alignment.
- **Exception:** Smectic LCs have layered order but still allow in-plane flow.

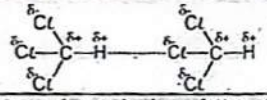
iii. **Surface Wetting Behavior**
- LCs spread and wet surfaces like liquids, forming droplets or films.
- Used in coatings and responsive sensors.

iv. **Diffusion and Mixing**
- LC molecules exhibit Brownian motion (random movement) and can diffuse, though slower than in isotropic liquids due to partial order.

c) Which property of liquid crystals make it possible to use them in temperature sensing devices?

Ans. The temperature-dependent optical properties of liquid crystals (especially cholesteric/chiral nematic phases) enable their use in temperature sensors.
- Their pitch (molecular twist length) changes with temperature, altering reflected/transmitted light wavelengths (visible as color shifts).
- **Example:** Thermochromic strips (e.g., forehead thermometers) use this to display temperature via color.
- The reversible, precise response to thermal energy makes LCs ideal for non-contact, visual temperature sensing.

Solution File — Rack Your Brain!

Sr. #	Option	Explanation
1.	C	Gases have large distances between molecules, making them more compressible compared to solids and liquids, which have molecules that are closely packed.
2.	D	The equation, known as the ideal gas law, relates the pressure (P), volume (V), and temperature (T) of a gas, with n being the number of mles and R the gas constant. It combines Boyle's Charles's and Avogadros' laws.
3.	S.Q	Iodine has a larger molecular mass and more electrons, which increases polarizability and strengthens id-id forces, due to that reason its boiling point increases.
4.	C	
5.	S.Q	**Anomalous Behaviour of Water Saves Aquatic Life:** The lower density of ice allows it to float and form an insulating layer on water, maintaining liquid water below and protecting aquatic organisms during winter.
6.	B	Surface tension decreases with increase in temperature because molecular motion weakens cohesive forces.
7.	C	Water seeps through the earthwnware and evaporates from the surface, taking heat away from the remaining water, thus cooling it down.
8.	S.Q	Earthenware vessels are porous. Water rises through these pores by capillary action and evaporates at the surface of the vessel. Remaining over water has low energy molecules so its temperature drops. Further, these earthenware vessels are insulators and do not allow the heat to move in them and hence, water remains cool in earthenware vessels.
9.	S.Q	The oppositely charged ions i.e. cations and anions in ionic crystals, are closely held together by strong attractive forces i.e. electrostatic force of attraction or ionic bond. That is why a very high energy or heat is required to separate cations and anions from each other and convert them into liquid. So, ionic crystalline solids have high melting points e.g., melting point of NaCℓ = 801°C
10.	S.Q	In crystals, the particles are arranged in a regular repeating three dimensional pattern. This arrangement of particles is different in different planes. It is due to the reason that cleavage of crystals occur differently in different directions. Hence, cleavage of crystals is itself anisotropic behaviour. Difference in physical properties with direction.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. **London dispersion forces are the only forces present among:**
a) molecules of water in liquid state b) atoms of helium in gaseous state at high temperature
c) molecules of solid iodine d) molecules of hydrogen chloride gas

II. **When the vapour pressure of a liquid equals the external pressure, what phenomenon occurs?**
a) Sublimation b) Condensation c) Boiling d) Freezing

III. **When water freezes at 0°C, its density decreases due to:**
a) cubic structure of ice b) empty spaces present in the structure of ice
c) decrease in volume d) decrease in viscosity

IV. **Which of following is the correct sequence of increasing ΔH_V values of substances mentioned?**
a) $H_2O > NH_3 > I_2$ b) $F_2 > NH_3 > H_2O$ c) $NH_3 > H_2O > F_2$ d) $H_2O > F_2 > NH_3$

V. **Surface tension of a liquid is due to:**
a) inward pull of surface molecules b) upward pull from the surface
c) collision of molecules d) repulsive forces

VI. **Which change of state involves overcoming only London dispersion forces?**
a) Melting of ice. ($H_2O_{(s)} \rightarrow H_2O_{(\ell)}$) b) Boiling of ethanol ($CH_3CH_2OH_{(\ell)} \rightarrow CH_3CH_2OH_{(g)}$)
c) Sublimation of iodine ($I_{(s)} \rightarrow I_{2(g)}$) d) Dissolving sodium chloride in water

VII. **In which of the following substances are London dispersion forces the only significant intermolecular forces present?**
a) Ammonia (NH_3) b) Water (H_2O) c) Methane (CH_4) d) Hydrogen fluoride (HF)

VIII. **Which of the following is a characteristic property of crystalline solids?**
a) They have a range of melting points. b) They are isotropic.
c) They have a definite and sharp melting point. d) They lack a regular arrangement of particles.

IX. **Which of the following liquids would you expect to have the highest viscosity at a given temperature?**
a) Water (H_2O) b) Ethanol (CH_3CH_2OH)
c) Diethyl ether ($CH_3CH_2OCH_2CH_3$) d) Glycerol ($CH_2(OH)CH(OHCH_2(OH)$)

X. **Which type of intermolecular force is present in all types of molecule regardless of their polarity?**
a) Dipole-dipole forces b) Hydrogen bonds c) London dispersion forces d) Ion-dipole forces

XI. **Liquid crystals exhibit properties:**
a) Only like solids. b) Only like liquids.
c) Between solids and liquids. d) Unlike solids or liquids

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	b	atoms of helium in gaseous state at high temperature	• Helium atoms are monoatomic and non-polar. They only exhibit temporary London dispersion forces. Water and HCℓ have hydrogen bonding or dipole–dipole forces; iodine has London forces, but also in a solid lattice.
II.	c	boiling	• Boiling starts when the vapour pressure inside the liquid equals the atmospheric pressure, allowing vapor bubbles to form inside the liquid.

III.	b	empty spaces present in the structure of ice	• Ice forms a hexagonal open structure with gaps due to hydrogen bonding, making it less dense than liquid water.
IV.	a	$H_2O > NH_3 > F_2$	ΔHv depends on intermolecular forces: • H_2O has strongest H-bonding → highest ΔHv • NH_3 has weaker H-bonding → moderate ΔHv • F_2 has only London forces → lowest ΔHv • Thus, the decreasing order (which matches option a) is: $H_2O > NH_3 > F_2$
V.	a	inward pull of surface molecules	• Surface molecules are pulled inward due to cohesive forces, causing the liquid to minimize surface area — this is surface tension.
VI.	c	Sublimation of iodine $I_{2(s)} \rightarrow I_{2(g)}$	• Iodine is non-polar; its molecules are held together only by weak London dispersion forces, which are overcome during sublimation.
VII.	c	Methane (CH_4)	• CH_4 is non-polar, and hence only exhibits London dispersion forces. The others have dipole or hydrogen bonding.
VIII.	c	They have a definite and sharp melting point	• Crystalline solids have an orderly arrangement, causing them to melt sharply at a specific temperature
IX.	d	Glycerol ($CH_2(OH)CH(OH)CH_2(OH)$)	• Glycerol has three –OH groups, forming many hydrogen bonds, increasing resistance to flow (viscosity).
X.	c	London dispersion forces	• London dispersion forces are present in all atoms and molecules due to temporary electron fluctuations.
XI.	c	Between solids and liquids	• Liquid crystals have properties intermediate between solids and liquids. They flow like liquids but have some molecular order like solids, making them unique and useful in display technologies (e.g., LCD screens).

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Explain, at a molecular level, why evaporation leads to a cooling effect.

Ans. Evaporation causes a cooling effect because of the loss of high-energy molecules from a liquid's surface.

1. **Molecules in a Liquid Have Varying Energies**
   - In any liquid, molecules are in constant motion and have different kinetic energies.
   - Some have high energy, others less — this distribution is random.
2. **Only the Fastest Molecules Escape**
   - The highest energy molecules (with enough kinetic energy to overcome intermolecular forces) escape from the liquid surface and become gas (vapour).
   - This process is evaporation.
3. **Loss of High-Energy Molecules Lowers Average Energy**
   - When these high-energy molecules leave, the average kinetic energy of the remaining molecules decreases.
   - Since temperature is a measure of average kinetic energy, the temperature of the liquid drops.

b. Explain why liquids with stronger intermolecular forces tend to have lower rates of evaporation at a given temperature compared to liquids with weaker intermolecular forces.

Ans. Liquids with stronger intermolecular forces (like hydrogen bonds or dipole-dipole forces) require more energy for molecules to escape the surface and become vapour.
At a given temperature, fewer molecules have enough energy to overcome these forces, so the rate of evaporation is lower compared to liquids with weaker intermolecular forces, where molecules escape more easily.

c. One feels sense of cooling under the fan after bath. Explain.

Ans. Evaporation is a cooling process and speed of air increases the rate of evaporation. After bath, a thin layer of water is formed on body. When one sits under the fan, the water gets energy from body and evaporates. Increase in the rate of evaporation is facilitated by speed of air. As a result, one feels sense of cooling due to decrease in body temperature.

d. How a dynamic equilibrium is established during evaporation of a liquid in a closed vessel at constant temperature.

Ans. When a liquid is placed in a **closed container** at constant temperature:
- **Evaporation starts:** Molecules at the surface escape into the vapour phase.
- **Condensation also begins:** Vapour molecules collide with the liquid surface and re-enter the liquid.

e. The boiling point of water is different at Lahore and Murree hills.

Ans. The boiling point of a liquid can be decreased by decreasing the external pressure.
Boiling Point of Water at Lahore:
At Lahore, the atmospheric pressure is 750.1 torr and boiling point of water is 99.1 °C (approx.) at this pressure.
Boiling Point of Water at Murree Hills:
At Murree Hills the pressure is 700 torr and boiling point of water is 98°C at this pressure.

f. Discuss two significant consequences of the lower density of ice compared to liquid water in natural environments.?

Ans. Two key consequences of ice being less dense than liquid water:
- **Ice Floats on Water:** This insulates lakes and ponds in winter, allowing aquatic life to survive beneath the frozen surface.
- **Prevention of Complete Freezing:** Since ice forms at the surface and floats, it prevents water bodies from freezing solid from the bottom up, preserving ecosystems.

g. Why boiling point (B.P) of a liquid increases when the external pressure rises?

Ans. The boiling point of a liquid increases with external pressure because:
Boiling occurs when the vapour pressure of the liquid equals the external pressure.
When the external pressure rises, the liquid must reach a higher temperature to produce enough vapour pressure to match it, thus raising the boiling point.

h. Mention four items in which liquid crystals are used.

Ans. Four common items that use liquid crystals:
- Digital watches and clocks
- Laptop and TV screens (LCDs)
- Thermometers (liquid crystal thermometers)
- Mobile phone displays

i. How do you differentiate between crystalline solids and amorphous solids?

Ans. Differences between Crystalline and Amorphous Solids

Property	Crystalline solids	Amorphous solids
Definition	Those solids in which atoms, ions or molecules are arranged in a definite three-dimensional pattern are called crystalline solids. This recurring regular geometrical pattern of structure extends three dimensionally.	Amorphous substances are those whose constituent atoms, ions or molecules do not possess a regular orderly arrangement.
Shape	They have definite characteristic geometrical shape.	They have irregular shape (Word Amorphous means shapeless).
Melting point	They melt at a sharp and characteristic temperature.	They gradually soften over a range of temperature.
Cleavage plane	When cut with a sharp edged tool, they into two pieces and the newly generated surfaces are plain and smooth.	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces.
Heat of fusion	They have a definite and characteristic heat of fusion.	They do not have definite heat of fusion.
Anisotropy	These are anisotropic in nature	These are isotropic in nature.
Nature	They are true solids	They are pseudo solids or super cooled liquids or highly viscous liquids.
Examples	NaCl, Sugar, Ice, Diamond etc.	Rubber, Plastic, Glue, Glass, Paper etc.

j. Propanone (CH_3COCH_3), propanol ($CH_3CH_2CH_2OH$) and butane ($CH_3CH_2CH_2CH_3$) have very similar relative molecular masses. List them in the expected order of increasing boiling points. Explain your answer.

Ans. Boiling Point:

"The temperature at which the vapour pressure of a liquid becomes equal to external pressure is called boiling point of that liquid."

Order of boiling points is:

$$\underset{0^\circ C}{\text{Butane}} < \underset{56^\circ C}{\text{Propanone}} < \underset{97^\circ C}{\text{Propanol}}$$

i. Butane is non-polar and it has London dispersion forces.
ii. Propanone has dipole-dipole forces.
iii. Propanol has hydrogen bonding.

The strongest intermolecular forces are hydrogen bonding and weakest are London forces, so ordered boiling points is same as given above.

k. Discuss how hydrogen bonding is responsible for the relatively high surface tension of water.

Ans. Hydrogen bonding is responsible for the relatively high surface tension of water due to the strong intermolecular attractions between water molecules. Each water molecule can form up to four hydrogen bonds with neighboring water molecules. At the surface, water molecules have fewer neighbouring molecules, so they form stronger bonds with the ones beside and below them. This creates an inward cohesive force, pulling surface molecules more tightly together. As a result, water's surface resists external force, leading to high surface tension.

In Short, Hydrogen bonding causes strong cohesive forces among water molecules, especially at the surface, resulting in high surface tension.

l. What type of intermolecular forces will dominate in the following liquids?
(i) NH_3 (ii) Ar (iii) CH_3COCH_3 (iv) CH_3OH

Ans. (i) NH_3 (Ammonia): Hydrogen bonding is present in ammonia molecules.
(ii) Ar (Argon): London dispersion forces are present in argon (which is a noble gas).
(iii) CH_3COCH_3 (Acetone): Hydrogen bonding is present in acetone molecules.
(iv) CH_3OH (Methanol): Hydrogen bonding is present in methanol molecules.

m. The boiling points and molar masses of hydrides of some first-row elements are tabulated below:

Substance	Boiling Point (K)	Molar Mass (g mol^{-1})
CH_4	112	16
NH_3	240	17
H_2O	373	18

Suggest reasons for the difference in their boiling points in terms of the type of molecules involved and the nature of the forces present between them.

Ans.
- **CH_4:** Methane is a symmetrical and non-polar molecule. It has **London dispersion forces.** Which are very weak so it has low bonding point.
- **NH_3:** Ammonia is a polar molecule. It has **hydrogen bonding** between its molecules. These intermolecular forces are stronger than London forces. Due to these forces, ammonia has high boiling point and heat of vapourization than methane.
- **H_2O:** Water is a polar molecule. In water molecule **strong hydrogen bonding** is present. Water forms two H-bonds per molecule as a result the affect of hydrogen bonding in water is more than in ammonia. Due to this, boiling point and heat of vapourization of water is very high as compared to methane and ammonia.

DESCRIPTIVE QUESTIONS

Q.3 What are London dispersion forces? Give examples, and discuss the factors affecting these forces.

Ans. See Page No. (142)

Q.4 Hydrogen bonding is present in H_2O, NH, HF, $(CH_3)_2$ CO and $CHCl_3$ molecules. Sketch structures and discuss briefly.

Ans. See Page No. (144)

Q.5 Discuss the structural changes when water turns into ice. Justify the empty spaces in its crystals as compared to H_2O at 4°C and lower density of ice.

Ans. See Page No. (146)

Q.6 How liquid crystals resemble liquids and solids? Give their uses in daily life.

Ans. See Page No. (158)

Q.7 Describe the following properties of crystalline solids.
i) Geometrical shape ii) Melting point iii) Cleavage plan iv) Habit of a crystal

Ans. See Page No. (156)

NUMERICAL PROBLEMS

Q.8 A sample of an unknown gas has a mass of 0.560 g. It occupies a volume of 2.87×10^{-4} m^3 at a temperature of 300 K and a pressure of 1.01×10^5 Pa. Calculate the molar mass of the gas. (Gas constant, $R = 8.31\ JK^{-1}\ mol^{-1}$)

Ans. Given data:

Mass (m) = 0.560 g
Volume (V) = 2.87×10^{-4} m^3
Temperature (T) = 300 K
Pressure (P) = 1.01×10^5 Pa
Gas constant (R) = 8.31 $J\ K^{-1}\ mol^{-1}$

To find:

Molar Mass of Unknown Gas = ?

Solution:

Step 1: Use the ideal gas law to find moles (n)

$$PV = nRT$$

$$n = PV/RT$$

$$n = \frac{(1.01\times10^5\ Pa)(2.87\times10^{-4}\ m^3)}{(8.31\ JK^{-1}mol^{-1})(300K)}$$

$$n = \frac{28.98}{2493} = 0.0116\ mol$$

Step 2: Calculate molar mass (M)

$$M = \text{mass / moles} = 0.560\ g / 0.0116\ mol$$

$$M = 48.3\ g\ mol^{-1}$$

Q.9 In a laboratory experiment, 150 cm^3 of a volatile liquid was completely vaporized at 98°C and a pressure of 1.01×10^5 Pa. The mass of the vapour was found to be 0.495 g. Determine the molecular mass of the liquid ($R = 8.314\ JK^{-1}\ mol^{-1}$).

Ans. Given data:

Volume (V) = 150 $cm^3 = 1.50 \times 10^{-4}$ m^3
Temperature (T) = 98 °C = 371 K
Pressure (P) = 1.01×10^5 Pa
Mass (m) = 0.495 g
Gas constant (R) = 8.314 $J\ K^{-1}\ mol^{-1}$

To find:

Molar Mass of Unknown Gas = ?

Solution:

Step 1: Use the ideal gas law to find moles (n)

$$PV = nRT$$

$$n = \frac{(1.01\times105\ Pa)(1.50\times10^{-4}\ m^3)}{(8.314\ JK^{-1}mol^{-1})(371\ K)}$$

$$n = \frac{15.15}{3083.6}$$

$$n = 0.00491\ mol$$

Step 2: Calculate molar mass (M)

$$M = \text{mass / moles}$$

$$M = 0.495\ g / 0.00491\ mol$$

$$M = 100.8\ g\ mol^{-1}$$

ADDITIONAL SLOs BASED MCQs

1. The temperature at which two or more than two types of crystals exist in equilibrium is called.
   A. Melting Point B. Transition temperature
   C. Eutectic temperature D. Boiling point
2. The solids in which atoms, ions or molecules have random non-repetitive three dimensional arrangements are termed as:
   A. Crystals B. Glasses C. Alloys D. Amalgams
3. The nature of bond in diamond is:
   A. Ionic B. Covalent C. Molecular D. Metallic
4. Crystal lattice is an arrangement of particles in:
   A. One dimension B. Two dimensions C. Three dimensions D. Four dimensions
5. Lattice energy is also called:
   A. Crystal energy B. Ionization energy C. Energy of affinity D. Bond Energy
6. When gaseous ions are allowed to form a crystal, energy.
   A. is evolved B. is absorbed
   C. is sometimes absorbed and sometimes released D. has no effect
7. NaF and MgO have both atomic ratio 1:1 in their crystals such property is:
   A. Polymorphism B. Isomorphism C. Isotropy D. Allotropy
8. Electric current can pass through graphite in one direction but not through other direction of crystal such a property is called:
   A. Allotropy B. Anisotropy C. Isomorphism D. Polymorphism
9. Iron acts as an electrical conductor due to:
   A. Electron cloud B. Free protons C. Free neutrons D. Free ions
10. A crystal of the purple compound, Potassium Permanganate, placed at the bottom of a beaker of water and the beaker left until there is no further change. What will be observed?
    A. A uniformly purple solution.
    B. A colourless liquid with the purple crystal unchanged.
    C. A purple layer below a colourless layer.
    D. A colourless layer below a purple layer.
11. Which of the following method is most suitable for obtaining a pure, dry sample of NaCl from a mixture of NaCl and sand?
    A. Shake the mixture with water. Filter and dry the substances on the filter paper.
    B. Shake the mixture with water. Filter and evaporate the filtrate.
    C. Shake the mixture with water and distill off the sand.
    D. Heat the mixture gently and collect the substances which boil off.
12. What method could be used to obtain copper from mixture of powdered copper and sodium chloride?
    A. Heating the mixture B. Fractional distillation of the mixture
    C. Passing an electric current through the mixture D. Adding excess water to the mixture and filtering
13. A bottle of copper oxide has been contaminated with some sodium chloride. How can the NaCl be removed from the copper oxide?
    A. Place the mixture in a separating funnel B. Heat the mixture and allow it to cool
    C. Add water to the mixture and filter D. Add aqueous $AgNO_3$ to the mixture
14. Lead and zinc can be separated by distillation because they have different.
    A. Boiling point B. Densities C. Mass numbers D. Reactivities

15. An insoluble solid was dropped into a measuring cylinder containing 50 cm^3 of water. What will be the effect on volume of water?
A. 15cm^3 B. 17 cm^3 C. 50 cm^3 D. 65 cm^3

Answer Key with Explanations

Q. No	Option	Explanation
1.	B	At transition temperature, one crystalline form of a substance changes to another. Above and below this temperature, only one form exists. The transition temperature of allotropic forms of an element is always less than its melting point.
2.	B	An amorphous solid is a substance in which atoms, molecules or ions assume a random and non-repetitive three dimensional arrangements e.g. Glass.
3.	B	Diamond is an allotrope of carbon. In diamond carbon atoms are covalently bonded with each other.
4.	C	An array of points representing the arrangement of particles (atoms, ions or molecules) in three dimensional spaces is called crystal lattice.
5.	A	The energy released when one mole of an ionic crystal is formed from the gaseous opposite ions is called lattice energy. e.g. $Na^{+1}_{(g)} + Cl^{-1}_{(g)} \longrightarrow NaCl_{(s)} \quad \Delta H_{Latt} = -787\ kJmol^{-1}$
6.	A	The energy released when one mole of the ionic crystal is formed from the gaseous ions is called lattice energy. e.g. $Na^{+1}_{(g)} + Cl^{-1}_{(g)} \longrightarrow NaCl_{(s)}\ \Delta H_{Latt} = -787\ kJmol^{-1}$
7.	B	The phenomenon in which two different substances exist in the same crystalline form is called isomorphism. e.g. NaF and MgO are isomorphs and having cubic shape.
8.	B	It is because crystal has different arrangements in different directions e.g. graphite exist in the form of layers, so it is conductor in one direction, parallel to layers but insulator across the layers.
9.	A	Iron is a metal. The electrical conductivity of metals is due to the presence of free or mobile electrons. These electrons form electron cloud in the metal lattice.
10.	A	Diffusion is a spontaneous movement of gas or liquid molecules from a region of a higher concentration to a region of lower concentration, until they are equally dispersed. • A deep purple layer below a pale purple layer is formed after about 15 minutes. • A uniform purple solution is formed after about 30 minutes.
11.	B	A mixture of NaCl and sand is mixed with water. NaCl is soluble while sand is insoluble in water. Filter the mixture. The filtrate is NaCl solution. It is evaporated. Water evaporates leaving behind solid NaCl.
12.	D	NaCl is soluble in water while copper is insoluble.
13.	C	When excess water is added in the mixture, NaCl dissolves in water while copper oxide remains insoluble. The solution is filtered. The copper oxide is obtained as residue on filter paper.
14.	A	Distillation is the technique to separate liquids from a mixture on the basis of boiling points. Zinc distilled first as it has low boiling point than lead.
15.	D	Addition of insoluble solid increase the volume of water.

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Write any four properties of gases.

Ans. Properties of Gases:
(i) **Indefinite Volume:** Gases have an indefinite volume and occupy all the available space. The volume of a gas is the volume of the container.
(ii) **Indefinite Shape:** They don't have a definite shape and take the shape of the container just like liquids.
(iii) **Low Densities:** Due to low densities of gases, as compared to those of liquids and solids but gases bubble through liquids and tend to rise up.
(iv) **Diffusion and Effusion:** Gases can diffuse and effuse. This property is negligible in solids but operates (works) in liquids as well.

Q.2 Write any four properties of liquids.

Ans. Properties of Liquids:
(i) **Volume:** Liquids have a fixed volume. The intermolecular forces in liquids are strong enough to maintain a fixed volume.
(ii) **Shape:** Liquids do not have a fixed shape. They always take the shape of the container in which they are placed. The intermolecular forces are present in liquids but they are not so strong that a liquid can have a fixed shape.
(iii) **Evaporation:** Due to constant movement and collisions between the liquid molecules, the high energy molecules leave the surface of liquid and the liquid is changed into its vapours. This process is called evaporation. Liquids evaporate at all temperatures.
(iv) **Diffusion:** A liquid can diffuse into another liquid with which it is miscible. However, the rate of diffusion in liquids is slower than in gases. This is due to less empty spaces between the liquid molecules.

Q.3 Give two statements of Boyle's law.

Ans. Boyle's Law:
Statement: "The volume of a given mass of a gas at constant temperature is inversely proportional to the pressure applied to the gas."

Mathematically: $V \propto \frac{1}{P}$ (at constant temperature and number of moles)

$V = \frac{k}{P}$ Here 'k' is proportionality constant

$PV = k$ (when 'T' and 'n' are constant)

The value of k is different for the different amounts of the same gas.

Another Statement: "The product of pressure and volume of a fixed amount of a gas at constant temperature is a constant quantity."

So, $P_1V_1 = k$ and $P_2V_2 = k$

Hence, $P_1V_1 = P_2V_2$

P_1V_1 are the initial values of pressure and volume while P_2V_2 are the final values of pressure and volume.

Q.4 State Charles's Law and write its mathematical form.

Ans. Charles's Law: "The volume of the given mass of a gas is directly proportional to the absolute temperature at constant pressure."

Mathematically:

$V \propto T$ (at constant pressure and number of moles)

or $V = kT$

or $\frac{V}{T} = k$

If temperature is changed from T_1 to T_2, and volume changes from V_1 to V_2, then

$$\frac{V_1}{T_1} = k \text{ and } \frac{V_2}{T_2} = k$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Another Statement:

"The ratio of volume to temperature remains constant for same amount of gas at same pressure."

Q.5 What is Avogadro's law (of gases)? Give an example.

Ans. Avogadro's Law:

"Equal volumes of all the ideal gases at the same temperature and pressure contains equal number of molecules."

At STP, one mole of all gases have volume 22.414 dm^3 and $N_A = 6.022 \times 10^{23}$ molecules.

Examples:

At STP,

$H_2 = 2g = 1$ mole $= 22.414\ dm^3 = 6.02 \times 10^{23}$ molecules

$O_2 = 32g = 1$ mole $= 22.414\ dm^3 = 6.02 \times 10^{23}$ molecules

Q.6 Derive molecular mass of a gas by general gas equation.

Ans. We can determine the molecular mass as follows:

Derivation:

$$PV = nRT \quad \text{(general gas equation)}$$

Where $$n = \frac{\text{mass of gas}}{\text{molecular mass}} = \frac{m}{M}$$

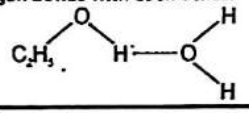
So $$PV = \frac{m}{M}RT$$

$$M = \frac{m}{V \times P}RT$$

So by knowing m, V, P, T for a gas, one can determine its molecular mass.

Q.7 Show hydrogen bonding in alcohol and water.

Ans. Lower alcohols like Ethyl alcohol (C_2H_5OH) has the tendency to form hydrogen bonds so they are soluble in water because both can form Hydrogen bonds with each other.



Q.8 What do you mean by liquid crystal? Write down any two uses of it.

Ans. Liquid Crystal:

"The turbid liquid phase of a solid that exists in between the melting and clearing temperature is called liquid crystal."

Crystal ⟹ Liquid Crystal ⟹ Liquid

Example: Cholesteryl benzoate.

- It is discovered by Frederick Reinitzer in 1888.

Uses of Liquid Crystals:

I. Like solid crystals, liquid crystals can diffract light. When one of the wavelengths of white light is reflected from a liquid crystal, it appears coloured. As the temperature changes, the distances between the layers of the molecules of liquid crystals change. Therefore, the reflected light changes accordingly. Thus liquid crystals can be used as temperature sensors.

II. Liquid crystals are used to find the point of potential failure in electrical circuits. Room thermometers also contain liquid crystals with a suitable temperature range. As the temperature changes, figures show up in different colours.

Q.9 Why ice occupies more volume than liquid water?

Ans. Ice Floats Over the Surface of Water:

When temperature of water is decreased and ice is formed then the molecules become more regular and this regularity extends throughout the whole structure. Empty spaces are created in the structure. That is why, when ice freezes it occupies 9% more space and its density decreases. The result is that ice floats on water.

Q.10 Evaporation takes place at all temperatures. Justify.

Ans. Evaporation:

"The spontaneous change of a liquid into its vapours at all temperatures is called evaporation."

Evaporation Takes Place at All Temperatures:

- Rate of evaporation is directly proportional to temperature. At high temperature, the kinetic energy of the molecules increases, so evaporation also increases.
- At low temperature, the kinetic energy of molecules is less, so rate of evaporation slows down. Thus evaporation continues at all temperatures whether low or high.

Q.11 Why are the vapour pressure of solids far less than those of liquids?

Ans. The magnitude of vapour pressure is inversely proportional to the strength of intermolecular attractive forces. These forces are stronger in solids as compared to the liquids. Hence, vapour pressure of solids is far less than liquids.

Q.12 Define Boiling point and molar heat of vapourization.

Ans. Boiling Point: "The temperature at which the vapour pressure of a liquid becomes equal to the atmospheric/external pressure is called boiling point"

Molar Heat of Vaporization: "The amount of heat absorbed when one mole of a liquid is changed into vapours at its boiling point, is called heat of vaporization." The pressure during the change is kept one atmosphere.

Example: Molar heat of vaporization of $H_2O = 40.7$ kJ/mol.

Q.13 What are ionic solids? Give two examples.

Ans. Ionic Solids:

"The crystalline solids in which the particles forming the crystal are positively and negatively charged ions which are held together by strong electrostatic forces of attraction (ionic bond) are called ionic solids."

Examples: The crystals of NaCl, KBr etc.

◆◆◆◆◆

SELF-ASSESSMENT Chapter # 05

Total Mark: 30

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) London dispersion forces are the only forces present among:
A. molecules of water in liquid state
B. atoms of helium in gaseous state at high temperature
C. molecules of solid iodine
D. molecules of hydrogen chloride gas

(ii) Identify equation which is used to determine the molar mass of a gas.
A. $PV = nRT$ B. $nV = RT$ C. $pV = KT$ D. $E = mc^2$

(iii) When water freezes at 0 °C, its density decreases due to:
A. cubic structure of ice B. empty spaces present in the structure of ice
C. decrease in volume D. decrease in viscosity

(iv) Which of following is the correct sequence of increasing ΔH_v values of substances mentioned?
A. $H_2O > NH_3 > F_2$ B. $F_2 > NH_3 > H_2O$ C. $NH_3 > H_2O > F_2$ D. $H_2O > F_2 > NH_3$

(v) Which type of intermolecular force is present in all types of molecule regardless of their polarity?
A. Dipole-dipole forces B. Hydrogen bonds C. London dispersion forces D. Ion-dipole forces

(vi) Which of the following is a crystalline solid?
A. Glass B. Plastic C. Quartz D. Wax

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) Why food cooking is difficult in the areas with high altitudes?
(ii) What is meant by habit of a crystal?
(iii) Discuss how hydrogen bonding is responsible for the relatively high surface tension of water.
(iv) Differentiate between crystalline and amorphous solids.
(v) One feels sense of cooling under the fan after bath.
(vi) Define vapour pressure and surface tension.
(vii) How does the heat of vaporization affect particle movement?
(viii) What are liquid crystals? Give two of their uses.

Q.3 Extensive Questions. (2 × 4 = 8)

(a) What are London dispersion forces? Give examples, and discuss the factors affecting these forces.
(b) A sample of an unknown gas has a mass of 0.560 g. It occupies a volume of 2.87×10^{-4} m^3 at a temperature of 300 K and a pressure of 1.01×10^5 Pa. Calculate the molar mass of the gas. (Gas constant, $R = 8.31 JK^{-1}mol^{-1}$)

Chapter 06 CHEMICAL ENERGETICS

Student Learning Outcomes

After studying this chapter, students will be able to:

- Describe those chemical reactions are accompanied by enthalpy changes and these changes can be exothermic (ΔH° is negative or endothermic ΔH° is positive). **(Understanding)**
- Interpret a reaction pathway diagram, in terms of the reaction and of the activation energy. **(Understanding)**
- Define terms such as standard conditions, enthalpy change, reaction, formation, combustion and neutralization. **(Understanding)**
- Explain that energy transfer occurs during chemical reactions because of the breaking and making of bonds. **(Understanding)**
- Calculate the bond energies for the enthalpy change of reaction ΔH°. **(Understanding)**
- Describe that some bond energies are exact and some bond energies are approximate. **(Understanding)**
- Calculate enthalpy changes from approximate experimental results, including the use of the relationships $q = mc\Delta T$ and $\Delta H^\circ = -mc\Delta T / n$. **(Application)**
- Define terms such as enthalpy change of atomization, lattice energy, ΔH°, first electron affinity, EA. **(Knowledge)**
- Use terms such as enthalpy change of atomization, lattice energy, first electron affinity. **(Application)**
- Construct Born Haber's Cycles for ionic solids. **(Application)**
- Perform calculations involving Born- Haber cycles. **(Understanding)**
- Explain the effect of ionic charge and ionic radius on the numerical magnitude of lattice energy. **(Understanding)**
- Apply enthalpy change with reference to hydration and solution. **(Application)**
- Construct an energy cycle involving enthalpy change of solutions and enthalpy change of hydration. **(Application)**
- Perform calculations involving energy cycles. **(Application)**
- Explain the effect of ionic charge and ionic radius on the numerical magnitude of an enthalpy change of hydration. **(Understanding)**
- Define the term entropy, S, as the number of possible arrangements of the particles and their energy in a given system. **(Understanding)**
- Explain the sign of entropy changes that occur during a change in state, temperature change and a reaction in which there is a change in the number of gaseous molecules. **(Understanding)**
- Calculate the entropy change for a reaction, ΔS°, given the standard entropies, S, of the reactants and the products. **(Application)**
- Explain the concept of heat as a form of energy. **(Understanding)**
- Explain the relationship between temperature and kinetic energy of particles. **(Understanding)**
- State that total energy is conserved in chemical reactions. **(Understanding)**

- Explain the concept of standard conditions and standard states in measuring energy changes. **(Understanding)**
- Explain Hess's Law. **(Understanding)**
- Apply Hess's Law to calculate enthalpy changes in a reaction carried out in multiple steps. **(Application)**
- Explain the relationship between bond formation energy and bond breaking energy. **(Understanding)**
- Explain Gibbs free energy. **(Understanding)**
- Apply the concept of Gibbs free energy to solve problems. **(Application)**
- Outline how enthalpy change relates to the calorie concept of the food we eat. **(Application)**
- Explain factors affecting the electron affinities of elements. **(Understanding)**

Thermochemistry

Thermochemistry is the study of the quantity of heat energy absorbed or evolved during physical or chemical changes. That is why it is also called *energetics* and is largely based on the first law of thermodynamics. Hess's law, a special case of 1st law of *thermodynamics*, is a remarkable tool in a chemist's hand and finds numerous applications in analytical chemistry. Moreover, thermodynamics allows us to predict whether a particular reaction can occur under specified conditions i.e., it discusses the spontaneity of a reaction.

ENTHALPY CHANGE

The energy possessed by a substance due to its structure (types of bonds) and physical state is called its heat content or enthalpy denoted by **H**. Every substance possesses a characteristic amount of enthalpy. This is the reason that the total enthalpy of products (H_p) is never equal to that of reactants (H_R). Hence during a chemical reaction, when reactants are converted into products, there occurs a change in enthalpy denoted as ΔH. In other words, enthalpy change is the net energy which is either evolved or absorbed in the form of heat.

Rack Your Mind!
1. What is a thermochemical equation?

Mathematically,

$$\Delta H = (\text{Heat content of products, } H_p) - (\text{Heat content of reactants, } H_R)$$

Exothermic Process Vs Endothermic Process

There are two cases:

I. $H_P < H_R$: such reactions involve a lowering of enthalpy and always take place with the evolution of heat which is equal to $H_p - H_R$ and ΔH carries negative sign.

"A chemical reaction or a physical change in which heat is evolved from the system to surroundings is called exothermic process."

For example, combustion of carbon in oxygen is an exothermic reaction.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H = -393.7 \text{ kJ mol}^{-1}$$

Rack Your Mind!
2. Which of the following is an endothermic reaction?
(A) $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)}$
(B) $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$
(C) $NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(\ell)}$
(D) $C_2H_5OH_{(aq)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(\ell)}$

II. $H_P > H_R$: such reactions involve an increase in enthalpy and always take place by the absorption of heat which is equal to $H_p - H_R$ and ΔH carries positive sign.

"A chemical reaction or a physical change in which heat is absorbed by the system from surroundings is known as endothermic process."

For example, The dissolution of ammonium chloride ($NH_4C\ell$) in water is an endothermic process.

$$NH_4C\ell_{(s)} \xrightarrow{H_2O_{(\ell)}} NH_4^+{}_{(aq)} + C\ell^-_{(aq)} \quad \Delta H = +16.2 \text{ kJ mol}^{-1}$$

Interesting Information!
The dissolution of ammonium chloride ($NH_4C\ell$) in water is an endothermic reaction. This reaction is used in cold packs (or ice packs) to treat internal injuries. When the pack is kneaded, water and $NH_4C\ell$ crystals mix and energy is absorbed from the surroundings, producing a cooling sensation.



Rack Your Mind!
3. Why in exothermic reactions heat is released from the system?

Following Figure shows the enthalpy diagram of exothermic and endothermic reactions.

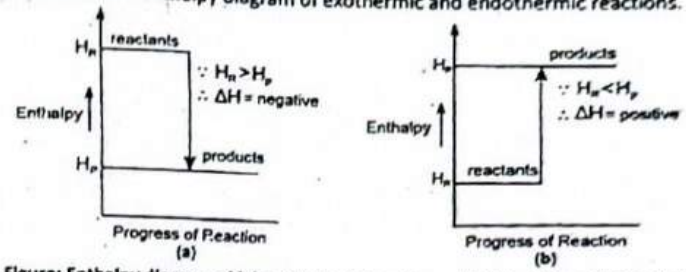
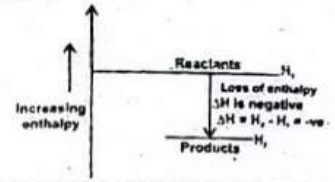
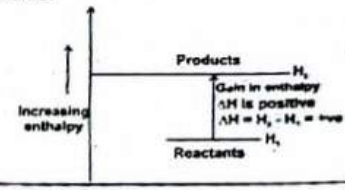


Figure: Enthalpy diagram of (a) Exothermic Reaction and (b) Endothermic Reaction

Exothermic reaction	Endothermic reaction
1. The reaction in which heat is evolved from the system is called exothermic reaction.	1. The reaction in which heat is absorbed by the system is called endothermic reaction.
2. The heat contents of product is less than that of reactants. 	2. The heat contents of products is more than that of reactants. 
3. ΔH is negative.	3. ΔH is positive.
4. The Number of bonds formed is greater than the bonds breakage during a reaction.	4. The number of bond breakage is greater than the bonds formation during a reaction.
5. The temperature of the system rises and eventually heat flows from system to surroundings.	5. The temperature of the system falls and eventually heat flows from surroundings to system.
6. The most spontaneous reactions are exothermic.	6. The most non-spontaneous reactions are endothermic.
Example: $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H = -393.7 \text{ kJ mol}^{-1}$	Examples: $N_{2(g)} + O_{2(g)} \longrightarrow NO_{(g)} \quad \Delta H = 180 \text{ kJ mol}^{-1}$

ENERGY PROFILE DIAGRAM

Energy of Activation

All chemical reactions involve the breaking of bonds in the reactant molecules before the formation of new bonds. This can be achieved only if the reactant molecules collide with sufficient amount of energy to overcome an energy barrier. This minimum amount of energy required by the reactant molecules just to cross that energy barrier is called **energy of activation** denoted by E_a.

Rack Your Mind!
4. In a reaction pathway diagram, the peak represents to:
A) Reactants B) Products
C) Activation energy D) Heat released

The energy profile diagram of exothermic and endothermic reactions are given in Figure.

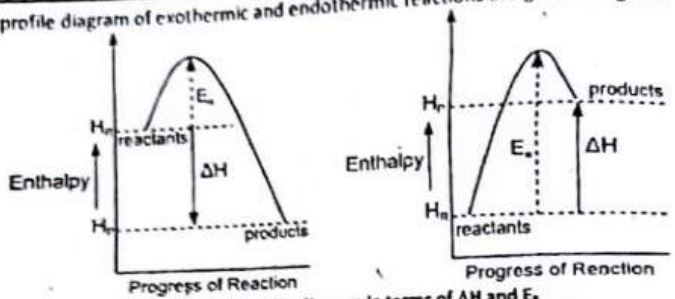


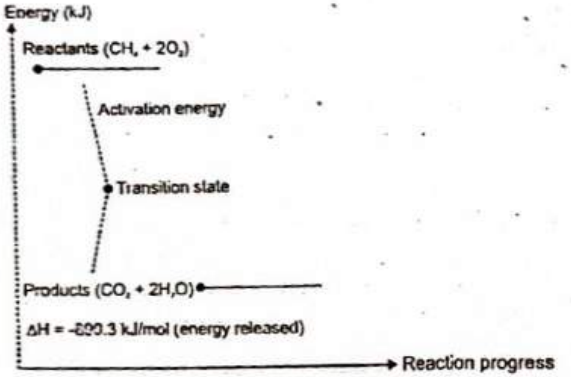
Figure: Energy profile diagram in terms of ΔH and E_a

QUICK CHECK 6.1

Draw the energy profile diagrams for the following reactions:

i. $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$ $\quad \Delta H = -890.3 \text{ kJ mol}^{-1}$

Ans.

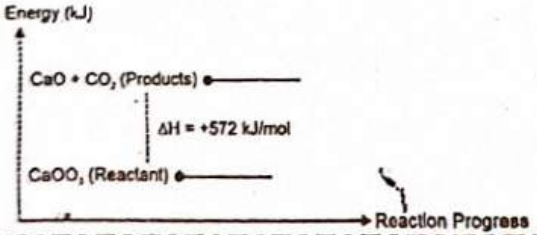


1. Reactants start at higher energy than products (exothermic)
2. Energy barrier represents activation energy
3. Vertical drop shows the large heat release (−890.3 kJ/mol)
4. Liquid water product is at lower energy than gaseous reactants

The downward slope shows this is highly exothermic, typical of combustion reactions. The exact activation energy isn't specified here, but the diagram shows there must be some energy input to initiate the reaction.

ii. $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$ $\quad \Delta H = +572 \text{ kJ mol}^{-1}$

Ans.



1. Reactants ($CaCO_3$) start at a lower energy level than products ($CaO + CO_2$).
2. **Energy absorbed:** The reaction requires +572 kJ/mol (endothermic), shown as an upward arrow.
3. **Activation energy (E_a):** Not specified, but implied by the curve's peak (not drawn here for simplicity).
   - Endothermic reactions always show products at a higher energy level than reactants.
   - The +ΔH value confirms energy is absorbed (e.g., thermal decomposition of limestone).

STANDARD ENTHALPY CHANGES

The enthalpy of a substance not only depends upon its physical state but also on the pressure and temperature. Hence, we must specify these conditions while writing an equation. Therefore, when making accurate comparisons of enthalpy changes for various reactions, ΔH is determined under certain standard conditions, which are summarized below:

a) **Temperature:** 25°C or 298 K
b) **Pressure:** 1 atm or 101 kPa

Did You Know?

The standard state of an element is its most stable form at 298 K and 1 atm pressure. For example, the standard state of C is graphite not diamond. By definition, the **standard enthalpy change** of formation of any element in its standard state is zero.

Rack Your Mind!

5. What is meant by atomization energy?

Enthalpy Change of Reaction (ΔH_r)

The standard enthalpy of a reaction is the enthalpy change involved when stoichiometric amounts of reactants in their standard states react together completely to form products under standard conditions.

Example: Consider the reaction between hydrogen and oxygen gases to form 1 mole of water:

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)} \qquad \Delta H_r = -286 \text{ kJ mol}^{-1}$$

Enthalpy Change of Combustion (ΔH_c°)

The standard enthalpy change of combustion of a substance is the enthalpy change involved when one mole of the substance is completely burnt in excess of oxygen, under standard conditions.
It is always exothermic.

Example: Standard enthalpy of combustion ΔH° C of ethanol is −1368 kJ mol^{-1}.

$$C_2H_5OH_{(\ell)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(\ell)} \qquad \Delta H_c^\circ = -1368 \text{ kJ mol}^{-1}$$

Enthalpy change of combustion is useful in calculating calorie content of foods and fuels.

Enthalpy Change of Formation (ΔH_f°)

Standard enthalpy change of formation of a compound is the enthalpy change involved when one mole of the compound is formed from its elements under standard conditions.
It can be exothermic or endothermic.

Example: ΔH_f° for methane is given below.

$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)} \qquad \Delta H_f^\circ = -74.8 \text{ kJ mol}^{-1}$$

Enthalpy Change of Atomization (ΔH_{at}°)

"The standard enthalpy change of atomization of an element is the enthalpy change involved when one mole of gaseous atoms is formed from the element, under standard conditions."

Example:

$$H_{2(g)} \longrightarrow 2H_{(g)} \qquad E_{H-H} = +436 \text{ kJ mol}^{-1}$$
$$1/2H_{2(g)} \longrightarrow H_{(g)} \qquad \Delta H_{at}^\circ = +218 \text{ kJ mol}^{-1}$$

Enthalpy Change of Neutralization (ΔH_n°)

The standard enthalpy change of neutralization is the enthalpy change involved when one mole of water is formed by the reaction of an acid with an alkali under standard conditions. It is always exothermic.

Example: The enthalpy of neutralization of NaOH by HCl is −57.1 kJ mol^{-1}.
When these solutions are mixed together during the process of neutralization, the only change that occurs is the formation of water molecules leaving Na^+ and Cl^- as free ions in solution. Thus, the enthalpy of neutralization is merely the heat of formation of one mole of liquid water from its ionic components and the actual neutralization reaction is:

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(\ell)} \qquad \Delta H^\circ = -57.1 \text{ kJ mol}^{-1}$$

For all strong acid-base reactions, ΔH° is always near −57.1 kJ mol^{-1}.

Electron Affinity (ΔH°_{ea})

The first electron affinity is the enthalpy change involved when 1 mole of electrons is added to 1 mole of gaseous atoms to form 1 mole of gaseous uni-negative ions under standard conditions.
Example: Electron affinity of chlorine atom.

$$Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)} \qquad \Delta H = -348.8 \text{ kJ mol}^{-1}$$

Since, energy is released, so first electron affinity carries negative sign.
Note: A detailed discussion of electron affinity is given in chapter 1.

Rack Your Mind!

6. Why is it necessary to mention the physical states of reactants and products in a thermo chemical reaction? Apply Hess's law to justify your answer.

QUICK CHECK 6.2

a) Write equations, including state symbols, that represent the enthalpy change of atomization of:
(i) Oxygen (ii) Barium (iii) Bromine

Ans. (i) Oxygen (O_2)

$$\frac{1}{2}O_{2(g)} \longrightarrow O_{(g)} \quad \Delta H = +249 \text{kJ/mol}$$

(ii) Barium (Ba)

$$Ba_{(s)} \longrightarrow Ba_{(g)} \quad \Delta H_a = +180 \text{kJ/mol}$$

(iii) Bromine (Br_2)

$$\frac{1}{2}Br_{2(\ell)} \longrightarrow Br_{(g)} \quad \Delta H_a = +112 \text{kJ/mol}$$

b) Classify the enthalpy change in each of the following reactions:

i) $C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)}$

Ans. Enthalpy Change of Formation (ΔH°_f)

ii) $HCl_{(g)} + NH_{3(g)} \longrightarrow NH_4Cl_{(s)}$

Ans. Enthalpy Change of Combustion (ΔH°_c)

iii) $H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O_{(\ell)}$

Ans. Enthalpy Change of Reaction (ΔH_r)

BOND ENERGY (BOND DISSOCIATION ENERGY) AND ENTHALPY CHANGES

Chemical reactions involve the breaking and making of chemical bonds. When a bond is formed between two atoms, energy is released. The same amount of energy is absorbed when the bond is broken to form neutral atoms; we call this, bond dissociation energy.

Bond Energy

It is defined as, "The average amount of energy required to break (dissociate) one mole of a particular bond in a substance."
It may be denoted as E. If we are determining bond energy of a particular bond in a particular substance, we call this exact bond energy.

This is to be noted that bonds between the same pair of atoms usually have different bond energy (B.E.) values, in all of their compounds. Actually, bond energy is affected by other atoms in a molecule. For example, C–C bonds usually have bond energy values of approximately 350 to 380 kJ/mol.

- In ethane: $[H_3C-CH_3]$; $E_{C-C} = 376$ kJ mol^{-1}
- In propane: $[H_3C-CH_2-CH_3]$; $E_{C-C} = 356$ kJ mol^{-1}
- In butane: $[H_3C-CH_2-CH_2-CH_3]$; $E_{C-C} = 352$ kJ mol^{-1}

In these examples, E_{C-C} for ethane is exact bond energy. Similarly for propane and butane, E_{C-C} are exact bond energies. When we take average of all E_{C-C} in different molecules, we obtain average C–C bond energy. Practically, average bond energy is used instead of exact bond energies. Average bond energies of some bonds are given in Table.

Rack Your Mind!

7. Energy is absorbed when:
A) Bonds are formed
B) Bonds are broken
C) Reaction is exothermic
D) Products form

Table: Average Bond Energies of Some Important Bonds (kJ mol^{-1})

	H–	C–	C=	C≡	N–	N=	N≡	O–	O=	F–	Cl–	Br–	I–
H	436	413			391			463					
C	413	348	615	812	292	615	891	351	728				
N	391	292	615	891	161	418	945	222	607				
O	463	351	728		222	607		139	498				
S	339	259	477					347		327	251	213	
F	563	441			270			185		159	255		
Cl	432	328			200			203			243	218	209
Br	366	276										192	180
I	299	240						201					151

ENTHALPY CHANGE OF REACTION (ΔH_r) AND CHEMICAL BONDS

A chemical reaction is defined as a process during which old bonds are broken and new bonds are formed. Therefore, the enthalpy change (ΔH_r) in a chemical reaction actually comes from the breaking and forming of chemical bonds.
A chemical bond represents a form of energy known as chemical energy (which, like the others, is interconvertible into all forms of energy). Bond breaking absorbs energy ($\Delta H = +ve$) while bond formation releases it ($\Delta H = -ve$) and their difference will decide the overall sign of ΔH. That is whether a reaction is exothermic or endothermic is determined by the net change.
Overall reaction is exothermic if the energy released in making of new bonds is greater than that absorbed in bond breaking. The reverse is true for an endothermic reaction.
Example:
Formation of Water:
In the formation of water, energy is needed to break the H–H bonds (of hydrogen molecules) and the O=O bonds (of oxygen molecules) while energy is released in the making of the H–O bonds (of water). However, the net reaction is exothermic because more energy is released in forming the H–O bonds than is absorbed in breaking the H–H and O=O bonds (Figure 6.5). Thus,

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)} \qquad \Delta H_r = -ve$$

Sample Problem 6.1

With the help of the following bond energy data; calculate the enthalpy change of the following reaction:

$$E_{H-H} = 436 \text{ kJ mol}^{-1}; E_{O=O} = 495 \text{ kJ mol}^{-1} \text{ and } E_{H-O} = 463 \text{ kJ mol}^{-1}$$

$$H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O_{(g)}$$

Solution:

$$\underbrace{H-H+1/2\,O=O}_{436+1/2(495)}$$ (bond breaking energy)

$$\overset{H}{\underset{H}{O}}$$ $2\times(463)$ (bond forming energy)

$$\because \Delta H_f^\circ = \sum E_R - \sum E_P$$
$$= [E_{H-H} + E_{O=O}] - [2E_{H-O}]$$
$$= [436 + 247.5] - [2(463)]$$
$$\Delta H_f^\circ = -242.5 \text{ kJ mol}$$

MEASUREMENT OF ENTHALPY CHANGE OF A REACTION

The amount of heat evolved or absorbed during a physical or chemical change can be measured by an instrument called calorimeter, which generally measures the change in temperature during the process. At its simplest, a calorimeter consists of an insulated vessel, a stirrer and a thermometer. There are various types of calorimeters but here we will describe only "Glass Calorimeter".

Rack Your Mind!

8. If $q = m\,c\,\Delta T$, what does 'c' represent?
A) Concentration
B) Specific heat capacity
C) Constant
D) Speed

Calorimetry relies on the fact that it takes 4.18 J of energy to increase temperature of 1 g of the water by 1°C. The amount of heat energy required to raise the temperature of substance of mass 1 kg through 1 K (or 1°C) is known as specific heat capacity, c, of the liquid. So the specific heat capacity of water is 4.18 $Jg^{-1}\,K^{-1}$ or $(Jg^{-1}\,°C^{-1})$.

The energy is transferred as heat and is shown by relationship

$$q = c \times m \times \Delta T$$

Where,

q = heat transferred in Joules
m = mass of water/solution in grams
c = specific heat of water = 4.184 J/g °C

ΔT is the temperature change in °C.

Here,

$(\Delta T = T_f - T_i)$

➲ Glass Calorimeter

A glass calorimeter is suitable for measuring heat-flow for reactions in solutions.

Construction:

It consists of a beaker, a stirrer, a thermometer and a loose-fitting lid to keep the contents at atmospheric pressure as shown in Figure 6.3. The outside walls of the calorimeter (beaker) are insulated using cotton wool to minimize the exchange of heat with the surrounding air.

Process:

The reaction is carried out inside the beaker and the heat evolved or absorbed is measured by the temperature change. Since the pressure inside the calorimeter is constant, the temperature measurement makes it possible to calculate the enthalpy change ΔH during the reaction.

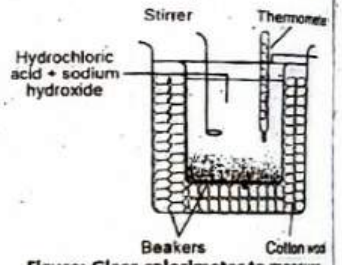


Figure: Glass calorimeter to measure enthalpy change of reactions

Calculation of ΔH:

ΔH is calculated as follows:

As all the heat evolved during the reaction remains within the calorimeter and absorbed by water, so

i) $q = m_{water} \times c_{water} \times \Delta T$

ii) Convert into kJ by dividing with 1000.

iii) Calculate ΔH for the reaction using relation:

The solutions we are using here are so dilute that almost all of their mass consists of water, therefore, we can simply use specific heat capacity of water. Such a calorimeter could be used to measure the heat of neutralization (ΔH_n°).

Limitation of glass calorimeter it cannot be used for reactions involving gases which would escape from the vessel, nor it would be appropriate for reactions in which the products reach high temperatures.

Sample Problem 6.2

Neutralization of 100 cm^3 of 0.5 mol dm^{-3} NaOH at 25°C with 100 cm^3 of 0.5 mol dm^{-3} HCl at 25°C raised the temperature of the reaction mixture to 28.5°C. Find the enthalpy of neutralization. Specific heat of water = 4.2 $Jg^{-1}\,K^{-1}$.

Solution:

Density of H_2O is around 1 g cm^{-3}, so total volume of solution which is 200 $cm^3 \approx 200$ g Rise in temperature,

$$\Delta T = 28.5 - 25.0 = 3.5°C = 3.5 \text{ K}$$

∴ Amount of total heat evolved, $q = m \times c \times \Delta T$
$= 200 \times 4.2 \times 3.5 = 2940 \text{ J}$
$= 2.94 \text{ kJ}$

➲ Calculation of n (No. of moles of H_2O formed)

Using $\text{mole} = \text{Concentration (mol/dm}^3) \times \text{Volume(dm}^3)$

$$n_{(HCl)} = n_{(NaOH)} = 0.5 \times 100/1000 = 0.05 \text{ mol}$$

Using equation, Number of moles of water formed, $n_{(H_2O)} = 0.05$ mol

Heat evolved in the formation of 0.05 mole of water, $q = -2.94$ kJ

$$\Delta H_n^\circ = q/n = -2.94 \text{ kJ}/0.05 \text{ mol}$$

So, Enthalpy of neutralization, $\Delta H_n^\circ = -58.8 \text{ kJ mol}^{-1}$

QUICK CHECK 6.3

Calculate ΔH_n° of the reaction of 50 cm^3 of HNO_3 with 50 cm^3 of 1.5 mol/dm^3 of NaOH. The change in temperature is 4°C.

Given Data:

- **Volume of HNO_3:** 50 cm^3 (0.050 dm^3)
- **Volume of NaOH:** 50 cm^3 (0.050 dm^3)
- **Concentration of NaOH:** 1.5 mol/dm^3
- **Temperature change (ΔT):** +4°C
- **Assumptions:**
  - HNO_3 is a strong acid (fully dissociates).
  - NaOH is a strong base (fully dissociates).
  - The density of the solution = 1 g/cm^3 (so total mass = 100 g).
  - Specific heat capacity (c) of the solution = 4.18 J/g°C (same as water).

Step 1: Determine Limiting Reagent (Moles of H^+ and OH^-)

- Both HNO_3 and NaOH are **monoprotic**, so moles of H^+ = moles of OH^-.
- **Moles of NaOH (and thus OH^-):**

$$n\text{NaOH} = C \times V = 1.5 \text{ mol/dm}^3 \times 0.050 \text{ dm}^3 = 0.075 \text{ moles}$$

Step 2: Calculate Heat Released (q)

$$q = m \times c \times \Delta T$$

- **Total mass (m):** 50 cm^3 + 50 cm^3 = 100 g
- **c:** 4.18 J/g°C
- **ΔT:** 4°C

$Q = 100\ g \times 4.18\ J/g\,°C \times 4\ °C = 1672\ J = 1.672\ kJ$

Step 3: Calculate ΔH_n° (per mole of H_2O formed)

- Moles of H_2O formed = moles of OH^- reacted = 0.075 mol
- ΔH_n° is heat released per mole:

$$\Delta H_n^\circ = \frac{-q}{n} = \frac{-1.672\ kJ}{0.075\ mol} = 22.29\ kJ/mol$$

ENTHALPY CHANGE AND CALORIE CONTENT OF FOOD

We will discuss foods as fuels. When food is digested, the chemical energy stored in the food (also called calorie content) is released as heat energy. In other words, digestion of food releases same amount of energy as it is burned outside the body. So, the overall enthalpy of combustion is the same as the heat of combustion, which can be determined in a calorimeter (typically in a bomb calorimeter).

Calorie Content: The calorie content of food is a measure of the energy 'released' when the food is completely consumed in the body.

Unit: This energy is typically expressed in units of kilocalories (k cal) or joules (J).

⊃ Relation between Enthalpy Change and Calorie Content

The enthalpy of combustion of a food (ΔH_c) is the calorie content of that food when it is translated or converted into kilocalories per gram.

Look at the energy provided from glucose.

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(\ell)} \qquad \Delta H^\circ = -2803\ kJ\ mol^{-1}$$

The calorie content of glucose can be calculated as follows: First, we find ΔH per gram of glucose. Molar mass of glucose is 180 g mol^{-1}. Above equation shows that;

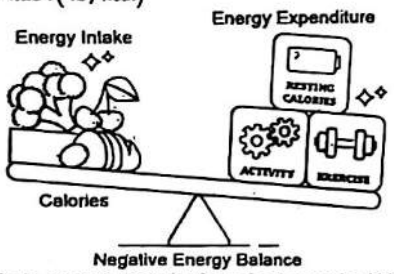
mol(180.0 g) of glucose burns to produce energy = 2803 kJ

$$1.0\ g\ of\ Glucose = \frac{2803\ kJ/g}{180\ g/mol} = 15.57\ kJ/g$$

Using the relation,

$$\Delta H(kJ/g) = -4.184 \times \text{calorie content}$$

$$\text{Calorie content} = -\frac{\Delta H(kJ/g)}{4.184(kJ/kcal)} = -\frac{15.57\ kJ/g}{4.184(kJ/kcal)} = -3.72\ kcal/g$$



Remember, the calorie content we take from food must be balanced by working, exercising and doing positive activities. Otherwise, our bodies will have imbalanced growth and maintenance

HESS'S LAW OF HEAT SUMMATION

Q. State and explain Hess' law. Give its two applications.

First law of thermodynamics is actually a manifestation of law of conservation of energy, which states, **"Energy can neither be created nor destroyed, but can be converted from one form to another."**

Germain Henri Hess applied the law of conservation of energy to enthalpy changes. There are many reactions, for which ΔH cannot be measured directly by calorimetric method. For example, tetrachloromethane CCl_4 cannot be prepared directly by combining carbon and chlorine. Hess's Law helps us calculating the enthalpy changes for such reactions or processes.

Statement:

"The total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same."

Explanation:

Hess's law can be illustrated by drawing enthalpy cycles, often called energy cycles or Hess cycles. Let A be converted to 'B' directly in a single step, which is the direct route; or in a series of two or three steps designated as indirect route 1 and indirect route 2 respectively as shown in Figure. The products formed in these routes (M, N and X, Y, Z) are called reaction intermediates.

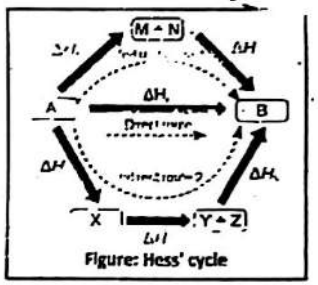


Figure: Hess' cycle

Then according to Hess' law,

For the indirect route 1, we can write: $\Delta H_i = \Delta H_1 + \Delta H_2$

For the indirect route 2, we can write: $\Delta H_i = \Delta H_3 + \Delta H_4 + \Delta H_5$

Below are few examples of it.

(i) Calculating Enthalpy of Formation (ΔH_f°) using Enthalpy of Combustion (ΔH_c°)

Sample Problem 6.3

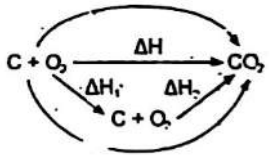
Calculate the enthalpy change of formation of CO using Hess cycle with the help of following combustion data.

Solution:

$$C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -393.5\ kJ\ mol^{-1}$$

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_2 = -283\ kJ\ mol^{-1}$$

$$C_{(graphite)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta H_1 = ?$$



Solution: Applying Hess's law, we can write

$$\Delta H = \Delta H_1 + \Delta H_2$$

$$\Delta H_1 = -393.5 - (-283)$$

$$= -110.5\ kJ\ mol^{-1}$$

(ii) Calculating Enthalpy Change of Reaction (ΔH°) using Enthalpies of formation (ΔH_f°)

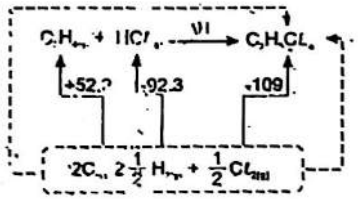
Sample Problem 6.4

Calculate the enthalpy change of reaction of

$$C_2H_4 + HCl \longrightarrow C_2H_5Cl + \Delta H_r$$

Using Hess cycle with the help of following combustion data.

Solution:



ΔH_f° of C_2H_4 = +52.2 kJ mol^{-1}

ΔH_f° of HCl = -92.3 kJ mol^{-1}

ΔH_f° of C_2H_5Cl = -109 kJ mol^{-1}

$$= -109 - [+52.2 + (-92.3)]$$

$$= -68.9\ kJ\ mol^{-1}$$

QUICK CHECK 6.4

Calculate the standard enthalpy change for the formation of methane (ΔH_f°):

$$6C_{(s)} + 3H_{2(g)} \longrightarrow C_6H_{6(\ell)} \qquad \Delta H_f^\circ = ?$$

The standard enthalpies of combustion of $C_{(s)}$, $H_{2(g)}$ are $-394\,kJmol^{-1}$, $-286\,kJmol^{-1}$ and enthalpy of formation of $C_6H_{6(\ell)}$ $-3267\,kJmol^{-1}$ respectively.

Given Data:

Combustion reactions and enthalpies:

- $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_c^\circ = -394$ kJ mol^{-1} (per mole of C)
- $H_{2(g)} + 1/2\,O_{2(g)} \rightarrow H_2O_{(\ell)}$ $\Delta H_c^\circ = -286$ kJ mol^{-1} (per mole of H_2)
- $C_6H_{6(\ell)} + 15/2\,O_{2(g)} \rightarrow 6CO_{2(g)} + 3H_2O_{(\ell)}$ $\Delta H_c^\circ = -3267$ kJ mol^{-1} (per mole of C_6H_6)

Target formation reaction:

$$6C_{(s)} + 3H_{2(g)} \rightarrow C_6H_{6(\ell)} \qquad \Delta H_f^\circ = ?$$

Step 1: Apply Hess's Law

The enthalpy of formation (ΔH_f°) of benzene can be calculated using the combustion enthalpies of the reactants and products:

$$\Delta H_f^\circ = \sum \Delta H_c^\circ(\text{reactants}) - \sum \Delta H_c^\circ(\text{products})$$

Here:

- **Reactants:** $6C_{(s)} + 3H_{2(g)}$
- **Product:** $C_6H_{6(\ell)}$

So:

$$\Delta H_f^\circ = \left[6 \times \Delta H_c^\circ(C) + 3 \times \Delta H_c^\circ(H_2)\right] - \left[1 \times \Delta H_c^\circ(C_6H_6)\right]$$

Step 2: Plug in the Values

$\Delta H_f^\circ = [6(-394) + 3(-286)] - [-3267]$

$\Delta H_f^\circ = [-2364 - 858] + 3267$

$\Delta H_f^\circ = -3222 + 3267$

$\Delta H_f^\circ = +45\,kJmol^{-1}$

iii) Calculating Enthalpy Change of Formation of a substance (ΔH_f°) using Enthalpy of Combustion and Enthalpies of Formation of other substances

Sample Problem 6.5

Propane ($C_3H_{8(g)}$) burns in oxygen according to the equation:

$$C_3H_{8(g)} + 5O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(\ell)}$$

When 14.64 g of propane is burned in an excess of oxygen in a calorimeter at 25°C and 1 atm pressure, 678.6 kJ of heat is evolved. Calculate the standard enthalpy of formation of propane. The standard enthalpies of formation of $CO_{2(g)}$ and $H_2O_{(\ell)}$ are -393.51 kJ mol^{-1} and -241.82 kJ mol^{-1} respectively.

Solution:

The first step is to find the enthalpy change when one mole of propane is burned.

Molar mass of propane, $C_3H_8 = 3(12.011) + 8(1.0079) = 36.033 + 8.0632 = 44.096$

No. of moles of propane $= 14.64 / 44.096 = 0.3320$ mol

So, 0.3320 mol propane evolves heat $= 678.6$ kJ

1.0 mol propane evolves heat $= 678.6 / 0.3320$ kJ mol^{-1} $= -2044$ kJ mol^{-1}

According to Hess's law:

$$\Delta H_r = \left[3 \times \Delta H_f^\circ(CO_2) + 4 \times \Delta H_f^\circ(H_2O)\right] - \left[1 \times \Delta H_c^\circ(C_3H_8) + 5 \times \Delta H_c^\circ(O_2)\right] - 2044\,kJ$$

$$= \left[3 \times (-393.51) + 4 \times (-241.82)\right] - \left[1 \times \Delta H_f^\circ(C_3H_8) + 5 \times (0)\right]$$

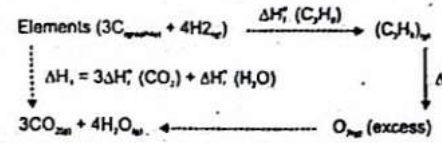
Taking the heat of combustion of $O_{2(g)}$ to be zero and solving this equation for $\Delta H_f^\circ(C_3H_8)$ gives,

$$\Delta H_f^\circ(C_3H_8) = -104\,kJ\,mol^{-1}$$

QUICK CHECK 6.5

Draw enthalpy cycle of sample problem 6.5 according to Hess's law to validate above calculation.

Solution:



1. **Path 1 (Formation Route):**
   - Elements → $C_3H_{8(g)}$ via $\Delta H_f^\circ(C_3H_8$ (unknown).
2. **Path 2 (Combustion Route):**
   - Elements combust to form $3CO_2 + 4H_2O$ directly.
   - $\Delta H_1 = 3(-393.51) + 4(-241.82) = -2147.81$ kJ/mol.
3. **Hess's Law Validation:**

$\Delta H_f^\circ(C_3H_8) + \Delta H_{comb}^\circ = \Delta H_1$

$\Delta H_f^\circ(C_3H_8) + (-2044) = -2147.81$

$\Delta H_f^\circ(C_3H_8) = -2047.81 + 2044 = -103.81$ kJ / mol

iv) Calculating Enthalpy Change of Reactions (ΔH_r) using Bond Energies

A special case of Hess's law involves the use of bond energies to estimate heats of reaction for gas-phase reactions.

First Step:

In the first step, the bonds in all the reactant molecules are broken to give free atoms in the gas phase. The enthalpy change for this step can be calculated by adding the bond enthalpies from Table.

Second Step:

In the second step, the product molecules are formed. The enthalpy change for this step can be estimated from the bond enthalpies of Table, which must now be taken with minus sign because the bonds are being formed instead of broken. In general, the heat of reaction for any gaseous chemical reaction can be calculated from average B.E.'s by use of the following version of Hess's law:

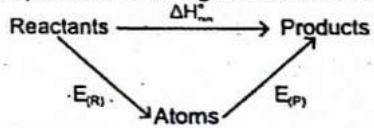


Figure: Hess Cycle; showing the relationship between B.E.'s and $\Delta H_r = \sum nE_R - \sum nE_P$

Sample problem 6.6

In the case of formation of $HC\ell_{(g)}$ from $H_{2(g)}$ and $C\ell_{2(g)}$, use B.E. data from Table 6.1 to estimate ΔH for the reaction:

$$H_{2(g)} + C\ell_{2(g)} \longrightarrow 2HC\ell_{(g)}$$

And finally calculate the heat of formation of $HC\ell$.

We replace this reaction by a hypothetical two-step process. The bonds in all the reactant molecules are first broken, and then the atoms are combined to make the products.

First Step:

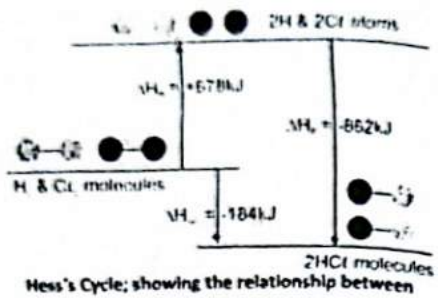
$H_{2(g)} + Cl_{2(g)} \longrightarrow 2H + 2Cl_{(g)}$

$E_{H-H} = 436\ kJ\ mol^{-1}$; $E_{Cl-Cl} = 242\ kJ\ mol^{-1}$

$E_a = \left(1\ mol \times 436 \frac{kJ}{mol}\right) + \left(1\ mol \times 242 \frac{kJ}{mol}\right)$

$= 436\ kJ + 242\ kJ$

$= 678\ kJ$



Hess's Cycle; showing the relationship between B.E.'s and ΔH.

Second Step:

$2H_{(g)} + 2Cl_{(g)} \longrightarrow 2HCl_{(g)}$

$E_{H-Cl} = 431\ kJ\ mol^{-1}$

$E_a = 2\ mol \times 431\ kJ\ mol^{-1} = 862\ kJ$

The standard enthalpy change in the reaction is obtained by the following formula:

$\Delta H^\circ = \sum E_a - \sum E_r$

$\Delta H^\circ = 678 - 862$

$\Delta H^\circ = -184\ kJ$ (for 2 mol of HCl)

$H_{2(g)} + Cl_{2(g)} \xrightarrow{\Delta H^\circ} 2HCl_{(g)}$

$\rightarrow 2H_{(g)} + 2Cl_{(g)} \rightarrow 2HCl_{(g)}$

Enthalpy of formation of $HCl = -184 / 2\ kJ = -92\ kJ\ mol^{-1}$

QUICK CHECK 6.6

a) The reaction for the Haber process is: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

The relevant bond energies are: $E_{N\equiv N} = 945\ kJ\ mol^{-1}$, $E_{N-H} = 436\ kJ\ mol^{-1}$, $E_{N-H} = 391\ kJ\ mol^{-1}$.

Calculate the enthalpy change of the above reaction.

Solution:

To calculate the enthalpy change (ΔH) for the Haber process reaction:

$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

We'll use bond enthalpies (bond energies) to determine the energy changes associated with breaking and forming bonds.

Step 1: Identify Bonds Broken and Formed

Bonds Broken (Endothermic, +ΔH):

- 1 N≡N triple bond (in N_2): $\Delta H = +945\ kJ\ mol^{-1}$
- 3 H-H single bonds (in H_2): $3 \times \Delta H = 3 \times (+436\ kJ\ mol^{-1}) = +1308\ kJ\ mol^{-1}$

Bonds Formed (Exothermic, −ΔH):

- 6 N-H single bonds (in $2NH_3$, since each NH_3 has 3 N-H bonds):

$6 \times \Delta H = 6 \times (-391\ kJ\ mol^{-1}) = -2346\ kJ\ mol^{-1}$

Step 2: Calculate Total Enthalpy Change

$\Delta H_{reaction} = Energy\ absorbed(bonds\ broken) + Energy\ released(bonds\ formed)$

$\Delta H = (+945 + 1308) + (-2346)$

$\Delta H = 2253 - 2346$

$\Delta H = -93\ kJ\ mol^{-1}$

b) Calculate the enthalpy change for the following reaction

$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$

The bond energies of various bonds (in $kJmol^{-1}$) are given below:

$E_{C-C} = +347$, $E_{C-H} = +410$, $E_{C-O} = +336$, $E_{O=O} = +496$, $E_{C=O} = +805$, $E_{O-H} = +465$

Given Data:

The enthalpy change (ΔH) for the combustion of ethanol (C_2H_5OH), we use bond energies:

Step 1: Bonds Broken (Reactants)

1. C_2H_5OH (Liquid Ethanol):
   - 1 C-C: 347 kJ/mol
   - 5 C-H: 5 × 410 = 2050 kJ/mol
   - 1 C-O: 336 kJ/mol
   - 1 O-H: 465 kJ/mol

   Total for C_2H_5OH = 347 + 2050 + 336 + 465 = 3198 kJ/mol
2. 3 O_2 (Gaseous Oxygen):
   - 3 O=O: 3 × 496 = 1488 kJ/mol

   Total Bonds Broken = 3198 + 1488 = 4686 kJ/mol

Step 2: Bonds Formed (Products)

1. 2 CO_2 (Gaseous):
   - 4 C=O: 4 × 805 = 3220 kJ/mol
2. 3 H_2O (Liquid):
   - 6 O-H: 6 × 465 = 2790 kJ/mol

   Total Bonds Formed = 3220 + 2790 = 6010 kJ/mol

Step 3: Calculate ΔH

ΔH = Energy Absorbed (Bonds Broken) − Energy Released (Bonds Formed)

ΔH = 4686 − 6010 = −1324kJ/mol

Note:

- Negative ΔH confirms exothermic reaction (heat released).

ENERGETICS OF SOLUTION

The process of dissolving a solute in a solvent is called dissolution. It is assumed that the formation of a solution, takes place in three steps.

i. Overcoming the intermolecular forces in the solvent to make room for the solute (expanding the solvent).
ii. Breaking up the solute into individual components (expanding the solute).
iii. Allowing the solute and solvent to interact to form the solution

In this process heat is either given out or taken in. Standard enthalpy change of solution is used to describe it.

➢ Standard enthalpy Change of Solution (ΔH°_{sol})

"The standard enthalpy of solution is the amount of heat absorbed or evolved when one mole of a substance is dissolved in a solvent to give an infinitely dilute solution."

It is denoted by ΔH°_{sol}. It may be exothermic or endothermic. The enthalpy changes of solution of sodium carbonate and ammonium chloride are described by the equations below:

$Na_2CO_{3(s)} + aq \longrightarrow 2Na^+_{(aq)} + CO^{2-}_{3(aq)} \quad \Delta H^\circ_{sol} = -25\ kJ\ mol^{-1}$

$NH_4Cl_{(s)} + aq \longrightarrow NH^+_{4(aq)} + Cl^-_{(aq)} \quad \Delta H^\circ_{sol} = +16.2\ kJ\ mol^{-1}$

In Table are given values of heats of solution of different ionic solids in water at infinite dilution. The magnitude of heat of solution gives information regarding the strength of intermolecular forces of attraction between components which mix to form a solution.

An ionic compound consists of oppositely charged ions, held together by strong electrostatic forces.

➢ Factors Governing Process of Dilution:

Two factors govern the process of dissolution

Table: Heats of solution of some important ionic solids

Substance	Heat of Solution
NaCl	4.98
KCl	17.8
KBr	19.9
KI	21.4
NH_4Cl	16.2
NH_4NO_3	26.0

i. Hydration energy (accounts for the attraction of solute ions with water molecules)
ii. Lattice energy (controls the breaking of the ionic compounds)

Hydration

When ionic compounds are dissolved in water, they are dissociated into ions, which are then surrounded by water molecules. **"The process in which water molecules surround and interact with the solute ions is called hydration."** The forces are created between water molecules and the ions which are called ion dipole forces as shown in Figure.
And as a result, all the ions in aqueous solution are said to be hydrated. The energy of attraction due to an ion-dipole force is known as enthalpy of hydration, defined as follows:

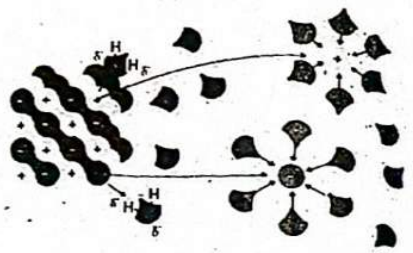


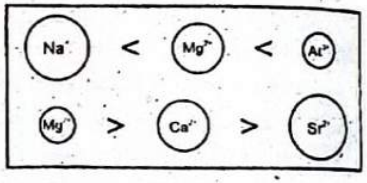
Figure: Dissolution of an ionic compound through the process of hydration.

Enthalpy of Hydration:

"The enthalpy change involved when one mole of a solute is dissolved in excess of water to make infinitely dilute solution under standard conditions is called enthalpy of hydration."
It is denoted by ΔH_{hyd}. This energy is always released as it is formation of ion-dipole bond.

Factors Affecting the magnitude of Hydration Energy

The heat of hydration depends on following factors:
i. Charge on the ion ii. Size of the ion
We usually use a combined term for these two factors i.e., **"charge density"** which is defined as charge per unit area. If greater charge is present on smaller ion, the charge density is large and vice versa. And large value of charge density means that ions are strongly attracted by water molecules during the process of hydration, thereby increasing the hydration energy values. For example, enthalpies of hydration of the given ions are in the order:



On the same basis we can explain the hydration energy of anions.

Exercise 1.Q.4

Q. What is lattice energy? How does Born-Haber cycle help to calculate the lattice energy of NaCl?

Lattice Energy (ΔH°_{latt})

"The lattice energy of an ionic crystal is the enthalpy change involved when one mole of the ionic compound is formed from gaseous ions under standard conditions."

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H^\circ_{latt} = -787 \text{ kJ mol}^{-1}$$

Factors Affecting the magnitude of Lattice Energy

The lattice energy depends on following factors:
i. Charge on the ion. ii. Size of the ion

Lattice energy and size of the Ions

Figure show the values of lattice energies of alkali metal halides. It is clear from the data that lattice energy decreases with the increase in the size of the cation/anion. With the increase in the size of either cations or anions, the packing of oppositely charged ions become less and less tight.

Lattice Energy and Charge on the Ions

Lattice energies is directly proportional to the charges on the ions i.e., greater the magnitude of the charge on an ion, greater is its lattice energy and vice versa.

Explanation

Let us try to understand this fact by comparing lithium fluoride, LiF, with magnesium oxide, MgO.
These compounds have the same arrangement of ions in their lattice structure and comparative sizes of cations and anions are same in both compounds.
The major physical difference between LiF and MgO is the ionic charge, which affects the lattice energy.

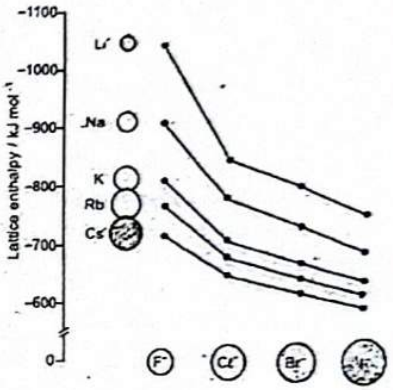


Figure: Lattice energies of alkali metal halides

Magnesium oxide $\Delta H_{latt[MgO]} = -3923 \text{ kJ mol}^{-1}$ is a greater than lithium fluoride $\Delta H_{latt[LiF]} = -1049 \text{ kJ mol}^{-1}$.

The doubly-charged Mg^{2+} and O^{2-} ions in MgO attract each other more strongly than the singly-charged ions of the same size in LiF. For ions of similar size, the greater the ionic charge, the higher the charge density. This results in stronger ionic bonds being formed.

Solubility Trends of Group II Hydroxides and Sulphates

ΔH°_{sol} depends on both lattice energy and hydration enthalpy.

- Look at the solubility trends of group II metal hydroxides. Both hydration energy and lattice enthalpy decreases down the group due to decrease in charge density of group 2 cations. But it is observed that the lattice energy decreases more rapidly in the series $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ than does the energy of hydration in ions
- Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}. For this reason, the lattice energy factor dominates this solubility trend. ΔH°_{sol} becomes more exothermic so solubility increase.
- **The solubility trends of group II metal sulphates:** As the SO_4^{2+} is much larger than the OH^-, the decrease in lattice energy going through the series of sulphates from $MgSO_4$ to $BaSO_4$ is less, but the energy of hydration of the cation decreases by a greater amount. Now the energy of hydration dominates the solubility trend, and the solubility decreases from $MgSO_4$ to $BaSO_4$. ΔH°_{sol} becomes more endothermic so solubility increase.

Calculating Enthalpy Change of Solution (ΔH°_{sol})

We can calculate the enthalpy change of solution or the enthalpy change of hydration by constructing an enthalpy cycle and using Hess's law (Figure).

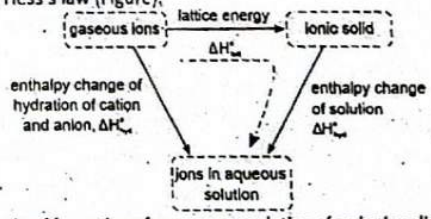


Figure: Energy cycle of formation of an aqueous solution of an ionic solid using Hess's law

We can see from this enthalpy cycle that:

$$\Delta H^\circ_{latt} + \Delta H^\circ_{sol} = \Delta H^\circ_{hyd}$$

We can use this energy cycle to calculate:

Sample Problem 6.6

Determine the enthalpy change of solution (ΔH°_{hyd} of sodium fluoride NaF) using the following data:

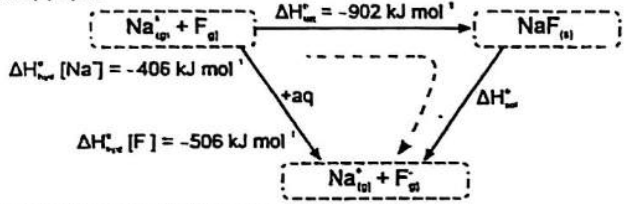
Lattice energy of sodium fluoride (NaF) = −902 kJ mol^{-1}

Heat of hydration of sodium ions (Na^+) = −406 kJ mol^{-1}

Heat of hydration of fluoride ions (F^-) = −506 kJ mol^{-1}

Solution:

Step 1: Draw the enthalpy cycle



Step 2: Rearrange the equation and substitute the values to find Δ

$$\Delta H^\circ_{latt} + \Delta H^\circ_{sol} = \Delta H^\circ_{hyd}$$

$$\Delta H^\circ_{sol} = (-406) + (-506) - (-902)$$

$$\Delta H^\circ_{hyd}[NaF] = -10 \text{ kJ mol}^{-1}$$

BORN-HABER CYCLE

- It is impossible to determine the lattice energy of a compound by a single direct experiment.
- We can, however, calculate the value for ΔH°_{latt} using several experimental data and an energy cycle called the **Born-Haber cycle.**
- Born-Haber cycle is an application of Hess's law.

➢ Calculation of Lattice Energy of NaCl:

Consider calculation of lattice energy of sodium Chloride using Hess's law and Born-Haber cycle.

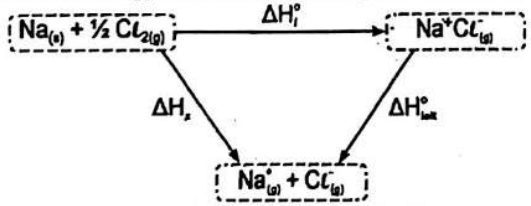


Figure: Enthalpy cycle of sodium chloride

where,

ΔH°_f : Standard enthalpy of formation of NaCl can be measured conveniently in a calorimeter.

ΔH_x : Total energy involved in changing sodium and chlorine from their standard physical states to gaseous ions. Applying Hess's law on the above energy cycle, we can write

$$\Delta H_x + \Delta H^\circ_{latt} = \Delta H^\circ_f$$

The above energy triangle has been extended to show the various stages involved in finding ΔH_x. The complete energy cycle is called the Born-Haber cycle and it is presented in Figure.

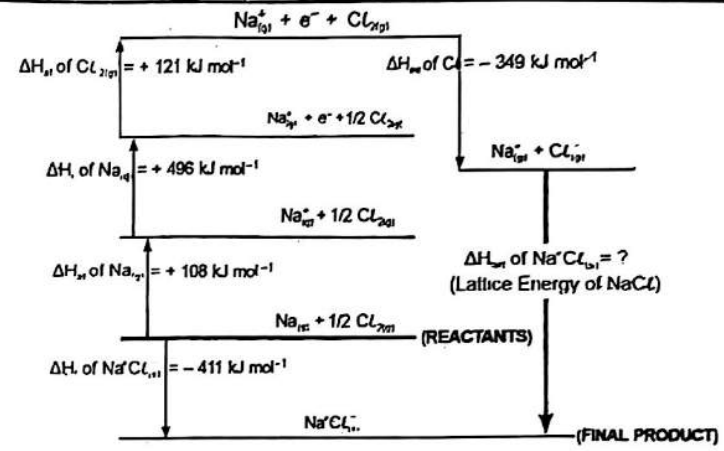


Figure: Born Haber cycle of sodium chloride (not according to scale)

➲ Calculation of ΔH_x

From above cycle we have,

$$\Delta H_x = \Delta H_{at(Na)} + \Delta H_{i(Na)} + \Delta H_{at(Cl_2)} + \Delta H_{ea(Cl)}$$

Using, $\Delta H^\circ_{latt} = \Delta H^\circ_f - \Delta H_x$

$$\Delta H^\circ_{latt} = -787 \text{ kJ mol}^{-1}$$

Sample Problem 6.7

Calculate the heat of formation of sodium fluoride, which crystallizes in the sodium chloride lattice. The heat of atomization of $Na_{(s)}$ is kJ / mol, half the bond energy of $F_{2(g)}$ is 79 kJ / mol, the ionization energy of sodium atoms is 494 kJ / mol, the electron affinity of fluorine atoms is −328 kJ / mol, and the lattice energy is −939 kJ / mol.

Solution: Values are given for all the quantities in the Born-Haber cycle, so we can apply Hess's law:

$$\Delta H^\circ_f = \Delta H^\circ_{latt} + \Delta H^\circ_{at(Na)} + \Delta H^\circ_{i(Na)} + \Delta H^\circ_{at(F2)} + \Delta H^\circ_{ea(F)}$$

$$= (-939 + 109 + 494 + 79 - 328) \text{ kJ mol}^{-1}$$

$$\Delta = -585 \text{ kJ mol}$$

☑ QUICK CHECK 6.7

a) Draw Born-Haber cycle for sample problem 6.7.

Ans. See quick check 6.7.

b) Calculate the heat of formation of lithium fluoride. The heat of atomization of $Li_{(s)}$ is 161 kJ/mol, half the bond energy of $F_{2(g)}$ is 79 kJ/mol, the ionization energy of lithium atoms is 520 kJ/mol, the electron affinity of fluorine atoms is −328 kJ/mol, and the lattice energy is 1107 kJ/mol.

Ans. Given Data:

1. **Heat of atomization of Li(s):**
   $Li_{(s)} \rightarrow Li_{(g)}$ $\quad \Delta H_{atom} = +161 \text{ kJ / mol}$
2. **Half the bond energy of F_2(g):**
   $1/2 F_{2(g)} \rightarrow F_{(g)}$ $\quad \Delta H_{bond} = +79 \text{ kJ / mol}$
   (Full bond energy of F_2 = 158 kJ/mol, but we use half since the cycle requires 1 F atom.)
3. **Ionization energy (IE) of Li(g):**
   $Li_{(g)} \rightarrow Li^+_{(g)} + e$ $\quad IE = +520 \text{ kJ / mol}$

4. **Electron affinity (EA) of F(g):**
   $F_{(g)} + e^- \rightarrow F^-_{(g)}$ $EA = -328 kJ/mol$
5. **Lattice energy (U) of LiF(s):**
   $Li^+_{(g)} + F^-_{(g)} \rightarrow LiF_{(s)}$ $U = -1107 kJ/mol$

Target Reaction (Heat of Formation):
$Li_{(s)} + 1/2F_{2(g)} \rightarrow LiF_{(s)}$ $\Delta Hf^\circ = ?$

ENTROPY

Entropy is a measure of the number of ways energy can be distributed within a system at a specific temperature.

➢ **Important Points:**

- When the energy is distributed in more ways, a system is more stable.
- Entropy is a measure of the randomness or disorder of a system.
- The higher the randomness or disorder, the greater the entropy of the system.
- The system becomes energetically more stable when it becomes more disordered.

➲ Entropy, Diffusion and Number of Ways of Arrangement

We can show that the molecules in a vapour diffuse by chance by thinking about the probability of finding them at one place at any one time. Consider the simplified model shown in Figure below.

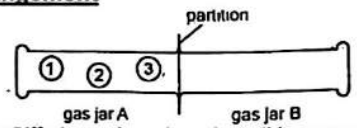


Figure: Diffusion and number of possible arrangements

There are 8 different ways for these molecules to arrange themselves in two jars by diffusion from Jar A to jar B that is:

- This is calculated as under
- Number of molecules in A = 3
- Number of Jars = 2
- Number of possible arrangements = $2^3 = 8$

Similarly, if there were 5 molecules initially in jar A, the possible ways of arrangement will be 2^5, i.e. 32. And if there were 100 molecules, the probability will be 2^{100}. A general formula x^y can be written for the calculation of probability, where x is the number of places and y is the number of particles to be arranged. Diffusion happens because there is a large number of ways of arranging the molecules. The concept of the 'number of ways' of arrangement either particles or the energy within these particles helps predict whether it can happen or not.

➲ Comparison of Entropy Values

Entropies of different substances can be compared based on the number of particles, physical properties, and state.

Small number of particles means low entropy and vice versa, for example $CaCO_3$ has higher standard entropy ($92.9 JK^{-1} mol^{-1}$) than CaO($39.7 JK^{-1} mol^{-1}$). This is because the number of possible arrangements is lower when the number of particles is smaller.

The entropy of substances having similar chemical nature is dictated by their hardness. Harder substances have lower entropy than softer ones. Diamond has lower entropy than graphite because it is much harder. Stronger forces result in limited vibrations in harder substances which decrease the probability of disorder. A substance has lower entropy in solid state than in liquid and gaseous states. The entropy of ice near its melting point is $48.0 JK^{-1} mol^{-1}$, for water, it is $69.9 JK^{-1} mol^{-1}$; whereas water vapour just above the boiling point is $188.7 JK^{-1} mol^{-1}$.



Dissolution of sugar in tea increases the entropy of both the solute and solvent

QUICK CHECK 6.8

Explain the difference in the entropy of each of the following pairs of substances in terms of their states and structures.

i. $Br_{2(g)}S^\circ = 151.6 J K^{-1} mol^{-1}$ and $I_{2(s)}S^\circ = 116.8 JK^{-1} mol^{-1}$

Ans. The difference in entropy (ΔS) between $Br_2(l)$ and $I_2(s)$ can be calculated and explained as follows:

Given: $S^\circ[Br_2(l)] = 151.6 J K^{-1} mol^{-1}$

$S^\circ[I_2(s)] = 116.8 J K^{-1} mol^{-1}$

Entropy Difference Calculation:

$\Delta S = S^\circ[Br_2(l)] - S^\circ[I_2(s)]$

$= 151.6 - 116.8$

$= +34.8 J K^{-1} mol^{-1}$

Explanation of the Difference:

1. **State Effect (Major Contribution):**
   - $Br_2(l)$ is a liquid → molecules have translational and rotational freedom
   - $I_2(s)$ is a solid → molecules are fixed in a crystal lattice
   - Liquids always have higher entropy than solids for the same substance
2. **Molecular Mass Effect (Minor Contribution):**
   - I_2 (254 g/mol) is heavier than Br_2 (160 g/mol) → would normally give I_2 higher entropy
   - However, the state difference (liquid vs solid) dominates here
3. **Structural Considerations:**
   - Both are simple diatomic molecules
   - $Br_2(l)$ has weaker London dispersion forces than $I_2(s)$
   - Less energy needed to disrupt order in $Br_2(l)$

In short, The $+34.8 J K^{-1} mol^{-1}$ difference shows that $Br_2(l)$ is significantly more disordered than $I_2(s)$, primarily because liquids have greater molecular freedom than solids, outweighing iodine's greater molecular mass.

ii. $H_{2(g)}S^\circ = 130.6 JK^{-1} mol^{-1}$ and $CH_{4(g)}S^\circ = 186.2 JK^{-1} mol^{-1}$

Ans. The standard molar entropy (S°) values are:

- $H_2(g)$: $130.6 J K^{-1} mol^{-1}$
- $CH_4(g)$: $186.2 J K^{-1} mol^{-1}$

$CH_4(g)$ has higher entropy due to:

1. **Molecular Complexity**
   - $H_2(g)$:
     - Simple diatomic molecule (2 atoms).
     - Only translational and rotational motion contribute to entropy.
   - $CH_4(g)$:
     - Tetrahedral structure (5 atoms).
     - More vibrational modes and rotational freedom → higher entropy.
2. **Degrees of Freedom**
   - $H_2(g)$:
     - 3 translational + 2 rotational = 5 degrees of freedom.
   - $CH_4(g)$:
     - 3 translational + 3 rotational + 9 vibrational = 15 degrees of freedom.
3. **Mass & Size**
   - CH_4 (M = 16 g/mol) is heavier than H_2 (M = 2 g/mol), leading to more energy states and higher entropy.

Calculation of Entropy Difference

$\Delta S^\circ = S^\circ(CH_4) - S^\circ(H_2) = 186.2 - 130.6 = 55.6 J K^{-1} mol^{-1}$

Conclusion

$CH_4(g)$ has higher entropy because:

- More atoms → more vibrational/rotational modes.
- Larger mass → more microstates.

iii. $Hg_{(\ell)}S^\circ = 76.00\,JK^{-1}mol^{-1}$ and $Na_{(s)}S^\circ = 51.20\,JK^{-1}mol^{-1}$

Ans. Substances:

- Hg(l) (liquid mercury), $S^\circ = 76.00\,J{\cdot}K^{-1}{\cdot}mol^{-1}$
- Na(s) (solid sodium), $S^\circ = 51.20\,J{\cdot}K^{-1}{\cdot}mol^{-1}$

Explanation:

Entropy (S°) is a measure of disorder or randomness in a system. The higher the entropy, the more disordered the system.

- Hg(l) is a liquid, meaning its atoms are more free to move and have greater positional and kinetic randomness than in a solid.
- Na(s) is a solid, where atoms are arranged in a fixed, orderly lattice with limited movement, hence lower entropy.

iv. $SO_{2(g)}S^\circ = 248.1\,JK^{-1}mol^{-1}$ and $SO_{3(\ell)}S^\circ = 95.60\,JK^{-1}mol^{-1}$

Given Data:

- S° of $SO_{2(g)} = 248.1\,JK^{-1}mol^{-1}$
- S° of $SO_{3(\ell)} = 95.60\,JK^{-1}mol^{-1}$

Entropy Difference (ΔS):

$\Delta S = S^\circ(SO_{2(g)}) - S^\circ(SO_{3(\ell)})$

$\Delta S = 248.1\,J\,K^{-1}mol^{-1} - 95.60\,J\,K^{-1}mol^{-1}$

$\Delta S = +152.5\,J\,K^{-1}mol^{-1}$

Positive ΔS confirms $SO_{2(g)}$ has higher disorder than $SO_{3(\ell)}$.

Reasons:

- Gaseous SO_2 has more translational/rotational freedom than liquid SO_3.
- Liquids have stronger intermolecular forces, reducing molecular randomness.

The $+152.5\,J\,K^{-1}mol^{-1}$ difference quantifies the entropy loss when SO_2 condenses into liquid SO_3.

➲ Entropy Changes in Reactions

In a chemical reaction, if we compare the entropies of the reactants and products, we can try to explain the magnitude of the entropy change and whether or not it increases or decreases.

➢ Rules about change in Entropy of Reaction:

The following rules must be followed to know about the change in entropy of a reaction.

- When a solid is converted to a liquid or a gas in the product, the entropy change is positive.
- If no. of moles in the products are more the entropy change is positive.
- If there is a change in the number of gaseous molecules in a reaction, due to high values of entropy are associated with gases.
- The more gas molecules, there are, the greater is the number of ways of arranging them and the higher the entropy.

For example:

$$CaCO_{(s)} \longrightarrow CaO_{(s)} + CO_{(g)}$$

There is an increase in entropy of the above system because the gas is being produced (high entropy) but the reactant, calcium carbonate, is a solid (low entropy). Such reactions are spontaneous.

Also, consider the reaction:

$$2N_2O_{(g)} \longrightarrow 4NO_{(g)} + O_{(g)}$$

We should expect an increase of entropy of the system because there are a greater number of moles of gas molecules in the products (5 molecules) than in the reactants (2 molecules). This is also a spontaneous process.

➢ The sign of Entropy Change and Spontaneity of a Process:

The entropy of a substance is always positive, however, when the entropy changes it may have positive or negative value.

A positive entropy change value ($\Delta S^\circ = +ve$) means a spontaneous process

A negative entropy change value ($\Delta S^\circ = -ve$) implies more ordered molecules and a decrease in disorder

For some reactions, however, the entropy change fails to tell about the spontaneity of the reaction and we need another quantity called free energy.

➲ Calculating the Entropy Change of the System (Reaction)

In order to calculate the entropy, change of the system we use the relationship:

$$\Delta S^\circ_{system} = S^\circ_{products} - S^\circ_{reactants}$$

Let us calculate the entropy change of the system for the reaction:

$$2Ca_{(s)} + O_{2(g)} \longrightarrow 2CaO_{(s)}$$

The standard entropy values are:

$$S^\circ_{[Ca(s)]} = 41.40\,J\,K^{-1}\,mol^{-1}$$

$$S^\circ_{[Ca(s)]} = 41.40\,J\,K^{-1}\,mol^{-1}$$

$$S^\circ_{[O2(g)]} = 205.0\,J\,K^{-1}\,mol^{-1}$$

$$S_{[CaO(s)]} = 39.70\,J\,K^{-1}\,mol^{-1}$$

As

$$\Delta S^\circ_{system} = S^\circ_{products} - S^\circ_{reactants}$$

$$= 2\times S^\circ_{[CaO(s)]} - \left\{2\times S^\circ_{[Ca(s)]} + S^\circ_{[O2(g)]}\right\}$$

$$= 2\times 39.70 - \left\{(2\times 41.40) + 205.0\right\}$$

$$= 79.40 - 287.8$$

The negative value for the entropy change shows that the entropy of the system has decreased. We know, however, that calcium reacts spontaneously with oxygen. So the entropy of the surroundings must also play a part because the total entropy change must be positive for the reaction to be feasible.

➲ Total Entropy Change, ΔS°_{total}

ΔS°_{total} is sum of standard entropy change of system and standard entropy change of surrounding. ΔS° for system can be found out by subtracting the standard entropies of reactants from the standard entropies of products (Similar to the way you obtained ΔH°).

$$\Delta S^\circ_{system} = \Sigma S^\circ_{(products)} - \Sigma S^\circ_{(reactants)}$$

Where, respective no. of moles of reactants and products in balanced chemical equation are multiplied with entropy of reactants and products.

ΔS° for surrounding is calculated using following equation:

$$\Delta S^\circ_{surrounding} = \frac{-\Delta H^\circ_f}{T}$$

Where,

- The value of ΔH°_f is in kJ/mol so must be multiplied with 1000. This is because entropy changes are measured in J/K mol.
- The negative sign is part of equation and not the sign of ΔH°_f

$\Delta S^\circ_{(total)}$ is calculated using following equation:

$$\Delta S^\circ_{total} = \Delta S^\circ_{system} + \Delta S^\circ_{surrounding}$$

$$\Delta S^\circ_{total} = \Sigma S^\circ_{(products)} - \Sigma S^\circ_{(reactants)} + \left[\frac{-\Delta H^\circ_f}{T}\right]$$

It is useful to be able to predict about spontaneity of reaction using the sign of $\Delta S°_{(total)}$

- $\Delta S°_{total}$ is +ve ⇒ entropy increases ⇒ reaction is spontaneous
- $\Delta S°_{total}$ is –ve ⇒ entropy decreases ⇒ reaction is nonspontaneous

Sample Problem 6.8

Calculate the entropy change of the system $\Delta S°$ system for the reaction:

$$2Ca_{(s)} + O_{2(g)} \rightarrow 2CaO_{(s)}$$

The standard entropy values are: $S°_{(Ca(s))} = 41.40\ JK^{-1}\ mol^{-1}$

$S°_{(O_2(g))} = 205.0\ JK^{-1}\ mol^{-1}$

$S°_{(CaO(s))} = 39.70\ JK^{-1}\ mol^{-1}$

As $\Delta S°_{system} = \Sigma S°_{(products)} - \Sigma S°_{(reactants)}$

$= 2 \times S°_{(CaO(s))} - \{2 \times S°_{(Ca(s))} + S°_{(O_2(g))}\}$

$= 2 \times 39.70 - \{(2 \times 41.40) + 205.0\}$

$= 79.40 - 287.8$

$\Delta S°_{system} = -208.4\ JK^{-1}\ mol^{-1}$

Sample Problem 6.9

Calculate the entropy change of the surroundings $\Delta S°_{surrounding}$ for the reaction at 298K:

$2Ca_{(s)} + O_{2(g)} \rightarrow 2CaO_{(s)}$ $\Delta H°_{reaction} = -1270.2\ kJ\ mol^{-1}$

Step 1: Convert the enthalpy change into J mol^{-1} by multiplying by 1000.

$-1270.2 \times 1000 = -1270\,200\ J\ mol^{-1}$

Step 2: Apply the relationship

$$\Delta S°_{surrounding} = \frac{-\Delta H°_{reaction}}{T}$$

$$\Delta S°_{surrounding} = \frac{-1270200}{298}$$

$$= +4262.4\ JK^{-1}\ mol^{-1}$$

Sample Problem 6.10

Calculate the total entropy change $\Delta S°_{total}$ for the reaction and check its spontaneity.

$2Ca_{(s)} + O_{2(g)}\ 2CaO_{(s)}$

$\Delta S°_{system} = -208.4\ JK^{-1}\ mol^{-1}$

$\Delta S°_{surrounding} = +4262.4\ JK^{-1}\ mol^{-1}$

As, $\Delta S°_{total} = -208.4 + 4262.4$

$\Delta S°_{total} = +4054.0\ JK^{-1}\ mol^{-1}$

The total entropy change is positive and the reaction is feasible.

THE FREE ENERGY CHANGE, (ΔG)

In determining whether a chemical reaction is likely to be spontaneous, we use the new quantity Gibbs free energy change, ΔG. The Gibbs free energy change is given by the relationship:

$$\Delta G = -T\Delta S_{total}$$

Multiplying the $\Delta S°_{(total)}$ expression by –T, we can also get the expression without having to consider the entropy changes of the surroundings. This expression is called Gibbs equation

$$-T \times \{\Delta S°_{total} = \Delta S°_{system} + \left[\frac{\Delta H°_r}{T}\right]\}$$

$$-T\Delta S_{total} = -T\Delta S_{system} + \Delta H°_r$$

$$\Delta G° = \Delta H°_r - T\Delta S°$$

Rack Your Mind!

9. What is the significance of Gibbs free energy in thermodynamics?
(A) Measures entropy change
(B) Predicts spontaneity of reactions
(C) Calculates enthalpy change
(D) Determines reaction rate

Extend your Knowledge

The unit of temperature times entropy ($T\Delta S$) is Joule. $\Delta S°$ represents $\Delta S°_{system}$.

And draw the following conclusion from it:

i. If $\Delta G < 0$ (–ve), the given process may occur spontaneously.

ii. If $\Delta G > 0$ (+ve), the indicated process cannot occur spontaneously; instead, the reverse of it may occur.

iii. If $\Delta G = 0$ neither the indicated process nor reverse of it can occur spontaneously. The system is in a state of equilibrium.

Rack Your Mind!

10. What are the information's given by Gibbs free energy for a reaction?

Calculating $\Delta G°$ for a Reaction

Sample Problem 6.11

For the Reaction:

$$CaSO_{4(s)} \longrightarrow Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

Calculate $\Delta H°$, $\Delta S°$ and $\Delta G°$ at 25°C using the following data; and discuss its spontaneity.

Heat of Formation:

$$\Delta H°_f\left[CaSO_{4(s)}\right] = -1432.7\ kJ,\ \Delta H°_f\left[Ca^{2+}_{(aq)}\right] = -543.0\ kJ,\ \Delta H°_f\left[SO^{2-}_{4(aq)}\right] = -907.5\ kJ$$

Standard Entropy:

$$S°\left[CaSO_{4(s)}\right] = 106.7\ J/K,\ S°\left[Ca^{2+}{}_{(aq)}\right] = -55.2\ J/K,\ S°\left[SO^{2-}_{4\,(aq)}\right] = +17.2\ J/K$$

Solution

i. $\Delta H° = \sum\Delta H_{f\,(products)} - \sum\Delta H_{f(\,reactants)} = \left[-543.0 - 907.5\right] - \left[-1432.7\right] = -17.8\ kJ$

ii. $\Delta S° = \sum S°_{(products)} - \sum S°_{(reactants)} = \left[(-55.2 + 17.2) - (106.7)\right] J/K = -1447\ J/K$

$\Delta S° = -0.1447\ kJ/K$

iii. $\Delta G° = \Delta H° - T\Delta S° = (-17.8\ kJ) - (298\ K) \times (-0.1447\ kJ/K) = +25.3 kJ$

Note that you substitute $\Delta S°$ in units of kJ/K in the formula of $\Delta G°$.

Result: We conclude that this process is nonspontaneous at standard conditions at 25°C.

Sample Problem 6.12

What is the standard free-energy, $\Delta G°$ for the following reaction (Haber's process) at 25°C? Also discuss its spontaneity.

$$N_{2(s)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

Heat of Formation: $\Delta H°_f\left[N_{2(g)}\right] = 0\ kJ,\ \Delta H°_f\left[H_{2(g)}\right] = 0\ kJ,\ \Delta H°_f\left[NH_{3(g)}\right] = -45.9\ kJ$

Standard Entropy: $S°\left[N_{2(g)}\right] = 191.5\ J/K,\ S°\left[H_{2(g)}\right] = 130.6\ J/K,\ S°\left[NH_{3(g)}\right] = +193\ J/K$

Solution:

$$\Delta H° = \sum\Delta H_{f(products)} - \sum\Delta H_{f\,(reactants)} = \left[2 \times (-45.9)\right] - \left[0 + 0\right] = -91.8\ kJ$$

$$\Delta S° = \sum nS°_{(products)} - \sum mS°_{(reactants)} = \left[2 \times (193)\right] - \left[191.5 + 3 \times 130.6\right] J/K = -197\ J/K$$

$\Delta S° = -0.197\ kJ/K$

$\Delta G° = \Delta H° - T\Delta S° = (-91.88\ kJ) - (298\ K) \times (-0.197\ kJ/K) = -33.1 kJ$

Result: Since $\Delta G°$ is a negative value, thus it is concluded that Haber's process is spontaneous at standard conditions, i.e. at 25°C.

Spontaneity and Temperature Change

Until now we obtained the free-energy for a reaction at 25°C. How do we find $\Delta G°$ at another temperature? For this purpose, we use the same equation i.e., $\Delta G° = \Delta H° - T\Delta S°$. We get the value of ΔG at any temperature by substituting values of $\Delta H°$ and $\Delta S°$ at 25°C. But in the method, we assume that $\Delta H°$ and $\Delta S°$ are essentially constant w.r.t temperature (this is only approximately true).

Remember that the superscript degree sign (°) refers to substances in standard states, which are substances at 1 atm and at the *specified temperature*. Although until now this was 25°C (298 K), we now consider other temperatures. Note that in general, ΔG depends strongly on temperature.

In Table, all of the four possible choices of signs for ΔH° and ΔS°, give different temperature behaviors for ΔG° are being discussed. In all this discussion temperature is always positive as it is taken on Kelvin scale.

Table: Effect of temperature on the spontaneity of reactions

ΔH°	ΔS°	ΔG°	Description*
–	+	–	Spontaneous at all T
+	–	+	Non-spontaneous at all T
–	–	+ or –	Spontaneous at low T; non-spontaneous at high T
+	+	+ or –	Non-spontaneous at low T; spontaneous at high T

*The term low temperature and high temperature are relative. For a particular reaction, high temperature could mean room temperature.

Sample Problem 6.13

Calculate ΔG° at 1000°C for the following reaction and discuss it spontaneity.

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_2$$

Solution:

For this reaction, ΔH° = +178.0 kJ and ΔS° = +160.4 J/K = 0.1604 kJ/K

Substituting $T = 1000 + 273 = 1273\ K$

$$\Delta G = \Delta H - T\Delta S = (+178.0\ kJ) - (1273\ K) \times (0.1604\ kJ/K)$$
$$= +178.0\ kJ - 204.2\ kJ$$
$$= -26.2\ kJ$$

We conclude that this reaction is spontaneous at 1000°C and 1 atm, since ΔG has negative sign. In other words, at 1000°C, limestone ($CaCO_3$) will decompose in an open container.

☑ QUICK CHECK 6.9

a) What do you expect about the entropy value of the following reactions, whether it would be positive or negative?

i) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Ans. Entropy Change (ΔS):

- **Reactants:** 1 mol N_2 + 3 mol H_2 = 4 moles of gas
- **Products:** 2 mol NH_3 = 2 moles of gas

Conclusion:

- The total number of gas molecules decreases.
- Therefore, disorder decreases, and entropy decreases.

ii) $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$

Ans. Entropy Change (ΔS): Positive or Negative?

Positive (ΔS > 0)

Reason:

- Number of gas molecules remains the same (2 moles of gas on both sides), but the products are different substances, leading to greater molecular randomness.
- The reaction results in increased disorder, as two different gas species (H_2 and I_2) are formed from a single type (HI), which increases entropy.

Conclusion:

ΔS = Positive

b) Which of the following changes are likely to be spontaneous?

i. The smell from an open bottle of aqueous ammonia diffusing throughout a room.

Ans. The smell from an open bottle of aqueous ammonia diffusing throughout a room.

Spontaneous

- Gas particles spread out to increase entropy (disorder).
- No energy input required.

ii. Water turning to ice at –10° C

Ans. Spontaneous

- Below 0 °C, freezing is thermodynamically favorable (exothermic).
- Even though it decreases entropy, the low temperature makes the process favorable.

iii. Ethanol vaporising at 20° C

Ans. Spontaneous

- Vaporization increases entropy.
- Ethanol has a low boiling point (~78 °C), and enough molecules have sufficient energy to evaporate slowly at 20 °C.

iv. Water mixing completely with salt

Ans. Spontaneous

- Dissolution increases entropy as ions disperse in water.
- No energy input needed.

v. Limestone (calcium carbonate) decomposing at room temperature

Ans. Not Spontaneous

- Endothermic reaction that requires heat input to break bonds.
- Doesn't occur naturally at room temperature.

Likely Spontaneous: i, ii, iii, iv

Not Spontaneous: v

Solution File — Rack Your Brain!

Sr. #	Option	Explanation
1.	S.Q	**Thermochemical Equation:** "A balanced chemical equation which fully describes the physical states of reactants and products in the form of state symbols along with an enthalpy change during the reaction is called a thermochemical equation." **Information from thermochemical equation:** It tells us about: i. Physical states of both reactants and products. ii. Exact number of moles of reactants and products. iii. Heat evolved or absorbed during a reaction. **Example:** $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ $\Delta H = -285.8\ kJ\ mol^{-1}$
2.	B	Energy is required to break the strong N ≡ N triple bond: $N_2 + O_2 \rightarrow 2NO$, ΔH = +ve (energy absorbed).
3.	S.Q	In exothermic reaction, the number of bonds formed is greater than bonds breakage during the reaction. Moreover heat content of products is less than that of reactants ($H_R > H_P$). That is why when reactants convert into product heat is released from system to surroundings. **Example:** $H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H = -285.5\ kJ\ mol^{-1}$
4.	C	The height of the peak in a reaction pathway diagram represents the activation energy, which is the minimum energy required for the reaction to occur.
5	S.Q	**Atomization Energy:** The energy required to convert a substance in atomic state is called atomization energy. It is always endothermic in nature. $\frac{1}{2}H_{2(g)} \longrightarrow H_{(g)}$ $\Delta H°_{at} = 218\ kJ\ mol^{-1}$

6.	S.Q	It is necessary to mention the physical state of reactants and products, because enthalpy is associated with a typical phase of a substance. With a change in physical state of reactants or products, enthalpy change of the reaction will be changed. So apparently two reactions are chemically same but thermo chemically, they may be different from each other. **Application of Hess's Law:** Steam is produced from H_2 and O_2 by two different routes. **Route I:** i. $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$ $\Delta H = -241.5$ kJ mol^{-1} **Route II:** ii. $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)}$ $\Delta H_2 = -285.8$ kJ mol^{-1}
7.	B	Energy is absorbed when bonds break because it requires energy to overcome the attractive forces between atoms in a molecule, allowing the bond to dissociate.
8.	B	In the equation $Q = mc\Delta T$, c represents the specific heat capacity, which is the amount of heat energy required to raise the temperature of a unit mass of a substance by 1 degree Celsius (or Kelvin).
9.	B	Gibbs free energy (ΔG) determines whether a reaction is spontaneous or not. If ΔG is negative, the reaction is spontaneous; if ΔG is positive, the reaction is non-spontaneous. This makes ΔG a crucial thermodynamic property in understanding reaction feasibility.
10.	S.Q	The sign of change in free energy (ΔG) of a process can be used to predict the spontaneity of that process. i. If $\Delta G < 0$(–ve), the given process may occur spontaneously. ii. If $\Delta G > 0$(+ve), the indicated process cannot occur spontaneously; instead, the reverse of it may occur. iii. If $\Delta G = 0$, neither the indicated process nor reverse of it can occur spontaneously. The system is in a state of equilibrium.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. Which of the following equations represents standard heat 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) $C(\text{graphite}) + H_{2(g)} \rightarrow 1/2\,C_2H_{4(g)}$ d) $2C(\text{diamond}) + 4H_{(g)} \rightarrow C_2H_{4(g)}$

II. Which of the following equations correctly defines lattice energy of $MgC\ell_2$?

a) $Mg_{(s)} + C\ell_{2(g)} \longrightarrow MgC\ell_2$ b) $Mg^{2+}_{(g)} + 2C\ell^-_{(g)} \longrightarrow MgC\ell_{2(g)}$

c) $Mg^{2+}_{(s)} + 2C\ell^-_{(g)} \longrightarrow MgC\ell_{2(s)}$ d) $Mg^{2+}_{(g)} + 2C\ell^-_{(g)} \longrightarrow MgC\ell_{2(s)}$

III. Suppose there are 100 molecules of a gas initially in jar A, which is connected to an evacuated jar B. When the stopcock is opened the possible ways of arrangement of molecules will be:

a) 100 b) 1/100 c) 2^{100} d) $1/2^{100}$

IV. For a reaction to occur spontaneously,

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.

V. The calorie content of food, often expressed in Calories (kcal), is fundamentally related to which thermodynamic quantity during its metabolism or combustion?

a) Entropy change (ΔS) b) Gibbs free energy change (ΔG)

VI. Which of the following quantities 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

VII. Which of the following factors would lead to a greater enthalpy change of hydration (more exothermic)?

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

VIII. The enthalpy of solution can be expressed in terms of which of the following enthalpy changes?

a) $\Delta H_{lattice} + \Delta H_{hydration}$ b) $\Delta H_{lattice} - \Delta H_{hydration}$ c) $-\Delta H_{lattice} + \Delta H_{hydration}$ d) $-\Delta H_{lattice} - \Delta H_{hydration}$

IX. Which of the following reactions has an enthalpy change that is equal to the standard enthalpy of formation of water, $\Delta H^\circ_f[H_2O_{(\ell)}]$?

a) $2H_{(g)} + O_{(g)} \rightarrow H_2O_{(\ell)}$ b) $H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)}$

c) $H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(\ell)}$ d) $2H^+_{(aq)} + O^{2-}_{(aq)} \rightarrow H_2O_{(\ell)}$

X. The enthalpy change for a reaction depends on:

a) Pathway taken from reactants to products

b) Presence of a catalyst

c) Initial and final states of the reactants and products

d) Rate of the reaction

XI. Which of the following processes would typically result in an increase in 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

XII. Consider a reaction with $\Delta H > 0$ and $\Delta S < 0$. This reaction will be:

a) Spontaneous at all temperatures b) Non-spontaneous at all temperatures

c) Spontaneous only at high temperatures d) Spontaneous only at low temperatures

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	c	$C_{(\text{graphite})} + H_{2(g)} \rightarrow 1/2\,C_2H_{4(g)}$	Standard heat of formation requires: • Elements in their most stable natural states (graphite for carbon, H_2 gas for hydrogen) • Formation of exactly 1 mole of the compound • Diamond and atomic hydrogen are not standard states • Option c only forms half mole of C_2H_4
II.	d	$Mg^{2+}_{(g)} + 2C\ell^-_{(g)} \longrightarrow MgC\ell_{2(s)}$	Lattice energy is: • The energy released when gaseous ions form 1 mole of solid ionic compound • Must start with separated gaseous ions (not elements or solid ions) • Must form solid crystalline compound
III.	c	2^{100}	• Each molecule has 2 choices (jar A or B) • For 100 independent molecules: total arrangements = $2 \times 2 \times \ldots \times 2$ (100 times) = 2^{100} • Demonstrates the statistical nature of entropy
IV.	a	$(\Delta H - T\Delta S)$ must be negative	• Gibbs free energy equation: $\Delta G = \Delta H - T\Delta S$ • For spontaneity: $\Delta G < 0$ • Thus $\Delta H - T\Delta S$ must be negative • Neither ΔH nor ΔS alone determines spontaneity

V.	c	Enthalpy change (ΔH)	• Calories measure heat released during combustion (ΔH) • 1 Calorie = 1 kcal = energy to raise 1kg water by 1°C • ΔG includes unusable energy; ΔH measures total heat
VI.	c	Activation energy	• Hess's Law calculates enthalpy changes (ΔH) only • Activation energy is kinetic parameter (energy barrier) • Can't be determined from reaction enthalpies
VII.	d	Smaller radius + larger charge	• Hydration enthalpy depends on ion-water attraction • **Smaller ions:** water molecules can approach closer • **Higher charge:** stronger electrostatic attraction • Most exothermic when ions are small and highly charged
IX.		$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(\ell)}$	• Standard formation requires: o Elements in standard states (H_2 gas, O_2 gas) o Formation of 1 mole of product o Correct physical state (liquid water) • Other options use non-standard states or form gas
X.	c	Initial and final states	• Enthalpy (ΔH) is a state function • Depends only on initial and final states • Independent of pathway or catalyst • Rate is kinetic property, unrelated to ΔH
XI.	c	Dissolving solid	• Dissolving increases disorder (solid → dispersed solution) • Freezing/condensing/crystallization decrease entropy (more ordered states) • Entropy generally increases when particles become more dispersed
XII.	b	Non-spontaneous at all temperatures	$\Delta G = (+\Delta H) - T(-\Delta S) = \Delta H + T\lvert\Delta S\rvert$ Since ΔH > 0 and TΔS adds positively, ΔG > 0 for all temperatures. So, ΔG is always positive → Reaction is non-spontaneous at all temperatures. When ΔH > 0 and ΔS < 0, no temperature can make ΔG negative.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Differentiate between exothermic and endothermic reactions.

Ans.

Property	Exothermic Reactions	Endothermic Reactions
Energy Change	Release energy (heat) to surroundings	Absorb energy (heat) from surroundings
Enthalpy (ΔH)	Negative (ΔH < 0)	Positive (ΔH > 0)
Temperature	Increases in the surroundings (heats up)	Decreases in the surroundings (cools down)
Example	Combustion of fuels, respiration, freezing water	Photosynthesis, melting ice, boiling water
Reaction Profile	Energy of products < energy of reactants	Energy of products > energy of reactants

b. What do you understand by the enthalpy of a system?

Ans. Enthalpy (H) of a system is the total heat content of the system at constant pressure.
It is defined as: $H = U + PV$

Where:
- H = enthalpy
- U = internal energy of the system
- P = pressure
- V = volume

c. Differentiate clearly between entropy (S) and Gibbs free energy (G).

Ans.

Property	Entropy (S)	Gibbs Free Energy (G)
Definition	Measure of disorder or randomness in a system	Measure of the usable energy available to do work
Symbol	S	G
Units	$J \cdot mol^{-1} \cdot K^{-1}$	$kJ \cdot mol^{-1}$
Nature	Tells how dispersed energy is in a system	Tells whether a process is spontaneous
Formula	No single formula (but used in ΔS)	$\Delta G = \Delta H - T\Delta S$
Interpretation	Higher S = more disorder	Negative ΔG = spontaneous process
Temperature Dependency	Affects spontaneity when multiplied by T in ΔG	Directly determines spontaneity of a reaction

d. Distinguish clearly between standard enthalpy of reaction and standard enthalpy of formation.

Ans.

Property	Standard Enthalpy of Reaction ($\Delta H^\circ_{reaction}$)	Standard Enthalpy of Formation (ΔH°_f)
Definition	Heat change during a chemical reaction under standard conditions	Heat change when 1 mole of a compound forms from its elements in their standard states
Reactants and Products	Any type of substances (elements or compounds)	Always starts from elements in standard states
Amount Involved	Varies depending on the reaction equation	Always forms exactly 1 mole of product
Symbol	ΔH°_{rxn}	ΔH°_f
Example	**Combustion of CH_4:** $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	**Formation of H_2O:** $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)}$

e. Define the following enthalpies and give one example of each.
(i) Standard enthalpy of solution **(ii) Standard enthalpy of hydration**
(iii) Standard enthalpy of atomization **(iv) Standard enthalpy of combustion**

Ans.

(i) Standard enthalpy Change of Solution (ΔH°_{sol})

"The standard enthalpy of solution is the amount of heat absorbed or evolved when one mole of a substance is dissolved in a solvent to give an infinitely dilute solution."
The enthalpy changes of solution of sodium carbonate and ammonium chloride are described by the equations below:

$$Na_2CO_{3(s)} + aq \longrightarrow 2Na^+_{(aq)} + CO^{2-}_{3\,(aq)} \qquad \Delta H^\circ_{sol} = -25 \text{ kJ mol}^{-1}$$

$$NH_4C\ell_{(s)} + aq \longrightarrow NH^+_{4\,(aq)} + C\ell^-_{(aq)} \qquad \Delta H^\circ_{sol} = +16.2 \text{ kJ mol}^{-1}$$

(ii) Standard enthalpy of hydration

"The enthalpy change involved when one mole of a solute is dissolved in excess of water to make infinitely dilute solution under standard conditions."

(iii) Enthalpy Change of Atomization (ΔH°_{at})

"The standard enthalpy change of atomization of an element is the enthalpy change involved when one mole of gaseous atoms is formed from the element, under standard conditions."

$H_{2(g)} \longrightarrow 2H_{(g)}$ $E_{H-H} = +436$ kJ mol^{-1}

$1/2H_{2(g)} \longrightarrow H_{(g)}$ $\Delta H^{\circ}_{at} = +218$ kJ mol^{-1}

(iv) Enthalpy Change of Combustion (ΔH°_{c})

The standard enthalpy change of combustion of a substance is the enthalpy change involved when one mole of the substance is completely burnt in excess of oxygen, under standard conditions.

For example, standard enthalpy of combustion ΔH° C of ethanol is -1368 kJ mol^{-1}.

$$C_2H_5OH_{(\ell)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(\ell)} \quad \Delta H^{\circ}_{c} = -1368 \text{ kJ mol}^{-1}$$

f. Explain why the lattice enthalpy of an ionic compound is typically a large negative value.

Ans. The lattice enthalpy of an ionic compound is typically a large negative value because:
It represents the energy released when gaseous ions combine to form one mole of a solid ionic crystal.
This process involves strong electrostatic attraction between oppositely charged ions. Since a large amount of energy is released during this bond formation, the lattice enthalpy is highly exothermic (negative value).

g. What factors influence the magnitude of the lattice enthalpy?

Ans. The magnitude of lattice enthalpy is mainly influenced by two key factors:

1. **Ionic Charge**
   - Greater ionic charge ⇒ Stronger electrostatic attraction between ions.
   - This leads to a more negative (larger) lattice enthalpy.

   Example:
   Lattice enthalpy of MgO (Mg^{2+} and O^{2-}) is much higher than that of NaCℓ (Na^{+} and $Cℓ^{-}$) due to higher charges.
2. **Ionic Radius (Size of Ions)**
   - Smaller ions ⇒ Ions are closer together ⇒ Stronger attraction.
   - Smaller size = more negative lattice enthalpy.

   Example:
   Lattice enthalpy of LiF is greater than that of CsF, because Li^{+} is smaller than Cs^{+}.

h. Explain why the enthalpy of hydration is always an exothermic process for gaseous ions. What are the main interactions responsible for the release of energy during hydration?

Ans. Enthalpy of Hydration: Always an exothermic process
The enthalpy of hydration is the heat released when gaseous ions dissolve in water and become surrounded by water molecules. It is always exothermic because:
When gaseous ions dissolve, the water molecules surround and stabilize the ions, leading to a decrease in the system's energy.
Main Interactions Responsible for Energy Release:

(i) **Ion-Dipole Interactions:**
The polar water molecules interact with the charged ions through their partial charges (δ^- on oxygen and δ^+ on hydrogen). This creates a stable interaction between the ion and the water molecules, releasing energy.

(ii) **Electrostatic Attraction:**
Water molecules are strongly attracted to the ions, especially smaller, highly charged ions (like Mg^{2+} or Na^{+}), which increases the energy released during hydration.

i. For the reaction $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$, identify all the bonds that need to be broken and all the bonds that need to be formed to carry out a bond energy calculation of ΔH.

Ans. To carry out a bond energy calculation for the reaction:

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$$

Bonds that need to be broken (in reactants):

1. **CH_4 (Methane):**
   4 C-H bonds (broken to form C and H atoms)

2. **O_2 (Oxygen):**
   2 O=O bonds (broken to form 2 oxygen atoms)

Bonds that need to be formed (in products):

1. **CO_2 (Carbon Dioxide):**
   2 C=O bonds (formed between carbon and oxygen)
2. **H_2O (Water):**
   2 O-H bonds in each H_2O molecule (2 molecules of H_2O, so 4 O-H bonds are formed)

To calculate ΔH we would use the bond energies (bond dissociation energies) for each of these bonds and apply the formula.

ΔH = Bonds Broken (Energy required) - Bonds Formed (Energy released)

j. For a reaction to be spontaneous, what is the required sign of the Gibbs free energy change (ΔG)? Under what conditions of enthalpy change (ΔH) and entropy change (ΔS) will a reaction always be spontaneous?

Ans. For a reaction to be spontaneous, the required sign of the Gibbs free energy change (ΔG) is:

$$\Delta G < 0$$

This means that the reaction must have a negative Gibbs free energy change for it to occur spontaneously under constant temperature and pressure.
In other words:

- $\Delta G < 0$ indicates a spontaneous reaction.
- $\Delta G > 0$ indicates a non-spontaneous reaction.
- $\Delta G = 0$ indicates a system in equilibrium.

The Gibbs free energy change (ΔG) must be negative, i.e., $\Delta G < 0$.
The relationship between ΔG, ΔH (enthalpy change), and ΔS (entropy change) is given by the equation:

$$\Delta G = \Delta H - T\Delta S$$

Where:

- ΔG = Gibbs free energy change
- ΔH = Enthalpy change
- T = Temperature (in Kelvin)
- ΔS = Entropy change

Conditions for Always Spontaneous Reaction:

1. $\Delta H < 0$ (Exothermic reaction)
2. $\Delta S > 0$ (Increase in disorder)

Explanation:

- Exothermic ($\Delta H < 0$) reactions release heat, making the system more stable.
- Increase in entropy ($\Delta S > 0$) means the system becomes more disordered, which also favours spontaneity.

These conditions ensure that ΔG will always be negative, regardless of the temperature. The negative ΔH and positive ΔS make both terms in the equation contribute to a negative value for ΔG.

k. The enthalpy of solution can be either positive or negative. Explain what a positive ΔH_{sol} and a negative ΔH_{sol} indicate about the energy changes during the dissolution process.

Ans. The enthalpy of solution (ΔH_{sol}) represents the heat change when a solute dissolves in a solvent. The sign of ΔH_{sol} gives us information about the energy changes that occur during the dissolution process.

(i) **Positive ΔH_{sol} (Endothermic Dissolution):**
- $\Delta H_{sol} > 0$ means the dissolution process is endothermic.
- Energy is absorbed from the surroundings to dissolve the solute.
- This occurs when the energy required to break the interactions between solute particles (like ionic or covalent bonds) is greater than the energy released when solvent particles interact with the solute.
- **Example:** When ammonium nitrate (NH_4NO_3) dissolves in water, it absorbs heat, making the solution feel cold.

(ii) **Negative ΔH_{sol} (Exothermic Dissolution):**
- $\Delta H_{sol} < 0$ means the dissolution process is exothermic.

- Energy is released into the surroundings as the solute dissolves.
- This occurs when the energy released during the interaction of solute particles with solvent molecules exceeds the energy needed to separate the solute particles.
- **Example:** When sodium hydroxide (NaOH) dissolves in water, heat is released, making the solution feel warm.

I. Consider two ions with similar charges but different sizes, or similar sizes but different charges. Explain how the concept of charge density can be used to predict which ion will have a more exothermic enthalpy of hydration and why.

Ans. The concept of charge density is essential for understanding which ion will have a more exothermic enthalpy of hydration.

- **Charge Density:**
  - Charge density is the charge of an ion divided by its size (radius).
  - Charge density = charge/radius.
- **Prediction of Enthalpy of Hydration:**
  - Higher charge density means stronger ion-dipole interactions between the ion and water molecules, leading to a more exothermic enthalpy of hydration (more energy released during hydration).
- **For ions with similar charges but different sizes:**
  - Smaller ions have a higher charge density because their charge is concentrated over a smaller area.
  - Smaller ions (higher charge density) will have a more exothermic enthalpy of hydration because they create stronger interactions with water molecules.
- **For ions with similar sizes but different charges:**
  - Ions with higher charges have a higher charge density, meaning they can interact more strongly with water molecules.
  - Higher charge (higher charge density) results in a more exothermic enthalpy of hydration.

DESCRIPTIVE QUESTIONS

Q.3 State and explain Hess's law. Give its two applications.

Ans. See Page No. (183)

Q.4 What is lattice energy? How does Born-Haber cycle help to calculate the lattice energy of NaCl?

Ans. See Page No. (188)

NUMERICAL PROBLEMS

Q.5 (a) When 0.400 g NaOH is dissolved in 100.0 g of water, the temperature rises from 25.00 to 26.03°C. Calculate: (i) q_{water}, (ii) ΔH for the solution process

Given Data:

Mass of NaOH (m_n) = 0.400 g
Mass of water (m) = 100.0 g
Initial temperature (T_1) = 25.00°C
Final temperature (T_2) = 26.03°C
Specific heat capacity of water (c) = 4.18 J/g°C

Step (i): Calculate q_{water} (Heat absorbed by water)

The heat absorbed by water (q_{water}) is given by:

$$q_{water} = m \cdot c \cdot \Delta T$$

Where:

$$\Delta T = T_2 - T_1 = 26.03°C - 25.00°C = 1.03°C$$

Substitute the values:

$$q_{water} = 100.0\ g \times 4.18\ J/g°C \times 1.03\ °C$$
$$q_{water} = 430.54\ J$$

So, the heat absorbed by water is 430.54 J.

Step (ii): Calculate ΔH for the solution process

The enthalpy change (ΔH) is the heat released or absorbed per mole of solute (NaOH).

Step 1: Calculate moles of NaOH

Molar mass of NaOH = 23 (Na) + 16 (O) + 1 (H) = 40 g/mol
Moles of NaOH = Mass / Molar Mass = 0.400 g/ 40 g/mol = 0.0100 mol

Step 2: Calculate ΔH

Since the temperature increased, the dissolution of NaOH is exothermic, meaning heat was released.
Therefore,

$$q_{solution} = -q_{water}$$
$$\Delta H = q_{solution} / \text{moles of NaOH} = -430.54\ J / 0.0100\ mol = -43054 J/mol$$

Convert to kJ/mol (since 1 kJ = 1000 J):

$$\Delta H = -43.05\ kJ/mol$$

So, the enthalpy change for the solution process is **–43.05 kJ/mol.**

Final Answers:

$$q_{water} = 430.54\ J$$
$$\Delta H = -43.05\ kJ/mol \text{ (exothermic)}$$

Q.6 By applying Hess's law, calculate the enthalpy change for the formation of an aqueous solution of NH_4Cl from NH_3 gas and HCl gas. The results for the various reactions are as follows.

(i) $NH_{3(g)} + aq \longrightarrow NH_{3(aq)}$ $\Delta H = -35.16\ kJ\ mol^{-1}$

(ii) $HCl_{(g)} + aq \longrightarrow HCl_{(aq)}$ $\Delta H = -72.41\ kJ\ mol^{-1}$

(iii) $NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}$ $\Delta H = -51.48\ kJ\ mol^{-1}$

Given data:

(i) $NH_{3(g)} + aq \rightarrow NH_{3(aq)}$ $\Delta H_1 = -35.16$ kJ/mol (Dissolution of NH_3 gas in water)
(ii) $HCl_{(g)} + aq \rightarrow HCl_{(aq)}$ $\Delta H_2 = -72.41$ kJ/mol (Dissolution of HCl gas in water)
(iii) $NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)}$ $\Delta H_3 = -51.48$ kJ/mol (Neutralization reaction forming NH_4Cl in solution)

To Find:

Find the enthalpy change for the overall reaction:

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(aq)}$$

$\Delta H_{overall} = ?$

Solution:

Step 1: Write the Target Reaction

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(aq)}$$

When we add all three reactions:

- The $NH_{3(aq)}$ from Reaction 1 cancels with the $NH_{3(aq)}$ in Reaction 3.
- The $HCl_{(aq)}$ from Reaction 2 cancels with the $HCl_{(aq)}$ in Reaction 3.

Thus, the net reaction is:

$$NH_{3(g)} + HCl_{(g)} + aq \rightarrow NH_4Cl_{(aq)}$$

Step 3: Add the Enthalpies

Since enthalpy is a state function, we simply add the enthalpies of the individual steps:

$$\Delta H_{overall} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Substitute the given values:

$\Delta H_{overall} = (-35.16) + (-72.41) + (-51.48) = -159.05$ kJ/mol

Q.7 Calculate the heat of formation of ethyl alcohol from the following information

(i) Heat of combustion of ethyl alcohol is $-1367\ kJ\ mol^{-1}$

(ii) Heat of formation of carbon dioxide is $-393.7\ kJ\ mol^{-1}$

(iii) Heat of formation of water is $-285.8\ kJ\ mol^{-1}$

Given Data:

1. **Heat of combustion of ethyl alcohol (C_2H_5OH):**
   $\Delta H_{comb} = -1367$ kJ/mol

2. **Heat of formation of carbon dioxide (CO_2):**
   $\Delta H_f^\circ (CO_2) = -393.7$ kJ/mol
3. **Heat of formation of water (H_2O):**
   $\Delta H_f^\circ (H_2O) = -285.8$ kJ/mol

Step 1:

Write the Combustion Reaction of Ethyl Alcohol

The combustion of C_2H_5OH (ethanol) produces CO_2 and H_2O:

$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)} \qquad \Delta H_{comb} = 1367 \text{ kJ/mol}$$

Step 2:

Express the Enthalpy of Combustion in Terms of Formation Enthalpies

The enthalpy change of a reaction can be calculated using the heats of formation of products and reactants:

$$\Delta H = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$$

For the combustion reaction:

$$\Delta H_{comb} = [2\Delta H_f^\circ (CO_2) + 3\Delta H_f^\circ (H_2O)] - [\Delta H_f^\circ (C_2H_5OH) + 3\Delta H_f^\circ (O_2)]$$

Since $O_{2(g)}$ is in its standard state, $\Delta H_f^\circ (O_2) = 0$

Substitute the known values:

$$-1367 = [2(-393.7) + 3(-285.8)] - [\Delta H_f^\circ (C_2H_5OH) + 3(0)]$$

Step 3:

Simplify the Equation

Calculate the sum of the products' enthalpies:

$$2(-393.7) + 3(-285.8) = -787.4 - 857.4 = -1644.8 \text{ kJ}$$

Now, substitute back:

$$-1367 = -1644.8 - \Delta H_f^\circ (C_2H_5OH)$$

$$\Delta H_f^\circ (C_2H_5OH) = -1644.8 + 1367 = -277.8 \text{ kJ/mol}$$

Final Answer:

The heat of formation of ethyl alcohol (C_2H_5OH) is: **-277.8 kJ/mol**

Q.8 Using the information given in the table below, calculate the lattice energy of potassium bromide.

Reactions	ΔH / kJmol^{-1}
$K_{(s)} + 1/2Br_{2(l)} \longrightarrow K^+Br^-$	−392
$K_{(s)} \longrightarrow K_{(g)}$	+90
$K_{(g)} \longrightarrow K^+_{(g)} + e^-$	+420
$1/Br_{2(l)} \longrightarrow Br_{(g)}$	+112
$Br + e^- \longrightarrow Br^-$	−342

Given Data:

Reactions	ΔH / kJmol^{-1}
Formation: $K_{(s)} + 1/2Br_{2(l)} \longrightarrow K^+Br^-$	−392
Sublimation: $K_{(s)} \longrightarrow K_{(g)}$	+90
Ionization: $K_{(g)} \longrightarrow K^+_{(g)} + e^-$	+420
Dissociation: $1/Br_{2(l)} \longrightarrow Br_{(g)}$	+112
Electron Affinity: $Br + e^- \longrightarrow Br^-$	-342

To find:

Lattice energy: $K^+ + Br^- \rightarrow KBr_{(s)} = ?$

Solution:

Born-Haber Cycle Equation:

ΔH_f = Sublimation + Ionization + Bond Dissociation + Electron Affinity + Lattice Energy

Substitute values: $-392 = 90 + 420 + 112 - 342 + U$

Add values: $-392 = 280 + U$

Solve for U: $U = -392 - 280 = -672$ kJ/mol

Final Answer:

Lattice energy of KBr = **−672 kJ/mol**

Q.9 Calculate the entropy change of the surroundings $\Delta S^\circ_{surrounding}$ for the reaction at 298K:

$$2Ca_{(s)} + O_{2(g)} \longrightarrow 2CaO_{(s)} \qquad \Delta H^\circ_{reaction} = -1270.2 \text{ kJ mol}^{-1}$$

Given Data:

- $\Delta H^\circ_{reaction} = -1270.2$ kJ/mol (exothermic)
- Temperature T = 298 K

Step 1: Understand the Key Concept

The entropy change of the surroundings (ΔH°_{surr}) is related to the heat transferred to the surroundings ($q_{surrounding}$) at constant temperature:

$$\Delta S^\circ_{surrounding} = \frac{q_{surrounding}}{T}$$

For an exothermic reaction, the system releases heat to the surroundings, so:

$$q_{surrounding} = -\Delta H^\circ_{rxn}$$

(Negative sign because the system loses heat, but the surroundings gain it.)

Step 2: Substitute the Given Values

$$\Delta H^\circ_{rxn} = -1270.2 \text{ kJ/mol},$$

The heat absorbed by the surroundings is:

$$q_{surrounding} = -(-1270.2) = +1270.2 \text{ kJ/mol}$$

(Positive sign indicates heat is added to the surroundings.)

Now, convert $q_{surrounding}$ to joules (since entropy units are J/K·mol):

$$q_{surrounding} = 1270.2 \text{ kJ/mol} \times 1000 = 1,270,200 \text{ J/mol}$$

Step 3: Calculate $\Delta S^\circ_{surrounding}$

Using the formula:

$$\Delta S^\circ_{surrounding} = \frac{q_{surrounding}}{T} = \frac{1,270,200 \text{ J/mol}}{298 \text{K}} = 4262.4$$

Q.10 For the reaction: $CaSO_{4(s)} \longrightarrow Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)}$

Calculate ΔH°, ΔS° and ΔG° at 25°C using the following data; and discuss its spontaneity.

Enthalpy of Formation:

$$\Delta H^\circ_{f(CaSO(s))} = -1432.7 \text{ kJ}, \Delta H^\circ_{f(Ca^{2+}(aq))} = -543.0 \text{kJ}, \Delta H^\circ_{f(SO_4^{2-}(aq))} = -907.5 \text{kJ}$$

[Standard entropy: $S^\circ_{(CaSO4(s))} = 106.7$ J/K, $S^\circ_{f(Ca^{2+}(aq))} = -55.2$ J/K, $S^\circ_{f(SO_4^{2-}(aq))} = +17.2$ J/K

Given Data:

Enthalpies of Formation (ΔH_f°):

- $\Delta H_f^\circ (CaSO_{4(s)}) = -1432.7$ kJ/mol
- $\Delta H_f^\circ (Ca^{2+}{}_{(aq)}) = -543.0$ kJ/mol
- $\Delta H_f^\circ (SO_4^{2-}{}_{(aq)}) = -907.5$ kJ/mol

Reaction:

$$CaSO_{4(s)} \rightarrow Ca^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Step 1: Calculate ΔH° (Enthalpy Change)

Using Hess's Law:

$$\Delta H^\circ_{reaction} = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ \text{ reactants})$$

Substitute values:

$$\Delta H^\circ_{reaction} = [\Delta H_f^\circ (Ca^{2+}) + \Delta H_f^\circ (SO_4^{2-})] - [\Delta H_f^\circ (CaSO_4)]$$
$$\Delta H^\circ_{reaction} = [(-543.0) + (-907.5)] - [-1432.7]$$
$$\Delta H^\circ_{reaction} = -1450.5 + 1432.7 = -17.8 \text{ kJ/mol}$$

(Negative sign indicates the reaction is **exothermic.**)

Step 2: Calculate ΔS° (Entropy Change)

Using standard entropies:

$$\Delta S^\circ_{reaction} = \sum S^\circ_{(products)} - \sum S^\circ_{(reactants)}$$

Substitute values:

$$\Delta S^\circ_{reaction} = [S^\circ Ca^{2+}) + S^\circ (SO_4^{2-})] - [S^\circ (CaSO_4)]$$
$$\Delta S^\circ_{reaction} = [(-55.2) + (17.2)] - [106.7]$$
$$\Delta S^\circ_{reaction} = -38.0 - 106.7 = -144.7$$

(Negative sign means the system becomes **more ordered.**)

Step 3: Calculate ΔG° (Gibbs Free Energy Change)

Using the Gibbs-Helmholtz equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S$$

Convert units for consistency:

$$\Delta H^\circ = -17.8 \text{ kJ/mol} = -17{,}800 \text{ J/mol}$$

Substitute values at T = 298 K

$$\Delta G^\circ = -17{,}800 - (298 \times -144.7)$$
$$\Delta G^\circ = -17{,}800 + 43{,}120.6 = +25{,}320.6 \text{ J/mol}$$
$$\Delta G^\circ = +25.32 \text{ kJ/mol}$$

(Positive sign means the reaction is **non-spontaneous** at 25°C.)

Step 4: Discussion on Spontaneity

- **ΔH° = −17.8 kJ/mol** (Exothermic, favorable)
- **ΔS° = −144.7 J/K·mol** (Decrease in entropy, unfavorable)
- ΔG° = +25.32 kJ/mol (Positive, non-spontaneous at 25°C)

ADDITIONAL SLOs BASED MCQs

1. **Which of the following substances have zero value for their standard enthalpy of formation?**
   A. O_3 B. H_2O C. ZnO D. None of these
2. **Calorie is equivalent to:**
   A. 4.18J B. 4.18kJ C. 0.418J D. 0.418kJ
3. **Enthalpy of neutralization of all the strong acids and strong basis has the same value due to:**
   A. The formation of salt and water B. The formation of salt
   C. The complete ionization of acids and bases D. The combination of H^+ and OH^- ions to form water
4. **Total heat content of a system is called:**
   A. Enthalpy B. Internal energy C. Heat D. State function
5. **Heat of_____ a substance is always negative:**
   A. Formation B. Combustion C. Decomposition D. Solution
6. **A balloon filled with oxygen is placed in a freezer. Identify system:**
   A. Balloon B. Oxygen C. Freezer D. All of these
7. **A bomb calorimeter is used in _____ calorimetry:**
   A. Constant volume B. Constant pressure C. Both a and b D. Constant temperature

8. **Born Haber cycle is used to determine lattice energies of:**
   A. Molecular solids B. Ionic solids C. Covalent solids D. Metallic solids
9. **Enthalpy of combustion for C is −393.5 kJ mol⁻¹**
   $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$
   $\Delta H^\circ_{combustion} = -393.5 \text{ kJmol}^{-1}$
   Enthalpy of formation of CO_2 would be:
   A. +393.5 kJ B. −393.5 kJ
   C. Zero D. Cannot be predicted form the given equation
10. **Which of the following is not a state function of a system:**
    A. Thermal energy at constant pressure B. Enthalpy
    C. Internal energy D. Work done
11. **For writing a thermochemical equation for enthalpy of combustion of an element requires:**
    A. 1 mole of element as reactant B. 1 mole of oxide of element as product
    C. Standard states of all the substances D. Balanced equation of 1 mole of element
12. **For the reaction** $NaCl_{(s)} \xrightarrow{water} Na^+_{aq} + Cl^-_{aq}$ **the change in enthalpy is called:**
    A. Heat of reaction B. Heat of formation C. Heat of combustion D. Heat of solution
13. **Which one of the following equations correctly defines the enthalpy change of formation of carbon monoxide?**
    A. $C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}$ B. $C_{(s)} + O_{(g)} \longrightarrow CO_{(g)}$
    C. $C_{(s)} + CO_{2(g)} \longrightarrow 2CO_{(g)}$ D. $C_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}$
14. **ΔH will be given a negative sign in:**
    A. Exothermic reactions B. Dissociation reactions
    C. Decomposition reactions D. Endothermic reactions
15. **Hess's law may be represented mathematically as:**
    A. $\Sigma\Delta H \neq 0$ B. $\Sigma\Delta G > 0$ C. $\Sigma\Delta H = 0$ D. $\Sigma\Delta H < 0$

Answer Key with Explanations

Q.#	Ans.	Explanations
1.	C	The standard enthalpy of formation of an element in molecular form is zero. Ozone (O_3) is molecular form of oxygen so its standard enthalpy of formation is zero.
2.	A	1 Calorie = 4.184 Joules 1J = 0.2390 cal
3.	D	Enthalpy of neutralization is merely the heat of formation of one mole of liquid water from its ionic components. $H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)} \quad \Delta H^\circ_n = -57.4 \text{ kJ mol}^{-1}$ Enthalpy of neutralization for any strong acid with a strong base is approximately the same i.e. −57.4 kJ mole⁻¹.
4.	A	The sum of internal energy (E) and the product of pressure and volume (PV) is called enthalpy of the system." $H = E + PV$ • Enthalpy is a state function. • Enthalpy is measured in "Joules."
5.	B	All combustion reactions are exothermic in nature so enthalpy of combustion is always negative.
6.	B	Oxygen is the system while balloon, freezer etc are surroundings.

7.	A	Constant volume calorimetry is used for accurate determination of the enthalpy of combustion for food, fuel and other compounds. A bomb calorimeter is used for this purpose. Chemical reaction in a bomb calorimeter takes place under constant volume conditions.
8.	B	Born Haber cycle is used to calculate lattice energy of binary ionic compounds like M^+X^-.
9.	B	The given reaction is combustion of carbon as well as formation of CO_2 from its elements. So $-393.5\ kJ\ mol^{-1}$ is not only enthalpy of combustion of carbon but also enthalpy of formation of CO_2.
10.	D	Work done depends upon path adopted to bring about change, so it is not state function. Similarly, heat, emf of cell are also not state functions.
11.	D	For writing thermochemical equation for enthalpy of combustion: (i) Write 1 mole of the element of compound and oxygen as reactant. (ii) Write oxides of the given element or oxides of elements present in the compound as products. (iii) Show standard states of all the substances. (iv) Finally, balance the atoms.
12.	D	1 mol of ionic solid is completely dissolved in minimum amount of H_2O so energy change is called enthalpy of solution.
13.	A	According to definition 1mol of CO is being formed from element in their standard state.
14.	A	For exothermic reaction, enthalpy of reaction is shown by negative sign.
15.	C	Definition of Hess's law, summation of enthalpies of cyclic process must be equal to zero.

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Define electron affinity. Give example.

Ans. Electron Affinity (ΔH°_{ea})

The first electron affinity is the enthalpy change involved when 1 mole of electrons is added to 1 mole of gaseous atoms to form 1 mole of gaseous uni-negative ions under standard conditions.

Example:

Electron affinity of chlorine atom.

$$Cl_{(g)} + e^- \longrightarrow Cl^- \qquad \Delta H = -348.8\ kJ\ mol^{-1}$$

Since, energy is released, so first electron affinity carries negative sign.

Q.2 What is calorie content?

Ans. Calorie content: The calorie content of food is a measure of the energy **'released'** when the food is completely consumed in the body.

- This energy is typically expressed in units of kilocalories (k cal) or joules (J).

Q.3 What is meant by lattice energy? Give example.

Ans. Lattice Energy (ΔH_{latt})

"The lattice energy of an ionic crystal is the enthalpy change involved when one mole of the ionic compound is formed from gaseous ions under standard conditions."

Example:

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H = -747 kJ mol^{-1}$$

Q.4 What do you know about entropy?

Ans. Entropy is a measure of the number of ways energy can be distributed within a system at a specific temperature.

(OR)

Entropy can also be thought of as a measure of the randomness or disorder of a system.

- When the energy is distributed in more ways, a system is more stable.
- The higher the randomness or disorder, the greater the entropy of the system.

Q.5 The sign of change in free energy (ΔG) of a process can be used to predict the spontaneity of that process. How?

Ans. The sign of change in free energy (ΔG) of a process can be used to predict the spontaneity of that process, when;

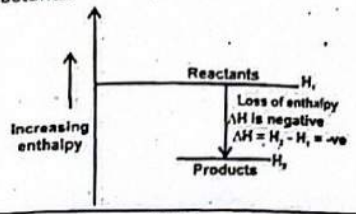
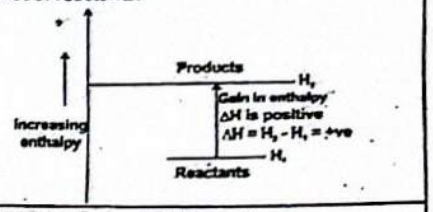
(i) If $\Delta G < 0$ (–ve), the given process may occur spontaneously

(ii) If $\Delta G > 0$ (+ve), the indicated process cannot occur spontaneously; instead, the reverse of it may occur.

(iii) If $\Delta G = 0$, neither the indicated process nor reverse of it can occur spontaneously. The system is in a state of equilibrium

Q.6 Differentiate between endothermic and exothermic reactions.

Ans.

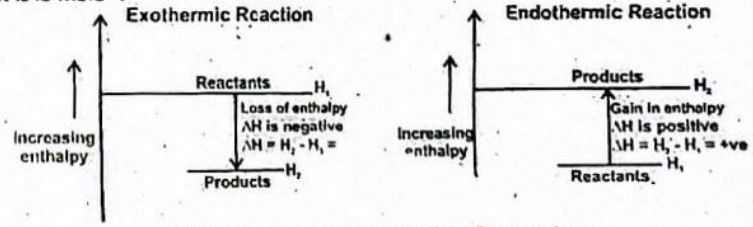
Exothermic Reaction	Endothermic Reaction
1. In this reaction, heat is evolved from the system.	1. In this reaction, heat is absorbed by the system.
2. The heat contents of product is less than that of reactants. 	2. The heat contents of products is more than that of reactants. 
3. Enthalpy change (ΔH) is negative.	3. Enthalpy change (ΔH) is positive.
4. The number of bonds formed is greater than the bonds breakage during a reaction.	4. The number of bonds breakage is greater than the bonds formation during a reaction.
5. The temperature of the system rises and eventually heat flows from system to surroundings.	5. The temperature of the system falls and eventually heat flows from surroundings to system.
6. Mostly the spontaneous reactions are exothermic.	6. Mostly the non-spontaneous reactions are endothermic.
Example: $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393.7\ kJ\ mol^{-1}$	Example: $N_{2(g)} + O_{2(g)} \longrightarrow NO_{(g)}$ $\Delta H = 180\ kJ\ mol^{-1}$

Q.7 Define: (i) Standard Enthalpy of reaction with one example.
(ii) Enthalpy of a system with an example.

Ans. (i) Standard Enthalpy of a Reaction:

"The enthalpy change which occurs when the certain number of moles of reactants react together completely to give the products under standard conditions i.e. 25°C (298K) and one atmosphere pressure is called standard enthalpy of reaction." It is represented by ΔH°. All the reactants and products must be in their standard physical states.

- Its unit is kJ $mole^{-1}$.



Enthalpy changes in thermochemical reactions.

Example:

$H_{2(g)} + 1/2\ O_{2(g)} \longrightarrow H_2O_{(l)}$ $\quad \Delta H^\circ = -285.8\ kJ\ mol^{-1}$

$-285.8 kJ\ mol^{-1}$ is standard enthalpy of reaction.

(ii) Enthalpy of the system:

"The sum of internal energy (E) and the product of pressure and volume (PV) is called enthalpy of the sy

Formula: $H = E + PV$

Q.8 Define enthalpy of formation (ΔH_f°). Give two example.

Ans. Enthalpy of Formation (ΔH_f°):

"The amount of heat evolved or absorbed when one mole of compound is formed from its element standard conditions of temperature and pressure is called standard enthalpy of formation (ΔH_f°) of a compo

- All the substances involved are in their standard physical states.
- The reaction is carried at standard conditions i.e. at 25oC (298K) and one atmospheric pressure.

Examples: (i) $Mg_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow MgO_{(s)}$ $\quad \Delta H_f^\circ = -692\ kJ\ mol^{-1}$

(ii) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta H_f^\circ = -393.7\ kJ\ mol^{-1}$

Q.9 State with one example enthalpy of combustion.

Ans. Enthalpy of Combustion:

"The amount of heat evolved when one mole of a substance is completely burnt in excess of oxygen standard conditions is called standard enthalpy of combustion of a substance (ΔH_c°)."

- Its unit is $kJ\ mol^{-1}$.

Example:

Standard enthalpy of ethanol is $-1368\ kJ\ mol^{-1}$.

$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\quad \Delta H_c^\circ = -1368\ kJ\ mol^{-1}$

Enthalpy of Solution:

"The amount of heat absorbed or evolved when one mole of a substance is dissolved in so much wa that further dilution results in no detectable heat change is called standard enthalpy of solution (ΔH_s)

- Its unit is $kJ\ mol^{-1}$.

Examples: (i) Enthalpy of a solution of $NH_4Cl = +16.2\ kJ\ mol^{-1}$.

(ii) Enthalpy of solution of $Na_2CO_3 = -25.0\ kJ\ mol^{-1}$.

Q.10 Define enthalpy of neutralization. Why is enthalpy of neutralization of strong acid and strong ba always $-57.5\ kJ\ mol^{-1}$?

Ans. Enthalpy of Neutralization:

Enthalpy of neutralization is the amount of heat evolved when one mole of hydrogen ions H^+ from an react with one mole of hydroxide OH^- ions from a base to form one mole of water.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)} \quad \Delta H = -57.4\ kJ\ mol^{-1}$$

All strong acids and bases ionize completely in aqueous solutions providing equal number of H^+ an ions depending upon concentration of solutions.

So a net result of neutralization is just the formation of water from its ionic components.

For all strong acids and bases with equimolar concentrations of ions, the value of heat of neutraliza same i.e., $-57.4\ kJ\ mol^{-1}$ or $13.2\ Kcal\ mol^{-1}$.

Q.11 Define the terms standard enthalpy of neutralization and standard enthalpy of atomization.

Ans. Enthalpy of Neutralization:

"The amount of heat evolved when one mole of hydrogen ions (H^+) from an acid, react with one mo hydroxide ions (OH^-) from a base to form one mole of water under standard conditions is called stan enthalpy of neutralization (ΔH_n°)."

Example:

A strong acid HCl and a strong base NaOH ionize completely in dilute solutions as follows:

$$HCl_{(aq)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

$$NaOH_{(aq)} \rightleftharpoons Na^+_{(aq)} + OH^-_{(aq)}$$

When these solutions are mixed together during the process of neutralization, the only change that actually occurs is the formation of water molecules leaving the sodium ions and the chloride ions as free ions in solution. Thus, enthalpy of neutralization is merely the heat of formation of one mole of liquid water from its ionic components.

$$H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)}$$

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)} \quad \Delta H_n^\circ = -57.4\ kJ\ mol^{-1}$$

Enthalpy of neutralization for any strong acid with a strong base is approximately the same. i.e. $-57.4\ kJ\ mole^{-1}$.

Enthalpy of Atomization:

"The amount of heat absorbed when one mole of gaseous atoms is formed from the element under standard conditions is called standard enthalpy of atomization of that element (ΔH_{at}°)."

- Its unit is $kJ\ mol^{-1}$.

Example: The standard enthalpy of atomization of hydrogen is

$\frac{1}{2}H_{2(g)} \longrightarrow H_{(g)}$ $\quad \Delta H_{at}^\circ = 218\ kJ\ mol^{-1}$

A wide range of experimental techniques are available for determining enthalpies of atomization of elements.

Q.12 Define Hess's law of constant heat summation.

Ans. Hess's Law:

"If a chemical change takes place by several different routes, the overall energy change is the same, regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same."

Mathematical Form: $\Sigma\Delta H(cycle) = 0$

Examples:

(i) Formation of Na_2CO_3:

Single Step Process:

$2NaOH_{(aq)} + CO_{2(g)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$ $\quad \Delta H = -89.08\ kJ$

Two Steps Process:

$NaOH_{(aq)} + CO_{2(g)} \longrightarrow NaHCO_{3(aq)}$ $\quad \Delta H_1 = -48.06\ kJ$

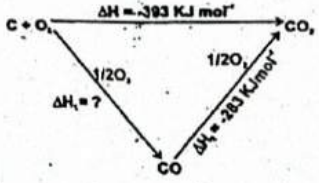
$NaHCO_{3(aq)} + NaOH_{(aq)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$ $\quad \Delta H_2 = -41.02\ kJ$

According to Hess's law $\Delta H = \Delta H_1 + \Delta H_2$

Putting the values of ΔH, ΔH_1 and ΔH_2 in the equation.

$-89.08 = -48.06 - 41.02$

$-89.08 = -89.08\ kJ$



(ii) Enthalpy of Formation of CO:

Single Step Process:

$C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta H_{(graphite)} = -393.7\ kJ\ mol^{-1}$

Two Steps Process:

$C_{(graphite)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}$ $\quad \Delta H\ (CO) = ?$

$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta H_2(CO_2) = -283\ kJ\ mol^{-1}$

According to Hess's law

$\Delta H = \Delta H_1 + \Delta H_2$

$\Delta H_1 = \Delta H_2 - \Delta H$

$= -393 - (-283)$

$= -110\ kJ\ mol^{-1}$

So, the enthalpy change for the formation of $CO_{(g)} = -110.0\ kJ\ mol^{-1}$

Q.13 Differentiate between Atomization energy and Lattice energy.

Ans. Atomization Energy:

The energy required to convert a substance in atomic state is called atomization energy. It is always endothermic in nature.

$$\frac{1}{2}H_{2(g)} \longrightarrow H_{(g)} \qquad \Delta H^\circ_{at} = 218\ kJ\ mol^{-1}$$

Lattice Energy:

"Enthalpy of formation of one mole of crystalline ionic compound from gaseous ions under standard conditions is called lattice energy."

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H_{latt} = -787\ kJ\ mol^{-1}$$

OR

"Energy required to break one mole of crystalline ionic compound into its gaseous ions at standard conditions is called lattice energy."

$$NaCl_{(s)} \longrightarrow Na^+_{(g)} + Cl^-_{(g)} \qquad \Delta H = +787\ kJ\ mol^{-1}$$

Q.14 Define heat capacity of a body. Give its mathematical expressions.

Ans. Heat Capacity: "The product of mass and specific heat of water is called heat capacity of the whole system." It is represented by 'c'.

$$c = m \times s$$

SELF-ASSESSMENT Chapter # 06

Total Mark: 30

Q.1 Encircle the correct option. **(1 × 6 = 6)**

(i) **Which of the following reactions is exothermic?**
A. Photosynthesis B. Electrolysis of water C. Combustion of methane D. Melting of ice

(ii) **The enthalpy change for a reaction depends on:**
A. Pathway taken from reactants to products
B. Presence of a catalyst
C. Initial and final states of the reactants and products
D. Rate of the reaction

(iii) **Which statement about bond energy is true?**
A. All bond energies are exact
B. Bond energy is always negative
C. Some bond energies are average values
D. Bond energy equals entropy change

(iv) **Which of the following processes would typically result in an increase in 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

(v) **For a reaction to occur spontaneously,**
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.

(vi) **The term "standard conditions" means:**
A. 273 K and 2 atm B. 100°C and 1 mol C. 298 K and 1 atm D. 298 K and 760 mmHg

Q.2 Write short answers of the following questions. **(2 × 8 = 16)**

(i) Define Standard enthalpy of atomization.
(ii) Explain why energy is released when new bonds are formed.
(iii) How does ionic radius affect the enthalpy change of hydration?
(iv) Write down the formula for calculating heat using mass, specific heat capacity, and temperature change.
(v) Differentiate clearly between entropy (S) and Gibbs free energy (G).
(vi) What factors influence the magnitude of the lattice enthalpy?
(vii) The enthalpy of solution can be either positive or negative. Explain what a positive ΔH_{sol} and a negative ΔH_{sol} indicate about the energy changes during the dissolution process.
(viii) How the calorie value of food is related to enthalpy change?

Q.3 Extensive Questions. **(2 × 4 = 8)**

(a) State and explain Hess's law. Give its two applications.
(b) When 0.400 g NaOH is dissolved in 100.0 g of water, the temperature rises from 25.00 to 26.03°C. Calculate: (i) q_{water}, (ii) ΔH for the solution process

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Chapter 07

REACTION KINETICS

Student Learning Outcomes

After studying this chapter, students will be able to:

- Explain the rate of reaction, and rate constant. **(Understanding)**
- Use experimental data to calculate the rate of a chemical reaction. **(Application)**
- Use the Boltzmann distribution curve to explain the effect of temperature on the rate of a reaction. **(Understanding)**
- Describe the effect of temperature change on the rate constant and rate of reaction. **(Understanding)**
- Explain the concept of activation energy and its role in chemical reactions. **(Understanding)**
- Explain the concept of catalyst and how they increase the rate of a reaction by lowering the activation energy. **(Understanding)**
- Interpret reaction pathway diagrams, including in the presence and absence of catalysts. **(Application)**
- Use rate equations, including orders of reaction and rate constant. **(Application)**
- Calculate the numerical value of a rate constant using the initial rates and half-life method. **(Application)**
- Suggest a reaction mechanism that is consistent with a given rate equation and rate determining step. **(Understanding)**
- Explain the relationship between Gibbs free energy change, ΔG° and the feasibility of a reaction. **(Understanding)**

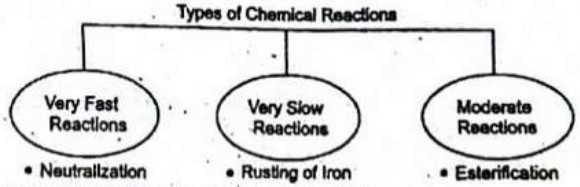
It is a common observation that rates of different chemical reactions differ greatly for example, the reaction of $NaCl$ with $AgNO_3$ is very fast. The hydrolysis of ester proceeds at a moderate rate. Whereas, rusting of iron is a slow process.

➢ **Reaction Kinetics:**

"The branch of chemistry which deals with rates of chemical reactions, factors that affect the rates of chemical reactions and the mechanisms of reactions is called reaction kinetics."

➢ **Chemical Reaction:**

"The breaking of pre-existing bonds and the formation of new bonds is called chemical change or chemical reaction."



Reaction kinetics is the study of the rates of chemical reactions.

➢ **Domain of Reaction Kinetics:**

It includes a variety of experimental methods for measuring reaction rates, orders and mechanisms of reactions.



An explosion is a swift reaction that happens within a fraction of a second, the rusting of iron is a slow process that may take days or months. The rates of reactions occurring during the explosion are enormous.

The rates of reactions and their control are often important in industry. They might be the deciding factors that determine whether a certain chemical reaction may be used economically or not. Many factors influence the rate of a chemical reaction. It is important to discover the conditions under which the reaction will proceed most economically.

COLLISION THEORY

Collision theory explains how reactions occur.

Main Postulates of Collision Theory

(I) According to this theory, for a chemical reaction to take place, the particles atoms, ions or molecules of reactants must form a homogeneous mixture and collide with one another. These collisions may be effective or ineffective depending upon the energy of the colliding particles. When these collisions are effective, they give rise to the products, otherwise the colliding particles just bounce back.

Rack Your Mind!

1. What conditions must be met for a collision to be effective according to collision theory?

(II) The effective collisions can take place only when the colliding particles possess certain amount of energy and they approach each other with the proper orientation.

Activation Energy: The minimum amount of energy, required for an effective collision between the reacting species, is called activation energy. Most of the reactions are slow, showing that all the collisions are not equally effective.

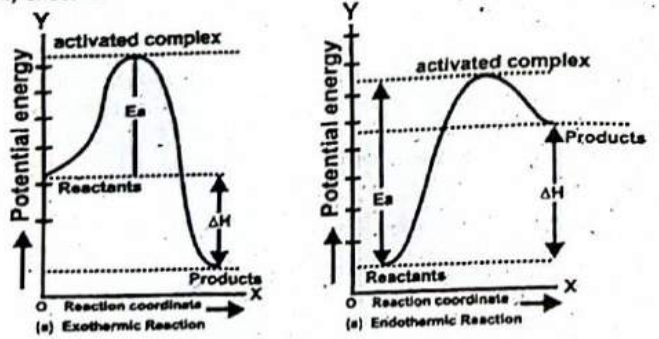


Figure: A graph between path of reaction and the potential energy of the reaction

It is important to note that the process can be understood with the help of a graph between the path of reaction and the potential energy of the reacting molecules. If the collision is effective, then the molecules flying apart are chemically different otherwise the same molecules just bounce back. The reactants reach the peak of the curve to form the activated complex. Only, the colliding molecules with proper activation energy, will be able to climb up the hill and give the products.

QUICK CHECK 7.1

a) What role does the activation energy play in chemical reactions?

Ans. Role of Activation Energy in Chemical Reactions

Activation energy (E_a) is the minimum energy required for reactant molecules to undergo a successful collision and form products. It plays three key roles:

1. Determines Reaction Feasibility
   - Only molecules with energy ≥ E_a can overcome the energy barrier and react.
   - Example: Combustion of paper requires heat (E_a) to start, even though it's exothermic.
2. Controls Reaction Rate
   - Higher E_a → Fewer molecules have enough energy → Slower reaction.
   - Lower E_a → More molecules can react → Faster reaction.
3. Explains Temperature Dependence
   - Increasing temperature raises the fraction of molecules with $E \geq E_a$ (per the Boltzmann distribution), speeding up reactions.
   - Catalysts lower E_a to accelerate reactions (e.g., enzymes in biology).
   - Explosions occur when E_a is very low (rapid release of energy).

Equation (Arrhenius):

$$k = Ae^{-Ea/RT}$$

Where:

- k = Rate constant
- A = Frequency factor (collision/orientation)
- R = Gas constant
- T_a = Temperature

In short: Activation energy is the "gatekeeper" of chemical reactions.

b) How does the activation energy affect the rate of reaction?

Ans. Effect of Activation Energy on Reaction Rate

Activation energy (E_a) directly controls how fast a reaction proceeds by determining the fraction of molecules with enough energy to react. Here's how:

1. Energy Barrier:
   - Only molecules with kinetic energy ≥ E_a can overcome the barrier and form products.
2. Boltzmann Distribution:
   - At a given temperature, fewer molecules have energy ≥ E_a if E_a is high → slower reaction.
   - Lowering E_a (e.g., with a catalyst) increases the fraction of "successful" collisions → faster reaction.
3. Arrhenius Equation:

$$\text{Rate} \propto e^{-Ea/RT}$$

   - Higher E_a → Exponential decrease in rate.
   - Lower E_a → Exponential increase in rate.

Example:

- Combustion (low E_a): Fast at room temperature.
- Diamond → Graphite (high E_a): Extremely slow (takes billions of years).

RATE OF REACTION

During a chemical reaction, reactants are converted into products. So, the concentration of the products increases with the corresponding decrease in the concentration of the reactants as they are being consumed.

Definition:

"The rate of a reaction is defined as the change in the concentration of a reactant or a product divided by the time taken for the change."

Formula:

$$\text{Rate of reaction} = \frac{\text{change in concentration of the substance}}{\text{time taken for the change}}$$

$$\text{Rate of reaction} = \frac{\Delta x}{\Delta t}$$

Where Δx is a very small change in the concentration of a reactant or a product in a very small time interval Δt.

Rock Your Mind!

2. If the concentration of HCL decreases from 1.0 mol/L to 0.6 mol/L in 20 seconds, what is the rate of reaction?
A) 0.02 mol/L·s B) 0.04 mol/L·s
C) 0.06 mol/L·s D) 0.08 mol/L·s

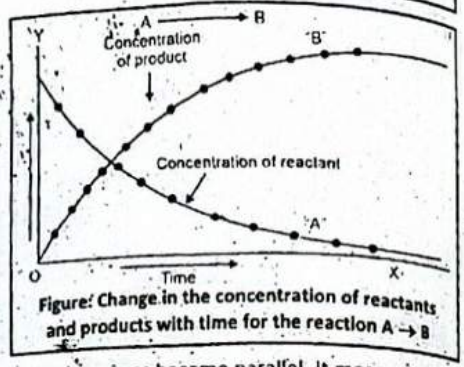


Figure: Change in the concentration of reactants and products with time for the reaction A → B

➢ **Explanation with the Help of Graph:**

The situation is explained graphically in Figure for the reactant A which is changing irreversibly to the product B.

$$A \longrightarrow B$$

The slope of the graph for the reactant or the product is steepest at the beginning. This shows a rapid decrease in the concentration of the reactant and consequently, a rapid increase in the concentration of the product. As the reaction proceeds, the slope becomes less steep indicating that the reaction is slowing down with time, ultimately both the curves become parallel. It means that the rate of a reaction is changing every moment. This is the stage of completion of reaction.

➢ **Units of Reaction Rate:**

The rate of reaction has the units of concentration divided by time. Usually, the concentration is expressed in mol dm^{-3} and the time in second, thus the units for the reaction rate are mol dm^{-3} s^{-1}.

$$\text{Rate of reaction} = \frac{\text{mol.dm}}{\text{seconds}} = \text{mol.dm}^{-3}\text{s}^{-1}$$

➢ **Units for Slow Reactions:**

For a slow reaction the units may be mol dm^{-3} min^{-1} or even mol dm^{-3} h^{-1}. For a gas phase reaction, units of pressure are used in the place of molar concentrations.

➢ **Rate of General Reaction:**

The rate of a general reaction, A → B, can be expressed in terms of rate of disappearance of the reactant A or the rate of appearance of the product B mathematically, where [A] and [B] are the concentrations of A and B, respectively.

$$\text{Rate of reaction} = -\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}$$

- The negative sign with indicates a decrease in the concentration of the reactant A.
- Since the concentration of product increases with time, the sign in rate expression involving the change of concentration of product is positive.

Instantaneous and Average Rate

- **Instantaneous Rate:** The rate at any one instant during the interval is called the instantaneous rate.
- **Average Rate:** The average rate of reaction is defined as, "The rate of reaction between two specific time intervals or the rate over a time period". The average rate and instantaneous rate are equal for only one instant in any time interval.

- At first, the instantaneous rate is higher than the average rate.
- At the end of the interval the instantaneous rate becomes lower than the average rate.

Differences Between Instantaneous Rate And Average Rate

Instantaneous rate	Average rate
• The rate at any one instant during the interval is called the instantaneous rate.	• The rate of reaction between two specific time intervals is called average rate.
• Instantaneous rate $= \frac{dx}{dt}$	• Average rate $= \frac{\Delta x}{\Delta t}$
• At first, the instantaneous rate is higher than the average rate.	• At the end, average rate is higher than instantaneous rate.

Sample Problem 7.1

The reaction for the formation of ammonia in Haber process is:

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

i. Calculate the instantaneous rate after 1.0 min

ii. What is the average rate of production of ammonia for the system, between 1.0 and 4.0 minutes?

Solution:

The instantaneous rate at 1.0 min can be calculated as:

$$\text{Instantaneous Rate} = \frac{\Delta C}{\Delta t} = \frac{2.7\ \text{mol·dm}^{-3}}{1\ \text{min}} = 2.7\ \text{mol·dm}^{-3}\ \text{min}^{-1}$$

If the concentration of ammonia is 3.5 mol dm^{-3} after 1.0 min and 6.2 mol.dm^{-3} after 4.0 minutes?

Solution:

$$\Delta C = \Delta[NH_3] = (6.2 - 3.5)\text{mol.dm}^{-3}; \quad \Delta c = 2.7\ \text{mol.dm}^{-3}$$

$$\Delta t = (4.0 - 1.0);\ \Delta t = 3.0\ \text{min}$$

$$\text{Rate of formation of } NH_3 = \frac{\Delta C}{\Delta t} = \frac{\Delta[NH_3]}{\Delta t} = \frac{2.7\ \text{mol.dm}^{-3}}{3\ \text{min}} = 0.90\ \text{mol dm}^{-3}\text{min}^{-1}$$

The rate of production of NH_3 gas over the given time interval is 0.90 mol dm^3 min^{-1}.

QUICK CHECK 7.2

The reaction of hydrogen and iodine to make hydrogen iodide at a particular temperature, $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$ was studied at various times. At 100.0 s after the start of the reaction, the iodine concentration had fallen from 0.010 mol dm^{-3} to 0.0080 mol dm^{-3}. What is the average rate of reaction during this period?

Given Data:

Reaction:

$$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$$

- Initial $[I_2]$ (at t = 0 s): 0.010 mol dm^{-3}
- Final $[I_2]$ (at t = 100.0 s): 0.0080 mol dm^{-3}
- Time interval (Δt): 100.0 s

Step 1: Calculate $\Delta[I_2]$ (Change in Concentration)

- $\Delta[I_2] = [I_2]_{final} - [I_2]_{initial} = 0.0080 - 0.010 = -0.0020\ \text{mol dm}^{-3}$

Step 2: Average Rate of Reaction (w.r.t. I_2)

Average rate $= -\Delta[I_2]/\Delta t$

$= -(-0.0020\ \text{mol dm}^{-3}/100.0\ \text{s})$

$= +2.0\times10^{-5}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

The average rate of reaction during this period is: 2.0×10^{-5} mol dm^{-3} s^{-1}

Measuring the Rate of a Chemical Reaction

The measurement of rate of a chemical reaction involves the determination of the concentration of reactants or products at regular time intervals as the reaction progresses.

Graph of Concentration Vs Time

To determine the rate of reaction for a given length of time, a graph is plotted between time on x -axis and concentration of a reactant on y-axis, whereby a curve is obtained.

Decomposition of HI:

To illustrate it, let us investigate the decomposition of HI to H_2 and I_2 at 50°C. By using the data, a graph is plotted as shown in Fig. The graph is between time on x-axis and concentration of HI in $mol dm^{-3}$ on y-axis. Since HI is a reactant, so it is a falling curve. The steepness of the concentration-time curve reflects the progress of reaction. Greater the slope of curve near the start of reaction, greater is the rate of reaction.

Table: Change in concentration of HI with regular intervals

$$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$$

Concentration of HI(mol dm^{-3})	Time (s)
0.100	0
0.0716	50
0.0558	100
0.0457	150
0.0387	200
0.0336	250
0.0296	300

In order to measure the rate of reaction, draw a tangent say, at 100 seconds, on the curve and measure the slope of that tangent. The slope of the tangent is the rate of reaction at that point i.e., after 100 seconds. A right-angled triangle ABC is completed with a tangent as hypotenuse. Figure shows that in 100 sec, the change in concentration is 0.04 $mol dm^{-3}$.

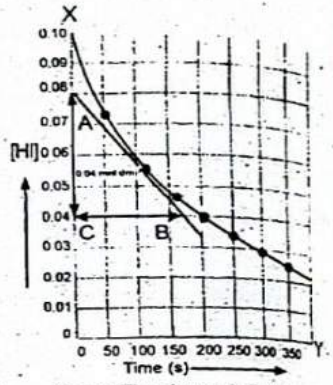


Figure: The change in the HI concentration with time to the reaction $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$ at 508°C

Rate Calculation Formula:

The rate is then calculated by using the following expression.

$$\text{Rate of reaction} = \frac{\Delta C}{\Delta T}$$

$$\text{Rate} = \frac{0.04\ mol dm^{-3}}{100\ sec} = 4 \times 10^{-4}\ mol dm^{-3} s^{-1}$$

This value of rate means that the concentration of HI is decreasing by 2.5 moles per dm^{-3} every second during the given interval.

If we plot a graph between time on x -axis and concentration of any of the products i.e., H_2 or I_2, then a rising curve is obtained. The value of the tangent at 100 seconds will give the same value of rate of reaction as 4×10^{-4} $mol dm^{-3} s^{-1}$.

QUICK CHECK 7.3

a) Plot the data in Table 7.1 for HI in your noe book.

Ans. There is no relevant data available in 7.1.

b) Calculate the rate after 300 sec (when the concentration is 0.03 $mol dm^{-3}$) by drawing a tangent.

Ans. Calculating Reaction Rate at 300 sec Using a Tangent

Given:

- At 300 sec, concentration of reactant = 0.03 mol dm^{-3}.
- Goal: Find the instantaneous rate at this point by drawing a tangent to the concentration-time curve.

Steps:

1. Plot the Graph

- X-axis: Time (sec)
- Y-axis: Concentration (mol dm^{-3})
- Mark the point (300 sec, 0.03 mol dm^{-3}) on the curve.

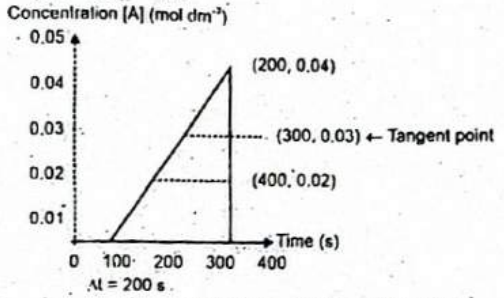
2. Draw the Tangent

- At t = 300 sec, sketch a straight line that *just touches* the curve (no crossing).

3. Calculate Slope (Rate)

- Choose two points on the tangent line (e.g., (200 sec, 0.04) and (400 sec, 0.02)).
- Slope (rate)

$$\text{Rate} = -\frac{\Delta[\text{Conc.}]}{\Delta\text{Time}} = -\frac{(0.02 - 0.04)}{(400 - 200)} = \frac{0.02}{200} = 1.0 \times 10^{-4}\ mol dm^{-3} s^{-1}$$



c) Use the same method to calculate the rate of reaction at HI concentrations of 0.10 $mol dm^{-3}$, 0.050 $mol dm^{-3}$ and 0.02 $mol dm^{-3}$.

Ans.

1. General Approach

For each HI concentration:

- Locate the point on the concentration-time curve.
- Draw a tangent at that point.
- Calculate the slope of the tangent ($\Delta[HI]/\Delta t$).

Since the exact curve isn't provided, we'll assume typical behaviour for the reaction:

$$H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$$

- HI formation rate is twice the I_2 consumption rate (stoichiometry).

2. Rate Calculations

(a) At [HI] = 0.10 mol dm^{-3}

Tangent points (example):

- (150 s, 0.08 mol dm^{-3})
- (250 s, 0.12 mol dm^{-3})

Slope (rate of HI formation):

$$\text{Rate} = \frac{\Delta[HI]}{\Delta t} = \frac{0.12 - 0.08}{250 - 150} = \frac{0.04}{100} = 4.0 \times 10^{-4}\ mol dm^{-3} s^{-1}$$

(b) At [HI] = 0.050 mol dm^{-3}

Tangent points (example):

- (100 s, 0.03 mol dm^{-3})
- (200 s, 0.07 mol dm^{-3})

Slope:

$$\text{Rate} = \frac{0.07 - 0.03}{200 - 100} = \frac{0.04}{100} = 4.0 \times 10^{-4}\ mol dm^{-3} s^{-1}$$

(c) At [HI] = 0.02 mol dm^{-3}

Tangent points (example):

- (50 s, 0.00 mol dm^{-3})
- (150 s, 0.04 mol dm^{-3})

Slope:

$$\text{Rate} = \frac{0.04 - 0.00}{150 - 50} = \frac{0.04}{100} = 4.0 \times 10^{-4} \text{ mol dm}^{-3}\text{s}^{-1}$$

3. Observations
   - Constant rate? The examples assume a linear concentration-time curve (constant rate).
   - Real-world cases: Rates typically decrease over time as reactants deplete. If the curve is nonlinear:
   - Early stage (low [HI]): Faster rate (e.g., 6.0×10^{-4}).
   - Late stage (high [HI]): Slower rate (e.g., 2.0×10^{-4}).
4. Key Notes
   - Units: Always in mol dm^{-3} s^{-1}.
   - Stoichiometry: For I_2 consumption, divide HI rates by 2.
   - Assumptions: Actual rates depend on experimental data.

Final Answers:

- At [HI] = 0.10 mol dm^{-3}: 4.0×10^{-4} mol dm^{-3} s^{-1}
- At [HI] = 0.050 mol dm^{-3}: 4.0×10^{-4} mol dm^{-3} s^{-1}
- At [HI] = 0.02 mol dm^{-3}: 4.0×10^{-4} mol dm^{-3} s^{-1}

d) What do you deduce about the rate of the reaction with time from these calculations?

Ans. From these calculations, we can deduce the following about the reaction rate over time:

1. Constant Rate (Linear Concentration-Time Curve)

   If the rate is the same (4.0×10^{-4} mol dm^{-3} s^{-1}) at all concentrations (0.02, 0.05, and 0.10 mol dm^{-3}), this suggests:
   - Zero-order kinetics with respect to HI (rate is independent of [HI]).
   - The reaction does not slow down as products accumulate or reactants deplete.
2. Practical Implications

   Likely controlled by external factors:
   - Example: A catalyst surface is saturated (e.g., $H_2 + I_2$ on platinum), where the rate depends only on catalyst sites, not concentrations.
   - Uncommon for elementary reactions: Most reactions slow over time due to fewer reactant collisions.
3. If Rates Were Different (Nonlinear Curve)

   In real-world cases (nonlinear [HI] vs. time):
   - Decreasing rate over time: Indicates first/second-order kinetics (rate depends on [reactants]).
   - Early stage (low [HI]): Faster rate (more reactants).
   - Late stage (high [HI]): Slower rate (reactants deplete).

   The constant rate here implies a zero-order mechanism for HI formation under these conditions.

e) At which concentration, the rate is highest, and lowest?

Ans. Highest and Lowest Reaction Rates –

From the given calculations (assuming a linear concentration-time curve):

- Rate is constant (4.0×10^{-4} mol dm^{-3} s^{-1}) at all [HI] (0.02, 0.05, 0.10 mol dm^{-3}).
- No difference in rate—neither highest nor lowest.

If the Curve is Nonlinear (Typical Behavior):

1. Highest Rate:
   - At low [HI] (e.g., 0.02 mol dm^{-3}) early in the reaction.
   - Reactants (H_2 and I_2) are abundant → more frequent collisions.

2. Lowest Rate:
   - At high [HI] (e.g., 0.10 mol dm^{-3}) later in the reaction.
   - Reactants are depleted → fewer collisions.

Key Idea:

- For non-zero-order reactions, rate decreases over time as reactants are consumed.
- The example assumes zero-order kinetics (rate = constant), which is rare unless conditions are controlled (e.g., catalyst saturation).

Final Answer:

- If zero-order: Rate is identical at all concentrations.
- Otherwise: Highest at low [HI], lowest at high [HI].

2 Measurement of Concentration

The change in concentrations of reactants or products can be determined by both physical and chemical methods depending upon the type of reactants or products involved.

a) Chemical Method

This is particularly suitable for reactions in solution. In this method, we do the chemical analysis of a reactant or a product.

Example:

The acid hydrolysis of an ester (ethyl acetate) in the presence of a small amount of an acid is one of the best examples.

$$CH_3COOC_2H_{5(\ell)} + H_2O_{(\ell)} \xrightarrow{H^+} CH_3COOH_{(\ell)} + C_2H_5OH_{(\ell)}$$

In case of hydrolysis of an ester, the solution of ester in water and the acid acting as a catalyst are allowed to react. After some time, a sample of reaction mixture is withdrawn by a pipette and run into about four times its volume of ice-cold water. The dilution and chilling stop the reaction. The acid formed is titrated against a standard alkali, say NaOH, using phenolphthalein as an indicator.

The analysis is repeated at various time intervals after the start of reaction. This would provide an information about the change in concentration of acetic acid formed during the reaction at different time intervals.

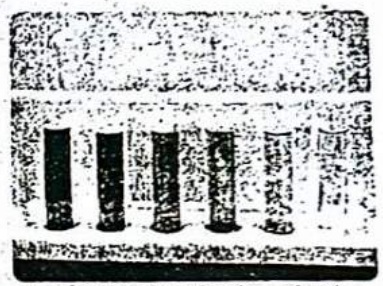


Figure: The concentration change for this reaction can be determined using colorimetry.

b) Physical Methods

Some of the methods used for the measurement of concentration are as follows:

i) Spectrophotometry or Colorimetry

This method is applicable if a reactant or a product absorbs ultraviolet, visible or infrared radiation. The rate of reaction can be measured by measuring the amount of radiations absorbed. For the reaction shown in Figure, the concentration can be measured using the colorimetry.

ii) Electrical Conductivity Method

The rate of a reaction involving ions can be studied by electrical conductivity method. The conductivity of such a solution depends upon the rate of change of concentration of the reacting ions or the ions formed during the reaction. The conductivity will be proportional to the rate of change in the concentration of such ions.

Electrical Conductivity $\propto$ Rate of change of concentration of ions

iii) Volume Change Method

This method is useful for those reactions, which involve changes in volumes of gases as shown in Figure. The volume change is directly proportional:

- The extent of reaction
- Changes in concentration

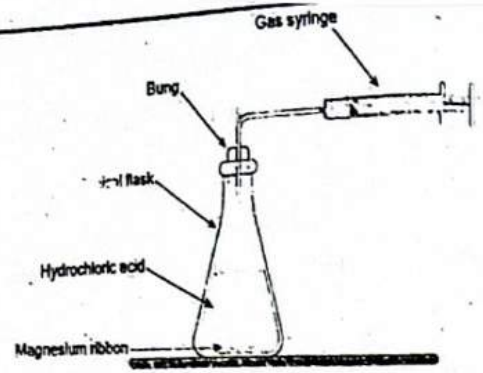


Figure: Rate of reaction can be followed by measuring the change in volume of a gas given off in a reaction.

Interesting Information!

Stopped-Flow Spectrophotometry

The rates of some very fast reactions can be monitored using stopped-flow spectrophotometry. In this technique, very small volumes of reactants are driven at high speed into a mixing chamber. From here they go to an observation cell, where the progress of the reaction is monitored (usually by measuring the transmission of ultraviolet radiation through the sample). A graph of rate of reaction against time can be generated automatically.

FACTORS AFFECTING RATE OF A CHEMICAL REACTION

In general, the rates at which reactants are consumed and products are formed during chemical reactions vary greatly. Even a chemical reaction involving the same reactants may have different rates under different conditions. The factors affecting the rates of reactions are:

i. Concentrations of the reactants
ii. Temperature of the system
iii. Surface area
iv. Catalyst

Did You Know?

Effect of Pressure on Rate of Reaction:

In the case of reactions that involve gaseous reactants, an increase in pressure increases the concentration of the gases which leads to an increase in the rate of reaction. However, pressure change has no effect on the rate of reaction if the reactants are either solids or liquids.

Higher concentration → More collisions → High rate of reaction

Concentration

According to the law of mass action, the greater the concentration of the reactants, the more rapidly the reaction proceeds. When the concentration of one or more reactants increases, rate of reaction increases. This is because increasing the concentration results in more collisions between the reacting particles, which speeds up the reaction.

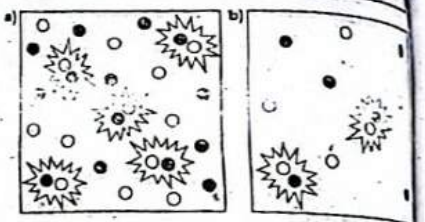


Figure: The reaction in box a) will occur faster than that in b) due to the higher concentration.

Temperature

(Maxwell-Boltzmann Distribution Curve)

- Increase in temperature increases the reaction rate. It has been observed that rate either doubles or triples for every 10°C rise in temperature.
- Temperature usually has a major effect on the rate of reaction. Molecules at higher temperatures have more thermal energy. So, they collide more frequently and with greater energy.

Rack Your Mind!

3. Explain how temperature affects the Boltzmann distribution curve.

- **The Boltzmann distribution curve** is a graph that shows the distribution of energies at certain temperature. In a reaction, a few particles will have very low energy, a few particles will have very high energy, and many particles will have energy in between. The distribution of energies at a given temperature can be shown on a graph as shown in Figure, this is called the Boltzmann distribution.
- **The activation energy** is the minimum energy required for colliding particles fruitfully to convert into the product. The shaded area under the graph as shown in Figure represents the proportion of molecules that have enough energy to cause a chemical change when they collide. The area under the curve represents the number of particles. The shaded area shows the number of particles with energy greater than the activation energy, E_a.

Higher Temperature → More Energetic Collisions → Faster Rate of Reaction

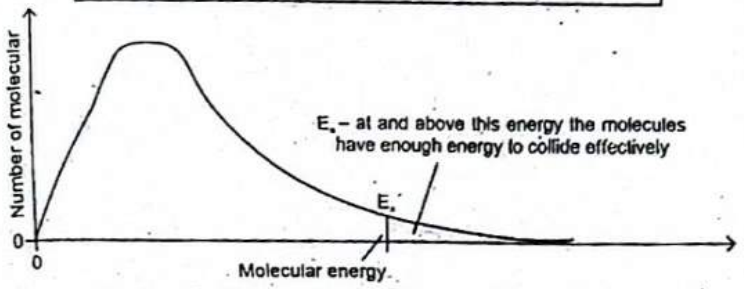


Figure: The Boltzmann distribution of molecular energies showing the activation energy

When Temperature Increases:

As the temperature of a reaction mixture is raised, the average kinetic (movement) energy of the particles increases. The reacting particles move around more quickly at a higher temperature, resulting in more frequent collisions. Therefore, the proportion of successful collisions also increases greatly as shown in Figure. The curve showing the Boltzmann distribution at the higher temperature flattens and the peak shifts to the right. For 10°C rise in temperature, the shaded area under the curve approximately doubles. In conclusion, increasing the temperature increases the rate of a reaction.

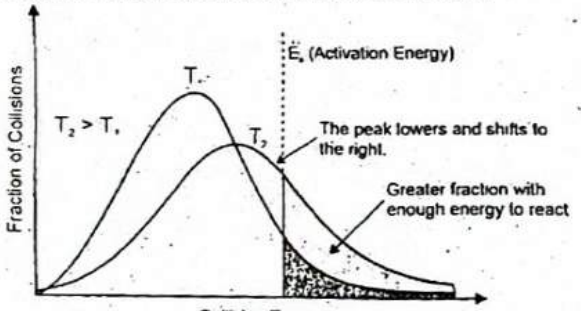


Figure: The Boltzmann distribution of molecular energies at temperatures T_1 and T_2

QUICK CHECK 7.4

a) **What is the Boltzmann distribution curve?**

Ans. The **Boltzmann distribution curve** is a fundamental concept in statistical mechanics that describes the distribution of kinetic energies among particles (e.g., molecules in a gas) at a given temperature.

Mathematical Form

The fraction of particles with energy E at temperature T is given by:

$$f(E) \propto e^{-E/kBT}$$

where:

- k_B = Boltzmann constant (1.38×10^{-23} J/K)
- T = Absolute temperature (Kelvin)

b) Explain why a 10°C rise in temperature approximately doubles the rate of a reaction.

Ans. The doubling of reaction rates with a 10 °C temperature rise is explained by the Arrhenius equation and the Boltzmann distribution of molecular energies. Here's why:

1. **Arrhenius Equation**
   The rate constant (k) depends on temperature (T) and activation energy (E_a):
   $$k = Ae^{-E_a/RT}$$
   - A = Frequency factor (collision/orientation),
   - R = Gas constant,
   - T = Temperature (Kelvin).

   A 10 °C rise (e.g., 298 K → 308 K) increases the exponential term, boosting k.
2. **Boltzmann Energy Distribution**
   At higher T, more molecules gain enough energy ($\geq E_a$) to react.
   - **Rule of thumb:** A 10°C rise increases the fraction of high-energy molecules by ~2 × (for typical E_a).
3. **Example Calculation**
   For E_a = 50 kJ/mol:
   - **At 298 K:**
   $$e^{-E_a/RT} = e^{-50000/(8.314\times298)} \approx e^{-20.2} \approx 1.6\times10^{-9}$$
   - **At 308 K:**
   $$e^{-50000/(8.314\times308)} \approx e^{-19.5} \approx 3.2\times10^{-9}$$

   Result: The exponential term doubles, doubling the rate.

Exercise L Q.5

Q. How does the activation energy profile of an uncatalyzed reaction compare with that of the catalyzed reaction?

Catalyst

A catalyst is defined as a substance which alters the rate of a chemical reaction, but remains chemically unchanged at the end of the reaction.

- A catalyst is often present in a very small amount.
- **Example:** The reaction between H_2 and O_2 to form water is very slow at ordinary temperature, but proceeds more rapidly in the presence of platinum. Platinum acts as a catalyst. Similarly, $KClO_3$ decomposes much more rapidly in the presence of a small amount of MnO_2. HCl is oxidized to Cl_2 in the presence of $CuCl_2$.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$
$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$
$$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$$

"The process, which takes place in the presence of a catalyst, is called catalysis."

Rack Your Mind!

4. The main role of a catalyst in a chemical reaction is to:
   A) Increases activation energy
   B) Lowers activation energy
   C) Increases enthalpy
   D) Raises temperature

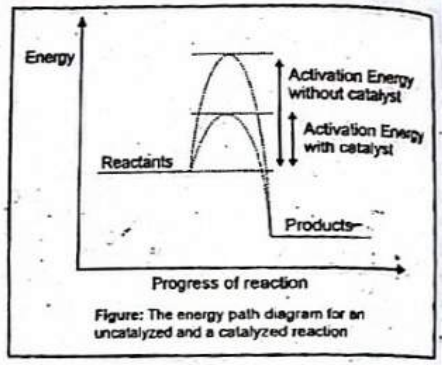


Figure: The energy path diagram for an uncatalyzed and a catalyzed reaction

Functions of Catalyst:

A catalyst provides a new reaction path with a low activation energy barrier. A greater number of molecules are now able to get over the new energy barrier and reaction rate increases.

Types of Catalysis

i) **Homogeneous Catalysis**

In this process, the catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout. The catalyst is distributed uniformly throughout the system.

For example:

- The formation of $SO_{3(g)}$ from $SO_{2(g)}$ and $O_{2(g)}$ in the contact process for the manufacture of sulphuric acid, needs $NO_{(g)}$ as a catalyst. Both the reactants and the catalyst are gases.
$$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO} 2SO_{3(g)}$$
- Esters are hydrolyzed in the presence of H_2SO_4. Both the reactants and the catalyst are in the solution state.
$$\underset{\text{Ethyl ethanoate}}{CH_3COOCH_2CH_{3(l)}} + H_2O_{(l)} \xrightarrow{H^+} \underset{\text{Ethanoic acid}}{CH_3COOH_{(l)}} + \underset{\text{Ethanol}}{CH_3CH_2OH_{(l)}}$$

ii) **Heterogeneous Catalysis**

In such systems, the catalyst and the reactants are in different phases. Mostly, the catalysts are in the solid phase, while the reactants are in the gaseous or liquid phase.

For example:

- **Oxidation of ammonia** to NO in the presence of platinum gauze helps us to manufacture HNO_3.
$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{Pt,\ 800\ °C} 4NO_{(g)} + 6H_2O_{(g)}$$
- **Hydrogenation of unsaturated organic compounds** are catalysed by finely divided Ni, Pd or Pt.
$$C_2H_{4(g)} + H_{2(g)} \xrightarrow{Ni,\ 150\ °C} C_2H_{4(g)}$$

Interesting Information!

Vitamins:
Vitamins are organic compounds that act as catalysts in biochemical reactions, especially when they function as coenzymes.

Coenzymes:
Coenzymes are organic molecules that help enzymes catalyze reactions more efficiently.

For example: Vitamin K, is necessary for blood clotting. Low levels of vitamin K can cause bleeding diathesis. A lack of vitamins can disrupt metabolic balance in cells and organisms. Vitamin deficiency is an example of a cofactor deficiency.

Did You Know?

Enzymes:
Biochemical catalysts, commonly known as enzymes (nature's catalyst) are essential molecules in living organisms.

Function: Its function is to lower the activation energy required for a chemical reaction to proceed, thereby increasing the reaction rate.

Enzymes are typically proteins.

Factors such as pH, temperature, and the concentration of substrate molecules can influence enzyme activity.

QUICK CHECK 7.5

a) Can a catalyst be consumed in a chemical reaction? Why or why not?

Ans. No, a catalyst is not consumed in a reaction.

1. **Regeneration:** Catalysts participate in intermediate steps but are reformed unchanged at the end generally.
   - **Example:** In the decomposition of H_2O_2, MnO_2 speeds up the reaction but remains intact.
2. **Role:** Lowers activation energy (E_a) by providing an alternative pathway

b) Explain whether the reaction below is an example of heterogeneous or homogeneous catalysis:

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5\ (solid)} 2SO_{3(g)}$$

Ans. The reaction $2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$ is typically an example of heterogeneous catalysis.

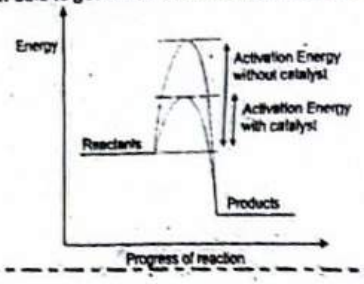
Reactants are in gaseous form and the catalysts Vanadium (V) oxide (V_2O_5) or platinum are in the solid form.

c) Draw an energy profile diagram to show a typical uncatalysed reaction and an enzyme-catalysed reaction.

On your diagram show the activation energy for:

i) Catalysed reaction ii) Uncatalysed reactions

Ans. A catalyst provides a new reaction path with a low activation energy barrier, as shown in figure. A greater number of molecules are now able to get over the new energy barrier and reaction rate increases.



RATE LAW, RATE CONSTANT AND ORDER OF REACTION

Rate Law and Rate Constant

The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products.

Rack Your Mind!

5. What does the order of a reaction indicate in the rate law expression?

➢ **Rate Law:**

"The representation of rate of a reaction in terms of concentration of the reactants is known as rate law."

(OR)

"A rate law is an equation that relates the rate of a reaction to the concentrations of reactants raised to various powers according to the experimental data."

➢ **General Reaction:**

For a general reaction between A and B where 'a' moles of A and 'b' moles of B react to form 'c' moles of C and 'd' moles of D.

$$aA + bB \longrightarrow cC + dD$$

We can write the rate equation as:

$$\text{Rate} = k[A]^x [B]^y$$

Where x and y are the experimentally determined values that may or may not be equal to the coefficient of reactants in the balanced chemical equation, as ' a ' and ' b ' in the above equation. This expression is called rate equation.

- The brackets [ ] represent the molar concentrations.
- The proportionality constant k is called rate constant for the reaction.

If $[A] = 1\ \text{moldm}^{-3}$ and $[B] = 1\ \text{moldm}^{-3}$

$\text{Rate of reaction} = k \times 1^x \times 1^y = k$

Rate Constant: It can be defined as **"The specific rate constant of a chemical reaction is the rate of reaction when the concentrations of the reactants are unity".**

- Under the given conditions, k remains constant, but it changes with temperature.

Exercise L.Q.3

Q. Relate the order of a reaction to the rate law for the reaction. How do you distinguish between zero order, first order and second order reaction?

Reaction Order

The exponents ' x ' or ' y ' in the above equation give the order of reaction with respect to the individual reactants.

"The order of a reaction with respect to a specific reactant is the exponent applied to that reactant's concentration within the rate equation".

➢ **Explanation:**

Reaction order tells how rate changes with reactants concentrations.

- Thus, the reaction is of order ' x ' with respect to A and of order ' y ' with respect to B.
- The overall order of reaction = x + y.
- The order of a reaction defines how the reactant concentration influences its rate.
- For a single-reactant, the order is simply the concentration's power in the rate equation.
- The chemical reactions are classified as zero, first, second and third order reactions.
- The order of reaction provides valuable information about the mechanism of a reaction.
- It is crucial to differentiate between the order concerning a single reactant and the overall reaction order.

Example: Take equation for the reaction of nitrogen (II) oxide (NO) with H_2 and oxygen:

$$2H_{2(g)} + 2NO_{(g)} \longrightarrow N_{2(g)} + H_2O_{(g)}$$

$$\text{Rate} = k[H_2][NO]^2$$

This reaction is:

i. first-order with respect to H_2
ii. second-order with respect to NO
iii. third-order overall (1 + 2 = 3)

KEEP IN MIND

Order of Reaction:

- The order of reaction is given by the sum of all the exponents to which the concentrations in the rate equation are raised.
- It is important to note that the order of a reaction is an experimentally determined quantity and cannot be inferred simply by looking at the reaction equation.
- The sum of the exponents in the rate equation may or may not be the same as in a balanced chemical equation.

QUICK CHECK 7.6

a) How order of reaction is derived from the rate law?

Ans. The order of reaction is derived from the rate law by analyzing how the reaction rate depends on the concentrations of reactants.

Steps to Determine Reaction Order

1. **Write the Rate Law:**
   For a reaction: aA+bB → Products,
   the rate law is: $\text{Rate} = k[A]^a[B]^b$
   - k = rate constant,
   - m, n = orders with respect to A and B (often integers, but can be fractions or zero).
2. **Experimental Data:**
   Measure how the **initial rate** changes when varying one reactant's concentration while keeping others constant.
3. **Derive Orders (m, n):**
   - If doubling [A] doubles the rate: m = 1 (first-order in A).
   - If doubling [A] quadruples the rate: m = 2 (second-order in A).
   - If rate is unchanged when [A] changes: m = 0 (zero-order in A).
4. **Overall Order:**
   Sum of individual orders:

   $$\text{Overall order} = m+n+\ldots$$

Example:

For the rate law $\text{Rate} = k[A][B]^2$:

- First-order in A (exponent = 1),
- Second-order in B (exponent = 2),
- Overall third-order (1 + 2 = 3).

b) Explain what is meant by the specific rate (rate constant) of a reaction and how it is represented in rate equation.

Ans. Specific Rate (Rate Constant, k)

- **Definition:** The rate constant (k) is a proportionality factor in the rate law that quantifies the reaction's speed at a given temperature, independent of reactant concentrations.
- **Role in Rate Equation:**

$$Rate = k[A]^a[B]^b$$

- k is specific to the reaction and temperature.

Units of Rate constants = various order

Order	Unit of K
nth	$\frac{1}{(mol.dm^{-3})^{1-n}.sec^{-1}}$
Zero	$mol\ dm^{-3}\ s^{-1}$
First	s^{-1}
Second	$dm^{-3}\ mol^{-1}\ s^{-1}$
Third	$dm^{6}\ mol^{-2}\ s^{-1}$

Types of Reaction Order

Zero Order Reaction:

The rate of a zero order reaction is independent of the concentration of the reactants. A change in the concentration has no effect on the speed of the reaction.

Rack Your Mind!

6. Give at least four examples of zero order reaction.

General Reaction:

$$A \rightarrow Product$$

$$Rate = k[A]^0$$

Examples:

i) $H_{2(g)} + C\ell_2 \longrightarrow 2HC\ell_{(g)}$

$$Rate = k[H_2]^0[C\ell_2]^0 = k$$

ii) $2NH_3 \longrightarrow N_2 + 3H_2$

$$Rate = k[NH_3]^0 = k$$

iii) Photochemical reactions are usually zero order.

Interesting Information!

Rate laws for Elementary Reaction		
Elementary Reaction	Molecularity	Rate Law
A → Product	Uni – molecular	Rate = k [A]
A + A → Product	Bi – molecular	Rate = k $[A]^2$
A + B → Product	Bi – molecular	Rate = k [A] [B]
A + B + C → Product	Ter – molecular	Rate = k $[A]^2[B]$

First Order Reaction:

In these reactions, there may be multiple reactants present, but concentration of only one reactant will change during the reaction.

First order means rate ∝ [Reactant]

Examples: Decomposition of nitrogen pentoxide involves the following equation.

$$2N_2O_{5(g)} \longrightarrow 2N_2O_{4(g)} + O_{2(g)}$$

The experimentally determined rate equation for this reaction is as follows:

$$Rate = k[N_2O_5]\ (n=1)$$

This equation suggests that the reaction is first order with respect to the concentration of N_2O_5.

Smart Thinking

Units of Rate constants = various order

Order	Unit of K
nth	$\frac{1}{(mol.dm^{-3})^{1-n}.sec^{-1}}$
Zero	$mol\ dm^{-3}\ s^{-1}$
First	s^{-1}
Second	$dm^{-3}\ mol^{-1}\ s^{-1}$
Third	$dm^{6}\ mol^{-2}\ s^{-1}$

Second Order Reaction:

Definition:

"A reaction for which sum of the exponents of the concentrations in the rate equation is 2."

(OR)

"A second order reaction is a reaction whose rate depends either on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power." The simpler type of reaction involves one kind of reactant molecule.

Rate Equation: $Rate = k[A]^2 \quad (n = 2)$

Example: $Rate = k[A]^1[B]^1 \quad (n = 1 + 1 = 2)$

Oxidation of nitric oxide with ozone has been shown to be first order with respect to NO and first order with respect to O_3. The sum of the individual orders gives the overall order of reaction as two.

$$NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)} \quad Rate = k[NO][O_3]$$

Third Order Reaction:

A third order reaction is the reaction for which sum of the exponents of the concentrations in the rate equation is three.

Rack Your Mind!

7. Given Rate = $k[A]^2[B]$, what is the overall order of reaction?
A) 1 B) 2
C) 3 D) 4

Rate Equation: $Rate = k[A]^3\ (n=3)$

or $Rate = k[A]^2[B]^1\ (n=2+1=3)$

or $Rate = k[A]^1[B]^1[C]^1\ (n=1+1+1=3)$

Example: $2FeC\ell_{3(aq)} + 6KI_{(aq)} \longrightarrow 2FeI_{2(aq)} + 6KC\ell_{(aq)} + I_2$

This reaction involves eight reactant molecules but experimentally it has been found to be a third order reaction.

$$Rate = k[FeC\ell_3][KI]^2$$

also, the following reaction is third order

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)} \quad Rate = k[NO]^2[O_2]^1$$

Fractional Order Reaction:

"A reaction in which the sum of exponents of rate equation is in fraction, is called the fractional order reaction."

Example: Consider the formation of carbon tetrachloride from chloroform.

$$CHC\ell_{3(\ell)} + C\ell_{2(g)} \longrightarrow CC\ell_{4(\ell)} + HC\ell_{(g)}$$

$$Rate = k[CHC\ell_3][C\ell_2]^{1/2} \quad n = 1 + 1/2 = 1.5$$

- Reactions involving free radicals frequently exhibit fractional orders.

Units of Rate Constant

The rate constant is specific for a particular reaction at a certain temperature. Since concentrations are in $mol\ dm^{-3}$ and the reaction rate is in units of $mol\ dm^{-3}\ s^{-1}$. The units for k depend on the order of the reaction and the units of time.

General Equation:

$$Rate = k[Reactants]^n \quad \text{where n = order of reaction}$$

$$k = \frac{Rate}{(Rectants)^n} = \frac{(moldm^{-3})s^{-1}}{(moldm^{-3})^n}$$

or $k = (mol.dm^{-3})^{1-n}s^{-1}$

or $k = (concentration)^{1-n}s^{-1}$

Rack Your Mind!

8. What are units for Zero and first order Reaction?

This equation can be used to determine units of any order of reaction.

For a zero order reaction (n = 0),

$$k = (mol \cdot dm^{-3})^{1-0}s^{-1}$$

$$k = mol^1 \cdot dm^{-3}s^{-1}$$

For a first order reaction (n = 1), the rate is directly proportional to the concentration of one reactant.

$$k = (mol \cdot dm^{-3})^{1-1}\ s^{-1}$$

$$k = (mol \cdot dm^{-3})^0 s^{-1}$$

$$k = s^{-1}$$

Therefore, the units of k for a first order rate constant are s^{-1}.

For a second order reaction (n = 2),

$$k = (\text{mol dm}^{-3})^{1-2}\,s^{-1}$$
$$= \text{mol}^{-1}\text{dm}^3\,s^{-1}$$
$$k = \text{dm}^3\,\text{mol}^{-1}\,s^{-1}$$

The units of k for a second order rate constant are $\text{dm}^3\,\text{mol}^{-1}\,s^{-1}$.

For a third order reaction (n = 3),

$$k = (\text{mol dm}^{-3})^{1-3}\,s^{-1}$$
$$= \text{mol}^{-2}\text{dm}^6\,s^{-1}$$
$$k = \text{dm}^6\,\text{mol}^{-2}\,s^{-1}$$

Therefore, the units of k for a third order rate constant are $\text{dm}^6\,\text{mol}^{-2}\,s^{-1}$.

QUICK CHECK 7.7

a) Calculate the overall order of reactions which have the rate expressions:

i) rate $= k[NO]^2[NH_3]^0$

Ans. Rate $= k[NO]^2[NH_3]^0$

- Order with respect to NO: 2 (exponent of [NO]).
- Order with respect to NH_3: 0 (exponent of $[NH_3]$).
- Overall order: 2 + 0 = 2 (Second-order overall).

As per text book order of reaction usually does not exceeds 3.

ii) rate $= k[BrO_3^-][Br^-][H^+]^2$

Ans. Rate $= k[BrO_3^-][Br^-][H^+]^2$

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br^2 + 3H_2O$$

Experimentally Determined Rate Law:

$$\text{Rate} = k[BrO_3^-][Br^-][H^+]^2$$

i) Calculate the overall order of reactions.

Ans. The given rate law is:

$$\text{Rate} = k\left[BrO_3^-\right]\left[Br^-\right]\left[H^+\right]^2$$

Overall order is the sum of these exponents: 1 + 1 + 2 = 4

Note: Overall order reaction comes out to be 4 but as per our syllabus order of reaction never exeeds 3. So, 3 is the maximum order the reaction and it is 3 for the above.

ii) What are the orders with respect to each reactant in the expression.

Ans. Rate $= k\left[BrO_3^-\right]\left[Br^-\right]\left[H^+\right]^2$

- The exponent of $\left[BrO_3^-\right] = 1$
- The exponent of $\left[Br^-\right] = 1$
- The exponent of $[H^+] = 2$

b) Why the sum of the coefficients of a balanced chemical equation is not necessarily important to give the order of a reaction?

Ans. Order of a chemical reaction is not necessarily the sum of the coefficients of the balanced chemical equation because the order of reaction is determined experimentally and not from the balanced chemical equation.

e.g., $2H_2 + 2NO_2 \longrightarrow 2H_2O_2 + N_2$

For this reaction, the sum of coefficients of balanced equation is 2 + 2 = 4 but the reaction is 3rd order. It is experimentally verified that rate of reaction is directly related to conc. of H_2 and to the square of concentration of NO_2. So the rate equation of this reaction is:

$$\text{Rate} \propto [H_2]^1[NO_2]^2$$
$$\text{Rate} = k[H_2]^1[NO_2]^2$$

Order of reaction is sum of exponents of rate equation. So

Order of reaction = 1 + 2 = 3

DETERMINATION OF RATE CONSTANT

(Exercise L.Q.4)

Q. How do you find the numerical value of a rate constant by initial and half-life methods?

The rate constant (k) of a reaction can be calculated using the following two methods:

Initial Concentration Method

In the presence of hydrogen ions, hydrogen peroxide, H_2O_2, reacts with iodide ions to form water and iodine:

$$H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \longrightarrow 2H_2O_{(\ell)} + I_{2(aq)}$$

The rate equation for this reaction is:

$$\text{Rate of reaction} = \frac{k[H_2O_2]}{[I^-]}$$

The progress of the reaction can be followed by measuring the initial rate of formation of iodine. Table shows the rates of reaction obtained using various initial concentrations of each reactant.

The procedure for calculating k is shown below, using the data for experiment 1.

Step 1: Write out the rate equation.

$$\text{Rate of reaction} = \frac{k[H_2O_2]}{[I^-]}$$

Step 2: Rearrange the equation in terms of k

$$k = \frac{\text{rate} \times [I^-]}{[H_2O_2]}$$

Step 3: Substitute the values

$$k = \frac{3.50\times10^{-6} \times (0.0100)}{(0.0200)}$$
$$= 1.75\times10^{-2}\,\text{dm}^3\,\text{mol}^{-1}\,s^{-1}$$

Table: Effect of change in concentrations of reactants on the rate of reaction

Experiment	$[H_2O_2]$ / mol dm$^{(-3)}$	$[I^-]$ / mol dm$^{(-3)}$	$[H^+]$ / mol dm$^{(-3)}$	Initial rate of reaction / mol dm$^{(-3)}$ s$^{(-1)}$
1.	0.0200	0.0100	0.0100	3.5×10^{-6}
2.	0.0300	0.0100	0.0100	5.3×10^{-6}
3.	0.0050	0.0200	0.0200	1.75×10^{-6}

The concentration of hydrogen ions is ignored because $[H^+]$ does not appear in the rate equation. The reaction is zero order with respect to $[H^+]$.

Half-Life Method

"Half life ($t_{1/2}$) is the time taken for the concentration of a reactant to fall to half of its original value".

Calculation of Rate Constant:

Calculating the rate constant (k) using the half-life method involves measuring the time it takes for the concentration of a reactant to decrease by half.

If the reaction is first-order, then the rate constant and the half-life of the reaction are related in the following way:

$$k = 0.693 / t_{1/2}$$

Example: A sample of hydrogen peroxide has a half-life of 2 hours. It decomposes in a first-order reaction. Calculate the rate constant, k, for this reaction.

To calculate k, we first need to convert the half-life, which is 2 hours, into seconds:

$$2 \times 60 \times 60 = 7200\ s$$

Rack Your Mind!

9. Hydrogen peroxide decomposes by a first-order reaction. If its half-life is 2 hours, what is the rate constant (k)?
A) $9.63 \times 10^{-5}\ s^{-1}$ B) $0.00072\ s^{-1}$
C) $0.00139\ s^{-1}$ D) $0.0036\ s^{-1}$

We then simply substitute this value into the equation:

$$k = \frac{0.693}{7200\ s}$$

$$k = 9.6\times10^{-5} s^{-1}$$

Sample Problem 7.2

The first-order reaction cyclopropane to propene, for which the half-life is 17.0 min, Calculate the rate constant of this reaction.

Solution:

Step 1: convert minutes to seconds

Step 2: substitute the half-life into the expression:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{17\times60\ s}$$

$$k = 6.79\times10^{-4}\ dm^3\ mol^{-1} s^{-1}$$

QUICK CHECK 7.8

Consider a first-order reaction with a half-life of 15 minutes. If the initial concentration of the reactant is 0.100 mol dm^{-3}, calculate the rate constant (k) for the reaction.

Solution:

- Half-life ($t_{1/2}$) = 15 minutes
- Initial concentration ($[A]_0$) = 0.100 mol dm^{-3}

Formula for First-Order Half-Life:

- $t_{1/2} = \ln(2)/k$

Step 1: Solve for k

- $k = \ln(2)/t_{1/2} = 0.693/15$ min
- $k = 0.0462$ min^{-1}

REACTION MECHANISM

➢ **Definition:**

"A reaction mechanism is a detailed, step by step description of how a chemical reaction occurs at the molecular level to yield the product(s)."

- Unlike the overall balanced chemical equation, which only shows the reactants and products, the reaction mechanism reveals the actually happening individual steps (called elementary steps) that lead to the formation of products.
- Each of these steps represents a single molecular event, such as the breaking or forming of bonds.
- Many reactions do not occur in a single step, but rather proceed through a series of steps.
- Each step is called an elementary reaction and is directly caused by the collision of atoms, ions or molecules.

Rack Your Mind!

10. Which of the following is most likely to be the rate-determining step in a multi-step reaction?

A) The fastest step
B) The step with the lowest activation energy
C) The step forming the product
D) The slowest step

➢ **Molecularity:**

The number of reactant molecules involved in an elementary step is called its molecularity.

- A unimolecular elementary reaction involves only a single reactant molecule.
- **Example:** Decomposition of N_2O_5.

$$N_2O_{5(g)} \longrightarrow NO_{2(g)} + NO_{3(g)}$$

- An elementary reaction that involves two atoms, ions or molecules and is called bimolecular.

- For example;

$$CO_{(g)} + NO_{3(g)} \longrightarrow NO_{2(g)} + CO_{2(g)}$$

$$NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$$

- **A ter-molecular reaction step involves the simultaneous reaction of three molecules.** Such reactions are rare. An example is the reaction between oxygen molecules and atomic oxygen to form ozone in the stratosphere or during smog formation.

$$2O_{2(g)} + O_{(g)} \longrightarrow O_{3(g)} + O_{2(g)}$$

➢ **Intermediates:**

Intermediates are short lived species (ions or free radicals) that are produced in one step of the mechanism and consumed in a subsequent step. They do not appear in the overall balanced equation because they are not stable products.

➢ **Rate Determining Step:**

In many reaction mechanisms, one step is significantly slower than all the others, this step is called the rate-determining step.

- This step controls the overall rate of the reaction because it limits the speed at which the reaction can proceed.
- The balanced equation for the overall reaction is equal to the net result of all the individual steps. In a chemical reaction, any step that occurs after the rate-determining step will not affect the rate, provided that it is compared with the rate-determining step.
- The atoms, ions or molecules taking part in the mechanism after the rate-determining step do not appear in the rate expression.
- All reactants that appear in the rate-determining step will also appear in the rate equation. Because the rate-determining step limits the rate of the overall reaction, the order of a reaction can be deduced from the rate determining step.

Example 1: Consider the following reaction:

$$2NO_{(g)} + 2H_{2(g)} \longrightarrow 2H_2O_{(g)} + N_{2(g)}$$

Table shows the results of six experiments. In the first three experiments the concentration of H_2 is increased by keeping the concentration of NO constant. By doubling the concentration of H_2, the rate is doubled and by tripling the concentration of H_2, the rate is tripled. So, the rate of reaction is directly proportional to the first power of concentration of H_2.

$$Rate \propto [H_2]$$

In the next three experiments, the concentration of H_2 is kept constant. By doubling the concentration of NO, the rate increases four times and by tripling the concentration of NO the rate is increased nine times. So, the rate is proportional to the square of concentration of NO.

$$Rate \propto [NO]^2$$

The overall rate equation of reaction is,

$$Rate \propto [H_2][NO]^2$$

or

$$Rate = k[H_2]^1[NO]^2$$

Table: Effect of change in concentrations of reactants on the rate of reaction

$[NO]$ in (mol dm^{-3})	$[H_2]$ in (mol dm^{-3})	Initial rate (atm min^{-1})
0.006	0.001	0.025
0.006	0.002	0.050
0.006	0.003	0.0075
0.001	0.009	0.0063
0.002	0.009	0.025
0.003	0.009	0.056

Hence, the reaction is a third order one

- This final equation is the rate law for this reaction.
- It should be kept in mind that rate law cannot be predicted from the balanced chemical equation.
- The possible mechanism consisting of two steps for the reaction is as follows.

Step 1: $2NO_{(g)} + H_{2(g)} \xrightarrow{Slow} N_{2(g)} + H_2O_{2(g)}$ (rate determining step)

Step 2: $H_2O_{2(g)} + H_{2(g)} \xrightarrow{Fast} 2H_2O_{(g)}$

The step 1 is slow and rate determining.

Example 2: The reaction between nitrogen dioxide and fluorine gas:

$$2NO_{2(g)} + F_{2(g)} \longrightarrow 2NO_2F_{(g)}$$

This reaction is first order in NO_2, first order in F_2 and second order overall.

Rate Law: The experimental rate law is first order in NO_2 and in F_2:

$$\text{Rate} = k[NO_2][F_2] \quad \text{(Observed)}$$

The accepted mechanism for the reaction is:

Step 1: $NO_{2(g)} + F_2 \xrightarrow{Slow} NO_2F_{(g)} + F_{(g)}$ $\quad$ Rate $= k_1[NO_2][F_2]$

Step 2: $NO_{2(g)} + F^*_{(g)} \xrightarrow{Fast} NO_2F_{(g)}$ $\quad$ Rate $= k_2[NO_2][F^*]$

- The first step is slow and determines the rate, in agreement with the observed rate expression.
- The second and fast step does not affect the reaction rate because fluorine atoms react with NO_2 as soon as they are produced.

QUICK CHECK 7.9

Q. **An acidified solution of hydrogen peroxide reacts with iodide ions.**

$$H_2O_{2(aq)} + 2H^+_{(aq)} + 2I^-_{(aq)} \rightarrow 2H_2O_{(l)} + I_{2(aq)}$$

The rate equation for this reaction is

$$\text{rate} = [H_2O_2][I^-]$$

The mechanism below has been proposed for this reaction.

$H_2O_2 + I^- \xrightarrow{Slow} H_2O + IO^-$

$H^+ + IO^- \xrightarrow{Fast} HIO$

$HIO + H^+ + I^- \xrightarrow{Fast} I_2 + H_2O$

Explain why this mechanism is consistent with the rate equation.

Ans. The proposed mechanism is consistent with the experimentally determined rate equation rate = $k[H_2O_2][I^-]$ because:

Rate-Determining Step (RDS):

- The slow step involves only H_2O_2 and I^-:

$$H_2O_2 + I^- \xrightarrow{Slow} H_2O + IO^-$$

Since the RDS determines the rate law, it directly gives:

$$\text{rate} = k_1[H_2O_2][I^-]$$

1. **Fast Steps:**
   The subsequent fast steps involve H^+ and IO^-/HIO, but these do not affect the rate law because:
   - They occur after the RDS.
   - H^+ acts as a catalyst (regenerated in the mechanism) and does not appear in the rate law.
2. **Consistency with Stoichiometry:**
   The mechanism sums to the overall reaction:

$$H_2O_2 + 2H^+ + 2I^- \longrightarrow 2H_2O + I_2$$

Why H^+ Doesn't Appear in the Rate Law:

- H^+ participates only in fast steps (after RDS) and is not involved in the slow step.
- Its concentration does not influence the rate.

Conclusion:

The mechanism aligns perfectly with the observed rate equation because:

- The slow step involves only the reactants that appear in the rate law (H_2O_2 and I^-).
- The fast steps reconcile the intermediates (IO^-, HIO) with the overall reaction.

Solution File — Rack Your Brain!

Sr. #	Option	Explanation
1.	S.Q	The conditions must be met for a collision to be effective according to collision theory are given below; A collision is effective only if; • The reacting particles have enough activation energy • Collide with the correct orientation
2.	A	0.02 mol/L-s
3.	S.Q	Temperature affects the Boltzmann distribution curve because higher temperature • shifts the curve to the right and flattens it, • increasing the number of particles with energy greater than the activation energy, • speeds up the reaction.
4.	B	A catalyst speeds up a reaction by providing an alternative reaction pathway with lower activation energy, allowing more reactant molecules to overcome the energy barrier and form products.
5.	S.Q	It shows how the concentration of a reactant affects the rate of the reaction. **For example,** if rate = $k[A]^2[B]$, the reaction is second order with respect to A and first order with respect to B.
6.	S.Q	**Examples** I. Photochemical reactions are usually zero order reactions. II. Enzyme catalysed reactions III. $H_2 + Cl_2 \xrightarrow{sunlight} 2HCl$ iv. $2NH_3 \xrightarrow{Pt} N_2 + 3H_2$ v. $2HI \xrightarrow{Au} H_2 + I_2$ vi. $N_2O \xrightarrow{Pt} N_2 + \frac{1}{2} O_2$
7.	C	Order of reaction = 2 + 1 = 3
8.	S.Q	**For a zero order reaction (n = 0),** $k = (mol \cdot dm^{-3})^{1-0} s^{-1}$ $k = mol^1 \cdot dm^{-3} s^{-1}$ **For a first order reaction (n = 1),** the rate is directly proportional to the concentration of one reactant. $k = (mol \cdot dm^{-3})^{1-1} s^{-1}$ $k = (mol \cdot dm^{-3})^0 s^{-1}$ $k = s^{-1}$
9.	A	For a first-order reaction, the half-life (t1/2) is related to the rate constant (k) by the equation: t1/2 = 0.693/k. Rearranging this equation give k = 0.693 / t1/2. The rate constant k is calculated as 0.3465 h^{-1}. To convert this to seconds, we multiply by (1h/3600s) giving k = $0.3465/3600 = 9.625 \times 10^{-5} s^{-1}$.
10.	D	This step determines the overall rate of the reaction, as the reaction cannot proceed faster than its slowest step.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. The rate of reaction:
a) Increases as the reaction proceeds
b) Decreases as the reaction proceeds
c) Remains the same as the reaction proceeds
d) May decrease or increase as the reaction proceeds

II. Increasing the temperature of a chemical reaction increases the rate of reaction because:
a) Both the collision frequency and collision energies of reactant molecules increase
b) Collision frequency of reactant molecules increases
c) Activation energy increase
d) Activation energy decrease

III. Consider two reactions with different activation energies at the same temperature. The reaction with the lower activation energy will have:
a) A smaller rate constant
b) A larger rate constant
c) The same rate constant
d) A rate constant that depends on the enthalpy change

IV. The order of a chemical reaction, that is independent of concentration is:
a) Second order reaction
b) First order reaction
c) Zero order reaction
d) Pseudo first order reaction

V. On a Boltzmann distribution curve, the area under the curve represents:
a) Activation energy of the reaction.
b) Total number of molecules in the sample.
c) Average kinetic energy of the molecules.
d) Rate constant of the reaction.

VI. On a Boltzmann distribution curve, the activation energy (E_a) is represented by:
a) The height of the peak
b) The area under the entire curve
c) A vertical line drawn at a specific kinetic energy value
d) The difference between the peak and the X-axis

VII. If we double the concentration of a reactant, the rate increases by four times, the reaction is:
a) Second order b) First order c) Third order d) Zero order

VIII. The rate determining step in a multi-step reaction is:
a) Always the first step b) Always the last step c) The slowest step d) The fastest step

IX. The reaction $NO_2 + CO \rightarrow NO + CO_2$ occurs in two steps. What is the rate law equation for this reaction?

$$2NO_2 \longrightarrow NO + NO_3 \ (k_1) \quad \text{slow}$$
$$NO_3 + CO \longrightarrow CO_2 + NO_2 \ (k_2) \quad \text{fast}$$

a) $R = k_1[NO_2]^3$ b) $R = k_1[NO_3][CO]$ c) $R = k_1[NO_2]$ d) $R = k_1[NO_2]^2$

X. How does the presence of a catalyst affect the rate of a chemical reaction?
a) It always decreases the rate of the reaction.
b) It always increases the rate of the reaction.
c) It increases the rate of the forward and decreases the rate of the reverse reaction.
d) It increases the rate of both the forward and reverse reactions.

XI. On an energy profile diagram, the presence of a catalyst is represented by:
a) A higher peak representing the activation energy.
b) A lower peak representing the activation energy.
c) A change in the energy level of the reactants or products.
d) A shift in the equilibrium position.

XII. The units of the rate constant (k) for a reaction depend on the:
a) Activation energy of the reaction
b) Temperature of the reaction
c) Overall order of the reaction
d) Stoichiometry of the balanced chemical equation

XIII. A first-order reaction has a half-life ($t_{1/2}$) of 20 minutes. What is the value of its rate constant (k)?
a) 0.05 min^{-1} b) 0.693 min^{-1} c) 0.0347 min^{-1} d) 13.86 min^{-1}

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	b	Decreases as the reaction proceeds	• Reactant concentrations decrease over time, reducing collision frequency and rate.
II.	a	Both the collision frequency and collision energies of reactant molecules increase	• Higher temperature boosts molecular speed (more collisions) and energy (more exceed E_a).
III.	b	A larger rate constant	• Lower E_a means more molecules have sufficient energy to react (faster rate, larger k).
IV.	c	Zero order reaction	• Zero-order rates are constant (e.g., catalytic surface reactions).
V.	b	Total number of molecules in the sample	• The integral of the curve equals the total molecules.
VI.	c	A vertical line drawn at a specific kinetic energy value	• E_a is the threshold energy (vertical line) beyond which molecules can react.
VII.	a	Second order	• Rate ∝ [Reactant]2 → 4 × 22 = rate increase.
VIII.	c	The slowest step	• The slowest step limits the overall rate.
IX.	d	$R = k_1[NO_2]^2$	• The slow step involves $2NO_2 \rightarrow$ products, so rate depends on $[NO_2]^2$.
X.	d	It increases the rate of both the forward and reverse reactions	• Catalysts lower E_a for both directions, speeding up equilibrium attainment.
XI.	b	A lower peak representing the activation energy	• Catalysts provide an alternative pathway with reduced E_a.
XII.	c	Overall order of the reaction	• For order n, k has units of $mol^{1-n}Ln^{-1}s^{-1}$.
XIII.	c	0.0347 min^{-1}	• $k = \frac{\ln(2)}{t_{1/2}} = \frac{0.693}{20} = 0.0347 min^{-1}$

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. What do you understand by the rate of a reaction?

Ans. The rate of a reaction refers to how fast or slow a chemical reaction occurs. It is defined as the change in concentration of a reactant or product per unit time.

Mathematically, the rate of reaction can be expressed as:

$$\text{Rate of reaction} = \frac{\text{Change in concentration of thr substance}}{\text{Time taken for the change}}$$

$$\text{Rate of reaction} = \frac{\Delta x}{\Delta t}$$

b. Give the difference between enthalpy change of reaction and energy of activation of reaction.

Ans. Difference between Enthalpy Change of Reaction and Energy of Activation of Reaction:

Property	Enthalpy Change of Reaction (ΔH)	Activation Energy (E_a)
Definition	The total heat change during a chemical reaction at constant pressure.	The minimum energy required for a reaction to occur.
Significance	It indicates whether a reaction is exothermic (ΔH < 0) or endothermic (ΔH > 0).	It represents the energy barrier that must be overcome for a reaction to proceed.
Effect on Reaction	Reflects the overall energy change between products and reactants.	Affects the rate of the reaction; higher E_a means slower reaction.
Energy Direction	ΔH can be positive (endothermic) or negative (exothermic).	E_a is always positive, indicating an energy input is needed.
Measurement	It is the difference in the enthalpy between reactants and products.	It is determined experimentally by studying reaction rates.
Example	In the combustion of methane: $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ ΔH is negative (exothermic).	For a reaction to occur, molecules must first overcome the activation energy, which can be lowered by a catalyst.

c. Differentiate clearly between order and molecularity of a reaction.

Ans. Differentiate between Order and Molecularity

Property	Order of a Reaction	Molecularity of a Reaction
Definition	The power to which the concentration of a reactant is raised in the rate law expression.	The number of reacting species (atoms, molecules, or ions) involved in the elementary step of a reaction.
Dependence on Concentration	Order depends on the experimental observation of how reaction rate changes with concentration of reactants.	Molecularity is based on the stoichiometric coefficients in the elementary reaction step.
Nature	Experimental: Determined by experimental data, can be fractional or zero.	Theoretical: Based on the nature of the reaction mechanism and the elementary steps.
Units	Depends on the rate law and overall reaction rate, and can vary with different reactions.	Always an integer (1, 2, 3, etc.), indicating the number of molecules or ions reacting in an elementary step.
Examples	For A → products, if rate = $k[A]^2$, the order is 2.	For A+B → products, the molecularity is 2 (because two molecules are involved).
Can It Be Fractional?	Yes, order can be fractional, zero, or a whole number.	No, molecularity must always be a whole number (1, 2, 3, ...).
Reactions	The order applies to overall reactions and depends on how concentration affects the rate.	Molecularity applies to the elementary step of a reaction mechanism.

d. Why the instantaneous rate changes during a reaction?

Ans. The instantaneous rate of a reaction changes during the course of the reaction because:

1. **Concentration of Reactants Changes:**
   - As the reaction proceeds, reactant molecules are consumed to form products. This causes a decrease in the concentration of the reactants over time.
   - According to the rate law, the rate of reaction depends on the concentration of reactants. As the concentration decreases, the rate of the reaction generally slows down (in the case of most reactions).
2. **Effect on Rate Law:**
   - The rate of the reaction is often directly proportional to the concentration of reactants raised to some power (the order of the reaction).
   - For example, if the rate law is rate = $k[A]^n$, as [A] decreases, the rate will decrease accordingly. This change in concentration over time causes the instantaneous rate to change as well.
3. **Transition from Fast to Slow Reactions:**
   - In initial stages, when reactants are present in higher concentrations, the reaction proceeds faster.
   - As reactants are consumed and their concentrations drop, the rate of reaction decreases.
4. **Reverse Reaction (if applicable):**
   - In reversible reactions, as products form, they can also react to regenerate reactants. This can affect the overall rate, especially as the reaction approaches equilibrium.

e. Briefly summarize the effects of temperature and surface area on the rates of reactions.

Ans.

1. **Effect of Temperature on Reaction Rate:**
   - Increase in Temperature ⇒ Increase in Rate of reaction.
   - At higher temperatures, molecules have more kinetic energy, leading to:
     - More frequent collisions between reactant molecules.
     - More energetic collisions, increasing the chances of successful reactions (i.e., collisions with enough energy to overcome the activation energy barrier).
   - **Arrhenius Equation:** The rate constant (k) increases with temperature, generally leading to a faster reaction.
2. **Effect of Surface Area on Reaction Rate:**
   - Increase in Surface Area ⇒ Increase in Rate of reaction.
   - Smaller particles or larger surface area of reactants result in:
     - More surface contact between reactants, leading to more collisions.
     - Faster reaction rate as more reactant particles are exposed to react with the other reactant molecules.
   - **Example:** Powdered solid reactants react faster than large chunks of the same substance because of the greater surface area available for collisions.

f. Justify that the radioactive decay is always a first order reaction.

Ans. Radioactive decay is always a first-order reaction due to the nature of the process, which can be justified as follows:

First-Order Reaction:

- A first-order reaction is one where the rate of reaction depends on the concentration of a single reactant raised to the power of 1.
- Mathematically: rate = k[A], where [A] is the concentration of the reactant, and k is the rate constant.

Dependence on the Number of Radioactive Nuclei:

- In radioactive decay, the rate at which a substance decays depends on the number of radioactive nuclei present at any given time.
- The probability that a single nucleus will decay within a given time interval is constant and independent of the number of decays that have already occurred.

- The rate of decay is proportional to the number of radioactive atoms that are still intact at any moment, i.e., the concentration of the substance.
- The half-life remains constant regardless of how much material is left, further proving that radioactive decay is a first-order process.

g. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration is doubled and reduced to half?

Ans. For a second-order reaction with respect to a reactant, the rate of the reaction is proportional to the square of the concentration of that reactant. This means that the rate law can be expressed as:

$$\text{Rate} = k[A]^2$$

Where:

- k is the rate constant,
- [A] is the concentration of the reactant.

h. What is meant by half-life and what is it used for?

Ans. Half-Life ($T_{1/2}$):

The half-life of a reaction is the time required for the concentration of a reactant to decrease to half of its initial value. It is a measure of how quickly a reaction occurs or how long it takes for a substance to undergo a certain amount of decay or transformation.

Uses:

It is used in various fields like radioactive decay, chemical reactions, and pharmacokinetics to measure the rate of processes or determine safe and effective dosages in medicine.

i. Why does wood burn more rapidly in pure oxygen than in air?

Ans.

1. **Increased Oxygen Concentration:**
   - In air, oxygen makes up about 21% of the atmosphere, with the rest primarily consisting of nitrogen and trace gases.
   - In pure oxygen, the oxygen concentration is 100%, meaning there is a much higher availability of oxygen molecules to react with the wood during combustion.
   - More oxygen molecules allow the combustion reaction to proceed more quickly and at a higher rate, as there are more molecules available to support the chemical reaction.
2. **Increased Rate of Combustion:**
   - Combustion is a chemical reaction between the fuel (in this case, wood) and oxygen. The reaction rate increases when the concentration of oxygen is higher.
   - Since the combustion of wood involves breaking bonds in the wood's cellulose structure, more oxygen molecules allow the reaction to happen more efficiently and rapidly.

The general combustion reaction of wood (which primarily consists of cellulose) is:

$$C_6H_{10}O_5 + O_2 \rightarrow CO_2 + H_2O$$

In pure oxygen, this reaction can proceed much faster than in air.

j. A catalyst lowers the activation energy of a chemical reaction. Illustrate it.

Ans. A catalyst is a substance that lowers the activation energy of a chemical reaction, thereby increasing the reaction rate without being consumed in the process.

k. The rate constant for a certain reaction is $3.5\times10^{-4}\ s^{-1}$ at 25°C. What is the order of the reaction? Explain based on the units of the rate constant.

Ans. It seems to a reaction with a given rate constant ($k = 3.5 \times 10^{-4}\ s^{-1}$) at a specific temperature (25°C). This rate constant suggests that the reaction may follow first-order kinetics, where the rate of reaction depends linearly on the concentration of the reactant.

Here are some key points about rate constants and their interpretation:

First-Order Kinetics:

For a reaction with first-order kinetics, the rate law is given by:

$$\text{rate} = k[A]$$

where:

- k is the rate constant (in this case, $3.5 \times 10^{-4}\ s^{-1}$)
- [A] is the concentration of the reactant.

The units of k for a first-order reaction are s^{-1} seconds inverse, which is consistent with the given rate constant.

"The number of reacting molecules whose concentration alters as a result of the chemical change is called order of reaction."

OR

"The sum of all the exponents to which the concentrations in the rate equation are raised is called order of reaction."

Order of a reaction decides the units of rate constant a reaction.

Explanation:

The units of the rate constant (k) reveal the reaction order:

- **First-order (s^{-1}):** Rate depends linearly on concentration (Rate = k[A]).
- **Second-order ($dm^3\ mol^{-1}s^{-1}$):** Rate depends on concentration squared ($\text{Rate} = k[A]^2$).
- **Zero-order ($k = mol.dm^{-3}\ s^{-1}$):** Rate is independent of concentration.

l. If the initial concentration of the reactant is 0.50 mol dm^{-3}, calculate the initial rate of the reaction.

Ans. For a first-order reaction, the rate law is:

$$\text{Rate} = k[A]$$

Where:

- Rate is the initial rate of the reaction,
- k is the rate constant (given as $3.5\times10^{-4}\ s^{-1}$)
- [A] is the initial concentration of the reactant (given as 0.50 mol/dm^3).

Substitute the Given Values:

$$\text{Rate} = (3.5 \times 10^{-4} s^{-1}) \times (0.50\ mol/dm^3)$$

$$\text{Rate} = 1.75 \times 10^{-4}\ mol/dm^3 s$$

m. How would the rate of this reaction change if the concentration of the reactant were doubled?

Ans. The reaction is first-order, the rate is directly proportional to the concentration of the reactant.

Rate law:

$$\text{Rate} = k[A]$$

If the initial concentration is doubled, say from [A to 2[A], then:

$$\text{New rate} = k[2[A]) = 2\cdot(k[A]) = 2\times\text{original rate}$$

n. A certain first-order reaction has a rate constant of $2.5\times10^{-3}\ s^{-1}$. Calculate the half-life of the reaction in minutes.

Ans. Half-life formula (for first-order reactions):

$$t_{1/2} = \ln 2/k$$

Where:

$t_{1/2}$ = half-life,

$\ln 2 \approx 0.693$

$k = 2.5\times10^{-3}\ s^{-1}$

Calculate in seconds: $t_{1/2} = 0.693/2.5\times10^{-3} = 277.2$ seconds

Convert seconds to minutes: $t_{1/2} = 277.2/60 \approx 4.62$ minutes

o. A radioactive isotope decays by a first-order process with a half-life of 12 hours. Calculate the rate constant for the decay in s^{-1}.

Ans.

$$k = \ln 2/t_{1/2}$$

Given: $t_{1/2} = 12$ hours

Convert to seconds: $12\ \text{hours} = 12 \times 60 \times 60 = 43{,}200$ s

$$K = 0.693/43{,}200s \approx 1.60 \times 10^{-5}\ s^{-1}$$

The rate constant k is approximately $1.60 \times 10^{-5}\ s^{-1}$

DESCRIPTIVE QUESTIONS

Q.3 Relate the order of a reaction to the rate law for the reaction. How do you distinguish between zero order, first order and second order reaction?

Ans. See Page No. (232)

Q.4 How do you find the numerical value of a rate constant by initial and half-life methods?

Ans. See Page No. (237)

Q.5 How does the activation energy profile of an uncatalyzed reaction compare with that of the catalyzed reaction?

Ans. See Page No. (230)

Q.6 The reaction between hydrogen peroxide (H_2O_2) and iodide ions (I^-) in acidic solution is believed to occur via the following mechanism:

Step 1: $H_2O_2 + I^- \longrightarrow H_2O + OI^-$ (slow)

Step 2: $OI^- + H^+ \longrightarrow HOI$ (fast)

Step 3: $HOI + I^- + H^+ \longrightarrow H_2O + I_2$ (fast)

i) Write the overall balanced equation for the reaction.

ii) Identify any intermediates and catalysts in this mechanism.

iii) What is the rate-determining step?

iv) Write the rate equation for the reaction, expressing it in terms of the reactants in the overall reaction.

Ans. See Quick Check 7.9

(ii) Possible Intermediates:

- Hypoiodous Acid (HOI) – May form transiently during iodide oxidation.
- Iodine Radical ($I^\bullet$) – A short-lived species in electron transfer steps.

And Catalysts for This Mechanism:

MoO_4^{2-} or Fe^{3+}

NUMERICAL PROBLEMS

Q.6 Calculate the reaction rate if the concentration of A is 0.5 M, the concentration of B is 0.2 and the rate constant k is 4.0 $M^{-2}s^{-1}$. Given the rate law for a reaction: Rate = $k[A][B]^2$.

Given Data:
Rate law = $k[A][B]^2$
Rate constant (k) = 4.0 $M^{-2}s^{-1}$
Concentration of A ([A]) = 0.5 M
Concentration of B ([B]) = 0.2 M

To find:
Reaction rate = ?

Solution:

The rate of the reaction is given by:

$$\text{Rate} = k[A][B]^2$$

Substitute the Given Values

$$\text{Rate} = (4.0\ M^{-2}s^{-1}) \times (0.5\ M) \times (0.2\ M)^2$$

Now, multiply all the terms step by step:

$$\text{Rate} = 4.0 \times 0.5 \times 0.04$$

$$\text{Rate} = 0.08\ Ms^{-1}$$

The reaction rate is: 0.08 $M\,s^{-1}$

Q.7 A first order reaction is found to have a rate constant, $k = 5.5\times10^{-14}s^{-1}$. Find the half-life of the reaction.

Temp. (K)	Rate constant ($cm^3\ mol^{-1}s^{-1}$)(K)
500	6.814×10^{-4}
550	2.64×10^{-2}
600	0.56×10^{0}
650	7.31×10^{0}
700	66.67×10^{0}

Given Data:
Rate constant (k) = $5.5 \times 10^{-14}\ s^{-1}$
Reaction order = First-order
Half-life ($t_{1/2}$) = ?

To find:

Solution:

Step 1 write formula

For a first-order reaction, the half-life is given by:

$$t_{1/2} = \frac{\ln(2)}{k}$$

where:

- ln(2) = 0.693
- k is the rate constant.

Step 2: Substitute the Given Rate Constant

By putting the value of k:

$$t_{1/2} = \frac{0.693}{5.5\times10^{-14}s^{-1}}$$

Step 3: Calculation

$$t_{1/2} = 1.26 \times 10^{13}\ s$$

Answer: The half-life of the reaction is 1.26×10^{13} s.

Q.8 Three experiments that have identical conditions were performed to measure the initial rate of the reaction. $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$

Experiment	[HI](M)	Rate (M/s)
1.	0.015	1.1×10^{-3}
2.	0.030	4.4×10^{-3}
3.	0.045	9.9×10^{-3}

Write the rate law for the reaction. Find the value and units of the specific rate constant, k.

Given Reaction:

$$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$$

Step 1: Rate Law Form

$$\text{Rate} = k[HI]^n$$

Use the data to find the order n.

Step 2: Determine Reaction Order (n)

Use experiments 1 and 2:

- **Exp 1:** [HI] = 0.015 = 0.015 Rate = 1.1×10^{-3}
- **Exp 2:** [HI] = 0.030 = 0.030 Rate = 4.4×10^{-3}

$$\frac{4.4\times10^{-3}}{1.1\times10^{-3}} = \left(\frac{0.030}{0.015}\right)^n \quad \Rightarrow 4 = 2^n \quad \Rightarrow n = 2$$

Order = 2

Step 3: Rate Law

$$\text{Rate} = k[HI]^2$$

Step 4: Rate constant (k)

Use any experiment (e.g., Exp 1):

$$\text{Rate} = k[HI]^2$$

$$1.1\times10^{-3} = k(0.015)^2$$

$$K = \frac{1.1\times10^{-3}}{0.000225} = 4.89 M^{-1}s^{-1}$$

Answer:

- **Rate Law:** Rate = $k[HI]^2$
  $k = 4.89\ M^{-1}s^{-1}$
- **Order:** Second order

ADDITIONAL SLOs BASED MCQs

1. The rate of a reaction ———— as the reaction proceeds.
   A. Increases B. Decreases
   C. Remains the same D. May increase or decrease
2. The unit of the rate constant is the same as that of the rate of reaction in ———— order reaction.
   A. First B. Second C. Third D. Zero
3. For the reaction:
   $2A + B \xrightarrow{slow} C$, the rate law for the reaction is
   A. rate = $k[A]^2[B]$ B. rate = $k[A][B]$ C. rate = $k[C]$ D. None of these
4. For the reaction: $2A + B \longrightarrow C + D$
   The expression for the rate law is, rate = $k[A]^2$, the order of reaction in B is
   A. First B. Second C. Third D. Zero
5. The activation energy for a reaction can be:
   A. Increased by increasing temperature
   B. Increased by decreasing temperature
   C. Decreased by increasing concentration of reactants
   D. None of these
6. Rate law for the reaction
   $R–X + H_2O \rightarrow R–OH + HX$ is, rate = k[R–X]. The rate of reaction will be doubled when
   A. Concentration of H_2O is doubled B. Concentration of R–X is reduced to half
   C. Concentration of both R–X and H_2O is doubled D. None of these
7. The rate of a catalyzed reaction is independent of the concentration of
   A. Reactants B. Products C. Catalyst D. Zero
8. If a reaction proceeds in such a way that order of reaction is independent of the reactants concentration, the overall order of reaction would be
   A. First B. Second C. Third D. Zero
9. Reactions with high activation energy are usually
   A. Fast B. Slow C. Exothermic D. Reversible
10. In a reversible reaction, catalyst lowers the activation energy of the
    A. Forward reaction B. Reverse reaction
    C. Forward as well as reverse reaction D. Forward reaction but increases for the reverse reaction
11. If rate of reaction doubles for every 10°C rise in temperature what is the increase in rate of reaction if temperature rises from 10°C to 100°C
    A. 112 times B. 100 times C. 400 times D. 512 times
12. Order of reaction is the number of reacting molecules whose concentration alters as a result of chemical change for which order of reaction the unit of rate constant (k) is the same as that of rate of reaction?
    A. 1st order reaction B. 2nd order reaction C. Zero order reaction D. 3rd order reaction

13. The hydrolysis of $(CH_3)_3CBr$ by OH^- ion proceed in two steps:
    $RBr \rightleftharpoons R^+ + Br^-$ slow
    $R^+ + OH^- \rightleftharpoons R–OH$ fast
    Which of the following rate equation is consistent with this scheme?
    A. rate = $k[RBr]^2$ B. rate = $k[RBr][OH^-]$ C. rate = $k[RBr][OH^-]^2$ D. rate = $k[RBr]$
14. Which one of the following correctly represents the units of the rate constant k for a first order reaction?
    A. s^{-1} B. mol $dm^{-3}s$ C. $mol.dm^{-3}s^{-1}$ D. $mol^{-1}dm^3s$
15. If the rate of decay of a radioactive isotope decreases from 200 counts per minutes to 25 counts per minute after 24 hours. What is half life?
    A. 3 hours B. 4 hours C. 6 hours D. 8 hours

Answer Key with Explanations

Q.#	Ans.	Explanations
1.	B	The rate of reaction is directly proportional to concentration of reactant. As reaction goes the amount of reactant decrease hence the rate of reaction decreases.
2.	D	A ⟶ Product Rate = k[A]o So, Rate = k = mol dm–3 s–1
3.	A	2A + B slow⟶ C Since two molecules of 'A' and one molecule of 'B' participate, so rate equation will be Rate = k[A]2[B] Order of reaction = 2 + 1 = 3
4.	D	Rate equation shows that concentration of reactant 'B' does not affect reaction rate. Therefore the order of reaction in 'B' is zero.
5.	B	k = Ae–Ea/RT Ea ∝ 1 T
6.	D	(i) Rate ∝ [R – X]. It means when concentration of R – X doubles, rate of reaction also doubles. (ii) Concentration of H2O does not affect the rate of reaction. So to increase rate of reaction, it is not necessary to increase conc. of H2O.
7.	B	According to Law of mass action: The rate of a chemical reaction is directly proportional to the active mass of the reactant or to the product of active masses if more than one reactants are involved in a chemical reaction. As the concentration of a catalyst increases its catalytic activity also increase.
8.	D	Such a reaction is zero order reaction: A + B ⟶ Product Rate = k[A]O[B]0 Order of reaction = zero
9.	B	According to Arrhenius equation: k = Ae–Ea/RT k = Rate of reaction (when molar concentration of reactants are in unity) Rate = Ae–Ea/RT Rate ∝ 1 Ea
10.	C	A catalyst cannot affect the equilibrium constant of a reaction but it helps the equilibrium to be established earlier. The rates of forward and backward steps are increased equally.
11.	D	For every 10°C Risk rate of reaction become double temp is increase 10°–100°(9 Time) 2^9 = 515 Time rate of reaction will increase
12.	C	R = K[cosc]° $\frac{mole/dm^3}{sec} = K$

13.	D	Rate expression is always according to slow step
14.	A	$R = K[conc]^1$ $mol/dm^3/sec = k.mole/dm^3$ $K = sec^{-1}$
15.	D	$200 \rightarrow 100 \rightarrow 50 \rightarrow 25$ Total 3half-life=24 hours 1 Half-life=8 hours

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Differentiate between instantaneous and average rate of reaction.

Ans. Differences between Instantaneous and Average Rate of Reaction:

Average Rate	Instantaneous Rate
"The rate at any one instant during the interval is called the instantaneous rate".	"The rate of reaction between two specific time intervals is called average rage".
Instantaneous rate $= \frac{dx}{dt}$	Average rate $= \frac{\Delta x}{\Delta t}$
At first instantaneous rate is higher than average rate.	At the end, average rate is higher than instantaneous rate.

Q.2 Differentiate between rate and rate constant of a reaction.

Ans. Differences between rate and rate constant of a reaction:

Rate of reaction	Rate constant
(i) It is the speed at which the reactants are converted into the products.	It is a constant of proportionality in the rate law expression.
(ii) Rate $= \frac{\Delta x}{\Delta t}$	Rate = k[Reactants] $\Rightarrow k = \frac{\text{Rate}}{[\text{Reactants}]}$
(iii) It depends upon the concentration of reactant species at that moment.	It refers to the rate of reaction at specific point when concentration of every reacting species is unity.
(iv) It decreases with the progress of reaction generally.	It is a constant and does not depend on the progress of the reaction.

Q.3 Radioactive decay is always first order reaction. Justify.

Ans. A radioactive substance has a single species at a moment, whose nucleus under goes disintegration. As only one reactant is involved, so it follows 1st order mechanism.

e.g., Half-life of $^{235}_{92}U$ is 710 million years. It means if one kg uranium is present at start, after 710 million years, 0.5 kg of it will disintegrate and after next 710 million years 0.25 kg of it will disintegrate and so on. Therefore we can say that half-life of a radioactive decay is always a 1st order reaction.

Q.4 What is zero order reaction? Give one example.

Ans. **Zero Order Reaction:** "The reaction which is entirely independent of the concentration of reactant molecules is called zero order reaction"

Mathematical Form:

$A \longrightarrow$ Products

$Rate = k[A]^0$

$Rate = k$

Example: All photosynthetic reactions are usually zero order reactions.

Q.5 The order of reaction may be in fraction. Explain.

Ans. **Fractional Order Reaction:**

The order of a reaction is usually positive integer or a zero, but it can also be in fraction or can have a negative value.

Example:

Consider the formation of carbon tetrachloride from chloroform.

$$CHCl_{3(L)} + Cl_{2(g)} \longrightarrow CCl_{4(l)} + HCl_{(g)}$$

$$Rate = k[CHCl_3]\ [Cl_2]^{1/2}$$

The sum of exponents will be $1 + 1/2 = 1.5$ so,

Order of reaction = 1.5

Q.6 Differentiate between order of reaction and rate of reaction.

Ans. **Order of Reaction:**

"The number of reacting molecules whose concentration alters as a result of the chemical change is called order of reaction." OR

"The sum of all the exponents to which the concentrations in the rate equation are raised is called order of reaction."

Rate of Reaction:

(i) It is the speed at which the reactants are converted into the products.

(ii) Rate $= \frac{\Delta x}{\Delta t}$

(iii) It depends upon the concentration of reactant species at that moment.

(iv) It decreases with the progress of reaction generally.

Q.7 Define half-life period of a reaction. Give one example.

Ans. **Half-Life Period:**

"The time which is required to convert 50% of the reactants into products is called half-life period ($t_{1/2}$)."

Example:

Decomposition of N_2O_5

The half-life period for the decomposition of N_2O_5 at 45°C is 24 minutes.

$$2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2 \qquad t_{1/2} = 24 \text{ min at } 45°C$$

[1st order reaction]

Importance:

- We can use the rate of decay of an item to determine the age of item.
- We can predict the amount of radioactive material that will remain after a given amount of time.

Half-Life and Order of Reaction:

"Half-life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction."

$$[t_{1/2}] \propto \frac{1}{a^{n-1}}$$

Half-Life and 2nd Order of Reaction:

For Second Order Reaction: n = 2

$[t_{1/2}]_2 \propto \frac{1}{a^{2-1}}$ or $[t_{1/2}]_2 \propto \frac{1}{a^1}$; Since $[t_{1/2}]_2 = \frac{1}{ka}$

Note: In case of second order reaction, the half-life period is inversely proportional to the initial concentration of the reactant.

Half-Life and 3rd Order of Reaction:

For Third Order Reaction: n = 3

$[t_{1/2}]_3 \propto \frac{1}{a^{3-1}}$ or $[t_{1/2}]_3 \propto \frac{1}{a^2}$; Since $[t_{1/2}]_3 = \frac{1.5}{ka^2}$

For a third order reaction, the half-life period is inversely proportional to the square of initial concentration of reactants.

Q.8 What is rate determining step? Give a suitable example.

Ans. Rate Determining Step:

"A slowest step in reaction mechanism which can determine the overall rate of reaction is called rate determining step."

Rate Determining Step:

"Rate-determining step is that step of a chemical reaction which controls the rate of reaction."

- If a reaction occurs in several steps, one of the steps is the slowest.
- The rate of this step determines the overall rate of reaction.
- This slowest step is called the rate determining or rate limiting step.
- The total number of molecules taking part in the rate determining step appear in the rate equation of the reaction.
- Let us consider the following reaction

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$$

The rate equation of the reaction is found to be:

$$\text{Rate} = K[NO_2]^2$$

- The reaction is second order with respect to $NO_{2(g)}$. Experiment shows that $CO_{(g)}$ is not taking part in the rate determining step. The proposed mechanism for this reaction is as follows:

Step 1: $NO_{2(g)} + NO_{2(g)} \xrightarrow{\text{Slow}} NO_{3(g)} + NO_{(g)}$ (It is a slow hence rate determining step)

Step 1: $NO_{3(g)} + CO_{(g)} \xrightarrow{\text{fast}} NO_{2(g)} + CO_{2(g)}$

- The first step is the rate determining step and NO_3 which does not appear in the balanced equation, is called the reaction intermediate.
- The reaction intermediate has a temporary existence and it is unstable relative to the reactants and the products.

Q.9 Differentiate between fast step and the rate determining step.

Ans.

Fast Step	Rate Determining Step
i. A step in a chemical reaction which proceeds so fastly that we are unable to determine the rate of reaction is called fast step. It has no effect on overall rate of reaction.	A slowest step in reaction mechanism which can determine the overall rate of reaction is called rate determining step.
ii. **For example:** For a reaction $2NO_{(g)} + 2H_{2(g)} \longrightarrow 2H_2O_{(g)} + N_{2(g)}$ The steps of reaction mechanisms are a. $2NO_{(g)} + H_2 \xrightarrow{\text{Slow}} H_2O_{2(g)} + N_{2(g)}$ b. $H_{2(g)} + H_2O_{2(g)} \xrightarrow{\text{fast}} 2H_2O_{(g)}$ Step (b) is fast step.	In the example given in left column, step (a) is the rate determining step. $2NO_{(g)} + H_{2(g)} \xrightarrow{\text{slow}} H_2O_{2(g)} + N_{2(g)}$ It is experimentally determined. It involves 2 moles NO and one mole H_2.
iii. Reactants of fast step are eliminated from rate equation. Moreover, in a multistep reaction, number of fast steps can be one or more than one.	Reactants of slow step are present in rate equation i.e., Rate = $k[H_2][NO_2]^2$. Moreover there is only one rate determining step in a multistep reaction.
iv. Fast step is unable to determine order of reaction.	Sum of reactant coefficients of slowest step is the order of reaction. e.g. in the above reaction: Order of reaction = 2 + 1 = 3.

Q.10 The sum of the co-efficient of a balanced chemical equation is no necessarily important to give the order of reaction. Give reasons in support of your answer.

Ans. Order of a chemical reaction is not necessarily the sum of the coefficients of the balanced chemical equation because the order of reaction is determined experimentally and not from the balanced chemical equation.

e.g., $2H_2 + 2NO_2 \longrightarrow 2H_2O_2 + N_2$

For this reaction, the sum of coefficients of balanced equation is 2 + 2 = 4 but the reaction is 3rd order. It is experimentally verified that rate of reaction is directly related to conc. of H_2 and to the square of concentration of NO_2. So the rate equation of this reaction is

$$\text{Rate} \propto [H_2]^1[NO_2]^2$$

$$\text{Rate} = k[H_2]^1[NO_2]^2$$

Order of reaction is sum of exponents of rate equation. So,

$$\text{Order of reaction} = 1 + 2 = 3$$

Q.11 Define energy of activation. How is it affected by temperature?

Ans. Energy of Activation:

The minimum amount of energy in addition to average kinetic energy which is just sufficient to convert the reactants into products is called energy of activation (E_a).

Effect of Temperature:

According to Arrhenius Equation:

$$k = Ae^{-E_a/RT}$$

k is exponentially related to activation energy E_a and temperature T. The equation shows that the increase in temperature, increase the rate constant and the reaction of high activation energy have low "k" values. It means that if we increase the temperature the activation energy of the reaction decreases.

Activated complex is an unstable combination of all the atoms involved in the reaction for which the energy is maximum. It is a short lived species and decomposes into products immediately. It has a transient existence that is why it is also called a transition state.

Q.12 Describe Half Life Method to determine order of reaction.

Ans. Half-Life Method:

"Half-life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction."

$$[t_{1/2}] \propto \frac{1}{a^{n-1}}$$

Let us perform a reaction twice by taking two different initial concentrations a_1 and a_2 and their half-life periods are found to be t_1 and t_2 respectively.

$$t_1 \propto \frac{1}{a_1^{n-1}} \quad \text{and} \quad t_2 \propto \frac{1}{a_2^{n-1}}$$

Dividing the above two equations:

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking log on both sides, we have

$$\log\left(\frac{t_1}{t_2}\right) = \log\left[\left(\frac{a_2}{a_1}\right)^{n-1}\right]$$

$$\log\left(\frac{t_1}{t_2}\right) = (n-1)\log\left(\frac{a_2}{a_1}\right)$$

$$n = 1 + \frac{\log\frac{t_1}{t_2}}{\log\frac{a_2}{a_1}}$$

Where, n = order of reaction

Q.13 Define Catalysis. Write two characteristics of a catalyst.

Ans. Catalysis:

"The process, which takes place in the presence of a catalyst, is called catalysis."

Characteristics of a Catalyst:

1. **Unchanged Chemical Composition:**
A catalyst remains unchanged in mass and chemical composition at the end of reaction. It may not remain in the same physical state.
Examples:
(i) MnO_2 is added as a catalyst for the decomposition of $KClO_3$. But MnO_2 is regenerated at the end in the form of a fine powder.
(ii) In some cases, the shining surfaces of the solid catalyst become dull.
2. **Effectiveness of a Catalyst:**
Sometimes, we use a trace of a metal catalyst to effect very large amount of reactants.
Examples:
(i) 1 mg of fine platinum powder can convert 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to water.
(ii) Dry HCl and NH_3 don't combine, but in the presence of trace of moisture, they give dense white fumes of NH_4Cl.
(iii) Thousands of dm^3 of H_2O_2 can be decomposed in the presence of 1 g of colloidal platinum.

Q.14 Define catalysis. Give its different types with one example in each case.

Ans. Catalysis:
"The process, which takes place in the presence of a catalyst, is called catalysis."
Types of Catalysis:
(a) Homogeneous Catalysis (b) Heterogeneous Catalysis

(a) Homogeneous Catalysis:
"When the catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout, then it is called homogeneous catalysis."
The catalyst is distributed uniformly throughout the system.
Examples:
The formation of SO_3 from SO_2 and O_2 in the lead chamber process for the manufacture of sulphuric acid needs NO as a catalyst. Both the reactants and the catalyst are gases.

(b) Heterogeneous Catalysis:
"When the catalyst and the reactants are in different phases, then it is called heterogeneous catalysis."
Examples:
Oxidation of ammonia to NO in the presence of platinum gauze helps us to manufacture HNO_3.

$$4NH_{3(g)} + 5O_{2(g)} \xrightleftharpoons{Pt_{(s)}} 4NO_{(g)} + 6H_2O_{(g)}$$

Q.15 Differentiate between homogeneous and heterogeneous catalysis. Give example.

Ans.

Homogeneous Catalysis	Heterogeneous Catalysis
(i) It is catalysis in which the catalyst and reacting substances are in same physical state/phase.	(i) It is catalysis in which the catalyst and reacting substances are in different phases.
(ii) Catalyst is uniformly distributed.	(ii) No uniform distribution of catalyst.
(iii) Mostly liquid or gaseous catalysts are used in homogeneous catalysis.	(iii) Catalyst is solid and reacting substances are either liquids or gases.
(iv) e.g., $2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{NO_{(g)}} 2SO_{3(g)}$	(iv) e.g., $4NH_{3(g)} + 5O_{2(g)} \xrightleftharpoons{Pt_{(s)}} 4NO_{(g)} + H_2O_{(g)}$

Q.16 Describe the effects of catalyst on reversible reaction.

Ans. Effect of Catalyst on Rate of Reversible Reaction:
In reversible chemical reaction, a catalyst, suitable for forward reaction may be used to carry out back reaction as it increases the rate of both forward and reverse processes by lowering the activation energy of both forward and reverse steps by giving new path to the reaction. This reduces the time to attain the equilibrium state. It does not affect the equilibrium state K_c.

SELF-ASSESSMENT Chapter # 07

Total Mark: 30

Q.1 Encircle the correct option. **(1 × 6 = 6)**

(i) **The rate of reaction:**
A. Increases as the reaction proceeds
B. Decreases as the reaction proceeds
C. Remains the same as the reaction proceeds
D. May decrease or increase as the reaction proceeds

(ii) **On a Boltzmann distribution curve, the area under the curve represents:**
A. Activation energy of the reaction.
B. Total number of molecules in the sample.
C. Average kinetic energy of the molecules.
D. Rate constant of the reaction.

(iii) **How does the presence of a catalyst affect the rate of a chemical reaction?**
A. It always decreases the rate of the reaction.
B. It always increases the rate of the reaction.
C. It increases the rate of the forward and decreases the rate of the reverse reaction.
D. It increases the rate of both the forward and reverse reactions.

(iv) **A first-order reaction has a half-life (t1/2) of 20 minutes. What is the value of its rate constant (k)?**
A. 0.05 min^{-1} B. 0.693 min^{-1} C. 0.0347 min^{-1} D. 13.86 min^{-1}

(v) **The reaction pathway diagram with a lower peak represents:**
A. A slower reaction B. A reaction with no catalyst
C. A catalyzed reaction D. A reversible reaction

(vi) **The order of a chemical reaction, that is independent of concentration is:**
A. Second order reaction B. First order reaction
C. Zero order reaction D. Pseudo first order reaction

Q.2 Write short answers of the following questions. **(2 × 8 = 16)**

(i) Differentiate clearly between order and molecularity of a reaction.
(ii) How does increasing temperature affect the rate of a reaction?
(iii) What is the significance of the rate constant in a rate equation?
(iv) Can a catalyst be consumed in a chemical reaction? Why or why not?
(v) The shape of the Boltzmann distribution curve change with temperature. How?
(vi) What is the order of the reaction? Explain based on the units of the rate constant.
(vii) Calculate the rate of reaction from the following data: 0.5 mol of reactant consumed in 10 s.
(viii) A radioactive isotope decays by a first-order process with a half-life of 12 hours. Calculate the rate constant for the decay in s^{-1}.

Q.3 Extensive Questions. **(2 × 4 = 8)**

(a) How does the activation energy profile of an uncatalyzed reaction compare with that of the catalyzed reaction?

(b) Calculate the reaction rate if the concentration of A is 0.5 M, the concentration of B is 0.2 and the rate constant k is 4.0 $M^{-2}s^{-1}$. Given the rate law for a reaction: Rate = $k[A][B]^2$.

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Chapter 08

CHEMICAL EQUILIBRIUM

Student Learning Outcomes

After studying this chapter, students will be able to:

- Describe the microscopic events that occur when a chemical system is in equilibrium. Define with examples. **(Understanding)**
- Differentiate between microscopic and macroscopic events in a chemical reaction. **(Understanding)**
- Propose microscopic that account for observed macroscopic changes that take place during a shift in equilibrium. **(Understanding)**
- Describe what is meant by a reversible reaction and dynamic equilibrium in terms of the rate of forward and reverse reactions being equal and the concentration of reactants and products remaining constant. **(Understanding)**
- Define dynamic equilibrium between two physical states. **(Knowledge)**
- Deduce the equilibrium constant expression (K_c) from an equation for homogeneous reaction. **(Understanding)**
- Determine the relationship between different equilibrium constants (K_c) for the same reaction at the same temperature. **(Understanding)**
- Write the equilibrium expression for a given chemical reaction in terms of concentration, K_c, partial pressure K_p, number of moles K_n and mole fraction K_x. **(Application)**
- State the necessary conditions for equilibrium and the ways that equilibrium can be recognized. **(Knowledge)**
- State Le Chatelier's Principle and be able to apply it to systems in equilibrium with changes in concentration, pressure, temperature, or the addition of catalyst. **(Knowledge)**
- Determine if Kc will increase or decrease when temperature is changed, given the equation for the reaction. **(Understanding)**
- Explain industrial applications of Le Chatelier's Principle using Haber's process and the contact process as an example. **(Understanding)**
- Discuss the industrial applications of chemical equilibria and how it can be used to optimize chemical reactions to maximize yields and minimize waste products. **(Understanding)**
- Use of concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic. **(Application)**

Irreversible Reactions:

The reactions in which the reactants are completely consumed and converted into products are called irreversible reactions. Such reactions stop when the limiting reactant is used up..

Reversible Reactions:

Those reactions which continue in both directions, i.e., forward and reverse, without changing the concentration of reactants and products under the existing conditions. Such reactions never stop and are called reversible reactions. When a reversible chemical reaction takes place in a container which prevents the entry or escape of any of the substances involved in the reaction, the quantities of these components change as some are consumed and others are formed. These reactions eventually reach a stage called chemical equilibrium.

At Chemical Equilibrium: The concentrations of reactants and products become constant and the rates of the forward and reverse reactions become equal.

Examples of some reversible reactions are given below:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

The double arrow tells that the reaction is reversible.

MACROSCOPIC EVENTS AND MICROSCOPIC EVENTS

Macroscopic Events

"Macroscopic events refer to the phenomena that can be observed with the naked eye without considering the individual particles or molecules involved in the process."

Examples:

Change in colour, the evolution or absorption of heat, the formation of precipitate, evolution of a gas, change in volume or pressure, change in the composition of a substance in a chemical reaction are examples of macroscopic properties.

Rack Your Mind!

1. Which of the following is a macroscopic property of a reaction at equilibrium?
   A) Molecules continue to collide.
   B) Forward and reverse rates are equal
   C) Concentrations remain constant
   D) Bonds are breaking and forming

Microscopic Events

"Microscopic events refer to the phenomena that cannot be observed with the naked eye."

Examples:

The collisions between molecules, breaking and forming bonds, rearrangement of atoms in molecules, loss or gain of electrons are examples of microscopic events.

REVERSIBLE REACTIONS, MICROSCOPIC EVENTS AND DYNAMIC EQUILIBRIUM

Reversible Reaction is at Equilibrium

It would apparently seem to be static. However, at microscopic level, the reaction never stops and molecules are continuously under change. The reactant molecules convert into products, while at the same time, the reverse process happens. To study at micro scale that affect the macroscopic properties of the system.

Example:

Consider the reaction between steam and carbon monoxide under appropriate conditions. On mixing these gases, macroscopic changes are observed (e.g., changes in concentration).

Suppose that the reaction is started with same number of moles of both reactants.

Rack Your Mind!

2. What is meant by dynamic equilibrium?

When steam and carbon monoxide are mixed, a maximum number of collisions per second between them will occur is microscopic events. Bonds in CO and H_2O are broken and new bonds are formed to produce H_2 and CO_2. Therefore, the forward reaction has its maximum rate at the beginning. This leads to a decrease in the concentration of the reactants. As H_2O and CO are gradually used up, the forward reaction slows down.

$$H_2O_{(g)} + CO_{(g)} \longrightarrow H_{2(g)} + CO_{2(g)}$$

Reverse Reaction

As the molecules of H_2 and CO_2 accumulate, the reverse reaction also starts. With the increase in the concentration of H_2 and CO_2, more and more collisions per second between these molecules will occur as microscopic events. As bonds in H_2 and CO_2 are broken, the bonds in CO and H_2O are formed.

This means that forward reaction starts with maximum rate and gradually slows down, whereas at the start, the rate of the reverse reaction is low, gradually increases, and finally becomes constant.

$$H_{2(g)} + CO_{2(g)} \longrightarrow H_2O_{(g)} + CO_{(g)}$$

Reaction at Equilibrium

Eventually, a time comes when both reactions proceed at the same rate. The reaction at this stage is said to be in chemical equilibrium and the concentration of reactants and products become constant.

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

Unless the system is somehow disturbed, no further changes in the concentrations will occur.

Chemical Equilibrium

"The state of a reversible reaction at which composition of the reaction mixture does not change and forward and reverse rates are equal is called the state of chemical equilibrium."

Graphical Explanation:

The plots of the concentrations of reactants and products versus time for a general reaction are shown in Figure.

Suppose the reactant A is converted into the product B in a chemical reaction. The graphs in the figure show different possibilities after the equilibrium is established. At the equilibrium position, the concentrations of the reactant and the product may be equal as shown in Figure (a), or the amount of reactant may be lower or greater than that of the product as shown in Figure (b and c). However, for all of these graphs, it is clear that after the equilibrium is established, the concentrations become constant.

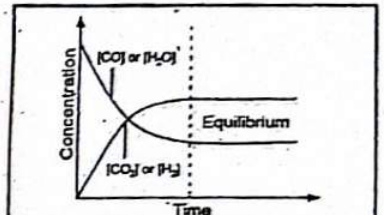


Figure: Plot of concentration vs time

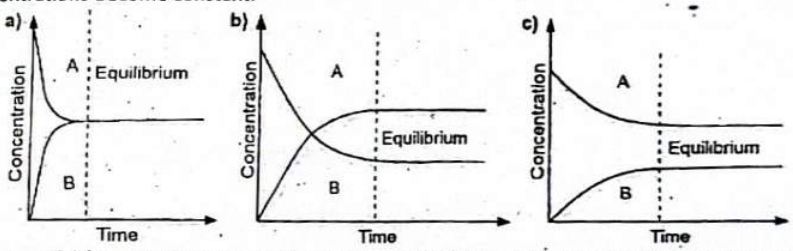


Figure: Plot of concentration vs time (a) Reactant = Product (b) Reactant < Product (c) Reactant > Product

- When the concentrations of reactants and products become constant, the reaction may apparently seem to have stopped. But it is not true.

At the Microscopic Level:

- There is intense activity. The individual molecules of the reactants continue to react. Individual product molecules also react to combine to go back to the reactants. The rate of forward process, is exactly equal to the rate of the reverse process.
- Therefore, it is a **dynamic equilibrium.** The system is dynamic because the individual molecules are constantly reacting, but the rates of forward and reverse reactions are the same.

RELATION BETWEEN MACROSCOPIC AND MICROSCOPIC EVENTS

Macroscopic events are the result of multiple simultaneous microscopic events. Understanding the microscopic events helps us to explain and predict the observed macroscopic changes in the equilibrium system.

When a change in equilibrium occurs in a chemical reaction, the microscopic events that explain the observed changes in equilibrium are the collisions and formation of new bonds between particles or molecules. These collisions change the rates of forward and reverse reactions, which are affected by activation energy and external factors. These microscopic events collectively appear as macroscopic changes which are observable by naked eye.

QUICK CHECK 8.1

a) Differentiate between macroscopic and microscopic events.

Ans. Difference Between Macroscopic and Microscopic Events:

Aspect	Macroscopic Events	Microscopic Events
Definition	Observable events visible to the naked eye.	Events at the atomic or molecular level.
Scale	Large scale.	Extremely small scale (atomic or subatomic).
Observation	Can be observed directly.	Cannot be seen directly; studied using instruments or models.
Relevance	Used in everyday applications and measurements.	Important for understanding fundamental chemical behavior.
Example	Melting of ice, boiling of water.	Movement of water molecules, vibration of atoms in ice.

b) The equilibrium is dynamic in nature, explain in terms of microscopic events.

Ans. Equilibrium is described as dynamic because even though the macroscopic properties (like concentrations of reactants and products) appear constant and unchanging, at the microscopic level, the reactions are still occurring.

In terms of microscopic events:

(i) **Continuous Forward Reaction:**
Individual reactant molecules are constantly colliding, breaking their existing bonds, and forming new bonds to become product molecules.

(ii) **Continuous Reverse Reaction:**
Simultaneously, individual product molecules are colliding, breaking their bonds, and re-forming the original reactant molecules.

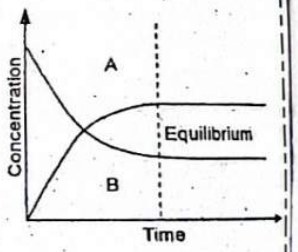
The "dynamic" aspect means these forward and reverse processes **never stop**. The equilibrium is maintained because the rate at which reactant molecules convert to products becomes exactly equal to the rate at which product molecules convert back to reactants. So, there's constant activity at the molecular level, but no net change in overall composition.

c) In the reaction $H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$, the concentration of the products is higher at the equilibrium stage.

i. Plot a graph between concentrations of reactants and products vs time.

Ans.

- **Reactants (H_2O and CO):** Start a curve for the concentration of reactants (e.g., labeled "[CO] or [H_2O]") at a high point on the Y-axis at Time = 0. This curve will decrease as time progresses, indicating reactants are being consumed. Eventually, the curve will become horizontal, showing that the concentration of reactants has become constant at equilibrium.
- **Products (H_2 and CO_2):** Start a curve for the concentration of products (e.g., labeled "[CO_2] or [H_2]") at the origin (Y=0, X=0) or a very low point on the Y-axis at Time = 0 (assuming no products initially). This curve will increase as time progresses, indicating products are being formed. Eventually, this curve will also become horizontal, showing that the concentration of products has become constant at equilibrium.
- **Equilibrium Condition:** Crucially, the horizontal line representing the constant concentration of products at equilibrium should be at a **higher level** on the Y-axis than the horizontal line representing the constant concentration of reactants. This fulfills the condition that "the concentration of the products is higher at the equilibrium stage." Both curves become horizontal at the same point in time (when equilibrium is reached).



(This graph would look like Figure (b) as shown below, where the line for 'B' (products) levels off higher than the line for 'A' (reactants)).

ii. Plot a graph between rate of the reaction with respect to time.

Ans. (You would draw a graph with "Rate of Reaction" on the Y-axis and "Time" on the X-axis. The description below explains how it should look).

- **Rate of Forward Reaction:** Start a curve for the rate of the forward reaction ($H_2O + CO \rightarrow H_2 + CO_2$) at a high point on the Y-axis at Time = 0 (since reactant concentrations are initially high). This rate will decrease as time progresses because the concentration of reactants decreases. Eventually, this curve will become horizontal when equilibrium is reached.
- **Rate of Reverse Reaction:** Start a curve for the rate of the reverse reaction ($H_2 + CO_2 \rightarrow H_2O + CO$) at the origin (Y=0, X=0) at Time = 0 (assuming no products initially, so the reverse rate is zero). This rate will increase as time progresses because the concentration of products increases. Eventually, this curve will also become horizontal.
- **Equilibrium Condition:** The point where the curve for the rate of the forward reaction and the curve for the rate of the reverse reaction meet and become a single horizontal line represents the attainment of equilibrium. At this point, the rate of the forward reaction is equal to the rate of the reverse reaction.

DYNAMIC EQUILIBRIUM BETWEEN TWO PHYSICAL STATES

Dynamic Equilibrium

It is a state in a reversible process where the rate of change in one direction is equal to the rate of change in the opposite direction. In other words, although there are continuous changes taking place, no net change in the system as a whole is observed. When a reversible phase change takes place for a substance, there is also a dynamic equilibrium between the two physical states.

Example: At 0°C, ice and water coexist in equilibrium. Water changes into ice whereas ice converts back into water at the same rate.

$$\text{Ice} \rightleftharpoons \text{Water}$$

Rack Your Mind!

3. Which of the following represents dynamic equilibrium between two physical states?
A) Ice melting into water
B) Sugar dissolving in water
C) Oxygen reacting with hydrogen
D) Carbon burning in air

Relationship between Dynamic Equilibrium and Vapor Pressure

Studying the behaviour of liquids and their vapour pressures is a significant concept in chemistry. When a liquid is placed in a closed container, some of the liquid molecules near the surface have enough energy to escape into the gaseous phase. This process is called **evaporation**. As more molecules escape into the gaseous phase, the pressure exerted by the gas molecules on the walls of the vessel increases. At the same time, molecules in vapour phase can also collide with the liquid surface and be captured again by the liquid, a process known as **condensation**.

$$\text{Liquid} \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \text{Gas}$$

As evaporation and condensation continue, the rate of these processes will eventually become equal, and a state of dynamic equilibrium is achieved. In this state, the number of liquid molecules transforming into the gas phase equals the number of gas molecules returning to the liquid phase.

At dynamic equilibrium, the vapor pressure remains constant at a given temperature, as long as the system is undisturbed.

When Temperature Increases

As the temperature increases, the average kinetic energy of the liquid molecules also increases. This leads to a higher rate of evaporation, which in turn increases the vapor pressure. Also, the rate of condensation increases at the higher temperature. Finally, the system will reach a new state of dynamic equilibrium, with a higher equilibrium vapor pressure. In short, dynamic equilibrium in terms of the vapor pressure of a liquid describes the state at which the rates of evaporation and condensation are equal.

QUICK CHECK 8.2

a) The dynamic equilibrium exists between water and its vapour at 100°C. Justify the statement.

Ans. Yes, dynamic equilibrium exists between liquid water and its vapor (steam) at 100°C in a closed system.

Justification:

1. **Constant Temperature (Boiling Point):** 100°C is the normal boiling point of water. At this temperature, if heat is continuously supplied, liquid water actively converts to steam.
2. **Reversible Process:** In a closed container, as steam forms, steam molecules also collide with the surface of the liquid water and condense back into liquid:

   Liquid Water $\rightleftharpoons$ Water Vapor (Steam)

   (Evaporation/Boiling) $\rightleftharpoons$ (Condensation)
3. **Equal Rates:** At 100°C in a closed system at equilibrium, the rate at which liquid water molecules gain enough energy to escape into the vapor phase (boiling/evaporation) becomes equal to the rate at which vapor molecules lose energy and return to the liquid phase (condensation).
4. **Dynamic Nature:** Although the overall amount of liquid water and steam might appear constant, individual water molecules are continuously transitioning between the liquid and vapor phases.
5. **Constant Vapor Pressure:** The pressure exerted by the water vapor at this equilibrium is constant (which would be 1 atm if the external pressure is 1 atm, as 100°C is the normal boiling point).

   Therefore, the continuous, balanced interchange of molecules between the liquid and vapor phases at equal rates signifies a dynamic equilibrium at 100°C.

b) Do you think that dynamic equilibrium exists between ice and water at 0°C? If yes, explain.

Ans. Yes, dynamic equilibrium exists between ice (solid water) and liquid water at 0°C in a closed system (or an open system where no heat is gained or lost from the surroundings).

Explanation:

1. **Constant Temperature (Melting/Freezing Point):** 0°C is the normal melting point (or freezing point) of water. At this temperature, both solid ice and liquid water can coexist.
2. **Reversible Process:** Ice can melt to form liquid water, and liquid water can freeze to form ice.

   Ice ($H_2O_{(s)}$) $\rightleftharpoons$ Liquid Water ($H_2O_{(l)}$)

   (Melting) $\rightleftharpoons$ (Freezing)
3. **Equal Rates:** At 0°C and equilibrium, the rate at which water molecules leave the solid ice structure and enter the liquid phase (melting) is exactly equal to the rate at which water molecules leave the liquid phase and join the solid ice structure (freezing).
4. **Dynamic Nature:** Even though the macroscopic amounts of ice and liquid water remain constant, at the microscopic level, there is a continuous exchange of molecules between the solid and liquid phases. Some ice molecules are melting, and simultaneously, some liquid water molecules are freezing.
5. **No Net Change:** Because these two opposing processes occur at the same rate, there is no net change in the amount of ice or liquid water.

   This continuous, balanced, and opposing transformation of molecules between the solid and liquid states at the same rate is characteristic of a dynamic equilibrium.

CONDITIONS FOR EQUILIBRIUM

The equilibrium should be studied when the following conditions are fulfilled:

1. The state of equilibrium only applies to reversible reactions.
2. **Closed Vessel:** The equilibrium can be established only if the reaction vessel is closed. No part of the reactants and products is allowed to escape out.

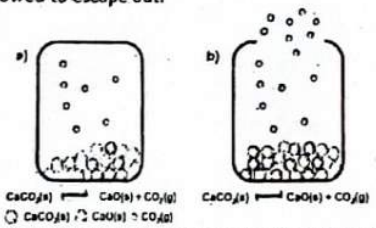


Figure (a): Equilibrium is established when the system is closed
(b) Equilibrium cannot be established in the open system.

CHARACTERISTICS OF CHEMICAL EQUILIBRIUM

Important features of equilibrium are as follows:

1. At the stage of chemical equilibrium, the concentrations of reactants and products remain constant.
2. The state of equilibrium in a reversible reaction can be approached from either side whether we start with reactants or products.
3. A catalyst does not change the equilibrium position and the equilibrium constant of the reaction. It helps to attain the equilibrium earlier.
4. The value of equilibrium constant does not depend upon the initial concentrations of reactants, rather it is constants and depends on temperature only.

KEEP IN MIND

If pure solids or pure liquids are involved in an equilibrium system, their concentrations are not included in the equilibrium constant expression. This is because the change in concentration of any pure solid or liquid has no effect on the equilibrium constant.

TYPES OF EQUILIBRIUM

With respect to the physical states of reactants and products, there are two types of chemical equilibrium.

Homogeneous Equilibrium

An equilibrium system in which all of the reactants and products are in the same phase.

Example: The following are examples of homogeneous equilibria:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

Heterogeneous Equilibrium

An equilibrium in which the reactants and products are in more than one phases is called heterogeneous equilibrium.

Example: The following are examples of heterogeneous equilibrium:

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

$$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$$

$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$$

QUICK CHECK 8.3

a) Differentiate between homogeneous and heterogeneous equilibria

Ans.

- **Homogeneous Equilibrium:** An equilibrium system where all the reactants and products are present in the **same physical phase.** For example, if all substances are gases, or all are dissolved in the same liquid solution.

  Example from Text: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ (All are gases)
- **Heterogeneous Equilibrium:** An equilibrium system where the reactants and products are present in **more than one physical phase.** For example, a reaction involving solids and gases, or liquids and gases, or immiscible liquids.

  Example from Text: $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ (Solids and a gas)

b) Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

Ans. The rates of forward reactions slow down as a reversible reaction approaches the equilibrium stage primarily because the concentration of the reactants decreases.

1. **Dependence on Concentration:** According to the Law of Mass Action, the rate of a reaction is directly proportional to the concentration of the reactants (raised to their respective powers).
2. **Consumption of Reactants:** As the forward reaction proceeds, reactants are converted into products. This leads to a gradual decrease in the concentration of the reactants.
3. **Reduced Collision Frequency:** With lower concentrations of reactants, there are fewer reactant molecules per unit volume. This results in fewer effective collisions between reactant molecules per unit of time, which are necessary for the reaction to occur.

Consequently, the rate of the forward reaction, which depends on these collisions and reactant concentrations, diminishes as the reaction moves towards equilibrium.

c) In capped soda water bottles, gaseous CO_2 is in equilibrium with the aqueous CO_2 (HCO_3^- and H^+).

$$CO_{2(g)} + H_2O_{(\ell)} \rightleftharpoons HCO^{3-}_{(aq)} + H^+_{(aq)}$$

Ans.

- **Closed Cap Required:** Equilibrium requires a closed system to prevent the escape of gaseous CO_2. If CO_2 escapes, the system cannot reach a state where the rates of dissolution and evolution of CO_2 are equal.
- **Cap Removed:** When the cap is removed, the pressure of CO_2 above the liquid decreases. According to Le Chatelier's principle, the equilibrium shifts to the left to produce more gaseous CO_2 to counteract the decrease in pressure. This results in the "fizzing" as dissolved CO_2 comes out of solution.

i. To which direction will the equilibrium shift if the bottle is opened?

Ans. When a bottle containing a gas in equilibrium with its dissolved form is opened, the equilibrium will shift to favor the gaseous phase. This occurs because the partial pressure of the gas in the headspace above the liquid decreases, causing more of the dissolved gas to escape into the gaseous phase to re–establish equilibrium. This principle is known as Le Chatelier's principle, which states that a system at equilibrium will shift to counteract any applied change.

ii. Condition for this equilibrium requires the closed cap of the bottle. Why?

Ans. A closed cap is required for this equilibrium because one of the components, $CO_2(g)$, is a gas.

1. **To Maintain Pressure of Gaseous CO_2:** The equilibrium involves gaseous CO_2 above the liquid. A closed cap maintains the pressure of this gaseous CO_2. If the cap is open, the gaseous CO_2 would escape into the atmosphere.
2. **To Prevent Escape of Reactant/Product:** According to Le Chatelier's principle, if gaseous CO_2 (a reactant in the dissolution process, or a "product" of the reverse decomposition of carbonic acid) escapes, the equilibrium will be disturbed. The system needs to be closed to allow the reverse reaction ($HCO_3^- + H^+ \rightarrow H_2O + CO_{2(g)}$) to build up enough CO_2 pressure to balance the forward dissolution rate.
3. **To Achieve Equilibrium:** For equilibrium to be established, the rate of CO_2 dissolving into the water (and reacting to form HCO_3^- and H^+) must become equal to the rate at which HCO_3^- and H^+ react to form H_2O and $CO_{2(g)}$ which then escapes from solution. If $CO_{2(g)}$ can escape, the reverse reaction cannot build up to match the forward rate, and equilibrium cannot be reached; the reaction would proceed largely to the left as CO_2 leaves.

iii. When the cap of the bottle is removed, to which direction the equilibrium shifts?

Ans. When the cap of the bottle is removed:

1. The pressure of gaseous CO_2 above the liquid suddenly decreases because the $CO_2(g)$ can now escape into the atmosphere (where its partial pressure is much lower).
2. According to Le Chatelier's principle, the system will try to counteract this decrease in $CO_2(g)$ pressure.
3. To do this, the equilibrium will shift to the **left** (reverse direction).

$$HCO^-_{3(aq)} + H^+_{(aq)} \longrightarrow CO2_{(g)} + H2O_{(\ell)}$$

4. This means that dissolved carbonic acid (formed from CO_2 and water, then ionized to HCO_3^- and H^+) will decompose to produce more gaseous CO_2, which then bubbles out of the solution. This is why soda water fizzes when the cap is opened.

EQUILIBRIUM CONSTANT AND POSITION OF EQUILIBRIUM

Position of Equilibrium:

The position of equilibrium refers to the relative amounts of products and reactants present in an equilibrium mixture.

Q. Define and explain the law of mass action and derive the expression for the equilibrium constant.

Law of Mass Action:

Introduction:

In 1864, the Norwegian chemists C. Guldberg (1836-1902) and P. Waage (1833-1900) carefully measured the compositions of many reaction systems at equilibrium.

Rack Your Mind!

4. Write the K_c expression for the reaction:
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Statement:

They discovered that for any reversible reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions.

General Reaction:

$$aA + bB \rightleftharpoons cC + dD$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation.

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Active Mass:

The rate of the chemical reaction is directly proportional to the active masses of the reactants, raised to the coefficients present in the balanced equation.

- The term active mass is used for the molar concentration.
- It is expressed in moles dm^{-3}.
- This concentration is expressed by square brackets [ ].

Let us consider a general reaction

$$A + B \rightleftharpoons C + D$$

According to the Law of mass action,

Rate of Forward Reaction:

$$\text{Rate of forward reaction} \propto [A][B] = k_f[A][B]$$

'k_f' is the proportionality constant, and is known as forward rate constant.

Rate of Reverse Reaction:

$$\text{Rate of reverse reaction} \propto [C][D] = k_r[C][D]$$

'k_r' is the proportionality constant and is known as reverse rate constant.

At the Equilibrium Stage: The forward and the reverse rates are equal. Hence,

$$k_f[A][B] = k_r[C][D]$$

Equilibrium Constant Expression:

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

The left side of this equation is the ratio of two rate constants, so it gives another constant called the equilibrium constant (K_c).

$$K_c = \frac{k_f}{k_r}$$

So, $$K_c = \frac{[C][D]}{[A][B]}$$

This equation is known as equilibrium constant expression.
Consider the following reversible reaction,

$$aA + bB \rightleftharpoons cC + dD$$

where a, b, c and d are the coefficients of balanced equation.

Then $$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

➲ Equilibrium Constant Expressions of Some Important Reactions

(i) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

(ii) $2\,N_2O_{5(g)} \rightleftharpoons 4NO_{2(g)} + O_{2(g)}$

$$K_c = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$$

Sample Problem 8.1

Ethanol reacts with ethanoic acid to form ethyl ethanoate and water.

$$\underset{\text{Ethanoic acid}}{CH_3COOH_{(1)}} + \underset{\text{Ethanol}}{C_2H_5OH_{(l)}} \rightleftharpoons \underset{\text{Ethyl Ethanoate}}{CH_3COOC_2H_{5(l)}} + \underset{\text{Water}}{H_2O_{(l)}}$$

500 cm^3 of the reaction mixture at equilibrium contained 0.235 mol of ethanoic acid and 0.0350 mol of ethanol together with 0.182 mol of ethyl ethanoate and 0.182 mol of water. Use this data to calculate a value of K_c for this reaction.

Step 1: Write out the balanced chemical equation with the concentrations beneath each substance.

$CH_3COOH_{(l)}$	+	$C_2H_5OH_{(l)}$	⇌	$CH_3COOC_2H_{5(l)}$	+	$H_2O_{(l)}$
$\frac{0.235\ mol}{0.5Hm^3}$		$\frac{0.0350\ mol}{0.5dm^3}$		$\frac{0.182\ mol}{0.5dm^3}$		$\frac{0.182\ mol}{0.5dm^3}$
$0.470\ mol\ dm^{-3}$		$0.070\ mol\ dm^{-3}$		$0.364\ mol\ dm^{-3}$		$0.364\ mol\ dm^{-3}$

Step 2: Write the equilibrium constant for this reaction in terms of concentrations.

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{(0.364\ mol\ dm^{-3})(0.0364\ mol\ dm^{-3})}{(0.470\ mol\ dm^{-3})(0.070\ mol\ dm^{-3})}$$

Step 3: Substitute the equilibrium concentrations into the expression

$$K_c = 4.03 \text{ (to3 significant figures)}$$

Step 4: Add the correct units by referring back to the equilibrium expression: The units of $mol\ dm^{-3}$ cancel out, so K_c has no units. Therefore, $K_c = 4.03$.

Sample Problem 8.2

Propanone reacts with hydrogen cyanide as follows:

$$\underset{\text{Propanone}}{CH_3COCH_{3(l)}} + \underset{\text{Hydrogen cyanide}}{HCN_{(g)}} \rightleftharpoons \underset{\text{Product}}{CH_3C(OH)(CN)CH_{3(l)}}$$

Propanone Hydrogen cyanide Product

A mixture of 0.0500 $moldm^{-3}$ propanone and 0.0500 $moldm^{-3}$ hydrogen cyanide is left to reach equilibrium at room temperature. At equilibrium the concentration of the product is 0.0233 $moldm^{-3}$. Calculate K_c for this reaction.

Solution:

Step 1: Write out the balanced chemical equation with all the data underneath:

	$CH_3COCH_{3(l)}$	+	$HCN_{(g)}$	⇌	$CH_3C(OH)(CN)CH_{3(l)}$
Initial conc.	$0.0500\ moldm^{-3}$		$0.0500\ moldm^{-3}$		$0\ moldm^{-3}$
Equilibrium. conc.	?		?		$0.0233\ moldm^{-3}$

Step 2: Calculate the equilibrium concentrations of the reactants. The chemical equation shows that for every mole of product formed, 1 mole of CH_3COCH_3 and 1 mole of HCN are consumed. So the equilibrium concentrations are as follows:

CH_3COCH_3; $0.0500 - 0.0233 = 0.0267\ moldm^{-3}$

HCN; $0.0500 - 0.0233 = 0.0267\ moldm^{-3}$

Step 3: Write the equilibrium constant for this reaction in terms of concentrations:

$$K_c = \frac{[CH_3C(OH)(CN)CH_3]}{[CH_3COCH_3][HCN]} = \frac{(0.0233\ mol\ dm^{-3})}{(0.05\ mol\ dm^{-3})(0.05\ mol\ dm^{-3})}$$

Step 4: Substitute the equilibrium concentrations into the expression

$$K_c = 32.7\ mol\ dm^{-3}$$

☑ QUICK CHECK 8.4

a) **Write K_c for the following reactions:**

i. $Sn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} \rightleftharpoons Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)}$

Ans. $K_c = \frac{[Product]}{[Reactants]} = \frac{[Sn^{+4}][Fe^{+2}]^2}{[Sn^{+2}][Fe^{+3}]^2}$

ii. $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

Ans. $K_c = \frac{[H_2O]^6[NO]^4}{[NH_3]^4[O_2]^5}$

iii. $PC\ell_{5(g)} \rightleftharpoons PC\ell_{3(g)} + C\ell_{2(g)}$

Ans. $K_c = \frac{[PC\ell_3][C\ell_2]}{[PC\ell_5]}$

b) **Calculate the value of K_c for the following reaction using the information below:**

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

Initial conc. of $H_{2(g)} = 10.00\ moldm^{-3}$.

Initial conc. of $CO_{2(g)} = 10.00\ moldm^{-3}$.

Equilibrium conc. of $CO_{(g)} = 9.47\ moldm^{-3}$.

Ans. $K_c = \frac{[H_2O][CO]}{[H_2][CO_2]}$

(As this value is not given in this question/textbook.) Supposed value of $H_2O_{(g)} = 1$ mol dm^{-3}

$$K_c = \frac{1\ moldm^{-3} \times 9.47\ moldm^{-3}}{10.00\ moldm^{-3} \times 10.00\ moldm^{-3}} = \frac{9.47}{100} = 0.0947$$

➲ Units of Equilibrium Constants

Case I: $n_r = n_p$

- When the number of moles of reactants and products in balanced chemical equations are equal, then units are canceled out, and equilibrium constant does not have any unit.
- **Example:** The ester formation reaction happens in solution state, and number of moles of reactants and products are equal. The K_c will have no units.

$$CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \rightleftharpoons CH_3COOC_2H_{5(aq)} + H_2O_{(l)}$$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH_{(aq)}][C_2H_5OH_{(aq)}]} = \frac{moldm^{-3} \times moldm^{-3}}{moldm^{-3} \times moldm^{-3}} = \text{no units}$$

Case II: $n_r \neq n_p$

- When the number of moles are unequal; then value of equilibrium constant depend upon the units of reactants and products used. In the synthesis of NH_3 by Haber's process, the units of reactants and products are not cancelled.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$K_c = \frac{[NH_{3(g)}]^2}{[N_{2(g)}][H_{2(g)}]^3} = \frac{[molsdm^{-3}]^2}{[moldm^{-3}][moldm^{-3}]^3} = \frac{1}{[mol\,dm^{-3}]^2} = mol^{-2}dm^6$$

RELATIONSHIPS BETWEEN VARIOUS EQUILIBRIUM CONSTANTS

There are four different types of quantities which may be used to calculate the equilibrium constants of reversible reaction. Let the general reaction be,

$$aA + bB \rightleftharpoons cC + dD$$

Rack Your Mind!

5. What happens to the value of K_p if $\Delta n = 0$?
   A) $K_p = 0$ B) $K_p = K_c$
   C) $K_p > K_c$ D) $K_p < K_c$

(1) **K_c:** When the concentrations of reactants and products are in mole dm^{-3}, then equilibrium constant is written as:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{_____ (1)}$$

Square brackets [ ] are used for mole dm^{-3}.

(2) **K_p:** When the concentrations are expressed in terms of partial pressures (p) for gaseous reactants and products, then

$$K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} \quad \text{_____ (2)}$$

(3) **K_n:** When the concentrations are expressed in terms of number of moles, then

$$K_n = \frac{n_C^c \cdot n_D^d}{n_A^a \cdot n_B^b} \quad \text{_____ (3)}$$

(4) **K_x:** When the concentrations are expressed in terms of mole fractions, (X) then

$$K_x = \frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b} \quad \text{_____ (4)}$$

The relationships between these equilibrium constants are as follows:

$$K_p = K_c(RT)^{\Delta n} \quad \text{_____ (5)}$$

$$K_p = K_x(P)^{\Delta n} \quad \text{_____ (6)}$$

$$K_p = K_n(N)^{\Delta n} \quad \text{_____ (7)}$$

Where:

R = General gas constant
T = Absolute temperature of the system
P = Pressure of the system
N = Total number of moles of reactants and products
Δn = Difference of number of moles of products and reactants in the balanced chemical equation

It depends upon the value of ' Δn ' that which of the equilibrium constants is bigger or smaller than the other. Anyhow, if the number of moles of reactants and products in a balanced chemical equation are equal, and all the constants have equal values.

That is, $\Delta n = 0$

then $K_p = K_c = K_x = K_n$

Hence, whichever concentration units are used, the equilibrium constants are same.

Sample Problem 8.3

$N_{2(g)}$ and $H_{2(g)}$ combine to form $NH_{3(g)}$. The value of K_c at 500°C is 6.0×10^{-2}. Calculate the numerical value of K_p for this reaction.

Solution:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$K_c = 6.0 \times 10^{-2}$

$T = 500°C + 273 = 773\ K$.

$R = 0.0821\ dm^3\ atm\ K^{-1}\ mol^{-1}$

$K_p = ?$

The formula for conversion of K_c to K_p is,

$$K_p = K_c(RT)^{\Delta n}$$

Δn = Number of moles of product − Number of moles of reactants

$\Delta n = 2 - 4 = -2$

Substituting these values in the expression

$$K_p = 6.0 \times 10^{-2}\left(0.0821 dm^3\ atm\ K{-}1\ mol^{-1} \times 773\ K\right)^{-2}$$

$$K_p = 6.0 \times 10^{-2}\left(63.5 dm^3\ atm\ mol^{-1}\right)^{-2}$$

$$K_p = \frac{6.0 \times 10^{-2}}{(63.5)^2} = \frac{0.06}{4032.25}$$

$$K_p = 1.4 \times 10^{-5}$$

So, the value of K_p is less than K_c.

Sample Problem 8.4

In the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

the equilibrium partial pressures at constant temperature are $SO_2 = 1.0 \times 10^6$ Pa, $O_2 = 7.0 \times 10^6$ Pa, $SO_3 = 8.0 \times 10^6$ Pa. Calculate the value of K_P for this reaction.

Solution

Step 1: Write the equilibrium expression for the reaction in terms of partial pressures.

$$K_p = \frac{P^2_{SO_3}}{P^2_{SO_2} \times P_{O_2}}$$

Step 2: Substitute the equilibrium concentrations into the expression.

$$K_p = \frac{(8.0 \times 10^6)^2}{(1.0 \times 10^6)^2 \times 7.0 \times 10^6} = 9.1 \times 10^{-6}\ Pa^{-1}$$

QUICK CHECK 8.5

a) Compare the magnitudes of K_c and K_p for the following reversible reactions.
i) Ammonia synthesis ii) Dissociation of PCl_5

Ans. Compare magnitudes of K_c and K_p

Use the formula:

$$K_p = K_c(RT)^{\Delta n}$$

Where:

Δn = moles of gaseous products – moles of gaseous reactants

$R = 0.0821\ dm^3 . atm . mol^{-1} . k^{-1}$

i) Ammonia Synthesis

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$\Delta n = 2 - (1 + 3) = -2 \quad \Rightarrow (RT)^{\Delta n} < 1 \quad \Rightarrow K_p < K_c$

ii) Dissociation of PCl_5

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

$\Delta n = 2 - 1 = +1 \Rightarrow (RT)^{\Delta n} > 1 \quad \Rightarrow K_p > K_c$

(b) Nitrogen reacts with hydrogen to form ammonia.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

The pressure exerted by this mixture of hydrogen, nitrogen and ammonia at constant temperature is 2.0×10^7 Pa. Under these conditions, the partial pressure of nitrogen is 1.5×10^7 Pa and the partial pressure of hydrogen is 0.4×10^7 Pa. Calculate the value of K_p for this reaction.

Ans. Calculate K_p for ammonia formation

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Given Data:

- Total pressure = 2.0×10^7 Pa (not needed directly)
- Partial pressure of $N_2 = 1.5 \times 10^7$ Pa
- Partial pressure of $H_2 = 0.4 \times 10^7$ Pa

Let the partial pressure of NH_3 be x

Use the balanced equation:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

So,

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$$

But the total pressure is the sum of partial pressure:

$$P_{total} = P_{N_2} + P_{NH_3} \Rightarrow 2.0\times10^7 = 1.5\times10^7 + 0.4\times10^7 + X \quad \Rightarrow X = 0.1\times10^7 = 1.0\times10^6\ Pa$$

Now plug into the Kp formula:

$$K_p = \frac{(1.0\times10^6)^2}{(1.5\times10^7)(0.4\times10^7)^3}$$

First, simplify:

Numerator: $(1.0\times10^6)^2 = 1.0\times10^{12}$

Denominator:

$$(1.5\times10^7)(0.4\times10^7)^3 = (1.5\times10^7)(6.4\times10^{20}) = 9.6\times10^{27}$$

$$K_p = \frac{1.0\times10^{12}}{9.6\times10^{27}} = 1.04\times10^{-16}$$

POSITION OF EQUILIBRIUM AND REACTION CONDITIONS

The position of equilibrium refers to the relative amounts of products and reactants present in an equilibrium mixture. If a system in equilibrium is disturbed.

- If the concentration of products is increased relative to the reactants, we say that the position of equilibrium has shifted to the left.
- If the concentration of products is decreased relative to the reactants, we say that the position of equilibrium has shifted to the right.

LE-CHATELIER'S PRINCIPLE

Le-Chatelier's principle can be stated as follows:

"If a system in equilibrium is disturbed, it behaves in such a way as to nullify the effect of that disturbance".

Le-Chatelier's principle describes what happens to a system when something momentarily takes it away from equilibrium



Applications of Le-Chatelier's Principle

Some of the most common applications of this principle with reference to certain physical and chemical equilibria are discussed below:

i) Effect of change in concentration
ii) Effect of change in pressure
iii) Effect of change in temperature.
iv) Effect of catalyst on equilibrium.

THE EFFECT OF CHANGE OF CONCENTRATIONS

If the system is at the equilibrium position and a certain amount of one of the reactants or products is added or removed, the equilibrium position is disturbed.

There are four possibilities for the change in concentrations of reactants and products.

Rack Your Mind!

6. In the reaction:
$BiCl_5 + H_2O \rightleftharpoons BiOCl + 2HCl$
what will happen if more $BiCl_5$ is added at equilibrium?
A) The reaction will stop
B) The equilibrium will shift to the left
C) The equilibrium will shift to the right
D) K_c will increase

(i) Hydrolysis of $BiCl_3$

Consider the following reversible reaction in which $BiCl_3$ reacts with water to give a white insoluble compound, BiOCl.

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

The expression for this reaction can be written as

$$K_c = \frac{[BiOCl][HCl]^2}{[BiCl_3][H_2O]}$$

When water is added in $BiCl_3$ solution, it becomes cloudy due to the formation of white precipitate of BiOCl. At equilibrium, a certain amount of BiOCl and HCl has been produced and certain number of moles of $BiCl_3$ are left behind.

Adding of the Reaction:

If a few moles of $BiCl_3$ are added at equilibrium, the reaction is pushed to the forward direction.

The addition of $BiCl_3$ or H_2O disturbs the equilibrium position. To re-establish the equilibrium, more BiOCl and HCl are produced. In other words, the reaction is pushed to the forward direction. K_c remains constant, but equilibrium position has changed.

The addition of BiOCl or HCl, or both disturbs the equilibrium position. To re-establish the equilibrium, more $BiCl_3$ is produced and the reaction moves in the reverse direction. The K_c remains the constant, but position of equilibrium changes.

If a certain amount of $BiCl_3$ is removed at equilibrium stage, the reaction will move in the reverse direction to compensate that change. A new equilibrium position is established, K_c being constant.

If a certain amount of BiOCl or HCl or both is removed at equilibrium stage, the reaction will move in the forward direction to compensate that change. A new equilibrium position is established; however, K_c remains constant.

THE EFFECT OF CHANGE IN PRESSURE OR VOLUME

The effect of change of volume or pressure is not applicable when

(a) The system does not involve gaseous components.

(b) The number of moles of reactants and products are equal in gaseous phase homogeneous equilibrium.

$$n_{reactants} = n_{products}$$

Rack Your Mind!

7. How does increasing pressure affect the equilibrium of ammonia synthesis?

This effect can only be discussed if the gaseous moles of reactants and products are unequal.

$$n_{reactants} \neq n_{products}$$

In order to explain this effect, let us consider the synthesis of ammonia by Haber's process.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

a) Increase in Pressure or Decrease in Volume

For the forward reaction, the number of moles and hence volume decreases. At equilibrium stage the volume occupied by the mixture is less than the volume at the initial stage under the given conditions. So, if pressure is increased at equilibrium, more ammonia is produced. It means, that reaction is shifted to the forward direction.

b) Decrease in Pressure or Increase in Volume

If the pressure is decreased or volume is increased, the reaction will move to that side, where the reaction occupies greater volume. Ammonia synthesis is shifted to the reverse direction.

QUICK CHECK 8.6

The change of volume or pressure for the following reactions only changes the equilibrium position but not the equilibrium constant. How the direction of reaction changes for each of the following reactions.

(a) $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$ (Increasing P)

(b) $2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$ (Increasing V)

(c) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ (Increasing P)

(d) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ (Increasing V)

Ans.

(a) $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$

- Increasing pressure (P): The equilibrium will shift to the right (toward the side with fewer moles of gas) to reduce the pressure.
  - Left side: 3 moles of gas ($2H_2 + 1O_2$)
  - Right side: 2 moles of gas ($2H_2O$)
  - Thus, the reaction favors the formation of $H_2O_{(g)}$ when pressure is increased.

(b) $2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$

- Increasing volume (decreasing pressure) shifts the equilibrium toward the side with more moles of gas to counteract the change.

- Here, the left side has 3 moles of gas ($2CO + 1O_2$), while the right side has 2 moles ($2CO_2$).
- Thus, the equilibrium shifts left (toward reactants) when volume increases.

(c) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

In this reaction, there is 1 mole of gaseous reactant (N_2O_4) and 2 moles of gaseous product (NO_2). Increasing the pressure will shift the equilibrium to the side with fewer moles of gas to reduce the pressure. Therefore, increasing pressure will shift the equilibrium to the left, favoring the formation of N_2O_4.

(d) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

- This gas phase reaction proceeds with the decrease in number of moles and hence decreases in volume at equilibrium stage.
- As the reaction approaches the equilibrium stage, the volume of the equilibrium mixture is less than the volume of reactants taken initially.
- When we decrease the volume further at equilibrium stage, the reaction is disturbed. It will move to the forward direction to minimize the effect of disturbance. It establishes a new equilibrium position while K_c remains constant.
- The reverse happens when the volume is increased or pressure is decreased at equilibrium stage.
- It is noted that the pressure is increased in a reaction having unequal number of moles of reactants and products then the reaction will move in that direction where the number of moles are less.

THE EFFECT OF CHANGE IN TEMPERATURE

Le-Chatelier's Principle can be used to predict the direction of a reaction with a change in temperature. **Temperature is the only factor that also affects the value of equilibrium constant (K_c).**

Rack Your Mind!

8. In the equilibrium:
$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $\Delta H^\circ = -198$ kJ
What happens if the temperature is increased?
A) Concentration of SO_3 increases
B) Concentration of SO_2 decreases
C) Equilibrium shifts to the left
D) Value of Kc increases

➢ **For an Exothermic Reaction:**

For an exothermic reaction, an increase in temperature (adding heat) favours the reverse reaction. A decrease in temperature (removing heat) favours the forward reaction.

The equation for the conversion of SO_2 to SO_3 is given below:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H^\circ = -198 \text{ kJ}$$

According to the Le-Chatelier's principle, an increase in temperature will shift the reaction from right to left.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

As a result of this change, the concentration of SO_3 will decrease and concentrations of SO_2 and O_2 will increase. Therefore, the value of the equilibrium constant will decrease. The equilibrium will shift towards left. The decrease in temperature will favour the forward reaction and the formation of the product. The production of SO_3 is favoured at a lower temperature. On the other hand, an increase in temperature will shift the reaction from left to right.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

Due to this change, the concentration of SO_3 will increase and concentrations of SO_2 and O_2 will decrease. Therefore, the value of the equilibrium constant will increase.

The equilibrium will shift towards right. The increase in temperature will favour the reverse reaction and the formation of the reactants. The production of SO_3 is not favoured at a higher temperature. K_c for this reaction is 2.8×10^2 at 1000 K; whereas, at 298 K the value of K_c is 1×10^{26}.

➢ **For an Endothermic Reaction:**

For an endothermic reaction, an increase in temperature (adding heat) favours the forward reaction. A decrease in temperature (removing heat) favours the reverse reaction.

The equation for the conversion of N_2O_4 to NO_2 is given below:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad \Delta H^\circ = +57.2 \text{ kJ}$$

According to the Le-Chatelier's Principle, an increase in temperature will shift the reaction from left to right.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

As a result of this change, the concentration of N_2O_4 will decrease and concentration of NO_2 will increase. Therefore, the value of the equilibrium constant (K_c) will increase. The equilibrium will shift towards right. The increase in temperature will favour the forward reaction and the formation of the product.

On the other hand, a decrease in temperature will shift the reaction from right to left. The decrease in temperature will favour the reverse reaction and the formation of the reactant.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

K_c for this reaction is 7.7×10^{-5} at 273 K, whereas 0.4 at 373 K.

EFFECT OF CATALYST ON EQUILIBRIUM

A catalyst is that substance which increases the rate of a chemical reaction without itself being consumed in the reaction.

- The catalyst does not change the equilibrium position and the equilibrium constant of a chemical reaction.
- A catalyst speeds up the rate at which equilibrium is attained. It means that the yield of the chemical reaction remains the same.
- A catalyst provides new path of lower activation energy for a reaction.
- If we plot a graph between reaction coordinate on x-axis and potential energy of the chemical reaction on y-axis, then the maxima of the curve become lower in the presence of a catalyst as shown in Figure 8.3.

Rack Your Mind!

9. How does a catalyst affect the rate of a reaction and its equilibrium?

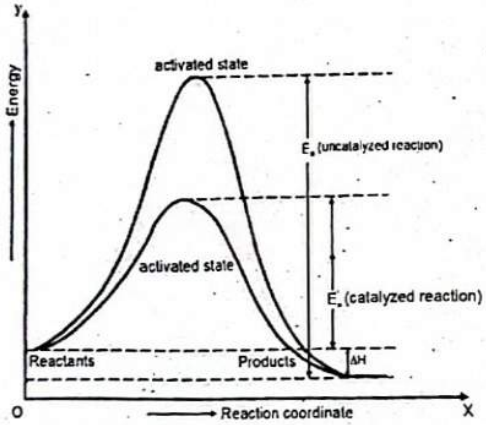


Figure: Effect of a catalyst on Reversible Reactions

INDUSTRIAL APPLICATIONS OF CHEMICAL EQUILIBRIUM

Synthesis of Ammonia by Haber's Process

It is one of the basic needs of industry to have maximum yield of the product. We can apply the concept of equilibrium in order to have the maximum yield from the industrial synthesis of ammonia.

Ammonia synthesis from nitrogen and hydrogen is a reversible process.

Rack Your Mind!

10. How can the yield of ammonia be increased in the Haber process using Le Chatelier's Principle?

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -46.11 \text{ kJ mol}^{-1}$$

The maximum yield of ammonia can be achieved by the following ways:

1. Decrease the concentration of ammonia by removing it from the reaction vessel from time to time. Equilibrium will shift to the forward direction in accordance with Le-Chatelier's principle.
2. Since, four moles of reactants combine to give two moles of products, reaction happens with the decreasing volume. High pressure will shift the equilibrium position to the right to give more and more ammonia.
3. This is an exothermic reaction. By decreasing temperature, it will shift to the forward direction according to Le-Chatelier's principle.

When we look at the Table given below and the Figure, then it becomes clear that the effect of pressure and temperature on the yield of ammonia is very prominent. The most complete conversion is 98.3% at 473 K(200°C) and 1000 atmospheric pressure.

Table: Effect of Temperature on K_c for Ammonia Synthesis.

T(K)	K_c
200	7.15×10^{15}
300	2.69×10^{8}
400	3.94×10^{4}
500	1.72×10^{2}
600	4.53×10^{0}
700	2.96×10^{-1}
800	3.96×10^{-2}

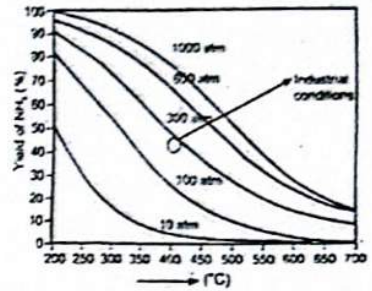


Fig: Percent yield of ammonia vs. Temperature (°C) at five different operating pressures. At very high pressure and low temperature (top left), the yield is high, but the rate of formation is low. Industrial conditions (circle) are between 200 and 300 atm at about 400°C.

At 200°C, the yield is being favoured but the rate of reaction becomes very slow and the process becomes uneconomical. So, the temperature is raised to a moderate level i.e. 400°C and a catalyst is used to increase the rate. If we want to achieve the same rate without a catalyst then we require much higher temperature, which lowers the yield.

Optimum Conditions to get Best Yield of Ammonia

The most suitable conditions to get maximum yield of ammonia are:

a) Pressure between 200-300 atmospheres

b) Temperature around 673 K(400°C)

c) Pieces of iron crystals present in a fused mixture of $MgO, A\ell_2O_3$ and SiO_2, as catalyst

Preparation of Sulphur Trioxide

To manufacture H_2SO_4, sulphur trioxide gas is produced from SO_2 and O_2, in a reversible process.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -97.9 \text{ kJ mol}^{-1}$$

According to Le-Chatelier's principle, a high pressure and low temperature are the essential conditions to have better yield of SO_3. At low temperature, the equilibrium constant for the formation of SO_3 is large, but equilibrium is achieved very slowly. As the temperature is raised, the rate increases but the yield of SO_3 drops off.

The following Table helps us to understand the parameters, when pressure is maintained at 1 atmosphere.

Table: Effect of temperature on equilibrium position of SO_3 formation

1. Temperature (°C)	200	300	400	500	600	700
2. K_c	5500	690	160	55	25	13
3. Mole % of SO_3	98	91	75	61	46	31

➢ **Optimum Conditions**

In order to have a best yield of SO_3, within a reasonable time, a mixture of $SO_{2(g)}$ and $O_{2(g)}$ (air) at one atmospheric pressure is passed over a solid catalyst, such as V_2O_5. But due to the exothermic reaction, the temperature of the gas increases to 60°C. The equilibrium mixture is recycled at low temperature of 400 – 500°C to increase the yield of $SO_{3(g)}$.

QUICK CHECK 8.7

Look at the information given in the table below:

$N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$ $\quad \Delta H^\circ = -92\ kJ\ mol^{-1}$ $\quad K_p=\frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3}$

$N_2O_4(g)\rightleftharpoons 2NO_2(g)$ $\quad \Delta H^\circ = +57\ kJ\ mol^{-1}$ $\quad K_p=\frac{(P_{NO_2})^2}{P_{N_2O_4}}$

$2SO_2(g)+O_2(g)\rightleftharpoons 2SO_3(g)$ $\quad \Delta H^\circ = -197\ kJ\ mol^{-1}$ $\quad K_p=\frac{(P_{SO_3})^2}{(P_{SO_2})^2 P_{O_2}}$

T/K	K_p / atm^{-2}	T/K	K_p / atm^{-2}	T/K	K_p / atm^{-1}
400	1.0×10^{2}	200	1.9×10^{-6}	600	3.2×10^{3}
500	1.6×10^{-1}	300	1.7×10^{-1}	700	2.0×10^{2}
600	3.1×10^{-3}	400	5.1×10	800	3.2×10
700	6.3×10^{-5}	500	1.5×10^{3}	900	6.3
800	7.9×10^{-6}	600	1.4×10^{4}	1000	2.0

i) How does the proportion of products in the above system change as the temperature increases?

Ans. In ammonia synthesis, increasing the temperature shifts the equilibrium towards the reactants, decreasing the proportion of products. This is because the reaction is exothermic, meaning it releases heat. According to Le Chatelier's principle, when the temperature of an exothermic reaction is increased, the equilibrium shifts to favor the endothermic direction, which in this case, is the reverse reaction that consumes heat and produces reactants. Therefore, a higher temperature results in a lower yield of ammonia.

In decomposition reaction of N_2O_4 to NO_2 i.e.:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

This reaction is endothermic in the forward direction (i.e., it absorbs heat). $\Delta H > 0$

According to Le Chatelier's Principle, increasing the temperature will favor the endothermic direction (the forward reaction). Therefore:

As temperature increases, the equilibrium shifts to the right. More NO_2 (product) is formed and less N_2O_4 reactant remains.

Contact process is used for the manufacturing of H_2SO_4 on industrial scale in which the conversion of SO_2 to SO_3 is achieved in a reversible reaction.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -194\ kJ\ mol^{-1}$$

At low temperature, the equilibrium constant for formation of SO_3 is large but equilibrium is reached very slowly.

- **As the temperature is raised the rate increases but the yield of SO_3 drops off according to Le-Chatelier's principle.**
- **High pressure tends to increase yield of SO_3. However, instead of using high pressure, the concentration of O_2 (air) is increased to increase the yield of SO_3.**

Effect of Temperature on the Yield of SO_3

The table helps to understand the effect of different conditions on the yield of SO_3. During the process pressure is kept at one atmosphere.

Temperature (°C)	K_c	Mole% of SO_3
200	5500	98
300	690	91
400	160	75
500	55	61
600	25	46
700	13	31

ii) Calculate the values of K_c for the reactions at 600 K?

Ans. To calculate the value of K_c at 600 K, the equilibrium concentrations of the reactants and products must be known. Since these concentrations are not provided, the exact value of Kc cannot be determined.

- In an endothermic reactions, rise in temperature (600 K) at equilibrium favours the reaction to shift to the forwards direction.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H^\circ = +57\ kJ\ mol^{-1}$$

- For an exothermic reaction, an increase in temperature shifts the equilibrium to the left, favoring the reactants. As a result, the proportion of products decreases e.g.

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H^\circ = -92\ kJ\ mol^{-1}$$

$$2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H^\circ = -197\ kJ\ mol^{-1}$$

Solution File — Rack Your Brain!

Sr. #	Option	Explanation
1.	C	At equilibrium, the concentration of reactants and products remains constant. This constancy is a key macroscopic property of equilibrium systems.
2.	S.Q	The state of equilibrium where forward and reverse reactions occur at the same rate, keeping the concentrations of all substances constant is called dynamic equilibrium.
3.	A	$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$ This represents the dynamic equilibrium between ice (solid) and water (liquid) at the melting point.
4.	S.Q	K_c expression for the reaction is given below; $K_c=\frac{[NH_3]^2}{[N_2][H_2]^3}$
5.	B	When $\Delta n = 0$, the number of moles of gaseous products equals the number of moles of gaseous reactants, so $K_p = K_c(RT)^0 = K_c$.
6.	C	Adding more $BiCl_3$ increases the concentration of reactants, causing the equilibrium to shift to the right to consume some of the added $BiCl_3$ and form more products.
7.	S.Q	In the reaction: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ Increasing pressure shifts the equilibrium **to the forward direction** (towards ammonia) because it reduces the number of gaseous moles from 4 moles to 2 moles.
8.	C	The reaction is exothermic, so increasing temperature favours the reverse reaction, shifting the equilibrium to the left. $2SO_2 + O_2 \rightleftharpoons 2SO_3$
9.	S.Q	A catalyst increases the rate of a chemical reaction by providing an alternative pathway with **lower activation energy. It does not affect the position of equilibrium or the value of the equilibrium constant,** but helps the system reach equilibrium faster.
10.	S.Q	The yield of ammonia can be increased by: 1. Removing ammonia regularly to shift equilibrium forward. 2. Applying high pressure because fewer gas molecules are formed. 3. Lowering temperature since the reaction is exothermic, favoring ammonia formation.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. For which system, does the equilibrium constant, K_c has units of $(\text{concentration})^{-1}$?

a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ b) $H_2 + I_2 \rightleftharpoons 2HI$ c) $2NO_2 \rightleftharpoons N_2O_4$ d) $2HF \rightleftharpoons H_2 + F_2$

II. Which statement about the following equilibrium is correct?

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H = -197.9\,kJmol^{-1}$$

a) The value of K_p falls with a rise in temperature.
b) The value of K_p falls with increasing pressure.
c) Adding V_2O_5 catalyst increase the equilibrium yield of sulphur trioxide.
d) The value of K_p is equal to K_c.

III. $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$

The conventional equilibrium constant expression (K_c) for the system as described by the above equation is:

a) $[SO_2]^2/[SO_3]$ b) $[SO_2]^2[O_2]/[SO_3]^2$ c) $[SO_3]^2/[SO_3]^2[O_2]$ d) $[SO_2][O_2]$

IV. A saturated solution represents a dynamic equilibrium. Macroscopically, the concentration of dissolved solute is constant. Microscopically, this occurs because:

a) No more solute particles are dissolving.
b) The rate of dissolution of solute is zero.
c) Solute particles are dissolving and precipitating at the same rate.
d) All solute particles have dissolved.

V. Which of the following statements correctly describes the effect of temperature on the equilibrium constant?

a) K_c is directly proportional to temperature.
b) K_c is inversely proportional to temperature.
c) K_c depends on the enthalpy change of the reaction.
d) Temperature has no effect on the value of K_c.

VI. Consider the gas-phase equilibrium system represented by the equation:

$$2H_2O_{(g)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$$

Given that the forward reaction is endothermic, which of the following changes will decrease the equilibrium amount of H_2O?

a) Adding more oxygen
b) Adding a solid phase catalyst
c) Decreasing the volume of the container (the total pressure increases)
d) Increasing the temperature at constant pressure

VII. $K_c = 0.040$ at 450°C for the given reaction, evaluate K_p for the reaction:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

a) 0.40 b) 0.64 c) 2.4 d) 0.052

VIII. In which of the following gaseous equilibria, pressure has no effect on the equilibrium position?

a) $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$ b) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

c) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$ d) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

IX. Consider the equilibrium $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. If the concentration of $H_2O_{(g)}$ is increased, the concentrations of $H_{2(g)}$ and $O_{2(g)}$ will:

a) Increase b) Decrease c) Remain the same d) Change irregularly

X. For a specific reaction, the value of the equilibrium constant, K_c:

a) Always remains the same at different reaction conditions.
b) Increases if the concentration of one of the products is increased.
c) Changes with changes in the temperature.
d) Increases if the concentration of one of the reactants is increased.

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	c	$2NO_2 \rightleftharpoons N_2O_4$	The units of Kc depend on the change in moles of gas (Δn) in the reaction: $K_c = \frac{[N_2O_4]}{[NO_2]_2} \Rightarrow \text{Units} = \frac{M}{M_2} = M^{-1} = (\text{concentration})^{-1}$ For option c, $\Delta n = 1-2 = -1$, leading to Kc units of M^{-1}.
II.	a	The value of K_p falls with a rise in temperature.	The reaction is exothermic ($\Delta H = -197.9$ kJ/mol). Le-Chatelier's Principle: Increasing temperature shifts equilibrium left (toward reactants), reducing K_p. Why other options are wrong: b) K_p is independent of pressure (only composition changes). c) Catalyst speeds up equilibrium but does not affect yield. d) $K_p \neq K_c$ because $\Delta n = 2-3 = -1$
III.	b	$[SO_2]^2[O_2]/[SO_3]^2$	K_c is products over reactants, raised to their stoichiometric coefficients.
IV.	c	Solute particles are dissolving and precipitating at the same rate.	Macroscopic constancy results from equal dissolution and precipitation rates at equilibrium.
V.	c	K_c depends on the enthalpy change of the reaction.	K_c changes with temperature only if $\Delta H \neq 0_{(exo/endothermic)}$
VI.	d	Increasing the temperature at constant pressure	Endothermic forward reaction favours products (more $H_2 + O_2$) when heated.
VII.	c	2.4	$K_p = K_c(RT)^{\Delta n}$, $\Delta n = 1$ $K_p = 0.040 \times (0.0821 \times 723)1 = 2.4$ (T = 450°C = 723K)
VIII.	c	$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$	$\Delta n = 0$ (2 gas moles ⇌ 2 gas moles), so pressure changes do not shift equilibrium.
IX.	a	Increase	Adding product (H_2O) shifts equilibrium left (Le-Chatelier's Principle), increasing $[H_2]$ and $[O_2]$.
X.	c	changes with changes in the temperature.	K_c is constant for a given temperature but varies with temperature (depends on ΔH).

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. What is meant by the state of chemical equilibrium?

Ans. Chemical equilibrium is the state in a reversible reaction when the rate of the forward reaction equals the rate of the reverse reaction, and the concentrations of reactants and products remain constant.

b. Define reversible reaction. Give an example.

Ans. A reversible reaction is a chemical reaction that proceeds in both forward and reverse directions under the same conditions.
Example:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

c. The change of volume disturbs the equilibrium position for some of the gas phase reactions but not the equilibrium constant.

Ans. Volume changes affect the pressure, thus shifting the equilibrium position (Le-Chatelier's principle), but the equilibrium constant K_c or K_p remains unchanged as long as temperature is constant.

d. Mention the characteristics of chemical equilibrium.

Ans. Characteristics of Chemical Equilibrium:
(i) Rate of forward reaction equals rate of reverse reaction.
(ii) Concentrations of reactants and products remain constant.
(iii) Dynamic in nature.
(iv) Can be established from either side.
(v) Only affected by temperature, not by pressure or concentration (for K_c).

e. Reversible reaction attains the position of equilibrium which is dynamic in nature and not static. Explain it.

Ans. At equilibrium, the forward and reverse reactions continue to occur, but at the same rate. This means particles are still reacting, but no net change occurs. Hence, it is dynamic, not static.

f. Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

Ans. As the concentration of reactants decreases and products increase, the forward reaction slows due to fewer collisions of reactant particles, while the reverse reaction rate increases.

g. Why ice at 0°C can be melted by applying pressure without supply of heat from outside?

Ans. Applying pressure favors the liquid phase (as it is denser than ice), shifting equilibrium towards melting even without external heat (Le-Chatelier's principle).

h. Write two conditions of equilibrium constant.

Ans.
(i) Temperature must remain constant.
(ii) The reaction must be in a closed system and reach equilibrium.

i. The reversible reaction:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

has come to equilibrium in a vessel of specific volume at a given temperature. Before the reaction began, the concentrations of the reactants were 0.060 mol/dm³ of SO_2 and 0.050 mol/dm³ of O_2. After equilibrium is reached, the concentration of SO_3 is 0.040 mol/dm³. What is the equilibrium concentration of O_2?

Ans.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

Given Data:
- Initial $[SO_2] = 0.060$ mol/dm³
- Initial $[O_2] = 0.050$ mol/dm³
- At equilibrium: $[SO_3] = 0.040$ mol/dm³

From Stoichiometry:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

$\Rightarrow$ If 0.040 mol of SO_3 formed, then 0.020 mol of O_2 used Equilibrium $[O_2] = 0.050 - 0.020 = 0.030$ mol/dm³

DESCRIPTIVE QUESTIONS

Q.3 (a) Define and explain the law of mass action and derive the expression for the equilibrium constant.

Ans. See Page No. (267)

(b) Write the expression for K_c for the following reactions:

i) $Sn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} \rightleftharpoons Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)}$ ii) $Ag^{1+}_{(aq)} + Fe^{2+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + Ag_{(s)}$

iii) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ iv) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

v) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

Ans.

(i) $Sn^{+2}_{(aq)} + 2Fe^{+3}_{(aq)} \rightleftharpoons Sn^{+4}_{(aq)} + 2Fe^{+2}_{(aq)}$

$$K_c = \frac{[\text{Product}]}{[\text{Reactants}]} = \frac{[Sn^{+4}][Fe^{+2}]^2}{[Sn^{+2}][Fe^{+3}]^2}$$

(ii) $Ag^{+}_{(aq)} + Fe^{+2}_{(aq)} \rightleftharpoons Fe^{+3}_{(aq)} + Ag^{0}$

$$K_c = \frac{[Fe^{+3}][Ag^0]}{[Ag^+][Fe^{+2}]}$$

(iii) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

(iv) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

$$K_c = \frac{[H_2O]^6[NO]^4}{[NH_3]^4[O_2]^5}$$

(v) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Q.4 Write down the K_c for the following reactions. Suppose that the reaction mixture in all the case is 'V' dm⁻³.

i) $CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

ii) $2HI \rightleftharpoons H_2 + I_2$ iii) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Ans.

(i) $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

moles at t = 0 "a" mol "b" mol $\rightleftharpoons$ "0" mol "0" mol

moles at t = equilibrium $(a-x) + (b-x) \rightleftharpoons (x) + (x)$

conc. in mol/v (dm^3) so $\left(\frac{a-x}{v}\right) + \left(\frac{b-x}{v}\right) \rightleftharpoons \left(\frac{x}{v}\right) + \left(\frac{x}{v}\right)$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} \Rightarrow K_c = \frac{\left(\frac{x}{v}\right)\times\left(\frac{x}{v}\right)}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)} \Rightarrow K_c = \frac{x^2}{v^2}\times\frac{v^2}{(a-x)(b-x)}$$

So $K_c = \frac{x^2}{(a-x)(b-x)}$

(ii) $2HI \rightleftharpoons H_2 + I_2$

t = 0 a mole $\rightleftharpoons$ 0 + 0

t = equilibrium $(a-2x) \rightleftharpoons x + x$

$$\left(\frac{a-2x}{v}\right) \rightleftharpoons \left(\frac{x}{v}\right) + \left(\frac{x}{v}\right)$$

$$K_c = \frac{[Products]}{[Reactant]} \Rightarrow K_c = \frac{[H_2][I_2]}{[HI]^2} \Rightarrow K_c = \frac{\left(\frac{x}{v}\right)\times\left(\frac{x}{v}\right)}{\left(\frac{a-2x}{v}\right)^2} \Rightarrow K_c = \frac{x^2}{(a-2x)^2}$$

(iii) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

moles at t = 0 $a + b \rightleftharpoons 0$

moles at t = equilibrium $(a-x) + (b-3x) \rightleftharpoons 2x$

concentration in moles/'V' dm^3 $\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right) \rightleftharpoons \frac{2x}{v}$

$$K_c = \frac{[Product}{[Reactant]} \Rightarrow K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]}$$

So $K_c = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right)^3} \Rightarrow K_c = \frac{4x^2v^2}{(a-x)(b-3x)^3}$

Q.5 In the equilibrium

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \quad \Delta H = 90 \text{ kJ mol}^{-1}$$

What is the effect on the following changes? Explain your answer.

i) If temperature is increased ii) volume of the container is decreased

iii) catalyst is added iv) chlorine is added

Ans. Equilibrium

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \quad \Delta H = 90 \text{ kJ mol}^{-1}$$

a. Position of equilibrium b. Equilibrium constant

If:

i. **Temperature is Increased:** Temperature change will affect both equilibrium position and equilibrium constant. This is endothermic reaction, the increase of temperature shifts equilibrium positon in forward direction to re-establish equilibrium. Hence, the value of K_c increase.

ii. **Volume is Decreased:** The volume change affects equilibrium position only. When volume is decreased, reaction moves in backward direction to establish equilibrium again.
Since equilibrium constant has a constant value at a particular temperature, it is not affected by change in volume.

iii. **Catalyst is Added:** Catalyst has no effect on the equilibrium position and equilibrium constant. When catalyst is added at equilibrium, it enhances both the rates equally. Hence, equilibrium is not affected.

iv. **Chlorine is Added:** The addition of a substance at equilibrium affects the equilibrium position only Equilibrium constant remains the same.
When Cl_2 is added at equilibrium, the conc. of products increases and equilibrium position is shifted in backward direction.

Q.6 Synthesis of ammonia by Haber's process is an exothermic reaction.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -92.46 \text{ kJ}$$

What should be the possible effect of change of temperature at equilibrium stage?

Ans. Since reaction is endothermic in backward direction, rise of temperature will shift equilibrium to left. Low temperature shifts the equilibrium to right and yield of NH3 will increase.

Q.7 K_c for the following reaction is 0.016 at 520°C

$$2HI_{(g)} \rightleftharpoons H_2 + I_{2(g)}$$

The equilibrium mixture contains HI = 0.08 M; H_2 = 0.01 M and I_2 = 0.01 M. To this mixture, more HI is added. So that its new concentration is 0.096 M. What will be the concentrations of HI, H_2 and I_2 when equilibrium is re-established?

Ans. Given Data:

Initial concentration of HI = 0.08 M

Initial concentration of H_2 = 0.01 M

Initial concentration of I_2 = 0.01 M

New concentration of HI = 0.096 M

Required: [HI], [H_2] and [I_2] = ?

Solution: $2HI \rightleftharpoons H_2 + I_2$

Initial concentration

$0.08\text{ M} \rightleftharpoons 0.01\text{ M} + 0.01\text{ M}$

At equilibrium, the new concentrations

$(0.096 - 2x) \rightleftharpoons (0.01 + x) + (0.01 + x)$

$$K_c = \frac{\text{concentration of product}}{\text{concentration of reactants}} = \frac{[H_2][I_2]}{[HI]^2}$$

$$0.016 = \frac{[0.01+x][0.01+x]}{[0.096-2x]^2}$$

$$0.016 = \frac{(0.01+x)^2}{(0.096-2x)^2}$$

Taking square root on both sides

$$\sqrt{0.016} = \sqrt{\frac{(0.01+x)^2}{(0.096-2x)^2}}$$

$$0.126 = \frac{0.01+x}{0.096-2x}$$

$$0.126(0.096-2x) = 0.01+x$$

$$0.012096 - 0.252x = 0.01 + x$$

$$0.012096 - 0.01 = x + 0.252x$$

$$0.002096 = 1.252x$$

$$x = \frac{0.002096}{1.252}$$

$$x = 1.68 \times 10^{-3}\text{ M} \text{ or } 0.00168\text{ M}$$

Concentrations at equilibrium can be calculated as follows

(i) $[HI] = (0.096 - 2x)$

$= 0.096 - 2 \times 0.00168 = 0.096 - 0.00336$

$= 0.09264$ M

(ii) $[H_2] = 0.01 + x = 0.01 + 0.00168$

$= 0.01168$ M

(iii) $[I_2] = 0.01 + x = 0.01 + 0.00168$

$= 0.01168$ M

[HI] = 0.0926 M

[H_2] = 001168 M

[I_2] = 0.01168

Q.8 The equilibrium constant for the reaction between acetic acid and ethyl alcohol is 4. A mixture of 3 moles of acetic acid and 1 mole of ethyl alcohol is allowed to come to equilibrium. Calculate the amount of ethyl acetate present at equilibrium.

Ans. Given Data: $K_c = 4$

Moles of acetic acid = 3

Moles of ethyl alcohol = 1

Required:

Moles of ethyl acetate = ? , Amount of ethyl acetate = ?

Moles of acid = ? , Amount of acid in gram = ?

Moles of alcohol = ? , Amount of alcohol in gram = ?

Solution: $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

at t = 0 3 mol + 1 mol $\rightleftharpoons$ 0 mol + 0 mol

at t = equilibrium $(3-x)$ mol + $(1-x)$ mol $\rightleftharpoons$ (x) mol + (x) mol

$$K_c = \frac{[Product]}{[Reactants]} = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$4 = \frac{(x)(x)}{(3-x)(1-x)} = \frac{x^2}{x^2-4x+3}$$

$$x^2 = 4(x^2-4x+3)$$

$$x^2 = 4x^2-16x+12$$

$$4x^2-x^2-16x+12 = 0$$

$$3x^2-16x+12 = 0$$

It is a quadratic equation. To evaluate the value of x, the formula used is:

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$$

Let us consider that [a = 3, b = –16, c = 12] for above reaction

Thus, $$x = \frac{-(16) \pm \sqrt{(16)^2-4\times3\times12}}{2\times3}$$

$$= \frac{16 \pm \sqrt{256-144}}{6} = \frac{16 \pm \sqrt{112}}{6} = \frac{16 \pm 10.58}{6}$$

So, $$x = \frac{16+10.58}{6} = 4.43 \text{ moles or}$$

$$x = \frac{16-10.58}{6} = 0.903 \text{ moles}$$

From the above two values of x

$x \neq 4$ as initial concentration of CH_3COOH is less i.e., 3 moles. So value of x = 0.903 moles.

(i) Concentration of (CH_3COOH) at equilibrium
= 3 – x = 3 – 0.903 = 2097 moles

(ii) Concentration of (C_2H_5OH) at equilibrium
= 1 – x = 1 – 0.903 = 0.097 moles

(iii) Concentration of ethyl acetate = x = 0.903 moles

(iv) Mass = Moles × Mol. mass

(a) Amount of CH_3COOH = 2.097 × 60 = 125.82 g

(b) Amount of C_2H_5OH = 0.1 × 46 = 4.6 g

(c) Amount of ethyl acetate = 0.9 × 88 = 79.46 g

Moles of ethyl acetate = 0.9 moles

Mass of ethyl acetate = 79.46 g

Mass of acid left behind = 126 g

Mass of alcohol left = 4.6 g

Q.9 Study the equilibrium

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

i) Write the expression of K_p.

ii) When 1.00 mole of steam and 1.00 mole of CO are allowed to reach equilibrium, 33.3% of equilibrium mixture is hydrogen. Calculate the value of K_p. State the units of K_p.

Ans. Given Data: Moles of steam = 1.00

Moles of CO = 1.00

% of H_2 at equilibrium = 33.3%

Required: (i) Value of K_p = ?

(ii) Unit of K_p = ?

Solution: $H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$

Concentration at t = 0 (1.00) mole + (1.00) mole $\rightleftharpoons$ 0 + 0

Concentration at t = eq (1 – x) mole + (1 – x) mole $\rightleftharpoons$ x + x

Total moles of reaction mixture = 1 + 1 = 2 mol.

Moles of H_2 at equilibrium = 33.3%

It means that $$\frac{x}{2} = \frac{\text{conc. of } H_2}{100}$$

$$\frac{x}{2} = \frac{33.3}{100}$$

$$x = \frac{2\times33.3}{100} = 0.666 \text{ moles}$$

So $[H_2O] = 1 - x$

$= 1 - 0.666 = 0.333$ moles

$[CO] = 1 - x$

$= 1 - 0.666 = 0.333$ moles

$[H_2] = [CO_2] = x = 0.666$ moles

$K_p = K_c(RT)^{\Delta n}$

as $\Delta n = 0$ so,

$K_p = K_c$

$$K_p = \frac{[Products]}{[Reactants]} = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{0.666\times0.666}{0.333\times0.333} = 4$$

Units of K_p $$= \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{\text{mol dm}^{-3}.\text{ mol dm}^{-3}}{\text{mol dm}^{-3}.\text{ mol dm}^{-3}} = \text{no unit}$$

$K_p = 4$

K_p has no unit.

ADDITIONAL SLOs BASED MCQs

1. Reactions that proceed in both forward and reverse directions without changing the concentration of reactants and products under existing conditions are called:
A. Irreversible reactions B. Reversible reactions C. Complete reactions D. Spontaneous reactions

2. The observation of a color change in a reaction is an example of a:
A. Microscopic event B. Macroscopic event C. Quantum event D. Nuclear event

3. In the reaction $H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$, the forward reaction rate is maximum:
A. At equilibrium B. At the beginning
C. When product concentration is high D. When the reverse reaction rate is maximum

4. Which of the following is an example of dynamic equilibrium between two physical states?
A. Burning of wood B. Rusting of iron
C. Evaporation of water in an open container D. Ice and water coexisting at 0°C in a closed container

5. At dynamic equilibrium between a liquid and its vapor, the rate of evaporation is:
A. Greater than the rate of condensation B. Less than the rate of condensation
C. Equal to the rate of condensation D. Zero

6. Which of the following is NOT a necessary condition for establishing chemical equilibrium?
A. The reaction must be reversible B. The system must be closed
C. A catalyst must be present D. Temperature should be constant

7. The concentration of pure solids and pure liquids are not included in the Kc expression because:
A. They do not react
B. Their concentrations are variable
C. Their concentrations (active masses) are considered constant
D. They are not part of the equilibrium

8. Which of the following is an example of heterogeneous equilibrium?
A. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_3(g)$
B. $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$
C. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
D. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

9. The term "active mass" in the Law of Mass Action refers to:
A. Total mass of the reactant B. Molar concentration
C. Number of moles D. Density

10. For the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, the correct Kc expression is:
A. $\frac{[NH_3]}{([N_2][H_2])}$ B. $\frac{[NH_3]^2}{([N_2][H_2]^3)}$ C. $\frac{([N_2][H_2]^3)}{[NH_3]^2}$ D. $\frac{[N_2][H_2]}{[NH_3]}$

11. For which reaction will K_c have units of $mol^{-2}\ dm^{+6}$?
A. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ B. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
C. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ D. $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$

12. For the Haber process $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, the value of Δn is:
A. −1 B. −2 C. +1 D. +2

13. Le Chatelier's principle is used to predict the effect of a disturbance on:
A. The rate of reaction only B. The equilibrium position
C. The activation energy D. The mechanism of reaction

14. For the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, increasing the pressure will shift the equilibrium:
A. To the left, favoring reactants B. To the right, favoring products
C. No effect D. To increase Δn

15. For an exothermic reaction (ΔH = −ve), increasing the temperature will:
A. Shift equilibrium to the right and increase K_c B. Shift equilibrium to the left and decrease K_c
C. Shift equilibrium to the right and decrease K_c D. Shift equilibrium to the left and increase K_c

16. A catalyst increases the rate of a chemical reaction by:
A. Increasing the activation energy B. Decreasing the activation energy
C. Shifting the equilibrium to the right D. Increasing the yield of products

17. To maximize the yield of ammonia in the Haber process ($N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$; ΔH = −ve), conditions should be:
A. High temperature, low pressure B. Low temperature, high pressure
C. High temperature, high pressure D. Low temperature, low pressure

18. In the Contact process for SO_3 production ($2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$; ΔH = −ve), a decrease in temperature favors:
A. Formation of SO_2 and O_2 B. Formation of SO_3
C. No change in equilibrium D. An increase in K_c value

Answers Key

1. B	2. B	3. B	4. D	5. C	6. C	7. C	8. C	9. B	10. B	11. B
12. B	13. B	14. C	15. B	16. B	17. C	18. B				

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Differentiate between Reversible and Irreversible reaction.

Ans.

Reversible Reaction	Irreversible Reaction
1. "The chemical reaction in which products of a reaction can react to form the original reactants under the same set of conditions is called a reversible reaction."	1. "A chemical reaction in which products of the reaction do not react to form the original reactants under same conditions is called irreversible reaction."
2. "The chemical reaction which takes place in both directions i.e. forward and reverse under same conditions is called reversible reaction." $A + B \rightleftharpoons C + D$ Reactants Products	2. "A chemical reaction which takes place in one direction only under same conditions is called irreversible reaction." $A + B \longrightarrow C + D$ Reactants Products
3. It is represented by writing a double headed arrow ($\rightleftharpoons$) between reactants and products.	3. It can be represented by an arrow ($\longrightarrow$) from reactants to products.
4. It can be carried out in a closed system.	4. It may or may not be carried out in a closed or an open system.
5. Chemical equilibrium is not established in it.	5. Chemical equilibrium is established in it.
Examples: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$.	**Examples:** $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ $2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$

Q.2 Define Law of Mass Action and Equilibrium Constant (K_c).

Ans. Law of Mass Action:
"The rate at which the reaction proceeds is directly proportional to the product of active masses of the reactants".
Equilibrium Constant (K_c):
The ratio of product of concentration of products and product of concentration of reactants is called equilibrium Constant (K_c).

$$K_c = \frac{[Products]}{[Reactants]}$$

Chemical Equilibrium:
"The state achieved by reversible chemical reaction in which the forward and reverse processes are occurring at the same rate is called state of chemical equilibrium or equilibrium state."

Q.3 Justify that Chemical Equilibrium is dynamic in nature.

Ans. A chemical equilibrium state in a reversible reaction is a state where the rate of forward reaction becomes equal to rate of reverse reaction. It shows that at this state both reaction are taking place simultaneously and not stop thus equilibrium is dynamic not static. If it would be static reaction would stop.

Q.4 What is effect of change in pressure on a system in equilibrium for gases?

Ans. (i) If reaction mixture is in gaseous state then at equilibrium if volume is changed it will effect the equilibrium.
(ii) If number of moles of reactants are not equal to number of moles of product then those gaseous reactions are effected by volume change at equilibrium.
For Example:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$
$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Q.5 What will be the effect of increase of pressure and temperature on the following reaction?

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -92.46\ kJ$$

Ans. (a) Since reaction is endothermic in backward direction, rise of temperature will shift equilibrium to left. Low temperature shifts the equilibrium to right and yield of NH_3 will increase.
(b) Increase of pressure decreases the volume and equilibrium position is shifted in forward direction. As a result yield of ammonia increases and vice versa.

Q.6 Briefly explain the effect of pressure on the equilibrium position for the dissociation of PCl_5.

Ans. Dissociation of PCl_5:
In the same way, effect of change of pressure on the equilibrium position can be explained for the dissociation of PCl_5. This is homogeneous gaseous phase reaction.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_2$$

K_c for this reaction is,

$$K_c = \frac{x^2}{(a-x)V}$$

Conclusion: In the dissociation of PCl_5 the factor of volume is present in the denominator. The reason is that number of moles of products are greater than those of reactants. So, increase in pressure will decrease the 'x' to keep the value of K_c constant and the reaction will be pushed to the backward direction. The equilibrium position is disturbed but not the K_c value.

Q.7 How does a catalyst affect on equilibrium constant?

Ans. Effect of Catalyst on Equilibrium Constant:
In most of the reversible reactions, the equilibrium is not always reached within a suitable short time. So an appropriate catalyst is used.

- A catalyst does not affect the equilibrium position of the reactions. It increases the rates of both forward and backward reactions and this reduces the time to attain the equilibrium state.
- A catalyst lowers the energy of activation of both forward and reverse steps by giving new path to the reaction.

Q.8 Write down equilibrium constant expression for the reactions:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

Ans. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
Equilibrium Constant Expression:

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Q.9 Write down K_c units for the reaction $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

Ans. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
Equilibrium constant for this reaction:

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{[mol\ dm^{-3}][mol\ dm^{-3}]}{[mol\ dm^{-3}]} = mol\ dm^{-3}$$

Q.10 State Le Chatelier's Principle.

Ans. Le-Chatelier's Principle:
"If a stress is applied to a system at equilibrium, the system acts in such a way so as to nullify, as far as possible, the affect of that stress is called Le-Chatelier's Principle".

Q.11 What are the optimum conditions of temperature and pressure to get maximum yield of ammonia?

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -92.46\ kJ$$

Ans. $N_2 + 3H_2 \rightleftharpoons 2NH_3 - 92.46\ kJ$ $\Delta H = -92.46\ kJ$
Optimum Conditions:
The optimum conditions for synthesis of Ammonia gas by Haber's processes are:

- **Temperature:** 400°C (673 K)
- **Pressure:** 200-300 atm
- **Catalyst:** pieces of iron crystals embedded in a fused mixture of MgO, Al_2O_3 and SiO_2.

Q.12 Why do the equilibrium constant value has its units for some of the reversible reactions but has no units for some other reactions?

Ans.

I. If number of moles of reactants and products are equal, then K_c has no units.

$$\underset{1\ mol}{H_{2(g)}} + \underset{1\ mol}{I_{2(g)}} \rightleftharpoons \underset{2\ mol}{2HI}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(mol\ dm^{-3})^2}{(mol\ dm^{-3}\ mol\ dm^{-3})} = \text{no units}$$

II. If the number of moles of reactants and products are not equal.

$$\underset{4\ mol}{N_{2(g)} + 3H_{2(g)}} \rightleftharpoons \underset{2\ mol}{2NH_{3(g)}}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[mol\ dm^{-3}]^2}{[mol\ dm^{-3}][mol\ dm^{-3}]^3} = mol^{-2}\ dm^{+6}$$

◆◆◆◆◆

SELF-ASSESSMENT Chapter # 08

Total Mark: 30

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) Consider the equilibrium $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. If the concentration of $H_2O_{(g)}$ is increased, the concentrations of $H_{2(g)}$ and $O_{2(g)}$ will:
A. Increase. B. Decrease. C. Remain the same. D. Change irregularly

(ii) For which system, does the equilibrium constant, K_C has units of (concentration)$^{-1}$?
A. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ B. $H_2 + I_2 \rightleftharpoons 2HI$
C. $2NO_2 \rightleftharpoons N_2O_4$ D. $2HF \rightleftharpoons H_2 + F_2$

(iii) The expression for Kc of the reaction: $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is:
A. $[NH_3]^2 / [N_2] + [H_2]^3$ B. $[N_2][H_2]^3 / [NH_3]^2$ C. $[NH_3] / [N_2][H_2]^3$ D. $[NH_3]^2 / [N_2][H_2]^3$

(iv) If the temperature of an exothermic reaction increases, then K_c:
A. Increases B. Decreases C. Remains same D. Becomes zero

(v) For a saturated solution of a salt in water, a dynamic equilibrium is between:
A. The dissolved ions and the undissolved solid salt
B. The solute and the solvent molecules
C. The solid salt and the water molecules
D. The hydrated ions and the water molecules in the bulk solvent

(vi) Which of the following condition will not change the equilibrium position?
A. Change in pressure B. Change in concentration
C. Adding catalyst D. Change in temperature

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) The dynamic equilibrium exists between water and its vapour at 100°C. Justify the statement.
(ii) Why ice at 0°C can be melted by applying pressure without supply of heat from outside?
(iii) Differentiate between macroscopic and microscopic changes with examples.
(iv) Mention the characteristics of chemical equilibrium.
(v) Derive the Kc expression for the reaction: $2SO_2 + O_2 \rightleftharpoons 2SO_3$.
(vi) Apply Le Chatelier's Principle when pressure is increased in a gaseous system.
(vii) If the reaction is endothermic, how does increase in temperature affect Kc?
(viii) Define dynamic equilibrium between two physical states with an example.

Q.3 Extensive Questions. (2 × 4 = 8)

(a) By using Le Chatelier's Principle, explain how concentration, pressure, and temperature changes affect equilibrium.
(b) Describe the industrial applications of equilibrium using Haber's process.

Chapter 09 ACID-BASE CHEMISTRY

Student Learning Outcomes

After studying this chapter, students will be able to:

- Define conjugate acid base pairs. **(Understanding)**
- Identify conjugate acid base pairs in reactions. **(Understanding)**
- Distinguish that Lewis acids accept lone pair, and Lewis bases donate lone pair to make a coordinate covalent bond. **(Understanding)**
- Define mathematically the terms K_w, pH, K_a and pK_a and use them in calculations. (K_b and the equation $K_w = K_a \times K_b$ will not be tested). **(Application)**
- Calculate $H^+_{(aq)}$ and pH values for: **(Application)**
- (a) strong acids (b) strong alkalis (c) weak acids (d) weak alkalies.
- Calculate the $[H_3O^+]$ given the K_a and molar concentration of weak acid. **(Application)**
- Apply the concept of the common ion effect to describe why the solubility of a substance changes when it is dissolved in a solution containing a common ion. **(Application)**
- Calculate the pH of buffer solutions in given appropriate data. **(Application)**
- Construct an expression for K_{sp}. **(Application)**
- Demonstrate the ability to comprehend and effectively apply the concept of solubility product K_{sp}. **(Application)**
- Perform calculations using K_{sp} values and concentration of a common ion. **(Application)**
- Calculate concentrations of ions of slightly soluble salts. **(Application)**
- Calculate K_{sp} from concentrations and vice versa. **(Application)**
- Use the concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic. **(Understanding)**
- Apply the concept of conjugate acid and conjugate base on salt hydrolysis. **(Application)**
- Select suitable indicators for acid-alkali titration, given appropriate data (pKa_a values will not be used). **(Understanding)**
- Perform acid-base titration to calculate molarity and strength of given sample solutions. **(Application)**

Differences between Common Acids and Bases

Sr.No.	Acids	Bases
1.	Acids were first recognized as having sour taste.	Bases were first recognized as having bitter taste.
2.	Acids change the litmus from blue to red.	Bases change the litmus from red to blue.
3.	Acids change the indicator "Phenophthalein" from pink to colourless.	Bases change the indicator "Phenophthalein" from colourless to pink.
	Note: Acids and bases neutralize each other and during neutralization, acids and bases react with each other to produce ionic substances called salts.	

Interesting Information!

Acidity in our stomachs is due to excess HCL. It is treated by taking mild bases such as, baking soda.

BRONSTED-LOWRY CONCEPT

Exercise L.Q.3

Q. Describe the Bronsted-Lowry theory of acids and bases. Provide examples of conjugate acid-base pairs and explain clearly their relationship.

The Danish chemist J.N. Bronsted and the English chemist T.M. Lowry in 1923 independently expanded the Arrhenius theory of acid-base.

The limitations of Arrhenius theory is that it describes the reaction of an acid and base only in the aqueous medium. There are many reactions that occur in solvents other than water or in the absence of any solvent. Bronsted-Lowry pointed out that acid-base reactions can be seen as proton transfer reactions and that acids and bases can be defined in terms of this proton (H^+) transfer.

➢ **Bronsted-Lowry Acid:**

According to the Bronsted-Lowry concept, **"an acid is the species donating a proton in a proton-transfer reaction":**

➢ **Bronsted-Lowry Base:**

According to Bronsted-Lowry concept, **"a base is the species accepting the proton".**

Example:

When HCℓ dissolves in Water:

When HCℓ dissolves in water, an H^+ ion (a proton) is transferred from HCℓ to water, where it becomes attached to a lone pair of electrons on the O atom and forms H_3O^+. In fact, HCℓ (the acid) has donated the H^+ and H_2O (the base) has accepted it.

$$\underset{\text{Proton donor}}{HCl_{(g)}} + \underset{\text{Proton acceptor}}{H_2O_{(\ell)}} \rightleftharpoons \underset{\text{Conjugate acid}}{H_3O^+} + \underset{\text{Conjugate base}}{Cl^-_{(aq)}}$$

Note:
- Chloride ion (Cl^-) is indeed the conjugate base of hydrochloric acid (HCl) because it is the species that remains after the acid (HCl) has lost its proton.

➢ **Conjugate Acid:**

"A species formed after a Bronsted base accepts a proton from the acid is called the conjugate acid". The hydronium ion (H_3O^+) is the conjugate acid of water.

- A Bronsted-Lowry acid is a proton donor.
- A Bronsted-Lowry base is a proton acceptor.

➢ **Conjugate Base:**

"A species formed when an acid donates a proton to a base is called the conjugate base". $HCl-Cl^-$ and $H_2O-H_3O^+$ are conjugate acid-base pairs.

Rack Your Mind!

1. In the reaction between HCℓ and water, which species acts as the conjugate base?
   A) H_3O^+ B) Cl^-
   C) HCℓ D) H_2O

Example:

When NH_3 dissolves in Water:

When ammonia dissolves in water, proton transfer also occurs. An H^+ from H_2O attaches to the N atom's lone pair and NH_4^+ and OH^- are formed. With fewer H^+, the water molecule becomes OH^- ion:

$$\underset{\text{Base}}{NH_{3(g)}} + \underset{\text{Acid}}{H_2O_{(\ell)}} \rightleftharpoons \underset{\text{Conjugate base}}{OH^-_{(aq)}} + \underset{\text{Conjugate base}}{NH^+_{4(aq)}}$$

Rack Your Mind!

2. Conjugate acid-base pair differs by:
   A) An electron pair B) A neutron
   C) An electron D) A proton

In this case, H_2O (the acid) has donated the proton and NH_3 (the base) has accepted it. $NH_3-NH_4^+$ and H_2O-OH^- are conjugate acid-base pair.

Amphoteric Substance: An amphoteric substance is a species that can act as either an acid and a base (it can lose or gain a proton), depending on the other reactant.

H_2O is Amphoteric in Nature: H_2O is amphoteric in nature because it acts as a base in one case and as an acid in the other (as shown in the above examples).

$$\underset{\text{base}}{H_2O} + \underset{\text{acid}}{H_2O} \longrightarrow \underset{\text{Conjugate acid}}{H_3O^+} + \underset{\text{Conjugate base}}{OH^-}$$

Application of Bronsted-Lowry Concept: The Bronsted-Lowry theory can be applied to acids in solvents other than water or even solventless reactions. The reaction between gaseous ammonia and HCℓ gives solid NH_4Cl.

$$HCl_{(g)} + NH_{3(g)} \longrightarrow NH_4Cl_{(s)}$$

HCℓ is an acid because in the reaction it donates a proton to the NH_3 molecule. The NH_3 acts as a base, even though hydroxide ion OH^- is not present, and accepts a proton from the HCℓ molecule. Similarly,

$$\underset{\text{Acid}}{HCl} + \underset{\text{base}}{H_2O} \longrightarrow \underset{\text{conjugate base}}{H_3O^+} + \underset{\text{conjugate acid}}{Cl}$$

Table: Conjugate Acid-Base Pairs of Common Species

Acid		Base		Conjugate Acid		Conjugate Base
HNO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NO_3^-
H_2SO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HSO_4^-
H_2O	+	CO_3^{2-}	$\rightleftharpoons$	HCO_3^-	+	OH^-

LEWIS CONCEPT OF ACIDS AND BASES

Exercise L.Q.4

Q. Define the Lewis theory of acids and bases. How does this theory differ from the Bronsted-Lowry theory? Give examples of Lewis acids and bases that do not involve proton transfer.

In 1923, G.N. Lewis proposed a generalized definition of acid-base behavior in which acids and bases are identified by their ability to accept or to donate a pair of electrons and form a coordinate covalent bond.

Rack Your Mind!

3. Why is BF_3 considered a Lewis acid?

➢ **Lewis Acid:**

"A Lewis acid is any species (molecule or ion) that can accept a pair of electrons".

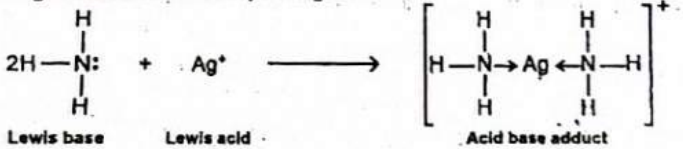
➢ **Lewis Base:**

"A Lewis base is any species (molecule or ion) that can donate a pair of electrons".

A Lewis acid-base reaction occurs when a base donates a pair of electrons to an acid.

Example 1:

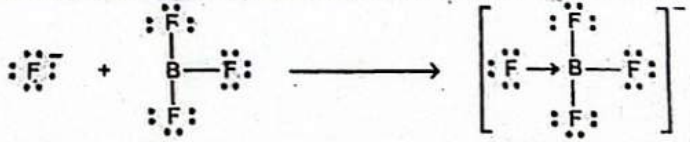
In the following reaction, each of two ammonia molecules, Lewis bases, donates a pair of electrons to a positively charged silver ion, the Lewis acid. The sum of charges on the left side is +1, so the acid-base adduct on the right hand side must carry a charge of +1:



Lewis base Lewis acid Acid base adduct

Example 2:

The boron atom in boron trifluoride, BF_3, has only six electrons in its valence shell. Boron atom has an incomplete octet. So it can behave as an electron pair acceptor. BF_3 is a very good Lewis acid and reacts with many Lewis bases e.g. a fluoride ion which is the Lewis base in this reaction, donates one of its lone pairs:

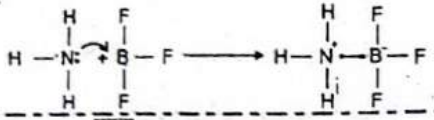


Lewis base Lewis acid Acid base adduct

The negative charge on the adduct is the sum of charges on the left hand side of the equation is −1, the sum of charges on the right hand side must also be −1.

In the following reaction NH_3 has a lone pair on N-atom so it is a Lewis base (electron pair donor) and boron accepts the lone pair and is a Lewis acid.

Example 3:



☑ QUICK CHECK 9.1

a) Identify the conjugate acid-base pairs in the following reactions:

i. $HCN_{(g)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + CN^-_{(aq)}$

Also write down the balanced chemical equation for the reaction and explain.

Ans. The conjugate acid-base pairs are:

1. HCN (acid) and CN^- (its conjugate base)
   HCN donates a proton (H^+) to become CN^-.
2. H_2O (base) and H_3O^+ (its conjugate acid)
   H_2O accepts a proton (H^+) to become H_3O^+.

Summary of Pairs:

Acid	Conjugate Base
HCN	CN^-
H_2O	H_3O^+

- Acid → Conjugate base by losing H^+.
- Base → Conjugate acid by gaining H^+.

ii. $CH_3COOH_{(\ell)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

Ans. The conjugate acid-base pairs are identified as follows:

Pair 1: CH_3COOH (Acid) and CH_3COO^- (Conjugate Base)

- CH_3COOH donates a proton (H^+) to become CH_3COO^-.
  - **Acid:** CH_3COOH (acetic acid).
  - **Conjugate Base:** CH_3COO^- (acetate ion).

Pair 2: H_2O (Base) and H_3O^+ (Conjugate Acid)

- H_2O accepts a proton (H^+) to become H_3O^+.
  - **Base:** H_2O (water).
  - **Conjugate Acid:** H_3O^+ (hydronium ion).

iii. $H_2S_{(g)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + HS^-_{(aq)}$

Ans. Conjugate Acid-Base Pairs:

- **H_2S (acid) / HS^- (Conjugate base):** H_2S donates a proton (H^+) to become HS^-. (Acid: Proton (H^+) donor.)
- **H_2O (base) / H_3O^+ (Conjugate acid):** H_2O accepts a proton (H^+) to become H_3O^+. (Base: Proton (H^+) acceptor.)
- **Pairs differ by one proton (H^+).**

Example:

- H_2S (acid) → HS^- (conjugate base)
- H_2O (base) → H_3O^+ (conjugate acid)

Note: H_3O^+ is the strongest acid here; HS^- is the weakest base.

iv. $HCl_{(g)} + HCO^-_{3(aq)} \rightleftharpoons H_2CO_{3(aq)} + Cl^-_{(aq)}$

Ans. Conjugate Acid-Base Pairs:

1. **HCl/Cl^-**
   - **HCl** (acid) donates a proton (H^+) to become **Cl^-** (its conjugate base).
2. **HCO_3^-/H_2CO_3**
   - **HCO_3^-** (base) accepts a proton (H^+) to become **H_2CO_3** (its conjugate acid).

Summary Table:

Acid	Conjugate Base
HCl	Cl^-
H_2CO_3	HCO_3^-

- **Acids** lose H^+ to form conjugate **bases**.
- **Bases** gain H^+ to form conjugate **acids**.

b) Identify the Lewis acid and Lewis base in the reaction between:

i. **SO_3 and O^{2-}**

Ans. Balanced Chemical Equation:

$SO_3 + O^{2-} \longrightarrow SO_4^{2-}$

Lewis Acid-Base Identification:

1. **Lewis Acid: SO_3**
   - **Reason: SO_3 accepts an electron pair** from O^{2-} (its sulfur atom has an incomplete octet and is electron-deficient).
2. **Lewis Base: O^{2-}**
   - **Reason: O^{2-} donates an electron pair to SO_3** (it has lone pairs available for bonding).

Mechanism Explanation:

1. SO_3 (electron-deficient due to polar S=O bonds) acts as the **electron-pair acceptor (Lewis acid).**
2. O^{2-} (a negatively charged ion with lone pairs) acts as the **electron-pair donor (Lewis base).**
3. The O^{2-} attacks the sulfur in SO_3, forming a **coordinate covalent bond** and creating **SO_4^{2-}** (sulfate).

Key Notes:

- SO_3 is a classic Lewis acid (e.g., in sulfuric acid production: $SO_3 + H_2O \longrightarrow H_2SO_4$).
- O^{2-} is a strong Lewis base (common in oxide reactions).

ii. **HCl and H_2O**

Ans. Balanced Equation:

$HCl_{(g)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

Lewis Acid-Base Identification:

1. **Lewis Acid: H^+ (from HCl)**
   - **Reason:** Accepts an electron pair from H_2O to form H_3O^+.
2. **Lewis Base: H_2O**
   - **Reason:** Donates an electron pair to H^+ to form a coordinate covalent bond in H_3O^+.

Explanation:

- HCl dissociates into H^+ (electron-pair acceptor, Lewis acid) and Cl^-.
- H_2O (with lone pairs on oxygen) acts as the **electron-pair donor (Lewis base)**, forming hydronium (H_3O^+).

iii. **BF_3 and NH_3**

Ans. Balanced Chemical Equation:

$BF_3 + NH_3 \longrightarrow H_3N{-}BF_3$

Lewis Acid and Base Identification:

- **Lewis Acid: BF_3** (electron pair acceptor).
  - Boron in BF_3 has an **empty 2p orbital**, making it electron-deficient.

- **Lewis Base:** NH_3 (electron pair donor).
  - Nitrogen in NH_3 has a lone pair it can donate.

Mechanism:

1. NH_3 donates its lone pair to the empty orbital of BF_3.
2. A dative covalent bond (coordinate bond) forms between N and B.

Key Points:

- BF_3 is a classic Lewis acid (no protons involved!).
- NH_3 is a Lewis base due to its lone pair.
- The product (H_3N-BF_3) is a stable adduct.

IONIC PRODUCT OF WATER

- Pure water is a poor conductor of electricity but its conductance is measurable.
- Water undergoes self-ionization reversibly as follows,

Net Reaction:

$$H_2O_{(\ell)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$H_2O_{(\ell)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

Rack Your Mind!

4. Why is the concentration of water considered constant in the K_c expression?

The equilibrium constant for this reaction can be written as follows:

$$K_c = \frac{[H^+][OH^-]}{[H_2O]} = 1.8\times10^{-16} \text{ mol dm}^{-3}$$

- The concentration of H_2O i.e. $[H_2O]$ in pure water may be calculated to be 1000 g dm^{-3} divided by 18 g mol^{-1} giving 55.5 moles dm^{-3} i.e. $\frac{1000 \text{ gdm}^{-3}}{18 \text{ gmol}^{-1}} = 55.5 \text{ mol dm}^{-3}$
- As water is present in very large excess and very few of its molecules undergo ionization, so its concentration remains effectively constant.
- Constant concentration of water is taken on L.H.S. and multiplied with K_c to get another constant called K_w.

$$K_c[H_2O] = [H^+][OH^-]$$

or $$= 1.8\times10^{-16}\times55.5 = 1.01\times10^{-14} = [H^+][OH^-]$$

This 1.01×10^{-14} is called K_w of water at 25°C.

$$K_c[H_2O] = [H^+][OH^-]$$

So, $K_w[H_2O] = [H^+][OH^-] = 10^{-14}$ at 25°C.

- K_w is called Ionic product of water or dissociation constant of water.

Table: K_w at various temperature.

Temp. (°C)	Value of K_w
0	0.11×10^{-14}
10	0.30×10^{-14}
25	1.0×10^{-14}
40	3.00×10^{-14}
100	7.5×10^{-14}

➢ **K_w of H_2O increases with increase of Temperature:**

- The value of K_w increases almost 75 times when temperature is increased from 0°C to 100°C.

For neutral water

$$[H^+] = [OH^-]$$

Or $$[H^+][H^+] = 10^{-14}$$

$$[H^+]^2 = 10^{-14} \text{ (at 25°C)}$$

$$[H^+] = 10^{-7} \text{ moldm}^{-3}$$

And $$[OH^-] = 10^{-7} \text{ moldm}^{-3}$$

The effect of temperature on K_w is shown in Table.

- Whenever some quantity of acid or base is added to water, then K_w remains the same, but $[H^+]$ and $[OH^-]$ are no more equal.

In case of addition of small amount of acid.

$$[H^+] > [OH^-]$$

While in the case of addition of few drops of a base.

$$[OH^-] > [H^+]$$

- During both of these additions, the values of K_w will remain the same, i.e. 10^{-14} at 25°C.

pH AND pOH

In 1909, Sorenson, a Danish biochemist, introduced the term pH and pOH. So, the scales of pH and pOH were developed.

➢ **pH:**

"The negative logarithm of hydrogen ion concentration in the solution is called pH."

$$pH = -\log[H^+]$$

➢ **pOH:**

"The negative logarithm of hydroxide ion concentration in the solution is called pOH."

$$pOH = -\log[OH^-]$$

For neutral water, $pH = -\log[10^{-7}] = 7$

$$pOH = -\log[10^{-7}] = 7$$

Also, $pH + pOH = 14$

Rack Your Mind!

5. If the pH of a solution is 3, then its $[H^+]$ is:
   A) 10^{-3} mol dm^{-3} B) 10^{-1} mol dm^{-3}
   C) 10^{3} mol dm^{-3} D) 3 mol dm^{-3}

Interesting Information!

Solutions of negative pH and having values more than 14 are also known.

In all the aqueous solutions, the concentration of H^+ and OH^- are too low to be conveniently expressed and used in calculations.

The value of pH normally varies between 0 → 14 at 25°C.

The pH values of some familiar aqueous solutions are shown in Figure. This table can help you to understand the acidic or basic nature of commonly used solutions.

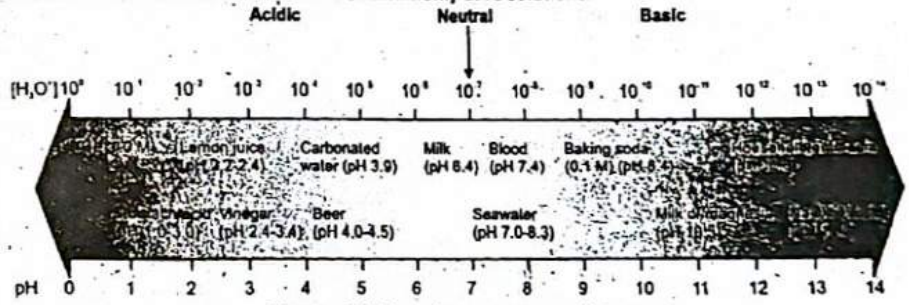


Figure: pH Values of some common substances

Sample Problem 9.1

In a solution, the pH is 9.2. Determine the ionic product of water K_w at 25°C.

Solution:

Calculate the pOH from the pH:

$$pOH = 14 - pH$$

$$pOH = 14 - 9.2$$

$$pOH = 4.8$$

Find the concentration of H^+ and OH^-,

Taking antilog of pH and pOH

$$\text{antilog pH} = \text{antilog}$$

$$[OH^-] = 10 - pH$$

$[H^+] = 10^{-9.2}$

$[OH^-] \approx 6.3\times10^{-10}$ M

Similarly, antilog pOH = antilog (4.8)

$[OH^-] = 10 - pOH$

$[OH^-] = 10^{-4.8}$

$[OH^-] \approx 1.6\times10^{-5}$ M

Sample Problem 9.2

The ionic product of water at a certain temperature is $K_w = 1.0\times10^{-14}$ at 25°C. If the concentration of H^+ ions in a solution is 1.0×10^{-7} M.
Calculate the concentration of OH^- ions, the pH and pOH of the solution.
Solution:
Use the expression for K_w:

$$K_w = [H^+][OH^-]$$

Substitute the known values of K_w and the concentration of H^+:

$$1.0\times10^{-14} = (1.0\times10^{-7})[OH^-]$$

Solve for the concentration of OH^-

$$[OH^-] = \frac{1.0\times10^{-14}}{1.0\times10^{-7}} = 1.0\times10^{-14}$$

Calculate the pH: $pH = -\log[H^+]$

$= -\log(1.0\times10^{-7}) = 7$

Calculate the pOH: $pOH = -\log[H^-]$

$= -\log(1.0\times10^{-7})$

$= 7$

QUICK CHECK 9.2

a) **A solution is prepared by mixing equal volumes of two solutions: one with a pH of 4.0 and another with a pH of 10.0. Calculate the K_w for this mixture at 25° C.**

Ans. **Given:**

- **Solution A:** pH = 4.0 → $[H^+] = 10^{-4}$ M
- **Solution B:** pH = 10.0 → $[OH^-] = 10^{-4}$ M (since pH 10 ⇒ pOH 4).

Step 1: Mix Equal Volumes

- [H+] from A and $[OH^-]$ from B neutralize each other:

$$H^+ + OH^- \longrightarrow H_2O$$

- **Result:** $[H^+] = [OH^-] = 10^{-4}$ M cancel out, leaving neutral water (pH 7).

Step 2: Final pH

- The mixture is neutral (pH = 7.0) because the H^+ and OH^- concentrations were equal and fully reacted.

Note on K_w:

- $K_w = [H^+][OH^-] = 1.0\times10^{-14}$ (constant at 25°C) for all aqueous solutions, including this mixture.

Final Answer:

The mixture has:

- pH = 7.0 (neutral).
- $k = 1.0\times10^{-14}$ (at 25°C).

b) **At a specific temperature, the ionic product of water K_w is 1.0×10^{-14}. If the concentration of OH^- ions in a solution is 2.5×10^{-8} M. Calculate the concentration of H^+ ions and the pH of the solution.**

Ans. **Given:**

$K_w = 1.0\times10^{-14}$ (at the given temperature).

$[OH^-] = 2.5\times10^{-8}$ M.

Step 1: Calculate $[H^+]$

Using the ionic product of water:

$$K_w = [H^+][OH^-]$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0\times10^{-14}}{2.5\times10^{-8}} = 4.0\times10^{-7}\text{ M}$$

Step 2: Calculate pH

$pH = -\log[H+] = -\log(4.0\times10^{-7})$

$pH = 6.40$ (since $\log(4.0) \approx 0.60$ and $\log(10^{-7}) = -7$)

Final Answer:

$[H+] = 4.0\times10^{-7}$ M

pH = 6.40 pH = 6.40

c) **Copper-plate etching solutions is prepared by diluting concentrated HNO_3 to 0.30 M HNO_3. Calculate $[H^+]$, pH, $[OH^-]$ and pOH of this solutions at 25° C.**

Ans. **Given:**

- **HNO_3 concentration:** 0.30 M (a strong acid, fully dissociates).
- **At 25°C:** $K_w = 1.0\times10^{-14}$.

1. **$[H^+]$ and pH:**
Since HNO_3 is a strong acid:

$[H^+] = 0.30$ M

$pH = -\log[H^+] = -\log(0.30) \approx 0.52$

2. **$[OH^-]$ and pOH:**
Using $K_w = [H^+][OH^-]$:

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0\times10^{-14}}{0.30} = 3.3\times10^{-14}\text{ M}$$

$pOH = -\log[OH^-] = -\log(3.3\times10^{-14}) \approx 13.48$

Final Results:

$[H+] = 0.30$ M

$pH = 0.52$

$[OH^-] = 3.3\times10^{-14}$ M

$pOH = 13.48$

- **HNO_3 fully dissociates,** so $[H^+]$ equals its initial concentration.
- **pH + pOH = 14** (verified: 0.52+13.48 = 14).
- **Highly acidic** (pH ≪ 7) due to concentrated HNO_3.

IONIZATION CONSTANTS OF ACIDS (K_a)

Acids and bases, when dissolved in water, may or may not be completely dissociated. Many acids are weak electrolytes and ionize to an extent which is much less than 100 %. The value of K_a called the dissociation constant of an acid, is the quantitative measure of the strength of the acid.

➢ **Mathematical Derivation of K_a**

Suppose we have an acid HA dissolved in water,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Rack Your Mind!

6. What is K_a in acid-base chemistry?

K_c for the reversible reaction will be written as follows:

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Let $K_c[H_2O] = K_a$

Hence $$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

This equation can be used to calculate K_a for any acidic solution if we know the pH or $[H^+]$ of that solution and the initial concentration of the dissolved acid [HA]. This can also be used to calculate the equilibrium concentration of H_3O^+ and A^- produced if we know the initial concentration of acid HA and its K_a value.

➤ **K_a and Strength of Acids:**

When $K_a < 10^{-3}$ acid is weak.

$K_a = 1$ to 10^{-3} acid is moderately strong.

$K_a > 1$ acid is strong.

The values of K_a for some acids are given in Table.

Table: The values of K_a for some acids

Acid	Dissociation	K_a	Relative strength
HCℓ	$HC\ell \rightleftharpoons H^+ + C\ell^-$	very large (10^{-2})	Very strong
HNO_3	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	very large (10^{-5})	Very strong
H_2SO_4	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	Large (10^{-2})	Very strong
HSO_4^-	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.3×10^{-4}	Strong
HF	$HF \rightleftharpoons H^+ + F^-$	6.7×10^{-5}	Week
CH_3COOH	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.85×10^{-5}	Week
H_2CO_3	$H_2CO_3 \rightleftharpoons H^+ + HS^-$	4.4×10^{-7}	Week
H_2S	$H_2S \rightleftharpoons H^+ + HS^-$	1.0×10^{-7}	Week
NH_4^+	$NH_4^+ \rightleftharpoons H^+ + NH_3$	5.7×10^{-10}	Week
HCO_3^-	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.7×10^{-12}	Week
H_2O	$H_2O \rightleftharpoons H^+ + OH^-$	1.8×10^{-15}	Very week

➲ Calculating H_3O^+ ions from K_a

The weak acids do not completely dissociate in water. Therefore, the concentration of hydronium ions is not equal to the initial concentration of the acid. So, the equilibrium expression is used to calculate the H_3O^+ concentration.

For a weak acid HA, the dissociation in water can be represented as:

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

In water, H^+ combines with water to form H_3O^+:

$$H^+_{(aq)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)}$$

So, the equilibrium equation in terms of $H_3O^+_{(aq)}$ is:

$$HA_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

Let the initial concentration of the weak acid HA be C mol dm^{-3}.

At equilibrium:

$$[H_3O^+] = x; [A^-] = x \text{ and } [HA] = C - x$$

The expression for the acid dissociation constant (K_a) is:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Substitute the equilibrium concentrations into this expression:

$$K_a = \frac{x.x}{C-x} = \frac{x^2}{C-x}$$

For weak acids, x is usually very small compared to C, so $C - x \approx C$. Therefore, the expression simplifies to:

$$K_a \approx \frac{x^2}{C}$$

Taking the square root of both sides:

$$x \approx \sqrt{K_a \times C}$$

Thus, the concentration of H_3O^+ is given by:

$$x \approx \sqrt{K_a \times C}$$

Sample Problem 9.3

Calculate the concentration of $[H_3O^+]$ in a 0.1 M (moldm^{-3}) solution of acetic acid $[CH_3COOH]$, given that the acid dissociation constant K_a is 1.8×10^{-5}.

Solution:

$$[H_3O^+] \approx \sqrt{K_a \times C}$$

$$[H_3O^+] \approx \sqrt{1.8\times10^{-5}\times0.1}$$

$$[H_3O^+] \approx \sqrt{0.18\times10^{-6}}$$

$$[H_3O^+] \approx 1.34\times10^{-3} \text{M(moldm)}$$

The concentration $[H_3O^+]$ in the solution is approximately 1.34×10^{-3} moldm^{-3}.

☑ QUICK CHECK 9.3

a) The pH of a 0.10 M solution of formic acid, HCOOH, at 25°C is 2.38. Calculate K_a for formic acid at this temperature.

Ans. **Given:**

- **Concentration of HCOOH ([HCOOH]: 0.10 M**
- **pH of the solution: 2.38**
- **Temperature: 25∘C**

Step 1: Calculate $[H^+]$ from pH

$$[H^+] = 10^{-pH} = 10^{-2.38} \approx 4.17\times10^{-3} \text{ M}$$

Step 2: Set Up the Equilibrium Expression

Formic acid dissociates as:

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$

At equilibrium:

- $[H^+] = [HCOO^-] = 4.17\times10^{-3}$ M
- $[HCOOH] \approx 0.10 - 4.17\times10^{-3} = 0.0958$ M (since $4.17\times10^{-3} \ll 0.10$, the approximation is valid).

Step 3: Calculate Ka

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{(4.17\times10^{-3})2}{0.0958} \approx 1.81\times10^{-4}$$

Final Answer:

$$K_a = 1.81\times10^{-4}$$

b) Calculate the concentration of $[H_3O^+]$ in a 0.1 M solution of nitrous acid $[HNO_2]$, given that the acid dissociation constant K_a is 4×10^{-4}.

Ans. **Step 1: Write the Dissociation Equation and K_a Expression**

$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} = 4\times10^{-4}$$

Step 2: Define Equilibrium Concentrations

Let $x = [H^+] = [NO_2^-]$ at equilibrium.

Since HNO_2 is a weak acid, its dissociation is small, so:

$[HNO_2] = 0.1 - x \approx 0.1$ M (assuming $x \ll 0.1$)

Step 3: Substitute into K_a and Solve for x

$$K_a = \frac{x\cdot x}{0.1} = 4\times10^{-4}$$

$$x^2 = 4\times10^{-5}$$

$$x = \sqrt{4\times10^{-5}} = 2\times10^{-2.5} \approx 6.32\times10^{-3}\,M$$

Step 4: Verify the Approximation

Check if $x \ll 0.1$:

$$\frac{6.32\times10^{-3}}{0.1} = 6.32\%$$ (<5% is ideal, but <10% is acceptable)

The approximation holds reasonably well. For higher precision, solve the quadratic equation:

$$(x^2 + 4\times10^{-4})(x - 4\times10^{-5}) = 0$$

Using the quadratic formula:

$$x = \frac{-b+\sqrt{b^2-4ac}}{2a} = \frac{-4\times10^{-4}+\sqrt{(4\times10^{-4})^2+1.6\times10^{-4}}}{2}$$

$x \approx 6.16\times10^{-3}$ M (minor correction)

Final Answer:

$[H_3O^+] = 6.32\times10^{-3}$ M (or 6.16×10^{-3} M with quadratic)

c) A vinegar sample is found to have 0.837 M CH_3COOH. Its hydronium ion concentration is found to be 3.86×10^{-3} mol dm^{-3}. Calculate K_a for acetic acid.

Ans. Given:

- Initial concentration of CH_3COOH ($[CH_3COOH]$): 0.837 M
- Hydronium ion concentration ($[H_3O+][H_3O+]$): 3.86×10−3 M

Step 1: Write the Dissociation Equation

Acetic acid partially dissociates in water:

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

Step 2: Determine Equilibrium Concentrations

At equilibrium:

- $[H_3O^+] = [CH_3COO^-] = 3.86\times10^{-3}$ M (from dissociation).
- $[CH_3COOH] \approx 0.837 - 3.86\times10^{-3} \approx 0.833$ M. (Approximation valid since $3.86\times10^{-3} \ll 0.837$)

Step 3: Calculate K_a

Using the equilibrium expression:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(3.86\times10^{-3})^2}{0.833}$$

$$K_a = \frac{1.49\times10^{-5}}{0.833} \approx 1.79\times10^{-5}$$

Final Answer:

$K_a = 1.79\times10^{-5}$

COMMON ION EFFECT

Exercise 9.5

Q. Discuss applications and implications of the common ion effect in various fields.

Definition:

"The suppression of ionization of a weak electrolyte by adding a common ion to it is called common ion effect".

Applications of Common Ion Effect

Purification of NaCl:

NaCl is purified by passing hydrogen chloride gas through the saturated brine. Sodium chloride is fully ionized in the solution. Equilibrium constant expression for this process can be written as follows:

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$K_c = \frac{[Na^+][Cl^-]}{[NaCl]}$$

HCl also ionizes in solution.

$$HCl \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

On passing HCl gas, concentration of Cl^- ions is increased. Therefore, NaCl crystallizes out of the solution to maintain the constant value of equilibrium constant. This type of effect is called common ion effect.

The addition of a common ion to the solution of less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitate.

$$Na^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons NaCl_{(s)}$$

Precipitation of $KClO_3$ by KCl:

The solubility of a less soluble salt $KClO_3$ in water is suppressed by the addition of more soluble salt KCl by common ion effect. K^+ is a common ion. The ionization of $KClO_3$ is suppressed and it settles down as precipitate.

$$KClO_{3(s)} \rightleftharpoons K^+_{(aq)} + ClO^{-1}_{3(aq)}$$

$$KCl \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$$

Precipitation of 2nd Group Basic Radicals of Salt Analysis:

The dissociation of a weak acid H_2S in water can be suppressed by the addition of stronger acid HCl. H^+ is a common ion. H_2S becomes less dissociated in acidic solution. In this way, low concentration of S^{-2} is developed.

$$H_2S \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$$

This low concentration of S^{2-} ions helps to do the precipitation of radicals of second group basic radicals during salt analysis.

$$HCl_{(aq)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

Precipitation of 3rd Group Basic Radicals of Salt Analysis:

An addition of NH_4Cl in NH_4OH solution suppresses the concentration of $OH^-_{(aq)}$ due to the presence of a large excess of NH_4^+ from NH_4Cl. Actually, NH_4Cl is a strong electrolyte. The combination of these two substances is used as reagent in third group basic radicals.

$$NH_4OH_{(aq)} \rightleftharpoons Na^+_{4(aq)} + OH^-_{(aq)}$$

$$NH_4Cl_{(aq)} \rightleftharpoons Na^+_{4(aq)} + Cl^-_{(aq)}$$

Uses in Qualitative Analysis and Preparation of Buffers:

Common ion effect has its extensive applications in the qualitative analysis and the preparation of buffers.

Note: In common ion effect, the term "Electrolyte" is used instead of acid, base or salt.

Define common ion effect with one example.

- We can suppress the ionization of an electrolyte by common ion effect.

Give applications of common ion effect. (any two)

- Common ion effect is an application of Le-Chatelier's principle.
- In it the term electrolyte is used instead of acid, base or salt.
- In a solution of weak acid, hydrofluoric acid ($K_a = 7.2\times10^{-4}$), its salt sodium fluoride produces the common ion (F^-).

$$HF_{(aq)} \xrightarrow{H_2O} H^+_{(aq)} + F^-_{(aq)}$$

$$NaF_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + F^-_{(aq)}$$

- Common ion effect is always in the reverse direction.

Rock Your Mind!

7. When ionization of a weak electrolyte is suppressed by a strong electrolyte having a common ion is called:
   A) Hydrolysis
   B) Buffering
   C) Common ion effect
   D) Precipitation reaction

BUFFER SOLUTIONS

The solutions which resist the change in their pH when a small amount of an acid or a base is added to them, are called buffer solutions.

- They have a specific constant value of pH. The pH values of buffer solutions do not change on dilution and on keeping for a long time.

Rock Your Mind!
8. What is a buffer solution?

Types of Buffer Solutions

Buffer solutions are mostly prepared by mixing two substances.

i. **Acidic Buffers:** By mixing a weak acid and its salt with a strong base. Such solutions give acidic buffers with pH less than 7. Mixture of acetic acid and sodium acetate is one of the best examples of acidic buffers.

ii. **Basic Buffers:** By mixing a weak base and its salt with a strong acid. Such solutions will give basic buffers with pH more than 7. Mixture of NH_4OH and NH_4Cl is one of the best examples of basic buffers.

Example:

An acidic buffer consisting of CH_3COOH and CH_3COONa. CH_3COOH being a weak electrolyte undergoes very little dissociation. When CH_3COONa, which is a strong electrolyte, is added to CH_3COOH solution, then the dissociation of CH_3COOH is suppressed, due to common ion effect of CH_3COO^-.

$$CH_3COOH_{(aq)} + H_2O_{(\ell)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

$$CH_3COONa_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

If one goes on adding CH_3COONa in CH_3COOH solution, then the added concentrations of CH_3COO^- decrease the dissociation of CH_3COOH and the pH of solution increases. The Table tells us how the pH value of a mixture of two compounds is maintained. Greater the concentration of acetic acid as compared to CH_3COONa, lesser is the pH of solution.

Table: Effect of addition of acetate ions on the pH of acetic acid solution

$[CH_3COOH]$ (mol dm^{-3})	$[CH_3COO^-]$ (mol dm^{-3})	% Dissociation	pH
0.10	0.00	1.3	2.89
0.10	0.05	0.036	4.44
0.10	0.10	0.018	4.74
0.10	0.15	0.012	4.92

Actually, a buffer mentioned above is a large reservoir of CH_3COOH and CH_3COO^- components. When an acid or H_3O^+ ions are added to this buffer, they will react with CH_3COO^- to give back acetic acid and hence the pH of the solution will almost remain unchanged. The reason is that CH_3COOH being a week acid will prefer to remain undissociated. Similarly, the buffer solution consisting of NH_4Cl and NH_4OH, can resist the change of pH and pOH, when acid or base is added from outside. When a base or OH^- ions are added in it, they will react with H_3O^+ to give back H_2O and the pH of the solution again will remain almost unchanged.

Acidic buffers	Basic buffers
• Those buffers which are formed by the mixing of a weak acid and a salt of it with a strong base are called acidic buffers.	• Those buffers which are formed by mixing of a weak base and a salt of it with a strong acid are called basic buffers.
• Their pH is usually less than 7.	• Their pH is more than 7.
• Henderson's equation for acidic buffers $pH = pK_a + \log\frac{[salt]}{[acid]}$	• Henderson's equation for basic buffers $pOH = pK_b + \log\frac{[salt]}{[base]}$
e.g. CH_3COOH + CH_3COONa (weak acid / salt of weak acid)	e.g. NH_4OH + NH_4Cl (weak base / salt of weak base)

Calculating the pH of a Buffer

Let us discuss preparation of a buffer of definite pH.

Example:

Consider a weak acid HA and its salt NaA with a strong base say NaOH. The reversible reactions for dissociation of HA and NaA are as follows:

$$HA \rightleftharpoons H^+ + A^-$$

$$NaA \rightleftharpoons Na^+ + A^-$$

Interesting Information!

The body's blood buffering system, involving bicarbonates, helps maintain a



Calculation of pH of a buffer solution by using Henderson equation:

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

Interchanging the numerator and denominator, the sign of log changes.

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

This relationship is called **Henderson's equation.**

Factors Affecting pH of a Buffer:

Henderson's equation shows that two factors which govern the pH of a buffer solution are as follows:

(i) pK_a of the acid used.

(ii) The ratio of the concentrations of the salt and the acid.

- The best buffer is prepared by taking equal concentration of salt and acid.
- So, pH is controlled by pK_a of the acid.

Example: For acetic acid - sodium acetate buffer, if

$$[CH_3COOH] = [CH_3COONa]$$

$$pK_a = 4.74$$

Then $$pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$pH = pK_a + \log(1)$$

So, $$pH = pK_a + 0 = pK_a$$

$$pH = 4.74$$

It means that the pH of this buffer is just equal to the pK_a of the acid.

QUICK CHECK 9.4

a) Explain the impact of common ion effect on solubility.

Ans. Effect of Common Ion on Solubility

The presence of a common ion decreases the solubility of a slightly soluble ionic compound. Consider a saturated solution of $PbCrO_4$, which is a sparingly soluble ionic salt.

$$PbCrO_{4(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO^{2-}_{4(aq)}$$

$$Na_2CrO_{4(aq)} \rightleftharpoons 2Na^+ + CrO^{2-}_4$$

Now add Na_2CrO_4 which is a soluble salt CrO^{2-}_4 is the common ion. It combines with Pb^{2+} to form more insoluble $PbCrO_4$. So equilibrium is shifted to the left to keep K_{sp} constant.

b) To a saturated solution of AgCl, some of NaCl solution was added.

I. State the effect of the concentration of Ag^+ on the equilibrium.

Ans. Effect on $[Ag^+]$:

The addition of NaCl (which provides Cl^- ions) to a saturated AgCl solution decreases the concentration of Ag^+ ions at equilibrium.

ii. Explain your answer with respect to the common ion effect.

Ans. Explanation (Common Ion Effect):

Equilibrium Shift:

- The dissolution equilibrium of $AgCl$ is:

$$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

- Adding $NaCl$ introduces excess Cl^-, shifting the equilibrium left (Le-Chatelier's Principle) to reduce the added Cl^-, causing more $AgCl$ to precipitate.

Mathematical Impact:

- The solubility product (K_{sp}) must remain constant:

$$K_{sp} = [Ag^+][Cl^-]$$

If $[Cl^-]$ increases, $[Ag^+]$ must decrease to maintain K_{sp}.

Result:

- Solubility of $AgCl$ decreases, and the solution becomes less saturated with Ag^+ ions.

c) How does a buffer maintain pH stability?

Ans. A buffer maintains pH stability by resisting changes in pH when small amounts of acid (H^+) or base (OH^-) are added. Here's how it works concisely:

Mechanisms:

1. Composition:
   - A buffer consists of a weak acid (HA) and its conjugate base (A^-) (e.g., CH_3COOH/CH_3COO^-) or a weak base (B) and its conjugate acid (BH^+) (e.g., NH_3/NH_4^+).
2. Action Against Added Acid (H^+):
   - The conjugate base (A^-) neutralizes H^+:

$$A^- + H^+ \longrightarrow HA$$

   - Example: In CH_3COO^-/CH_3COOH buffer, CH_3COO^- consumes H^+ to form CH_3COOH.
3. Action Against Added Base (OH^-):
   - The weak acid (HA) neutralizes OH^-:

$$HA + OH^- \longrightarrow A^- + H_2O$$

   - Example: CH_3COOH donates H^+ to OH^-, forming water and CH_3COO^-.
4. pH Stability:
   - The equilibrium between HA and A^- ensures $[H^+]$ (and thus pH) changes minimally.
   - The Henderson-Hasselbalch equation predicts buffer pH:

$$pH = pK_a + \log([HA][A^-])$$

Example:

A phosphate buffer ($H_2PO_4^-/HPO_4^{2-}$) maintains blood pH (~7.4) by:

- Neutralizing added H^+:

$$HPO_4^{2-} + H^+ \longrightarrow H_2PO_4^-$$

- Neutralizing added OH^-:

$$H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O$$

Conclusion:

Buffers stabilize pH by shifting equilibrium to consume added H^+ or OH^-, keeping the $[HA]/[A^-]$ ratio (and thus pH) nearly constant.

d) Calculate the pH of a buffer consisting of 0.50 M HF and 0.45 M of a fluoride (F^-) salt before and after addition of 0.40 g NaOH to 1.0 dm^3 of the buffer (K_a of HF = 6.8×10^{-4}).

Ans. Given Buffer Solution:

$[HF] = 0.50\ M$

$[F^-] = 0.45\ M$

Volume = 1.0 dm^3

K_a of HF = 6.8×10^{-4}

- Added NaOH = 0.40 g (Molar mass = 40 g/mol → 0.01 mol NaOH in 1.0 dm^3 → $[OH^-] = 0.01\ M$)

Step 1: Calculate Initial pH (Before NaOH Addition)

Using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log([F^-]/[HF])$$

$$pK_a = -\log(6.8\times10^{-4}) \approx 3.17$$

$$pK_a = -\log(6.8\times10^{-4}) \approx 3.17$$

$$pH = 3.17 + \log(0.450.50) = 3.17 + \log(0.9) \approx 3.17 - 0.046 = 3.12$$

Step 2: Calculate pH After Adding NaOH (0.01 M OH^-)

NaOH reacts with HF (weak acid) in the buffer:

$$HF + OH^- \rightarrow F^- + H_2O$$

- HF consumed: 0.50−0.01 = 0.49 M
- F^- produced: 0.45+0.01 = 0.46 M

New pH:

$pH = 3.17 + \log(0.46/0.49) = 3.17 + \log(0.94) \approx 3.17 - 0.027 = 3.14$

e) Calculate the pH of a buffer solution in which 0.11 molar CH_3COONa and 0.09 molar acetic acid solutions are present. K_a for CH_3COOH is 1.85×10^{-5}.

Given Data: $[CH_3COONa] = 0.11M$

$[CH_3COOH] = 0.09M$

K_a of $CH_3COOH = 1.85\times10^{-5}$

Required: pH of Buffer solution = ?

Solution:

$$pK_a = -\log K_a$$

$$= -\log 1.8\times10^{-5} = 4.74$$

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

$$pH = 4.74 + \log\frac{0.11}{0.09}$$

$$pH = 4.74 + 0.087$$

$$pH = 4.83$$

SOLUBILITY PRODUCT

(For slightly soluble ionic compounds)

Exercise L.Q.6

Q. What is the solubility product for sparingly soluble salts? Give its two applications.

Definition:

"The solubility product is the product of the concentrations of ions raised to an exponent equal to the coefficient of the balanced equation".

OR

"The product of the equilibrium concentration of ions raised to an exponent equal to the coefficient of the balanced equation at given temperature is called solubility product (K_{sp})".

When a soluble ionic compound is dissolved in water, like $NaCl$, it dissociates completely into ions. But for slightly soluble salts the dissociation is not complete at equilibrium stage.

➢ Example 1, Lead Sulphate:

When Lead Sulphate ($PbSO_4$) is shaken with water the solution contains Pb^{2+}, SO_4^{2-} and undissociated $PbSO_4$. It means that equilibrium exists between solid solute, $PbSO_4$ and the dissolved ions, SO_4^{2-} and SO_4^{2-}. Lead sulphate is a well-known sparingly soluble compound and it dissociates to a very small extent like $PbCl_2$.

$$PbSO_{4(s)} \xrightleftharpoons{-H_2O} Pb^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

$$K_c = \frac{[Pb^{2+}][SO_4^{2-}]}{[PbSO_4]}$$

Being a sparingly soluble salt, the concentration of lead sulphate ($PbSO_4$) almost remains constant. Bring $[PbSO_4]$ on L.H.S. with K_c:

$$K_c[PbSO_4] = [Pb^{2+}][SO_4^{2-}]$$

if $K_c[PbSO_4] = K_{sp}$

then $K_{sp} = [Pb^{2+}][SO_4^{2-}] = 1.6\times10^{-8}$ at 25°C

K_{sp} is called the solubility product of $PbSO_4$. It is the product of molar solubilities of two ions at equilibrium stage.

Rack Your Mind!

9. What is the effect of temperature on the K_{sp} value?
A) It always remains constant
B) It decreases with temperature
C) It changes with temperature
D) It increases with pressure

Example 2, Lead Chloride:

Consider a sparingly soluble salt, $PbCl_2$. $K_{sp} = [Pb^{2+}][Cl^-]^2$

K_{sp} is usually a very small quantity at room temperature. The value of K_{sp} is temperature dependent. The value of K_{sp} is a measure of the dissociation of sparingly soluble salt.

The following Table shows the K_{sp} values of some slightly soluble ionic compounds.

Table: K_{sp} values for some ionic compounds

Salt	Ion Product	K_{sp}	Salt	Ion Product	K_{sp}
AgBr	$[Ag^+][Br^-]$	5.0×10^{-13}	CuS	$[Cu^{2+}][S^{2+}]$	8×10^{-36}
AgCl	$[Ag^+][Cl^-]$	1.8×10^{-10}	Fe_2S_3	$[Fe^{3+}]^2[S^{2-}]^3$	1.4×10^{-85}
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	3×10^{-34}	$MgCO_3$	$[Mg^{2+}][CO_3^{2-}]$	3.5×10^{-8}
$BaSO_4$	$[Ba][CO_4^{2-}]$	1.1×10^{-10}	MnS	$[Mn^{2+}][S^{2-}]$	3×10^{-11}
$CaCO_3$	$[Ca^{2+}][Ca_3^{2-}]$	3.3×10^{-9}	$PbCrO_4$	$[Pb^{2+}][CrO_4^{2-}]$	2.3×10^{-13}
CaF_2	$[Ca^{2+}][F^-]^2$	3.2×10^{-11}	$PbSO_4$	$[Pb^{2+}][SO_4^{2-}]$	1.6×10^{-8}

Applications of Solubility Product

a) Determination of Solubility from K_{sp}

For this purpose, we need the formula of the compound and K_{sp} value. Then the unknown molar solubility S is calculated and the concentration of the ions is determined. Table shows the relationship between the K_{sp} values and the solubility of some sparingly soluble compounds.

Table: The relation between solubility and solubility products of some salts

Formula	No. of Ions	K_{sp}	Solubility g dm^{-3}
$PbSO_4$	2	1.69×10^{-4}	1.3×10^{-4}
$Ca(OH)_2$	3	6.5×10^{-6}	1.175×10^{-2}
CaF_2	3	3.2×10^{-11}	2.0×10^{-4}
Ag_2CrO_4	3	2.6×10^{-12}	8.7×10^{-5}

Smart Thinking

Relationship Between K_{sp} and Molar Solubility (s)				
Compound	Cation	Anion	Ksp Expression	Relation Between Ksp and s
AgCl	s	s	$[Ag^+][Cl^-]$	$K_{sp} = s^2 \Rightarrow s = (K_{sp})^{\frac{1}{2}}$
$BaSO_4$	s	s	$[Ba^{2+}][SO_4^-]$	$K_{sp} = s^2 \Rightarrow s = (K_{sp})^{\frac{1}{2}}$
PbF_2	s	2s	$[Pb^{2+}][F^-]^2$	$K_{sp} = 4s^3 \Rightarrow s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
Ag_2CO_3	2s	s	$[Ag^+]^2[CO_3^{2-}]$	$K_{sp} = 4s^3 \Rightarrow s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
$Al(OH)_3$	s	3s	$[Al^{3+}][OH^-]^3$	$K_{sp} = 27s^4 \Rightarrow s = \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$
$Ca_3(PO_4)_2$	3s	2s	$[Ca^{2+}]^3[PO_4^{3-}]^2$	$K_{sp} = 108s^5 \Rightarrow s = \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$

Sample Problem 9.4

$Ca(OH)_2$ is a sparingly soluble compound. Its solubility product is 6.5×10^{-6}. Calculate the solubility of $Ca(OH)_2$.

Solution:

Let the solubility be represented by S in terms of mol dm^{-3}.

The balanced equation is:

$$Ca(OH)_{2(aq)} \rightleftharpoons Ca_{(aq)} + 2OH^-_{(aq)}$$

$Ca(OH)_{2(aq)} \rightleftharpoons 0 + 0$ Initial Stage

$Ca(OH)_2 \rightleftharpoons S + S$ Equilibrium Stage

The concentration of OH^- is double than the concentration of Ca^{2+}, so

$$K_{sp} = [Ca^{2+}][OH^-]^2 = S\times(2S)^2$$

$$4S^3 = 6.5\times10^{-6}$$

$$S^3 = \frac{6.5\times10^{-6}}{4}$$

$$S = (1.625)^{1/3}\times10^{-2}$$

$$S = 1.18\times110^{-2} \text{ mol dm}^{-3}$$

Hence, at equilibrium stage 1.18×10^{-2} moldm^{-3} moldm^{-3} of Ca^{2+} and $2\times1.18\times10^{-2}$ mol dm $= 2.36\times10^{-2}$ mol dm^{-3}. OH^- are present in the solution. In this way, we have calculated the individual concentrations of Ca^{2+} and OH^- ions from the solubility product of $Ca(OH)_2$.

b) Common Ion Effect

The presence of a common ion decreases the solubility of a slightly soluble ionic compound. In order to explain it, consider a saturated solution of $PbCrO_4$, which is a sparingly soluble ionic salt.

$$\text{Solubility} \propto \frac{1}{\text{concentration (no.) of common ions}}$$

$$PbCrO_{4(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)}$$

Now add Na_2CrO_4 which is a soluble salt.

$$Na_2CrO_{4(aq)} \rightleftharpoons 2Na^+ + CrO_4^{2-}$$

CrO_4^{2-} is the common ion. It combines with Pb^{2+} to form more insoluble $PbCrO_4$. So equilibrium is shifted to the left to keep K_{sp} constant.

c) Predicting Precipitation

The solubility product (K_{sp}) helps in predicting whether the precipitation of a salt will occur or not. For example, the solubility product of $CaSO_4$ is 2×10^{-5}. If we add 10^{-2} moldm^{-3} solution Ca^{2+} to 10^{-2} mol dm^{-3} solution of SO_4^{2-} ions at 25°C. The concentrations of each ionic species can be calculated as:

Ionic Product	Type of Solution	Precipitation
$>K_{sp}$	Supersaturated	Yes
$=K_{sp}$	Saturated	No
$<K_{sp}$	Unsaturated	No

$$[Ca^{2+}]=[SO_4^{2-}]=\frac{10^{-2}}{2}=5.0\times10^{-3}\ \text{mol dm}^{-3}$$

$$[Ca^{2+}][SO_4^{2-}]=5.0\times10^{-3}\ \text{moldm}^{-3}\times5.0\times10^{-3}\ \text{moldm}^{-3}$$

$$=2.5\times10^{-5}\ \text{mol}^2\text{dm}^{-6}$$

$$=2.5\times10^{-5}\ \text{mol}^2\text{dm}^{-6} > K_{sp}\ \text{of}\ CaSO_4$$

As the product of concentrations is greater than K_{sp}, therefore $CaSO_4$ will precipitate out.

QUICK CHECK 9.5

a) The solubility product constant (K_{sp}) of silver chloride (AgCℓ) is 1.77×10^{-10} at 25°C. A solution already contains 0.10 M of sodium chloride (NaCℓ). Find the solubility of AgCℓ in a solution that contains 0.10 NaCℓ.

Ans. Given:

- Ksp of AgCℓ = 1.77×10^{-10}
- [Cℓ$^-$] from NaCℓ = 0.10 M (this is the common ion).

Step 1: Define Solubility (S) of AgCℓ

Let S = molar solubility of AgCℓ (mol/dm^3) in the presence of NaCℓ.

- **Dissolution equation:**

$$AgCℓ_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cℓ^-_{(aq)}$$

- **At equilibrium:**

$$[Ag^+] = S\ (\text{from AgCℓ})$$

$$[Cℓ^-] = 0.10\ \text{M (from NaCℓ)} + S = 0.10\ \text{M (since } S \ll 0.10)$$

Step 2: Apply K_{sp} Expression

$$K_{sp} = [Ag^+][Cℓ^-]$$

$$1.77\times10^{-10} = S\times0.10$$

$$S = 1.77\times10^{-10}/0.10 = 1.77\times10^{-9}\ \text{M}$$

1. **Common Ion Effect:**
   The pre-existing 0.10 M Cℓ$^-$ from NaCℓ drastically reduces AgCℓ solubility (from $1,33\times10^{-5}$ M in pure water to 1.77×10^{-9} M).
2. **Assumption Valid:**
   S << 0.10, so [Cℓ$^-$]=0.10 M is justified.

Conclusion:

The solubility of AgCℓ in 0.10 M NaCℓ is 1.77×10^{-9} M.

b) Predict whether $CaSO_4$ will be precipitated or not when 10^{-3} moldm^{-3} of each of Ca^{2+} and SO_4^{2-} is mixed together.

Ans. Given:

$$[Ca^{2+}] = 10^{-3}\ \text{mol dm}^{-3}$$

$$[SO_4^{2-}] = 10^{-3}\ \text{mol dm}^{-3}$$

$$K_{sp}\ \text{of}\ CaSO_4 = 2.4\times10^{-5}\ \text{(at 25°C, literature value).}$$

Step 1: Calculate the Ion Product (Q)

$$Q = [Ca^{2+}][SO_4^{2-}]=(10^{-3})(10^{-3})=10^{-6}$$

Step 2: Compare Q to K_{sp}

- If $Q > K_{sp}$: Precipitation occurs.
- If $Q < K_{sp}$: No precipitation.

Here: $Q = 10^{-6}$ vs. $K_{sp} = 2.4\times10^{-5}$

Since $10^{-6} < 2.4\times10 = 10^{-6} < 2.4\times10^{-5}$, $Q < K_{sp}$.

Conclusion:

$CaSO_4$ will NOT precipitate under these conditions because the ion product (Q) is less than K_{sp}.

c) Solution of potassium carbonate is basic.

i. Explain why the solution is alkaline.

Ans. **Solution is Alkaline:**

Potassium carbonate (K_2CO_3) dissolves in water to produce CO_3^{2-}, which hydrolyzes to form OH^- ions, making the solution basic:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

- CO_3^{2-} (a strong base) reacts with water, accepting protons (H^+) and releasing OH^-.
- K^+ (from K_2CO_3) is a spectator ion and does not hydrolyze.

ii. Also give the equation for the hydrolysis of the above salt.

Ans. **Hydrolysis Equation:**

$$K_2CO_3 \rightarrow 2K^+ + CO_3^{2-} \quad \text{(Dissociation)}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \quad \text{(Hydrolysis)}$$

The OH^- generated during hydrolysis raises the pH (>7), making the solution alkaline.

Example pH: ~11 for 0.1 M K_2CO_3.

Interesting Information!

The shell of this nautilus is composed mainly of calcium carbonate. The nautilus adjusts conditions so shell material is formed when the concentration of calcium ions and carbonate ions in seawater are high enough to precipitate calcium carbonate.



SALT HYDROLYSIS

When a salt dissolves in water, it dissociates into its constituent ions. These ions can interact with water, affecting the solution's pH depending on the nature of the acid and base from which the salt is derived.

➢ **Hydrolysis:**

"The interaction between salts and water are called hydrolytic reactions and this phenomenon is called hydrolysis".

➲ **Salts of Strong Acids and Strong Bases**

For salts derived from strong acids and strong bases (e.g., sodium chloride, NaCℓ), the conjugate base of a strong acid (e.g., Cℓ$^-$ from HCℓ) is very weak and does not significantly react with water. The conjugate acid of a strong base (e.g., Na^+ from NaOH) is also very weak and does not significantly react with water.

$$NaCl_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + Cl^-_{(aq)}$$

Na^+ is the conjugate acid of NaOH (a strong base) and does not affect the pH.

Cl^- is the conjugate base of HCl (a strong acid) and does not affect the pH.

The solution remains neutral.

Examples are KCl (HCl + KOH), $KNO_3(HNO_2 + KOH)$, $Na_2SO_4(H_2SO_4 + NaOH)$ etc.

Salts of Strong Acids and Weak Bases

For salts derived from strong acids and weak bases (e.g., ammonium chloride, NH_4Cl), The conjugate base of the strong acid (e.g., Cl^-) does not react with water. The conjugate acid of the weak base (e.g., NH_4^+ from NH_3) reacts with water to produce H_3O^+ ions, making the solution acidic.

$$NH_4Cl_{(s)} \rightleftharpoons NH^+_{4(aq)} + Cl^-_{(aq)}$$

NH_4^+ is the conjugate acid of NH_3 (a weak base) and reacts with water:

$$NH^+_{4(aq)} + H_2O_{(\ell)} \rightleftharpoons NH_{3(g)} + H_3O^+_{(aq)}$$

Cl^- is the conjugate base of HCl (a strong acid) and does not affect the pH.

The solution is acidic due to the NH_4^+ ion.

Examples: $AlCl_3$, $CuSO_4$, NH_4NO_3 etc.

Salts of Weak Acids and Strong Bases

The example of salt of weak acid and strong base is sodium acetate.

$$CH_3COONa_{(s)} + H_2O_{(\ell)} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

CH_3COO^- is the conjugate base of CH_3COOH (a weak acid) and reacts with water:

$$CH_3COO^-_{(aq)} + H_2O_{(\ell)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

Na^+ is the conjugate acid of NaOH (a strong base) and does not affect the pH . The solution is basic due to the CH_3COO^- ion.

Examples: $Na_2CO_3(H_2CO_3 + NaOH)$, $Na_3PO4(H_3PO_4 + NaOH)$

Salts of Weak Acids and Weak Bases

For salts derived from weak acids and weak bases (e.g., ammonium acetate, NH_4CH_3COO): The conjugate acid (NH_4^+) and the conjugate base (CH_3COO^-) both affect the pH .

$$NH_4CH_3COO_{(aq)} \rightleftharpoons NH^+_{4(aq)} + CH_3COO^-_{(aq)}$$

NH_4^+ hydrolyzes to produce H_3O^+.

$$NH^+_{4(aq)} + H_2O_{(\ell)} \rightleftharpoons NH_{3(aq)} + H_3O^+_{(aq)}$$

CH_3COO^- hydrolyzes to produce OH^-.

$$CH_3COO^-_{(aq)} + H_2O_{(aq)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

The resultant pH of the solution depends on the relative strengths of the conjugate acid and conjugate base. The solution may be acidic, basic, or nearly neutral, depending on which reaction is more dominant.

Examples: $NH_4CN(NH_4OH + HCN)$, $(NH_4)_2CO_3(H_2CO_3 + NH_3)$

ACID-BASE INDICATORS

An indicator is a substance that changes color to mark a titration's endpoint. Acid-base indicators exhibit one color in acid and another in base. Most indicators used in acid-base titration are weak organic acids or weak organic bases. In solution, a weak-acid indicator (HIn) can be represented by the equation below.

$$HIn \rightleftharpoons H^+ + In^-$$

In^- is the symbol of the anion part of the indicator. Because the reaction is reversible, both HIn and In^- are present. The colors displayed result from the fact that HIn and In^- have different colors.

In acidic solutions, any In^- ions that are present act as Bronsted bases and accept protons from the acid. The indicator is then present in largely unionized form, HIn. In basic solutions, the OH^- ions from the base combine with the H^+ ions produced by the indicator. The indicator molecules further ionize to equalize the loss of H^+ ions. The indicator is thus present largely in the form of its anion, In^-. The solution now shows the base-indicating color, which for litmus is blue.

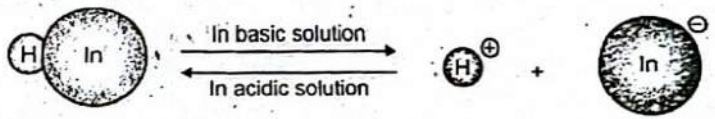


Figure: Unionized acid-base indicators and their ionised forms exist in an equilibrium

Different indicators change color at different pH values. The color depends on the relative amounts of HIn and In^- at a given pH. For example, methyl red changes from red to yellow between pH 4.4 and 6.2. At pH 4.4, the indicator exists mostly as HIn molecules, which appear red in the solution. The indicator ranges are given below for some of the indicators commonly used.

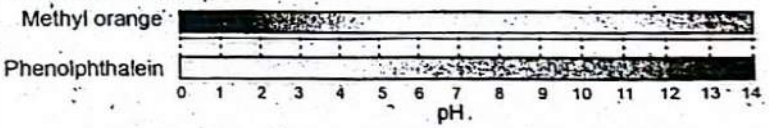


Figure: Range and color changes of some common Acid-Base Indicators

Selecting a Suitable Indicator

The two general criteria for an indicator to be used in a titration are:

- The pH at the end of the titration should be close to the indicator's neutral point.
- The indicator should indicate a sharp color change near the equivalence point of the titration.

Each pH indicator changes color over a defined range of pH, known as the indicator range. An indicator changes color over a range of about 2 pH units.

Exercise I, Q.7

Q. Describe the general shape of a titration curve for a strong acid titrated with a strong base. How can you identify the equivalence point on this titration curve?

Titration Curve and Equivalence Point

A pH curve is a graph of the pH of the solution verses the volume of titrant added. **The equivalence point is the point at which the amount of titrant added is just enough to neutralize the analyte solution completely.** Titration curves show how the pH of an acidic or basic solution changes as a basic or acidic solution is added to it. We can use the titration curve to choose an indicator that will show when the titration is complete and we reach the equivalence point. The end point of the titration occurs when the indicator changes color. We choose an indicator with an end point close to the equivalence point.

1. Strong Acid-Strong Base Titration Curve:

Consider the titration of HCℓ with NaOH. Initially, the solution contains only the strong acid. Since the acid is strong, it completely dissociates, leading to a high concentration of H^+ ions and the pH is very low.

As NaOH is added, OH^- ions from NaOH begin to neutralize the H^+ ions from HCℓ and pH of the solution rises.

The equivalence point is reached when the amount of OH^- added is stoichiometrically equal to the amount of H^+ originally present in the acid. **The pH at the equivalence point in a strong acid-strong base titration is 7.0.**

The titration curve at this stage shows a steep rise in pH, changing quickly from acidic to neutral. The pH value at the endpoint changes about from 4.0 to 10.0. These titrations have a pH of 7.0 at equivalence, so, such phenolphthalein as indicator can be used as they show different colours in this range.

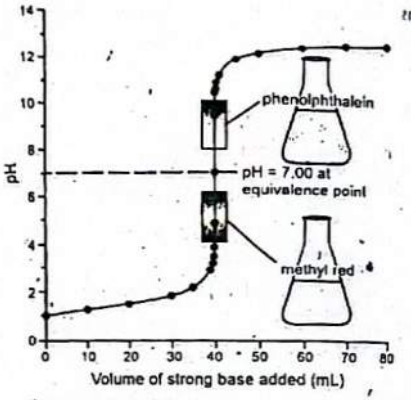


Figure: Strong acid-strong base titration curve

2. Strong Acid-Weak Base Titration Curve

Consider the titration of aqueous NH_3 with HCℓ. Initially, the solution contains only the weak base and it only partially dissociates, with a lower concentration of OH^- ions compared to a strong base. The initial pH will be greater than 7 but lower than the pH of a strong base. As HCℓ is added, the concentration of OH^- decreases, causing a further decrease in pH.

Before reaching the equivalence point, the solution is in a buffer-like region where the pH changes more gradually. The presence of the weak base and its conjugate acid (from the salt formed) creates a buffering effect, which helps to moderate the pH change as the base is added.

The pH at the equivalence point will be less than 7(pH = 5.27) because the conjugate acid slightly dissociates, releasing H^+ ions making the solution acidic ($NH_4^+ \rightarrow NH_3 + H^+$).

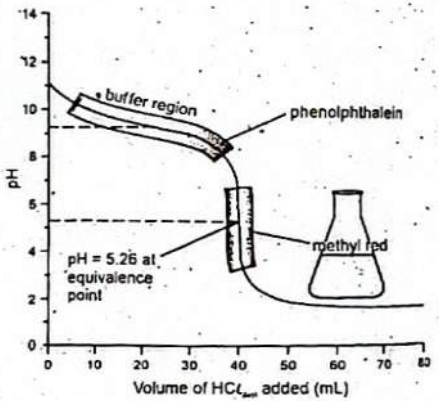


Figure: strong acid-weak base titration curve

After the equivalence point, the pH of the solution decreases rapidly. This is because the strong acid dissociates completely in water, providing a high concentration of hydrogen ions H^+, which significantly lowers the pH, Methyl orange has its colour change in this range, therefore, it can be used as an indicator for strong acid-weak base titrations.

Rack Your Mind!

10. What is the equivalence point in a titration?

Table: pH ranges of common Indicators

Indicators	Acid color	Base color	pH Range	Type of Titration
Methyl orange	orange	yellow	3.2 – 4.5	strong acid-strong base strong acid-weak base
Phenolpthalein	colorless	red	8.2 – 10.0	weak acid-strong base

QUICK CHECK 9.6

a) Differentiate end point and equivalent point.

Ans. The difference between Endpoint and Equivalence:

Feature	Equivalence Point	Endpoint
Definition	The point where stoichiometrically equivalent amounts of analyte and titrant react.	The point where the indicator changes color, signaling completion of titration.
Theoretical vs. Experimental	Theoretical (calculated from stoichiometry).	Experimental (observed visually or instrumentally).
Dependence on Indicator	Independent of indicator.	Depends on the choice of indicator.
pH (Acid-Base Titration)	pH is determined by the salt formed (e.g., pH = 7 for strong acid-strong base).	pH may slightly differ due to indicator range (e.g., phenolphthalein changes at pH 8.2–10).
Precision	Exact (based on reaction stoichiometry).	Approximate (may not perfectly match equivalence point).

b) Explain how an indicator changes its colour in acidic and basic solution.

Ans. An Indicator Changes Color in Acidic vs. Basic Solutions:

1. **Chemical Structure:**
   - Indicators are **weak acids (HIn)** or **weak bases (InOH)** with **different colors** in protonated (acidic) and deprotonated (basic) forms.
2. **Acidic Solution ($pH < pK_a$):**
   - Excess H^+ ions shift equilibrium left:
   $$HIn \rightleftharpoons H^+ + In^-$$
   - The **protonated form (HIn)** dominates (e.g., **red** for methyl orange).
3. **Basic Solution ($pH > pK_a$):**
   - OH^- ions remove H^+, shifting equilibrium right:
   $$HIn \longrightarrow In^- + H^+$$
   - The **deprotonated form (In^-)** dominates (e.g., **yellow** for methyl orange).
4. **Transition Range ($pH \approx pK_a \pm 1$):**
   - Color change occurs (e.g., phenolphthalein turns pink at pH 8.2–10).

Example:

- **Methyl Orange:**
  Acidic (red, HIn) → Basic (yellow, In^-).
- **Phenolphthalein:**
  Acidic (colorless, HIn) → Basic (pink, In^-).

Key Idea: The indicator's color reflects the dominant form (HIn or In^-) based on pH.

c) Suggest a suitable indicator for weak acid and strong base titration.

Ans. For the titration of a weak acid (e.g., CH_3COOH) with a strong base (e.g., NaOH), the best indicator is:

Phenolphthalein

- **pH Range: 8.2–10.0** (colorless → pink).
- **Reason:** The equivalence point pH is >7 (due to hydrolysis of the conjugate base, e.g., CH_3COO^-). Phenolphthalein's range matches this alkaline pH.

d) **Suggest a suitable indicator for weak acid and weak base titration.**

Ans. For weak acid-weak base titrations, no indicator is ideal due to the gradual pH change near the equivalence point. However, if required:

Suggested Indicator: Bromothymol Blue

- **pH Range:** 6.0 (yellow) to 7.6 (blue).
- **Reason:** Covers the neutral pH (≈7) typical for weak acid-weak base titrations (e.g., acetic acid + ammonia).

Limitation:

Weak acid-weak base titrations often lack a sharp pH jump, making pH meters more reliable than visual indicators.

Solution File — Rack Your Brain!

Sr. #	Option	Explanation
1.	B	HCℓ (acid) → H^+ + $Cℓ^-$ (conjugate base) HCl donates a proton, making Cl– its conjugate base.
2.	D	When an acid donates a proton, it forms its conjugate base, and when a base accepts a proton, it forms its conjugate acid.
3.	S.Q	BF_3 is a Lewis acid because the boron atom has only six electrons in its valence shell, which is less than an octet. This incomplete octet makes BF_3 electron-deficient and able to accept a lone pair from a Lewis base like fluoride ion.
4.	S.Q	Water concentration remains effectively constant (about 55.5 mol dm^{-3}) because water is present in large excess and only a tiny fraction ionizes; so its concentration does not change significantly.
5.	A	H+ = 10(–pH) = $10^{(-3)}$ = 0.001 M or $1 \times 10^{(-3)}$M pH is defined as the negative logarithm of the hydrogen ion concentration.
6.	S.Q	K_a is the acid dissociation constant. It represents the extent to which an acid donates protons in water. A higher K_a value means a stronger acid,
7.	C	Presence of a common ion from a strong electrolyte reduces the ionization of a weak electrolyte, shifting the equilibrium towards the reactants.
8.	S.Q	• A buffer solution resists a change in pH when a small amount of acid or base is added. • It maintains a constant pH and is stable over time and on dilution. • Buffers are made from a weak acid/base and its salt.
9.	C	Based on "Le Chatelier's Principle" the system shifts to oppose the temperature change. So "temperature can increase or decrease Ksp" depending on the heat change of the dissolution reaction.
10.	S.Q	• The equivalence point is when the amount of acid equals the amount of base. • It is where complete neutralization occurs. • It is not always at pH 7, depending on acid and base strength.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 **Four choices are given for each question. Select the correct choice.**

I. **Given the following reaction:**

$$NH_{3(g)} + H_2O_{(\ell)} \longrightarrow NH_{4(aq)}^+ + OH_{(aq)}^-$$

a) NH_3 is the acid, H_2O is the base
b) NH_3 is the base, H_2O is the acid
c) NH_4^+ is the base, OH^- is the acid
d) H_2O is the base, OH^- is the acid

II. **The pH of 10^{-3} mol dm^{-3} of an aqueous solution of H_2SO_4 is:**
a) 3.0 b) 2.7 c) 2.0 d) 1.5

III. **The solubility product of AgCℓ is 2.0×10^{-10} moldm^{-6}. The maximum concentration of Ag^+ ions in the solution is:**
a) 2.0×10^{-10} moldm^{-3} b) 1.41×10^{-5} moldm^{-3} c) 1.0×10^{-10} moldm^{-3} d) 4.0×10^{-20} moldm^{-3}

IV. **Which indicator is typically used for titrations involving strong acids and strong bases?**
a) Methyl red b) Phenolphthalein c) Bromothymol blue d) Litmus solution

V. **Which of the following is the conjugate base of water?**
a) $OH_{(aq)}^-$ b) $OH_{(aq)}^+$ c) $H_2O_{(\ell)}$ d) $H_3O_{(aq)}^+$

VI. **Which of the following is a Lewis acid but not a Bronsted-Lowry acid?**
a) HCℓ b) NH_3 c) $AlCℓ_3$ d) H_2O

VII. **In an acid-base titration, the equivalence point is reached when:**
a) pH of the solution is 7.0. b) The indicator changes color.
c) Equal volumes of acid and base have been added. d) The reaction stops.

VIII. **If the concentration of $Cℓ^-$ ion in a solution is increased, the solubility of silver chloride (AgCℓ) will:**
a) Decrease b) Increase c) Remain unchanged d) Become zero

IX. **Which of the following pairs of substances can act as a conjugate acid-base pair according to the Bronsted-Lowry theory?**
a) HCℓ and NaOH b) NH_3 and NH_4^+ c) H_2O and H_2SO_4 d) H_2O and CH_4

X. **If the pH of a solution is 11, what is the $[OH^-]$ concentration in the solution?**
a) 1×10^{-3} M b) 1×10^{-11} M c) 1×10^{-2} M d) 1×10^{-14} M

XI. **Which of the following pairs forms a buffer solution?**
a) (HCℓ) and (NaCℓ) b) (CH_3COONa) and (CH_3COOH)
c) (NaOH) and (HCℓ) d) (NH_3) and (Na_2SO_4)

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	b	NH_3 is the base, H_2O is the acid	• NH_3 accepts H^+, making it a base; H_2O donates H^+, making it an acid.
II.	b	2.7	• $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{-2}$ $[H^+] = 2 \times 10^{-3}$ pH = –log $[H^+]$ pH = $-\log 2 \times 10^{-3} = -(\log 2 - 3 \log 10) = -(0.301 - 3)$ pH = 2.67 Or 2.7

III.	b	1.41×10^{-5} moldm^{-3}	• $AgCl \rightleftharpoons Ag^{+1} + Cl^-$ $K_{sp} = [Ag^{+1}][Cl^{-1}]$ $2.0\times10^{-10} = [Ag^{+1}][Cl^{-1}]$ Since $[Ag^{+1}] = [Cl^{-1}]$ $2.0\times10^{-10} = [Ag^{+1}]^2$ $\sqrt{2.0\times10^{-10}} = \sqrt{[Ag^{+1}]^2}$ $[Ag^{+1}] = 1.414\times10^{-5}$ mol dm^{-3}
IV.	b	Phenolphthalein	• Changes color near pH 7–9, ideal for strong acid-strong base titrations.
V.	a	$OH^-_{(aq)}$	• H_2O loses H^+ to form OH^- so OH^- is its conjugate base.
VI.	c	$AlCl_3$	• Accepts an electron pair but does not donate H^+.
VII.	c	Equal volumes of acid and base have been added.	• Equivalence point is stoichiometric, not necessarily pH 7.
VIII.	a	Decrease	• Common ion effect reduces solubility.
IX.	b	NH_3 and NH_4^+	• NH_3 gains H^+ to form NH_4^+
X.	a	1×10^{-3} M	• pH = 11 → pOH = 3 → $[OH^-] = 10^{-3}$ M.
XI.	b	Sodium acetate (CH_3COONa) and acetic acid (CH_3COOH)	• Weak acid (CH_3COOH) + its conjugate base (CH_3COO^-) forms buffer.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Define the following with an example for each:
i) Ionization constant **ii) Solubility product**
iii) Common ion effect **iv) Acid-base Indicator**

Ans.

(i) Ionization Constant: The quantitative measure of the strength of the acid and base is called ionization constant.

Example: we have an acid HA dissolved in water,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

(ii) Solubility Product: The solubility product is the product of the concentrations of ions raised to an exponent equal to the co-efficient of the balanced equation,

Example: For $AgCl$

$$AgCl \rightleftharpoons Ag^+ + Cl^-, \quad K_{sp} = [Ag^+][Cl^-]$$

(iii) Common ion Effect: The suppression of ionization of a weak electrolyte by adding a common ion to it is called common ion effect.

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$HCl_{(g)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

(iv) Acid-base Indicator: An indicator is a substance that changes colour to mark a titration's endpoint. Acid-base indicators exhibit one colour in acid and another in base. Most indicators used in acid-base titration are weak organic acids or weak organic bases.

Example:
Phenolphthalein: Colorless (pH < 8.3) to Pink (pH > 10.0)

b. Differentiate between:
i) Hydrolysis and dissolution **ii) Acidic and basic buffer solutions**

Ans. i) Hydrolysis and Dissolution

Feature	Hydrolysis	Dissolution
Definition	A chemical reaction where water breaks bonds in a compound.	A physical process where a solute dissolves in a solvent.
Nature	Chemical process (forms new substances).	Physical process (no new substances formed).
Involves	Reaction with water molecules (H^+ and OH^- may participate).	Mixing of solute and solvent (e.g., salt in water).
Energy Change	May release or absorb energy (exo/endothermic).	Often absorbs energy (endothermic, but not always).
Result	Forms new products (e.g., acids, bases, or ions).	Forms a homogeneous mixture (solution).
Example	$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3H^+ + 3Cl^-$	$NaCl_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

(ii) Acidic and Basic Buffer Solutions

Acidic buffers	Basic buffers
• Those buffers which are formed by the mixing of a weak acid and a salt of it with a strong base are called acidic buffers.	• Those buffers which are formed by mixing of a weak base and a salt of it with a strong acid are called basic buffers.
• Their pH is less than 7.	• Their pH is more than 7.
• Henderson's equation for acidic buffers $pH = pK_a + \log\frac{[salt]}{[acid]}$	• Henderson's equation for basic buffers $pOH = pK_b + \log\frac{[salt]}{[base]}$
e.g. CH_3COOH (weak acid) + CH_3COONa (salt of weak acid)	e.g. NH_4OH (weak base) + NH_4Cl (salt of weak base)

c. Explain the concept of conjugate acid-base pairs. How are they related in terms of proton transfer?

Ans. Conjugate Acid:

"A species formed after a Bronsted base accepts a proton from the acid is called the conjugate acid". The hydronium ion (H_3O^+) is the conjugate acid of water.

Example:

When NH_3 dissolves in Water:

When ammonia dissolves in water, proton transfer also occurs. H^+ from H_2O attaches to the N atom's lone pair and NH_4^+ and OH^- are formed. With fewer H^+, the water molecule becomes OH^- ion:

$$\underset{\text{Base}}{NH_{3(g)}} + \underset{\text{Acid}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{Conjugate base}}{OH^-_{(aq)}} + \underset{\text{Conjugate acid}}{NH^+_{4(aq)}}$$

In this case, H_2O (the acid) has donated the proton and NH_3 (the base) has accepted it. $NH_3 - NH_4^+$ and $H_2O - OH^-$ are conjugate acid-base pair.

Conjugate Base:

"A species formed after a Bronsted base accepts a proton from the acid is called the conjugate acid."

Example: The hydronium ion (H_3O^+) is the conjugate acid of water. A species formed when an acid donates a proton to a base is called the conjugate base. $HCl + Cl^-$ and $H_2O \rightarrow H_3O^+$ are conjugate acid-base pairs.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \longrightarrow \underset{\text{conjugate acid}}{H_3O^+} + \underset{\text{conjugate base}}{Cl^-}$$

d. What is the relationship between the strength of an acid and the strength of its conjugate base?

Ans. A strong acid has a weak conjugate base because it donates protons easily. A weak acid has a stronger conjugate base as it holds onto protons.

Example: HCl (strong acid) forms Cl^- (very weak base).

- **Strong Acid (HCl):** Weak conjugate base (Cl^-).
- **Weak Acid (CH_3COOH):** Strong conjugate base (CH_3COO^-).

e. For the following three reactions, identify the reactants that are Arrhenius bases, Bronsted-Lowry bases, and/or Lewis bases. State which type(s) of bases each reactant is. Explain your answers.

i) $NaOH_{(s)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$ ii) $HF_{(aq)} + H_2O_{(l)} \longrightarrow F^-_{(aq)} + H_3O^+_{(aq)}$ iii) $H^+_{(aq)} + NH_{3(aq)} \longrightarrow NH^+_{4(aq)}$

Ans. (i) OH^- is an Arrhenius and Bronsted-Lowry base (accepts H^+).
(ii) H_2O is a Bronsted-Lowry base (accepts H^+) and Lewis base (donates lone pair).
(iii) NH_3 is a Bronsted-Lowry and Lewis base (accepts H^+ and donates lone pair).

f. An amphoteric substance can behave as either an acid or a base. Identify whether water behaves as an acid or a base in each of the following reactions.

i) $H_2O + HCl \longrightarrow H_3O^+ + Cl^-$ ii) $NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$

iii) $HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$ iv) $CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+$

Ans.

Reaction	H_2O Role	Reason
i) $H_2O + HCl \longrightarrow H_3O^+ + Cl^-$	Base	Accepts H^+ from HCl.
ii) $NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$	Acid	Donates H^+ to NH_3.
iii) $HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$	Base	Accepts H^+ from HNO_3.
iv) $CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+$	Base	Accepts H^+ from CH_3COOH.

g. Which salt would you expect to dissolve more readily in acidic solution: Barium sulfate or Barium fluoride? Explain. $K_{sp(BaCO_3)} = 1.1 \times 10^{-10}$, $K_{sp(BaSO_4)} = 1.1 \times 10^{-10}$

Ans. Barium fluoride (BaF_2) dissolves more in acid.

Reason: F^- reacts with H^+ to form HF:

$$BaF_2 \rightleftharpoons Ba^{2+} + 2F^- \qquad F^- + H^+ \longrightarrow HF$$

$BaSO_4$ is unaffected because SO_4^{2-} doesn't react with H^+.

h. Why does common ion effect decrease solubility of a less soluble salt?

Ans. The solubility of a less soluble salts $KClO_3$ in water is suppressed by the addition of a more soluble salt KCl by common ion effect. K^+ is a common ion. The ionization of $KClO_3$ is suppressed and it settles down as precipitate.

$$KClO_{3(s)} \rightleftharpoons K^+_{(aq)} + ClO^-_{(aq)}$$
$$KCl_{(s)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$$

i. State the basic principle of solubility product. Mention factors affecting solubility product.

Ans. It is the product of molar solubilities of two ions at equilibrium stage.

For example: sparingly soluble salt, $PbCl_2$, $K_{sp} = [Pb^{2+}][Cl^-]^2$

K_{sp} is usually a very small quantity at room temperature. The value of K_{sp} is temperature dependent.

Factors Affecting K_{sp}:

- Temperature
- Presence of common ions
- pH (if salt has basic/acidic ions)

j. Prove by equations what happens when Na_2CrO_4 is added to saturated solution of $PbCrO_4$.

Ans. When Na_2CrO_4 is added to a saturated $PbCrO_4$ solution, it increases the concentration of CrO_4^{2-} ions. According to Le Chatelier's Principle, the equilibrium shifts left to reduce the added CrO_4^{2-} ions:

$$PbCrO_{4(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO^{2-}_{4(aq)}$$
$$Na_2CrO_{4(aq)} \rightleftharpoons 2Na^+ + CrO_4^{2-}$$

- **Result:** More $PbCrO_4$ precipitates out, decreasing its solubility.
- **Reason:** The common ion (CrO_4^{2-}) suppresses the dissociation of $PbCrO_4$.

This is an example of the common ion effect reducing solubility.

k. According to the Lewis acid-base concept, Boron trifluoride (BF_3) can act as an acid. Is this statement correct?

Ans. Correct, BF_3 is a Lewis acid.

Reason: Boron in BF_3 has an empty p-orbital and can accept an electron pair (Lewis acid).

Example: When BF_3 reacts with NH_3 (a Lewis base), it forms a coordinate covalent bond:

$$BF_3 + NH_3 \longrightarrow H_3N \longrightarrow BF_3$$

Here, BF_3 accepts the lone pair from NH_3.

l. If the concentration of hydrogen ions in a solution is 1×10^{-5} M, what is the pH of the solution?

Given Data:

Concentration of hydrogen ions, $[H^+] = 1 \times 10^{-5}$ M

To Find:

pH of the solution = ?

Solution:

Step 1: pH formula:

$pH = -\log[H^+]$

Step 2: Substitute the given $[H^+]$ into the formula:

$pH = -\log(1 \times 10^{-5})$

Step 3: Simplify the logarithm:

$pH = -(-5) = 5$

Answer: The pH of the solution is 5.

DESCRIPTIVE QUESTIONS

Q.3 Describe the Bronsted-Lowry theory of acids and bases. Provide examples of conjugate acid-base pairs and explain clearly their relationship.

Ans. See Page No. (294)

Q.4 Define the Lewis theory of acids and bases. How does this theory differ from the Bronsted-Lowry theory? Give examples of Lewis acids and bases that do not involve proton transfer.

Ans. See Page No. (295)

Q.5 Discuss applications and implications of the common ion effect in various fields.

Ans. See Page No. (305)

Q.6 What is the solubility product for sparingly soluble salts? Give its two applications.

Ans. See Page No. (309)

Q.7 Describe the general shape of a titration curve for a strong acid titrated with a strong base. How can you identify the equivalence point on this titration curve?

Ans. See Page No. (315)

NUMERICAL PROBLEMS

Q.8 A buffer solution has a pH of 5.0. It is made from a weak acid HA with a pK_a of 4.8. What is the ratio of the concentration of the conjugate base $[A^-]$ to the concentration of the weak acid [HA] in this buffer?

Given Data: $pH = 5.0$, $pK_a = 4.8$

Formula: $pH = pK_a + \log\frac{[salt]}{[acid]}$

Putting the values: $5.0 = 4.8 + \log\left(\frac{[A^-]}{[HA]}\right)$

Solve for the log term: $\log\left(\frac{[A^-]}{[HA]}\right) = 5.0 - 4.8 = 0.2$

Convert log to ratio (antilog):

$$\frac{[A^-]}{[HA]} = 10^{0.2} = 1.58$$

Final Result: $\frac{[A^-]}{[HA]} \approx \boxed{1.58}$

The buffer contains 1.58 times more conjugate base (A^-) than weak acid (HA) to maintain pH 5.0.

Q.9 Calculate the solubility of a sparingly salt lead (II) iodide (PbI_2) in water. It has $K_{sp} = 1.4 \times 10^{-8}$.

Given Data: $K_{sp} = 1.4 \times 10^{-8}$

$$PbI_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2I^-_{(aq)}$$

Define Solubility (s):

Let s = molar solubility of PbI_2 (mol/dm³).

At equilibrium: $[Pb^{2+}] = s$

$[I^-] = 2s$ (2 moles of I^- are produced per mole of PbI_2).

K_{sp} Expression: $K_{sp} = [Pb^{2+}][I^-]^2$

$= (s)(2s)^2 = 4s^3$

Solve for s: $4s^3 = 1.4 \times 10^{-8}$

$$s^3 = \frac{1.4\times10^{-8}}{4} = 3.5 \times 10^{-9}$$

$$s = \sqrt[3]{3.5\times10^{-9}} = \boxed{1.52 \times 10^{-3}\ mol/dm^3}$$

Final Answer: The solubility of PbI_2 is 1.52×10^{-3} mol/dm³.

Q.10 The molar solubility of silver chromate (Ag_2CrO_4) in pure water at 298 K is 6.5×10^{-5} mol dm⁻³. Calculate the K_{sp} of silver chromate at this temperature.

Given Data:

Molar solubility (s) of $Ag_2CrO_4 = 6.5 \times 10^{-5}$ mol dm⁻³

$$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^+_{(aq)} + CrO^{2-}_{4(aq)}$$

Ion Concentrations in Terms of s

$[Ag^+] = 2s$ (2 moles of Ag^+ per mole of Ag_2CrO_4).

$[CrO_4^{2-}] = s$ (1 mole of CrO_4^{2-} per mole of Ag_2CrO_4).

K_{sp} Expression: $K_{sp} = [Ag^+]_2[CrO_4^{2-}]$

$= (2s)^2(s) = 4s^3$

Substitute s and Solve for K_{sp}: $K_{sp} = 4 \times (6.5 \times 10^{-5})^3$

$K_{sp} = 4 \times (2.746 \times 10^{-13})$

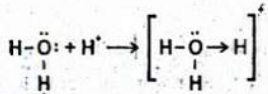
$K_{sp} = 1.10 \times 10^{-12}\ mol^3\ dm^{-9}$

Final Answer: $K_{sp} = \boxed{1.1 \times 10^{-12}}$

ADDITIONAL SLOs BASED MCQs

1. Water cannot act as:
   A. Lewis acid B. Lewis base C. Bronsted acid D. Bronsted base
2. pH of 0.01 M HCl solution is:
   A. 10^{-2} B. 10^{+2} C. 2.0 D. 1.0
3. An aqueous solution of ammonium chloride is:
   A. Basic B. Acidic C. Neutral D. Amphoteric
4. An aqueous solution of which compound is basic.
   A. Ammonium nit ate B. Calcium chloride C. Ammonium acetate D. Potassium carbonate
5. Which statement about acids is not correct? An acid:
   A. Contains hydrogen ions in solution B. Contains Oxygen
   C. Has a pH of less than 7 then D. Gives off carbon dioxide from a carbonate
6. If a liquid has a pH of 7 then:
   A. It must be colourless B. It has boiling point of 100°C
   C. It must be a solution D. It must be neutral
7. When air is bubbled through pure water, the pH is lowered from 7.0 to 5.6, which gas in the air is responsible for this change.
   A. Argon B. Carbon dioxide C. Nitrogen D. Oxygen
8. Which of the following oxides is classified incorrectly?
   A. Zinc oxide (ZnO) amphoteric B. Carbon dioxide (CO_2) acidic
   C. Carbon monoxide (CO) neutral D. Lead oxide (PbO) basic
9. If 25cm³ of 1 mole. dm⁻³ nitric acid is added to 50 cm³ of 0.5 potassium hydroxide solution, what would be the pH of the resulting solution?
   A. 5 B. 7 C. 9 D. 14
10. If dry citric acid crystals are placed on dry litmus paper they will:
    A. turn yellow B. turn green C. turn red D. remain unchanged
11. A base is a substance which will neutralize an acid. Which of these substances is not a base?
    A. Aqueous ammonia B. Copper oxide C. Potassium chloride D. Sodium carbonate
12. A strong acid:
    A. Is always partially ionized when in solution B. Is always fully ionized when in solution
    C. Always decomposes carbonates D. Always contains oxygen
13. Which one of the following oxides dissolves in water to form acidic solution?
    A. MgO B. Na_2O C. SO_2 D. SiO_2
14. When crystals of copper sulphate are heated, the colour changes from blue to white. This is caused by:
    A. Loss of water only B. Loss of water and SO_2
    C. Reaction with CO_2 in the air D. Loss of water, sulphur dioxide and oxygen
15. The oxide of a metal was found to react with HCl and aqueous NaOH solution. Which of the following is the best description of the oxide?
    A. Acidic B. Amphoteric C. Basic D. Neutral

Answer Key with Explanations

Q. No	Ans.	Explanation
1.	A	• Water can donate and accept proton (H^+). So it can act as Bronsted acid as well as base. $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ • Similarly, in water, oxygen has electron pairs which it can donate to other species, so water acts as Lewis base.  But water cannot act as Lewis acid.
2.	C	$HCl \rightleftharpoons H^+O + Cl^-$ 0.01M 0.01M Since HCl is a strong acid, it ionized completely giving $[H^+] = 0.01M = 10^{-2}M$ $pH = -\log [H^+]$ $pH = -\log 10^{-2}$ $pH = 2 \log 10$ $\log 10 = 1$ $pH = 2$
3.	B	$HCl + NH_3 \rightleftharpoons NH_4Cl$ Strong acid weak base Acidic salt When NH_4Cl is added, the solution becomes acidic.
4.	D	Salt: NH_4NO_3 Ammonium Nitrate — Type: Acidic Salt — Nature of Solution: Acidic solution Salt: $CaCl_2$ Calcium chloride — Type: Neutral salt — Nature of Solution: Somewhat neutral solution Salt: K_2CO_3 Potassium carbonate — Type: Basic salt — Nature of Solution: Basic solution
5.	B	HCl, HBr, BF_3, $AlCl_3$ etc are acids but they do not contain oxygen. Anyhow H_2SO_4, HNO_3, CH_3COOH etc have oxygen in them
6.	D	Solution: pH = 7 (Neutral); pH > 7 (Basic); pH < 7 (Acidic)
7.	B	When air is bubbled through pure water, CO_2 combines with water and forms carbonic acid. $CO_{2(g)} + H_2O_{(l)} \longrightarrow H_2CO_{3(aq)}$ As a result, pH of the solution decreases
8.	D	Lead oxide (PbO) is an amphoteric oxide. $PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O$ (base) (acid) $PbO + 2NaOH + H_2O \longrightarrow Na_2[Pb(OH)_4]$ (acid) (base)
9.	B	Concentration = Molarity × Volume of H^+ or OH^- Since $[H^+] = [OH^-]$ in both cases, so a neutral solution having pH = 7 is formed.
10.	D	Moisture is necessary to effect the litmus paper. In moist, the litmus paper turns red with citric acid.
11.	C	$KOH + HCl \longrightarrow KCl + H_2O$ Strong base Strong acid Neutral salt KCl will not hydrolyse, so solution remains neutral.
12.	B	The strength of an acid depends upon its extent of ionization. A strong acid fully ionizes in solution.
13.	C	Generally – Metals form basic oxides; Non-metals form acidic oxides $SO_2 + H_2O \longrightarrow H_2SO_3$ (sulphurous acid) Acidic oxide
14.	A	Blue vitriol is deep blue solid copper (II) sulphate pentahydrate is heated to drive off water vapours to form white solid copper (II) sulphate.
15.	B	Aluminum oxide (Al_2O_3) is amphoteric and it reacts with both acidic and basic solution. $Al_2O_{3(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_2O_{(l)}$ (basic) $Al_2O_{3(s)} + 2NaOH_{(aq)} \longrightarrow 2NaAlO_{2(aq)} + H_2O_{(l)}$ (acidic)

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Why do the equilibrium constant value has its units for some of the reversible reactions but has no units for some other reactions?

Ans. i. If number of moles of reactants and products are equal, then K_c has no units.

$$\underset{1\text{ mol}}{H_{2(g)}} + \underset{1\text{ mol}}{I_{2(g)}} \rightleftharpoons \underset{2\text{ mol}}{2HI}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})} = \text{no units}$$

ii. If the number of moles of reactants and products are not equal.

$$\underset{4\text{ mol}}{N_{2(g)} + 3H_{2(g)}} \rightleftharpoons \underset{2\text{ mol}}{2NH_{3(g)}}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}][\text{mol dm}^{-3}]^3} = \text{mol}^{-2}\,\text{dm}^{+6}$$

Q.2 Define pH and pOH with mathematical expressions. What is the sum of pH and pOH?

Ans. **pH:** "The negative log of hydrogen ion concentration is called pH."

$$pH = -\log[H^+]$$

pOH: "The negative log of concentration of hydroxide ion is called pOH."

$$pOH = -\log[OH^-]$$

Relationship between pH and pOH:

$pH + pOH = 14$ at 25°C

The sum of pH and pOH for a solution must be equal to 14 at 25°C.

Q.3 Write the relationship of pH and pOH with pK_w.

Ans. **Relation of pH and pOH with pK_w:**

From the concept of ionic product of water we have

$$K_w = [H^+][OH^-]$$

Taking log: $\log K_w = \log[H^+] \log[OH^-]$

Now multiply with (–1)

$$-\log K_w = -\log[H^+] + (-\log[OH^-])$$

$$pK_w = pH + pOH$$

$pH + pOH = 14$ at 25°C (Since, $pK_w = 14$ at 25°C)

Thus, the sum of pH and pOH is equal to pK_w i.e., 14 at 25°C.

Q.4 What is ionization constant of acids.

Ans. Ionization Constant of Acids:

The ionization constants of the acids is the quantitative measure of the strength of the acid. Acids and bases when dissolved in water may or may not be completely dissociated. Many acids are weak electrolytes and they ionize to an extent which is less than 100%.

Q.5 Define Lowry Bronsted concept of acids and bases.

Ans. Bronsted Acid:

"Those species (ions or molecules) which donate or have a tendency to donate proton (H^+) are called acids."

Example: $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

(Acid: HCl; Base: H_2O; H^+ transferred)

Bronsted Base:

"These species (ions or molecules) which accept or have a tendency to accept proton (H^+) are called bases."

Q.6 What are conjugate acids and bases?

Ans. Conjugate Acid:

A conjugate acid is the specie (molecule or ion) formed when a proton is added to a base. **e.g.,**

When a weak acid or a weak base is dissolved in water, the conjugate acid base pair is produced.

e.g., $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

(acid: CH_3COOH; base: H_2O; conjugate base: CH_3COO^-; conjugate acid: H_3O^+)

Conjugate base: The species (ions or molecules) formed when acid loses its H^+ ions and resulting species become its conjugate base.

Example:

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

(Base: NH_3; Acid: H_2O; H^+ transferred)

Conjugate acid-base Pair

When a weak acid or a weak base is dissolved in water, the conjugate acid base pair is produced.

Example:

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

(acid: CH_3COOH; base: H_2O; conjugate base: CH_3COO^-; conjugate acid: H_3O^+)

Q.7 What is the formula to calculate the percentage ionization of weak acid? (LHR 2018 GII)

Ans. Percentage of Ionization of Weak Acids:

We can calculate the percentage of ionization of weak acid and the formula is as follows:

$$\% \text{ ionization} = \frac{\text{Amount of acid ionized}}{\text{Amount of acid initially available}} \times 100$$

Q.8 Define pK_a and pK_b. Give its significance.

Ans. pK_a:

"The negative log of dissociation constant of acid (K_a) is called pK_a".

$$pK_a = -\log K_a$$

$$pK_a \propto \frac{1}{k_a}$$

pK_b:

"The negative log of K_b is called pK_b".

$$pK_b = -\log K_b$$

Significance:

- pK_a and pK_b gives us the quantitative strength of acids and bases respectively.
- Larger the value of pK_a, weaker will be the acid and vice versa.
- Larger the value of pK_b, weaker will be the base and vice versa.

Q.9 Prove that $pK_a + pK_b = 14$ at 25°C.

Ans. Let us take the log of equation:

$$\log(K_a \times K_b) = \log(K_w)$$

$$\log K_a + (\log K_b) = \log K_w$$

Multiply both sides by '–1'

$$-\log K_a - \log K_b = -\log K_w$$

Since, $pK_a = -\log K_a$ and $pK_b = -\log K_b$

So, $pK_a + pK_b = pK_w = 14$

Hence pK_a and pK_b of conjugate acid base pair has a very simple relation with each other.

$$pK_a + pK_b = 14 \text{ at } 25°C$$

Q.10 What is ionic product of water? Write its value at 25°C.

Ans. Ionic Product of Water:

The product of molar concentration of H^+ and OH^- in pure water is called ionic product of water. It is represented by K_w and its value is 10^{-14} at 25°C.

$$K_w = [H^+][OH^-]$$

$$K_w = 10^{-14} \text{ at } 25°C$$

Q.11 What is buffer solution? Give types of buffer solution with one example each.

Ans. Buffer Solutions:

"These solutions which resist the change in their pH when a small amount of an acid or a base is added to them are called Buffer solution."

The buffer solutions have a specific constant value of pH.

The pH values of buffer solutions do not change on dilution and on keeping for a long time.

Types of Buffer Solutions: Buffer solutions are mostly prepared by mixing two substances.

Acidic Buffers	Basic Buffers
• These buffers which are formed by the mixing of a weak acid and a salt of it with a strong base are called acidic buffers.	• These buffers which are formed by mixing of a weak base and a salt of it with a strong acid are called basic buffers.
• Their pH is usually less than 7.	• Their pH is more than 7.
• Henderson's equation for acidic buffers $pH = pK_a + \log \frac{[salt]}{[acid]}$	• Henderson's equation for basic buffers $pOH = pK_b + \log \frac{[salt]}{[base]}$
e.g., CH_3COOH (weak acid) + CH_3COONa (salt of weak acid)	**e.g.,** NH_4OH (weak base) + NH_4Cl (salt of weak base)

Q.12 Define buffer capacity. Write down the Henderson's equation for acidic buffers.

Ans. Buffer Capacity:

"The capability of a buffer solution to resist the change in its pH when a small amount of acid or a base is added in it is called buffer capacity."

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

Q.13 Define common ion effect. How can NaCl be purified by common ion effect?

Ans. Common Ion Effect:

"The suppression of ionization of a weak electrolyte by adding a common ion from outside is called common ion effect."

Example: Purification of NaCl:

NaCl is purified by passing hydrogen chloride gas through the saturated brine. Sodium chloride is fully ionized in the solution. Equilibrium constant expression for this process can be written as follows:

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$K_c = \frac{[Ha^+][Cl^-]}{[NaCl]}$$

HCl also ionizes in solution.

$$HCl \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

On passing HCl gas, concentration of Cl^- ions is increased. Therefore, NaCl crystallizes out of the solution to maintain the constant value of equilibrium constant. This type of effect is called common ion effect.

$$Na^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons NaCl_{(s)}$$

The addition of a common ion to the solution of less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitate.

Q.14 Give applications of common ion effect (any two).

Ans. Applications of Common Ion Effect:

- **Precipitation of 2nd Group Basic Radicals of Salt Analysis:**
  Similarly the dissociation of a weak acid H_2S in water can be suppressed by the addition of stronger acid HCl. H^+ is a common ion. H_2S becomes less dissociated in acidic solution. In this way, low concentration of S^{-2} is developed.

$$H_2S \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$$

  This low concentration of S^{2-} ions helps to do the precipitation of radicals of second group basic radicals during salt analysis.

$$HCl_{(aq)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

- **Precipitation of 3rd Group Basic Radicals of Salt Analysis:**
  An addition of NH_4Cl in NH_4OH solution suppresses the concentration of $OH^-_{(aq)}$ due to the presence of a large excess of NH_4^+ from NH_4Cl. Actually, NH_4Cl is a strong electrolyte. The combination of these two substances is used as reagent in third group basic radicals.

$$NH_4Cl_{(aq)} \rightleftharpoons Na^+_{4(aq)} + Cl^-_{(aq)}$$

$$NH_4OH_{(aq)} \rightleftharpoons Na^+_{4(aq)} + OH^-_{(aq)}$$

Q.15 Write the effect of common ion on solubility. Prove by equations that what happens when Na_2CrO_4 is added to saturated solution of $PbCrO_4$?

Ans. Effect of Common Ion on Solubility:

The presence of a common ion decreases the solubility of a slightly soluble ionic compound. In order to explain it, consider a saturated solution of $PbCrO_4$, which is a sparingly soluble ionic salt.

$$PbCrO_{4(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO^{2-}_{4(aq)}$$

$$Na_2CrO_{4(aq)} \rightleftharpoons 2Na^+_{(aq)} + CrO^{2-}_4$$

Now add Na_2CrO_4, which is a soluble salt. CrO^{2-}_4 is the common ion. It combines with Pb^{2+} to form more insoluble $PbCrO_4$. So equilibrium is shifted to the left to keep K_{sp} constant.

Q.16 Define Solubility Product Constant (K_{sp}). Give two examples.

Ans. Solubility Product:

"The product of the equilibrium concentration of ions raised to an exponent equal to the coefficient of the balanced equation at given temperature is called solubility product (K_{sp})."

Mathematical Form:

$$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$$

$$K_c = \frac{[A^{+y}]^x[B^{-x}]^y}{[A_xB_y]}$$

$$K_c[A_xB_y] = [A^{+y}]^x[B^{-x}]^y$$

$$K_{sp} = [A^{+y}]^x[B^{-x}]^y$$

- K_{sp} is the product of molar solubilities of two ions at equilibrium.

Examples:

1. When Lead Chloride ($PbCl_2$) is shaken with water the solution contains Pb^{+2}, Cl^- and un-dissociated $PbCl_2$. It means an equilibrium exists between $PbCl_2$ (solid solute) and the dissolved ions, Pb^{+2} and Cl^-.

$$PbCl_{2(s)} \rightleftharpoons PbCl_{2(aq)} \rightleftharpoons Pb^{+2}_{(aq)} + 2Cl^-_{(aq)}$$

According to law of mass action:

$$K_c = \frac{[Pb^{+2}][Cl^-]^2}{[PbCl_2]}$$

$$K_c[PbCl_2] = [Pb^{+2}][Cl^-]^2$$

$$K_{sp} = [Pb^{+2}][Cl^-]^2 = 1.6 \times 10^{-5} \text{ at } 25°C$$

2. **Solubility Product Expression for Ag_2CrO_4:**

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO^{-2}_4$$

$$K_c = \frac{[Ag^+]\,[CrO^{-2}_4]}{[Ag_2CrO_4]}$$

$$K_{sp} = K_c[Ag^+]^2\,[CrO_4]^{-2}$$

◆◆◆◆◆

SELF-ASSESSMENT Chapter # 09

Total Mark: 30

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) Given the following reaction:

$$NH_{3(g)} + H_2O_{(l)} \longrightarrow NH_{4(aq)}^{+} + OH_{(aq)}^{-}$$

A. NH_3 is the acid, H_2O is the base
B. NH_3 is the base, H_2O is the acid
C. NH_4^+ is the base, OH^- is the acid
D. H_2O is the base, OH^- is the acid

(ii) In the given reaction, the conjugate base is:

$$NH_3 + HCl \longrightarrow NH_4^+ + Cl^-$$

A. NH_3 B. Cl^- C. NH_4^+ D. HCl

(iii) Which statement correctly describes a Lewis acid?
A. Accepts a lone pair of electrons
B. Donates a lone pair of electrons
C. Always donates protons
D. Has a negative charge

(iv) If the pH of a solution is 11, what is the $[OH^-]$ concentration in the solution?
A. 1×10^{-3} M B. 1×10^{-11} M C. 1×10^{-2} M D. 1×10^{-14} M

(v) The solubility product of $AgCl$ is 2.0×10^{-10} mol dm^{-6}. The maximum concentration of Ag^+ ions in the solution is:
A. 2.0×10^{-10} mol dm^{-3} B. 1.41×10^{-5} mol dm^{-3} C. 1×10^{-10} mol dm^{-3} D. 4.0×10^{-20} mol dm^{-3}

(vi) Which indicator is typically used for titrations involving strong acids and strong bases?
A. Methyl red B. Phenolphthalein C. Bromothymol blue D. Litmus solution

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) Identify the Lewis acid and Lewis base in the reaction between:
(a) SO_3 and O^{2-} (b) HCl and H_2O
Also write down the balanced chemical equation for the reaction and explain

(ii) Calculate the pH of a 0.01 M NaOH solution.

(iii) Determine $[H_3O^+]$ in a 0.01 M HA solution given $K_a = 1.0 \times 10^{-6}$.

(iv) Define common ion effect. Give a suitable example.

(v) Differentiate end point and equivalent point.

(vi) A solution is prepared by mixing equal volumes of two solutions: one with a pH of 4.0 and another with a pH of 10.0. Calculate the K_W for this mixture at 25°C.

(vii) How does a buffer maintain pH stability?

(viii) Why is aqueous solution of NH_4Cl slightly acidic?

Q.3 Extensive Questions. (2 × 4 = 8)

(a) Describe the Bronsted-Lowry theory of acids and bases. Provide examples of conjugate acid-base pairs and explain clearly their relationship.

(b) The molar solubility of silver chromate (Ag_2CrO_4) in pure water at 298 K is 6.5×10^{-5} mol dm^{-3}. Calculate the K_{sp} of silver chromate at this temperature.

Chapter 10 ELECTROCHEMISTRY

Student Learning Outcomes

After studying this chapter, students will be able to:

- Define the terms redox, oxidation, reduction, and disproportionation (in terms of electron transfer and changes in oxidation number). **(Knowledge)**
- Apply the concept of oxidation numbers in identifying oxidation and reduction reactions. **(Application)**
- Identify the oxidizing and reducing agents in a redox reaction. **(Knowledge)**
- Describe the role of oxidizing and reducing agents in the redox reaction. **(Understanding)**
- Apply the concept of changes in oxidation numbers to balance chemical equations. **(Application)**
- Explain how electrolytic cells convert electrical energy to chemical energy, with oxidation at the anode and reduction at the cathode. **(Understanding)**
- Predict the identities of substances liberated during electrolysis based on the state of the electrolyte, position in the redox series, and concentration. **(Knowledge)**
- Apply the relationship between the Faraday constant, Avogadro constant, and the charge on the electron to solve problems. **(Application)**
- Calculate the quantity of charge passed during electrolysis and the mass or volume of substance liberated during electrolysis. **(Application)**
- Deduce the Avogadro constant by an electrolytic method. **(Application)**
- Define the terms standard electrode potential and standard cell potential. **(Knowledge)**
- Describe the standard hydrogen electrode (SHE) and methods used to measure standard electrode potentials. **(Understanding)**
- Calculate the standard cell potentials by combining the potentials of two standard electrodes and then use these to predict the feasibility of a reaction and the direction of electron flow in a simple cell. **(Application)**
- Deduce the relative reactivity of elements compounds, and ions as oxidizing agents or reducing agents from their electrode potential values. **(Application)**
- Construct redox equations using relevant half-equations. **(Application)**
- Explain how voltaic (galvanic) cells convert energy from spontaneous, exothermic chemical processes to electrical energy, with oxidation at the anode and reduction at the cathode. **(Understanding)**
- Explain how voltaic cells convert chemical energy from redox reactions to electrical energy using Cu – Zn galvanic cell as an example. **(Understanding)**
- Explain how electrode potentials vary with the concentrations of aqueous ions and use the Nernst equation to predict this quantitatively. **(Understanding)**
- Explain the concept of the activity series of metals and how it relates to the ease of oxidation. **(Understanding)**
- Deduce the feasibility of redox reactions from activity series or reaction data. **(Understanding)**
- Explain the merits of photovoltaic cells as sustainable ways of meeting energy demands by making reference to the photovoltaic principle. **(Understanding)**
- Explain the use of the Winkler Method to measure biochemical oxygen demand (BOD) and its use as a measure of water pollution. **(Understanding)**

The branch of chemistry which deals with inter conversion of electrical and chemical energy i.e., electrical energy into chemical energy and chemical energy into electrical energy is called **electrochemistry**.

OXIDATION, REDUCTION, AND REDOX REACTIONS

Oxidation is a process involving loss of electron or electrons.

$$Fe^{+2} \longrightarrow Fe^{+3} + e^-$$
$$Zn^0 \longrightarrow Zn^{+2} + e^-$$

Here Fe^{+2} and Zn^0 have lost electrons, therefore they are oxidized.

Reduction is a process involving gain of electron or electrons.

$$C\ell^0 + e^- \longrightarrow C\ell^{-1}$$
$$Cu^{+2} + 2e^- \longrightarrow Cu^0$$

In these examples, $C\ell^0$ and Cu^{+2} have gained electrons; therefore, they are reduced.

Interesting Information!

Photosynthesis is a redox reaction which provides food for the entire planet, and another one is respiration that keeps you alive, both are redox reactions.

Rock Your Mind!

1. Calculate the oxidation number of Cr in K_2CrO_4.

Differences between Oxidation and Reduction:

Sr. No.	Oxidation	Reduction
1.	The addition of oxygen in a specie is called oxidation. e.g., $S + O_2 \longrightarrow SO_2$; $C + O_2 \longrightarrow CO_2$; $2CO + O_2 \longrightarrow 2CO_2$. In these examples, oxygen is added to S, C and CO.	The removal of oxygen or an electronegativity element from a specie is called reduction. e.g., $ZnO + C \longrightarrow Zn + CO$; $CuO + C \longrightarrow Cu + CO$; $2FeC\ell_3 + H_2 \longrightarrow 2FeC\ell_2 + 2HC\ell$
2.	The removal of hydrogen is also called oxidation. e.g., $H_2S + C\ell_2 \longrightarrow 2HC\ell + S$; $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$. So, H_2S and CH_4 are oxidized.	The addition of hydrogen to a specie is called reduction. e.g., $H_2S + Br_2 \longrightarrow 2HBr + S$. Here bromine gets reduced as it gains hydrogen to form HBr. $H_2C = CH_2 + H_2 \longrightarrow H_3C - CH_3$
3.	Loss of electron/s and hence decrease in oxidation number is called oxidation. e.g., $Zn \longrightarrow Zn^{2+} + 2e^-$. Here Zn is oxidized to form Zn^{2+} ions.	Gain of electrons and hence decrease in oxidation number is called reduction. e.g., $Zn^{2+} + 2e^- \longrightarrow Zn$. Here Zn^{2+} is reduced to form Zn.
4.	In electrochemical cells, oxidation takes place at anode.	In electrochemical cells, reduction takes place at cathode.

Redox Reactions

"Those reactions in which one species (atom, ion or molecule) is oxidized while other is reduced are called redox reactions".

There are two ways of finding out whether or not a substance has been oxidized or reduced during a chemical reaction:

- Electron transfer
- Changes in oxidation number

Oxidation Number rules can be applied to any compound, whether ionic or covalent species.

OXIDATION NUMBER AND ITS SIGNIFICANCE

Definition

"An oxidation number is a number given to each atom or ion in a compound that shows us its degree of oxidation."

Or

"It is the apparent charge on an atom (per atom) of an element in a molecule or an ion."

- The oxidation numbers are also called oxidation states.
- Oxidation numbers can be positive, negative or zero. The + or – sign must always be included.
- Higher positive oxidation numbers mean that an atom or ion is more oxidized.
- Higher negative oxidation numbers mean that an atom or ion is more reduced.

Oxidation Number Rules

The oxidation number of any atom or ion can be deduced by using oxidation number rules. It is important to note that an oxidation number refers to a single atom in a compound.

i. The oxidation number of any uncombined element is zero. For example, the oxidation number of each atom in $S_8, H_2, C\ell_2$, Na, Mg and Zn is zero.

ii. In either a compound or an ion, the more electronegative element is given the negative oxidation number. In HF, fluorine has –1 oxidation number.

iii. In compounds, many atoms or ions have fixed oxidation numbers, group 1 alkali metals are always +1, group 2 alkaline earth elements are always +2, group 17 halogens in binary compounds are always –1, hydrogen is +1 (except in metal hydrides, such as NaH, where it is –1), oxygen is –2 (except in peroxides, where it is –1, and in F_2O, where it is +2).

iv. The oxidation number of an element in a mono-atomic ion is always the same as the charge on the ion, for example, $C\ell^-$ is –1, Al^{3+} is +3.

v. The sum of the oxidation numbers in a compound is zero. In neutral molecules, the algebraic sum of the oxidation numbers of all the elements is zero. e.g., In $HC\ell$ (+1 – 1 = 0), $NaC\ell$ (+1 – 1 = 0).

vi. In polyatomic ions, the algebraic sum of oxidation number equals the charge on the ion. e.g., NH_4^+, CO_3^{-2} and SO_4^{-2}.

vii. For transition metals and many non-metals, Ox. No. cannot be fixed as they show variable Ox states. Therefore, there Ox. Nos. are always determined by calculations.

While applying the oxidation number rules in the following examples, 'Ox. No.' as an abbreviation for oxidation number is used.

Rock Your Mind!

2. In all oxidation reactions, atoms of an element in a chemical species lose electrons and increase their:
(a) Oxidation state
(b) Electrode
(c) Reductions
(d) Negative charges

KEEP IN MIND

- Hydrogen shows –1 oxidation state with all metals.
- Hydrogen shows +1 oxidation state with all non-metals.
- Oxygen shows negative oxidation state with all metals.
- Oxygen shows negative oxidation state with all non-metals except fluorine.
- Oxygen shows –2, –1 and –1/2 in H_2O, Na_2O_2, and KO_2 respectively.

Finding Oxidation Number of an Element in a Compound or a Radical

The oxidation number or state of any atom of an element present in a compound or a radical can be determined by making use of the above-mentioned rules.

Compounds of a Metal with a Non-metal

A metal always has the positive Ox. No. and nonmetals have the negative Ox. State. For example, in sodium sulfide, Na_2S:

$$2(+1) + S = 0$$
$$+2 + S = 0$$
$$S = -2$$

➢ **Compounds of a Non-metal with a Non-metal**

In compounds containing two different non-metals, the sign of the Ox. No. depends on the electronegativity of each atom. The most electronegative element is given the negative sign.

Sample Problem 10.1

Find the oxidation No. of S in Sulfur dioxide, SO_2.

Ox. No. of each O atom = −2

For two oxygen atoms = 2 × (−2) = −4

SO_2 has no charge, so the total Ox. No. is zero. So,

$$S + 2(-2) = 0$$
$$S - 4 = 0$$
$$S = +4$$

Ox. No. of S = +4

➲ Compound Ions

Compound ions are ions with two or more different atoms. **Examples** are the sulfate ion, SO_4^{2-}, and the nitrate ion, NO_3^-.

Sample Problem 10.2

Calculate the oxidation number (Ox. No.) of Sulphur in SO_4^{2-}.

Solution:

$$[\text{Ox. No. of S}] + 4[\text{Ox. No. of 0}] = -2$$
$$S + 4(-2) = -2$$
$$S = +6$$

Thus, the oxidation number of sulphur in SO_4^{2-} is +6.

Rock Your Mind!

3. In SO_4^{2-} the oxidation number of Sulphur is:
(a) −8 (b) +8
(c) −6 (d) +6

☑ QUICK CHECK 10.1

a) Define oxidation and reduction in terms of electron transfer with examples.

Ans. Oxidation: The loss of electrons by a substance.

Example:

$$Na \longrightarrow Na^+ + e^-$$

Sodium loses one electron — **oxidation.**

Reduction: The gain of electrons by a substance.

Example:

$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$

Chlorine gains electrons — **reduction.**

b) Define oxidation and reduction in terms of change in oxidation number with examples.

Ans. Oxidation: Increase in oxidation number.

Example:

$$Fe_2^{+} \longrightarrow Fe_3^{+} + e^-$$

Oxidation number increases from +2 to +3 — **oxidation.**

Reduction: Decrease in oxidation number.

Example:

$$Cl_2 \longrightarrow 2Cl^-$$

Oxidation number decreases from 0 to −1 — **reduction.**

c) Determine Ox. No. of:

I) Oxygen (N) in Na_2O

Ans. Oxygen (O) in Na_2O

Let oxidation number of oxygen = x

Na = +1

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

ii) Iodine (I) in ICl_3

Ans. Iodine (I) in ICl_3

Let Iodine = x, Chlorine = −1

$x+3(-1) = 0 \quad \Rightarrow x-3 = 0 \quad \Rightarrow x = +3x + 3(-1) = 0 \quad \Rightarrow x-3 = 0 \quad \Rightarrow x = +3$

iii) Nitrogen (N) in NO_3^{1-}

Ans. Nitrogen (N) in NO_3^-

Let N = x, O = −2

$x+3(-2) = -1 \quad \Rightarrow x-6 = -1 \quad \Rightarrow x = +5x + 3(-2) = -1 \quad \Rightarrow x-6 = -1 \quad \Rightarrow x = +5$

iv) Chromium (Cr) in $K_2Cr_2O_7$

Ans. Chromium (Cr) in $K_2Cr_2O_7$

K = +1, O = −2, Cr = x

$2(+1)+2(x)+7(-2) = 0 \quad \Rightarrow 2+2x-14 = 0 \quad \Rightarrow 2x = 12 \quad \Rightarrow x = +62(+1) + 2(x) + 7(-2) = 0$

$\Rightarrow 2 + 2x - 14 = 0 \quad \Rightarrow 2x = 12 \quad \Rightarrow x = +6$

v) Manganese (Mn) in $KMnO_4$.

Solution:

$$[\text{Ox. No. of K}] + [\text{Ox. No. of Mn}] + 4[\text{Ox. No. of 0}] = 0$$
$$+1 + Mn + 4(-2) = 0$$
$$(+1) + Mn - 8 = 0$$
$$\text{or} \quad Mn = +7$$

Thus, the oxidation number (Ox. No.) of Mn in $KMnO_4$ is +7.

DISPROPORTIONATION REACTION

➲ Disproportionation Reaction

A chemical reaction where a single substance (a species i.e. molecule, atom or ion) acts as both the oxidizing and reducing agent, resulting in two different products with different oxidation states.

This type of reaction involves the simultaneous oxidation and reduction of the same element.

➢ **Example 1:**

The decomposition of hydrogen peroxide (H_2O_2) to form water (H_2O) and oxygen (O_2) is a disproportionation reaction:

$$2H_2O_2 \longrightarrow H_2O^{-1} + O_2^0$$

Rock Your Mind!

4. What are redox reactions? Give an example.

Oxidation number of oxygen in H_2O_2 = −1

Oxidation number of oxygen in H_2O = −2 (Oxygen is reduced from −1 to −2)

Oxidation number of oxygen in O_2 = 0 (Oxygen is oxidized from −1 to 0)

➢ **Example 2:**

$$6NaOH_{(aq)} + 3Cl^0_{2(g)} \rightarrow 5NaCl^{-1}_{(aq)} + NaCl^{+5}O_{3(aq)} + 3H_2O$$

Oxidation number of chlorine atoms in Cl_2 = 0

Oxidation number of chlorine in NaCl = −1 (Cl is reduced from 0 to −1)

Oxidation number of chlorine in $NaClO_3$ = +5 Cl is (oxidized from 0 to +5)

Important: Disproportionation reactions can occur where ions or molecules can exist in multiple oxidation states in a reaction.

OXIDIZING AGENT (OXIDANT) AND REDUCING AGENT (REDUCTANT)

Oxidizing Agent	Reducing Agent
An oxidizing agent (atom, ion or molecule) is that substance which oxidizes some other substance, and is itself reduced to a lower oxidation state by gaining one or more electrons.	A reducing agent (atom, ion or molecule) is that substance which reduces some other substance, and is itself oxidized to a higher oxidation state by losing one or more electrons.
If an element M gains one or more electrons and is converted into M^- anion, the element M is said to be acting as an oxidizing agent, since it withdraws an electron from the other atom, in this process oxidation number of M has decreased that is: **For oxidizing agent** $X + e^- \longrightarrow X^-$ [Ox. No. = 0] [Ox. No. = −1] (Higher Oxidation State) (Lower Oxidation State) **For example,** $Cl + e^- \longrightarrow Cl^-$	If an element M loses one electron and is converted to M^+ cation, the element M is said to be acting as a reducing agent, since it is providing electrons, it gets higher oxidation state. Thus, **For reducing agent** $M \longrightarrow M^+ + e^-$ [Ox. No. = 0] [Ox. No. = −1] (Lower Oxidation State) (Higher Oxidation State) **For example,** $Na \longrightarrow Na^+ + e^-$

QUICK CHECK 10.2

a) **Identify the oxidized species and reduced species in the following equation. Also identify the oxidizing and reducing agents on the reactant side.**

i. $Fe_2O_{3(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$

Ans.

1. **Assign Oxidation Numbers (O.N.):**
   - Fe_2O_3: O is −2. So, 2(O.N. of Fe) + 3(−2) = 0 ⇒ 2(O.N. of Fe) = +6 ⇒ O.N. of Fe = +3.
   - CO: O is −2. So, O.N. of C + (−2) = 0 ⇒ O.N. of C = +2.
   - Fe: O.N. of Fe = **0** (elemental form).
   - CO_2: O is −2. So, O.N. of C + 2(−2) = 0 ⇒ O.N. of C = +4.
2. **Identify Changes in O.N.:**
   - Fe: O.N. changes from +3 in Fe_2O_3 to 0 in Fe. (Decrease in O.N.)
   - C: O.N. changes from +2 in CO to +4 in CO_2. (Increase in O.N.)
   - O: O.N. remains −2 throughout.
3. **Identify Oxidized and Reduced Species:**
   - **Reduced Species:** Fe in Fe_2O_3 is reduced (its O.N. decreases from +3 to 0). So, Fe_2O_3 is the species containing the element that is reduced.
   - **Oxidized Species:** C in CO is oxidized (its O.N. increases from +2 to +4). So, CO is the species containing the element that is oxidized.
4. **Identify Oxidizing and Reducing Agents (on reactant side):**
   - **Oxidizing Agent:** The species that causes oxidation and gets reduced itself. Fe_2O_3 gets reduced. So, Fe_2O_3 is the oxidizing agent.
   - **Reducing Agent:** The species that causes reduction and gets oxidized itself. CO gets oxidized. So, CO is the reducing agent.

ii. $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

Ans.

1. **Assign Oxidation Numbers (O.N.):**
   - CH_4: H is +1. So, O.N. of C + 4(+1) = 0 ⇒ O.N. of C = −4.
   - O_2: O.N. of O = **0** (elemental form).

   - CO_2: O is −2. So, O.N. of C + 2(−2) = 0 ⇒ O.N. of C = +4.
   - H_2O: H is +1, O is −2. O.N. of O = −2.
2. **Identify Changes in O.N.:**
   - C: O.N. changes from −4 in CH_4 to +4 in CO_2. (Increase in O.N.)
   - O: O.N. changes from 0 in O_2 to −2 in CO_2 and H_2O. (Decrease in O.N.)
   - H: O.N. remains +1 throughout.
3. **Identify Oxidized and Reduced Species:**
   - **Oxidized Species:** C in CH_4 is oxidized (its O.N. increases from −4 to +4). So, CH_4 is the species containing the element that is oxidized.
   - **Reduced Species:** O in O_2 is reduced (its O.N. decreases from 0 to −2). So, O_2 is the species that is reduced.
4. **Identify Oxidizing and Reducing Agents (on reactant side):**
   - **Oxidizing Agent:** The species that causes oxidation and gets reduced itself. O_2 gets reduced. So, O_2 is the oxidizing agent.
   - **Reducing Agent:** The species that causes reduction and gets oxidized itself. CH_4 gets oxidized. So, CH_4 is the reducing agent.

b) **Identify the species in the following reaction which undergoes both oxidation and reduction.**

i. $2NaO_{2(s)} + 2H_2O_{(l)} \rightarrow 4NaOH_{(aq)} + O_{2(g)}$

Ans.

1. **Identify oxidation states:**
   - In NaO_2 (Sodium superoxide)
   - Na is always +1
   - Let the oxidation state of O be x.
   - So: $+1 + 2x = 0 \Rightarrow 2x = -1 \Rightarrow x = -\frac{1}{2}$

   Each oxygen in O_2^-
   - In NaOH:
     O is −2
   - In O_2 (oxygen gas)
     O is 0
2. **What happening to oxygen**
   - In NaO_2:
     Oxygen starts at −1/2

   Products:
   - Some oxygen atoms become −2 in NaOH → reduction
   - Some become 0 in O_2 gas → oxidation

   The species that undergoes both oxidation and reduction is:
   The superoxide ion (O_2^-) in NaO_2
   It disproportionate:
   - Part of it is oxidaized to O_2 (0)
   - Part of it is reduced to OH^- (via NaOH, where O is −2)

ii. $P_{4(s)} + 3OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow PH_{3(g)} + 3H_2PO^-_{2(aq)}$

Ans.

1. **Assign Oxidation Numbers (O.N.) of Phosphorus in each species:**
   - P_4 (White phosphorus): O.N. of P = **0** (elemental form).
   - PH_3 (Phosphine): H is +1. So, O.N. of P + 3(+1) = 0 ⇒ O.N. of P = −3.
   - H_2PO_2 (Hypophosphite ion): H is +1, O is −2. So, 2(+1) + O.N. of P + 2(−2) = −1 (charge of the ion)
     ⇒ +2 + O.N. of P − 4 = −1 ⇒ O.N. of P − 2 = −1 ⇒ O.N. of P = +1.
   - (O and H in OH^- and H_2O do not change their usual oxidation states).

2. Analyze the changes for Phosphorus:
   - In the reactant P_4, P has an O.N. of 0.
   - In the product PH_3, P has an O.N. of −3 (Reduction: 0 → −3, decrease).
   - In the product H_3PO_2, P has an O.N. of +1 (Oxidation: 0 → +1, increase).
3. Conclusion:
   The species that undergoes both oxidation and reduction is Phosphorus in P_4. (Or you can say the species is P_4 itself).

BALANCING OF REDOX EQUATIONS BY OXIDATION NUMBER METHOD

The following steps are carried out for balancing of redox equations by oxidation number method:

i. Write down the skeleton equation of the redox reaction under consideration.
ii. Identify the elements, which undergo a change in their oxidation number during the reaction.
iii. Record the oxidation number above the symbols of the element, which have undergone a change in the oxidation number.
iv. Indicate the change in oxidation number by arrows joining the atoms on both sides of the equation to shows number of electrons gained or lost.
v. Equate the increase or decrease in the oxidation number, i.e., electrons gained or lost by multiplying with a suitable digit.
vi. Balance the rest of the equation by inspection (hit and trial) method.

Did You Know?

Sequence of the balancing the chemical equation using inspection (hit and trial) method.
- Firstly, balance atoms of all elements except nitrogen, oxygen and hydrogen.
- Secondly, balance atoms of nitrogen (if in the equation).
- Thirdly, balance atoms of oxygen (if in the equation).
- Lastly, balance atoms of hydrogen (if in the equation).

KEEP IN MIND

a) If an element in a species undergoes only increase in oxidation number or decrease in oxidation number in a reaction. The specie containing such element is written once on the RHS of the equation.

$$Zn_{(s)} + HC\ell_{(aq)} \longrightarrow ZnC\ell_{2(aq)} + H_{2(g)}$$

b) If an element in a species undergoes both increase in oxidation number or decrease in oxidation number simultaneously in a reaction (as in case of self-redox or disproportionation reaction). The specie containing such element is written twice on the RHS of the equation. First for increase in oxidation number while second is written for decrease in oxidation number.

$$C\ell_2 + NaOH + C\ell_2 \longrightarrow NaC\ell + H_2O + NaOC\ell$$

c) If an element in a species undergoes increase or decrease in oxidation number as well as no change in oxidation number in a reaction. The specie containing such element is also written twice. First, for change in oxidation number while second is for no change in oxidation number.

$$HNO_3 + Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O + NO_2$$
$$HC\ell + K_2Cr_2O_7 + HC\ell \longrightarrow C\ell_2 + KC\ell + CrC\ell_3 + H_2O$$

Sample Problem 10.4

Balance the following equation by oxidation number method.

$$K_2Cr_2O_7 + HC\ell \rightarrow KC\ell + CrC\ell_3 + C\ell_2 + H_2O$$

Solution:

1. Write down the skeleton of chemical equation.
$$K_2Cr_2O_7 + HC\ell \longrightarrow C\ell_2 + KC\ell + CrC\ell_3 + H_2O$$
2. Write down the oxidation number of each element.
$$K_2^{1+}Cr_2^{6+}O_7^{2-} + H^{1+}C\ell^{1-} \longrightarrow C\ell_2^0 + K^{1+}C\ell^{1-} + Cr^{3+}C\ell_3^{1-} + H_2^{1+}O^{2-}$$
3. Identify the elements that show change in oxidation number on both sides.
$$K_2^{1+}Cr_2^{6+}O_7^{2-} + H^{1+}C\ell^{1-} \rightarrow C\ell_2^0 + K^{1+}C\ell^{-} + Cr^{3+}C\ell_3^{-} + H_2^{1+}O^{2-}$$
(6e⁻ : Cr⁶⁺ → Cr³⁺; 2e⁻ : 2Cl⁻ → Cl₂⁰)

Here, Cr undergoes a change in oxidation state from +6 to +3 and it is reduced (acts as an oxidizing agent) while Cl undergoes a change in oxidation state from −1 to 0 and it is oxidized (acts as a reducing agent).

4. Write two half reactions separately i.e., reduction and oxidation reactions
$$K_2Cr_2^{6+}O_7 \longrightarrow 2Cr^{3+}C\ell_3 \text{ Half reduction reaction} _____ \text{(ii)}$$
$$2HC\ell^{1-} \longrightarrow C\ell_2^0 \text{ Half oxidation reaction} _____ \text{(iii)}$$

Decrease in Ox. No. of Cr is 6 units for one molecule of $K_2Cr_2O_7$.
Increase in Ox. No. of Cl is 2 units for 2 molecules of HCl.
Eq. (iii) is multiplied by 3 in order to equalize the loss of electrons and the gain of electrons i.e., 6 electrons in this equation.

$$3 \times 2HC\ell \longrightarrow 3C\ell_2$$
$$6HC\ell \longrightarrow 3C\ell_2 _____ \text{(iv)}$$

Now eq. (i) becomes:

$$K_2Cr_2O_7 + 6HC\ell \longrightarrow 3C\ell_2 + KC\ell + 2CrC\ell_3 + H_2O$$

5. Rest of the following equation is balanced by inspection method:
$$K_2Cr_2O_7 + 6HC\ell \longrightarrow 3C\ell_2 + 2KC\ell + 2CrC\ell_3 + H_2O$$

To balance Cl and K, 14 molecules of HCl and 2 KCl molecules are required, therefore, we add 8 HCl to left hand side

$$8HC\ell + K_2Cr_2O_7 + 6HC\ell \longrightarrow 2CrC\ell_3 + 3C\ell_2 + 2KC\ell + H_2O$$

To balance hydrogen and oxygen, $6H_2O$ are added to RHS.
Hence, the balanced equation is,

$$K_2Cr_2O_7 + 14HC\ell \longrightarrow 2KC\ell + 2CrC\ell_3 + 3C\ell_2 + 7H_2O$$

QUICK CHECK 10.3

Balance the given equations by oxidation number method.

I. $Fe_2O_{3(s)} + CO_{(g)} \longrightarrow Fe_{(s)} + CO_{2(g)}$

Ans. Step 1: Oxidation numbers
- Fe in Fe_2O_3: +3 → Fe: 0 (reduced)
- C in CO: +2 → C in CO_2: +4 (oxidized)

Step 2: Determine changes
- Fe: +3 → 0 (gain of 3 electrons per Fe, 2 Fe atoms = 6 e^- gain)
- C: +2 → +4 (loss of 2 electrons per C atom)

Step 3: Equallze e^- transfer
- Multiply CO by 3 and Fe_2O_3 by 1.

Balanced equation:

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

ii $MnO_2 + HCl \rightarrow MnCl_2 + H_2O + Cl_2$

Ans. **Step 1: Oxidation numbers**

- Mn in MnO_2: +4 → Mn in $MnCl_2$: +2 (reduced)
- Cl in HCl: −1 → Cl_2: 0 (oxidized)

Step 2: Determine changes

- Mn: +4 → +2 (gain of 2 electrons)
- Cl: −1 → 0 (loss of 1 electron per Cl atom; Cl_2 = 2 Cl atoms = $2e^-$ lost)

Step 3: Equalize e^- transfer

- $2Cl^-$ oxidized = $2e^-$ loss
- 1 Mn^{4+} reduced = $2e^-$ gain → already equal

Balanced equation:

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

iii. $Fe^{2+}_{(aq)} + MnO^{-}_{4(aq)} \longrightarrow Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)}$

Ans. **Step 1: Oxidation numbers**

- $Fe^{2+} \rightarrow Fe^{3+}$ (oxidation, loss of 1 e^-)
- Mn^{7+} in $MnO_4^- \rightarrow Mn^{2+}$ (reduction, gain of 5 e^-)

Step 2: Equalize electrons

- Multiply $Fe^{2+} \rightarrow Fe^{3+}$ by 5

Step 3: Balance rest (acidic medium)

- $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Balanced equation:

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

iv. $K_2Cr_2O_{7(aq)} + FeSO_{4(aq)} + H_2SO_{4(aq)} \longrightarrow Cr_2(SO_4)_{3(aq)} + Fe_2(SO_4)_{3(aq)} + K_2SO_{4(aq)} + H_2O_{(l)}$

Ans. **Step 1: Oxidation numbers**

- Cr in $Cr_2O_7^{2-}$: +6 → Cr^{3+}: +3 (reduction, gain of $3e^-$ per Cr)
- $Fe^{2+} \rightarrow Fe^{3+}$: oxidation (loss of $1e^-$)

Step 2: $Cr_2O_7^{2-}$ contains 2 Cr → $6e^-$ gained

- Therefore, 6 Fe^{2+} needed (each loses $1e^-$)

Balanced half reactions:

- $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
- $6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$

Combine:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Include sulphates and potassium:

- $Cr_2O_7^{2-} \rightarrow Cr_2(SO_4)_3$
- $Fe^{2+} \rightarrow Fe_2(SO_4)_3$ (needs 6 $Fe^{2+} \rightarrow 3\ Fe_2(SO_4)_3$)
- K^+ and SO_4^{2-} balance with K_2SO_4

Full Balanced equation:

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

ELECTROLYTIC CELL

An electrolytic cell is a device that converts electrical energy into chemical energy through a process called electrolysis.

➢ **Construction:**

It consists of two electrodes, typically made of metal or another conductive material, which are immersed in an electrolyte-a substance containing free ions that carry electric current.

➢ **Process:**

When a direct electric current is applied, one electrode becomes negatively charged (the cathode) and the other positively charged (the anode).

In an electrolytic cell, positive ions in the electrolyte migrate towards the cathode, where they gain electrons (a reduction process), while negative ions move towards the anode, where they lose electrons (an oxidation process). This movement of ions and transfer of electrons results in chemical changes at the electrodes, effectively converting electrical energy into chemical energy.

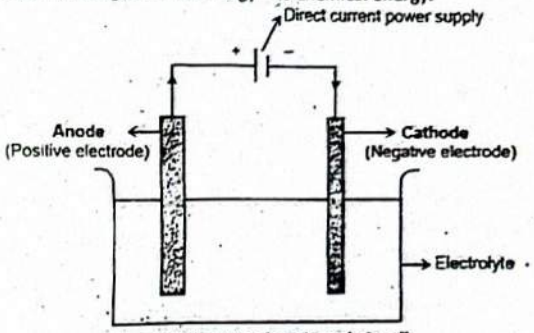


Figure: Main parts of an electrolytic cell

➢ **Applications of Electrolytic Cells:**

Electrolytic cells are used in the electrolysis of sodium chloride to produce sodium metal and chlorine gas, the refining and plating of metals, and the production of chemicals like caustic soda. Electrolysis is also used to produce non-metals such as chlorine and to purify metals. Electrolysis is generally carried out in an electrolysis cell as shown in Figure.

In the electrolysis cell:

- **Electrolyte:** The electrolyte is the compound that is decomposed; it is either a molten ionic compound or a concentrated aqueous solution of ions
- **Electrodes:** The electrodes are, made from either carbon (graphite) or metal, which conduct electricity to and from the electrolyte - the anode is the positive electrode - the cathode is the negative electrode
- **DC:** The power supply must be direct current.

(Note: The actual structure of the cell will vary according to the element extracted).

REDOX REACTIONS IN ELECTROLYSIS

During electrolysis, the positive ions (cations) move to the cathode. When they reach the cathode, they gain electrons from the cathode.

For example:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

Gain of electrons is reduction and it always occurs at the cathode. If metal atoms are formed, they may be deposited as a layer of metal on the cathode. Alternatively, they may form a molten layer in the cell. If hydrogen gas is formed, it bubbles off.

The negative ions **(anions)** move to the anode. When they reach the anode, they lose electrons to the anode. Loss of electrons is oxidation. Oxidation always occurs at the anode.

For example:

$$2C\ell^-_{(aq)} \longrightarrow C\ell_{2(g)} + 2e^-$$

$$4OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(\ell)} + 4e^-$$

Electrolysis is a redox reaction. For example, when molten zinc chloride ($ZnC\ell_2$) is electrolyzed, the electrode reactions are:

- **Cathode:** $Zn^{2+}_{(\ell)} + 2e^- \longrightarrow Zn_{(s)}$ (Reduction)
- **Anode:** $2C\ell^-_{(\ell)} \longrightarrow C\ell_{2(g)} + 2e^-$ (Oxidation)

The electron loss at the anode balances the electron gain at the cathode. The overall reaction is

$$ZnC\ell_{2(\ell)} \longrightarrow Zn_{(s)} + C\ell_{2(g)}$$

QUICK CHECK 10.4

Molten copper (II) bromide ($CuBr_2$) is electrolyzed using inert electrodes.

i. Which ions are present in this solution?

Ans. The ions present are Cu^{2+} and Br^-.

ii. Name the electrode on which the formation of copper metal occurs?

Ans. Copper metal forms on the cathode.

iii. Give the half-equation that represents the formation of copper metal.

Ans. $Cu^{2+} + 2e^- \longrightarrow Cu$

iv. Write the half-equation for the formation of bromine on the other electrode.

Ans. $2Br^- \longrightarrow Br_2 + 2e^-$ (occurs at the anode)

MASS OF A SUBSTANCE DEPOSITED DURING ELECTROLYSIS

The mass of a substance produced at an electrode during electrolysis is proportional to the time over which a constant electric current pass and the strength of the electric current.

Combining current and time, we get the relationship:

$$Q = I \times t$$

Where Q = Charge (in coulombs, C)
I = Current (in amperes, A)
t = Time (in seconds, s)

The mass of a substance produced at (or removed from) an electrode during electrolysis is proportional to the quantity of electricity (in coulombs) which passes through the electrolyte.

➢ **Faraday:**

The quantity of electricity is often expressed in terms of a unit called the **Faraday** (symbol F). 1 Faraday is the quantity of electric charge carried by 1 mole of electrons or 1 mole of singly charged ions. Its value is 96500 C mol^{-1}.

➢ **Electrolysis of Silver Nitrate Solution:**

During the electrolysis of silver nitrate solution, silver is deposited at the cathode.

$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$$

1 mol 1 mol 1 mol

1 Faraday of electricity (96500 C) is required to deposit 1 mole of silver.

➢ **Electrolysis of Copper(II) Sulphate:**

During the electrolysis of copper (II) sulphate solution, copper is deposited at the cathode.

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

1 mol 2 mol 1 mol

The equation shows that 2 moles of electrons are needed to produce 1 mole of copper from Cu^{2+} ions. So, it requires 2 Faradays of electricity (2×96500 C) to deposit 1 mole of copper.

No. of Faraday = No. of moles of electrons gained or lost

AMOUNT OF SUBSTANCE PRODUCED DURING ELECTROLYSIS

The value of F can be used to calculate the mass of substance deposited at an electrode and the volume of gas produced at an electrode.

Sample Problems 10.5

Calculate the mass of lead (Pb) deposited at the cathode during electrolysis when a current of 1.50 A flows through molten lead (II) bromide ($PbBr_2$) for 20.0 min. (relative atomic mass, Ar value: [Pb] = 207; F = 96500 C mol^{-1})

Solution:

Step 1: Write the half-equation for the reaction.

$$Pb^{2+}_{(aq)} + 2e^- \longrightarrow Pb_{(s)}$$

Step 2: Find the number of coulombs required to deposit 1 mole of product at the electrode.

2 moles of electrons are required per mole of Pb formed = 2F

$= 2 \times 96500$

$= 193000$ C mol^{-1}

Step 3: Calculate the charge transferred during the electrolysis.

$Q = I \times t$

$= 1.50 \times 20 \times 60$

$= 1800$ C

Step 4: Calculate the mass by simple proportion using the relative atomic mass.

193000 C deposits 1 mole Pb, which is 207 g Pb

so, 1800 C deposits $= \frac{207}{193000} \times 1800 = 1.93$ g Pb

AVOGADRO'S CONSTANT BY THE ELECTROLYTIC METHOD

Exercise L.O 4

Q. How Avogadro's number can be derived using an electrolytic cell?

A **Avogadro's Constant:**

- The Avogadro's constant, L, is the number of specified particles (atoms, molecules, or ions) in 1 mole. An electrolytic method can be used to find a value for the Avogadro's constant by calculating the charge associated with 1 mole of electrons.

$$N_A = \frac{\text{Charge on 1 mole of electrons}}{\text{Charge on 1 electron}}$$

- The charge on the electron can be calculated by experiment. The results show us that the charge on the electron is approximately 1.60×10^{-19} C.

Finding the Charge on 1 Mole of Electrons

- The charge on 1 mole of electrons can be found from a simple electrolytic experiment. The apparatus for this is shown in Figure.

Procedure:

- The procedure is to weigh the pure copper anode and pure copper cathode separately arrange the apparatus during the electrolysis of aqueous copper(II) sulfate as shown in Figure.

- The variable resistor is used to keep the current constant pass about 0.2 amperes.
- Pass a constant electric current for a measured time interval, e.g., 40 min.
- Remove the cathode and anode and wash and dry them with distilled water and then with propanone.
- Reweigh the cathode and anode.

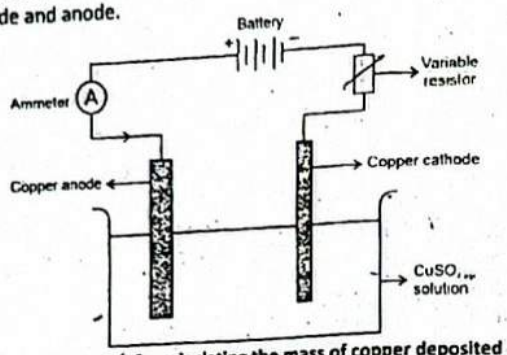


Figure: Apparatus for calculating the mass of copper deposited

- The cathode increases in mass because copper is deposited.
- The anode decreases in mass because the copper goes into solution as copper ions. The decrease in the mass of the anode is measured. This is preferred because the copper does not always stick to the cathode very well.

Calculating Charge on An Electron

A sample calculation is shown below, using a current of 0.20 A for 34 min.

mass of anode at start of the experiment = 56.53 g
mass of anode at end of experiment = 56.40 g
mass of copper removed from anode = 0.13 g
quantity of charge passed Q = I x t
= 0.20 × 34 × 60
= 408 C

As the amount of copper removed is 0.13 g
So, 0.13 g of copper requires = 408 C

1 g of copper requires = $\frac{408}{0.13}$

63.5 g of copper requires = $\frac{408}{0.13} \times 63.5 = 99646$ C

But the equation for the electrolysis shows that 2 moles of electrons are needed to produce 1 mole of copper:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

The charge on 1 mole of electrons = $\frac{190500}{2} = 95{,}250$ C

If the charge on one electron is 1.60×10^{-19} C,

Charge on an electron = $\frac{95250}{6.02 \times 10^{23}} = 1.58 \times 10^{-19}$ C

QUICK CHECK 10.5

a) An aqueous solution of silver nitrate is electrolysed. Calculate the mass of silver deposited at the cathode when the electrolysis is carried out for exactly 35 min using a current of 0.18 A. (Ar[Ag] = 108; F = 96500 Cmol^{-1})

Ans. **Electrolysis of Silver Nitrate ($AgNO_3$)**

According to Faraday's First Law of Electrolysis:

Mass (m) = Q × Mn × F

Where:

Q = I × t Q = I times t = charge in coulombs
M = molar mass of Ag = 108 g/mol
N = number of electrons per ion ($Ag^+ \rightarrow Ag = 1e^-$)
F = Faraday's constant = 96,500 C/mol

Step 1: Calculate Q

I = 0.18 A
t = 35 min = 35 × 60 = 2100 s
Q = I × t = 0.18 × 2100 = 378 C

Step 2: Calculate Mass of Ag

$$m = \frac{Q \times M}{n \times F} = \frac{378 \times 108}{1 \times 96500} \approx \frac{40824}{96500} \approx 0.423 \text{ g}$$

b) An electric current of 1.04 A was passed through a solution of dilute sulfuric acid for 6.00 min. The volume of hydrogen produced at STP was 41.5 cm^3.

i. How many coulombs of charge were passed during the experiment?

Ans. Calculate total charge passed

I = 1.04 A
t = 6.00 min = 6 × 60 = 360 s
Q = I × t = 1.04 × 360 = 374.4 C

ii. How many coulombs of charge are required to liberate 1 mole of hydrogen gas? (F = 96 500 Cmol^{-1})

Ans. Charge required to liberate 1 mole of H_2 gas

Reaction at Cathode:

$$2H^+ + 2e^- \longrightarrow H_2$$

So, 2 moles of electrons are required for 1 mole of H_2.

Charge = 2 × F = 2 × 96500 = 193000 C

ELECTRODE POTENTIALS
(Ease of oxidation and reduction)

During the redox processes, a redox equilibrium exists between two chemically related species that are in different oxidation states.

Definition:

"When a metal is put into a solution of its ions, an electric potential (voltage) is established between the metal and the metal ions in solution. This is called electrode potential".

It indicates the ease of oxidation or reduction of a substance.

Example: When a copper rod is placed in contact with an aqueous solution of its ions, the following equilibrium exists:

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$$

Explanation:

There are two opposing reactions in this equilibrium.

a) Metal atoms from the rod entering the solution as metal ions. This leaves electrons behind on the surface of the electrode.

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$$

b) Ions in solution accepting electrons from the metal rod and get deposited as metal atoms on the surface of the electrode.

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

The redox equilibrium is established when the rate of electron gain equals the rate of electron loss.

For unreactive metals such as copper, if this equilibrium is compared with the equilibrium set up by other metals, the equilibrium set up by copper lies further over to the right.

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

$Cu^{2+}_{(aq)}$ ions are therefore relatively easy to reduce. They gain electrons readily to form copper metal.

For reactive metals such as vanadium, the equilibrium lies further over to the left.

$$V^{2+}_{(aq)} + 2e^- \longrightarrow V_{(s)}$$

$V^{2+}_{(aq)}$ ions are therefore relatively difficult to reduce. They gain electrons much less readily by comparison.

The position of equilibrium differs for different combinations of metals placed in solutions of their ions.

Electrical Double Layer

It is thought that the **absolute electrode potentials** cannot be measured due to the formation of an electrical double layer, when an element is placed in a solution of its ions.

Example:

A strip of Zinc in a solution containing Zn ions:

- When zinc is placed in a solution containing zinc ions, a tiny number of zinc atoms on the surface of the metal is converted to zinc ions, which go into solution. This leaves an excess of electrons on the surface of the zinc.
- The solution around the metal now has excess Zn^{2+} ions. Some of these cations near the surface of the zinc are attracted to its surface. So, an electrical double layer is formed.
- This buildup of charge causes an electric potential (voltage) between the metal and the metal ions in solution as shown in Figure 10.3.
- Due to the formation an electrical double layer, the potential cannot directly be measured.
- The difference in potential between the metal/metal ion system and another system can be measured. We call this value the **electrode potential**, E. Electrode potential is measured in volts. The system we use for comparison is the **standard hydrogen electrode (SHE).**

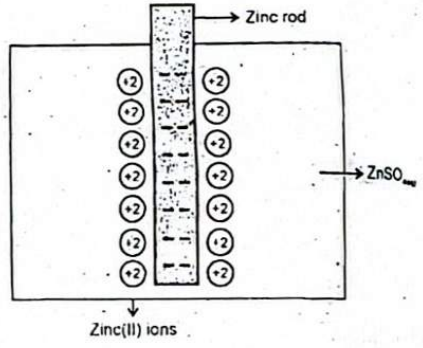


Figure: Formation of electrical double layer

STANDARD HYDROGEN ELECTRODE (SHE)

(Exercise L.Q.6)

Q. What is meant by Standard Hydrogen Electrode (SHE)? How it is used to measure the electrode potential of another electrode?

The **Standard Hydrogen Electrode (SHE)** is one of several types of half-cell that can be used as reference electrode.

➢ **Construction:**

Figure shows a standard hydrogen electrode.

SHE is a reversible electrode.

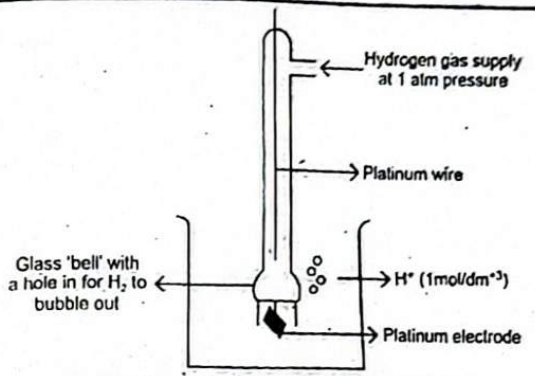


Figure: Standard hydrogen electrode (SHE)

S/Q. Why platinum black is a preferred catalyst?

Ans. Platinum black is a highly preferred catalyst due to its exceptionally high surface area, which significantly enhances its catalytic activity. This high surface area, achieved through a fine powder form, provides numerous active sites for chemical reactions to occur. It boosts reaction rates and overall efficiency.

Standard Hydrogen Electrode consists of:

- Hydrogen gas at 101 kP_a pressure, in equilibrium with H^+ ions of concentration 1.00 mol dm^{-3}
- A platinum electrode covered with platinum black in contact with the hydrogen gas and the H^+ ions.

The **platinum black** is finely divided platinum, which allows close contact of hydrogen gas and H^+ ions in solution so that equilibrium between H_2 gas and H^+ ions is established quickly. The platinum electrode is inert so it does not take part in the reaction. Standard electrode potential E° values for all half-cells are measured relative to this electrode.

When connected to another half-cell, the value read on the voltmeter gives the standard electrode potential for that half-cell. The half-equation for the hydrogen electrode can be written:

Reduction (Acts as cathode): $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ $\quad E^\circ = 0.00$ V

Oxidation (Acts as anode): $H_2 \longrightarrow 2H^+ + 2e$ $\quad E^\circ = 0.00$ V

The way that the half-equation is balanced makes no difference to the value of E°. The equation does not affect the tendency for the element to gain electrons.

Electrode Potential: Its voltage is arbitrarily fixed at 0.00 V.

STANDARD ELECTRODE POTENTIAL (E°)

The voltage of an electrochemical cell will also depend on concentration, temperature, and pressure of the gas. Therefore, we should use standard conditions when comparing electrode potentials.

Conditions:

- Concentration of ions at 1.00 mol dm^{-3}
- A temperature of 25°C(298 K)
- Any gases should be at a pressure of 1 atmosphere (101 kP_a)
- The value of the electrode potential of the half-cell is measured relative to the standard hydrogen electrode.

Under these conditions, the electrode potential we measure is called the standard electrode potential. This has the symbol, E°. It is spoken of as ' E standard'.

"The standard electrode potential for a half-cell is the voltage measured under standard conditions with a standard hydrogen electrode (SHE) as the other half-cell".

MEASURING STANDARD ELECTRODE POTENTIALS

There are three main types of half-cell whose E° value can be obtained when connected to a standard hydrogen electrode (SHE):

- metal/metal ion half-cell (Cu^{2+}/Cu°)
- non-metal/non-metal ion half-cell ($C\ell^{1-}/C\ell_2$)
- ion/ion half-cell. (Fe^{2+}/Fe^{3+})

Measurement of Standard Electrode Potential of a Cu^{2+}/Cu half Cell:

Figure 10.5 shows how to measure the E° value for a Cu^{2+}/Cu half-cell. The Cu^{2+}/Cu half cell is connected to the SHE and the voltage measured. The voltage is +0.34 V. The copper is the positive terminal (positive pole) of the cell and the SHE is the negative terminal. The two half-equations are:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \quad E^\circ = +0.34\ V$$

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)} \quad E^\circ = 0.00\ V$$

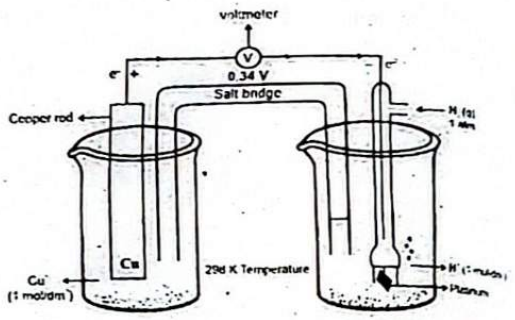


Figure: Measuring the standard electrode potential of a Cu^{2+}/Cu half-cell

The E° values show us that Cu^{2+} ions are easier to reduce than H^+ ions (they have a more positive E° value). Cu^{2+} ions are more likely to gain electrons than H^+ ions. So Cu^{2+} ions will accept electrons from the H^+/H_2 half-cell and H_2 will lose electrons to the Cu^{2+}/Cu half-cell.

Measurement of Standard Electrode Potential of a Zn^{2+}/Zn Half Cell:

Figure 10.6 shows how to measure the E° value for a Zn^{2+}/Zn half cell. The voltage of the Zn^{2+}/Zn half-cell is -0.76 V. Zinc metal is the negative terminal (negative pole) of the cell and the hydrogen electrode is the positive terminal.

The two half-equations are:

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)} \quad E^\circ = 0.00\ V$$

$$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)} \quad E^\circ = -0.76\ V$$

Rack Your Mind!

5. The standard oxidation potential of Zn is 0.76 volts and reduction potential -0.76 volts. Explain.

The E° values show us that Zn^{2+} ions are more difficult to reduce than H^+ ions (they have a more negative E^0 value). Zn^{2+} ions are less likely to gain electrons than H^+ ions. So, Zn will lose electrons to the H^+/H_2 half-cell and H^+ ions will gain electrons from the Zn^{2+}/Zn half-cell.

From these two examples, we can see that:

- Reduction takes place at the positive terminal of the cell. For example, in the Zn^{2+}/Zn; H^+/H_2 cell:

$$2H^+_{(aq)} + 2e^{-1} \longrightarrow H_{2(g)}$$

- Oxidation takes place at the negative terminal of the cell. For example, in the Zn^{2+}/Zn; H^+/H_2 cell:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

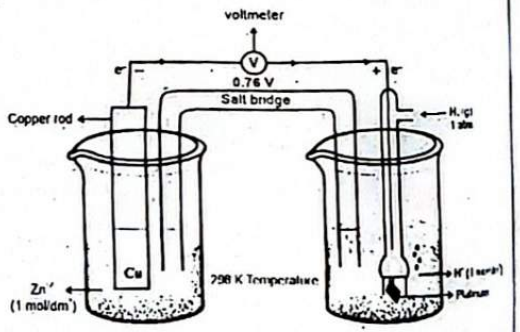


Figure: Measuring the standard electrode potential of a Zn^{2+}/Zn half-cell

ELECTROCHEMICAL CELL (GALVANIC CELL)

Exercise LO 5

Q. Describe the construction and working principle of the Zn-Cu Galvanic cell.

Galvanic Cell:

A cell in which the conversion of chemical energy into electrical energy takes place spontaneously in exothermic redox process with oxidation at anode and reduction at cathode.

For Example:

$$Cu^{2+}/Cu//Z^{2+}/Zn \text{ cell} \qquad E^\circ = 1.10\ V$$

- A galvanic cell is designed to take advantage of spontaneous transfer of electrons.
- A Galvanic Cell, is also known as a Voltaic Cell.

Examples: Daniel cell, dry cell etc.

For example: $Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$ voltage = 0.76 V

In order to measure the electrode potential relating to the half-equation

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

A pure copper rod is placed in a solution of $Cu^{2+}_{(aq)}$ ions (for example copper(II) sulfate solution). This Cu^{2+}/Cu system is called a half-cell.

The following standard conditions are used to make the half-cell:

- The $Cu^{2+}_{(aq)}$ ions have a concentration of 1.00 mol dm^{-3}
- The temperature is 25°C (298 K)
- The copper rod must be pure.

If we connect two half-cells together, we have made an electrochemical cell. We can measure the voltage between these two half-cells. Figure 10.7 shows a Cu^{2+}/Cu half-cell connected to a Zn^{2+}/Zn half-cell to make a complete electrochemical cell.

Half-cells are connected together using:

- Wires connecting the metal rods in each half-cell to a high-resistance voltmeter; the electrons flow round this external circuit from the metal with the more negative (or less positive) electrode potential to the metal with the less negative (or more positive) electrode potential
- **Salt Bridge:** A salt bridge to complete the electrical circuit allowing the movement of ions between the two half cells so that ionic balance is maintained; a salt bridge does not allow the movement of electrons. A salt bridge can be made from a strip of filter paper (or other inert porous material) soaked in a saturated solution of potassium nitrate.
- The voltages for the half cells in Figure can be represented by the following half-equations:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \quad E^\circ = +0.34\ V$$

$$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)} \quad E^\circ = -0.76\ V$$

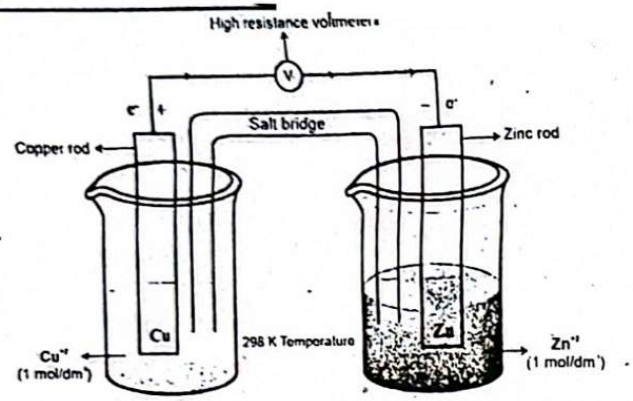


Figure: An electrochemical cell, made by connecting a Cu^{2+} / Cu half-cell to a Zn^{2+} / Zn half-cell.

An electrochemical cell is made by connecting a Cu^{2+} /Cu half-cell to a Zn^{2+} /Zn half-cell. The relative values of these voltages tell us that Zn^{2+} ions are more difficult to reduce than Cu^{2+} ions.

At the anode, zinc undergoes oxidation, losing electrons to form zinc ions:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

These electrons travel through an external circuit to the cathode, where copper ions gain electrons and are reduced to form copper metal:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

The overall cell reaction can be represented as:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

Rack Your Mind!

6. What is emf and how we calculate the emf of a galvanic cell?

This process effectively converts the chemical energy of the redox reaction into electrical energy, which can be connected to perform work.

The voltage generated by this cell is +1.10 V.

$$E^\circ_{cell} = E^\circ_{red} + E^\circ_{oxd} = +0.34 - (-0.76) = +1.10\,V$$

In a Cu-Zn galvanic cell, zinc(Zn) **serves as the anode, and copper ions (Cu^{2+}) in solution serve as the cathode.** The E° value for the Ag^+ / Ag half-cell is more positive than for the $Zn^{(2+)}$ / Zn half-cell. So, the Ag^+/Ag half-cell is the positive pole and the Zn^{2+} /Zn half-cell is the negative pole of the cell.

Functions of Salt Bridge:

i. The purpose of the salt bridge is to prevent any net charge accumulation in either beaker by allowing negative ions to leave the right beaker, diffuse through the bridge and enter the left beaker. If this diffusional exchange of ions does not occur, the net charge accumulating in the beakers would immediately stop the flow of electrons through the external circuit and oxidation reduction reaction would stop.

ii. Keeps the electrolyte solution neutral.

iii. Minimizes or eliminates the liquid junction potential.

☑ QUICK CHECK 10.6

a) What is the function of salt bridge in the voltaic cell?

Ans. A salt bridge is a crucial component in a voltaic cell. Its functions are:

- **Maintains electrical neutrality** in both half-cells by allowing the flow of **inert ions.**
- Prevents the solutions from becoming charged (e.g., accumulation of positive or negative ions).
- **Completes the electrical circuit,** allowing electrons to continue flowing through the external wire.
- Minimizes **liquid junction potential,** ensuring a stable cell voltage.

A typical salt bridge contains a neutral electrolyte (e.g., KNO_3, KCl) that doesn't react with either half-cell.

b) Calculate the voltage of a cell having iron and copper electrodes.

$$Fe_{(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2e^- \quad E^\circ = -0.44\,V$$

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \quad E^\circ = -0.44\,V$$

Given Data:

$Fe^{2+} + 2e^- \rightarrow Fe_{(s)}$ $E^\circ = -0.44$ V

$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ $E^\circ = +0.34$ V

It looks like you might have written $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ also as −0.44 V by mistake, but the standard value is +0.34 V.

Step 1: Identify the anode and cathode

- The electrode with lower E° is the anode (oxidation).
- The electrode with higher E° is the cathode (reduction).

So

- **Anode:** $Fe \rightarrow Fe^{2+} + 2e^-$ $(E^\circ = -0.44\,V)$
- **Cathode:** $Cu^{2+} + 2e^- \rightarrow Cu$ $(E^\circ = +0.34\,V)$

Step 2: Calculate Cell Potential

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$E^\circ_{cell} = (+0.34\,V) - (-0.44\,V) = +0.78\,V$$

Final Answers:

i) A salt bridge maintains charge balance and completes the circuit in a voltaic cell.

ii) The standard cell voltage for Fe–Cu voltaic cell is **0.78 V**

APPLICATIONS OF E° VALUES

➲ Direction of Electron Flow

- We can infer (deduce) the direction of electron flow in the wires in the external circuit by comparing the E° values for the two half-cells which make up the electrochemical cell. For example, in Figure 10.9 these voltages are:

$$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)} \quad E^\circ = +0.80\,V$$

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \quad E^\circ = -0.76\,V$$

- The relative values of these voltages tell us that Zn^{2+} ions are more difficult to reduce than Ag^+ ions.
- So, Zn metal will lose electrons to the Ag^+ / Ag half-cell and Ag^+ ions will accept electrons from the Zn^{2+} / Zn half-cell.
- The electrons move through the wires in the external circuit. They do not travel through the electrolyte solution.
- So, the electron flow is from the Zn^{2+} /Zn half-cell to the Ag^+ / Ag half-cell.
- In other words, the flow is from the negative pole to the positive pole. Remember that the more positive pole attracts the negative electrons.

➲ Feasibility of A Reaction Using E° Values

- Standard electrode potential values, E°, give us a measure of how easy or difficult it is to oxidize or reduce a species. The E° values are listed in order of increasingly negative values.
- For each half-equation, the more oxidized form is on the left and the more reduced form is on the right.
- The more positive the value of E°, the greater the tendency for the half-equation to proceed in the forward direction, and the easier it is to reduce the species on the left of the half-equation.

- The less positive the value of E°, the greater the tendency ... to proceed in the reverse direction, and the easier it is to oxidize the species on the right of the half-equation.
- To check the feasibility of reaction between Mg^{2+} and Ag

$$Mg^{2+} + Ag \longrightarrow ?$$

We need half cell equations and E° values

$$Mg^{2+} + 2e^- \rightleftharpoons Mg \qquad E^\circ = -2.32\ V$$
$$Ag^+ + 1e^- \rightleftharpoons Ag \qquad E^\circ = +0.80\ V$$

Mg^{2+} are supposed to be reduced here and Ag is supposed to get oxidized, So calculating E° cell gives us

$$E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox}$$
$$= (-2.32) - (+0.80)$$
$$= -1.52\ V$$

Negative value of E°_{cell} indicates the reaction is not feasible.

On the other hand reaction between Ag^+ and Mg is feasible as for this reaction E° cell will be positive as given below.

$$E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox}$$
$$= (-0.80) - (-2.32)$$
$$= +1.52\ V$$

Therefore, the feasible reaction is

$$2Ag^+ + Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + Ag_{(s)}$$

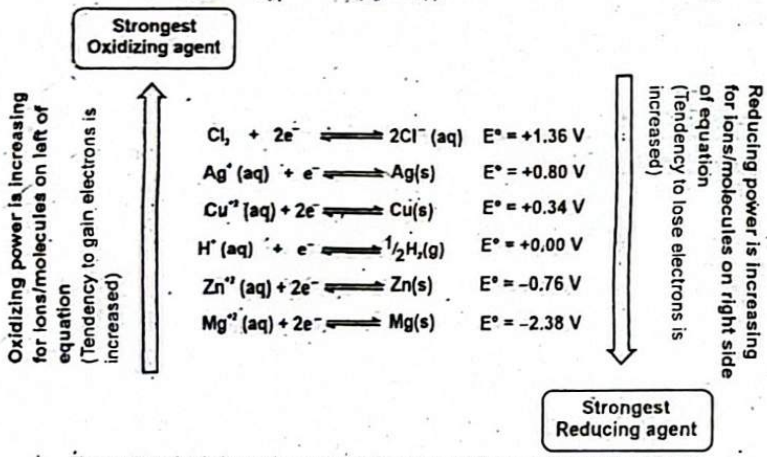


Figure: Standard electrode potentials for some oxidizing and reducing agents

QUICK CHECK 10.7

a) **Explain the following keeping in view the standard electrode potential values**

$$E^\circ_{Cl_2/2Cl^-} = +1.36\ V,\ E^\circ_{Br_2/2Br^-} = +1.07\ V,\ E^\circ_{I_2/2I^-} = +0.54\ V$$

Ans. Explanation using standard electrode potentials:

We are given:

- $E^\circ_{Cl_2/2Cl^-} = +1.36\ V$
- $E^\circ_{Br_2/2Br^-} = +1.07\ V$
- $E^\circ_{I_2/2I^-} = +0.54\ V$

These values indicate how easily the halogens act as oxidizing agents. The higher the E° value, the stronger the oxidizing agent.

i. **The aqueous solution of iodine can be oxidized with bromide or iodide ions.**

Ans. This statement is incorrect as written. It likely means:

"The aqueous solution of iodine can be oxidized by chlorine or bromine ions."

But using the actual meaning with the given standard potentials:

- Iodine (I_2) has a lower E° value than both bromine and chlorine.
- Hence, **iodine is a weaker oxidizing agent** than both chlorine and bromine.
- So, **iodide ions** (I^-) can be oxidized to iodine by both Cl_2 and Br_2 (which have higher E° values).
- But **iodine cannot oxidize** Br^- or Cl^- because it is not strong enough as an oxidizing agent.

Corrected Explanation:

Aqueous iodine cannot oxidize bromide or chloride ions because its standard electrode potential (+0.54 V) is lower than that of bromine (+1.07 V) and chlorine (+1.36 V). Therefore, I_2 is not strong enough to pull electrons from Br^- or Cl^- ions.

ii. **Why bromine does not react with chloride ions?**

Ans.

- Bromine (Br_2) has an $E^\circ = +1.07\ V$
- Chlorine (Cl_2) has an $E^\circ = +1.36\ V$

Since Cl_2 is a stronger oxidizing agent than Br_2, Br_2 cannot oxidize Cl^- ions to Cl_2.

Explanation:

Bromine does not react with chloride ions because the standard electrode potential of chlorine is higher than that of bromine. Therefore, Br_2 is not strong enough to oxidize Cl^- to Cl_2.

Oxidizing and Reducing Agents Using E° Values

Look back at Figure. Note the following as the values of E° for each of these reduction reactions gets more negative.

The species on the left of the equation become weaker oxidizing agents. They accept electrons less readily.

The species on the right of the equation become stronger reducing agents. They release electrons more readily.

Cu will not reduce Zn^{2+} ions to Zn. So how can we reduce Zn^{2+} ions? The answer is to react the Zn^{2+} ions with a stronger reducing agent, which should have an E° value more negative than the E° value for Zn^{2+}/Zn. In Figure we see that the half-equation Mg^{2+}/Mg has a more negative E° value. So, Mg is a suitable reducing agent.

$$Zn^{2+}_{(aq)} + e^- \longrightarrow Zn_{(s)} \qquad E^\circ = -0.76\ V$$
$$Mg^{2+}_{(aq)} + 2e^- \longrightarrow Mg_{(s)} \qquad E^\circ = -2.38\ V$$

Zn^{2+} is the better oxidizing agent. It is more likely to accept electrons than Mg^{2+} ions. Mg is the better reducing agent. It is more likely to release electrons than Zn.

Compounds can also act as oxidizing and reducing agents. **For example** $KMnO_4$ (+0.54 V) $K_2Cr_2O_7$ (+1.33 V) are oxidizing agent because of their higher E° values. Whereas, KI and $FeSO_4$ are reducing gents due to their lower E° values.

Few compounds, such as H_2O_2 can act both as oxidizing as well as reducing agents.

Rack Your Mind!

7. **During a redox reaction, an oxidizing agent:**
   (A) Gains electrons
   (B) Is oxidized
   (C) Loses electrons
   (D) Is hydrolyzed

Rack Your Mind!

8. **The reduction potential of Zn is:**
   (A) −0.76 Va (B) −0.34 V
   (C) +0.34 V (D) +0.76 V

VARIATION OF E° VALUE WITH ION CONCENTRATION

The position of an equilibrium reaction is affected by changes in concentration, temperature and pressure. If we change the concentration or temperature of half-cell X, the electrode potential also changes. Under these conditions standard conditions we use the symbol E for the electrode potential. Let us take an example of a metal/metal ion equilibrium:

Table: Variation of Potential with Ion Concentration

$[Fe^{3+}]$(mol dm^{-3})	$[Fe^{2+}]$(mol dm^{-3})	E^0(V)	Effect
> 1.00	1.00	+ 0.85	More positive
< 1.00	1.00	+ 0.70	Less positive
1.00	> 1.00	+0.70	Less positive
1.00	< 1.00	+0.85	More positive

$Zn^{2+}_{(aq)} + e^- \longrightarrow Zn_{(s)}$ $\quad E^\circ = -0.76$ V

- If $[Zn^{2+}]$ is greater than 1.00 mol dm^{-3}, the value of E becomes less negative / more positive (say −0.61 V)
- If $[Zn^{2+}]$ is less than 1.00 mol dm^{-3}, the value of E becomes more negative / less positive (say −0.80 V)

Le-Chatelier's principle can be applied to redox equilibria. If we increase the concentration of the species on the left of the equation, the position of equilibrium will shift to the right. So, the value of E becomes more positive / less negative change in contraction of ions and its effect on E° is shown in Table 10.1. If two different ions are present in the half-cell, we have to consider both ions. Let us take the equilibrium between Fe^{3+} ions and Fe^{2+} ions as an example.

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \quad E^\circ = +0.77 \text{ V}$$
1.00 mol dm^{-3} 1.00 mol dm^{-3}

NERNST EQUATION

Exercise Q.6

Q. How electrode potential varies with concentration of an aqueous solution? Use the Nernst equation to explain this variation.

If we consider a cell made up from a silver/silver ion electrode and a copper/copper(II) ion electrode, the reaction taking place is:

$$Cu_{(s)} + 2Ag^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)} \qquad E^\circ = +0.46 \text{ V}$$

When E°_{cell} is plotted against concentration, we obtain a graph as shown in Figure.

Note that we have plotted the value of E_{cell} (non-standard conditions for the cell as a whole) against the logarithm of the silver ion concentration. The above redox cell reaction makes the value of E_{cell} more positive.

Interesting Information

Nernst Equation:
The Nernst equation is an equation relating the capacity of an atom/ion to take up one or more electrons (reduction potential) measured at any conditions to that measured at standard conditions (standard reduction potential of 298 K and one molar or one atmospheric pressure)

The effect of concentration and temperature on the value of E_{cell} can be deduced using the Nernst equation. For a given electrode, e.g., a $Cu_{(s)} / Cu^{2+}_{(aq)}$ electrode, the relationship is:

$$E = E^\circ + \frac{RT}{zF} \ell n \frac{[\text{oxidized form}]}{[\text{reduced form}]}$$

where,

E is the electrode potential under non-standard conditions

E° is the standard electrode potential

R is the gas constant, 8.314 $J K^{-1}$ mol^{-1}

T is the kelvin temperature

Z is the number of electrons transferred in the reaction

F is the value of the Faraday constant in C mol^{-1}

ln is the natural logarithm

[oxidized] refers to the concentration of the oxidized form in the half-equation

[reduced] refers to the concentration of the reduced form in the half-equation.

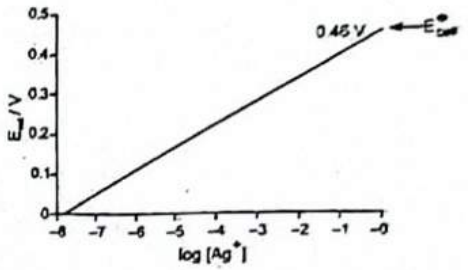


Figure: Increasing the concentration of silver ions in the cell reaction

Fortunately, for a metal/metal ion electrode, we can simplify this equation in three ways:

- The natural logarithm, ℓn, is related to log to the base 10 by the relationship $\ell n x = 2.303 \log_{10} x$
- At standard temperature the values of R, T and F are constant, The equation then becomes

$$E = E^\circ + \frac{0.059}{z} \ell og \frac{[\text{oxidized form}]}{[\text{reduced form}]}$$

Sample Problem

What is the electrode potential of a Zn electrode dipped in a solution containing Zn^{2+} ions (0.1 M), The e° value of Zn^{2+} / ZnO is −0.76 V.

Using Half equation and E°,

$$Zn^{2+} + 2e^- \longrightarrow Zn \qquad E^\circ = -0.76 \text{ V}$$

$$E = (-0.76) + \frac{8.31 \times 298}{2 \times 96500} \ell n (0.1)$$

$$E = -0.76 + (-0.029) = -0.78 \text{ V}$$

Since, Concentration of Zn^{2+} is decreased to shift equilibrium backward and electrode potential decreases to −0.78 V.

ACTIVITY SERIES OF METALS

- The activity series of metals is a ranking of metals based on their reactivity, particularly their tendency to lose electrons and undergo oxidation.
- Metals higher in the activity series have more negative standard reduction potentials, meaning they are more likely to lose electrons and undergo oxidation. Hence such metals act as reducing agents.
- Metals at the top of the series are the most reactive with water, oxygen and acid. For example, alkali metals like cesium and sodium are highly reactive and oxidize readily, reacting vigorously with substances like water to form ions and release hydrogen gas.
- In contrast, metals lower in the activity series, such as noble metals like gold and silver, do not oxidize easily. They are less reactive and do not readily lose electrons, that is why they do not react with water. Metals at the bottom of the series are the least reactive with water, oxygen and acid. Thus, the position of a metal in the activity series directly correlates with its ease of oxidation and overall reactivity. Conversely, metals lower in the activity series have more positive standard reduction potentials, indicating a greater tendency to gain electrons and undergo reduction. Hence such metals act as oxidizing agents.
- Activity series of metals is actually reactivity series.
  Thus, the activity series can be understood in terms of standard reduction potentials: metals with more negative potentials are more reactive and oxidize more readily, while those with more positive potentials are less reactive and oxidize less readily as given in Table.

Table: Activity Series of Metals

Metals	Ions	E°(V)	Reaction Occurring	Trend
Li	Li^{1+}	−3.05	React with cold water, replacing hydrogen $2M_{(s)} + 2H_2O_{(\ell)} \longrightarrow 2MOH_{(aq)} + H_{2(g)}$	Decreasing ease of oxidation, reactivity and acting reducing agent
K	K^{1+}	−2.93		
Ba	Ba^{2+}	−2.90		
Sr	Sr^{2+}	−2.89		
Ca	Ca^{2+}	−2.87		
Na	Na^{1+}	−2.71		
Mg	Mg^{2+}	−2.37	Reacts with steam (but not with cold water) replacing hydrogen. $M_{(s)} + H_2O_{(\ell)} \longrightarrow MO_{(aq)} + H_{2(g)}$	
Aℓ	$Aℓ^{3+}$	−1.66		
Zn	Zn^{2+}	−0.76		
Cr	Cr^{3+}	−0.74		
Fe	Fe^{2+}	−0.44		
Cd	Cd^{2+}	−0.40		
Co	Co^{2+}	−0.28	Do not react with water. React with acids, replacing hydrogen. $M_{(s)} + HCℓ_{(aq)} \longrightarrow MCℓ_{(aq)} + H_{2(g)}$	
Ni	Ni^{2+}	−0.25		
Sn	Sn^{2+}	−0.14		
Pb	Pb^{2+}	−0.13		
H_2	H^+	0.00	Included as reference	
Cu	Cu^{2+}	+0.34	Unreactive with water or acids	
Hg	Hg^{2+}	+0.92		
Ag	Ag^{1+}	+0.80		
Pt	Pt^{2+}	+1.18		
Au	Au^{3+}	+1.50		

For Entry Test: Increasing strength as an oxidizing agents / Increasing reduction potential

FEASIBILITY OF REDOX REACTIONS FROM ACTIVITY SERIES OR REACTION DATA

- The activity series is actually a reactivity series of metals, in order of reactivity from highest to lowest.
- It is used to determine the products of single displacement reactions; whereby metal M_1 will replace another metal M_2 in a solution if M_1 is higher in the series.

Rack Your Mind!

9. Na and K can displace hydrogen from acids but Pt, Cu cannot. Explain.

➲ Feasibility of a Reaction

From the activity series of metals, we can determine whether the reaction is feasible or not. We sum up the potentials of half reactions, if potential of the cell is positive it means the reaction is possible, however if emf is negative, the reaction is not feasible. Let us see the reactions:

$$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)} \qquad E^\circ_{(ox)} = -0.44\ V$$

$$Ag^+_{(aq)} + 1e^- \rightleftharpoons Ag_{(s)} \qquad E^\circ_{(ox)} = +0.080\ V$$

The overall reaction is

$$Fe_{(s)} + 2Ag^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + 2Ag_{(s)} \qquad E^\circ_{(cell)} = 0.080 - (-0.44) = +1.24\ V$$

The cell potential is positive; hence the reaction is feasible.

$Fe_{(s)} + 2Ag^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + ZAg_{(s)}\ E^\circ_{(cell)} = 0.080 - (-0.44) = +1.24$ V From the activity series of metals, we have

$$Aℓ^{3+}_{(aq)} + 3e^- \rightleftharpoons Aℓ_{(s)} \qquad E^\circ_{(red)} = -1.66\ V$$

$$Ag^+_{(aq)} + 1e^- \rightleftharpoons Ag_{(s)} \qquad E^\circ_{(ox)} = +0.080\ V$$

$$Aℓ^{3+}_{(aq)} + Ag_{(s)} \rightleftharpoons Aℓ_{(s)} + Ag^+_{(aq)} \qquad E^\circ_{(red)} = -1.66 + 0.080 = -0.86\ V$$

The sum of E° values of the two half-cell reactions is negative. Hence the reaction is not feasible.

☑ QUICK CHECK 10.8

a) State the Nernst equation, why is it significant in electrochemistry.

Ans. State the Nernst Equation and Its Significance

Nernst Equation:

For a half-cell reaction at 25°C (298 K), the Nernst equation is:

$$E = E^\circ - \frac{0.0591}{n}\log\frac{[Red]}{[Ox]}$$

or, more commonly written for oxidation-reduction reactions:

$$E = E^\circ - \frac{0.0591}{n}\log Q$$

Where:

- E = electrode potential at non-standard conditions
- E° = standard electrode potential
- n = number of electrons transferred
- Q = reaction quotient (ratio of product to reactant concentrations)

Significance in Electrochemistry:

- It allows the calculation of cell/electrode potentials under non-standard conditions.
- Explains how electrode potential changes with concentration, pressure, or temperature.
- Crucial for predicting direction of redox reactions, and in designing electrochemical cells.

b) What is the effect of variation in ion concentration on the standard electrode potential of a half reaction?

Ans. Effect of Ion Concentration on Standard Electrode Potential

- Standard electrode potential (E°) is fixed, measured at standard conditions (1 M, 1 atm, 25°C).
- However, the actual electrode potential (E) varies with ion concentration, as shown by the Nernst equation.
- **Increase in ion concentration (oxidant):** shifts equilibrium → increases E.
- **Decrease in ion concentration:** shifts equilibrium → decreases E.

So, electrode potential becomes more positive or more negative depending on concentration changes.

c) Give answers using E° values ($E^\circ_{Ag^+/Ag} = +0.80$ V, $E^\circ_{Cr^{2+}/Cr} = -0.91$ V, $E^\circ_{Fe^{2+}/Fe} = -0.44$ V).

I. Which of Ag^+, Cr^{2+} and Fe^{2+}, is the strongest oxidizing agent? Which is the least oxidizing? Explain with reason.

Ans. $E^\circ_{Ag^+/Ag} = +0.80$ V

$E^\circ_{Fe^{2+}/Fe} = -0.44$ V

$E^\circ_{Cr^{2+}/Cr} = -0.91$ V

Strongest and Weakest Oxidizing Agent:

- Oxidizing agents = species that gain electrons (i.e., get reduced).
- Higher E° → more easily reduced → stronger oxidizing agent.

So:

- Strongest oxidizing agent: Ag^+ ($E^\circ = +0.80$ V)
- Weakest oxidizing agent: Cr^{2+} ($E^\circ = -0.91$ V)

ii. Arrange Ag, Cr and Fe in increasing order of their reducing powers.

Ans. Increasing order of reducing power (Ag, Cr, Fe):

Reducing agents = metals (Ag, Fe, Cr) that lose electrons (get oxidized).

Lower E° of their conjugate ion → better reducing agent.

Order (increasing reducing power):

$$Ag < Fe < Cr$$

d) What is the electrode potential of a Cu electrode dipped in a solution containing Cu^{2+} ions (0.01 M). The E° value of Cu^{2+}/Cu^0 is +0.34 V?

Ans. Electrode potential of Cu electrode in 0.01 M Cu^{2+} Solution:

Given Data:

- $E^\circ_{Cu^{2+}/Cu} = +0.34\,V$
- $[Cu^{2+}] = 0.01M$
- $n = 2$

Using the Nernst Equation:

$$E = E^\circ - \frac{0.0591}{n}\log\frac{1}{[Cu^{2+}]}$$

$$E = 0.34 - \frac{0.0591}{2}\log\left(\frac{1}{0.01}\right)$$

$$E = 0.34 - 0.02955 \times \log(100)$$

$$E = 0.34 - 0.02955 \times 2 = 0.34 - 0.0591 = 0.2809\ V$$

e) What is the electrode potential of $C\ell^-/C\ell_2$ half cell at 25 °C, if concentration of $C\ell^-$ is 0.05 mol dm^{-3}.

$$C\ell_2 + 2e^- \rightleftharpoons 2C\ell^- \qquad E^\circ = 1.36\ V$$

To Find: The electrode potential of the $C\ell_2/C\ell^-$ half-cell at 25°C, we use the Nernst equation:

Given:

Half-cell: $C\ell_{2(g)} + 2e^- \rightleftharpoons 2C\ell^-$

Standard Electrode Potential: $E^\circ = 1.36$ V

$[C\ell^-] = 0.05$ mol dm^{-3}

$T = 25°C = 298$ K

Assume: $PC\ell_2 = 1$ atm

Nernst Equation (at 25°C):

$$E = E^\circ - \frac{0.0591}{n}\log\left(\frac{1}{[C\ell^-]^2}\right)$$

$n = 2$ (number of electrons transferred)

$[C\ell^-] = 0.05$

Calculations:

$$E = 1.36 - \frac{0.0591}{2}\log\left(\frac{1}{(0.05)^2}\right)$$

$$E = 1.36 - 0.02955\log\left(\frac{1}{0.0025}\right)$$

$$E = 1.36 - 0.02955\log(400)$$

$$\text{Log}\,(400) \approx 2.60$$

$$E = 1.36 - 0.02955 \times 2.60$$

$$E = 1.36 - 0.0768 = 1.28\ V$$

In short, the electrode potential of the $C\ell_2/C\ell^-$ half-cell decreases from the standard 1.36 V to 1.28 V when the $C\ell^-$ concentration is lower (0.05 M), as calculated using the Nernst equation.

PHOTOVOLTAIC CELLS

The word 'photovoltaic' is composed of photo (light) and volt (electrical potential). The cell which converts light energy into electrical energy is called photovoltaic cell.

Principle of Photovoltaic Cells

- The central principle behind the operation of PV cells is the photovoltaic effect, which involves the generation of voltage and electric current in a material upon exposure to light.
- The photovoltaic effect involves the excitation of electrons from the valence band to the conduction band in semiconductors, facilitated by the energy from photons.
- This process is improved by the presence of a PN junction, which separates the electrons and holes, creating a voltage that drives an electric current.

Merits of Photovoltaic Cell as Sustainable Source of Energy

i. The photovoltaic effect continues as long as light is present, making it a sustainable method for generating electricity.

ii. A photovoltaic system is a renewable energy source that converts sunlight into electrical energy.

iii. The photovoltaic systems use the sun's energy, making them a sustainable energy source that is independent of fossil fuels.

WINKLER METHOD, BOD AND DO

Biochemical Oxygen Demand (BOD)

"Biochemical oxygen demand (BOD) is the capacity of organic matter in natural water to consume oxygen within a period of five days."

- The value of BOD is the amount of oxygen consumed as a result of biological oxidation of dissolved organic matter in the sample.
- The oxidation reaction is catalyzed by microorganisms which are already present in the natural water.
- It is measured experimentally through **Winkler method** by calculating the concentration of oxygen at the beginning and at the end of five days period, in which a sealed water sample is maintained in the dark at constant temperature at 25°C.

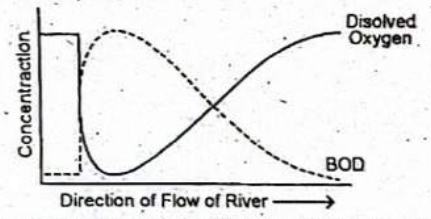


Figure 10.12: Inverse relationship between BOD and DO

Rack Your Mind!

10. The capacity of organic matter in natural water to consume oxygen within five days is called:

A) DO B) BOD

C) COD D) PAN

Dissolved Oxygen (DO)

"Dissolved oxygen (DO) is defined as the amount of oxygen dissolved in water. It is dissolved either from the atmosphere or released by plants during photosynthesis in water."

- Its concentration is between 5 to 8mg / dm^3. The minimum level of DO should be 5mg / dm^3.
- Below 5mg / dm^3, the water supposed to be polluted.
- Dissolved Oxygen (DO) and Biochemical Oxygen Demand (BOD) have an inverse relationship as shown in Figure.
- As bacteria consume oxygen in the water while decomposing organic matter, BOD increases, leading to lower dissolved oxygen (DO) level.

Winkler Method

- Winkler method is a technique used to measure the amount of dissolved oxygen (DO) in water samples.
- It is based on the idea that dissolved oxygen (DO) in the sample solution, has oxidizing properties and reacts with KI.
- The amount of iodine formed is measured by titrating with sodium thiosulfate using starch as an indicator which turns the solution dark blue, indicating the endpoint.
- The amount of iodine formed is proportional to the amount of dissolved oxygen in the solution.

Solution File — Rack Your Brain!

Sr. #	Option	Explanation
1.	S.Q	**Given Data:** K_2CrO_4: Oxidation Number of O = −2 Oxidation Number of K = +1 **Required:** Oxidation Number of Cr = x = ? **Solution:** 2(O.S of K) + (O.S of Cr) + 4(O.S of O) = 0 2(+1) + (x) + 4(−2) = 0 +2 + x − 8 = 0 x = +8 − 2 = +6 Oxidation Number of Cr is +6 in K_2CrO_4.
2.	A	In all oxidation reactions, atoms of an element in a chemical species lose electrons and increase their oxidation state.
3.	D	SO_4^{2-} (O.No of S) + 4 (O.No. of O) = −2 = O.No of S + 4(−2) = −2 = O.No of S − 8 = O.No of S = −2 + 8 = +6
4.	S.Q	**Redox Reactions:** "Those reactions in which one species (atom, ion or molecule) is **oxidized** while other is **reduced** are called redox reactions". **Example:** $2Fe + 3Cl_2 \longrightarrow 2FeCl_3$ In this reaction, Iron (Fe) is **oxidized** while chlorine (Cl_2) is **reduced**. So, this is a redox reaction.
5.	S.Q	Standard oxidation potential of Zn means that Zn has a greater tendency of 0.76 volts than SHE to oxidize or to lose electrons when connected to it. $Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$ $\quad E^\circ_{oxi} = 0.76$ volts For the reverse reaction, which is reduction of Zn^{+2} ion by gain of two electrons the E°_{red} is with a reverse sign i.e., $Zn^{+2}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$ $\quad E^\circ_{red} = -0.76$ volts As both the reactions are opposite to each other, therefore their values of E°_{oxi} and E°_{red} are same but with an opposite sign. $Zn_{(s)} \rightleftharpoons Zn^{+2}_{(aq)} + 2e^-$
6.	S.Q	**Electromotive force (emf):** The force with which electrons moves from anode towards the cathode through an external circuit in a galvanic cell is called the electromotive force (emf).

		It measures the tendency of the cell reaction to takes place. **Calculation of emf of a Cell:** Let us find the emf or cell potential of Daniel cell. The half-cell reactions are $Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$ (Oxidation half) $Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ (Reduction half) The overall cell reaction is $Zn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Cu_{(s)} + Zn^{+2}_{(aq)}$ The cell voltage or emf of the cell is given by $E^\circ_{cell} = E^\circ_{oxid} + E^\circ_{red}$ $= 0.76V + 0.34V$ $= 1.10V$
7.	A	During a redox reaction, an oxidizing agent Gains electrons.
8.	A	The reduction potential of Zn is −0.76 V
9.	S.Q	Displacement of hydrogen from acids involve oxidation of metal and reduction of H^+ to H_2 gas from acid. $M \rightarrow M^+ + 1e^-$ (Oxidation) $2H^+ + 2e^- \rightarrow H_2$ (Reduction) In electrochemical series, those metals which are listed above H_2 have lesser values of reduction potential than H_2 electrode so they possess high values of oxidation potentials. Na and K possess high values of oxidation potential so they liberate H_2 when react with acids as they are present above H_2 in electrochemical series $Na \rightarrow Na^+ + 1e^-$ $\quad E^\circ_{oxi} = 2.714$ volt $K \rightarrow K^+ + 1e^-$ $\quad E^\circ_{oxi} = 2.925$ volt On the other hand Pt, Cu, Au, Ag etc. are listed below H_2 indicating greater reduction potential so they have negative potential to undergo oxidation. e.g. $Cu \rightarrow Cu^{+2} + 2e^-$ $\quad E^\circ_{oxi} = -0.34$ volt Therefore these metals are not able to liberate H_2 gas when treated with acids.
10.	B	BOD (Biochemical Oxygen Demand) measures the amount of oxygen consumed by microorganisms to decompose organic matter in water over five days.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. **The activity series of metals arranges metals in order of their:**
a) Atomic mass b) Density c) Ease of oxidation d) Ease of reduction

II. **According to the activity series, which of the following metals would most readily displace hydrogen gas from dilute acids?**
a) Copper (Cu) b) Silver (Ag) c) Magnesium (Mg) d) Platinum (Pt)

III. **The salt bridge allows transfer of _____ in Zn – Cu voltaic cell.**
(a) Zn^{2+} ions b) SO_4^{2-} Ions (c) Both d) None of these

IV. **If Zn–Cu galvanic cell works ideally after complete discharge, both compartments will have:**
a) $CuSO_4$ solution b) $ZnSO_4$ solution c) Cu^{+2} Ions d) Zn solid

V. Which of the following half-reactions represents a reduction process?
a) $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ b) $Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$ c) $Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$ d) $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

VI. Which of the following half-reactions represents the oxidation process occurring in the disproportionation of Cu^+?
a) $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ b) $Cu^+_{(aq)} + e^- \rightarrow Cu_{(s)}$ c) $Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + e^-$ d) $2Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$

VII. If salt bridge is not used between two half cells in a Galvanic cell, then the voltage
a) Decrease slowly b) Decrease rapidly c) Does not change d) Drop to zero

VIII. In an electrolysis experiment, if a charge of 96,500 Coulombs is passed through a solution, the amount of substance liberated or deposited at the electrode is directly related to:
a) Mass number of the ion b) One mole of electrons being transferred
c) Avogadro's number of ions being discharged d) Standard electrode potential of the metal ion

IX. The experimental determination of Avogadro's number through electrolysis typically involves measuring:
a) The current and voltage applied.
b) The mass of the substance deposited or liberated by a known charge.
c) The conductivity of the electrolytic solution.
d) The temperature changes during electrolysis.

X. The principle of measuring DO by Wrinkler's Method is based on
a) Iodimetry b) Iodometry c) Acid-Base titration d) Complexometry

XI. A positive value for the standard electrode potential (E°) of a metal ion/metal half-cell (e.g., Cu^{2+}/Cu) indicates that:
a) The metal is a strong reducing agent.
b) The metal ion is readily oxidized.
c) The metal ion is readily reduced.
d) The metal will readily displace hydrogen from dilute acids.

XII. Which of the following changes would typically lead to an increase in the rate of electrolysis?
a) Decreasing the concentration of the electrolyte
b) Increasing the distance between the electrodes
c) Decreasing the surface area of the electrodes
d) Increasing the current passed through the electrolytic cell

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I	c)	Ease of oxidation	Metals are arranged based on how easily they lose electrons. More reactive metals oxidize easily and appear higher in the series.
II	c)	Magnesium (Mg)	Magnesium is more reactive than hydrogen in the series. It donates electrons to H^+ ions, releasing hydrogen gas quickly.
III	b)	SO_4^{2-} ions	The salt bridge carries SO_4^{2-} ions to maintain charge balance. It completes the circuit by allowing ion flow without mixing solutions.
IV	b)	$ZnSO_4$ solution	Zn oxidizes and Cu^{2+} reduces to Cu, consuming Cu^{2+} ions. The leftover electrolyte in both half-cells becomes $ZnSO_4$.
V	c)	$Cl_2 + 2e^- \rightarrow 2Cl^-$	In reduction, a species gains electrons. Cl_2 gains electrons to form Cl^-, so it's a reduction.
VI	d)	Drop to zero	Without a salt bridge, charge builds up in the half-cells. This stops electron flow, and the cell immediately loses voltage.
VII	d)	$2Cu^+ \rightarrow Cu^{2+} + Cu$	In disproportionation, the same element is oxidized and reduced. One Cu^+ loses an electron (oxidized), and the other gains (reduced).

VIII	b)	One mole of electrons	96,500 C is 1 Faraday, the charge of 1 mole of electrons. The amount of substance deposited depends on electrons transferred.
IX	b)	Mass deposited by known charge	Mass of metal deposited for a known charge gives moles of atoms. This helps calculate the number of atoms (Avogadro's number).
X	b)	Iodometry	Winkler's method involves titration of iodine formed by DO. It is a redox reaction measured using iodometric titration.
XI	c)	Ion is reduced	A positive E° means the ion gains electrons easily. It is more likely to be reduced than hydrogen.
XII	d)	Increase current	More current increases the number of electrons flowing per second. This speeds up ion discharge and increases the rate of electrolysis.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. How and why electrical double layer is formed?

Ans. An electrical double layer forms at the interface between a solid electrode and an electrolyte solution. It consists of two layers: a layer of charge on the electrode surface and a layer of opposite charge in the solution. This structure arises due to electrostatic interactions between the electrode and the ions in the solution.

b. Why electrode potential of Cu is called reduction potential?

Ans. The electrode potential of Cu is called a reduction potential because it represents the tendency of Cu^{2+} ions to gain electrons (reduction) and form solid copper. A positive value indicates a strong tendency to gain electrons.

c. What are the advantages of salt bridge in a galvanic cell?

Ans. A salt bridge:
- Maintains electrical neutrality by allowing ion flow between half-cells.
- Prevents the solutions from mixing while completing the circuit.
- Enables continuous electron flow, allowing the cell to produce electricity.

d. How can we predict the feasibility of a chemical reaction using the cell voltage?

Ans. The feasibility of a reaction can be predicted by calculating the standard cell potential (E°_{cell}). A positive E°_{cell} indicates a spontaneous reaction, while a negative E°_{cell} suggests a non-spontaneous reaction.

e. During electrolysis of aqueous NaCl, why Na is not liberated at the cathode?

Ans. Sodium (Na) is not liberated at the cathode during the electrolysis of aqueous NaCl because water has a lower reduction potential than Na^+ ions. Therefore, water is reduced to hydrogen gas instead of Na^+ being reduced to Na metal.

f. Calculate the Ox. No. of chromium (Cr) in the following compounds:
(i) $CrCl_3$ (ii) $Cr_2(SO_4)_3$ (iii) $Cr_2O_7^{2-}$

Ans. Oxidation Number of Chromium (Cr)
(i) $CrCl_3$:
Given Data: Oxidation Number of Cl = −1
Required: Oxidation Number of Cr = x = ?
Solution:
Oxidation No. of Cr + 3(Oxidation No. of Cl) = 0
$x + 3(-1) = 0$
$x - 3 = 0$
$x = +3$
Oxidation Number of Cr is +3 in $CrCl_3$.

(ii) $Cr_2(SO_4)_3$:

Given Data: Oxidation Number of O = −2
Oxidation Number of S = +6
Required: Oxidation Number of Cr = x = ?
Solution:

2(Oxidation No. of Cr) + 3(Oxidation No. of S) + 12(Oxidation No. of O) = 0

$$2x + 3(+6) + 12(-2) = 0$$
$$2x + 18 - 24 = 0$$
$$2x = 24 - 18 = +6$$
$$x = +3$$

Oxidation Number of Cr is +3 in $Cr_2(SO_4)_3$.

(iii) $Cr_2O_7^{2-}$:

Given Data: Oxidation Number of O = −2
Required: Oxidation Number of Cr = x = ?
Solution:

2(Oxidation No. of Cr) + 7(Oxidation No. of O) = −2

$$2x + 7(-2) = -2$$
$$2x - 14 = -2$$
$$2x = +14 - 2 = +12$$
$$x = +6$$

Oxidation Number of Cr is +6 in $Cr_2O_7^{-2}$.

g. The order of decreasing reactivity of metals based on their position is K > Mg > Zn > Fe > Cu. Write balanced chemical equations for the reactions that would occur (if any) when:

i) Copper is added to a solution of magnesium sulphate.

ii) Iron is added to a dilute solution of hydrochloric acid.

Ans. i) Copper is added to a solution of magnesium sulphate:
No reaction occurs because copper is less reactive than magnesium.

ii) Iron is added to a dilute solution of hydrochloric acid:

$$Fe_{(s)} + 2HC\ell_{(aq)} \longrightarrow FeC\ell_{2(aq)} + H_{2(g)}$$

h. Explain why some metals higher in the activity series can displace hydrogen from acids, while others lower in the series cannot.

Ans. Metals higher in the activity series (e.g., Zn, Mg) are more reactive and have a greater tendency to lose electrons (oxidize) compared to hydrogen. When reacted with acids, these metals displace H^+ ions (reducing them to H_2 gas) because their reduction potential is lower than hydrogen's.
Metals lower in the series (e.g., Cu, Ag) are less reactive than hydrogen. Their reduction potential is higher, meaning they cannot supply electrons to reduce H^+ ions, so they do not displace hydrogen from acids.
In short, electrochemical reactivity (position in the series) determines whether a metal can reduce H^+ to H_2.

i. Calculate the number of Faradays required to deposit 108 g of Ag^{1+}, 63.5 g of Cu^{2+} and 27 g of $A\ell^{3+}$.

Ans. Number of Faradays=Mass of substance (g)/Equivalent mass of substance
The equivalent mass (E) is calculated as:

$$E = \frac{\text{Molar mass (M)}}{\text{Valency (n)}}$$

1. For 108 g of Ag^+ (Silver)

Molar mass (Ag) = 108 g/mol
Valency (n) = 1

$$\text{Equivalent mass (E)} = \frac{108}{1} = 108\ \text{g/equivalent}$$

$$\text{Number of Faradays} = \frac{108\text{g}}{108\text{g/equivalent}} = 1\text{F}$$

2. For 63.5 g of Cu^{2+} (Copper)

Molar mass (Cu) = 63.5 g/mol
Valency (n) = 2

$$\text{Equivalent mass (E)} = \frac{63.5}{2} = 31.75\ \text{g/equivalent}$$

$$\text{Number of Faradays} = \frac{63.5\text{g}}{31.75\text{g/equivalent}} = 2\text{F}$$

3. For 27 g of $A\ell^{3+}$ (Aluminum)

Molar mass ($A\ell$) = 27 g/mol
Valency (n) = 3

$$\text{Equivalent mass (E)} = \frac{27}{3} = 9\ \text{g/equivalent}$$

$$\text{Number of Faradays} = \frac{27\text{g}}{9\text{g/equivalent}} = 3\text{F}$$

Final Answer:

- **Ag^+ (108 g):** 1 Faraday
- **Cu^{2+} (63.5 g):** 2 Faradays
- **$A\ell^{3+}$ (27 g):** 3 Faradays

(Each Faraday = 96,485 C/mol, but here we only calculate the number of Faradays.)

j. In an electrolysis experiment, a current of 0.500 A was passed through a solution of $AgNO_3$ for 30.0 minutes. The mass of silver deposited on the cathode was found to be 0.503 g. Given that the molar mass of silver is 107.87 g mol^{-1} and the charge on a silver ion is +1. Calculate the value of Avogadro's number (N_A) from this data.

Ans. Given Data:

Current (I) = 0.500 A
Time (t) = 30.0 minutes = 1800 seconds
Mass of Ag deposited (m) = 0.503 g
Molar mass of Ag (M) = 107.87 g mol^{-1}
Charge on Ag^+ ion (n) = 1

Step 1: Calculate the total charge passed (Q)

$$Q = I \times t = 0.500\ \text{A} \times 1800\ \text{s} = 900\ \text{C}$$

Step 2: Determine moles of Ag deposited

$$\text{Moles of Ag} = \frac{m}{M} = \frac{0.503\text{g}}{107.87\text{g mol}^{-1}} = 4.663 \times 10^{-3}\ \text{mol}$$

Step 3: Relate charge to moles of electrons (Faraday's Law)

Since $Ag^+ + e^- \rightarrow Ag$, **1 mole of Ag requires 1 mole of electrons (1 Faraday = 96,485 C).**
Total charge required for 4.663×10^{-3} mol Ag:

$$Q_{theory} = \text{Moles of Ag} \times F = 4.663 \times 10^{-3} \times 96{,}485\ \text{C}$$

But the **actual charge used (Q) = 900 C**, so:

$$F = \frac{Q}{\text{Moles of Ag}} = \frac{900}{4.663 \times 10^{-3}} = 1.930 \times 10^5\ \text{C mol}^{-1}$$

Step 4: Calculate Avogadro's number (N_A)

Since $F = N_A \times e$ (where $e = 1.602 \times 10^{-19}$ C):

$$N_A = \frac{F}{e} = \frac{1.930 \times 10^5}{1.602 \times 10^{-19}} = 6.02 \times 10^{23} \text{ mol}^{-1}$$

Final Answer: $N_A = 6.02 \times 10^{23}$ mol^{-1}

k. A cell is set up with a standard nickel electrode ($Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)}$ $E^\circ = -0.25$ V) and a standard cobalt electrode ($Co^{2+}_{(aq)} + 2e^- \rightleftharpoons Co_{(s)}$ $E^\circ = -0.28$ V).

i) Identify which metal will be the anode and which will be the cathode. Justify your answer.

ii) Write the balanced overall cell reaction.

iii) Calculate the standard cell potential (E°_{cell}).

Solution:

i) Identifying Anode and Cathode

- **Standard Reduction Potentials (E°):**
  - $Ni^{2+} + 2e^- \rightleftharpoons Ni_{(s)}$ $E^\circ = -0.25$ V
  - $Co^{2+} + 2e^- \rightleftharpoons Co_{(s)}$ $E^\circ = -0.28$ V
- **Comparison:**
  - Nickel has a less negative (higher) reduction potential than cobalt.
  - **Cathode (Reduction):** The electrode with the higher reduction potential (Ni^{2+}/Ni).
  - **Anode (Oxidation):** The electrode with the lower reduction potential (Co^{2+}/Co), where oxidation occurs.

Justification:

Since, $E^\circ_{(Ni^{2+}/Ni)} > E^\circ_{(Co^{2+}/Co)}$, Ni^{2+} gains electrons (reduction) at the cathode, while Co loses electrons (oxidation) at the anode.

ii) Balanced Overall Cell Reaction

- **Oxidation at Anode (Co):** $Co_{(s)} \longrightarrow Co^{2+}_{(aq)} + 2e^-$
- **Reduction at Cathode (Ni):** $Ni^{2+}_{(aq)} + 2e^- \longrightarrow Ni_{(s)}$
- **Overall Reaction:** $Ni^{2+}_{(aq)} + 2e^- \longrightarrow Ni_{(s)}$

iii) Standard Cell Potential (E°cell)

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$E^\circ_{cell} = (-0.25\text{ V}) - (-0.28\text{ V}) = +0.03\text{ V}$$

- The positive E°_{cell} confirms the reaction is spontaneous.
- Cobalt (anode) dissolves, while nickel (cathode) deposits.

Final Answers:

i) Anode: $Co_{(s)}$ (oxidation)
Cathode: $Ni^{2+}_{(aq)}$ (reduction)

ii) $Ni^{2+}_{(aq)} + Co_{(s)} \rightarrow Ni_{(s)} + Co^{2+}_{(aq)}$

iii) $E^\circ_{cell} = +0.03$ V

DESCRIPTIVE QUESTIONS

Q.3 How electrode potential varies with concentration of an aqueous solution? Use the NERNST equation to explain this variation.

Ans. See Page No. (356)

Q.4 How Avogadro's number can be derived using an electrolytic cell?

Ans. See Page No. (345)

Q.5 Describe the construction and working principle of the Zn – Cu Galvanic cell.

Ans. See Page No. (351)

Q.6 What is meant by Standard Hydrogen Electrode (SHE)? How it is used to measure the electrode potential of another electrode?

Ans. See Page No. (348)

NUMERICAL PROBLEMS

Q.7 Calculate the electrode potential for a zinc electrode immersed in a 0.010 mol dm^{-3} solution of zinc sulfate ($ZnSO_4$) at 298 K. The standard electrode potential (E°) for $Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ is −0.76 V. (Gas constant, R = 8.31 J K^{-1} mol^{-1}, Faraday constant, F = 96500 C mol^{-1})

Given Data:

- Standard electrode potential (E°) = −0.76 V (for $Zn^{2+} + 2e^- \rightleftharpoons Zn_{(s)}$)
- Concentration of Zn^{2+} ($[Zn^{2+}]$) = 0.010 mol dm^{-3}
- Temperature (T) = 298 K
- Gas constant (R) = 8.31 JK^{-1} mol^{-1}
- Faraday constant (F) = 96500 C mol^{-1}
- n (number of electrons transferred) = 2

Nernst Equation:

$$E = E^\circ - \frac{RT}{nF} \ln\left(\frac{1}{[Zn^{2+}]}\right)$$

Since the activity of solid Zn(s) is 1, the equation simplifies to:

$$E = E^\circ - \frac{0.0591}{n} \log_{10}[Zn^{2+}]$$

(At 298 K, $\frac{RT\ln(10)}{F} = 0.0591$ V)

Substitute Values

$$E = -0.76 - \frac{0.0591}{2} \log_{10}(0.010)$$

$$E = -0.76 - \frac{0.0591}{2} \times (-2) \qquad (\because \log_{10}(0.010) = -2)$$

$$E = -0.76 + 0.0591$$

$$E = -0.7009\text{V}$$

Final Answer: $E = -0.70$ V

Q.8 A constant current of 2.00 A is passed through a solution of copper(II) sulfate ($CuSO_4$) for 30.0 minutes. Calculate the mass of copper deposited at the cathode. (Molar mass of Cu = 63.5 g mol^{-1}, Faraday constant, F = 96500 C mol^{-1})

Given Data:

Current (I) = 2.00 A
Time (t) = 30.0 minutes = 1800 seconds
Molar mass of Cu = 63.5 g mol^{-1}
Faraday constant (F) = 96500 C mol^{-1}

Reaction at Cathode:

$$Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$$

Step 1: Calculate Total Charge Passed (Q)

$$Q = I \times t$$
$$= 2.00\ A \times 1800\ s = 3600\ C$$

Step 2: Determine Moles of Electrons Transferred

$$\text{Moles of } e^- = \frac{Q}{F} = \frac{3600}{96500} = 0.0373 \text{ mol}$$

Step 3: Relate Moles of Electrons to Moles of Cu Deposited

Since 2 moles of e– deposit 1 mole of Cu.

$$\text{Moles of Cu} = \frac{\text{Moles of } e^-}{2} = \frac{0.0373}{2} = 0.01865 \text{ mol}$$

Step 4: Calculate Mass of Copper Deposited

Mass of Cu = Moles of Cu × Molar mass
$= 0.01865 \times 63.5 = 1.184$ g

Final Answer: 1.18 g

Q.9 A galvanic cell consists of a standard hydrogen electrode (SHE) and a $Ni^{2+}_{(aq)}/Ni_{(s)}$ half-cell. The measured cell potential at 298 K is 0.25 V, and the nickel electrode is the negative terminal.

a) Write the balanced overall cell reaction.

b) Determine the standard electrode potential (E°) of the $Ni^{2+}_{(aq)}/Ni_{(s)}$ half-cell.

c) Identify which electrode is the anode and which is the cathode.

Ans.

a) Balanced Overall Cell Reaction

Since the nickel electrode is negative, it acts as the anode (oxidation), and SHE is the cathode (reduction).

Oxidation (Anode):

$$Ni_{(s)} \longrightarrow Ni^{2+}_{(aq)} + 2e^-$$

Reduction (Cathode):

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

Overall Reaction:

$$Ni_{(s)} + 2H^+_{(aq)} \longrightarrow Ni^{2+}_{(aq)} + H_{2(g)}$$

b) Standard Electrode Potential (E°) of Ni^{2+}/Ni

Given Data:

Measured E°_{cell} = 0.25 V

SHE reference potential:

$$E^\circ_{H^+/H_2} = 0\ V$$

Using $E_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$$0.25 = 0 - E^\circ_{Ni^{2+}/Ni}$$

$$E^\circ_{Ni^{2+}/Ni} = -0.25V$$

c) Anode and Cathode Identification

- **Anode (Negative terminal):** $Ni_{(s)}$ (oxidation).
- **Cathode (Positive terminal):** SHE (reduction).

ADDITIONAL SLOs BASED MCQs

1. **By electrolysis of brine solution which of the following is deposited at anode?**
   A. H_2 B. Cl_2 C. O_2 D. Na
2. **Which of the following is reducing agent?**
   A. $KMnO_4$ B. HI C. $K_2Cr_2O_7$ D. H_2SO_4
3. **The oxidation number of Mn in potassium manganate is:**
   A. +7 B. +6 C. +5 D. +2
4. **All of the following statements about (oxidation) state is / are correct EXCEPT:**
   A. It is apparent charge on an atom in a compound B. Its value is either zero, positive or negative
   C. It can be variable D. Maximum oxidation state can be +7
5. **In the extraction of Al by electrolysis. Why it is necessary to dissolve Al_2O_3 in molten cryolite?**
   A. Cryolite provides the ions needed to carry current B. To decrease high melting point of the electrolyte
   C. Cryolite reacts with Al_2O_3 to form ions D. Molten Al_2O_3 would not conduct electricity
6. **All of the following is / are characteristic of electrolytic cell except:**
   A. Electrical energy into chemical energy B. Anode has negative charge and cathode positive charge
   C. Reverse of addition reaction D. Endothermic process
7. **A solution of copper (II) sulphate is electrolyzed using copper electrode, which of the following would be happen?**
   A. The anode loses weight B. The cathode loses weight
   C. The solution darkens in colour D. The solution lighters in colour
8. **Which is not a galvanic cell?**
   A. Daniel cell B. NICAD C. Fuel cell D. Dry Cell
9. **Voltage of silver oxide battery is:**
   A. 1.5V B. 1.8V C. 2V D. 2.2
10. **Coinage metal Cu, Ag, Au, are the least reactive because they have:**
    A. Negative reduction potential B. Positive reduction potential
    C. Negative oxide potential D. Positive oxide potential
11. **The following standard half cells are connected**

$$Cd^{+2}_{(aq)} + 2e^- \rightleftharpoons Cd_{(s)} E^\circ red = -0.40v$$
$$Ag^{+2}_{(aq)} + e^- \rightleftharpoons Ag_{(s)} E^\circ red = +0.80v$$

What is cell potential of the Cd electrode relative to the Ag electrode?
A. -2 .0v B. - 0.04v C. +1.2v D. +0.40v

12. **Zinc displaced copper from copper sulphate solution because:**
    A. Atomic no. of zinc is higher than that of copper
    B. Zinc has more negative electrode potential than copper
    C. Zinc has positive electrode potential than copper
    D. Zinc sulphate is more soluble in water than copper sulphate
13. **The cell reaction $Zn + Cu^{2+}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Cu$, is best represented by:**
    A. $Cu|Cu^{2+}||Zn^{2+}|Zn$ B. $Pt|Zn^{2+}||Cu^{2+}|Cu$ C. $Zn|Zn^{2+}||Cu^{2+}|Cu$ D. $Zn|Cu^{2+}||Zn^{2+}|Cu$
14. **Which of the following is type of electrolytic cell?**
    A. Ni – Cd cell B. Down's Cell C. Silver oxide cell D. Dry alkaline cell

15. If the salt bridge is not used between two half cells, then the voltage:
A. Decrease rapidly B. Decrease slowly C. Does not change D. Drops to zero

Answer Key with Explanations

Sr.No.	Option	Explanations
1.	B	In Electrolysis of brine soln. Cl and OH are present at anode according to E.C series should oxidize to give O_2 but to high cone. Cl is oxidized to give Cl_2 at anode.
2.	B	Among the following the reducing agent is HI.
3.	B	The oxidation number of Mn in K_2MnO_4 is+6.
4.	D	The correct statement among the following is maximum oxidation state can be +7.
5.	B	In the extraction of Al by electrolysis. It is necessary to dissolve Al_2O_3 in molten cryolite decrease high melting point of the electrolyte.
6.	B	The incorrect statement about electrolytic cell is anode has negative charge and cath positive charge.
7.	D	A solution of copper (II) sulphate is electrolyzed using copper electrode then solution Light in colour.
8.	C	Fuel is not a galvanic cell.
9.	A	Voltage of silver oxide battery is 1.5V.
10.	B	Coinage metal Cu, Ag, Au, are the least reactive because they have positive reducti potential.
11.	C	Element with low R.P will be oxidized oxidation pot of Cd will be=+0.40 Ag with high R.P w be reduced red pot of Ag is = 0.40 + 0.80 by adding both weight = +1.20V
12.	B	Zinc displaced copper from copper sulphate solution because Zinc has more negati electrode potential than copper.
13.	C	$Zn\|Zn^{2+}\|\|Cu^{2+}\|Cu$
14.	B	Electrolytic cell like Down's cell uses electricity to carry out non-spontaneous chemic reaction.
15.	D	Due to charge accumulation, flow of e is stopped and voltage drop to zero.

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 What is Winkler method?

Ans. Winkler method is a technique used to measure the amount of dissolved oxygen (DO) in wat samples. It is based on the idea that dissolved oxygen (DO) in the sample solution, has oxidiz properties and reacts with KI. The amount of iodine formed is measured by titrating with sodi thiosulfate using starch as an indicator which turns the solution dark blue, indicating the endpoi The amount of iodine formed is proportional to the amount of dissolved oxygen in the solution.

Q.2 Differentiate between dissolve and biological oxygen demand.

Ans. Dissolved oxygen (DO) is defined as the amount of oxygen dissolved in water. It is dissolved eithe from the atmosphere or released by plants during photosynthesis in water. Its concentration between 5 to 8 mg/dm³. The minimum level of DO should be 5 mg/ dm³. Below 5 mg/dm³, the wat supposed to be polluted.

The capacity of organic matter in natural water to consume oxygen within a period of five days. Th value of BOD is the amount of oxygen consumed as a result of biological oxidation of dissolv organic matter in the sample is called biological oxygen demand.

Q.3 What is the principle of photovoltaic cell?

Ans. **Principle of Photovoltaic Cells**
The central principle behind the operation of PV cells is the photovoltaic effect, which involves the generation of voltage and electric current in a material upon exposure to light. The photovoltaic effect involves the excitation of electrons from the valence band to the conduction band in semiconductors, facilitated by the energy from photons. This process is improved by the presence of a PN junction, which separates the electrons and holes, creating a voltage that drives an electric current.

Q.4 Define electrochemistry.

Ans. **Electrochemistry:**
"The branch of chemistry concerned with the conversion of electrical energy into chemical energy in electrolytic cells and chemical energy into electrical energy in galvanic or voltaic cells is called electrochemistry."

$$\text{Chemical energy} \underset{\text{Electrolytic cell}}{\overset{\text{Galvanic cell}}{\rightleftharpoons}} \text{Electrical energy}$$

Q.5 Differences between oxidizing agent and reducing Agent.

Ans.

Oxidizing Agent	Reducing Agent
(i) A specie which oxidize a substance in a redox reaction is called an oxidizing agent or oxidant.	(i) A specie which reduces a substance in a redox reaction is called as a reducing agent or reductant.
(ii) In the process, the oxidizing agent is reduced itself.	(ii) In the process, the reducing agent is oxidized itself.
(iii) An oxidizing agent gain electrons and its oxidation number decreases in the reaction, e.g., $KMnO_4/H_2SO_4$, $K_2Cr_2O_7/H_2SO_4$, HNO_3, Cl_2, Br_2 etc.	(iii) The reducing agent lose electrons and its oxidation number is increased. e.g., $FeSO_4$, HI, SO_2, Na, K etc.

Q.6 Define Oxidation and Oxidation number. Give two examples.

Ans. **Oxidation:** There are three definitions
(i) Loss of electron (ii) Loss of hydrogen (iii) Gain of oxygen
Oxidation Number/Oxidation State:
"The apparent charge on an atom of an element in a molecule or in an ion is called oxidation number or oxidation state."
Examples:
(i) Oxidation number of Cr is +6 in $K_2Cr_2O_7$. (ii) Oxidation of P is + 5 in Na_3PO_4.

Q.7 What is difference between oxidation and reduction process, give one example of each?

Ans.

Oxidation	Reduction
"Addition of oxygen or removal of hydrogen is called oxidation"	"Addition of hydrogen or removal of oxygen is called oxidation".
• Loss of electron and hence increase in oxidation number is called oxidation. e.g., $Zn \longrightarrow Zn^{+2} + 2e^-$	• Gain of electron and hence decrease in oxidation number is called reduction. e.g., $Cu^{+2} + 2e^- \longrightarrow Cu$
• In electrochemical cells oxidation takes place at anode.	• In electrochemical cells reduction takes place at cathode.

Q.8 Write down the oxidation states of oxygen in peroxide and super oxides.

Ans. **Oxidation States of Oxygen in Peroxides and Super Oxides:**
In peroxides, oxygen has – 1 oxidation state e.g. $H_2^{2(+1)}O^{2(-1)}$.
In superoxide it has –1/2 oxidation state e.g. $K^{+1}O^{(-1/2)}$.

Q.9 Calculate the oxidation number of underlined elements: $H\underline{N}O_3$: $\underline{Cr}O_3$

Ans. $H\underline{N}O_3$

Given Data: Oxidation Number of O = −2
Oxidation Number of H = +1
Required: Oxidation Number of N = x = ?
Solution:

(Oxidation No. of H) + (Oxidation No. of N) + 3(Oxidation No. of O) = 0

$(+1) + x + 3(-2) = 0$

$+1 + x - 6 = 0$

$x = +6 - 1 = +5$

Oxidation Number of N is +5 in HNO_3.

$\underline{Cr}O_3$

Given Data: Oxidation Number of O = −2
Required: Oxidation Number of Cr = x = ?
Solution:

(Oxidation No. of Cr) + 3(Oxidation No. of O) = 0

$x + 3(-2) = 0$

$x - 6 = 0$

$x = +6$

Oxidation Number of Cr is +6 in CrO_3.

Q.10 Define anode and cathode.

Ans. Anode:
An anode is an electrode of a polarized electrical device through which conventional current enters the device.
Cathode:
An electrode of the device through which conventional current leaves the device.

Q.11 Define electrolytic cell. Give example.

Ans. Electrolytic Cell:
In this cell, electrical energy is converted into chemical energy. Non-spontaneous redox reaction takes place. Electrical energy is used to carry out reaction. Electrolysis takes place. Anode is positive and cathode is negative. **e.g.,** Down's cell (to prepare pure Na-metal), Nelson's cell (to prepare caustic soda commercially) etc.

Q.12 Define electrode potential and standard electrode potential.

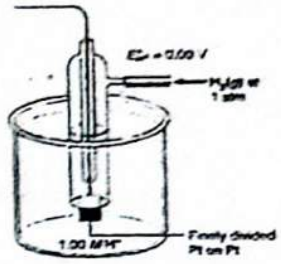
Ans. Electrode Potential:
The tendency of a metal to form its ions or get deposited on the metal when it is dipped into solution of its own ions is called electrode potential.
Standard Electrode Potential:
"The potential set up when an electrode is in contact with one molar solution of its own ions at 298 K is known as standard electrode potential or standard reduction potential of the element."
It is represented as E°.
For example, a rod of Zn will have an accumulation of negative charge owing to the net ionization of some of its atoms. This layer of negative charge will attract Zn^{+2} ions around the rod. In this way, an electrical double layer is formed around the Zn rod as shown in figure. The equilibrium state is represented as:

$$Zn_{(s)} \rightleftharpoons Zn^{+2}_{(aq)} + 2e^-$$

Q.13 What is Standard Hydrogen Electrode (SHE)? Explain with the help of diagram.

Ans. Standard Hydrogen Electrode (SHE):
A standard hydrogen electrode consists of a piece of platinum foil, coated with a layer of finally divided platinum black (to give it a large surface area) and is connected with a platinum wire. It is immersed in 1 M HCl solution. Pure H_2 gas at one atmospheric pressure is continuously bubbled into 1 M HCl solution.
The platinum acts as an electrical conductor and also facilitates the attainment of equilibrium between the gas and its ions in solution. The electrode potential (oxidation or reduction) of this standard hydrogen electrode is arbitrarily taken as zero at all temperatures.

$E^\circ = 0.00$ V



Q.14 Write down the importance of standard Hydrogen Electrode (SHE).

Ans. Importance of Standard Hydrogen Electrode (SHE):
- SHE is used as a standard electrode.
- Standard Hydrogen Electrode is used as a reference electrode and has a potential of 0.0 volts.
- SHE is used to find the reduction potential of different electrodes.
- SHE serves as a medium for cell potential calculations.

Q.15 Differentiate between Galvanic cell and Electrolytic cell.

Ans. Differences between Galvanic Cell and Electrolytic Cell:

Electrolytic Cell	Voltaic/Galvanic Cell
• In this cell, electrical energy is converted into chemical energy.	• In this cell, the chemical energy is converted into electrical energy.
• Non-spontaneous redox reaction takes place.	• Spontaneous redox reaction takes place.
• Electrical energy is used to carry out reaction.	• Electrical energy is generated by a chemical reaction.
• Electrolysis takes place.	• No electrolysis takes place.
• Anode is positive and cathode is negative.	• Anode is negative and cathode is positive.
• **Example:** Down's cell (to prepare pure Na-metal), Nelson's cell (to prepare caustic soda commercially) etc.	• **Example:** Zn-Cu cell (Daniel cell), lead storage battery, silver oxide cell etc.

SELF-ASSESSMENT Chapter # 10

Total Marks: 30

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) **Which of the following half-reactions represents a reduction process?**
A. $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ B. $Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$ C. $Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$ D. $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

(ii) **The activity series of metals arranges metals in order of their:**
A. Atomic mass B. Density C. Ease of oxidation D. Ease of reduction

(iii) **The Nernst equation relates electrode potential to:**
A. Temperature only B. Ion concentration and temperature
C. Pressure only D. Volume only

(iv) **In the Cu-Zn galvanic cell, metal which oxidized is:**
A. Copper B. Zinc C. Both D. Neither

(v) **The principle of measuring DO by Wrinkler's Method is based on**
A. Iodimetry B. odometry C. Acid-Base titration D. Complexometry

(vi) **Which of the following changes would typically lead to an increase in the rate of electrolysis?**
A. Decreasing the concentration of the electrolyte
B. Increasing the distance between the electrodes
C. Decreasing the surface area of the electrodes
D. Increasing the current passed through the electrolytic cell

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) Determine Oxidation No. of Oxygen (O) in Na_2O
(ii) What is the function of salt bridge in the voltaic cell?
(iii) Why bromine does not react with chloride ions?
(iv) Calculate Number of Faradays required to deposit 108 g of Ag^{1+}, 63.5 g of Cu^{2+} and 27 g of Al^{3+}.
(v) How and why electrical double layer is formed?
(vi) Write the principle of the Winkler Method for measuring BOD.
(vii) What is meant by the term standard electrode potential?
(viii) The photovoltaic cells generate electricity. How?

Q.3 Extensive Questions. (2 × 4 = 8)

(a) How electrode potential varies with concentration of an aqueous solution? Use the NERST equation to explain this variation.

(b) Calculate the electrode potential for a zinc electrode immersed in a 0.010 mol dm^{-3} solution of zinc sulfate ($ZnSO_4$) at 298 K. The standard electrode potential (E°) for $Zn^{2+} + 2e^- \rightleftharpoons Zn$ is −0.76 V. (Gas constant, R = 8.31 J K^{-1} mol^{-1}, Faraday constant, F = 96500 C mol^{-1})

Chapter 11

HYDROCARBONS

Student Learning Outcomes

After studying this chapter, students will be able to:

- Classify hydrocarbons as aliphatic and aromatic. **(Understanding)**
- Describe the nomenclature of alkanes and cycloalkanes. **(Understanding)**
- Explain the shapes of alkanes and cycloalkanes exemplified by ethane and cyclopropane. **(Understanding)**
- Explain the unreactive nature of alkanes towards polar reagents. **(Understanding)**
- Define homolytic and heterolytic fission, free radical initiation, propagation and termination. **(Understanding)**
- Describe the mechanism of free radical substitution in alkanes exemplified by methane and ethane. **(Understanding)**
- Identify organic redox reactions. **(Understanding)**
- Explain the nomenclature of alkenes. **(Understanding)**
- Explain the shape of the ethene molecule in terms of s and p C−C bonds. **(Understanding)**
- Describe the structure and reactivity of alkenes as exemplified by ethene. **(Understanding)**
- Explain with suitable examples the terms isomerism, stereoisomerism, and structural isomerism. **(Understanding)**
- Explain the dehydration of alcohols and dehydrohalogenation of RX for the preparation of ethene. **(Understanding)**
- Describe the chemistry of alkenes by the following reactions of ethene: hydrogenation, hydrohalogenation, hydration, halogenation, halo hydration, epoxidation, ozonolysis, and polymerization. **(Understanding)**
- Explain the concept of conjugation in alkenes having alternate double bonds. **(Understanding)**
- Describe the mechanism of electrophilic addition in alkenes, using bromine/ ethene and hydrogen bromide propene as examples. **(Understanding)**
- Use the IUPAC naming system for alkenes. **(Understanding)**
- Explain the inductive effects of alkyl groups on the stability of primary, secondary and tertiary cations formed during electrophilic addition (this should be used to explain Markovnikov addition). **(Understanding)**

- **Hydrocarbons** is a class of organic compounds that consists of only carbon and hydrogen. Hydrocarbons are abundantly found in petroleum and natural gas.
- **Uses of Hydrocarbons:** They are frequently used as domestic and industrial fuels. Generally, hydrocarbons have many synthetic applications.
- **Unsaturated hydrocarbons**, especially alkenes, are used as the starting materials for a number of industrial products. Most of the products in the form of medicines, plastics, perfumes, polymers have their origins in hydrocarbons.
- **Classification:** Hydrocarbons are broadly divided into two classes:
  (i) Aliphatic hydrocarbons (ii) Aromatic hydrocarbons

ALIPHATIC AND AROMATIC HYDROCARBONS

Aliphatic Hydrocarbons

The compounds that are not aromatic are called aliphatic hydrocarbons. Aliphatic compounds may be open chain and cyclic, also they may be saturated or unsaturated. If there are only carbon and hydrogen atoms in an aliphatic compound, it is called aliphatic hydrocarbon. Alkanes are acyclic aliphatic hydrocarbons, whereas cycloalkanes are cyclic aliphatic hydrocarbons. Alkenes and alkynes are acyclic and unsaturated aliphatic hydrocarbons. Figure shows some examples of aliphatic hydrocarbons.

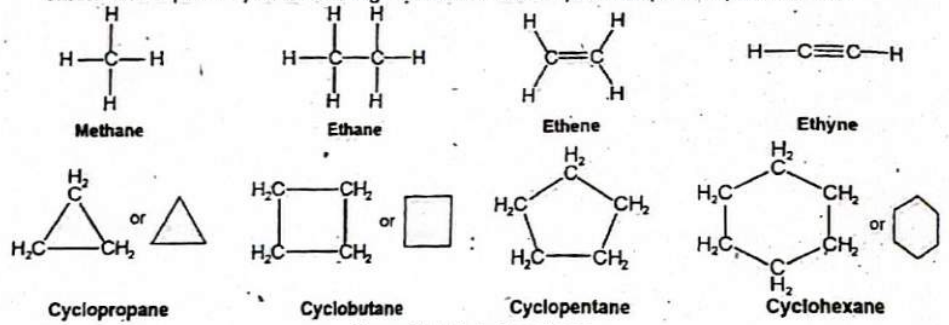


Figure: Aliphatic hydrocarbons

Aromatic Hydrocarbons

Aromatic hydrocarbons is a special class of cyclic hydrocarbons that have high carbon to hydrogen ratio and are based on benzene (C_6H_6) or resembling compounds. Benzene is the basic aromatic compound and other compounds such as toluene and phenol are its derivatives. Figure presents the structures of some aromatic hydrocarbons.

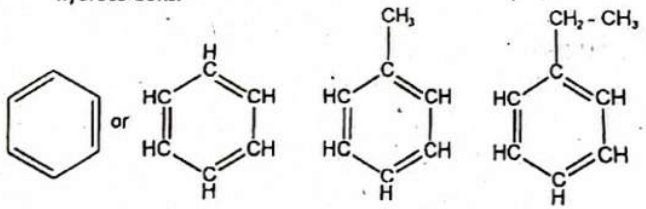


Figure: Some aromatic hydrocarbons

Rack Your Mind!

1. Methyl benzene is also called:
   A) Xylene B) Toluene
   C) Cyclohexane D) n-heptane

Interesting Information

The term aromatic was derived from the Greek word 'aroma' meaning "fragrant" and is used in organic chemistry for a special class of compounds (aromatic compounds) having characteristic odour.

NOMENCLATURE

Alkanes or Paraffins (Latin Parum-Little, affins = affinity)

Alkanes are saturated hydrocarbons with the general formula C_nH_{2n+2}. Methane (CH_4) is the simplest member of this family. The homologous series of alkanes with condensed structural formulae and molecular formulae are shown in Table

Table: Condensed structural formulae and molecular formulae of alkanes

IUPAC Name	Molecular formula	Condensed structure
Methane	CH_4	CH_4
Ethane	C_2H_6	CH_3CH_3
Propane	C_3H_8	$CH_3CH_2CH_3$
Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$
Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$
Hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$
Heptane	C_7H_{10}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
Octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Did You Know?

Butane is a fuel used in lighters. Isobutane is used as a propellant in products such as shaving gel.

Alkyl Group:

The group obtained after the removal of one hydrogen atom from an alkane is called an alkyl group. The resulting alkyl groups are named by replacing –ane of the alkanes with –yl. Few examples are shown in Table2 & Table 3.

Table: alkyl groups, their names and abbreviations

Alkane	Alkyl group	Abbreviation
CH_4 Methane	CH_3 – Methyl	Me–
CH_3-CH_3 Ethane	CH_3-CH_2 – Ethyl	Et–

For alkanes with more than two carbon atoms, more than one alkyl groups can be derived.

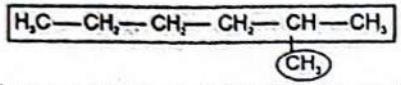
Table: Alkyl groups, straight chain and branched and their names

Alkane	Possible Alkyl Groups			
$CH_3CH_2CH_3$ Propane	$CH_3CH_2CH_2-$ n-Propyl group (Propyl)		$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_3$ isoPropyl group (1-Methylethyl)	
$H_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2-$ n-Butyl group (Butyl)	$CH_3CH_2\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_3$ sec-Butyl group (1-Methylpropyl)	$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_2-$ isoButyl group (2-Methylpropyl)	$H_3C-\underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}-CH_3$ tert-Butyl group (1,1-Dimethylpropyl)

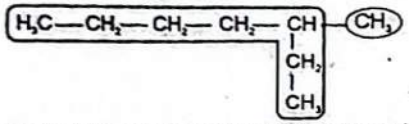
Nomenclature of Alkanes

Branched chain alkanes are named according to the following rules.

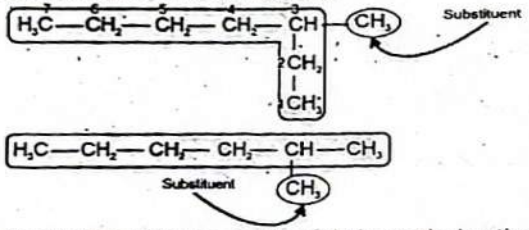
1. Locate the longest continuous chain of carbon atoms; this chain determines the parent name for the alkane. We designate the following compound as a hexane because the longest continuous chain contains six carbon atoms.



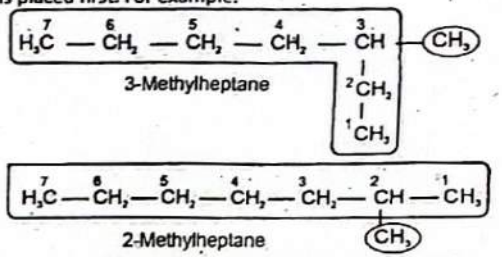
The longest continuous chain may not always be obvious from the way the formula is written. Notice, for example, that the following alkane is designated as a heptane because the longest chain contains seven carbon atoms.



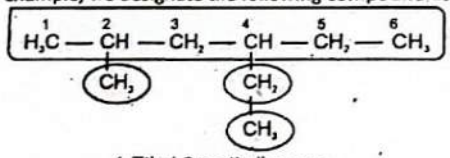
2. Number the longest chain beginning from the end nearest to the substituent. Applying this rule, we number the two alkanes shown above in the following way.



3. Use the numbers obtained by the application of rule 2 to designate the location of the substituent group. The parent name is placed last, and the substituent group, preceded by the number designating its location on the chain, is placed first. For example:



4. When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain. For example, we designate the following compound as 4-Ethyl-2-methylhexane.



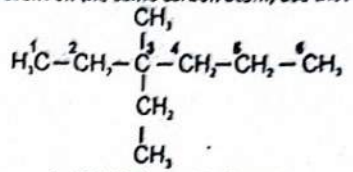
4-Ethyl-2-methylhexane

The substituent groups should be listed alphabetically (i.e. ethyl before methyl). While deciding on alphabetical order ignored multiplying prefixes such as "di" and "tri".

Rack Your Mind!

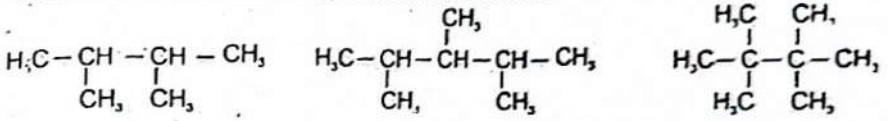
2. Write down names of the following compounds according to IUPAC system.
(a) $(CH_3CH_2)_3CH$ (b) $(C_6H_5)_3CH$

5. When two substituents are present on the same carbon atom, use that number twice.



3 - Ethyl - 3 - methylhexane

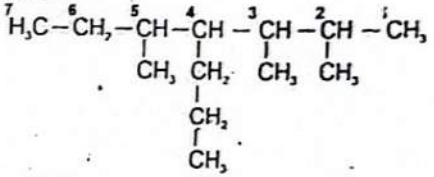
6. When two or more substituents are identical, indicate this by the prefixes di, tri, tetra, and so on. Then make certain that each and every substituent has a number.



2, 3 - Dimethylbutane 2, 3, 4 - Trimethylpentane 2, 2, 3, 3 - Tetramethylbutane

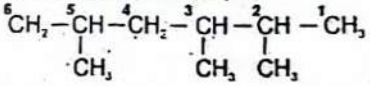
Application of these six rules allows us to name most of the alkanes that we shall encounter. Two other rules, however, may be required occasionally.

7. When two chains of equal length compete for selection as the parent chain, choose the chain with the greater number of substituents.



2, 3, 5 - Trimethyl - 4 - n - propylheptane

8. When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference.



2, 3, 5 - Trimethylhexane (not 2, 4, 5 - Trimethylhexane)

Nomenclature of Cycloalkanes

Cycloalkanes are named by attaching the prefix 'cyclo' to the names of the alkanes possessing the same number of carbon atoms. Figure 11.3

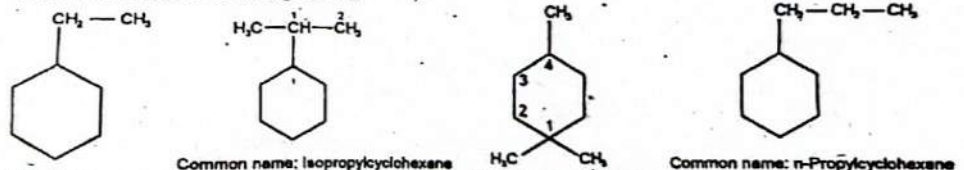
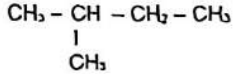


Figure: Naming cycloalkanes

QUICK CHECK 11.1

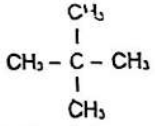
a) Write down the structural formulas for 2-methylbutane and 2,2-dimethylpropane.

Ans. 2-Methylbutane (Isopentane)



2-Methylbutane

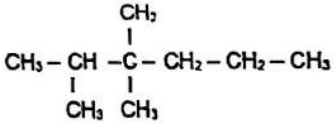
2,2-Dimethylpropane (Neopentane)



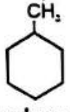
2,2-Dimethylpropane

b) Write down displayed formula of 2,3,3-trimethylhexane and methylcyclohexane.

Ans. 2,3,3-trimethylhexane



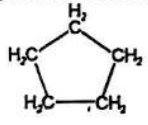
Methylcyclohexane



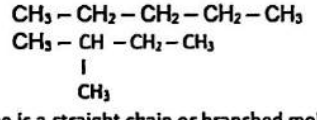
c) Give two differences between molecules of cyclopentane and pentane?

Ans.

1. **Chemical Formulas**
   Cyclopentane: C_5H_{10}, **Pentane:** C_5H_{12}
   Pentane has two hydrogen atom more than cyclopentane.
2. **Structure**
   Cyclopentane: It is a cyclic (ring-shaped) molecule with five carbon atoms forming a closed ring.



3. **Pentane**



A pentane is a straight chain or branched molecule.

d) Eicosane is a straight chain alkane whose molecules contain 20 carbon atoms. What is the molecular formula of eicosane?

Ans. The molecular formula of eicosane (a straight-chain alkane with 20 carbon atoms) is:

$$C_{20}H_{42}$$

Explanation:

General formula for alkanes: C_nH_{2n+2}

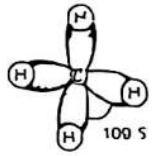
For n = 20:

$$H = (2 \times 20) + 2 = 42$$

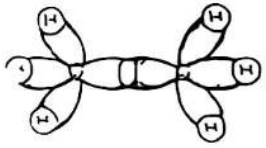
Shapes of Alkanes and Cycloalkanes

The carbon atom in an alkane has four sp^3 hybridized orbitals and forms four single bonds that are equidistant from each other Figure. Alkane molecules have a tetrahedral shape around carbon atoms. Carbon atoms in alkane molecules form sigma bonds with surrounding carbon and hydrogen atoms.

As a result, carbon atoms in alkanes are surrounded by 4 pairs of bonding electrons which equally repel each other to form 109.5° bond angles and a C–C bond length of 1.54 Å. The shapes of organic molecules are generally represented using ball and stick formula. The shapes of some straight chain alkanes



Methane



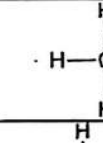
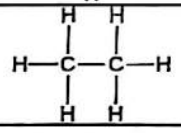
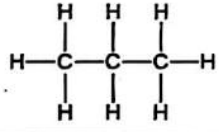
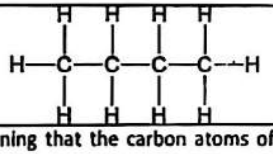
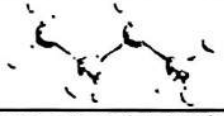
Ethane

sp^3 hybridized tetrahedral

Figure: sp^3 hybridised methane and ethane are shown

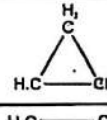
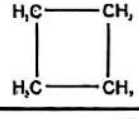
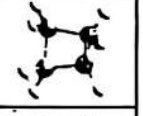
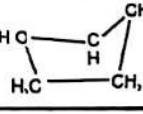
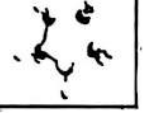
[Table].

Table: Shapes of some straight chain alkanes

IUPAC name & Molecular Formula	Structural Formula	3D Structure
Methane CH_4		
Ethane C_2H_6		
Propane C_3H_8.		
Butane C_4H_{10}.		

Cycloalkanes are cyclic, meaning that the carbon atoms of the molecule are arranged in the form of a ring. Cycloalkanes are also saturated, meaning that all of the carbons atoms that make up the ring are singly bonded to other atoms. The structural shapes of cyclopropane, cyclobutane and cyclopentane are shown below (Table)

Table: Shapes of few cycloalkanes

IUPAC name & Molecular formula	Structural formula	3D Structure
Cyclopropane C_3H_6		
Cyclobutane C_4H_8		
Cyclopentane C_5H_{10}		

Physical Properties of Alkanes

1. **Physical State:**
Alkanes containing upto four carbon atoms are colourless, odourless, gases while pentane to heptadecane (C_5 to C_{17}) are colourless, odourless liquids. The higher members from C_{18} onwards are waxy solids which are also colourless and odourless.
2. **Non-Polarity and Solubility:**
Alkanes are non-polar or very weakly polar and are insoluble in polar solvents like water, but soluble in non-polar solvents, such as hexane, benzene, ether, etc.
3. **Effect of Increase in Number of C-atoms on Physical Constants:**
Their physical constants, e.g. boiling points, melting points, density, etc. increase with the increase in number of carbon atoms, whereas solubility decreases with the increase in molecular mass. The boiling points of alkanes having branched chain structures are lower than their isomeric normal chain alkanes.

normal) Iso) neo

e.g., straight change butane has a higher boiling point –0.50°C than 2-Methylpropane (isobutane, –11.7°C)

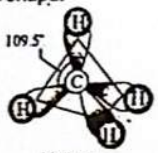
QUICK CHECK 11.2

a) Why do branched alkanes have lower boiling points than the straight-chain alkanes?

Ans. The straight chain alkanes have greater polarizability and greater inter molecular forces than the branched chain alkanes. e.g., Boiling points of

n-pentane) isopentane) neo pentane
309K 301K 283K

b) Explain why alkanes have a tetrahedral shape.

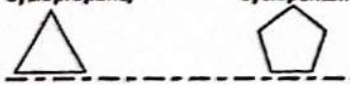


Methane

- Tetrahedral symmetry ensures maximum separation of bonds, minimizing electron repulsion.
- Free rotation around C–C single bonds allows flexible conformations.

c) Draw the shapes of cyclopropane and cyclopentane.

Ans. Cyclopropane, Cyclopentane



REACTION MECHANISM AND MODES OF BOND BREAKING

Reaction mechanism is the series of steps that take place in the course of the overall reaction. Like all chemical reactions organic reactions involve the breaking of chemical bonds. There are two ways in which covalent bonds can break.

(a) *Homolytic Fission (Homolysis)*

Homolytic fission occurs when the covalent bond breaks evenly to produce free radicals. Free Radical is species that contains an unpaired electron and is very reactive. Free radicals are extremely reactive because of the tendency of unpaired electrons to become paired.

Homolytic Cleavage

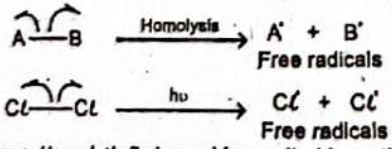


Figure: Homolytic fission and free radical formation

(b) Heterolytic Fission (Heterolysis)

Heterolytic fission occurs when the covalent bond breaks in such a way that the originally shared pair of electrons is gained by one atom only and oppositely child ions are produced. This bond fission is shown by full curly arrows in mechanisms.

Heterolytic cleavage

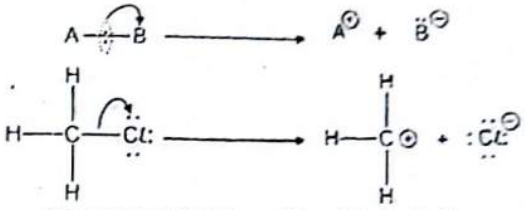


Figure: Heterolytic fission and formation of radical ions

UNREACTIVE NATURE OF ALKANES TOWARDS POLAR REAGENTS

The alkanes or paraffins (Latin: parum = little, affins = affinity) are inert towards acids, alkalis, oxidizing and reducing agents under ordinary condition.

(i) **Non-Polar Nature**

The lack of reactivity of alkanes under normal conditions may be explained on the basis of the non-polarity of the bonds forming them. The electronegativity values of carbon (2.5) and hydrogen (2.1) do not differ appreciably and the bonding electrons between C–H and C–C are equally shared making them almost non-polar and generally unreactive.

(ii) **Inertness of a Sigma Bond**

The unreactive nature of alkanes can also be explained on the basis of inertness of a sigma bond. In a sigma bond the electrons are very tightly held between the nuclei which makes it a very stable bond. A lot of energy is required to break it. e.g., C – H bond energy is about 412 kJ/mol.

Did You Know?

Hydrocarbon combustion produces CO_2, a greenhouse gas contributing to climate change. Incomplete combustion can release carbon monoxide (CO) and particulate matter, which have serious health and environmental consequences.

REACTIONS OF ALKANES

Under high temperature or suitable conditions, alkanes undergo two types of reactions.

I. Thermal and Catalytic Reactions, e.g., Combustion and cracking
II. Free radical substitution reactions are the reactions that involve replacement of one atom, or group of atoms by another through the free radical mechanism.

Exercise Q.3

Q. Describe the free radical halogenation of methane using Cl_2 as an example.

Free radical Substitution Reactions

Substitution reactions of alkanes take place in the presence of light energy through the formation of highly reactive free radicals.

The extent of halogenation of alkanes depends upon the concentration of X_2 used.

➢ **Example:**

Halogenation:

- The substitution of a halogen atom with a hydrogen of an alkane, called halogenation.
- **With Chlorine and Bromine:** Alkanes react with chlorine and bromine in the presence of sunlight or UV light resulting in the successive replacement of hydrogen atoms with halogens.

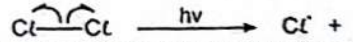
- **With Fluorine:** Reaction of alkanes with fluorine is highly violent and results in a mixture of carbon, fluorinated alkanes and hydrofluoric acid.
- **With Iodine:** Iodine does not substitute directly because the reaction is too slow and reversible.
- The extent of halogenation depends upon the amount of halogen used.
- **Order of Reactivity:** The order of reactivity of halogens is:

$$F_2 > Cl_2 > Br_2 > I_2$$

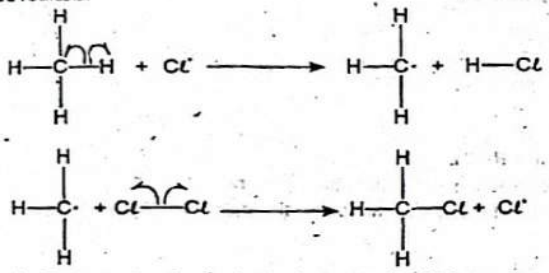
Free Radical Substitution Mechanism of Alkanes:

Halogenation involves the following three steps.

i) **Initiation** step is the first step in the mechanism of free radical substitution of alkanes by halogens. It involves the breaking of the halogen-halogen bond using energy from the UV light. It is homolytic fission.



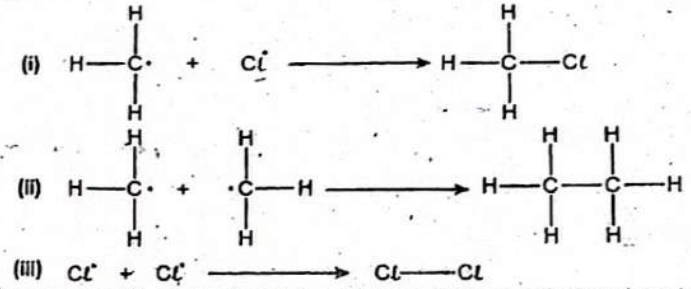
ii) **Propagation** step is the second step in the free radical substitution in which the initially formed radicals attack the alkane molecule generating more free radicals.



iii) **Termination** step is the final step in a free radical substitution in which two free radicals react together to form a product.

The termination step may take place in different ways. The chloride and alkyl radicals may combine to form a chloroalkanes or two chloride radicals may also react to make the chlorine molecule.

Another termination mode is the formation of alkane with double number of carbon atoms which takes place when two alkyl radicals merge together. This type of termination is rare and the alkanes with double carbon atoms are formed in traces. However, its presence is evident of free radical substitution mechanism.



By repetition of step (ii), propagation step, a mixture of halogen substituted products (chloroalkanes) is obtained. The more the chlorine gas in reaction mixture to start with, the greater the proportions of chlorine atoms in the chloroalkane molecules formed.

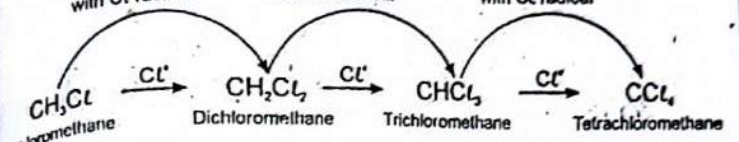
MCQ

The slowest and rate determining step in halogenation of alkane is:
(a) Initiation
(b) Propagation
(c) Termination
(b) Cannot be predicted

Smart Thinking

The final product obtained by heating $H_3C - CH_3$ with excess of chlorine in the presence of sunlight is:
(a) Monochloro ethane
(b) Dichloro ethane
(c) Tetrachloro ethane
(d) Hexachloro ethane

Note: Trichloromethane is also known as chloroform. Tetrachloromethane is also known as carbon tetrachloride and it is used as a non-polar inert solvent.



Interesting Information!
Haloalkanes are anaesthetic in nature. The anesthetic power of a haloalkane increases with the number of halogen atoms. Use of these as organic solvents in lab is strictly monitored due to their toxic nature.

QUICK CHECK 11.3

a) **Explain why alkanes have high stability?**

Ans. **Stability of Alkanes is due to:**

1. **Strong C–C and C–H Bonds:**
   High bond dissociation energies (e.g., C–C: 348 kJ/mol, C–H: 413 kJ/mol).
2. **Nonpolar Bonds:**
   Electronegativity difference between C and H is negligible ($\Delta EN \approx 0.4$), making them resistant to electrophilic/nucleophilic attacks.
3. **Saturated Hydrocarbons:**
   Only single bonds (σ-bonds) with no reactive π-electrons (unlike alkenes/alkynes).
4. **Tetrahedral Symmetry:**
   sp^3 hybridization minimizes steric strain and electron repulsion.
5. **Inertness to Common Reagents:**
   Unreactive toward acids, bases, and oxidizing agents at room temperature.
6. **Combustion Requires High Energy:**
   Need strong ignition sources (e.g., heat/sparks) to break stable σ-bonds.

Conclusion: Stability arises from strong, nonpolar, single bonds and lack of functional groups.

b) **What are major types of reactions that alkanes undergo?**

Ans.

1. **Combustion:**
   Burns in oxygen to form $CO_2 + H_2O$ + energy (e.g., methane: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$).
2. **Halogenation (Free Radical Substitution):**
   Reacts with halogens (Cl_2/Br_2) under UV light to form alkyl halides (e.g., $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$).
3. **Cracking (Thermal Decomposition):**
   Breaks into smaller alkanes/alkenes at high temperatures (e.g., $C_{10}H_{22} \rightarrow C_8H_{18} + C_2H_4$).
4. **Isomerization:**
   Converts straight-chain alkanes to branched isomers (catalyzed by acids/metal catalysts).
5. **Reforming:**
   Converts alkanes to cycloalkanes/aromatics (e.g., hexane → benzene).

Conclusion: Alkanes are unreactive except under extreme conditions (heat/light).

c) **How the termination step occurs in the halogenation of alkenes?**

Ans. See Free Radical Substitution Mechanism of Alkanes: (iii. Termination Step)

d) **State the conditions under which a mixture of halogenoalkanes is obtained from the halogenation of alkanes.**

Ans. A mixture of halogenoalkanes is obtained during the halogenation of alkanes under the following conditions:

1. **Excess Alkane (Low Halogen Concentration)**
   Prevents complete substitution, yielding mono-, di-, tri-, etc., halogenated products.
2. **Non-Selective Free Radical Mechanism**
   - **Initiation:**

$$X_2 \xrightarrow{UV/hv} 2X^{\bullet}$$

- **Propagation:**

$$RH + X^{\bullet} \longrightarrow R^{\bullet} + HX$$
$$R^{\bullet} + X_2 \longrightarrow RX + X^{\bullet}$$

- **Multiple substitutions** occur as any remaining C–H bonds can react further.

3. **No Controlled Stoichiometry**
Halogen (Cl_2/Br_2) reacts randomly with available C – H bonds, producing mixed products (e.g., CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4 from methane).

4. **Example (Chlorination of Methane):**

$$CH_4 \xrightarrow{Cl_2/UV} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + HCl$$

e) Predict the products of the free radical chlorination of ethane.

Ans.

1. **Monochlorination:**
Chloroethane (Ethyl chloride)

$$CH_3CH_3 + Cl_2 \xrightarrow{UV/h\nu} CH_3CH_2Cl + HCl$$

2. **Dichlorination:**
1,1-Dichloroethane

$$CH_3CH_2Cl + Cl_2 \longrightarrow CH_3CHCl_2 + HCl$$

1,2-Dichloroethane

$$CH_3CH_2Cl + Cl_2 \longrightarrow CH_2ClCH_2Cl + HCl$$

3. **Trichlorination:**
1,1,1-Trichloroethane

$$CH_3CHCl_2 + Cl_2 \longrightarrow CH_3CCl_3 + HCl$$

1,1,2-Trichloroethane

$$CH_2ClCH_2Cl + Cl_2 \longrightarrow CH_2ClCHCl_2 + HCl$$

4. **Tetrachlorination:**
1,1,1,2-Tetrachloroethane

$$CH_3CCl_3 + Cl_2 \longrightarrow CH_2ClCCl_3 + HCl$$

1,1,2,2-Tetrachloroethane

$$CH_2ClCHCl_2 + Cl_2 \longrightarrow CHCl_2CHCl_2 + HCl$$

5. **Pentachlorination & Hexachlorination:**
Pentachloroethane ($CHCl_2CCl_3$)

6. **Hexachloroethane (CCl_3CCl_3)**

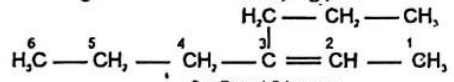
ALKENES

Alkenes are unsaturated hydrocarbons, ***unsaturated hydrocarbons*** are compounds of hydrogen and carbon only whose molecules contain carbon to carbon double bonds (or triple bonds). Alkenes have two hydrogen atoms less than the corresponding saturated hydrocarbons.

➲ Nomenclature of Alkenes

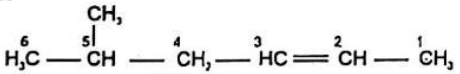
The IUPAC rules for naming alkenes are similar in many respects to those for naming alkanes.

1. Select the longest continuous chain that contains the C = C as the parent chain. Change the ending of the name of the alkane of identical length from –ane to –ene, e.g.,



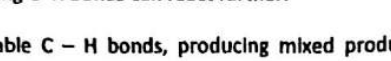
3-n-Propyl-2-hexene

2. Number the chain so as to include both carbon atoms of the double bond. Numbering begins from the end nearer to the double bond.



5-Methyl-2-hexene

3. Designate the location of the double bond by using the number of the first atom of the double bond as a prefix.

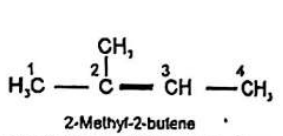


1-butene

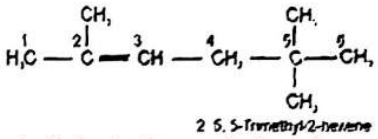


1-pentene

4. Indicate the locations of the substituent groups by the numbers of the carbon atoms to which they are attached.



2-Methyl-2-butene



2, 5, 5-Trimethyl-2-hexene

5. If the parent chain contains more than one double bonds, they are alkadienes for two, alkatrienes for three and so on.

Q. Describe the following methods for the preparation of alkenes:
i) Dehydrohalogenation of alkyl halides **ii) Dehydration of alcohols**

➲ Preparation of Alkenes

Alkenes are prepared by the removal of small atoms (H, OH, X) from the adjacent carbon atoms of the saturated compounds, so as to create a double bond between carbon atoms. These reactions are known as elimination reactions.

In such reactions, a small molecule such as H_2O or HCl, is removed from adjacent carbons in an organic molecule. Preparation of ethene through various methods is being discussed below.

i) Dehydration of Alcohols

Ethene is prepared by heating a mixture of ethanol and excess of concentrated sulphuric acid at 180°C. The reaction involves the removal of a water molecule from the alcohol molecule.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{heat}]{H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + \underset{\text{water}}{H_2O}$$

In the first step, ethyl hydrogen sulphate is formed which decomposes on heating to produce ethene.

$$CH_3-CH_2OH + H_2SO_4 \xrightarrow{180°C} CH_3-CH_2-OSO_3H + H_2O$$
$$CH_3-CH_2OSO_3H \xrightarrow{heat} H_2C=CH_2 + H_2SO_4$$

ii) Dehydrohalogenation of Alkyl Halides

On heating, ethyl bromide with alcoholic KOH, ethene is formed. Removal of hydrogen and halogen takes place from adjacent carbon atoms to create a double bond.

$$H_3C-CH_2-Br + KOH_{(alcoholic)} \xrightarrow{heat} H_2C=CH_2 + KBr + H_2O$$

$$H_3C-CH_2-CH_2-Br + KOH \xrightarrow{Alcohol} H_3C-CH=CH_2 + KBr + H_2O$$

➲ Physical Properties

i. First three members i.e. ethene, propene and butene are gases at room temperature while C_5 to C_{15} are liquids and the higher members are solids.
ii. They are insoluble in water but soluble in alcohol.
iii. They have characteristic smell and burn with luminous flame.
iv. Unlike alkanes, Alkenes show weakly polar properties because of sp^2 hybridization

☑ QUICK CHECK 11.4

a) Give the reactions of propanol with H_2SO_4, write down all the reaction involved.

Ans.

1. **Dehydration to Alkene (Elimination Reaction)**
Condition: Conc. H_2SO_4, heat (170 °C)
Reaction: $CH_3CH_2CH_2OH \xrightarrow{H_2SO_4,\Delta} CH_3CH=CH_2 + H_2O$
Propene (alkene)

2. Formation of Alkyl Hydrogen Sulphate (Addition Reaction)

Condition: Cold conc. H_2SO_4 (0–20 °C)

Reaction: $CH_3CH_2CH_2OH + H_2SO_4 \longrightarrow CH_3CH_2CH_2OSO_3H + H_2O$

Propyl hydrogen sulphate

3. Oxidation:

In presence of oxidizing agents like $K_2Cr_2O_7/H_2SO_4$, propanol is oxidized:

Primary alcohol → Aldehyde → Carboxylic acid

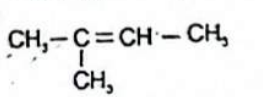
$$CH_3CH_2CH_2OH \xrightarrow{[O]} CH_3CH_2CHO \xrightarrow{[O]} CH_3CH_2COOH$$

Propanal (aldehyde), propanoic acid

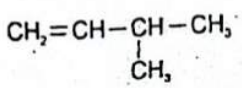
b) Name the following alkenes

i) $CH_3C(CH_3)=CH-CH_3$ **ii)** $CH_2=CHCH(CH_3)_2$

Ans:



2-methyl-2-butene

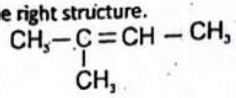


3-methyl-1-butene

c) Draw the structural formulas of the following alkenes.

i) 3-Methyl-2-butene

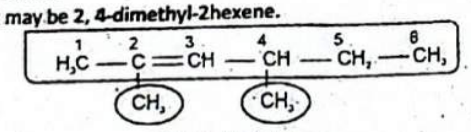
Ans: Correction: 2-Methyl-2-butene is the right structure.



2-methyl-2-butene

ii) 2-Methyl-4-ethyl-2-pentene

Ans. (This is not correct). It may be **2, 4-dimethyl-2hexene.**



2, 4-dimethyl-2-hexene

d) Give the dehydrohalogenation reaction of bromopropane?

Ans. $CH_3-CH_2-CH_2-Br + KOH_{(alcoholic)} \longrightarrow \underset{\text{Propene}}{CH_3-CH=CH_2} + KBr + H_2O$

e) Can propanol undergo dehydration? If yes give reactions involving dehydration.

Ans. $CH_3-CH_2-CH_2-OH \xrightarrow[140-170°C]{75\%H_2SO_4} CH_3-CH=CH_2 + H_2O$

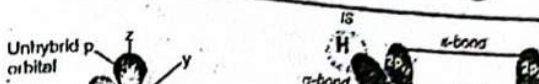
STRUCTURE AND REACTIVITY OF ALKENES

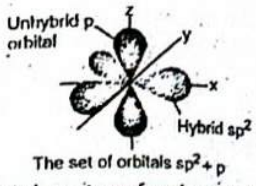
Structure of Alkenes

- Ethene (C_2H_4) is the simplest alkene. Each carbon atom in ethene is **sp^2 hybridized** and forms three equivalent sp^2 hybrid orbitals which lie in the same plane. The unhybrid p orbital lies perpendicular (90°) to the plane of hybrid orbitals shown in Figure.
- These sp^2 orbitals are formed by mixing of the 2s orbital with two 2p orbitals leaving one unhybrid p orbital. In ethene, each carbon uses two sp^2 orbitals to form two C – H bonds each. The remaining sp^2 orbital on each carbon is used to form a carbon-carbon σ bond by linear overlap as in Figure.
- The unhybrid p-orbitals of each carbon atom which are parallel to each other overlap laterally to form another carbon-carbon bond. This bond formed by the lateral overlap of p-orbitals is called a π bond.

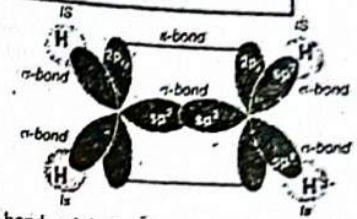
Interesting Information

Plants produce ethene as a natural ripening hormone. For efficiency harvesting and transportation to market, fruits and vegetables are often picked unripe and exposed to ethene so they could ripen in short time.





The set of orbitals sp^2 + p



- The two carbon atoms forming a double bond and the four atoms attached directly to them lie in the same plane. The remaining p-orbital on each carbon is used to form the π bond.
- The sp^2 hybridization results in a trigonal planar arrangement around each carbon atom. The bond angles are approximately 120°, leading to a planar molecule as shown in Figure.

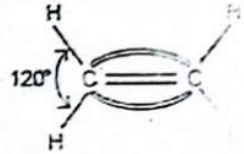


Figure: Structure of ethene

Reactivity of π bond

Comparison of Reactivity of Alkanes and Alkenes: Alkenes are more reactive than alkanes due to the presence of the double bond. The probability of finding electron is away from the line joining the two nuclei. Due to this reason π-electrons are less firmly held between the nuclei. A π bond is, therefore, a weak bond as compared to a σ-bond. During a reaction it breaks comparatively easily rendering alkenes as reactive group of compounds. Moreover, the loosely held π-electrons are more exposed to attack by the electrophilic reagents. Alkenes, therefore, undergo electrophilic addition reactions very easily.

Rack Your Mind!

3. Differentiate between electrophiles and nucleophiles.

Did You Know?

Electrophile is a species that can act as electron pair acceptor, it is represented by E^+. Alkenes act as nucleophile because they contains pi electrons. Nucleophile is a species that can act as a donor of a pair of electrons, it is represented by $Nu^{\ominus}$.

Rack Your Mind!

4. Which of the following is not a nucleophile?

(A) H_2O (B) H_2S

(C) BF_3 (D) NH_3

QUICK CHECK 11.5

a) How does an alkane differ from an alkene in stability?

Ans. Alkanes are more stable than alkenes because:

- Alkanes have only single bonds (σ^- bonds), which are stronger and less reactive.
- Alkenes contain a double bond ($\sigma^+ \pi$ bond), the π bond is weaker and more reactive, making alkenes less stable.

b) Which of the following species is likely to act as a nucleophile? Why?

i) H_2 ii) H^+ iii) OH^-

Ans. iii) OH^-

Explanation:

Nucleophile:

A nucleophile is a species that donates a pair of electrons to form a bond.

OH^- has a lone pair and a negative charge and is a strong nucleophile

c) Which of the following species is likely to act as an electrophile?

i) H_2 ii) H^+ iii) OH^-

Ans. ii) H^+

Explanation:

Electrophiles are electron-deficient species that "accept electrons" (Lewis acids).

H^+ has an empty 1s orbital and strongly attracts electrons.

The reactions of alkenes mostly proceed through the formation of carbocations. Therefore, before studying the addition reactions of alkenes, the concept of carbocations and their stability is very important.

➲ Carbocation Stability and Inductive Effect of Alkyl Group

Carbocation is an alkyl group with a single positive charge on one of its carbon atoms.

Classification: Carbocations are classified into following types.

i. **Methyl Carbocation:** Carbocation which is bonded to H only is named as methyl carbocation.
ii. **Primary 1° Carbocation:** If carbocation is bonded to one C or alkyl substituent then it is named as primary 1° carbocation.
iii. **Secondary 2° Carbocation: If it is bonded to 2 carbons** (alkyl substituent) directly, then it is named as secondary 2° carbocation.
iv. **Tertiary 3° Carbocation:** It is named as tertiary 3° carbocation if it is directly bonded to 3 carbons (alkyl substituent).

➢ Role of Inductive Effect:

The inductive effect of alkyl groups plays an important role in the stability of carbocation. The polarization of a σ bond due to electron withdrawing or electron donating effect of adjacent groups or atoms is referred to as inductive effect.

Electron Donating Inductive Effect: Alkyl groups have a slightly electron donating inductive effect. Electron donating species, are said to have **positive inductive effect (+I),** whereas electron withdrawing species, such as a halogen atom, have a negative inductive effect (–I).

The alkyl groups attached to the positively charged carbon atoms are electron donating groups. Due to the positive charge on the carbon atom, carbocation is electrophile. The inductive effect is shown by the arrowheads on the bonds to show the alkyl groups pushing electrons towards the positively charged carbon.

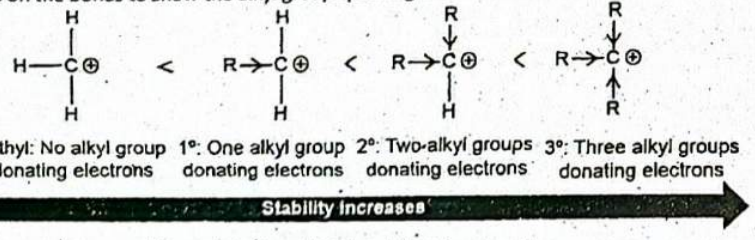


Figure: Inductive effect & stability of carbocation

As a result of this, the carbocation become less positively charged which makes it energetically more stable. The stability of carbocation ions increases with a number of alkyl groups due to their +I effect. This means that tertiary carbocation is the most stable as they have three electron-donating alkyl groups which energetically stabilize the carbocation Figure.

➲ Electron withdrawing Inductive Effect

Electron withdrawing groups, such as a halogen atom, have a negative inductive effect (–I). Halogen withdraws bonded electrons from carbon to carbon bond and thus displays negative inductive effect. This causes a permanent dipole to arise in the molecule wherein the halogen atom holds a negative charge and carbon become partial positive Figure.

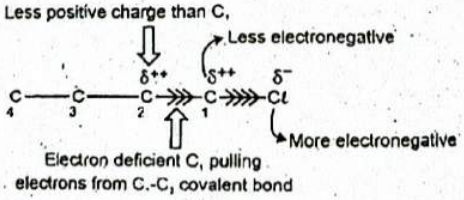


Figure: Inductive effect: Polarization of sigma bond

REACTIONS OF ALKENES

Alkenes are unsaturated hydrcarbons and they undergo electrophilic addition reactions mostly. Other minor types of reactions include oxidation, combustion and polymerization reactions.

➲ Electrophilic Addition Reactions

The reactions in which an electrophile is added to the double bond of an alkene is called electrophilic addition reaction.

➢ Mechanism of Electrophilic Addition in Alkenes

The C = C in alkenes is a region of high electron density making susceptible to attack by electrophiles. Alkenes reacts with an electrophile to give a carbocation intermediate that then reacts with a nucleophile. In the generalized mechanism Figure, X^+ represents an electrophile and Y^- represents a nucleophile.

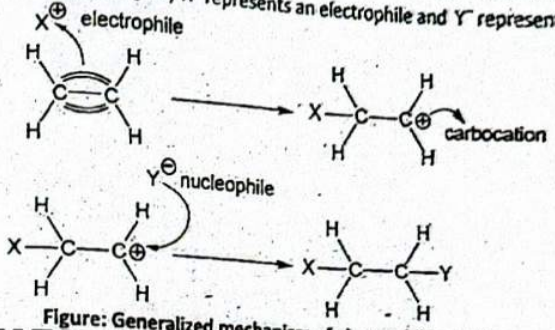


Figure: Generalized mechanism of electrophilic addition

☑ QUICK CHECK 11.6

a) **How do alkenes react with an electrophile?**

Ans. **Alkenes react with electrophiles through electrophilic addition. The general steps are:**

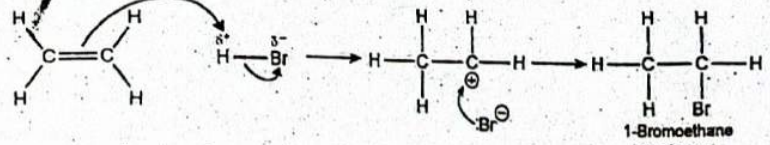
1. **Attack by π-electrons:** The alkene's π-electrons attack the electrophile (E^+), forming a carbocation intermediate.
2. **Nucleophilic attack:** A nucleophile (Nu^-) attacks the carbocation, forming the final product.

Example with HBr:

- **Step 1:** π-electrons attack H^+, forming a carbocation.
- **Step 2:** Br^- attacks the carbocation, yielding a bromoalkane.

Key Points:

- Follows Markovnikov's rule (H adds to the less substituted carbon).
- Carbocation stability determines the major product.



b) **Why the order of stability of carbocation is 3° > 2° > 1°?**

Ans. The stability of carbocations follows 3° > 2° > 1° due to:

1. **Hyperconjugation** – More alkyl groups donate electron density via σ bonds, stabilizing the positive charge.
2. **Inductive Effect** – Alkyl groups are electron-donating (+I effect), dispersing the positive charge.
3. **Resonance (if applicable)** – Delocalization further stabilizes the carbocation.

3° carbocations have the most alkyl groups, providing maximum stabilization, while 1° has the least.

In this chapter, only the mechanism of halogen addition and hydrogen halide addition will be learnt.

1. Halogenation

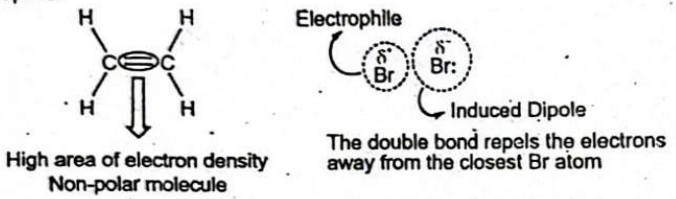
Halogenation means addition of halogens like chlorine or bromine. When bromine water (a solution of bromine in water having red-brown colour) is added to ethene in an inert solvent like carbon tetrachloride, its reddish brown colour is discharged at once. This reaction is used to identify the unsaturation of an organic compound.

$$CH_2=CH_2 + Br_2 \xrightarrow{CCl_4} Br-CH_2-CH_2-Br$$

Mechanism:

The above reaction proceeds through a three-steps mechanism as given below:

i) Bromine (Br_2) is a non-polar molecule, however, when a bromine molecule gets closer to the double bond of an alkene, the high electron density in the double bond repels the electron pair in Br – Br away from the Br atom. As a result of this, the Br atom closest to the double bond is slightly positive and acts as an electrophile.



ii) The δ^+ bromine of Br_2 is attacked by the π electrons in the double bond and the partial positive bromine accepts a pair of electrons from the C = C bond in the alkene. This results in the formation of a highly reactive carbocation intermediate.

iii) This carbocation intermediate reacts with the Br^- (nucleophile) to make the product. Mechanism is shown below Figure.

Mechanism:

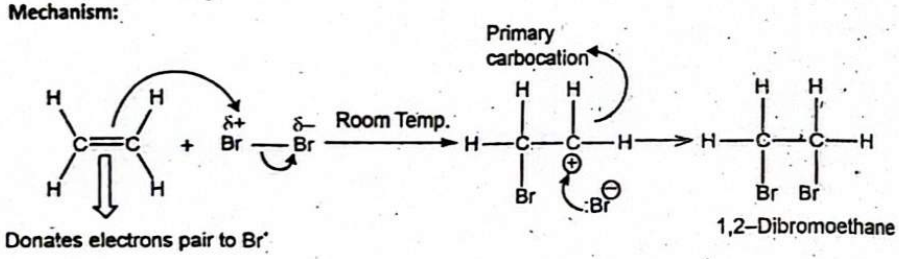


Figure: Electrophilic addition mechanism of ethene and Br_2

2. Hydrohalogenation

When an alkene reacts with dry gaseous hydrogen halide at room temperature, the product is a halogenoalkane.

$$\underset{\text{Ethene}}{CH_2=CH_2} + HBr \longrightarrow \underset{\text{Bromoethane}}{CH_3-CH_2-Br}$$

Hydrogen halides are among the simplest examples of polar substances having permanent dipoles that add to alkenes Figure 11.15. All hydrogen halides (HBr, HCl, HI, HF) give this reaction and add across C = C exactly the same way. But, the rate of reaction increases from HF to HI. The actual product formed depends upon whether the alkene is symmetrical or unsymmetrical.

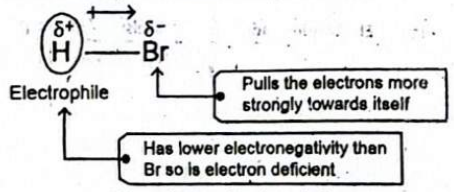


Figure: HBr molecule polarity

Q. Describe the mechanism of electrophilic addition of hydrogen halides to alkenes. Discuss Markovnikov's Rule in the context of hydrogen halide addition.

i) **Addition to Symmetrical Alkenes:** When the alkene (e.g. ethene) is symmetrical only one product is theoretically possible. Let us look at the mechanism of addition of HBr to ethene.

Mechanism:

I. Nucleophilic pi-bond attacks the hydrogen in hydrogen halide. Hydrogen bromide gives a bromide ion (Br^-). Ethene is converted to carbocation by adding hydrogen to one of the double bonded carbons.

II. The bromide ion (nucleophile) attacks the carbocation to give the addition product Figure.

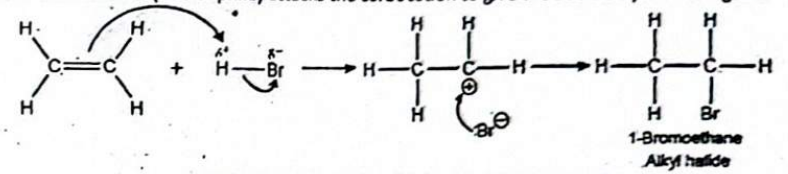


Figure: Electrophilic addition mechanism of HBr to ethene

ii) **Addition to Unsymmetrical Alkenes:** When the alkene is unsymmetrical, two products are theoretically possible. For example, the addition of HBr to propene can give two products. But experimentally, it has been found that under these conditions, the major product is 2-bromopropane and the minor product is 1-bromopropane.

Markovnikov's Rule:

Markovnikov's Rule is applicable for addition reactions in alkenes. According to this rule, "When a polar reagent adds to an unsymmetrical alkene, the negative part of the reagent attach to the double bonded carbon which bears the lesser number of hydrogen."

Mechanism:

Propene reacts with HBr in two ways. The mechanism of this reaction involves the following steps.

i. The pi electrons of C = C attacks on partial positive end of H – Br. Hydrogen bromide breaks heterolytically creating bromide ion (electrophile) and hydrogen is added to double bonded carbon with more number of hydrogen, creating a 2° carbocation.

ii. The bromide ion attacks the secondary carbocation to give the major product. The minor product is formed by the attack on primary carbocation Figure.

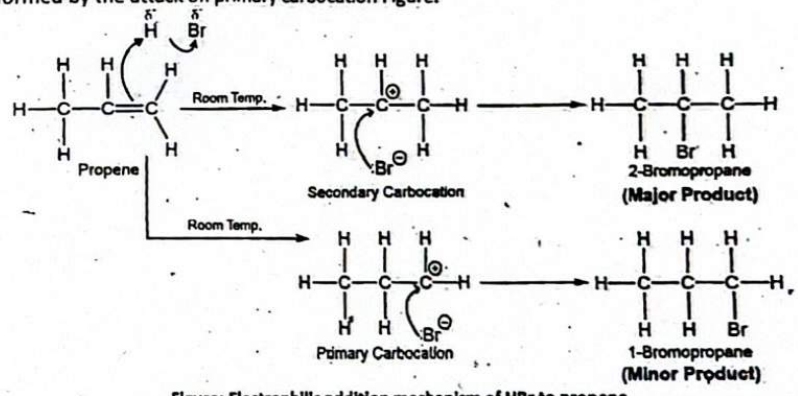


Figure: Electrophilic addition mechanism of HBr to propene

QUICK CHECK 11.7

a) Compare and explain the relative rates of addition to alkenes (reactivities) of HCl, HBr and HI

Ans. Order of Halogen Acid:

The **reactivity order** for addition of hydrogen halides to alkenes is:

HI ⟩ HBr ⟩ HCl

Explanation:

1. **Bond Strength** – The H-X bond strength decreases down the group (HCl > HBr > HI), making HI the easiest to break (fastest reaction).
2. **Electrophilicity** – Iodine (I) is less electronegative than Br or Cl, so HI is a better proton (H^+) donor, increasing its reactivity.
3. **Carbocation Stability** – The larger halide (I^-) stabilizes the intermediate carbocation better via polarizability, speeding up the reaction.

b) Explain the difference between an addition reaction and an elimination reaction?

Ans.

Feature	Addition Reaction	Elimination Reaction
Definition	Two molecules combine to form a single product.	A molecule splits into two or more products.
Substrate	Usually alkenes/alkynes (π bonds).	Usually alkyl halides/alcohols (sp^3 C–X).
Mechanism	Electrophilic/nucleophilic addition.	E1, E2 (unimolecular/bimolecular).
Bond Changes	π bond breaks; new σ bonds form.	σ bond breaks; new π bond forms.
Reagents	HX, X_2, H_2O (electrophiles/nucleophiles).	Base (OH^-, RO^-) + heat (for E2/E1).
Example	$C=C + HBr \rightarrow C-C-Br$	$R-CH_2-CH_2-Br \rightarrow C=C + HBr$
Product	Saturated (alkane) or functionalized molecule.	Unsaturated (alkene/alkyne) or smaller molecule.

c) How alkene react with an electrophile?

Ans. See Mechanism of Halogenation of Alkenes (a)

d) Explain how Markovnikov's rule is applied in addition of HBr to 2-pentene.

Ans.

$$H_3C-CH_2-CH_2-CH=CH_2 + H-Br \longrightarrow \underset{\text{2-Bromopentane}}{CH_3-CH_2-CH_2-\overset{\overset{Br}{|}}{CH}-CH_3}$$

3. Hydrogenation

Hydrogenation means addition of molecular hydrogen to an alkene in the presence of a catalyst (Ni/Pt) to form a saturated compound at 250–300°C.

$$H_2C=CH_2 + H_2 \xrightarrow[250-300^\circ C]{Ni} H_3C-CH_3$$

On industrial scale, this reaction is used to convert vegetable oil into margarine (Banaspati ghes).

$$Oil + H_2 \xrightarrow{Ni} \text{Margarine (Banaspati ghee)}$$

4. Hydration

Gaseous alkenes react with steam at high temperature and pressure in the presence of concentrated acid (H_2SO_4) as the catalyst to form alcohols.

$$H_2C=CH_2 + H_2O \xrightarrow{H_2SO_4} C_2H_5OH$$

Similar to hydrohalogenation, the alkene forms a carbocation intermediate, which is then attacked by OH^-.

5. Halohydration

Halohydration is a reaction where an alkene reacts with a halogen (such as bromine or chlorine) in the presence of water to form a halohydrin. For ethene (C_2H_4), the reaction specifically produces a bromohydrin or chlorohydrin, depending on the halogen used.

$$H_2C=CH_2 + Br_2 + H_2O \longrightarrow \underset{\text{2-Bromoethanol}}{\underset{OH}{\overset{|}{H_2C}}-\underset{Br}{\overset{|}{CH_2}}}$$

Rack Your Mind!

5. Write down the reaction of $H_2C = CH_2$ with HOCl.

Rack Your Mind!

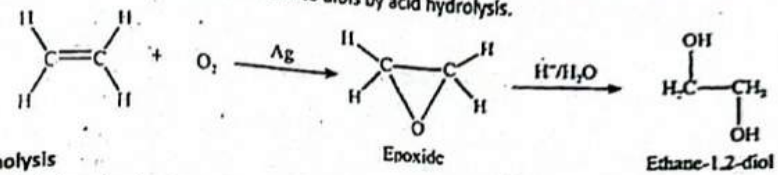
6. Write down the reaction of $CH_3 - CH = CH_2$ with HOCl.

6. Epoxidation

The epoxidation of alkenes gives an oxygen-containing three-membered cyclic ether called epoxide. In the case of ethene (C_2H_4), this reaction can be accomplished using various oxidizing agents.

Catalyst: Ethene can also be converted to ethylene oxide using molecular oxygen and metal catalysts. A transition metal catalyst facilitates the reaction, forming an epoxide directly from the alkene.

Use: The epoxides can be converted in to diols by acid hydrolysis.



7. Ozonolysis

Ozonolysis is a method of oxidatively cleaving alkenes using ozone (O_3), a reactive allotrope of oxygen. Alkenes react with ozone (O_3) to form ozonides, which can be further reduced to carbonyl compounds (aldehydes or ketones), and ultimately to alcohols.

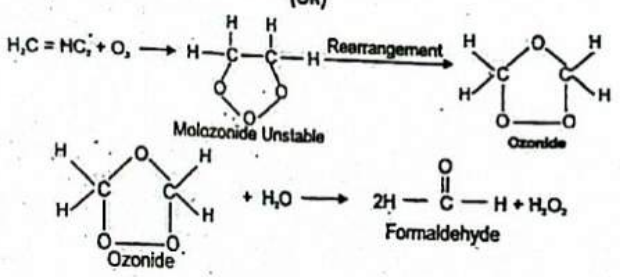
Use: Ozonolysis is often used to identify the structure of unknown alkenes by breaking them down into smaller, more easily identifiable pieces.

Ozonolysis is used to detect the position and number of multiple bonds and structure of compounds.

Examples:

(i) Ozonolysis of Ethene: $C_2H_4 + O_3 \longrightarrow C_2H_4O_3 \longrightarrow 2CH_2O$

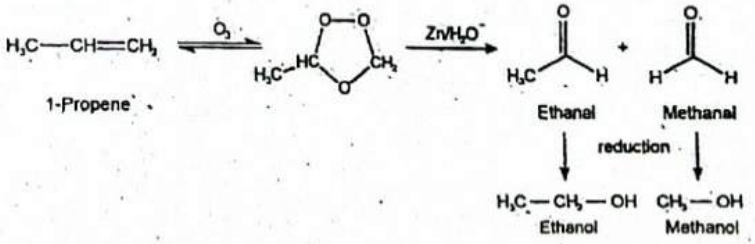
(OR)



$$H_3C-HC=CH_2 + O_3 \xrightarrow{Zn-H_2O} CH_3-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H$$

Acetaldehyde Formaldehyde

(ii) Ozonolysis of Propene:



QUICK CHECK 11.8

a) Write the equation for the ozonolysis of ethene.

Ans. See Above Point 7 Ozonolysis.

b) Give the epoxidation reaction of 2-Butene.

Ans.

$$CH_3 - CH = CH - CH_3 + \frac{1}{2} O_2 \xrightarrow[300°C]{Ag,O} CH_3 - \underset{\diagdown O \diagup}{CH - CH} - CH_3$$

c) How ozonolysis can indicate the position of a double bond in an alkene? Explain with the help of an example.

Ans. Position of double bond will affect the type of carbonyl compounds. e.g., if a double bond is at the end of alkene chain aldehyde will be formed. e.g., Ozonolysis of 1-butene.

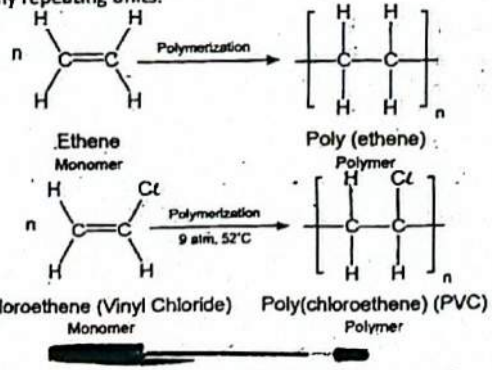
$$CH_3 - CH_2 - CH = CH_2 + O_3 \xrightarrow{Zn/H_2O} CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - H + H - \overset{O}{\overset{\|}{C}} - H$$

8. Polymerization

Polymerization is the formation of extremely long molecules (polymers) from small reactive molecules that join together (monomers). Addition polymerization is one of the most important addition reactions of alkenes which form the basis of the plastics industry.

Addition polymerization is the reaction in which many monomers containing at least one C = C double bond form long chains of polymers as the only product.

Just like in other addition reactions of alkenes, the π-bond in each C–C bond breaks and then the monomers link together to form new C–C single bonds. A polymer is a long-chain molecule that is made up of many repeating units.



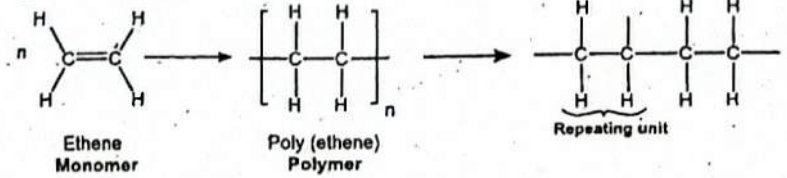
Interesting Information!

Alkenes, like ethene and propene, are used to create plastics through polymerization. Ethene, for instance, is polymerized to make polyethylene, one of the world's most common plastics used in bags, bottles, and packaging.

This ball pen is made of PVC

➢ Deducing Repeating Units

- A repeating unit is the smallest group of atoms that when connected one after the other make up the polymer chain. It is represented by square brackets in the displayed and general formula.
- In poly(alkenes) (such as poly(ethene)) and substituted poly(alkenes) (such as PVC) made of one type of monomer, the repeating unit is the same as the monomer except that the C – C double bond is changed to a C – C single bond.



QUICK CHECK 11.9

a) (i) Discuss how the chemical structure of ethene makes it suitable for polymerization.

Ans. See Above Topic Polymerization of Alkenes (Point 8).

(ii) Discuss the change in hybridization and bond angle during this reaction.

Ans.

Property	Ethene (Monomer)	Polyethylene (Polymer)
Hybridization (Carbon)	sp^2	sp^3
Geometry	Trigonal planar	Tetrahedral
Bond angle	120°	109.5°
Bonding	C = C double bond	C – C single bonds

b) Explain why an addition reaction increases the saturation of a molecule.

Ans. An addition reaction increases the saturation of a molecule because it involves the conversion of multiple bonds (double or triple bonds) into single bonds, allowing more atoms (typically hydrogen or halogens) to attach to the carbon atoms.

Example: Ethene + Hydrogen → Ethane

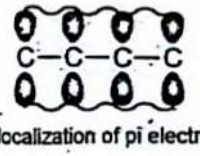
$$CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$$

CONJUGATED DIENES

As the name indicates, a diene is a molecule containing two double bonds between carbon atoms. In a conjugated diene, the double bonds in the carbon chain are separated by a single bond. The adjacent double bonds in conjugated dienes allow for the overlap of p-orbitals on three or more adjacent atoms. This overlap leads to a delocalization of electrons, which can stabilize the molecule and affect its reactivity. In conjugated dienes pi-bond overlap extends over the entire system.

$CH_2 = CH - CH = CH_2$
But-1,3-diene

$CH_2 = \underset{CH_3}{\underset{|}{C}} - CH = CH_2$
2-Methylbut-1,3-diene (Isoprene)


Delocalization of pi electrons

➢ Significance:

Conjugated alkenes are an important class of compounds in organic chemistry, featuring unique properties due to the arrangement of their double bonds. Conjugated dienes like 1,3-butadiene are used in the production of synthetic rubber. The conjugated structure allows for polymerization, leading to long chains that exhibit rubber-like properties.

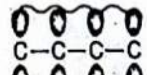
QUICK CHECK 11.10

a) Draw the structure of simple conjugated dienes such as Penta-1, 3-diene.

Ans. $H_3C - CH = CH - CH = CH_2$
Pent-1,3-diene

b) Illustrate the delocalization of electrons in conjugated dienes.

Ans.


Delocalization of pi electrons

ISOMERISM

The concept of isomerism is an important feature of organic compounds.

Definition: Two or more compounds having the same molecular formula but different structural formulas and properties are said to be isomers and the phenomenon is called isomerism.

- The structural formula of a compound shows the arrangement of atoms and bonds present in it.
- The simplest hydrocarbon to have structural isomers is butane (C_4H_{10}). If we study the structural formula of butane or other higher hydrocarbons of the alkane family, we will observe that it is possible to arrange the atoms present in the molecule in more than one way to satisfy all valencies. This means that it is possible to have two or more different arrangements for the same molecular formula.
- **Example:** Chlorobutane molecule has two structural formulas:

$CH_3CH_2CH_2CH_2C\ell$ and $CH_3CHC\ell CH_2CH_3$

1–Chlorobutane 2–Chlorobutane

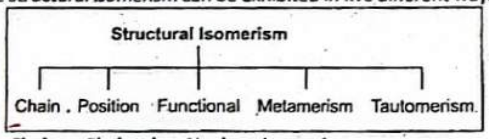
This fact has been supported by an experimental evidence that there are two compounds with different physical properties but with the same molecular formula of $C_4H_9C\ell$. Isomerism is not only possible but common if the compound contains more than three carbon atoms. As the number of carbon atoms in a hydrocarbon increases, the number of possible isomers increase very rapidly. The five carbon compound, pentane, has three isomers.

Tip Formula to find no. of chain isomers of Alkanes up to carbon no.7 is $2^{nc-4}+1$
e.g., if nc = 6 (Hexane)
then,
$2^{6-4}+1 = 2^2+1 = 5$
- For carbon no. 8 (Octane)
$2^{nc-4}+2 = 2^{8-4}+2 = 2^4+2 = 16+2 = 18$
- For carbon no. 9 (Nonane)
$2^{nc-4}+3$
$= 2^{9-4}+3 = 2^5+3$
$= (2\times2\times2\times2\times2)+3 = 32+3 = 35$

Types of Isomerism

A. Structural Isomerism:

The structural isomerism is not confined to hydrocarbons only. In fact, all classes of organic compounds and their derivatives show the phenomenon of structural isomerism. The structural isomerism arises due to the difference in the arrangement of atoms within the molecule. The structural isomerism can be exhibited in five different ways.



Rack Your Mind!

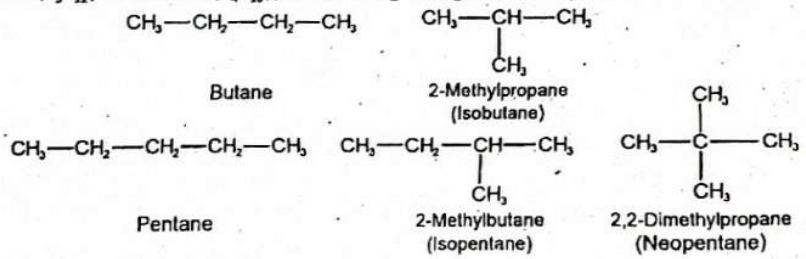
7. Number of Isomers of C_4H_{10} is:
(A) 1 (B) 2
(C) 3 (D) 4

Rack Your Mind!

8. Five carbon compound, pentane has number of isomers:
(A) Five (B) Four
(C) Three (D) One

1. The Chain or Skeletal or Nucleus Isomerism

This type of isomerism arises due to the difference in the nature of the carbon chain. For example, for pentane (C_5H_{12}) and butane (C_4H_{10}), the following arrangements are possible.



Alkanes	No. of Isomers	Alkanes	No. of Isomers
Methane, Ethane, Propane	No. of Isomers	Methane, Ethane, Propane	No. of Isomers
Butane (C_4H_{10})	2	Pentane (C_5H_{12})	3
Hexane (C_6H_{14})	5	Heptane (C_7H_{16})	9
Octane (C_8H_{18})	18	Nonane (C_9H_{20})	35
Decane ($C_{10}H_{22}$)	75	Icosane ($C_{20}H_{42}$)	366319
Triacontane ($C_{30}H_{62}$)	More than 4 billions	Tetracontane ($C_{40}H_{82}$)	625 Trillions

2. Position Isomerism

This type of isomerism arises due to the difference in the position of the same functional group or multiple bonds on the carbon chain. The arrangement of carbon atoms remains the same.

Examples:

$C_3H_7C\ell$: $CH_3-CH_2-CH_2-C\ell$ (1-Chloropropane); $CH_3-CH(C\ell)-CH_3$ (2-Chloropropane)

C_3H_7OH: $CH_3-CH_2-CH_2-OH$ (1-Propanol); $CH_3-CH(OH)-CH_3$ (2-Propanol)

C_4H_8: $CH_3-CH_2-CH=CH_2$ (1-Butene); $CH_3-CH=CH-CH_3$ (2-Butene)

Pentane and 2-methyl butane have the same percentage composition.

Ethanal (acetaldehyde) does not show position isomerism.

Rack Your Mind!

9. Write down three position isomers of xylene.

3. Functional Group Isomerism

The compounds having the same molecular formula but different functional groups are said to exhibit functional group isomerism.

Examples

In the following examples, there are two or more compounds having the same molecular formulae but different arrangement of atoms.

C_2H_6O: CH_3-O-CH_3 (Dimethyl ether); CH_3-CH_2-OH (Ethyl alcohol)

C_3H_6O: $CH_3-CH_2-C(=O)-H$ (Propionaldehyde (Propanal)); $CH_3-C(=O)-CH_3$ (Acetone (Propanone))

C_3H_8O: $CH_3-CH_2-CH_2-OH$ (1-Propanol); $CH_3-O-CH_2-CH_3$ (Methoxy ethane)

Rack Your Mind!

10. Both CH_3COOH and $HCOOCH_3$ show isomerism:
(A) Position (B) Chain
(C) Geometric (D) Functional group

Sr.No.	Formula	Functional Group Isomers
(i)	C_nH_{2n}	Alkene and cycloalkane
(ii)	C_nH_{2n-2}	Alkadiene, Alkyne and cycloalkene
(iii)	$C_nH_{2n+2}O$	Alcohol, ether
(iv)	$C_nH_{2n}O$	Aldehyde, ketone
(v)	$C_nH_{2n}O_2$	Carboxylic Acid, ester
(vi)	$C_6H_{12}O_6$	Glucose (aldohexose), Fructose (Ketohexose)
(vii)	$C_nH_{2n+1}CN$	Cyanides and iso-cyanides e.g., CH_3CN = Ethanenitrile, CH_3NC = Methane isonitrile

4. Metamerism

This type of isomerism arises due to the unequal distribution of carbon atoms on either side of the functional group. Such compounds belong to the same homologous series.

- Such compounds belong to the same homologous series or class of compounds.
- It is due to the presence of different alkyl groups attached to the same polyvalent functional group or atom.

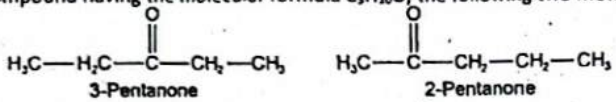
i.e., $-O-$, $-S-$, $-NH-$, $-\overset{O}{\overset{\|}{C}}-$, $-\overset{O}{\overset{\|}{C}}-O-$.

- It is shown by ethers, thioether, ketones, esters, secondary amines, tertiary amines.
- Metamerism is due to the difference in alkyl groups joined with same divalent functional group present in the molecule.
- **Examples:** Diethyl ether and Methoxy methane.

$H_3C-H_2C-O-CH_2-CH_3$ (Ethoxy ethane) $\qquad H_3C-O-CH_2-CH_2-CH_3$ (Methoxy propane)

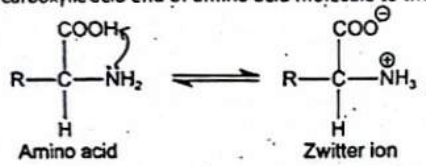
- Alkenes do not show metamerism.
- Butanone do not show metamerism.

For a ketonic compound having the molecular formula $C_5H_{10}O$, the following two metamers are possible.



5. Tautomerism

This type of isomerism arises due to shifting of proton (H^+) from one atom to another in the same molecule. This is commonly seen in amino acids. They exist as zwitter ions which are formed when a proton is shifted from the carboxylic acid end of amino acid molecule to the amine group.



➢ **Keto-Enol Isomerism:**

Keto-enol isomerism is exhibited only by such aldehydes and ketones which contain at least one α-hydrogen. Here one isomer has the carbonyl group and the other has an – OH group attached to a doubly bonded carbon known as enol. **E.g.,**

$H_2C=C(OH)-CH_3 \rightleftharpoons H_3C-C(=O)-CH_3$

Prop-1-en-2-ol $\qquad$ Acetone

Rack Your Mind!

11. Which type of structural isomerism involves differences in the arrangement of the carbon skeleton?
(A) Chain isomerism
(B) Positional isomerism
(C) Metamerism
(D) Stereoisomerism

B. Stereoisomerism:

Stereoisomers are such compounds which possess the same structural formula, but differ with respect to the positions of the identical groups in space.

There are two types of stereoisomerism:

i. Geometrical or cis trans isomerism
ii. Optical isomerism

Note: It is part of class 12 syllabus and will be covered there.

ORGANIC REDOX REACTIONS

Oxidation-Reduction reactions that involve organic compounds are called organic **redox reactions**. These reactions are characterized by the addition or removal of atoms/bonds. Normally, during organic oxidation, oxygen is added or hydrogen is removed. During organic reduction, hydrogen is added or oxygen is removed. Some examples of oxidation and reduction reactions are given below:

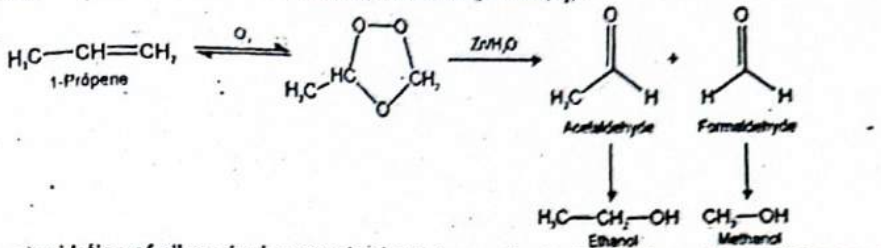
➲ Oxidation

Oxidation of organic compounds involving reaction with oxygen is usually the combustion reaction:

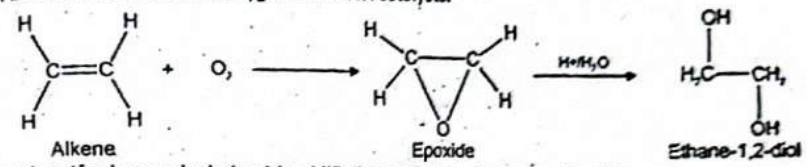
$$2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$$

Reactions of organic compounds with oxidizing agents. e.g.,

i) Ozonolysis is a method of oxidatively clearing alkenes using ozone (O_3).



ii) The epoxidation of alkene is also example of oxidation reaction. In this reaction various oxidizing agents can be used like molecular oxygen and metal catalysts.



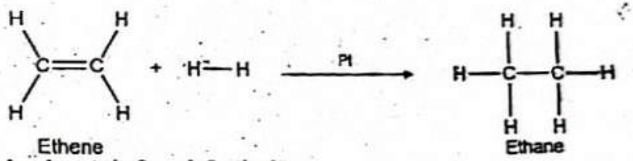
iii) Reaction of primary alcohols with acidified $K_2Cr_2O_7$ to make carboxylic acids.

(**Note:** Detail will be discussed in class 12 syllabus).

$$C_2H_5OH + 2[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH + H_2O$$

➢ **Reduction**

Addition of hydrogen to carbon-carbon double bond to form alkane is an example of organic reduction reaction.



Role of Reducing Agents in Organic Synthesis:

Various reducing agents are used in Organic synthesis. e.g.; $LiAlH_4$, $NaBH_4$,.

(**Note:** Reduction of nitriles to amines, amides to amines, carboxylic acid to primary alcohols, nitrobenzene to phenylamine are all examples of reduction and will be studied in class 12 syllabus).

$$CH_3-\overset{O}{\overset{\|}{C}}-H + 2[H] \xrightarrow{LiAlH_4} CH_3-CH_2-OH$$

QUICK CHECK 11.11

a) **Draw the displayed formula and name an isomer of C_4H_8 that could be an example of positional isomerism?**

Ans. C_4H_8 $\quad CH_3-CH_2-CH=CH_2$ (1-Butene) $\quad CH_3-CH=CH-CH_3$ (2-Butene)

b) **What type of isomers are ethoxy methane ether and propanol?**

Ans. C_3H_8O $\quad CH_3-CH_2-O-CH_3$ (Ethoxy Methane (Methoxy ethane)) $\quad CH_3-CH_2-CH_2-OH$ (1-propanol)

c) **What are the different types of structural isomerism in alkenes?**

Ans. **The types of structural isomerism in alkenes are:**

1. **Chain Isomerism** – Different carbon skeletons (e.g., 1-butene and 2-methylpropene).

2. **Position Isomerism** – Double bond at different positions (e.g., 1-butene and 2-butene).
3. **Functional Isomerism** – Same molecular formula but different functional groups (e.g., butene and cyclobutane).

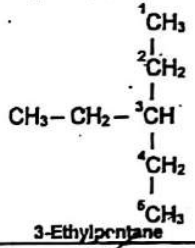
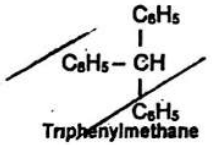
d) Write down different isomers of the compound $C_4H_9NH_2$.

Ans. The molecular formula $C_4H_9NH_2$ represents **butylamine** (a primary amine with four carbons). It has four structural isomers due to different carbon chain arrangements and positions of the $-NH_2$ group.

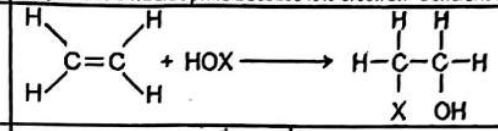
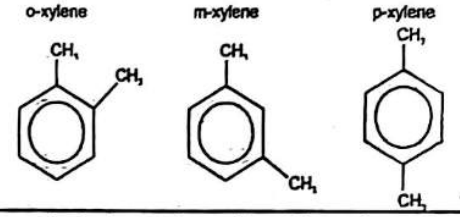
Isomers of $C_4H_9NH_2$ (Butylamine):

1. **Straight-Chain Amines:**
   - (a) 1-Butanamine (n-Butylamine)
     $CH_3–CH_2–CH_2–CH_2–NH_2$
   - (b) 2-Butanamine (sec-Butylamine)
     $CH_3–CH_2–CH(NH_2)–CH_3$
2. **Branched-Chain Amines:**
   - (c) 2-Methyl-1-propanamine (Isobutylamine)
     $(CH_3)2CH–CH_2–NH_2$
   - (d) 2-Methyl-2-propanamine (tert-Butylamine)
     $(CH_3)3C–NH_2$

Solution File Rack Your Brain!

Sr. #	Option	Explanation
1.	B	Toluene is the common name for methyl benzene, which is a benzene ring with one methyl group attached.
2.	S.Q	(a)  3-Ethylpentane (b)  Triphenylmethane
3.	S.Q	**Differences between Nucleophile and Electrophile:**

Nucleophile	Electrophile
• Nucleophile means nucleus loving. This is the reagent which seeks for a nucleus. • It has an unshared electron pair available for bonding. • In most cases it is basic in character. • It may be negatively charged or neutral. • Nucleophile is also called Lewis base. **Examples:** • It may be negatively charged e.g., $C_2H_5O^-$ Ethoxide, H_2S^- Hydrogen Sulphide ion, SCN^- Thiocyanate ion, Cl^- Chloride ion, Br^- Bromide ion, I^- Iodine ion, It may be neutral e.g. $H_2\ddot{O}:$, $:\ddot{N}H_3$ • π-electron system $H_2C = CH_2$, $HC \equiv CH$	• It is a specie which attracts electrons (electron loving). • In most cases, it is acidic in character. • The carbon atom of an alkyl group attached with the halogen atom and bearing a partial positive charge is called an electrophile or electrophilic center. • An electrophile may be neutral or positively charged. • Electrophile is also called Lewis acid. **Examples:** • It may be neutral or electron deficient e.g. $AlCl_3$, SO_3, BF_3, • It may be positively charged e.g., NH_4^+, Cl^+, Br^+, NO_2^+, R^+ etc.

4.	C	BF_3 is not a nucleophile because it is electron-deficient and acts as an electrophile.
5.	S.Q	
6.	S.Q	$CH_3—HC = CH_2 + \overset{\delta-}{HO}—\overset{\delta+}{Cl} \longrightarrow CH_3—HC(OH)—CH_2—Cl$ (Propylene chlorohydrin or 1-Chloro-2-propanol)
7.	B	C_4H_{10} has two chain isomers, n-butane and iso-butane
8.	C	Pentane has three structural isomers: n-pentane, isopentane (methylbutane), and neopentane (dimethylpropane).
9.	S.Q	**Xylenes (C_8H_{10})** 
10.	D	They have the same molecular formula ($C_2H_4O_2$) but different functinal group: carboxylic acid (–COOH) and ester (–COO–).
11.	A	Chain isomerism involves differences in the carbon skeleton (e.g., straight-chain vs. branched).

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. An alkene undergoes ozonolysis followed by reduction with zinc dust and water to yield propanone and methanal. The alkene is:
a) 1-Butene b) 2-Butene c) 2-Methylpropene d) 2-Methyl-2-butene

II. Which of the following reagents is typically used for the acid-catalyzed hydration of alkenes to form alcohols?
a) H_2 / Ni b) O_3 followed by Zn/H_2O
c) Dilute H_2SO_4 d) Br_2 in CCl_4

III. Halogenation of alkanes is an example of:
a) Electrophilic substitution b) Nucleophilic substitution
c) Free-radical substitution d) Oxidation

IV. Which of the following reactions can an alkane undergo?
a) Addition b) Substitution c) Polymerization d) Nitration

V. What is the first step in the electrophilic addition reaction of alkenes?
a) Formation of a carbocation b) Attack by a nucleophile
c) Attack by an electrophile on the double bond d) Formation of a free radical

VI. The addition of unsymmetrical reagent to an unsymmetrical alkene is in accordance with the rule/principle?
a) Markovnikov's Rule b) Hund's Rule c) Le Chatelier's Principle d) Aufbau Principle

VII. The most stable carbonium ion among the following is:
a) CH_3^+ b) $CH_3CH_2^+$ c) $(CH_3)_2CH^+$ d) $(CH_3)_3C^+$

VIII. Markownikov's rule is applicable to:
a) $CH_2=CH_2$ b) $CH_3-CH_2-CH_3$ c) $CH_3-CH=CH-CH_3$ d) $(CH_3)_2C=CH_2$

IX. What intermediate is formed during the electrophilic addition of HBr to an alkene?
a) Carbocation b) Carbanion c) Radical d) Epokide

X. The enhanced stability of conjugated dienes compared to isolated dienes is primarily attributed to:
a) Inductive effects of the double bonds.
b) Increased s-character of the hybridised orbitals.
c) Delocalisation of π electrons across the conjugated system.
d) Steric hindrance between the double bonds.

XI. Which of the following carbocations would be the least stable?
a) $(CH_3)_2CH^+$ b) $CH_3CH_2^+$ c) CH_3^+ d) $(CH_3)_3C^+$

XII. Which of the following is the repeating unit in the polymer poly(ethene) (polyethylene)?
a) $-CH_2CH_3-$ b) $-CH=CH-$ c) $-CH_2CH_2-$ d) $-CH(CH_3)CH_2-$

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	c	2-Methylpropene	• Ozonolysis of 2-methylpropene ($(CH_3)_2C=CH_2$) gives propanone (CH_3COCH_3) and methanol (HCHO).
II.	c	Dilute H_2SO_4	• Dilute H_2SO_4 catalyzes the hydration of alkenes to form alcohols.
III.	c	Free-radical substitution	• Halogenation of alkanes (e.g., $CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl$) proceeds via free-radical chain mechanism.
IV.	b	Substitution	• Alkanes undergo substitution (e.g., halogenation) but not addition (no π bonds) or polymerization.
V.	c	Attack by an electrophile on the double bond	• The first step is electrophilic attack (e.g., H^+ in HBr) on the π electrons of the alkene.
VI.	a	Markovnikov's Rule	• Unsymmetrical reagents (e.g., HBr) add to unsymmetrical alkenes such that the H attaches to the less substituted carbon.
VII.	d	$(CH_3)_3C^+$	• Tertiary carbocations (3°) are most stable due to hyperconjugation and inductive effects.
VIII.	d	$(CH_3)_2C=CH_2$	• Markovnikov's rule applies to unsymmetrical alkenes (e.g., $(CH_3)_2C=CH_2$.
IX.	a	Carbocation	• Electrophilic addition of HBr forms a carbocation intermediate (e.g., CH_3CH^+CH).
X.	c	Delocalisation of π electrons across the conjugated system	• Conjugated dienes (e.g., buta-1,3-diene) are stabilized by π-electron delocalization over 4+ carbons.
XI.	c	CH_3^+	• Methyl cation (CH_3^+) is least stable (no alkyl groups to stabilize the positive charge).
XII.	c	$-CH_2CH_2-$	• Poly(ethene) is formed by polymerization of ethene ($CH_2=CH_2$), with repeating unit $-CH_2-CH_2-$.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Define the following:
i) Cycloalkanes ii) Isomerism iii) Conjugated dienes iv) Inductive effect

Ans.

(i) **Cycloalkanes:** Cycloalkanes are saturated hydrocarbons with carbon atoms arranged in a ring structure, containing only single bonds.
General formula: C_nH_{2n}

ii) **Isomerism**
Two or more compounds having the same molecular formula but different structural formulas and properties are said to be isomers and the phenomenon is called isomerism.

iii) **Conjugated dienes**
Conjugated dienes are organic compounds that contain two double bonds separated by a single bond. The double bonds are alternating (i.e., conjugated) in the carbon chain.

iv) **Inductive effect**
The inductive effect refers to the transmission of charge through a chain of atoms in a molecule by the polarization of sigma bonds. It occurs when an atom or group of atoms in a molecule either donates electron density (electron-donating) or withdraws electron density (electron-withdrawing) through the sigma bonds.

b. Differentiate between:
i) Aliphatic and Aromatic hydrocarbons ii) Homolytic and Heterolytic Fission
iii) Electrophile and Nucleophile

Ans.

i) **Aliphatic and Aromatic hydrocarbons**

Property	Aliphatic Hydrocarbons	Aromatic Hydrocarbons
Structure	Open-chain (straight or branched) or non-aromatic rings	Contain one or more benzene rings (aromatic rings)
Bonding	May have single, double, or triple bonds	Contain delocalized π-electrons in a ring structure
Stability	Less stable than aromatics	Highly stable due to resonance
Types	Alkanes, alkenes, alkynes, and cycloalkanes	Benzene, toluene, naphthalene, etc.
Reactivity	Generally more reactive	Less reactive toward addition reactions
Examples	Ethane (C_2H_6), Propene (C_3H_6), Butyne (C_4H_6)	Benzene (C_6H_6), Toluene (C_7H_8)

ii) **Homolytic and Heterolytic Fission**

Feature	Homolytic Fission	Heterolytic Fission
Bond breaking	Bond breaks evenly	Bond breaks unevenly
Electron distribution	Each atom gets one electron	One atom gets both bonding electrons
Produces	Free radicals	Ions (cation and anion)
Occurs in	Non-polar solvents or under high energy (e.g. UV light)	Polar solvents or in presence of electrophiles/nucleophiles
Example	$Cl-Cl \rightarrow Cl^{\cdot} + Cl^{\cdot}$	$H-Cl \rightarrow H^+ + Cl^-$

iii) **Electrophile and Nucleophile**

Property	Electrophile	Nucleophile
Definition	Electron-deficient species	Electron-rich species
Electron behavior	Accepts electron pairs	Donates electron pairs
Charge	Often positively charged or neutral	Often negatively charged or neutral
Affinity	Attracted to electron-rich centers	Attracted to electron-deficient centers
Role in reactions	Acts as a Lewis acid	Acts as a Lewis base
Examples	H^+, NO_2^+, $AlCl_3$, BF_3	OH^-, NH_3, Cl^-, CN^-

c. Explain why alkanes do not undergo addition reactions.

Ans. **Alkanes do not undergo addition reactions because:**

- **They are saturated hydrocarbons**, meaning all carbon-carbon bonds are **single (σ) bonds.**
- **These σ-bonds are strong and stable, and there are no regions of high electron density like double or triple bonds for an electrophile to attack.**
- **Addition reactions typically occur with unsaturated compounds (like alkenes or alkynes), which have π-bonds that are more reactive.**

In short, Alkanes lack π-bonds, making them chemically inert toward addition reactions and more likely to undergo substitution reactions instead.

d. How elimination reaction is considered the opposite of an addition reaction.

Ans. An elimination reaction is considered the opposite of an addition reaction because:

- **In an addition reaction, atoms or groups are added to a molecule, typically converting a double or triple bond into a single bond.**
- **In an elimination reaction, atoms or groups are removed from a molecule, typically forming a double or triple bond from a single bond.**

Alkanes do not undergo elimination reactions under normal conditions because:

- **Elimination reactions require a molecule to have a leaving group (like –OH, –Br, –Cℓ) on one carbon and a β-hydrogen (on an adjacent carbon).**
- **Alkanes consist of only C–C and C–H single bonds and do not have good leaving groups naturally.**
- **They are also non-polar and chemically stable, making it hard to break bonds without strong reagents or high energy.**

In short, Alkanes lack both the leaving groups and reactive centres needed for elimination, so they do not undergo elimination reactions unless first converted to more reactive derivatives (like alkyl halides).

e. Compare the carbocation stability in propene and 2-butene.

Ans.

(i) Propene (CH_3–CH=CH_2)

- **If a proton is removed from the double bond, the most likely carbocation formed is the allyl carbocation (CH_2 = CH–CH_2^+).**
- **This allylic carbocation is resonance-stabilized, meaning the positive charge is delocalized over two carbon atoms.**
- **Stability: Relatively stable due to resonance.**

(ii) 2-Butene (CH_3–CH = CH–CH_3)

- **Ionization typically leads to a secondary carbocation (CH_3–C^+H–CH=CH_3).**
- **There is no resonance stabilization unless rearrangement occurs.**
- **Stability: Less stable than the allylic carbocation of propene.**

f. Given the molecular formula C_5H_{10}, list all possible structural isomers that are alkenes.

Ans. C_5H_{10} Alkene Isomers:

(i) Pent-1-ene
CH_2=CH–CH_2–CH_2–CH_3

(ii) Pent-2-ene
CH_3–CH=CH–CH_2–CH_3

(iii) 2-Methylbut-1-ene
CH_2=C(CH_3)–CH_2–CH_3

(iv) 3-Methylbut-1-ene
CH_2=CH–CH(CH_3)–CH_3

(v) 2-Methylbut-2-ene
CH_3–C(CH_3)=CH–CH_3

g. When propene (C_3H_6) undergoes electrophilic addition with HBr, it forms 2-bromopropane as the major product. Explain why 2-bromopropane is favored over 1-bromopropane, using the concept of carbocation stability.

Ans. When propene (CH_3–CH=CH_2) reacts with HBr, the reaction proceeds via an electrophilic addition mechanism. The major product is 2-bromopropane, and this can be explained using carbocation stability:

Explanation:

1. **Electrophilic attack:**
   The π electrons of the double bond attack the H^+ from HBr.
   This can lead to two possible carbocations:
   - Path A (less stable): H^+ adds to the CH_2 end, forming a primary carbocation (CH_3–CH–CH_2^+)
   - Path B (more stable): H^+ adds to the CH end, forming a secondary carbocation (CH_3–C^+H–CH_3)
2. **Carbocation stability:**
   - Primary carbocations are less stable
   - Secondary carbocations are more stable due to hyperconjugation and inductive effects from surrounding alkyl groups
3. **Nucleophilic attack:**
   - Br^- then attacks the more stable secondary carbocation, leading to 2-bromopropane.

Conclusion:
2-bromopropane is the major product because its formation proceeds through a more stable secondary carbocation, following Markovnikov's rule.

h. Explain why conjugated alkenes may show different reactivity compared to isolated alkenes.

Ans. Conjugated alkenes show different reactivity compared to isolated alkenes due to delocalization of π-electrons across alternating double and single bonds.

Aspect	Conjugated Alkenes	Isolated Alkenes
Structure	Alternating double and single bonds.	Double bonds separated by two or more single bonds.
Electron delocalization	π-electrons are delocalized across the system.	π-electrons are localized between two atoms.
Stability	More stable due to resonance.	Less stable.
Reactivity	Can undergo special reactions (e.g. 1, 4-addition).	React through normal electrophilic addition only.
UV/Visible absorption	Often absorb at longer wavelengths.	Less likely to absorb in the visible range.

i. Explain how inductive effects from alkyl groups stabilize carbocations in alkenes.

Ans. Inductive effects from alkyl groups help stabilize carbocations in alkenes by donating electron density through sigma (σ) bonds toward the positively charged carbon.

- Carbocations are electron-deficient species (positively charged carbon).
- Alkyl groups (like $–CH_3$ or $–CH_2CH_3$) have a slight electron-releasing character.
- Through the inductive effect, they push electron density toward the carbocation, reducing its positive charge and making it more stable.

Relative stability of carbocations due to inductive effects:

- **Tertiary carbocation** (3 alkyl groups) → Most stable
- **Secondary carbocation** (2 alkyl groups)
- **Primary carbocation** (1 alkyl group)
- **Methyl carbocation** (no alkyl groups) → Least stable

j. Write the equation for each reaction.

i. $CH_3CH_2CH = CH_2$ with H_2 (Ni catalyst)

ii. $CH_3CH = CH_2$ with $C\ell_2$

iii. $CH_3CH_2CH = CHCH_2CH_3$ with H_2O(H_2SO_4 catalyst)

Ans.

i. $CH_3CH_2CH = CH_2$ with H_2 (Ni catalyst)

This is a hydrogenation reaction of an alkene.

$$CH_3CH_2CH = CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_2CH_3$$

ii. $CH_3CH = CH_2$ with $C\ell_2$

This is an electrophilic addition of chlorine to an alkene.

$$CH_3CH = CH_2 + C\ell_2 \longrightarrow CH_3CHC\ell CH_2C\ell$$

iii. $CH_3CH_2CH = CHCH_2CH_3$ with $H_2O(H_2SO_4$ catalyst)

It is Hydration of hex-2-ene with H_2O in the presence of H_2SO_4 catalyst

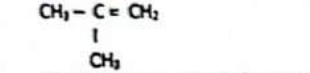
$$CH_3CH_2CH = CHCH_2CH_3 + H_2O \xrightarrow{H_2SO_4} CH_3CH_2CH(OH) - CH_2CH_2CH_3$$

k. Write structural formulas for each of the following compounds.

(i) Isobutylene (ii) 2,3,4,4-Tetramethyl-2-pentene (iii) 2,5-Heptadiene
(iv) 4,5-Dimethyl-2-hexene (v) Vinyl acetylene (vi) 1,3-Pentadiene
(vii) 1-Butyne (viii) 3-n-Propyl-1,4-pentadiene (ix) Vinyl bromide
(x) But-1-en-3-yne (xi) 4-Methyl-2-pentyne (xii) Isopentane

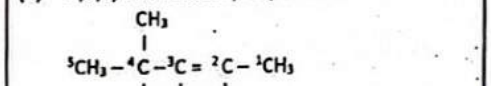
Ans. Structural Formulae

(i) Isobutylene

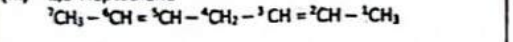


(IUPAC Name = 2-Methylpropene)

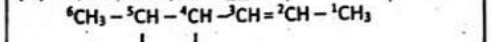
(ii) 2,3,4,4-Tetramethyl-2-pentene



(iii) 2,5-Heptadiene



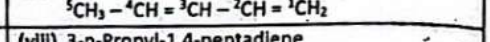
(iv) 4,5-Dimethyl-2-hexene



(v) Vinyl acetylene



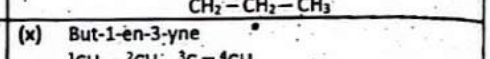
(vi) 1,3 – Pentadiene



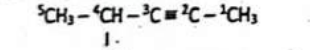
(vii) 1-Butyne



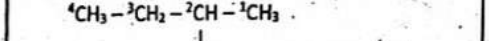
(viii) 3-n-Propyl-1,4-pentadiene



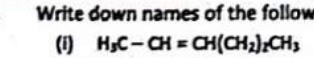
(ix) Vinyl bromide



(x) But-1-en-3-yne



(xi) 4-Methyl-2-pentyne



(xii) Isopentane



l. Write down names of the following compounds according to IUPAC-System.

(i) $H_3C - CH = CH(CH_2)_2CH_3$ (ii) $(CH_3)_2C = CH_2$

(iii) $CH_3 - CH_2 - CH_2 - C = CH_2$ (iv) $CH_2 = CH - CH = CH_2$

$CH(CH_3)_2$

(v) $CH_2 = C - CH_2CH_2CH_3$ (vi) $(CH_3CH_2)_3CH$

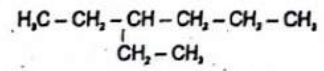
C_2H_5

(vii) $CH_3CH_2C(CH_3)2CH(CH_2CH_3)CH_3$ (viii) $CH_2 = CH - C \equiv C - CH = CH_2$

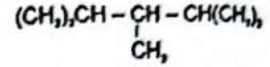
(ix) $(CH_3)_3C - CH_2 - C(CH_3)_3$ (x) $CH_2 = CH - C \equiv CH$

(xi) $CH_3C(CH_3)_2(CH_2)CH_3$

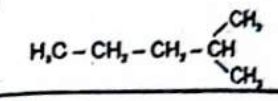
(a)



(b)

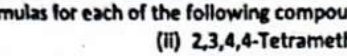


(c)



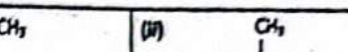
Ans. IUPAC Names

(i)



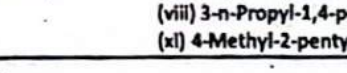
2-Hexene

(ii)



2-Methylpropene

(iii)



2-Isopropyl-1-pentene

(iv)

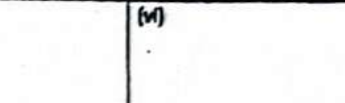


1,3-Butadiene

(v)

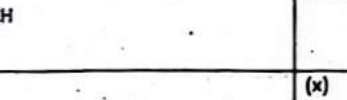
2-Ethyl-1-pentene

(vi)



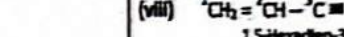
3-Ethylpentane

(vii)



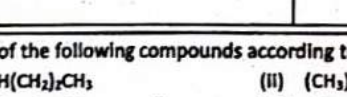
3,3,4-Trimethylhexane

(viii)



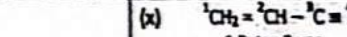
1,5-Hexadien-3-yne

(ix)



2,2,4,4 - tetramethylPentane

(x)



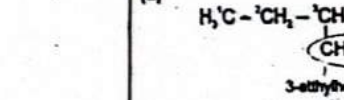
1-Buten-3-yne

(xi)



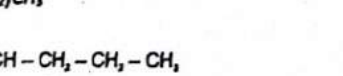
2,2 - dimethylbutane

(a)



3-ethylhexane

(b)



2, 3, 4 - trimethylpentane

(c)



2-MethylPentane

DESCRIPTIVE QUESTIONS

Q.3 Describe the free radical halogenation of methane using Cl_2 as an example.

Ans. See Page No. (385)

Q.4 Describe the following methods for the preparation of alkenes:
i) Dehydrohalogenation of alkyl halides ii) Dehydration of alcohols

Ans. See Page No. (389)

Q.5 Describe the mechanism of electrophilic addition of hydrogen halides to alkenes. Discuss Markovnikov's Rule in the context of hydrogen halide addition.

Ans. See Page No. (395)

Q.6 Explain the following reactions of alkenes with examples:
a) Halogenation b) Ozonolysis c) Epoxidation d) Polymerization

Ans. See Reactions of Alkenes (Point No. 1, 7, 6, 8) in theory.

ADDITIONAL SLOs BASED MCQs

1. The most likely reaction alkanes undergo is:
A. electrophilic addition B. free radical substitution
C. nucleophilic addition D. electrophilic substitution

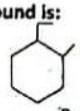
2. The condensed structural formula of the major product obtained by hydrobromination of 2-methylpent-2-ene is:
A. $CH_3CH(Br)CH(CH_3)CH_2CH_3$ B. $(CH_3)_2C(Br)(CH_2)_2CH_3$
C. $(CH_3)_2CHCH(Br)CH_2CH_3$ D. $CH_2(Br)CH(CH_3)(CH_2)_2CH_3$

3. Which one of the following is a possible propagation step in chlorination of ethane?
A. $C_2H_6 + Cl \rightarrow C_2H_5Cl + H$ B. $C_2H_5Cl + Cl \rightarrow C_2H_4Cl + HCl$
C. $C_2H_5 + Cl \rightarrow C_2H_5Cl$ D. $C_2H_4Cl_2 + Cl \rightarrow C_2H_4Cl + Cl_2$

4. Which one of the following is the most stable (least reactive) hydrocarbon?
A. hex-1-ene B. propene C. penta-1,2-diene D. hepta-1,3,5-triene

5. The most striking factor held responsible for the less reactivity of alkanes is:
I. their non-polar bonds II. absence of functional group
III. their strong sigma (δ) bonds IV. Long C – C bond lengths
A. I &II only B. II & III only C. I, II & III only D. III & IV only

6. The systematic name of the following compound is:



A. 2-ethylmethylcyclohexane B. 2-methyethylcyclohexane
C. 1-ethylmethylcyclohexane D. 1-ethyl-2-methylcyclohexane

7. Dehydration of propan-1-ol gives:
A. propene B. propane C. propanone D. propanal

8. Which one of the following compounds can show geometric isomerism?
A. 2,2-dimethylbut-2-ene B. 2-methylhex-1-ene C. hex-3-ene D. 2-methylpropene

9. A racemic mixture must contain:
A. 90 levorotatory isomers
B. equimolar quantities of levorotatory and dextrorotatory isomers
C. meso isomers and levorotatory isomers
D. 80 dextrorotatory and 20% levorotatory isomers

10. Which set of compounds are consecutive members of same homologous series?
A. CH_3OH, CH_3CHO, HCHO B. CH_3COOH, C_2H_5COOH, C_3H_7COOH
C. CH_4, CH_2Cl, CH_2Cl_2 D. C_2H_2, C_2H_4, C_2H_6

11. The molecule of ethane possesses which hybridization;
A. sp^3 B. sp^2 C. sp D. sp^3d

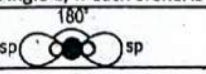
12. The sp^2 hybrid orbitals are oriented in space at one angle;
A. 109.5° B. 180° C. 100° D. 120°

13. The geometry of acetylene is:
A. angular B. bent C. trigonal D. linear

14. Which reaction is used as test for the presence of alkene;
A. reaction of cold diluted alkaline $KMnO_4$ B. combustion
C. polymerization D. catalytic hydrogenation

15. The general formula of alkane is;
A. C_nH_{2n-2} B. C_nH_n C. C_nH_{2n} D. C_nH_{2n-2}

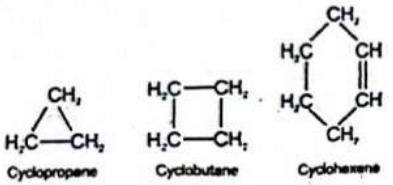
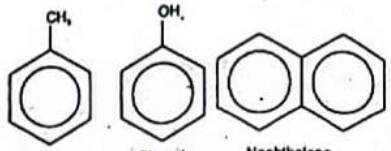
Answer Key with Explanations

Sr. #	Ans.	Explanations
1.	B	Alkanes are most likely to undergo free radical substitution reactions, such as the chlorination and bromination of alkanes, which involve the formation of free radicals.
2.	C	The hydrobromination of 2-methylpent-2-ene follows Markownikov's rule, where the bromine atom attaches to the more substituted carbon atom, resulting in 3-bromo-2-methylpentane.
3.	C	During the chlorination of ethane, a propagation step involves the ethyl radical (C_2H_5) reacting with a chlorine atom to form chloroethane (C_2H_5Cl).
4.	B	Stability decreases with increasing number of double bonds and conjugation. Propene, with a single double bond, is more stable than dienes or trienes.
5.	C	Alkanes are less reactive due to their non-polar bonds, absence of functional groups, and strong sigma bonds.
6.	D	The correct IUPAC name indicates the substituents' positions and follows the alphabetical order of naming.
7.	A	Dehydration of propan-1-ol results in the formation of propene through the elimination of water.
8.	C	Geometric isomerism (cis-trans) can occur in compounds with double bonds that have different substituents on each carbon of the double bond. Hex-3-ene fits this criterion.
9.	B	A racemic mixture contains equal amounts of both enantiomers, which cancel out each other's optical activity.
10.	B	These compounds are carboxylic acids and differ by a CH_2 unit, fitting the definition of a homologous series.
11.	A	In ethane, there is C – C so each carbon is sp^3 hybridized.
12.	D	Angle b/w each orbital is 120°.
13.	D	
14.	A	When alkenes are treated with mild oxidizing reagents like dilute (1%) alkaline $KMnO_4$ solution (Baeyer's Reagent) at low temperature, hydroxylation of double bond occurs resulting in the formation of dihydroxy compounds known as vicinal glycols. The pink colour of $KMnO_4$ solution is discharged during the reaction.
15.	A	The general formula of alkane is C_nH_{2n+2}.

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Differentiate between Alicyclic and Aromatic compounds.

Ans.

Alicyclic Compounds	Aromatic Compounds
• The homocyclic compounds which contain ring of three or more carbon atoms and resembling the aliphatic compounds are called alicyclic compounds.	• The homocyclic compounds which contain atleast one benzene ring are called aromatic compounds.
• They may be saturated or unsaturated.	• They may contain one or more benzene rings.
• They have low percentage of carbon.	• They have high percentage of carbon.
Examples:  Cyclopropane, Cyclobutane, Cyclohexane	**Examples:**  Toluene, Phenol, Naphthalene

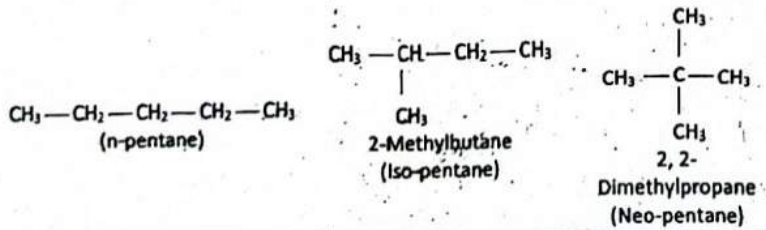
Q.2 Define the term isomerism. Give examples.

Ans. Isomerism:

"Two or more compounds having the same molecular formula but different structural formulas and properties are said to be isomers and the phenomenon is called isomerism."

Examples:

C_5H_{12}:



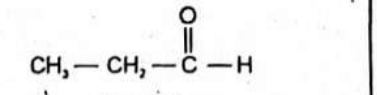
$CH_3-CH_2-CH_2-CH_2-CH_3$ (n-pentane)

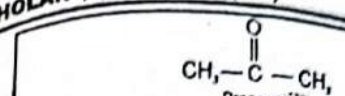
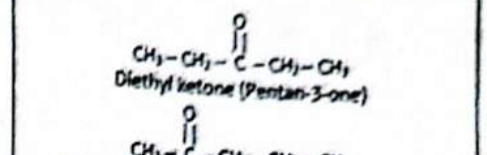
$CH_3-CH(CH_3)-CH_2-CH_3$ 2-Methylbutane (Iso-pentane)

$C(CH_3)_4$ 2, 2-Dimethylpropane (Neo-pentane)

Q.3 How functional group isomerism differs from metamerism? Give examples.

Ans.

Functional Group Isomerism	Metamerism
• The compounds having the same molecular formula but different functional groups are said to exhibit functional group isomerism.	• This type of isomerism arises due to the unequal distribution of carbon atoms on either side of the functional group.
• Such compounds belong to different homologous series.	• Such compounds belong to the same homologous series.
Examples: C_3H_6O:  Propanal	**Example:** $C_4H_{10}O$: $CH_3-CH_2-O-CH_2-CH_3$ Diethyl ether; $CH_3-O-CH_2-CH_2-CH_3$ Methyl-n-propyl ether

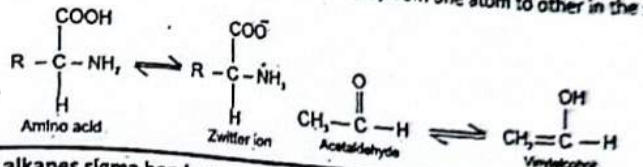
C_3H_6O:  Propanone; $CH_3CH_2-CH_2-OH$ 1-Propanol; $CH_3-O-CH_2-CH_3$ Methoxy Ethane	$C_5H_{10}O$:  Diethyl ketone (Pentan-3-one); Methyl-n-propyl ketone (Pentan-2-one)

Q.4 Define Tautomerism with an example.

Ans. Tautomerism:

This type of isomerism arises due to shifting of proton (H^+) from one atom to other in the same molecule.

Examples:



Amino acid ⇌ Zwitter ion; Acetaldehyde ⇌ Vinylalcohol

Q.5 Justify that in alkanes sigma bonds are inert.

Ans. Inertness of σ-bond:

In a σ–bond, the electrons are very tightly held between the two nuclei which makes it a very stable bond. A lot of energy is required to break it. Moreover, the electrons present in a σ–bond can neither attack on any electrophile nor a nucleophile can attack on them. Due to the inertness of σ–bonds, alkanes are unreactive.

Q.6 Why alkanes are called paraffins?

Ans. Alkanes are Paraffins:

The word "paraffins" is derived from Latin words 'parum' = little, 'affins' = affinity. Alkanes are called paraffins due to:

(i) Non-polar Nature:

The electronegativity values of carbon (2.5) and hydrogen (2.1) do not differ appreciably and the bonding electrons between C – H and C – C are equally shared making them almost non-polar. In view of this, the ionic reagents such as acids, alkalies, oxidizing agents, etc. find no reaction site in the alkane molecules to which they could be attached.

(ii) Inertness of σ-bond:

In a σ – bond, the electrons are very tightly held between the nuclei which makes it a very stable bond. A lot of energy is required to break it. Moreover, the electrons present in a σ – bond can neither attack on any electrophile nor a nucleophile can attack on them.

Q.7 Differentiate between hydrogenolysis and hydrogenation.

Ans.

Hydrogenolysis	Hydrogenation
1. The addition of hydrogen accompanied by bond cleavage is called hydrogenolysis."	1. The addition of hydrogen to an unsaturated compound in the presence of a catalyst is called hydrogenation."
2. It is carried out in Pd-charcoal cavity.	2. It is carried out in the presence of Ni, Pt or Pd etc.
Examples: (i) $R-X+H-H \xrightarrow[\Delta]{Pd-Charcoal} R-H + HX$ Alkane; (ii) $CH_3-Cl+H-H \xrightarrow[\Delta]{Pd-Charcoal} CH_4+HCl$	**Examples:** (i) $CH_2=CH_2+H_2 \xrightarrow[200°C]{Ni} CH_3-CH_3$ Ethene → Ethane; (ii) Vegetable oil $+H_2 \xrightarrow[200°C]{Ni}$ vegetable Ghee

Q.8 Give general mechanism of electrophilic addition reactions of alkene.

Ans. General Mechanism of Electrophilic Addition Reactions of Alkene:

It involves three steps:

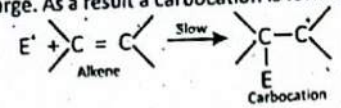
Step 1: To Generate Electrophile:

The reagent E – Nu ionizes to give an electrophile and nucleophile.

$$E - Nu \longrightarrow E^{+} + :Nu^{-}$$

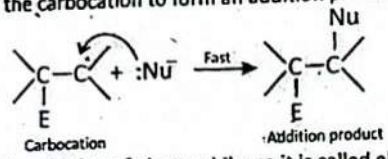
Step 2: Attack of Electrophile and Formation of Carbocation:

The electrophile attacks the carbon – carbon double bond and forms a covalent bond with one carbon and other carbon bears positive charge. As a result a carbocation is formed.



Step 3: Attack of Nucleophile:

The nucleophile now attacks the carbocation to form an addition product.



Since the reaction is initiated by addition of electrophile, so it is called electrophilic addition reaction.

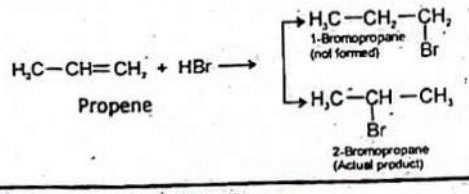
Q.9 What is Markownikov's rule? Give example also.

Ans. Markownikov's Rule:

Statement:

"In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, constituting the double bond, which has least number of hydrogen atoms."

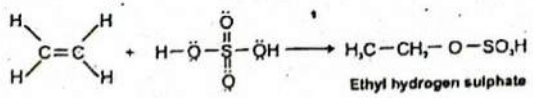
Example:



Q.10 How would you convert ethene into ethyl alcohol?

Ans. Conversion of Ethene into Ethyl Alcohol:

When ethene is treated with cold concentrated sulphuric acid (H_2SO_4), it is dissolved because it forms ethyl hydrogen sulphate.



The ethyl hydrogen sulphate on boiling with water decomposes to give ethyl alcohol.

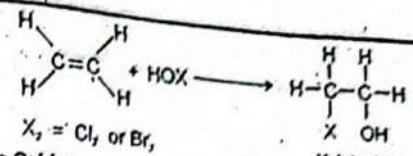
$$H_3C-CH_2-O-SO_3H + H_2O \xrightarrow{100^{\circ}C} H_3C-CH_2-OH + H_2SO_4$$

Q.11 Convert ethene to (a) Halohydrin (b) Ethylene oxide

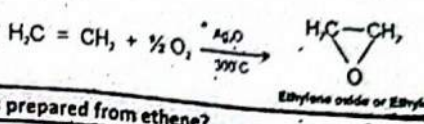
Ans. (a) Ethene to Halohydrin:

If the halogenation of an alkene is carried out in an aqueous solution, haloalcohol is formed called a Halohydrin. In this reaction, molecules of the solvent become reactants too.

$$X_2 + H_2O \longrightarrow HOX + HX$$



(b) Ethene to Ethylene Oxide:



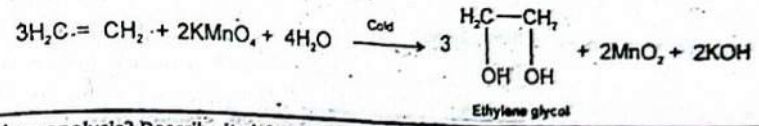
Q.12 How Ethylene Glycol is prepared from ethene?

Ans. Baeyer's Test:

- Dilute 1% alkaline $KMnO_4$ solution is called Baeyer's reagent.
- It is pink in colour and acts as mild oxidizing agent.
- Baeyer's reagent is used to test the presence of unsaturation in the molecules.

Reaction:

When alkenes are treated with Baeyer's reagent at low temperature, hydroxylation of double bond occurs resulting in the formation of dihydroxy compounds known as vicinal glycols. The pink colour of $KMnO_4$ is discharged during the reaction.



Q.13 What is ozonolysis? Describe it giving example. Also give its mechanism.

Ans. Ozonolysis:

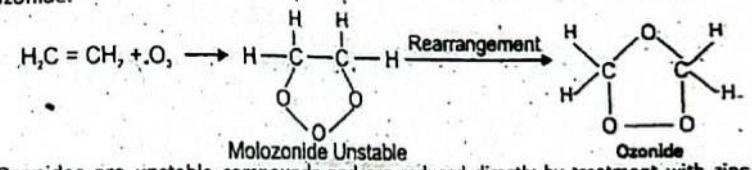
"The cleavage of an unsaturated molecule by reacting with ozone is called ozonolysis."

Ozone (O_3) is a highly reactive allotropic form of oxygen. It reacts vigorously with ethene (or other alkenes) to form formaldehyde (or other carbonyl compounds.)

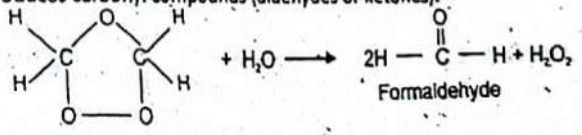
$$CH_2=CH_2 + O_3 \xrightarrow{Zn} 2HCHO$$

Mechanism:

(i) Ozone reacts with ethene to form molozonide. Molozonoide rearranges spontaneously to form an ozonide.



(ii) Ozonides are unstable compounds and are reduced directly by treatment with zinc and H_2O. The reduction produces carbonyl compounds (aldehydes or ketones).



$$Zn + H_2O_2 \longrightarrow ZnO + H_2O$$

◆◆◆◆◆

SELF-ASSESSMENT Chapter # 11

Total Mark: 30

Q.1 . Encircle the correct option. (1 × 6 = 6)

(i) What intermediate is formed during the electrophilic addition of HBr to an alkene?
A. Carbocation B. Carbanion C. Radical D. Epoxide

(ii) Markownikov's rule is applicable to :
A. $CH_2 = CH_2$ B. $CH_3 - CH_2 - CH_3$ C. $CH_3 - CH = CH - CH_3$ D. $(CH_3)_2 - C = CH_2$

(iii) Which of the following reagents is typically used for the acid-catalyzed hydration of alkenes to form alcohols?
A. H_2/Ni B. O_3 followed by Zn/H_2O C. Dilute H_2SO_4 D. Br_2 in CCl_4

(iv) Alkanes are generally unreactive toward polar reagents because:
A. They have double bonds B. They are aromatic
C. Their bonds are non-polar D. They are ionic

(v) An alkene undergoes ozonolysis followed by reduction with zinc dust and water to yield propanone and methanal. The alkene is:
A. 1-Butene B. 2-Butene C. 2-Methylpropene D. 2-Methyl-2-butene

(vi) What type of isomerism exists in but-2-ene?
A. Chain B. Geometrical C. Functional D. Position

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) Differentiate between aliphatic and aromatic hydrocarbons with one example each.
(ii) Write the IUPAC name of the following:
a) $CH_2 = CH - CH = CH_2$ b) $CH \equiv C - CH = CH - C \equiv CH$
(iii) Why do branched alkanes have lower boiling points than the straight-chain alkanes?
(iv) What is homolytic and heterolytic bond fission?
(v) Why the order of stability of carbocation is $3^\circ > 2^\circ > 1^\circ$?
(vi) Write down the structural formulas for 2-methylbutane and 2, 2-dimethylpropane.
(vii) Give the dehydrohalogenation reaction of bromopropane?
(viii) Given the molecular formula C_5H_{10}, list all possible structural isomers that are alkenes.

Q.3 Extensive Questions. (2 × 4 = 8)

(a) Explain the following reactions of alkenes with examples:
a) Halogenation b) Ozonolysis c) Polymerization
(b) Describe the free radical halogenation of methane using Cl_2 as an example.

Chapter 12 NITROGEN AND SULPHUR

Student Learning Outcomes

After studying this chapter, students will be able to:

- Explain the lack of reactivity of nitrogen due to its triple bond strength and lack of polarity. **(Understanding)**
- Describe the basicity of ammonia using the Bronsted-Lowery theory. **(Understanding)**
- Identify the structure of the ammonium ion and explain how it is formed by an acid-base reaction. **(Understanding)**
- Describe how ammonia can be displaced from ammonium salts through an acid-base reaction. **(Understanding)**
- Describe natural and man-made occurrences of oxides of nitrogen and their catalytic removal from exhaust gases of internal combustion gases. **(Understanding)**
- Explain the role of NO and NO_2 in the formation of photochemical smog, specifically in th ion with unburned hydrocarbons to form peroxyacetyl nitrate (PAN). **(Understanding)**
- Differentiate between nitrification and de-nitrification. **(Knowledge)**
- Explain the lack of reactivity of sulfur, with reference to its bonding and stability of its compounds. **(Understanding)**
- Describe the different oxidation states of sulfur and their relative stability. **(Understanding)**
- Describe the properties and uses of sulfuric acid, including its production and industrial applications. **(Understanding)**
- Describe the chemical reactions and processes involving sulfur, such as combustion and oxidation. **(Understanding)**
- Explain the uses of sulfur compounds in industry and everyday life, such as in fertilizers, gunpowder, and rubber, and in synthetic organic chemistry, including the synthesis of dyes, drugs, and fragrances. **(Understanding)**

NITROGEN

➢ **Occurrence:**
Nitrogen belongs to group 15 of the periodic table.

➢ **Preparation:**

(i) In industrial processes, nitrogen is typically obtained by cooling air until it becomes a liquid. Liquid nitrogen is commonly used for rapid cooling purposes.

(ii) In laboratory settings, nitrogen can be generated by slowly heating a solution of ammonium nitrite.

$$NH_4NO_{2(aq)} \xrightarrow{\Delta} N_{2(g)} + 2H_2O_{(\ell)}$$

Table: Physical Properties of Nitrogen ($_7N^{14}$)

Atomic number	7	Ionic radius (3-)	171 pm
Relative atomic mass	14.007 Da	1st Ionization energy	1402 kJ/mol
Physical appearance	Colourless Gas	Electronegativity	3.0
Electronic configuration	$[He]2s^2 2p^3$	Electron affinity	−8.0 kJ/mol
Melting point	−210°C	Density	0.001145 g/cm³
Boiling point	−195.8°C	Principal oxidation states	3+ and 5+
Covalent radius	74 pm		

REACTIVITY OF NITROGEN (N_2)

Reasons for Inertness of Nitrogen

Nitrogen is a significant component of the air, known for its low reactivity due to its small size, symmetrical electronic cloud, and nonpolar triple bond.

Rack Your Mind!

1. Summarize the reasons for inertness of nitrogen.

(i) High bond Energy

- Nitrogen has electronic configuration of $1s^2 2s^2 2p^3$.
- Nitrogen requires three electrons to complete its octet, forming a triple bond by sharing the electrons with another nitrogen atom (as shown in Figure). The bond has a bond enthalpy of +944 kJ mol^{-1}. High energy is required to break this bond to form new bonds, making N_2 very unreactive.

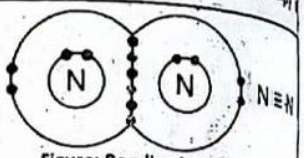


Figure: Bonding in N_2 molecule

(ii) Non-Polar Nature of N_2

- N≡N is nonpolar.
- Both the atoms are the same having zero electronegativity difference. This causes equal sharing of the three bonded electrons between the two atoms making the bond nonpolar.

Interesting Information!

Uses of Nitrogen:

(i) The high concentration of nitrogen in the air serves to dilute oxygen, preventing every spark in our atmosphere from igniting a massive fire.
(ii) In the case of large shipments of hydrocarbons or edible oils, it is crucial to utilize blankets of Nitrogen or any other inert gas on ships to safeguard them from oxygen and moisture.
(iii) It is also used in laboratory to carry out the reactions which require inert atmosphere.

AMMONIA (NH_3)

Exercise Q.1

Q. Explain the preparation and basicity of ammonia.

Preparation of Ammonia:

- Ammonia (NH_3) is an important industrial compound of nitrogen, which is mainly used as a fertilizer.
- Ammonia is prepared industrially by Haber-Bosch process.

$$N_{2(g)} + 3H_{2(g)} \overset{\Delta}{\rightleftharpoons} 2NH_{3(g)}$$

Q. Ammonia behaves as a Lowry Bronsted base. Explain.

Basicity of Ammonia

Ammonia behaves as a Lowry-Bronsted base by accepting a proton (H^+) from an acid to form ammonium ion.

$$NH_{3(aq)} + H^+_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)}$$

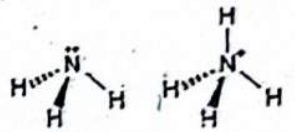
Ammonia dissolves in water to form ammonium hydroxide (NH_4OH) and equilibrium is established between ammonia molecules and ammonium ions in the solution.

$$NH_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons NH_{4(aq)}^+ + OH_{(aq)}^- \qquad K_b = 1.8 \times 10^{-5}$$

Ammonia solution is a weak base due to the low basicity constant (K_b) and the equilibrium position being towards the far left side.

Structure of Ammonium (NH_4^+)

Ammonia molecule has pyramidal shape due to lone pair of nitrogen. But when nitrogen atom in ammonia utilizes this lone pair of electrons to form ammonium ion, this ion adopts a tetrahedral shape in which all the bonds are of equal length and strength, (as depicted in Figure).


Figure: Pyramidal and tetrahedral shapes of ammonia and ammonium

Synthesis of Ammonia from Ammonium Salts

Preparation of Ammonia

- **In Laboratory:**

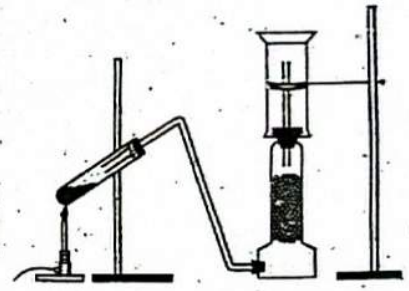
In the laboratory, ammonia gas can be synthesized by heating an ammonium salt such as ammonium chloride ($NH_4Cℓ$) with a base like calcium hydroxide ($Ca(OH)_2$) as shown in Figure.

$$2NH_4Cℓ_{(s)} + Ca(OH)_{2(aq)} \longrightarrow CaCℓ_{2(aq)} + 2H_2O_{(ℓ)} + 2NH_{3(g)}$$

In this acid-base reaction, NH_4^+ acts as an acid by donating H^+ ions, while OH^- acts as a base by accepting H^+ ions. This reaction displaces ammonia gas from the ammonium salt and produces salt and water.

- **Use in Salt Analysis:**

It is commonly used to identify ammonium in salt analysis. If a gas with a pungent smell is released and turns moistened red litmus paper blue, it indicates the presence of ammonium in the compound.


Figure: Synthesis of ammonia gas

QUICK CHECK 12.1

a) Why N_2 gas is used in food packaging?

Ans. N_2 gas is used in food packaging because it is inert and prevents oxidation and bacterial growth. By replacing oxygen (O_2) inside the package, N_2 slows down spoilage and keeps food fresh for longer. It is especially useful for snacks, chips, and ready-to-eat meals to maintain crispness and flavor.

b) Both CO and N_2 have triple bonds in their molecules. Why do you think CO is more reactive than N_2?

Ans. Although both CO and N_2 have triple bonds, CO is more reactive because:

- The bond is slightly weaker (bond energy 1072 kJ/mol as compared to bond energy of N_2 which is 946 kJ/mol).
- CO has a polar structure (C slightly positive, O slightly negative), making it more likely to react with other molecules compared to nonpolar N_2.

c) Ammonium salts such as $(NH_4)_2SO_4$ or $(NH_4)_2NO_3$ are commonly used as fertilizers. Why a farmer wouldn't treat a field with an ammonium fertilizer at the same time as using lime? What would be the chemical reactions?

Ans. Ammonium fertilizers like $(NH_4)_2SO_4$ react with lime ($Ca(OH)_2$ or CaO) to release ammonia gas (NH_3), reducing nitrogen content in the soil:

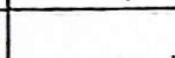
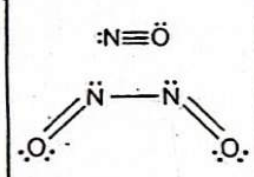
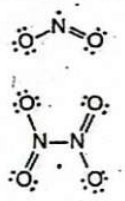
$$2NH_4^+ + Ca(OH)_2 \longrightarrow 2NH_3\uparrow + Ca^{2+} + 2H_2O$$

This reaction makes the fertilizer less effective and causes nitrogen loss, harming crop growth.

OXIDES OF NITROGEN

Oxides of nitrogen are NO, N_2O, NO_2, N_2O_4 and N_2O_5 in which oxidation states range from 1+ to V+. N_2O_4 and N_2O_5 decay quickly to other oxides. NO and NO_2 are collectively called as NO_x. The structures, properties and uses of these oxides are given in Table.

Table: Properties of some common oxides of nitrogen

Name and formula of oxide	Structure	Formal oxidation state	Properties	Uses
Nitrous oxide/ Nitrogen oxide (Laughing gas) N_2O		1+	Colourless gas, water-soluble, neutral, sweet smelling, helps in combustion.	Dental anaesthetic, propellant for whipped ice cream, synthesis of NaN_3.
Nitic oxide, Nitrogen dioxide NO, N_2O_2		2+	Colourless gas, slightly water-soluble, neutral, NO is paramagnetic while N_2O_2 is diamagnetic, oxidizing as well as reducing in nature.	Biochemical messenger (Lowers blood pressure and role in other body functions), synthesis of nitrosyl carbonyls.
Nitrogen dioxide/Nitrogen peroxide, Nitrogen tetraoxide NO_2, N_2O_4 $2NO_2 \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} N_2O_4$ (Brown / Colourless)		4+	NO_2 is a reddish brown gas, paramagnetic, and reacts with water to form HNO_3 and HNO_2, N_2O_4 is colourless liquid or solid.	Rocket propellant, HNO_3 formation by Ostwald process, explosives.

Did You Know?

Name of Ammonia by IUPAC:
Another recommended name for ammonia by the International Union of Pure and Applied Chemistry (IUPAC) is Azane and for ammonium is Azanium. These names have been derived from Azote, a Greek name for nitrogen, meaning "no life". These names are used in naming derivatives of ammonia and ammonium e.g. sodium azide (NaN_3).

Rack Your Mind!

2. Peroxy acetyl nitrate (PAN) is an irritant to human being and it effects:
A) Ears B) Stomach
C) Eyes D) Nose

SOURCES OF OXIDES OF NITROGEN

The main categories of NO_x sources are:

Natural Sources of NO_x

Natural sources include lightning, volcanoes, biological decay, forest fires, soil microorganisms, oceans, etc. NO is produced when N_2 and O_2 in the air react during lightning. It is produced by microorganism using air N_2.

Anthropogenic (Man-made) Sources of NO_x

The main anthropogenic sources of NO_x are the combustion of fossil fuels in vehicles and power plants. Other sources include chemical plants, biomass burning, welding, etc.

ROLE OF NO & NO_2 IN SMOG & PAN FORMATION

Exercise 12.4

Q. How oxides of nitrogen (NO_x) cause the formation of photochemical smog and PAN? Give its mechanism.

NO_x is responsible for numerous harmful effects on living organisms.

Photochemical Smog

Photochemical smog (Los Angeles smog) forms in the atmosphere from NO_x and volatile organic compounds (VOCs) in the sunlight. It is oxidizing in nature. Photochemical oxidants, such as NO_2, ozone, and peroxyacyl nitrates (PANs) can react and oxidise specific compounds in the atmosphere. Photochemical smog is becoming more common than classical smog (London smog) due to increasing NO_x emissions.

Chemical Reactions:

The formation of photochemical smog involves the following chemical reactions.

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$$

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

$$NO_{2(g)} \xrightarrow{h\upsilon} NO_{(g)} + O_{(g)}$$

$$O_{(g)} + O_{2(g)} \longrightarrow O_{3(g)}$$

$$RCH{=}CHR_{(g)} + O_{3(g)} \longrightarrow RCO^{\cdot}_{3(g)} + RCH^{-}_{2(g)} \longrightarrow RC(O)OONO_2$$

Did You Know?

Lahore smog consists of volatile organic compounds (VOCs), NO_x, ground level ozone (O_3), particulate matter PM 2.5, CO and SO_2.

Rack Your Mind!

3. The yellow colour in photochemical smog is due to:
A) NO B) NO_2
C) N_2O D) N_2O_5

Alternate Reactions

$RCH = CHR + O_3 \longrightarrow 2RCHO + O_2$
$RCHO + OH^{\cdot} \longrightarrow RC(O)O^{\cdot} + H_2O$
$RC(O)O^{\cdot} + NO_2 \longrightarrow RC(O)OONO_2$

Formation of Peroxyacyl Nitrates (PANs)

NO_x take part in a series of reactions leading to the formation of ozone (O_3), aldehydes, peroxyacyl nitrates (PANs) and peroxybenzoyl nitrate (PBN). PAN is one of the members of peroxyacyl nitrates as shown in Figure.

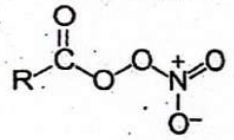


Figure: General structure of PANs

The R group in peroxyacetyl nitrate is $-CH_3$, but other hydrocarbon chains may also be present.

Rack Your Mind!

4. Mention the conditions which are required for the formation of smog?

Rack Your Mind!

5. Differentiate between oxidizing and reducing smog.

Formation of PAN:

The main component of oxidizing smog is ozone, which oxidizes hydrocarbon to produce aldehyde. The aldehyde then reacts with hydroxyl radical to produce acyl radical. The acyl radical reacts with oxygen to produce peroxyacyl radical, which finally reacts with nitrogen peroxide to form peroxyacyl nitrate.

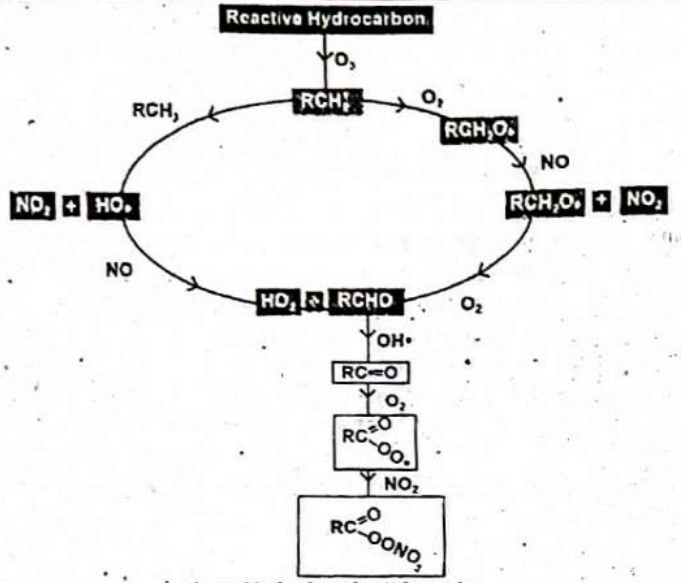


Figure: Mechanism of PAN formation

QUICK CHECK 12.2

a) Draw the structures of the following oxides of nitrogen. Also, briefly explain their bonding.
i) N_2O ii) NO iii) NO_2

Ans.

(i) N_2O (Nitrous oxide / Laughing gas)

Structure:

$[N = N = O \longleftrightarrow N \equiv N - O]$

Dinitrogen Oxide, N_2O (nitrous oxide) Or $:N \equiv N^+ - O^-$ (linear molecule)

Bonding explanation:

- N_2O is linear, with a triple bond between the two nitrogen atoms and a coordinate bond to oxygen.
- It has resonance forms, and the terminal nitrogen carries a positive charge, while oxygen has a negative charge.

(ii) NO (Nitric oxide)

Structure:

$:\dot{N} = \dot{O}:$

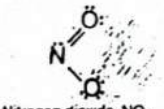
Nitrogen Oxide, NO (nitric oxide) Or $N = O^{\bullet}$ (linear with one unpaired electron)

Bonding explanation:

- NO is a diatomic, linear molecule with a double bond and one unpaired electron, making it a free radical.
- It is paramagnetic due to this lone unpaired electron.

(iii) NO_2 (Nitrogen dioxide)

Structure:



Nitrogen dioxide, NO_2 (nitrogen peroxide) Or $O = N - O^{\bullet}$ (bent molecule, 134°)

Bonding Explanation:

- NO_2 is angular (bent) and also a free radical with one unpaired electron. It has resonance structures and is paramagnetic due to the unpaired electron.

What does PAN stand for? Give its general formula.

Ans.

- PAN stands for Peroxyacetyl Nitrate. It is a toxic compound found in photochemical smog.
- Its general formula is $CH_3C(O)OONO_2$. It irritates eyes and affects plants and human health.

Write down the formulas of the compounds responsible for the formation of PAN.

Ans. PAN is formed from the reaction of the following compounds:

- Hydrocarbons (RH) $\rightarrow$ R – CHO (aldehydes)
- Nitrogen oxides (NO and NO_2)
- Oxygen (O_2) and sunlight

These react to form peroxyacyl radicals and then PAN.

If magnesium ribbon is ignited and placed in a jar containing N_2O, it continues to burn brightly, how does the product form in this reaction confirm the structure of N_2O?

Ans. When magnesium burns in N_2O, it produces magnesium oxide (MgO) and nitrogen gas (N_2). This reaction proves N_2O contains oxygen, as the flame is sustained by O release, confirming its structure $N \equiv N^+ - O^-$.

CATALYTIC CONVERTER

- A catalytic converter is a ceramic or metallic monolith with a honeycomb-like structure (as shown in Figure).
- Its inner channels have a layer of alumina to provide a high surface area.
- Noble precious (expensive) metals such as Pt (Platinum), Pd (Palladium), and Rh (Rhodium) are dispersed on the alumina.
- These metals catalyze three redox reactions to remove the half harmful exhaust gases.
- The three-way converter converts harmful CO, NO, and hydrocarbons into CO_2, N_2, and water.
- These precious metals can also be recycled.

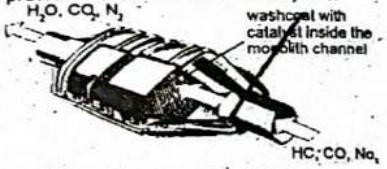


Figure: Three-way Catalytic Converter

Reduction: $2NO_{(g)} + 2CO_{(g)} \xrightarrow{Pt/Rd} N_{2(g)} + 2CO_{2(g)}$

Oxidation: $2CO_{(g)} + O_{2(g)} \xrightarrow{Pt/Rh} 2CO_{2(g)}$

$2C_2H_4 + 6O_{2(g)} \xrightarrow{Pt/Rd} 4CO_{2(g)} + 4H_2O_{(g)}$

Rack Your Mind!

6. What is the primary function of a catalytic converter in an automobile?
A) Increase engine
B) Improve fuel efficiency
C) Reduce harmful emissions
D) Enhance vehicle speed

Rack Your Mind!

7. What is catalytic convertor?

Rack Your Mind!

8. Which of the following gases are primarily reduced or oxidized by a catalytic converter?
A) Carbon dioxide, oxygen, and nitrogen
B) Methane, ammonia, and hydrogen
C) CO, nitrogen oxides, and hydrocarbons
D) Sulphur dioxide, ozone, and water vapour

NITRIFICATION AND DENITRIFICATION

- Nitrification and denitrification are the two phases of the nitrogen cycle.
- Nitrification involves the conversion of ammonium (NH_4^{1+}) to nitrite (NO_2^{1-}) and nitrate (NO_3^{1-}), while denitrification involves the conversion of nitrate (NO_3^{1-}) to Nitrogen (N_2).
- These two processes are also involved in the wastewater treatment to remove nitrogen. Some differences between nitrification and denitrification are given in Table.

Table: Differences between Nitrification and Denitrification

Nitrification	Denitrification
In nitrification Ammonia ion (NH_4^{1+}) is converted into nitrite (NO_2^{1-}) and nitrate (NO_3^{1-}).	Nitrite (NO_2^{1-}) and nitrate (NO_3^{1-}) are converted back to N_2 that is released into the atmosphere.
Nitrifying bacteria aerobic conditions, pH 6.5 – 8.0, optimum temperature 20°C – 30°C.	Denitrifying bacteria anaerobic conditions, pH 7.0 – 9.0, optimum temperature 26°C – 38°C.
Plants absorb these nitrites and nitrates for their nutrition as they cannot assimilate nitrogen directly from the atmosphere.	It is important in wastewater treatment and useful for aquatic life, to oxidize NH_4^+ with NO_2^- to form N_2 gas.
Oxidation of nitrogen $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$ $2NH^{1+}_{4(aq)} + 3O_{2(ac)} \rightarrow 2NO^{1-}_{2(aq)} + 4H^+_{(aq)} + 2H_2O_{(\ell)}$ $2NO^{1-}_{2(aq)} + O_{2(aq)} \rightarrow 2NO^{1}_{3(aq)}$	Reduction of nitrogen $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$ $2NO^{1-}_{3(aq)} + 10e^- + 12H^+_{(aq)} \rightarrow N_{2(g)} + 6H_2O_{(\ell)}$

QUICK CHECK 12.3

a) Write down the reduction and oxidation reactions that occur in the catalytic converter in the vehicle exhausts.

Ans. These metals catalyze three redox reactions to remove the half harmful exhaust gases. The three-way converter converts harmful CO, NO, and hydrocarbons into CO_2, N_2, and water. These precious metals can also be recycled.

Reduction: $2NO_{(g)} + 2CO_{(g)} \longrightarrow N_{2(g)} + 2CO_{2(g)}$

Oxidation: $2CO_{(g)} + O_{2(g)} \xrightarrow{Pt/Rh} 2CO_{2(g)}$

$2CH_{4(g)} + 6O_{2(g)} \xrightarrow{Pt/Rd} 4CO_{2(g)} + 4H_2O_{(g)}$

b) What is the basic principle of catalytic converter? Describe the role of catalyst in the catalytic converter.

Ans. These metals catalyze three redox reactions to remove the half harmful exhaust gases. The three-way converter converts harmful CO, NO, and hydrocarbons into CO_2, N_2, and water. These precious metals can also be recycled.

c) Do hybrid and electric cars have catalytic converters? Explain why or why not.

Ans. **Hybrids:** Yes, because they still use gasoline engines that produce emissions.

Electric cars: No, since they run on batteries and produce no exhaust gases to treat.

SULPHUR

Sulphur is a member of group 16 which is also called the Chalcogen family. Some physical properties of sulphur are listed in Table.

Table: Physical properties of Sulphur

Atomic number	16	Ionic radius	184 pm
Relative atomic mass	32.06 a.m.u.	1st Ionization energy	1000 kJ/mol
Physical appearance	Solid Yellow	Electronegativity	2.5
Electronic configuration	[Ne]3 $s^2 3p^4$	Electron affinity	–200 kJ/mol
Melting point	113°C (honey yellow)	Density	2.07 g / cm^3
Boiling point	445°C (dark brown)	Common oxidation states	4+ and 6+
Covalent radius	104 pm	Common Bonding	Covalent bond

Reactivity of Sulphur

Sulphur usually forms single bonds with other sulphur atoms instead of double bonds due to poor overlapping of the orbitals. As a result, it forms larger molecules and structures through a process called catenation. S_8 is a crown-like molecule, as shown in Figure 12.7.

Oxidation States of Sulphur

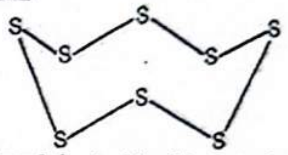


Figure: Cyclo-octasulphur, (S_8) crown molecule

Sulphur exhibits oxidation states of –2, 0, +2, +4, and +6. The electronic configuration of sulphur is depicted in Figure, where the oxidation state is determined by the number of unpaired electrons. Under standard conditions, sulphur and oxygen react to produce Sulphur dioxide (SO_2) in which sulphur has an oxidation state of +4. However, to form sulphur trioxide (SO_3) with an oxidation state of +6, high energy is required.

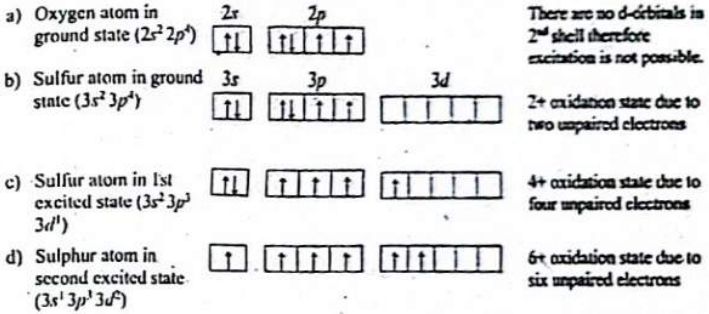


Figure: Electronic configurations of sulphur for attaining different oxidation states

STABILITY OF OXIDATION STATES OF SULPHUR

Sulphur displays a range of oxidation states, principally from -2 to +6. The stability of these states is influenced by the factors like pH, temperature, nature of the compound and the chemical environment.

pH

In general, under acidic conditions, reduced forms (like H2S, -2 oxidation state) are more stable, while under basic or neutral conditions, oxidized forms (like SO_4^{2-}, +6 oxidation state) become more stable in water.

Thermodynamics and Kinetics

Although Sulphur (+6), as in SO_3, is thermodynamically the most stable, kinetic limitations can prevent it from forming readily at standard temperatures, making Sulphur (+4), as in SO_2, the more frequent form.

Nature of the Compound

The stability of Sulphur's oxidation state can be affected by the elements it is bonded to, and the overall chemical environment. In acidic environment SO_4^{2-} is kinetically stable due to strong O-S bonds.

Catalyst

A catalyst can also enhance the rate of formation of a specific oxidation state, for example vanadium in the contact process increases the rate of formation of SO_3.

QUICK CHECK 12.4

a) Determine the oxidation state of S in the following species.

i. SO_3 ii. H_2SO_4 iii. SO_4^{2-} iv. $S_2O_3^{2-}$

Ans.

(i) Oxidation state of SO_3

S(O.S) + O(O.S) = 0
X + 3(−2) = 0
X − 6 = 0
X = +6
So, the oxidation state of S in SO_3 is + 6.

(ii) Oxidation state of H_2SO_4

H(O.S) + S(O.S) + O(O.S) = 0
2(1) + X + 4(−2) = 0
2 + X − 8 = 0
X = 8 − 2
X = +6
So the oxidation state of S in H_2SO_4 is + 6.

(iii) Oxidation state of SO_4^{-2}

S(O.S) + O(O.S) = 0
X + 4(−2) = −2
X − 8 = −2
X = 8 − 2
X = +6
So the oxidation state of S in SO_4^{-2} is + 6.

(iv) Oxidation state of $S_2O_3^{-2}$

S(O.S) + O(O.S) = 0
2X + 3(−2) = −2
2X − 6 = −2
2X = 6 − 2
2x = 4
X = 4/2 = +2
So the oxidation state of S in $S_2O_3^{-2}$ is + 2.

b) Which oxidation states of sulphur are the most common? Explain your answer with reason.

Ans. The most common oxidation states of sulfur are −2, +4, and +6.

- −2 is found in sulfides (e.g., H_2S).
- +4 in SO_2 and +6 in H_2SO_4.

Reason: These are common due to sulfur's ability to gain or lose electrons easily depending on bonding.

c) Explain the involvement of d orbital in variable oxidation states of S in its compounds.

Ans. Sulphur has vacant 3d orbitals that allow it to form expanded octets and make multiple bonds. This helps sulfur to show oxidation states higher than +2, such as +4 and +6, in compounds like SO_2 and SO_3 respectively.

REACTIONS OF SULPHUR

Sulphur can combine with many elements to form a wide variety of inorganic and organic compounds. It is unreactive to water under normal conditions, dilute non-oxidizing acids, and noble gases. Its ability to catenate allows it to form ring structures and linear chains. Here are some important reactions of sulphur:

(i) Reaction with Air: Sulphur burns in the air to form SO_2 with a blue colour flame. The other main sulphur oxide is SO_3 which requires higher temperature and a catalyst for its formation.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

$$2SO_{2(g)} + O_{2(g)} \xrightarrow[Pt]{\Delta} 2SO_{3(g)}$$

(ii) Reaction with Nitric Acid: Sulphur can be oxidised by nitric acid to produce NO_2 and H_2SO_4.

$$S_{(s)} + 6HNO_{3(\ell)} \longrightarrow H_2SO_{4(\ell)} + 6NO_{2(g)} + 2H_2O_{(\ell)}$$

(iii) Reaction with Ion Electronegative Element: When sulphur reacts with elements that have lower electronegativity, it acts as an oxidizing agent and forms their sulfides. It tarnishes Ag, Cu, and Zn by forming a coating of metal sulfide. Sulphur does not react with Au and Pt.

$$2Ag_{(s)} + S_{(s)} \longrightarrow Ag_2S_{(s)}$$

$$Hg_{(\ell)} + S_{(s)} \longrightarrow HgS_{(s)}$$

$$2Cu_{(s)} + S_{(s)} \longrightarrow Cu_2S_{(s)}$$

(iv) Reaction with Cyanide: Sulphur converts cyanide into thiocyanate which is also known as **pseudohalide**. It is used to analyse Fe^{3+}.

$$KCN_{(s)} + S_{(s)} \xrightarrow{\Delta} KSCN_{(s)}$$

(v) Reaction with Halogens: Sulphur reacts directly with F_2 to form SF_4 and SF_6. Sulphur hexafluoride (SF_6) is a gas and is very unreactive. It is used as an insulator gas in electric devices. Sulphur readily reacts with $C\ell_2$ to form $S_2C\ell_2$ (yellow liquid) which further reacts with $C\ell_2$ to form $SC\ell_2$ (red liquid).

$$S_{(s)} + 3F_{2(g)} \longrightarrow SF_{6(g)}$$

$$2S_{(s)} + C\ell_{2(g)} \longrightarrow S_2C\ell_{2(\ell)}$$

$$S_{(\ell)} + SC\ell_{2(g)} \longrightarrow S_2C\ell_{2(\ell)}$$

USES OF SULPHUR AND ITS COMPOUNDS

Vulcanization

Sulphur is used as a cross linker for the rubber molecular chains. This is called vulcanization and it improves the strength of rubber as shown in Figure.

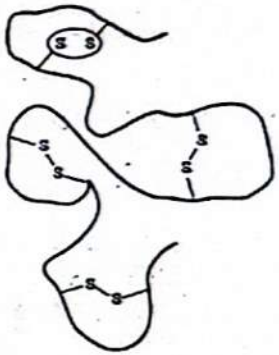


Figure: S-S cross-linkages between polymer chains

Fertilizer

Sulphur is an essential nutrient for plant growth. When soils become depleted in sulfate, sulphur can be restored in soil by applying sulphur containing N/P fertilizers, or sulphur-coated fertilizers such as sulphur-coated urea. Soil components and microbes convert elemental sulphur into soluble forms for the use of plants. Gypsum ($CaSO_4 \cdot 2H_2O$) is also used as a fertilizer.

Gun powder

Gun powder is a coarse blend of 75% potassium nitrate (KNO_3), 15% wood charcoal, and 10% sulphur. Charcoal carbon is the main fuel, nitrate is the oxidiser and sulphur is the additional fuel that burns the powder faster. The following reaction in burning takes place:

$$10KNO_{3(s)} + 3S_{(s)} + 8C_{(s)} \longrightarrow 2K_2CO_{3(s)} + 3K_2SO_{4(s)} + 6CO_{2(g)} + 5N_{2(g)}$$

QUICK CHECK 12.5

a) What is the function of SO_2 and sulfite (SO_3^{2-}) salt in preserving the food?

Ans. SO_2 and sulfites act as antimicrobial agents and antioxidants, preventing bacterial/fungal growth and slowing food discoloration. They inhibit enzyme activity that causes spoilage in dried fruits, wines, and processed foods. Sulfites also maintain freshness by preventing oxidation reactions.

b) Give the reaction of S with HCl and NaOH.

Ans. **With HCl:** Sulfur does not react with HCl because it's non-reactive to non-oxidizing acids at normal conditions.

With NaOH: Sulfur reacts in hot NaOH solution, forming sulfides (Na_2S) and sulfites (Na_2SO_3).

$$3S + 6NaOH \longrightarrow 2Na_2S + Na_2SO_3 + 3H_2O$$

ROLE OF SULPHUR IN ORGANIC SYNTHESIS

Carbon-Sulphur bonds are present in a wide range of compounds with biological, pharmaceutical, and material properties. These bonds form a large number of organic compounds containing a variety of functional groups such as thiols or mercaptans, thioethers, sulfoxides, sulfones, etc.

Drugs

Sulfa drugs are the antibacterial sulfonamides such as penicillins and cephalosporins contain sulphur. The common drug omeprazole, used in GERD (Gastroesophageal reflux disease) contains sulfoxide group.

Dyes

Sulphur dyes are synthesised by the process of thionation or sulphurization of organic compounds that contain nitro or amino groups. These compounds contain sulphur linkages. They generally give black, brown, khaki, blue, and green colours.

Examples are sulphur black 1, sulphur blue and sulphur brilliant green.

Odorants/Fragrances

Mercaptans are used to give odour to natural gas. Some thiols have pleasant odours on high dilution, for example, thioterpineol is the key ingredient in the aroma of grapefruit. cisglabanum oxathiane is a fragrant compound. It is used in fine fragrances, soaps, shampoos and shower gels. Many naturally occurring odorants are produced synthetically and also applied as flavouring agents.

SULPHURIC ACID (H_2SO_4)

Sulphuric acid is called 'King of Chemicals'.

The major portion of sulphur, around 85% is used for the production of sulphuric acid (H_2SO_4). It has tetrahedral structure with two S – O and two S = O bonds as shown in Figure.

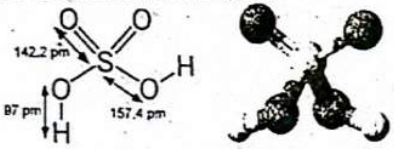


Figure: Structure of H_2SO_4

EXERCISE Q.5

Q. Give flowsheet diagram and equations involved in the contact process.

Contact Process (For the Manufacture of Sulphuric Acid)

Sulphuric acid is produced by the contact process.

➢ **Flow Sheet Diagram:**

A flow sheet diagram of the contact process is shown in Figure.

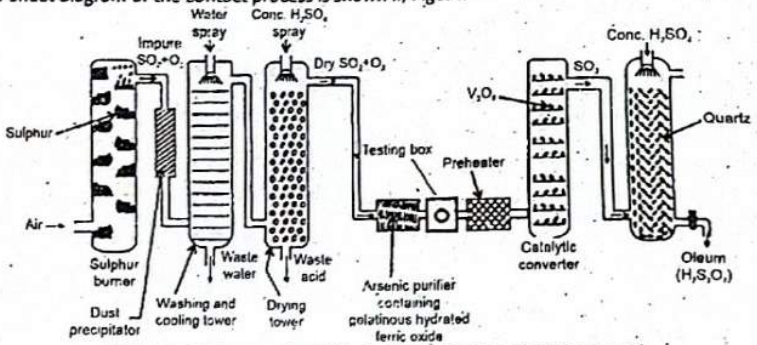


Figure: Contact process for the industrial production of sulphuric acid

➢ **Stages:**

The Contact process can be divided into the following stages.

Sulphur/pyrite Burners

The process starts with the combustion of molten sulphur or by heating pyrites such as iron pyrite (FeS) in excess of air to produce sulphur dioxide SO_2.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)} \qquad \Delta H = -297.03\ kJ/mol$$

$$4FeS_{(s)} + 6O_{2(g)} \longrightarrow 2Fe_2O_{3(s)} + 4SO_{2(g)}$$

Purification Unit

If pyrite ore is used as a sulphur source, the SO_2 gas formed may contain contaminants like dust particles, vapours, and arsenic oxide. These contaminants affect the efficiency of the catalyst. Hence, the gas needs to pass through the purification unit. In an arsenic purifier, gelatinous ferric hydroxide $Fe(OH)_3$ present in horizontal shelves, absorbs arsenic oxide As_2O_3.

$$As_2O_{3(g)} + 2Fe(OH)_{3(s)} \longrightarrow 2FeAsO_{3(s)} + 3H_2O_{(l)}$$

Ferric arsenite

Rack Your Mind!

9. Arsenic oxides are removed during manufacture of H_2SO_4 by passing through:
A) Ferric hydroxide B) Sodium hydroxide
C) Calcium hydroxide D) Potassium hydroxide

Contact Tower and Heat Exchangers

Purified SO_2 and air, preheated at 420°C–450°C, are fed to the first converter stage of the contact tower at 1 – 2 atm pressure. Here, these gases come in contact with vanadium pentoxide (V_2O_5) catalyst.

$$SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad \Delta H = -98.98\ kJ\ mol^{-1}$$

The catalyst works in two steps:

Oxidation of SO_2 into SO_3 by V^{5+}:

$$SO_{2(g)} + V_2O_{5(s)} \longrightarrow SO_{3(g)} + 4\,V_2O_{4(s)}$$

Oxidation of V^{4+} back into V^{5+} by oxygen (catalyst regeneration):

$$V_2O_{4(s)} + \frac{1}{2}O_{2(g)} \longrightarrow V_2O_{5(s)}$$

QUICK CHECK 12.6

a) **Why is high temperature and catalyst needed to form SO_3?**

Ans: The reaction in which SO_3 formed is an exothermic but slow at low temperatures. A high temperature (450°C) provides activation energy, on the other hand, the V_2O_5 (vanadium pentoxide) catalyst speeds up the reaction without being consumed, making the process industrially viable. The reaction is given below,

$$2SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad \Delta H = -98.98\ kJ/mol$$

b) **Write down dehydration reactions of conc. H_2SO_4 with starch and oxalic acid.**

Ans. The dehydration reactions of conc. H_2SO_4 with starch and oxalic acid are given below,

- **With starch $(C_6H_{10}O_5)_n$:** $(C_6H_{10}O_5)_n \xrightarrow{H_2SO_4} 6Cn + 5nH_2O$
- **With oxalic acid $(H_2C_2O_4)$:** $H_2C_2O_4 \xrightarrow{H_2SO_4} CO + CO_2 + H_2O$

c) **How does the catalyst V_2O_5 function in the conversion of SO_2 to SO_3.**

Ans. Vanadium(V) pentoxide V_2O_5 provides a surface for the reaction and helps in transferring oxygen: V_2O_5 temporarily forms V_2O_4, which is reoxidized by O_2, so it remains unchanged overall.

The catalyst works in two steps:

Oxidation of SO_2 into SO_3 by V^{5+}: $SO_{2(g)} + V_2O_{5(s)} \longrightarrow SO_{3(g)} + 4V_2O_{4(s)}$

Oxidation of V^{4+} back into V^{5+} by oxygen (catalyst regeneration): $\frac{1}{2}O_{2(g)} + V_2O_{4(s)} \longrightarrow V_2O_{4(s)}$

Absorption Tower

Sulphur trioxide (SO_3) is cooled and can be converted to sulphuric acid by reacting with water.

$$H_2O_{(l)} + SO_{3(g)} \longrightarrow H_2SO_{4(l)} \qquad \Delta H = -176.6\ kJ/mol$$

Mixing SO_3 with water is not feasible because the reaction is extremely exothermic and acidic vapour mist is produced rather than a liquid solution. Mainly, sulphur trioxide is dissolved in recirculating 98.5% sulphuric acid. The term fuming sulphuric acid or oleum is used for the mixtures of sulphur trioxide with 100 percent sulphuric acid.

Oleum undergoes a reaction with water to make a highly concentrated solution of H_2SO_4 whose concentration can be adjusted.

$$H_2SO_{4(\ell)} + SO_{3(g)} \longrightarrow H_2S_2O_{7(\ell)} \quad \text{(Oleum)}$$

$$H_2S_2O_{7(\ell)} + H_2O_{(\ell)} \longrightarrow 2H_2SO_{4(\ell)}$$

➲ Physical Properties

Sulphuric acid is soluble in water and hygroscopic in nature. It readily absorbs water vapour from the air. Anhydrous H_2SO_4 is a very polar liquid. It is highly corrosive to various materials. On contacting the skin, it causes chemical burns. Some physical properties of sulphuric acid are given in Table.

Table: Physical Properties of Sulphuric Acid

Molar mass	98.08 g/mol
Physical appearance	colourless viscous liquid
Odour	odourless
Melting point	10°C
Boiling point	290°C
Specific gravity (15°C)	1.83 g / cm^3
Viscosity	25.24 centipoise
Vapour pressure (25°C)	0.001 torr
Sulphuric acid is a highly corrosive substance. It can badly burn cloths, plastic, rubber and injured the human skin, eyes, etc,. Handle it very carefully.	

➲ Chemical Properties

i. Autoprotolysis

It self-ionizes or undergoes autoprotolysis as follows.

$$H_2SO_{4(\ell)} + H_2SO_{4(\ell)} \rightleftharpoons H_3SO^{+}_{4(aq)} + HSO^{-}_{4(aq)} \qquad K = 2.7\times10^{-4}$$

The equilibrium constant value is greater than that of water which makes it to be used as a non-aqueous protic solvent.

Sulphuric acid is a strong acid as shown by its pK_{a1} value:

$$H_2SO_{4(aq)} \rightleftharpoons H_3O^{+}_{(aq)} + HSO^{-}_{4(aq)} \quad (pK_{a1} = -2)$$

But hydrogensulphate (HSO_4^{1-}) is a far weaker acid due to a positive pK_{a2} value:

$$HSO^{1-}_{4(aq)} + H_2O_{(\ell)} \rightleftharpoons H_3O^{+}_{(aq)} + SO^{2-}_{4(aq)} \quad (pK_{a2} = 1.92)$$

Rack Your Mind!

10. Discuss Sulphuric acid as dibasic acid.

(Exercise Q)

Q. Discuss sulphuric acid as an oxidizing agent and a dehydrating agent with three reactions for each.

ii. Sulphuric Acid as Dehydrating Agent

Concentrated sulphuric acid is a powerful dehydrating agent that removes water from many substances such as sucrose, starch, wood, and paper to produce carbon, steam, and heat.

It also dehydrates ethyl alcohol to ethene or ethoxyethane depending upon the reaction conditions.

$$C_2H_5OH_{(\ell)} + H_2SO_{4(\ell)} \longrightarrow C_2H_{4(s)} + H_2O_{(\ell)} + H_2SO_{4(aq)}$$

Interesting Information

Dehydration of Table Sugar:
A common laboratory demonstration is the dehydration of table sugar, where a black porous carbon mass called carbon snake protrudes out of the apparatus.

$$C_{12}H_{22}O_{11(s)} + H_2SO_{4(\ell)} \longrightarrow 12C_{(s)} + 11H_2O_{(\ell)} + H_2SO_{4(aq)}$$

Rack Your Mind!

11. When Conc. H_2SO_4 comes in contact with sugar later becomes black due to:
A) Hydrolysis B) Hydration
C) Decolorization D) Dehydration

iii. Reaction with NaCl

Hydrochloric acid (HCl) gas, is formed when sulphuric acid reacts with sodium chloride.

$$NaCl_{(s)} + H_2SO_{4(\ell)} \longrightarrow NaHSO_{4(s)} + HCl_{(g)}$$

iv. Reaction with Metals

Reactions of sulphuric acid with metals depend upon the metal, concentration of the acid, and temperature. Metals that are above hydrogen in electrochemical series such as Fe, Al, Zn, Mn, Ni, and Mg react directly with dilute sulphuric acid to produce hydrogen gas and metal sulfates. But with cold conc. H_2SO_4, they liberate SO_2 and form sulphates.

$$Zn_{(s)} + H_2SO_{4(aq)} \longrightarrow H_{2(g)} + Zn^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

$$Zn_{(s)} + H_2SO_{4(\ell)} \longrightarrow SO_{2(g)} + Fe^{2+}_{(aq)} + SO^{2-}_{4(aq)} + 2H_2O_{(\ell)}$$

v. Sulphuric Acid as Oxidizing Agent

Metals like Cu, Ag, and Hg react with hot conc. H_2SO_4 to form metal sulfates. Sulphuric acid is not regarded as a typical oxidizing agent due to the stability of SO_4^{2-} anion. This anion is weakly oxidizing. However hot concentrated sulphuric acid is a moderately strong oxidizing agent due to high temperature, high concentration of protons (H^+), and formation of nascent oxygen. Hot concentrated sulphuric acid oxidises Cu, as given below:

$$Cu_{(s)} + 2H_2SO_{4(\ell)} \longrightarrow SO_{2(g)} + 2H_2O_{(\ell)} + SO^{2-}_{4(aq)} + Cu^{2+}_{(aq)}$$

☑ QUICK CHECK 12.7

a) Write down dehydration reactions of conc. H_2SO_4 with starch and oxalic acid.

Ans. Starch

$$(C_6H_{10}O_5)n_{(s)} \xrightarrow{\text{conc. } H_2SO_4} 6nC_{(s)} + 5nH_2O_{(g)}$$

Oxalic acid:

$$\begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow{\text{conc. } H_2SO_4} CO_{2(g)} + CO_{(g)} + H_2O_{(\ell)}$$

Paper and Sugar on reaction with conc.H_2SO_4 becomes black due to dehydration.

b) How does conc. H_2SO_4 react with NaCl? What is the importance of this reaction?

Ans. Hydrochloric acid (HCl) gas, is formed when sulphuric acid reacts with sodium chloride

$$NaCl_{(s)} + H_2SO_{4(\ell)} \longrightarrow NaHSO_{4(s)} + HCl_{(g)}$$

Sulfuric acid displaces the weaker acid (HCl) from its salt. This is important because it is used to prepare pure HCl gas in laboratories

c) What is the difference between the oxidizing power of cold and hot sulphuric acid?

Ans.

- Cold concentrated H_2SO_4 mainly acts as a dehydrating acid and shows weak oxidizing ability.
- Hot concentrated H_2SO_4 acts as a strong oxidizing agent, reacting with metals and nonmetals.

For example:

$$Cu + 2H_2SO_4 \xrightarrow{\text{hot}} CuSO_4 + SO_2 + 2H_2O$$

The heat increases its reactivity and helps release SO_2 gas.

➲ Uses and Industrial Applications of Sulphuric Acid

➢ **King of Chemicals:**

Sulphuric acid is considered a king of chemicals and its consumption is an indicator of the industrial progress of a country.

1. **Fertilizer Formation:** A major portion of the acid is used in making fertilizers, normally 77.67% is us to digest the phosphate rock containing calcium phosphate ($Ca_3(PO_4)_2$).
2. **Extraction of Metals:** It is used in the extraction of metals from ores such as Cu, Ni, steel etc.
3. **As a Catalyst:** It is utilized as a catalyst in oil and coal refining, polymers, synthetic rubber, and pla industries.
4. It is used in the pulp and paper industry and involved in the production of pesticides, insecticid herbicides, varnishes, dyes, pharmaceuticals, soaps and detergents.
5. **Formation of Explosive:** It is used for nitration in making explosives such as trinitrotoluene (TN nitroglycerine, picric acid, nitrocellulose, etc.
6. **Food Industry:** It is involved in the food industry for making sugar, starch, and corn syrup.
7. **Paint Industry:** It is used in the paint industry for making titanium dioxide (TiO_2)-pigment.
8. **Dry Gases:** It is used to dry gases in industrial processes.
9. **Lead Storage Batteries:** 35.67% acid is used in lead storage batteries.
10. **Laboratory Reagent:** It is used as a laboratory reagent.

Even though it is used in various industries, it is rarely contained in the final product.

Did You Know?

Fluorapatite ($Ca_5(PO_4)_3F$) to make single superphosphate $Ca(H_2PO_4)_2$ and phosphoric acid (H_3PO_4). H_3PO_4 is further used to make double and triple superphosphates and ammonium phosphate. Sulphuric acid also reacts with ammonia to make ammonium sulfate fertilizer.

Solution File — Rack Your Brain!

Sr. #	Option	Explanation
1.	S.Q	(i) High bond Energy (941 kJ/mol) (ii) Non-Polar Nature of N_2 (iii) Electronic configuration stability (iv) Triple bond strength (v) No permanent dipole
2.	C	PAN causes eye irritation, leading to redness, itching, and tearing due to its oxidizing properties.
3.	B	NO_2 absorbs light and appears yellow-brown due to its molecular structure and absorption spectrum.
4.	S.Q	**Conditions for the Formation of Smog:** Following conditions are required for the formation of Smog. i. There must be sufficient NO, hydrocarbons and volatile organic compounds (VOC) emitted by the vehicular traffic. ii. There must be sunlight, so that some of the chemical reactions may occur at a rapid rate. iii. The movement of air mass must be little so that reactions are not disturbed.
5.	S.Q	There are two types of smog: (i) Reducing smog (ii) Oxidizing smog

Reducing Smog (Classical Smog)	Oxidizing Smog (Photochemical Smog)
It is formed due to the build up of sulphur dioxide from combustion of Coal.	It is formed due to photochemical reaction of sunlight on the nitrogen oxides and hydrocarbons produced by automobile and factories.
It involves smoke and fog.	It does not involve smoke and fog.
It mostly occurs in cool humid climate.	It occurs in warm, dry and sunny climate.
It has high concentration of SO_2 and is therefore reducing in character.	It has high concentration of oxidants like O_3 and therefore is oxidizing in nature.
It causes bronchitis and irritation i.e. problem in lungs.	It causes irritation in eyes and toxic to plants.

6.	C	It converts pollutants like CO, NOx, and Hydrocarbons into harmless gases like CO_2, N_2, and H_2O, reducing emission and minimizing environmental impact.
7.	S.Q	A catalytic convertor is an emission control device to reduce harmful pollutants in exhaust gases from internal combustion engine.
8.	C	It converts pollutants gases into harmless gases: $NOx \rightarrow N_2$, $CO \rightarrow$, and $HC \rightarrow CO_2 + H_2O$
9.	A	$As_2O_{3(g)} + 2Fe(OH)_{3(\ell)} \longrightarrow 2FeAsO_{3(\ell)} + 3H_2O_{(\ell)}$ Ferric arsenite
10.	S.Q	Sulphuric acid is a strong acid. In an aqueous solution, it completely ionizes to give hydronium ions and sulphate ions. The dissociation takes place in two steps. $H_2SO_{4(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + HSO^-_{4(aq)}$ $HSO^-_{4(aq)} + H_2O_{(\ell)} \longrightarrow SO^{2-}_{4(aq)} + H_3O^+_{(aq)}$
11.	D	The acid removes water from the sugar molecules, leading to the formatin of carbon, which appears black.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. **Despite being the most abundant gas in the Earth's atmosphere, nitrogen does not readily participate in combustion reactions because:**
a) It is denser than oxygen.
b) It has a high specific heat capacity.
c) Breaking the N≡N bond requires a large amount of energy.
d) It is a noble gas.

II. **A student heats a solid ammonium salt with a solution of a strong alkali. The gas produced turns damp red litmus paper blue and has a characteristic pungent smell. The gas is:**
a) Hydrogen (H_2) b) Carbon dioxide (CO_2) c) Ammonia (NH_3) d) Sulphur dioxide (SO_2)

III. **The shape of ammonium (ion) is:**
a) pyramidal b) triangular planar c) tetrahedral d) linear

IV. **In a catalytic converter, the conversion of nitrogen oxides (NO_x) into nitrogen gas (N_2) and oxygen gas (O_2) is a process of:**
a) Oxidation b) Reduction c) Combustion d) Neutralization

V. **PAN formation starts when reacts with the hydrocarbon.**
a) NO b) NO_2 c) O_3 d) HO^-

VI. **Nitrification is the process by which:**
a) Atmospheric nitrogen is converted into ammonia.
b) Nitrate is converted into nitrogen gas.
c) Ammonia is converted into nitrite and then nitrate.
d) Organic nitrogen is converted into ammonia.

VII. **The most stable species in an acidic environment is:**
a) SO_4^{2-} b) SO_2 c) H_2S d) S

VIII. **Which gas is used in separating hard water from normal water?**
a) SO_2 b) H_2S c) NH_3 d) NO_2

IX. The oxidation state of sulphur in H_2SO_4 is:
a) +1 b) +2 c) +4 d) +6

X. The drug omeprazole contains _____ group.
a) Thiol b) Sulfoxide c) Bisulfide d) Sulfone

XI. Sulphur dioxide (SO_2) produced from the combustion of sulphur can be further oxidized to sulphur trioxide (SO_3) under specific conditions, such as in the presence of a:
a) Catalyst (e.g., vanadium (V) oxide) and high temperature.
b) Catalyst (e.g., iron) and low temperature.
c) Strong reducing agent and high pressure.
d) Dilute acid and room temperature.

XII. Sulphur trioxide (SO_3) is not directly dissolved in water to produce sulphuric acid in the Contact Process because this reaction is:
a) Too slow.
b) Reversible and would result in a low yield.
c) Highly exothermic and produces a mist of sulphuric acid.
d) Requires very high pressures.

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	c	Breaking the N≡N bond requires a large amount of energy	• The N≡N triple bond has very high bond energy (946 kJ/mol), making nitrogen inert in combustion.
II.	c	Ammonia (NH_3)	• Heating ammonium salts with alkali produces NH_3, which turns damp red litmus blue (basic) and has a pungent smell.
III.	c	Tetrahedral	• NH_4^+ has sp^3 hybridization with 4 bond pairs, resulting in a tetrahedral shape.
IV.	b	Reduction	• In catalytic converters, $NO_x \rightarrow N_2 + O_2$ involves reduction of nitrogen (e.g., $NO \rightarrow N_2$).
V.	b	NO_2	• Peroxyacetyl nitrate (PAN) forms when NO_2 reacts with hydrocarbons in photochemical smog.
VI.	c	Ammonia is converted into nitrite and then nitrate	• Nitrification: $NH_3 \rightarrow NO_2^-$ (by Nitrosomonas) $\rightarrow NO_3^-$ (by Nitrobacter).
VII.	a	SO_4^{2-}	• Sulphate (SO_4^{2-}) is stable in acidic conditions, while H_2S/SO_2 may oxidize further.
VIII.	c	NH_3	• Ammonia precipitates Mg^{2+}/Ca^{2+} as hydroxides, softening hard water.
IX.	d	+6	• In H_2SO_4, sulphur has +6 oxidation state (O.N. calculation: $2(+1) + x + 4(-2) = 0 \rightarrow x = +6$).
X.	B	Sulfoxide	• Omeprazole is a PPI that reduces stomach acid by irreversibly inhibiting the H^+/K^+–ATPase enzyme. Its activity relies on a sulfoxide group (–S=O), making it a sulfoxide derivative of benzimidazole.
XI.	a	vanadium(V) oxide) and high temperature	• **Contact Process:** $SO_2 \rightarrow SO_3$ uses V_2O_5 catalyst at 450°C for optimal yield.
XII.	c	Highly exothermic and produces a mist of sulfuric acid	• Directly dissolving SO_3 in water creates an uncontrollable mist; instead, SO_3 is absorbed in conc. H_2SO_4 (oleum).

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. List two reasons for the inertness of N_2.

Ans.
(i) **High Bond Energy:** The nitrogen molecule (N_2) is inert primarily due to its strong triple covalent bond (N≡N), which has a very high bond dissociation energy of 946 kJ/mol. This makes the bond extremely difficult to break under normal conditions.
(ii) **Non-Polar Nature:** N_2 is nonpolar because both nitrogen atoms have equal electronegativity, reducing its tendency to react with polar or ionic substances. The absence of lone pair availability for donation further contributes to its chemical inertness.

b. How is nitrogen isolated from air?

Ans. Nitrogen is isolated from air through a process called fractional distillation of liquefied air. First, air is filtered to remove dust and then compressed and cooled to very low temperatures (–200°C), turning it into a liquid. Since nitrogen has a lower boiling point (–196°C) than oxygen (–183°C), it evaporates first when the liquid air is gradually warmed. The nitrogen gas is then collected, while the remaining liquid contains oxygen, argon, and other trace gases. Further purification steps may be applied to obtain high-purity nitrogen.

c. Why ammonia (NH_3) is a weak base?

Ans. Reasons:
- **Partial Dissociation in Water:** NH_3 reacts with water to form NH_4^+ and OH^-, but only a small fraction dissociates, making it a weak base.
- **Lone Pair Availability:** The nitrogen lone pair can accept a proton (H^+), but it does so weakly compared to strong bases like NaOH.
- **Equilibrium Lies to the Left:** The reaction $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ favors the reactants, resulting in a low concentration of OH^- ions.

d. Write down the reactions of photochemical smog formation?

Ans. **Chemical Reactions:**
The formation of photochemical smog involves the following chemical reactions.

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$$
$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$
$$NO_{2(g)} \xrightarrow{h\nu} NO_{(g)} + O_{(g)}$$
$$O_{(g)} + O_{2(g)} \longrightarrow O_{3(g)}$$
$$RCH{=}CHR_{(g)} + O_{3(g)} \longrightarrow RCO^{\bullet}_{3(g)} + RCH^{-}_{2(g)} \longrightarrow RC(O)OONO_2$$

Alternate For the Last Reaction:

$$RCH = CHR + O_3 \longrightarrow 2RCHO + O_2$$
$$RCHO + OH^{\bullet} \longrightarrow RC(O)O^{\bullet} + H_2O$$
$$RC(O)O^{\bullet} + NO_2 \longrightarrow RC(O)OONO_2$$

e. Write down the reactions of photochemical smog formation.

Ans. Photochemical smog (Los Angeles smog) forms in the atmosphere from NO_x and volatile organic compounds (VOCs) in the sunlight. It is oxidizing in nature. Photochemical oxidants, such as NO_2, ozone, and peroxyacyl nitrates (PANs) can react and oxidise specific compounds in the atmosphere.

Photochemical smog is becoming more common than classical smog (London smog) due to increasing NO_x emissions. The formation of photochemical smog involves the following chemical reactions.

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$$
$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$
$$NO_{2(g)} \xrightarrow{h\nu} NO_{(g)} + O_{(g)}$$
$$O_{(g)} + O_{2(g)} \longrightarrow O_{3(g)}$$

f. What is the construction and function of a catalytic converter?

Ans. Construction:

A catalytic converter is a ceramic or metallic monolith with a honeycomb-like structure, its inner channels have a layer of alumina to provide a high surface area. Noble expensive metals such as Pt (Platinum), Pd (Palladium), and Rh (Rhodium) are dispersed on the alumina.

Functions:

It functions in two stages:

(i) **Reduction Catalyst (Rh):** Converts harmful nitrogen oxides (NO_x) into nitrogen (N_2) and oxygen (O_2).

(ii) **Oxidation Catalyst (Pt/Pd):** Oxidizes carbon monoxide (CO) and unburned hydrocarbons into carbon dioxide (CO_2) and water (H_2O).

This process significantly reduces the toxicity of exhaust gases.

g. Why sulphur is quite unreactive at room temperature?

Ans. Sulfur is unreactive at room temperature because it exists as cyclic S_8 molecules (crown-shaped rings) held together by strong covalent S–S bonds. Breaking these bonds requires significant energy, making sulfur inert under mild conditions. Additionally, the nonpolar nature of S_8 reduces its interaction with polar solvents or reactants.

h. Which are the most stable oxidation states of sulphur in water at pH = 0 and pH=14?

Ans.

- At pH = 0 (strongly acidic conditions), sulfur's most stable oxidation states are:
  - +6 (sulfate, SO_4^{2-}) – Dominant due to high thermodynamic stability.
  - +4 (sulfur dioxide, SO_2 or sulfite, SO_3^{2-}) – Stable but can be oxidized further.
- At pH = 14 (strongly alkaline conditions), the stable forms shift to:
  - +6 (sulfate, SO_4^{2-}) – Remains stable.
  - –2 (sulfide, S^{2-}) – Favored in reducing environments.

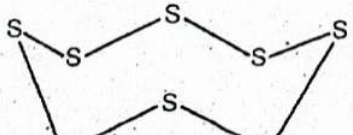
i. How does sulphur react with halogens?

Ans. Sulfur reacts directly with F_2 to form SF_4 and SF_6. Sulfur hexafluoride (SF_6) is a gas and is very unreactive. It is used as an insulator gas in electric devices. Sulfur readily reacts with Cl_2 to form S_2Cl_2 (yellow liquid) which further reacts with Cl_2 to form SCl_2 (red liquid).

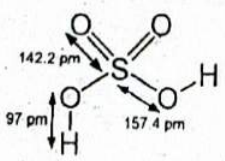
$$S_{(s)} + 3F_{2(g)} \longrightarrow SF_{6(g)}$$
$$2S_{(s)} + Cl_{2(g)} \longrightarrow S_2Cl_{2(l)}$$

j. Draw the structures of cyclo-octasulphur (S_8) and sulphuric acid.

Ans.



Cyclo-octasulphur, (S_8) crown molecule





Structure of H_2SO_4

k. What is the role of sulphur in the vulcanization of rubber?

Ans. Sulphur is used as a cross linker for the rubber molecular chains. This is called vulcanization and it improves the strength of rubber.

l. What is the composition and the chemical reaction of gunpowder combustion?

Ans. Gun powder is a coarse blend of 75% potassium nitrate (KNO_3), 15% wood charcoal, and 10% sulfur. Charcoal carbon is the main fuel, nitrate is the oxidiser and sulfur is the additional fuel that burns the powder faster. The following reaction in burning takes place:

$$10KNO_{3(s)} + 3S_{(s)} + 8C_{(s)} \longrightarrow 2K_2CO_{3(s)} + 3K_2SO_{4(s)} + 6CO_{2(g)} + 5N_{2(g)}$$

m. What is the importance of disulfide bridges?

Ans. Disulfide bridges (–S–S–) are covalent bonds between sulfur atoms in cysteine residues of proteins. They stabilize protein structures (e.g., keratin in hair, insulin) by linking distant parts of the polypeptide chain, ensuring proper folding and mechanical strength. Disruption of these bonds (e.g., by reducing agents) can denature proteins.

n. Write down self-ionization equation of sulphuric acid and its ionization in water.

Ans. It self-ionizes or undergoes autoprotolysis as follows.

$$H_2SO_{4(\ell)} + H_2SO_{4(\ell)} \rightleftharpoons H_3SO^{1+}_{4(aq)} + HSO^{1-}_{4(aq)} \qquad K = 2.7\times10^{-4}$$

The equilibrium constant value is greater than that of water which makes it to be used as a non-aqueous protic solvent.

Sulphuric acid is a strong acid as shown by its pK_{a1} value:

$$H_2SO_{4(aq)} \rightleftharpoons H_3O^{+}_{(aq)} + HSO^{1-}_{4(aq)} \qquad (pK_{a1} = -2)$$

But hydrogen sulphate (HSO_4^{1-}) is a far weaker acid due to a positive pK_{a2} value:

$$HSO^{1-}_{4(aq)} + H_2O_{(\ell)} \rightleftharpoons H_3O^{+}_{(aq)} + SO^{2-}_{4(aq)} \qquad (pK_{a2} = 1.92)$$

o. Give two examples where sulphuric acid acts as a dehydrating agent.

Ans. Dehydration of Alcohol:

H_2SO_4 dehydrates ethyl alcohol to ethene or ethoxyethane (Diethyl ether) depending upon the reaction conditions.

$$C_2H_5OH_{(\ell)} + H_2SO_{4(\ell)} \longrightarrow C_2H_{4(g)} + H_2O_{(\ell)} + H_2SO_{4(aq)}$$

Dehydration of sugar (sucrose):

$$C_{12}H_{22}O_{11} + H_2SO_4 \longrightarrow 12C + 11H_2O$$

p. How does V_2O_5 catalyze the formation of SO_3?

Ans. Vanadium pentoxide (V_2O_5) catalyzes the oxidation of SO_2 to SO_3 in the Contact Process:

(i) SO_2 reduces V_2O_5 to V_2O_4:

$$SO_2 + V_2O_5 \longrightarrow SO_3 + V_2O_4$$

(ii) O_2 reoxidizes V_2O_4 back to V_2O_5:

$$2V_2O_4 + O \longrightarrow 2V_2O_5$$

q. What is purpose of formation of oleum?

Ans. Oleum ($H_2S_2O_7$) is produced to safely transport and store sulfuric acid. Since concentrated H_2SO_4 tends to crystallize, oleum (a solution of SO_3 in H_2SO_4) prevents this problem. When diluted with water, oleum releases SO_3, which reacts to form additional H_2SO_4:

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

This ensures high-purity sulfuric acid delivery.

DESCRIPTIVE QUESTIONS

Q.3 Explain the preparation and basicity of ammonia.

Ans. See Page No. (420).

Q.4 How oxides of nitrogen (NO_x) cause the formation of photochemical smog and PAN? Give its mechanism.

Ans. See Page No. (423)

Q.5 Give flowsheet diagram and equations involved in the contact process.

Ans. See Page No. (430)

Q.6 Discuss sulphuric acid as an oxidizing agent and a dehydrating agent with three reactions for each.

Ans. See Page No. (432)

ADDITIONAL SLOs BASED MCQs

1. **Which equations represent stages in the Contact process for manufacturing sulphuric acid?**
   A. $S + O_2 \rightarrow SO_2$ B. $H_2O + SO_2 \rightarrow H_2SO_3$ C. $H_2SO_3 + O_2 \rightarrow H_2SO_4$ D. $SO_3 + H_2O \rightarrow H_2SO_4$
2. **Nitrogen is absorbed by the plants in the form of:**
   A. Ammonium B. Nitrites C. Nitrates D. All
3. **Nitrogen fixation is the conversion of:**
   A. N_2 to N B. N_2 to NH_3 C. N_2 to NO_3^- D. N_2 to urea
4. **Sulphur dioxide is an important food preservative. Which property makes sulphur dioxide useful in this role?**
   A. It is a gas. B. It is a reducing agent.
   C. It reacts with oxygen to form sulphur trioxide. D. It reacts with water to form an acidic solution.
5. **Most modern cars are fitted with three-way catalytic converters in the exhaust system. Which three gases are removed by such a catalytic converter?**
   A. carbon monoxide, hydrocarbons, nitrogen oxides B. carbon monoxide, carbon dioxide, nitrogen oxides
   C. carbon monoxide, nitrogen oxides, sulphur dioxide D. hydrocarbons, nitrogen oxides, sulphur dioxide
6. **Conversion of nitrates to nitrogen gas is called:**
   A. Ammonification B. Nitrification C. Nitrogen fixation D. Denitrification
7. **In the Contact process, what is the nature of the gaseous product and what is the identity of the catalyst?**

	Nature of gaseous product	Catalyst
A.	acidic	Fe^2
B.	acidic	V_2O_5
C.	basic	Fe_3
D.	basic	V_2O_5

8. **Conversion of nitrites to nitrates is called:**
   A. Nitrosococcus B. Clostridium C. Nitrobacter D. Nitrosomonas
9. **Which oxide of nitrogen is released from car engines?**
   A. Nitrogen dioxide B. Nitric oxide C. Nitrous oxide D. Nitrogen tetroxide
10. **Which compound of sulphur is used to bleach wood pulp?**
    A. Sulphuric Acid B. Sodium sulphate C. Sulphur dioxide D. Sodium sulphite

Sr. #	Ans.	Explanations
1.	A	The Contact process involves the oxidation of sulphur to sulphur dioxide (SO_2), the further oxidation of SO_2 to sulphur trioxide (SO_3).
2.	D	Plants can absorb nitrogen in the form of ammonium (NH_4^+), nitrites (NO_2^-), and nitrates (NO_3^-), although nitrates are the most common form absorbed.
3.	B	Nitrogen fixation is the process of converting nitrogen gas (N_2) from the atmosphere into ammonia (NH_3), which can be used by plants.
4.	B	Sulphur dioxide acts as a reducing agent and inhibits the growth of bacteria and other microorganisms, making it useful as a food preservative.
5.	A	Three-way catalytic converters reduce emissions of carbon monoxide (CO), hydrocarbons (HC), and nitrogen oxides (NOx) from car exhaust.
6.	D	Denitrification is the process by which nitrates (NO_3^-) are converted to nitrogen gas (N_2), typically by bacteria, releasing nitrogen back into the atmosphere.
7.	B	The gaseous product (SO_3) formed in the Contact process is acidic, and the catalyst used is vanadium (V) oxide (V_2O_5).
8.	C	Nitrobacter bacteria are responsible for converting nitrites (NO_2^-) to nitrates (NO_3^-) in the nitrification process.
9.	B	Car engines typically release nitric oxide (NO) as part of the exhaust gases, which can further react to form nitrogen dioxide (NO_2).
10.	C	Sulphur dioxide (SO_2) is used in the bleaching of wood pulp because of its reducing properties, which help in removing lignin from the pulp.

SHORT ANSWER QUESTIONS

Q.1 What are the main categories of sources of NO_x?

Ans. The main categories of NO_x sources are:

- **Natural Sources of NO_x**
  Natural sources include lightning, volcanoes, biological decay, forest fires, soil microorganisms, oceans, etc. NO is produced when N_2 and O_2 in the air react during lightning. It is produced by microorganism using air N_2.
- **Man-made Sources of NO_x**
  The main anthropogenic sources of NO_x are the combustion of fossil fuels in vehicles and power plants. Other sources include chemical plants, biomass burning, welding, etc.

Q.2 Differentiate between nitrification and denitrification.

Ans.

Nitrification	Denitrification
Ammonia NH_3 / NH_4^{1+} is converted into nitrite (NO_2^{1-}) and nitrate (NO_3^{1-}).	Nitrite (NO_2^{1-}) and nitrate (NO_3^{1-}) are converted back to N_2 that is released into the atmosphere.
Nitrifying bacteria aerobic conditions, pH 6.5 – 8.0, optimum temperature 20 °C – 30 °C.	Denitrifying bacteria anaerobic conditions, pH 7.0 – 9.0, optimum temperature 26 °C – 38 °C.

Q.3 What is catalytic converter?

Ans. **Catalytic Converter**
A catalytic converter is a ceramic or metallic monolith with a honeycomb-like structure. Its inner channels have a layer of alumina to provide a high surface area.

Q.4 Write down the natural sources of oxides of nitrogen.

Ans. Natural sources include lightning, volcanoes, biological decay, forest fires, soil microorganisms, oceans, etc. NO is produced when N_2 and O_2 in the air react during lightning. It is produced by microorganism using air N_2.

Q.5 Ammonia is basic in nature. How?

Ans. Ammonia behaves as a Lowry-Brønsted base by accepting a proton (H^+) from an acid to form ammonium:

$$NH_{3(aq)} + H^{+1}_{(aq)} \rightleftharpoons NH^{+1}_{4(aq)}$$

It dissolves in water to form ammonium hydroxide (NH_4OH) and equilibrium is established between ammonia molecules and ammonium ions in the solution.

$$NH_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons NH^{1+}_{4(aq)} + OH^{1-}_{(aq)} \qquad K_b = 1.8\times10^{-5}$$

Ammonia solution is a weak base due to the low basicity constant (K_b) and the equilibrium position being towards the far left side.

Q.6 Write down the equation for the reaction between conc. H_2SO_4 and copper and explain what type of reaction is it.

Ans. Reaction between Conc.H_2SO_4 and Copper:

Hot conc. Sulphuric acid reacts with Cu to form Copper Sulphate and SO_2.

$$Cu^{0} + 2H_2\overset{+6}{S}O_4 \xrightarrow[\text{Reduction}]{\overset{\text{Oxidation}}{\longrightarrow}} Cu^{+2}SO_4 + 2H_2O + \overset{+4}{S}O_2$$

In this reaction, the oxidation state of Cu is changed from "zero" to "2" in $CuSO_4$ and thus Cu is oxidized. The oxidation state of S in H_2SO_4 is +6 whereas in SO_2 it is +4. This show that sulphur is reduced. Therefore the reaction is an oxidation reduction.

Q.7 Give the advantages of contact process for the manufacturing of sulphuric acid (H_2SO_4).

Ans. The advantages of contact process for the manufacture of H_2SO_4 are given below:-

(i) By using this process, we can get H_2SO_4 of any required concentration.
(ii) As no by product is obtained during this process. So, it is a environment friendly process.
(iii) It is used in commercial preparations.
(iv) The catalyst used i.e. V_2O_5 is solid. So, it can be handled easily.

Q.8 Why is SO_3 dissolved in H_2SO_4 and not in water?

Ans. When SO_3 is dissolved in 98% H_2SO_4, pyrosulphuric acid (oleum) is obtained.

$$H_2SO_{4(aq)} + SO_{3(g)} \longrightarrow H_2S_2O_{7(\ell)}$$

Oleum can be converted to sulphuric acid of any required concentration. By mixing adequate amount of water.

$$H_2S_2O_{7(\ell)} + H_2O_{(\ell)} \longrightarrow 2H_2SO_{4(aq)}$$

SO_3 is not dissolved in water directly because

(i) The reaction is highly exothermic.
(ii) SO_3 is less soluble in H_2O at high temperature.
(iii) A dense fog is produced which does not easily condense.
(iv) Sulphuric acid of required concentration cannot be prepared.

Q.9 H_2SO_4 is dehydrating agent. Write down some chemical equations to prove it.

Ans. Reactions as a Dehydrating Agent:

H_2SO_4 has a great affinity for water, so it acts as dehydrating agent and eliminates water from different compounds.

- $C_6H_{12}O_6 \xrightarrow{\text{Conc.}H_2SO_4} 6C + 6H_2O$
- $C_2H_5OH \xrightarrow[100°C]{\text{Conc.}H_2SO_4} C_2H_4 + H_2O$

- With oxalic acid it forms CO_2 and CO.

$$\begin{matrix}COOH\\|\\COOH_{(aq)}\end{matrix} \xrightarrow{\text{Conc.}H_2SO_4} CO_{2(g)} + CO_{(g)} + H_2O_{(\ell)}$$

- With formic acid, CO is formed,

$$HCOOH_{(aq)} \xrightarrow{\text{conc.}H_2SO_4} CO_{(g)} + H_2O_{(\ell)}$$

Q.10 Prove that H_2SO_4 acts as an oxidizing agent.

Ans. H_2SO_4 acts as a strong oxidizing agent.

(i) It oxidizes C and S giving CO_2 and SO_2 respectively.

$$C_{(s)} + 2H_2SO_{4(aq)} \longrightarrow CO_{2(g)} + 2SO_{2(g)} + 2H_2O_{(g)}$$
$$S_{(s)} + 2H_2SO_{4(aq)} \longrightarrow 3SO_{2(g)} + 2H_2O_{(\ell)}$$

(ii) H_2S is oxidized to S.

$$H_2S_{(g)} + H_2SO_{4(aq)} \longrightarrow S_{(s)} + SO_{2(g)} + 2H_2O_{(g)}$$

(iii) Reactions of H_2SO_4 with HBr and HI produce bromine and iodine respectively.

$$2HBr_{(aq)} + H_2SO_{4(aq)} \longrightarrow Br_{2(g)} + SO_{2(g)} + 2H_2O_{(g)}$$
$$2HI_{(aq)} + H_2SO_{4(aq)} \longrightarrow I_{2(g)} + SO_{2(g)} + 2H_2O_{(g)}$$

Q.11 Write reactions of H_2SO_4 with $NaCl_{(s)}$ and $NaBr_{(s)}$.

Ans. $2NaCl_{(s)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)}$
$2NaBr_{(s)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + 2HBr_{(g)}$

Q.12 Write four physical properties of sulphuric acid.

Ans. Physical Properties:

1. Pure sulphuric acid is a colourless oily liquid without an odour.
2. Its specific gravity is 1.834 at 18°C.
3. It freezes at 10.5°C.
4. Its boiling point is 338°C.
5. It dissolves in water liberating a lot of heat which raises the temperature of the mixture up to 120°C. H_2SO_4 should always be poured in water in a thin stream to avoid any accident.
6. Pure acid is a nonconductor of electricity but the addition of a little water makes it a good conductor.
7. It is extremely corrosive to skin and causes very serious burns to all the tissues.

Q.13 How does H_2SO_4 react with: (i) Zn (ii) Cu

Ans. (i) $H_2SO_{4(aq)} + Zn_{(s)} \longrightarrow ZnSO_{4(aq)} + H_2$
(ii) $Cu_{(s)} + 2H_2SO_{4(aq)} \longrightarrow CuSO_{4(aq)} + 2H_2O_{(\ell)} + SO_{2(\ell)}$
(It is an oxidation-reduction reaction).

Q.14 How Arsenic is removed in contact process?

Ans. Arsenic Purifier:

Arsenic oxide is then removed in the form of Ferric arsenite by passing the dry gases through a chamber provided with shelves packed with freshly prepared ferric hydroxide.

$$As_2O_3 + 2Fe(OH)_3 \longrightarrow 2FeAsO_3 + 3H_2O$$
(Ferric arsenite)

Q.15 Write four uses of sulphuric acid.

Ans. Uses of Sulphuric Acid (King of Chemicals):

It is used

(i) In the manufacture of fertilizers like ammonium sulphate and calcium superphosphate.
(ii) In refining of petroleum to remove nitrogen and sulphur compounds.
(iii) In electrical batteries and storage cells.
(iv) As a dehydrating agent for drying gases.

SELF-ASSESSMENT Chapter # 12

Total Mark: 30

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) **The oxidation State of S in $S_2O_3^{-2}$ is:**
A. +1 B. +2 C. +3 D. +4

(ii) **Despite being the most abundant gas in the Earth's atmosphere, nitrogen does not readily participate in combustion reactions because:**
A. It is denser than oxygen.
B. It has a high specific heat capacity.
C. Breaking the N≡N bond requires a large amount of energy.
D. It is a noble gas.

(iii) **The shape of ammonium (ion) is:**
A. pyramidal B. triangular planar C. tetrahedral D. linear

(iv) **Nitrification is the process by which:**
A. Atmospheric nitrogen is converted into ammonia.
B. Nitrate is converted into nitrogen gas.
C. Ammonia is converted into nitrite and then nitrate.
D. Organic nitrogen is converted into ammonia.

(v) **The most stable species in an acidic environment is:**
A. SO_4^{2-} B. SO_2 C. H_2S D. S

(vi) **Sulphur trioxide (SO_3) is not directly dissolved in water to produce sulphuric acid in the Contact Process because this reaction is:**
A. Too slow.
B. Reversible and would result in a low yield.
C. Highly exothermic and produces a mist of sulphuric acid.
D. Requires very high pressures.

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) If magnesium ribbon is ignited and placed in a jar containing N_2O, it continues to burn brightly. Explain this observation with reason.
(ii) Why N_2 gas is used in food packaging?
(iii) Write down the reduction and oxidation reactions that occur in the catalytic converter in the vehicle exhausts.
(iv) What is the basic principle of catalytic converter? Describe the role of catalyst in the catalytic converter.
(v) Give the reaction of S with NaOH.
(vi) Write down self-ionization equation of sulphuric acid and its ionization in water.

Q.3 Extensive Questions. (2 × 4 = 8)

(a) Discuss sulphuric acid as an oxidizing agent and a dehydrating agent with three reactions for each.
(b) How oxides of nitrogen (NO_x) cause the formation of photochemical smog and PAN? Give its mechanism.

Chapter 13

HALOGENS

Student Learning Outcomes

After studying this chapter, students will be able to:
- Describe the colours and the trends in volatility of chlorine, bromine and iodine. (Understanding)
- Describe the trend in bond strength of halogen molecules. (Understanding)
- Interpret the volatility of the elements in terms of instantaneous dipole-induced dipole forces. (Understanding)
- Describe the relative reactivity of halogen elements as oxidizing agents. (Understanding)
- Describe the reactions of elements with hydrogen and explain their relative reactivity in these reactions. (Understanding)
- Describe the relative thermal stabilities of hydrogen halides and explain these in terms of bond strength. (Understanding)
- Describe the relative reactivity of halide ions as reducing agents. (Understanding)
- Explain the reactions of halide ions with aqueous silver nitrate and concentrated sulphuric acid. (Understanding)
- Describe the reactions of halides with aqueous silver ions followed by aqueous ammonia. (Understanding)
- Interpret the reaction of Chlorine with cold and hot aqueous sodium hydroxide as disproportion reactions. (Understanding)
- Explain the use of chlorine in water purification, including the production of the active species HOCl and ClO^- which kill bacteria. (Understanding)

Elements present in Group 17 or VIIA of the periodic table are termed as halogens.
- It includes fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At) and tennessine (Ts).
- The halogen elements form a group of very reactive non-metals and are quite similar to each other in their chemical properties.
- First four elements are the common elements of the halogen family but last two astatine (At) and tennessine (Ts) are very rare and radioactive elements.

Physical States of Halogens

- Halogens exist as diatomic molecules (X_2 = F_2, Cl_2, Br_2, I_2) in all phases (gas, liquid or solid).
- Fluorine (F_2) and chlorine (Cl_2) are gases of pale yellow and greenish yellow colours respectively at room temperature and pressure.
- Bromine (Br_2) is a volatile liquid of reddish-brown colour at room temperature. It has corrosive and toxic fumes.
- Iodine (I_2) is shiny greyish black solid at room temperature. It sublimes directly from solid to a violet vapour. The colors of halogens (X_2) darken progressively from chlorine to iodine.

Rack Your Mind!
1. Why I_2 is solid while F_2 is gas?

Rack Your Mind!
2. Which halogen occurs naturally in a positive oxidation state?
(A) Fluorine (F) (B) Chlorine (Cl)
(C) Bromine (Br) (D) Iodine (I)

Reason:
The trends of colour changes from chlorine to iodine is due to changes in the absorption of light as a result of electron transitions within the molecules of respective halogens.

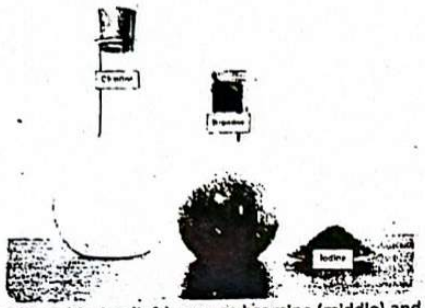


Figure: The greenish yellow chlorine (left), orange bromine (middle) and purple iodine (right).

Did You Know?

The name halogen comes from the Greek words "halos", meaning "salt", and "gen", meaning "to make." The first halogen to be isolated and recognized as an element was chlorine. Despite the fact that chlorine is poisonous, small amount is essential to human health and life in the form of chloride.

Table: Atomic and Physical properties of the common halogens.

Element	Fluorine	Chlorine	Bromine	Iodine
Proton number	9	17	35	53
Electron shell structure	2, 7	2, 8, 7	2, 8, 18, 7	2, 8, 18, 18, 7
Outer shell electron configuration	$2s^2 2p^5$	$3s^2 3p^5$	$4s^2 4p^5$	$5s^2 5p^5$
Relative atomic mass	19.0	35.5	79.9	126.9
Physical state at of 20°C	gas	gas	liquid	solid
Colour	pale yellow	pale green	red-brown	dark gray
Melting point/°C	−220	−101	−7	113
Boiling point/°C	−188	−35	59	183
Enthalpy change of vaporization/kJ mol^{-1}	+3.3	+10.2	+15	+30
Solubility /g per 100 g of water at 20°C	reacts readily with water	0.59 (reacts slightly)	3.6	0.018

VOLATILITY OF CHLORINE, BROMINE AND IODINE

- **Chlorine:**
  Chlorine being a liquid is very volatile at room temperature and it disperses quickly in the air.
- **Bromine:**
  Bromine being a liquid is less volatile than chlorine but more volatile than iodine. It evaporates readily releasing toxic fumes at room temperature. Iodine is the least volatile among the three. At room temperature, its solid states show lower volatility as compared to chlorine and bromine. Generally, volatility decreases from chlorine to iodine. This trend is due to the increasing molecular mass, increase in size of outer shell and stronger intermolecular forces (London dispersion forces) as we move down the group in the periodic table.

Rack Your Mind!

3. Which of the following halogens is solid at room temperature?
   A) F_2 B) Cl_2
   C) Br_2 D) I_2

Interesting Information!

Bromine liquid evaporates easily at room temperatures emitting an orange vapour. Bromine has a very strong and bad odour. It gets its name from the Greek word "bromos" which means "stench."

TREND IN VOLATILITY OF THE HALOGENS

Halogens are non-polar and instantaneous dipole-induced forces play a significant role in determining the volatility of halogens.

Factors:

- The forces depend on factors like molecular size, shape and polarizability, with stronger forces leading to lower volatility and higher boiling points.
- Substances with weak id-id forces, smaller and less polarizable molecule have lower boiling points and higher volatility.
- Larger, more polarizable molecules with stronger London dispersion forces have higher boiling points and lower volatility.
- Volatility is inversely related to the boiling point of a substance.
- A more volatile substance will have a lower boiling point.
- Stronger intermolecular forces require more energy to separate the molecules from the liquid phase to the gaseous phase. A summary is given in Table.

Table: Effect of London forces on physical properties

Size	Polarizability	Instantaneous dipole-induced dipole forces	Boiling Point	Volatility
Small	Small	Weak	Lower	Higher
Large	High	Strong	Higher	Lower

- The first two halogens, i.e., fluorine (colourless or very light green) and chlorine (greenish yellow) are gases due to weaker id-id forces. Bromine is a liquid as its size is bigger and it possesses stronger intermolecular forces than fluorine and chlorine. Iodine has the strongest forces among the group, so it is in solid state at room temperature.

QUICK CHECK 13.1

a) **Which halogens elements are radioactive?**

Ans. Astatine (At) and Tennessine (Ts) are radioactive halogens.
- Astatine is the only naturally occurring radioactive halogen, but it's extremely rare.
- Tennessine is artificially produced and is also radioactive.

b) **What is the reason behind the different colours of halogens?**

Ans. The different colours of halogens are due to:
- Electron transitions between energy levels.
- As we go down the group, the energy gap between molecular orbitals decreases, allowing absorption of longer wavelengths of visible light.

Example:
- **Fluorine** – pale yellow (absorbs violet light)
- **Chlorine** – yellow-green
- **Bromine** – reddish-brown
- **Iodine** – violet

c) **Why chlorine is more volatile than bromine and iodine?**

Ans. Chlorine is more volatile because:
- It has weaker intermolecular forces (London dispersion forces) due to its smaller molecular size and lower molar mass.
- Volatility decreases down the group as the halogen molecules get larger and heavier, increasing the strength of dispersion forces.

So, Cl_2 (gas) > Br_2 (liquid) > I_2 (solid) in terms of volatility.

THE BOND STRENGTH OF HALOGEN MOLECULES

Bond strength in halogens decreases as we move down the group from chlorine to iodine.

➢ **Reason:**

This is due to the increase in the atomic size down the group which results in longer bond lengths and weaker bonds. Moving from top to bottom in group 17, the bond energy of halogens decreases gradually from chlorine to iodine.

➢ **Exceptional Behaviour of Fluorine:**

Fluorine is an exception in this group. In the case of fluorine, the bond strength is relatively weak because fluorine atoms are very small. Due to the small size, there is significant electron-electron repulsion between the lone pairs on the fluorine atoms, which weakens the bond despite the high electronegativity of fluorine. The bond energy of halogens is listed in Table.

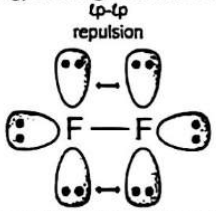


Figure: F_2 molecule with lone pairs of electrons

Table: Bond energies of halogen molecules

Halogen Molecule	Bond Energy (kJ mol^{-1})
F_2	156
$C\ell_2$	243
Br_2	193
I_2	151

RELATIVE REACTIVITIES OF THE HALOGENS AS OXIDIZING AGENTS

(Exercise L Q 4)

Q. Discuss the relative reactivity of the halogen elements as oxidizing agents. Arrange $F_2, C\ell_2, Br_2, I_2$ in increasing order of the oxidizing power.

- All the free halogens act as oxidizing agents when they react with metals and most of non-metals.
- On forming ionic compounds with metals, the halogens gain electrons and are converted to negative halide ions.

$$2Na_{(s)} + C\ell_{2(g)} \longrightarrow 2NaC\ell_{(s)}$$

- The oxidizing power of halogens decreases down the group. Fluorine has the highest oxidizing power and iodine the least.
- The order of decreasing power as an oxidizing agent is:

$$F_2 > C\ell_2 > Br_2 > I_2$$

Rack Your Mind!

4. $C\ell_2$ cannot oxidize:
A) F^- B) Br^-
C) I^- D) Na-metal

- The reactivity of halogens is directly related to their ability to acquire an electron and form halide ions ($F^-, C\ell^-, Br^-$ and I^-) when they react with other elements.
- Fluorine has the highest tendency to acquire an electron and form fluoride.
- Fluorine molecule can oxidize and displace all the halide ions from their solutions ($C\ell^-, Br^-$ and I^-) to free halogens.

$$F_{2(g)} + C\ell^{1-}_{(aq)} \longrightarrow F^{1-}_{(aq)} + C\ell_{2(g)}$$
$$F_{2(g)} + Br^{1-}_{(aq)} \longrightarrow F^{1-}_{(aq)} + Br_{2(g)}$$
$$F_{2(g)} + I^{1-}_{(aq)} \longrightarrow F^{1-}_{(aq)} + I_{2(g)}$$

- Chlorine can oxidize and displace Br^- and I^-. Bromine can oxidize and displace I^-. Iodine cannot oxidize any halide ion.
- The oxidizing power of halogens can be related to standard electrode potential (E°) values. Fluorine is the most reactive halogen and the most powerful oxidizing agent. The standard electrode potential $E^\circ(X_2/X^-)$ for halogens shown in Table become less positive from fluorine to iodine.

Table: Standard electrode potential $E^\circ(X_2/X^-)$

Halogen Molecule (X_2)	Standard Reduction Potential, E° (V)
F_2	+2.87
$C\ell_2$	+1.36
Br_2	+1.07
I_2	+0.54

- This shows the decreasing oxidizing power.

Factors affecting Oxidizing Power of Halogen:

- The oxidizing power of halogens depends upon various factors, i.e., energy of dissociation, electron affinity of atoms, hydration energies of ions, and heats of vaporization (for Br_2 and I_2). A halogen having low energy of dissociation, high electron affinity and higher hydration energy of its ions, will have a high oxidizing power.

QUICK CHECK 13.2

a) The F–F bond is weaker than $C\ell$–$C\ell$ bond although fluorine is the most electronegative element, Explain.

Ans. Yes, despite fluorine being the most electronegative:

- The F–F bond is weaker due to strong repulsion between the lone pairs of electrons on the small fluorine atoms.
- The small atomic radius of fluorine causes the non-bonding electrons to be closer, increasing electron–electron repulsion.
- In contrast, $C\ell$–$C\ell$ has a larger bond length, reducing repulsion and making the bond stronger.

b) Is the reaction between $NaC\ell_{aq}$ and F_2 gas possible?

i) Give reason whether yes or no.

Ans. **Reason:**

Yes, the reaction is possible.

- Fluorine is more reactive and has a higher oxidizing power than chlorine.
- Therefore, fluorine can displace chlorine from sodium chloride solution.

ii) If yes, write the equation for this reaction.

Ans. **Reaction Equation:**

$$F_{2(g)} + 2NaC\ell_{(aq)} \longrightarrow 2NaF_{(aq)} + C\ell_{2(g)}$$

c) What is the relationship between the oxidizing power of halogens and their standard reduction potential values?

Ans.

- The oxidizing power of a halogen is directly related to its standard reduction potential (E°).
- A higher E° value means the halogen is a stronger oxidizing agent (more likely to gain electrons).

Order of oxidizing power (strongest to weakest):

$$F_2 > C\ell_2 > Br_2 > I_2$$

Corresponding E° values (approx.):

- F_2: + 2.87 V
- $C\ell_2$: +1.36 V
- Br_2: +1.07 V
- I_2: +0.54 V

REACTIONS OF THE HALOGENS WITH HYDROGEN

➢ **Hydrogen Halides:**

- When halogen elements react with hydrogen, they produce hydrogen halides.

$$H_2 + X_2 \longrightarrow 2HX \qquad \text{Where } X_2 = F_2, C\ell_2, Br_2 \text{ and } I_2$$

- Hydrogen halides are colourless gases that dissolve in water to form hydrohalic acid. When we mo down the group from fluorine to iodine, the reactivity of halogens with hydrogen decreases.

$$F_2 > C\ell_2 > Br_2 > I_2$$

- At low temperature and in the dark, fluorine reacts explosively with hydrogen.

$$H_{2(g)} + F_{2(g)} \longrightarrow 2HF_{(g)}$$

- When this gas is dissolved in water, it forms hydrofluoric acid.
- In the presence of UV light or a spark, chlorine reacts readily with hydrogen and produces colourless H gas which forms hydrochloric acid in water.

$$H_{2(g)} + C\ell_{2(g)} \xrightarrow{h\nu} 2HC\ell_{(g)}$$

- Hydrogen bromide (HBr) gas is produced when bromine reacts with the hydrogen upon heating. HBr is less reactive than HCℓ and HF. It forms a strong hydrobromic acid in water. This is an exotherm reaction.

$$H_{2(g)} + Br_{2(g)} \xrightarrow{\Delta} 2HBr_{(g)}$$

- At high temperature and in presence of a catalyst, iodine reacts with hydrogen to form hydrogen iodi (HI) gas, which forms hydroiodic acid in water.

$$H_{2(g)} + I_{2(g)} \underset{}{\overset{\text{catalyst}}{\rightleftharpoons}} 2HI_{(g)}$$

- This is a reversible reaction and occurs very slowly.

Rack Your Mind!

5. Maximum bond energy is of:
A) HF B) HBr
C) HCℓ D) HI

RELATIVE THERMAL STABILITIES OF HYDROGEN HALIDES IN TERMS OF THEIR BOND STRENGTH

Exercise Q.6

Q. Describe and explain the relative thermal stabilities of the halogen hydrides in terms of bonds strength.

- As we move down the halogen group from fluorine to iodine, the thermal stabilities of hydrogen halide (H-X) decrease due to decrease in bond dissociation energies as given in Table 13.5. The order of therma stability of HX is as follows:

$$HF > HC\ell > HBr > HI$$

- Bond strength between the hydrogen and the halogen atom in the H – X molecule explain this trend.
- Hydrogen fluoride (HF) is the most thermally stable hydrogen halide. Due to the high electronegativity of fluorine and its small atomic radius, a strong overlap of orbitals produces a very strong H – F bond.
- The bond dissociation energy of H – F (569 kJ/mol) is the highest among the hydrogen halides.
- Hydrogen chloride (HCl) is less thermally stable than hydrogen fluoride but more stable than oth hydrogen halides.
- Due to the larger atomic radius of chlorine than fluorine H – Cℓ bond is weaker than H – F bond. Its bo dissociation energy is less than that of H – F.

Rack Your Mind!

6. Which of the following hydrogen halide is the most thermally stable?
A) HF B) HCℓ
C) HBr D) HI

- Its bond dissociation energy is 431 kJ/mol. Hydrogen bromide (H – Br) bond is weaker than H – F and H – Cℓ due to the larger atomic radius of bromine. There is a reduced overlapping of orbitals. Its bond dissociation energy is 366 kJ/mol.
- Among the common hydrogen halides, hydrogen iodide (HI) is the least thermally stable. Atomic radius of iodine is very large leading to poor orbital overlap due to which hydrogen iodide bond is the weakest among H – F, HCℓ and HBr.
- The bond dissociation energy of hydrogen iodide is 299 kJ/mol.

Table: Bond dissociation energy of H – X bonds

Hydrogen halide (HX)	Bond dissociation energy (kJ mol^{-1})
H – F	569
H – Cℓ	431
H – Br	366
H – I	299

QUICK CHECK 13.3

a) The reaction between H_2 and F_2 is explosive but that between H_2 and I_2 is slow and reversible. Explain why.

Ans.
- The H–F bond is very strong and releases a large amount of energy when formed, making the reaction with F_2 highly exothermic and explosive.
- The activation energy for the $H_2 + F_2$ reaction is also very low.
- In contrast, the H–I bond is weaker, the reaction is less exothermic, and it has a higher activation energy, making it slow and reversible.

b) Refer to Table 13.4 and 13.5 to predict which of the following reactions would be more exothermic. Explain your answer.

$$H_{2(g)} + C\ell_{2(g)} \longrightarrow 2HC\ell_{(g)} \text{ and } H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr_{(g)}$$

Ans. Reaction 1 is more exothermic.

Reason:
- The H–Cℓ bond is stronger than the H–Br bond.
- More energy is released when forming strong H–Cℓ bonds compared to H–Br.
- Also, $C\ell_2$ has a weaker bond than Br_2, requiring less energy to break.
- So, overall energy change is more negative (exothermic) for the HCℓ reaction.

c) How thermal stability of hydrogen halides is related to their bond dissociation energies?

Ans.
- Thermal stability of hydrogen halides increases with higher bond dissociation energy.
- Stronger H–X bonds (higher bond energy) are harder to break, so the compound is more stable under heat.

Trend:

$$HF > HC\ell > HBr > HI$$

This trend corresponds to decreasing bond dissociation energy and thermal stability.

d) HF is the most thermally stable hydrogen halide. Give reasons.

Ans.
- The H–F bond has the highest bond dissociation energy among hydrogen halides.
- Fluorine is small and highly electronegative, forming a strong, short bond with hydrogen.
- This makes HF harder to decompose on heating → most thermally stable.

RELATIVE REACTIVITY OF HALIDE IONS AS REDUCING AGENTS

Exercise I, Q1

Q. Discuss the reducing power of halide ions with relevant reactions. Also explain the factors affecting it.

- The reducing ability of halide ions increases as we move down the group from fluorine to iodine.
- This trend is mostly due to the decreasing electronegativity and increasing atomic radius down the group. This result in lower charge density and greater ease of electron donation.
- Fluoride ion is the weakest reducing agent while iodide is the strongest reducing agent among the halides.
- The order of decreasing power as a reducing agent is $I^- > Br^- > C\ell^- > F^-$.

The following is an explanation of this trend in terms of their properties.

- The high electronegativity of fluorine and the strong bond between the fluorine atom and its extra electron make it difficult for fluoride ion (F^-) to donate electrons. The small size of fluoride ion results in a high charge density, further stabilizing the fluoride ion and reducing its tendency to lose an electron.
- Chloride ion ($C\ell^-$) is a stronger reducing agent than fluoride but still weaker than bromide and iodide. This is due to its larger size and lower electronegativity.
- Bromide (Br^-) is a stronger reducing agent than chloride. Bromine is less electronegative than chlorine. Bromide ion (Br^-) has a larger ionic radius and lower charge density due to which it easily loses an electron and act as a reducing agent.
- Iodide (I^-) is much stronger reducing agent than both chloride and bromide. Electronegativity of iodine is much lower than chlorine and bromine. Iodide ion (I^-) is large in size. This results in a lower charge density and a tendency to donate an electron by the iodide ion, making it strong reducing agent.

REACTIONS OF HALIDES WITH AQUEOUS SILVER ION FOLLOWED BY AQUEOUS AMMONIA

Reactions of Halides with Aqueous Silver Ion (Silver Nitrate Test for Halide Ions)

Insoluble silver halides (AgX) are formed when halide ions react with aqueous silver nitrate ($AgNO_3$). These reactions are used in qualitative analysis to identify halides ions. The general reaction is given below:

$$X^{1-}_{(aq)} + Ag^{1-}_{(aq)} \longrightarrow 2AgX_{(s)}$$

Rock Your Mind!

7. Why AgF does not form precipitates with water while other silver halides form?

- **AgF:** No reaction is visible when silver ions and fluoride ions are mixed in the aqueous medium. As silver fluoride is soluble in water, **Fluoride (F^-) does not form precipitate as silver fluoride.**
- **AgCℓ:** When silver ions and chloride ions are mixed in the aqueous medium a white precipitate of silver chloride forms, which is soluble in dilute ammonia.

$$Ag^{1+}_{(aq)} + C\ell^{1-}_{(aq)} \longrightarrow AgC\ell_{(s)}$$

- **AgBr:** On mixing of aqueous silver ions with aqueous Bromide ions, a cream-coloured precipitate of silver bromide forms. This precipitate of silver bromide is sparingly soluble in concentrated ammonia.

$$Ag^{1+}_{(aq)} + Br^{1-}_{(aq)} \longrightarrow AgBr_{(s)}$$

- **AgI:** A yellow precipitate of silver iodide forms on mixing aqueous silver ion with aqueous halide solution. The product AgI is insoluble in ammonia.

$$Ag^{1+}_{(aq)} + I^{1-}_{(aq)} \longrightarrow AgI_{(s)}$$

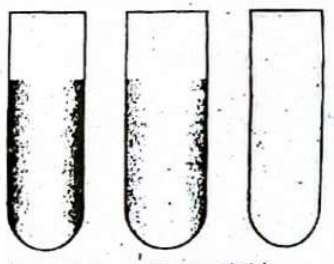


Figure: Colours of the silver halide precipitates: silver chloride (left), silver bromide (middle) and silver iodide (right).

This type of reactions is used to identify halide ions and is called silver nitrate test.

Reaction of Silver Halides (AgX) with Aqueous Ammonia

Addition of aqueous ammonia tests the solubility of initially formed silver halide precipitates.

AgF is soluble in water so it does not form precipitate, so ammonia has no effect. Silver chloride dissolves in dilute ammonia to form diamminesilver (1) complex. The white precipitate of AgCℓ dissolves in dilute ammonia forming a colourless solution.

$$AgC\ell_{(s)} + 2NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]^+_{(aq)} + C\ell^{1-}_{(aq)}$$

The cream-coloured precipitate of AgBr dissolves in concentrated ammonia, forming a colourless solution.

$$AgBr_{(s)} + 2NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]^+_{(aq)} + Br^{1-}_{(aq)}$$

The yellow precipitate of silver iodide (AgI) does not dissolve in both dilute and concentrated ammonia, so there is no change in the presence of ammonia.

The below sequence of reactions in Table provides a systematic way to differentiate between halide ions using their solubility with aqueous silver ions and ammonia.

QUICK CHECK 13.4

a) F^- is a weaker reducing agent than $C\ell^-$. Explain why.

Ans.

- A reducing agent donates electrons (gets oxidized).
- To be a good reducing agent, the halide ion must easily lose electrons to form the halogen.

Reason F^- is weaker:

- F^- has a very strong bond with its electron due to its small size and high electronegativity.
- It is less willing to give up electrons.
- Therefore, F^- is a poor reducing agent, $C\ell^-$ is better at losing electrons (i.e., stronger reducing agent).

b) What is the cause of the different solubilities of silver halides in ammonia?

Ans.

- Solubility in ammonia depends on the ability of the silver halide to form a complex ion with ammonia: $[Ag(NH_3)_2]^+$
- AgCℓ and AgBr form this complex and dissolve in ammonia (AgCℓ is more soluble than AgBr).
- AgI is insoluble because it forms a very insoluble salt and does not readily form a complex with ammonia.

Trend of solubility in NH_3:

$$AgC\ell > AgBr > AgI$$

c) Write down the equation for the reaction of KI with Ag^+ followed by NH_3. What would you observe at the completion of this reaction?

Ans. Step 1: Reaction with silver nitrate (Ag^+):

$$KI_{(aq)} + AgNO_{3(aq)} \longrightarrow AgI_{(s)} + KNO_{3(aq)}$$

- A yellow precipitate of AgI forms.

Step 2: Addition of NH_3 (aqueous ammonia):

- AgI does not dissolve in ammonia:

$$AgI_{(s)} + 2NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]^+ + I^-$$

Observation:

- Yellow precipitate remains unchanged on adding ammonia.

Table: Action of Ag^+ followed by Ammonia on Silver Halides

Halide ion	Action of aq. Ag^+ ion	Action of Aqueous Ammonia
Fluoride ion (F^-)	No precipitate	No reaction with aq. NH_3
Chloride ion ($C\ell^-$)	White precipitate ($AgC\ell$)	Soluble in dil. aq. NH_3
Bromide ion (Br^-)	Cream colour precipitate (AgBr)	Soluble in conc. aq. NH_3
Iodide ion (I^-)	Pale yellow precipitate(AgI)	Insoluble in aq. NH_3

REACTIONS OF HALIDES (X^-) WITH CONCENTRATED SULFURIC ACID

The reactions of different halide ions with concentrated sulfuric acid are different from one another. The nature of the product and nature of reaction changes down the group from fluoride to iodide.

Fumes of hydrogen fluoride gas are produced when concentrated sulfuric acid reacts with NaF. HF is a weak reducing agent, therefore, it does not react with H_2SO_4 further.

$$NaF_{(s)} + H_2SO_{4(\ell)} \longrightarrow NaHSO_{4(\ell)} + HF_{(g)}$$

When concentrated sulfuric acid reacts with sodium chloride, fumes of hydrogen chloride gas are produced.

$$NaC\ell_{(s)} + H_2SO_{4(\ell)} \longrightarrow NaHSO_{4(\ell)} + HC\ell_{(g)}$$

In case of Br^{1-} ion, steamy fumes of hydrogen bromide (HBr) gas and brown fumes of bromine (Br_2) are produced along with the smell of sulfur dioxide (SO_2). It is a redox reaction. Hydrogen bromide acts as a reducing agent by reducing sulfuric acid to sulfur dioxide and is self-oxidized to bromine.

$$NaBr + H_2SO_{4(\ell)} \longrightarrow NaHSO_{4(\ell)} + HBr_{(g)}$$

$$2HBr_{(s)} + H_2SO_{4(\ell)} \longrightarrow Br_{2(g)} + 2SO_{2(g)} + 2H_2O_{(\ell)}$$

When concentrated sulfuric acid reacts with sodium iodide, fumes of hydrogen iodide gas, purple fumes of solid iodine I_2 and smell of H_2S gas produced. HI acts as a strong reducing agent. It reduces H_2SO_4 to H_2S and is itself oxidized to I_2.

$$NaI_{(aq)} + H_2SO_{4(\ell)} \longrightarrow NaHSO_{4(\ell)} + HI_{(g)}$$

$$8HI_{(s)} + H_2SO_{4(\ell)} \longrightarrow 4I_{2(s)} + H_2S_{(g)} + 4H_2O_{(\ell)}$$

The trend of increasing reducing power of the halide ions (X^-) from fluoride to iodide, leads to more complex reactions with concentrated sulfuric acid.

REACTIONS OF CHLORINE WITH COLD AND HOT AQUEOUS SODIUM HYDROXIDE

Disproportionation Reaction:

Those reactions in which a single element undergoes both oxidation and reduction simultaneously are known as disproportionation reactions. When chlorine reacts with cold and hot aqueous sodium hydroxide (NaOH), it undergoes disproportion and form different products according to the temperature of the reaction.

Rack Your Mind!

8. Give chemical reaction of NaOH and Cl_2 in hot state at 70°C.

➲ Reaction with Cold Aqueous Sodium Hydroxide

Chlorine undergoes disproportion when it reacts with cold aqueous sodium hydroxide (NaOH) forming sodium chloride (NaCl) and sodium chlorate (I) (NaClO).

$$C\ell_{2(g)} + 2NaOH_{(aq)} \longrightarrow NaC\ell_{(aq)} + NaC\ell O_{(aq)} + H_2O_{(\ell)}$$

Oxidation states of chlorine in the above reaction are given below:

Chlorine in $C\ell_2$ = 0

Chlorine in $NaC\ell$ = −1

Chlorine in $NaC\ell O$ = +1

KEEP IN MIND

Sodium chlorate (I) was previously called sodium hypochlorite.

Chlorine in $C\ell_2$ is oxidized from 0 to +1 in $NaOC\ell$. Chlorine in $C\ell_2$ is reduced from 0 to 1 in $NaC\ell$.

The above reaction shows the simultaneous oxidation and reduction of chlorine and is example of disproportionation reaction.

➲ Reaction with Hot Aqueous Sodium Hydroxide

When chlorine reacts with hot aqueous sodium hydroxide (NaOH), it forms sodium chloride (NaCl) and sodium chlorate (V) ($NaC\ell O_3$). It is another example of disproportionation reaction.

$$3C\ell_{2(g)} + 6NaOH_{(aq)} \longrightarrow NaC\ell_{(aq)} + NaC\ell O_{3(aq)} + 3H_2O_{(\ell)}$$

Chlorine in $C\ell_2 = 0$

Chlorine in $NaC\ell = -1$

Chlorine in $NaC\ell O_3 = +5$

Chlorine is oxidized from 0 to +5 in $NaC\ell O_3$. Chlorine is reduced from 0 to −1 in NaCl. This disproportionation reaction shows how the temperature of the reaction influences the products formed, demonstrating the versatility of chlorine in undergoing redox reactions.

☑ QUICK CHECK 13.5

a) **How would KI react with conc. H_2SO_4. What does this reaction indicate about the reducing power of Iodide?**

Ans. When potassium iodide (KI) reacts with concentrated sulfuric acid (H_2SO_4), it shows strong reducing behavior:

Reaction:

$$2KI + H_2SO_4 \longrightarrow 2HI + KH_2SO_4$$

Then, HI reduces H_2SO_4:

$$8HI + H_2SO_4 \longrightarrow H_2S + 4I_2 + 4H_2O$$

Observation:

- Purple iodine vapor (I_2) appears
- Rotten egg smell of hydrogen sulfide (H_2S) may be detected

Conclusion:

- Iodide (I^-) is a very strong reducing agent
- It reduces sulfur in H_2SO_4 from +6 to −2 (H_2S)

b) **Show that the reaction of $C\ell_2$ with cold and hot aqueous KOH is a disproportionation reaction.**

Ans. A disproportionation reaction is where the same element is both oxidized and reduced.

Cold KOH (Cl_2 in cold, dilute alkali):

$$C\ell_2 + 2KOH \longrightarrow KC\ell + KC\ell O + H_2O$$

- Chlorine (0) ⟶ $C\ell^-$ (−1) ⟶ reduced
- Chlorine (0) ⟶ $C\ell O^-$ (+1) ⟶ oxidized

Disproportionation

Hot KOH ($C\ell_2$ in hot, concentrated alkali):

$$3C\ell_2 + 6KOH \rightarrow 5KC\ell + KC\ell O_3 + 3H_2O$$

- $C\ell_2$ (0) ⟶ $C\ell^-$ (−1) ⟶ reduced
- $C\ell_2$ (0) ⟶ $C\ell O_3^-$ (+5) ⟶ oxidized

c) **HI acts as strong reducing agent. Explain it with chemical reactions.**

Ans. HI (hydrolodic acid) is a strong reducing agent because Iodide ions (I^-) easily donate electrons.

Examples:

1. **Reduction of Fe^{3+} to Fe^{2+}: $Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$**
2. **Reduction of H_2SO_4 to H_2S (as in part a): $8HI + H_2SO_4 \longrightarrow H2S + 4I_2 + 4H_2O$**
3. **Reduction of MnO_4^- to Mn^{2+}: $2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$**

Conclusion:

- HI reduces a variety of substances.
- Its strong reducing power is due to the ease of oxidation of I^- to I_2.

USE OF CHLORINE IN WATER PURIFICATION

Chlorine gas is very poisonous. However, in small quantities, they are harmless to humans but poisonous to bacteria which cause diseases. Due to its strong disinfectant properties, chlorine is widely used at the treatment plants for water purification. The process involves adding chlorine to water, where it forms active species that kill bacteria and other pathogens. Water in the swimming pools is also chlorinated with slightly higher concentration of chorine because there is likely to be a higher concentration of bacteria in the water. The primary active species are chloric (I) acid or hypochlorous acid (HOCl) and the chlorate (I) or hypochlorite ions (OCl^-). Chlorination is a relatively inexpensive method of water disinfections.

Chlorine Addition to Water

When chlorine gas (Cl_2) is added to water, it undergoes hydrolysis to form a mixture of hydrochloric acid (HCl) and chloric (I) acid (HClO).

$$Cl_{2(g)} + H_2O_{(l)} \longrightarrow HCl_{(aq)} + HClO_{(aq)}$$

Chloric (I) acid (HOCl) is a weak acid and partially dissociate in water to form hydrogen ions (H^+) and chlorate (I) ion (OCl^-).

Rack Your Mind!

9. Discuss harmful effects of chlorinated water.

Disinfection Activity

HOCl and OCl^- are effective disinfectants, but HOCl is more effective due to its neutral charge. The neutral charge of HOCl allows to penetrate the cell walls of micro-organisms easily. Essential cellular components such as proteins and lipids are oxidized by HOCl and OCl^-, which disrupt the cell function leading to cell death. HOCl and OCl can oxidize and inactivate enzymes that are crucial for survival and replication of bacteria.

Interesting Information!

Nucleic acids (DNA and RNA) can be oxidized by HOCl and OCl^- and thus preventing bacteria from replicating and vital cellular functions.

Factors Affecting Disinfection

pH

- At pH around 6 – 7.5, HOCl predominates and makes the disinfection process more effective.
- At higher pH (above 7.5), OCl^- predominates, its less effective but still provides disinfection.

Rack Your Mind!

10. Which one is frequently used to disinfect water?
A) Sodium chloride B) Hydrochloric acid
C) Chlorine D) Sodium hydroxide

Chorine Dose

The higher the amount of chlorine, the more effective the disinfection. Sufficient chlorine must be added to get enough HOCl and OCl^- to kill bacteria.

Contact Time

Contact time of water with chlorine must be long enough, to allow the disinfectants to penetrate and kill bacteria, viruses and protozoa.

QUICK CHECK 13.6

a) **Why HOCl is more effective disinfectant than OCl^- to kill bacteria in water?**

Ans.

- HOCl (hypochlorous acid) is more effective because:
- It is neutral and penetrates bacterial cell walls more easily than the negatively charged OCl^- (hypochlorite ion).
- Once inside the cell, HOCl can disrupt vital cell processes and oxidize cell components.

Conclusion:

HOCl is 80–100 times more effective than OCl^- in killing microorganisms.

b) **What are the factors that affect disinfection of bacteria in water?**

Ans. Key factors include:

1. pH of water
   - Lower pH favors HOCl formation, which is more effective.
   - At higher pH, more OCl^- is formed (less effective).
2. Temperature
   - Higher temperatures generally increase the rate of disinfection.
3. Contact time
   - Longer exposure allows more time for disinfection.
4. Concentration of disinfectant
   - More chlorine or HOCl increases effectiveness.
5. Presence of organic matter
   - Organic compounds can consume chlorine, reducing its availability for disinfection.

c) **What are the primary active species in the chlorination of water? Give equation that shows their production.**

Ans. The primary active species are:

- Hypochlorous acid (HOCl).
- Hypochlorite ion (OCl^-).

These are produced when chlorine reacts with water:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

Then, depending on the pH:

$$HOCl \rightleftharpoons H^+ + OCl^-$$

Summary:

- HOCl is the main active disinfectant at low to neutral pH.
- OCl^- predominates at higher pH, but is less effective.

Solution File — Rack Your Brain!

Sr.#	Option	Explanation
1.	S.Q	All the halogens exist as non-polar diatomic molecules and their molecules are held together by London dispersion force. The physical state of a molecular substance depends upon the strength of these forces. Fluorine at the top to group VII A has small size and low polarizability, therefore the intermolecular forces between F_2 molecules are weak and it exist as a gas. Iodine at the bottom of group VIIA has relatively large size, high polarizability, and there are very strong forces of attraction between I_2 molecules. Hence it exists as a solid at room temperature.
2.	D	Iodine show positive oxidation states of +1, +3, +5 and +7 e.g. In HIO_3, its oxidation state = +5; HIO_4, its oxidation state = +7
3.	D	Iodine is a solid halogen because as we move down the group, strength of van der waals forces increases and Iodine is at the bottom having strongest intermolecular force.
4.	A	Chlorine cannot oxidize F^- (Fluoride ion) to F_2 between Fluorine is more electronegative.
5.	A	HF has the maximum bond energy because the bond between hydrogen and fluorine is the shortest and strongest due to flurine's high electronegativity and small atomic size.
6.	A	Thermal stability decreases down the group due to increasing bond length and decreasing bond dissociation energy. HF has the strongest H–X bond, making it the most stable.
7.	S.Q	AgF is highly soluble in water. All other silver fluorides are form precipitates i.e. insoluble in water.

8.	S.Q	Sodium hypochlorite which is produced in cold state in the above reaction decomposes forming sodium chloride and sodium chlorate at 70°C. $3NaClO_{(aq)} \longrightarrow 2NaCl_{(aq)} + NaClO_{3(aq)}$
9.	S.Q	Chlorinated water has also some harmful effects which are discussed below: 1. Hypochlorous acid or chlorine of water reacts with dissolved ammonia to form chloramines NH_2Cl, $NHCl_2$ and especially NCl_3 (nitrogen trichloride). NCl_3 is a powerful eye irritant. $NH_3 + 3HOCl \longrightarrow NCl_3 + 3H_2O$ The alkaline pH can prevent the formation of chloramines. 2. If phenol is present in water then chlorinated phenols are formed which have offensive odour and taste and are toxic.
10.	C	Chlorine reacts with water to form hypochlorous acid (HOCl) and hypochlorite ions (OCl^-) which are powerful oxidizing agents that destory microorganisms.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. Which halogen molecule has the strongest bond?
a) F_2 b) Br_2 c) I_2 d) Cl_2

II. The volatility of the halogens (Group 17) generally as you move down the group (from Fluorine to Iodine).
a) Increases b) Decreases c) Remains the same d) Fluctuates unpredictably

III. Which one of the following halogen molecules has strongest oxidizing power?
a) Br_2 b) F_2 c) I_2 d) Cl_2

IV. The decreasing thermal stability of the halogens down the group is primarily due to the:
a) Increasing electronegativity of the atoms.
b) Decreasing bond length between the halogen atoms.
c) Increasing atomic radius, leading to a weaker covalent bond.
d) Increasing strength of van der Waals forces

V. Which one of the following halides has strongest reducing power?
a) F^- b) Cl^- b) Br^- d) I^-

VI. Which statement about the reaction between halogens and hydrogen is correct?
a) Iodine reacts most vigorously with hydrogen
b) Chlorine and hydrogen explode in darkness
c) Fluorine combines explosively with hydrogen even in cold and dark conditions
d) Bromine and hydrogen do not react at all

VII. How does the acidic strength of hydrogen halides change as you move down the group?
a) It remains constant. b) It decreases from HF to HI.
c) It increases from HF to HI. d) It fluctuates erratically

VIII. Why is fluorine the most reactive halogen?
a) Bond length in the halogen molecule b) Bond strength in the halogen molecule
c) Electronegativity of the halogen d) Number of electrons in the halogen molecule

IX. When aqueous silver nitrate is added to a solution containing bromide ions, a cream precipitate forms. What is the solubility of this precipitate in ammonia solution?
a) Soluble in dilute ammonia solution. b) Partially soluble in dilute ammonia solution.
c) Insoluble in dilute ammonia solution. d) Soluble only upon heating with ammonia.

X. Concentrated sulfuric acid is added to solid sodium chloride. What is the initial observation?
a) Reddish-brown fumes are evolved.
b) A purple vapor is evolved.
c) Steamy white fumes of hydrogen chloride are evolved.
d) A black solid is formed.

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	c	I_2	• Bond strength increases down Group 17 due to greater orbital overlap (larger atomic size). • Iodine (I_2) has the strongest bond (bond energy: $F_2 < Cl_2 < Br_2 < I_2$).
II.	b	Decreases	• Volatility decreases down the group as van der Waals forces increase with larger atomic size (F_2 gas → I_2 solid).
III.	b	F_2	• Fluorine (F_2) is the strongest oxidizer due to its highest electronegativity and weak F–F bond (easily breaks to oxidize others).
IV.	c	Increasing atomic radius, leading to a weaker covalent bond	• Larger atomic size reduces orbital overlap, weakening the X-X bond (e.g., $F_2 > Cl_2 > Br_2 > I_2$ stability).
V.	b	It decreases from HF to HI	• HF has strong hydrogen bonding, while HI has weak dipole forces. Boiling points: HF > HI > HBr > HCl.
VI.	c	Electronegativity of the halogen	• Fluorine is most reactive due to its highest electronegativity (attracts electrons aggressively) and low bond energy (F–F bond weak).
VII.	c	It increases from HF to HI	• Acidic strength order: HI > HBr > HCl > HF. • Reason: Bond strength decreases down the group (HF has the strongest H–F bond due to high electronegativity and small size of F), making HX dissociation easier.
VIII.	b	Bond strength in the halogen molecule	• Fluorine (F_2) is the most reactive halogen because its weak F–F bond (due to lone pair repulsions in small atoms) is easily broken, facilitating reactions.
IX.	b	Partially soluble in dilute ammonia solution	• Cream Precipitate: AgBr (silver bromide). • Solubility: AgBr is partially soluble in dilute NH_3 (unlike AgCl, which dissolves completely, and AgI, which is insoluble).
X.	c	Steamy white fumes of hydrogen chloride are evolved	• Reaction: $NaCl_{(s)} + H_2SO_4 \rightarrow NaHSO_4 + HCl_{(g)}\uparrow$ • Observation: Steamy white fumes of HCl gas (due to HCl reacting with moisture in air).

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Which halogen is the least reactive, which is the most reactive? Give reason.

Ans.
- **Most reactive halogen:** Fluorine (F_2)
- **Least reactive halogen:** Iodine (I_2)

Reason:

As we go down Group 17 in the periodic table:
- Atomic size increases.
- Electronegativity decreases.
- Bond energy decreases.

This makes fluorine the most reactive because it attracts electrons strongly. Iodine is the least reactive because its larger atoms hold electrons less tightly.

b. The ionic equation for a reaction is: $Br_2 + 2I^- \longrightarrow Br^- + I_2$

Explain which species is oxidized in this reaction. Why?

Ans. The given reaction is a redox (displacement) reaction:

$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

Observations:

Oxidation: $I^- \longrightarrow I_2 + 2e^-$ (Iodide is oxidized, losing electrons).

Reduction: $Br_2 + 2e^- \longrightarrow 2Br^-$

Displacement:
- Br_2 (stronger oxidant) displaces I^- from its compound, confirming the trend:
- Br_2 is more reactive than I_2 in the halogen reactivity series.

In short:
- Spontaneous reaction (Br_2 has higher reduction potential than I_2).
- Net ionic form (spectator ions omitted).

Species is oxidized in this Reaction:
- Iodide ion (I^-) is oxidized.
- It loses electrons and forms iodine (I_2).
- Oxidation means loss of electrons.

So, iodide is oxidized and bromine is reduced.

c. What is role of London dispersion forces in the trend of volatility of halogens?

Ans. Role of London dispersion forces in the trend of volatility of Halogens:
- London dispersion forces are weak forces between molecules.
- As you move down the group, atoms become larger, so dispersion forces become stronger.
- Stronger forces mean lower volatility (less easily turned to gas).

This is the reason that fluorine (gas) is most volatile and iodine (solid) is least volatile.

d. How does the reactivity of halogens with hydrogen vary?

Ans. Reactivity **decreases down the group:**
- Fluorine reacts explosively with hydrogen.
- Chlorine reacts quickly in light.
- Bromine reacts slowly.
- Iodine reacts very slowly and incompletely.

This is due to decreasing bond strength and oxidizing power down the group.

e. Which halogen is used as an antiseptic? How does it work?

Ans. Halogen is used as an Antiseptic:
- Iodine is used as an antiseptic.
- It kills bacteria by oxidizing their cell contents.
- Often used in the form of tincture of iodine (iodine + alcohol).

f. What is the colour change when chlorine displaces bromine?

Ans. Chlorine displaces bromine from a solution of potassium bromide:

$$Cl_2 + 2KBr \rightarrow 2KCl + Br_2$$

Observation:
- Colourless solution turns reddish-brown due to the formation of bromine.

g. How the halogen acids are ionized in water?

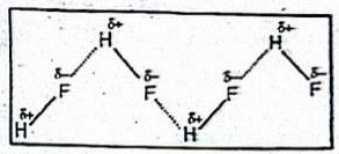
Ans. Halogen acids ionize in water and form Halide ions and hydronium ions (H_3O^+).

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$
$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
$$HBr + H_2O \rightleftharpoons H_3O^+ + Br^-$$
$$HI + H_2O \rightleftharpoons H_3O^+ + I^-$$

h. Why HF is weaker acid than HCl?

Ans. HF is a weaker acid than HCl (Acidic strength ∝ Ionization)

A substance which has a tendency to give proton (H^+) in an aqueous solution is called acid. The strength of an acid is directly proportional to its proton (H^+) releasing power.



HF has weak acidic properties in aqueous solution to incomplete dissociation of HF molecule in water. In HF, strong hydrogen bonding is present and partially positive hydrogen is entrapped between two strong electronegative fluorine atoms. Moreover, HF has a strong polar covalent bound with high bond energy (566 kJ/mol). So, Hydrogen ions (H^+) are not released easily.

As a result it becomes difficult for proton (H^+) to be ionized (released) resulting in lower concentration of hydrogen ions compared to stronger acids like HCl in water making HF a weaker acid.

On the other hand in HCl dipole-dipole interaction is present which is weaker than hydrogen bonding. Therefore proton (H^+) releasing power of HCl is more which makes it strong acid.

$$\cdots\cdots \overset{\delta+}{H}\text{—}\overset{\delta-}{Cl}\cdots\cdots \overset{\delta+}{H}\text{—}\overset{\delta-}{Cl}\cdots\cdots \overset{\delta+}{H}\text{—}\overset{\delta-}{Cl}\cdots\cdots$$

Therefore, it is not easy for HF to release H^+ as compared to HCl. It makes HF weaker acid than HCl.

i. Describe a simple chemical test that could be used to distinguish between aqueous solutions of potassium bromide and potassium iodide. Include the reagents and expected observations.

Ans. Reagents:
- Chlorine water
- Organic solvent (like carbon tetrachloride or hexane)

Procedure & Observation:
- Add chlorine water to both solutions.
- Then shake with organic solvent.

Solution	Observation	Conclusion
KBr	Reddish-brown layer	Br_2 formed
KI	Purple/violet layer	I_2 formed

j. Explain the chemical principles behind the use of chlorine as a disinfectant in water purification. Include relevant chemical equations in your explanation.

Ans. Chlorine kills bacteria by forming hypochlorous acid (HOCl):

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

HOCl is a strong oxidizing agent. It penetrates and destroys bacterial cells.

k. Describe one significant disadvantage associated with the use of chlorine in water purification.

Ans. Disadvantage:

- Chlorine reacts with organic matter in water to form harmful by-products called trihalomethanes (THMs).
- These can be carcinogenic (cancer-causing).

l. What is disproportionation reaction? Give an example.

Ans. A disproportionation reaction is when one element is both oxidized and reduced in the same reaction.

Example:

$$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$$

Chlorine goes from 0 to −1 (reduced) and 0 to +1 (oxidized).

m. Chlorine gas reacts differently with sodium hydroxide solution depending on the temperature and concentration.

Ans. Yes. It forms different products with cold and hot NaOH.

n. Write balanced chemical equations for the reaction of chlorine (Cl_2) with:

i) Cold, dilute sodium hydroxide (NaOH).

ii) Hot, concentrated sodium hydroxide (NaOH).

Ans. i) Cold, dilute NaOH: $Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$

ii) Hot, concentrated NaOH: $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

o. For each reaction in question 1), identify the oxidation states of chlorine in the reactant (Cl_2) and in each of the chlorine-containing products. Use these oxidation states to explain why both reactions are classified as disproportionation reactions.

Ans. Cold reaction:

- $Cl_2(0) \longrightarrow Cl^-(-1)$ = reduction
- $Cl_2(0) \longrightarrow ClO^-(+1)$ = oxidation

Hot reaction:

- $Cl_2(0) \longrightarrow Cl^-(-1)$ = reduction
- $Cl_2(0) \longrightarrow ClO_3^-(+5)$ = oxidation
- In both reactions, chlorine is oxidized and reduced — a disproportionation reaction.

DESCRIPTIVE QUESTIONS

Q.3 Describe and explain the relative thermal stabilities of the halogen hydrides in terms of bonds strength.

Ans. See Page No. (450)

Q.4 Discuss the relative reactivity of the halogen elements as oxidizing agents. Arrange F_2, Cl_2, Br_2, I_2 in increasing order of the oxidizing power.

Ans. See Page No. (448)

Q.5 Discuss the reducing power of halide ions with relevant reactions. Also explain the factors affecting it.

Ans. See Page No. (452)

ADDITIONAL SLOs BASED MCQs

1. **Which halogen has greenish yellow colour?**
   A. F_2 B. Cl_2 C. Br_2 D. I_2
2. **Which halogen exist in liquid state?**
   A. F_2 B. Cl_2 C. Br_2 D. I_2
3. **Which of the following is a strongest reducing agent?**
   A. F^- B. Br^- C. Cl^- D. I^-
4. **Oxidizing power of which halogen is highest?**
   A. F_2 B. Cl_2 C. Br_2 D. I_2
5. **Which is strongest acid?**
   A. HF B. HCl C. HBr D. HI
6. **Highest electron affinity is shown by?**
   A. F B. I C. Br D. Cl
7. **Which is the strongest reducing agent?**
   A. HF B. HCl C. HI D. HBr
8. **Substance boiling at higher temperature among following is?**
   A. HI B. HF C. HCl D. HBr
9. **Group VII-A elements are generally called:**
   A. halogens B. noble gases C. inert gases D. metalloids
10. **The radioactive element in halogen group is:**
    A. radon B. radium C. astatine D. bromine

Answer Key with Explanations

Sr. #	Ans.	Explanations
1.	B	Chlorine (Cl_2) is a greenish-yellow gas.
2.	C	Bromine (Br_2) is the only halogen that exists as a liquid at room temperature.
3.	D	Iodide (I^-) is the strongest reducing agent among the halide ions due to its larger size and lower ionization energy, making it easier to donate electrons.
4.	A	Fluorine (F_2) has the highest oxidizing power among the halogens due to its high electronegativity and small atomic size.
5.	D	Hydroiodic acid (HI) is the strongest acid among the hydrohalic acids due to the weak bond between hydrogen and iodine, which makes it easier to dissociate in water.
6.	D	Electron affinity, of halogens is F (−322kJmol^{-1}); Cl (−349 kJ mol^{-1}), Br (−325 kJ mol^{-1}) and I (−295 kJ mol^{-1})
7.	C	HF, HCl, HBr and HI act as reducing agents in the following order: HF < HCl < HBr < HI
8.	B	The boiling points of hydrogen halides are as follow: HF = 19.5°C, HCl = −85.0°C, HBr = −66.7°C, HI = −35.3°C
9.	A	Group VIIA elements are called the halogens from Greek hals, "salt" and gennan, "to form or generate", because they are literally the salt formers.
10.	C	Astatine is a rare halogen. It is radioactive and its most stable isotope has a half life of 8.3 hrs.

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 The reducing power of halide ions decreases in the order: $I^- > Br^- > Cl^- > F^-$. Give reason.

Ans. Iodide is the best reducing agent due to its large size and low electronegativity, making electron loss easier. Fluoride, being small and highly electronegative, holds its electrons tightly and resists oxidation. As size increases and electronegativity decreases, the tendency to donate electrons (reducing power) increases.

Q.2 The thermal stability of hydrogen halides decrease down the group. Why?

Ans. The thermal stability of hydrogen halides decreases in the order: **HF > HCl > HBr > HI.**
This is because the **H–X bond strength decreases down the group.**
HF has the strongest bond due to the small size of fluorine, making it more stable to heat.
As the size of halogen increases from F to I, the H–X bond becomes weaker and easier to break on heating.

Q.3 Bond strength in halogens decreases as we move down the group from chlorine to iodine. WHY?

Ans. Bond strength in halogens decreases as we move down the group from chlorine to iodine. This is due to the increase in the atomic size down the group which results in longer bond lengths and weaker bonds. Moving from top to bottom in group 17, the bond energy of halogens decreases gradually from chlorine to iodine.

Q.4 The thermal stability of hydrogen halides decrease down the group. Why?

Ans. Halogens are non-polar and instantaneous dipole-induced forces play a significant role in determining the volatility of halogens. The forces depend on factors like molecular size, shape and polarizability, with stronger forces leading to lower volatility and higher boiling points. The first two halogens, i.e., fluorine (colourless or very light green) and chlorine (greenish yellow) are gases due to weaker id-id forces. Bromine is a liquid as its size is bigger and it possesses stronger intermolecular forces than fluorine and chlorine. Iodine has the strongest forces among the group, so it is in solid state at room temperature.

Q.5 The reactivity of halogens with hydrogen decreases down the group. Why?

Ans. The reactivity of halogens with hydrogen decreases down the group: $F_2 > Cl_2 > Br_2 > I_2$.
This is because **bond dissociation energy of H–X decreases and halogens become less electronegative** down the group.
Fluorine forms a strong H–F bond and is highly reactive due to its small size and high electronegativity. As we move down, halogens form weaker H–X bonds and react less readily with hydrogen.

Q.6 What is disproportionation reaction?

Ans. Those reactions in which a single element undergoes both oxidation and reduction simultaneously are known as disproportionation reactions. When chlorine reacts with cold and hot aqueous sodium hydroxide (NaOH), it undergoes disproportion and form different products according to the temperature of the reaction.

Q.7 The thermal stability of hydrogen halides decrease down the group. Why?

Ans. Chlorine undergoes disproportion when it reacts with cold aqueous sodium hydroxide (NaOH) forming sodium chloride (NaCl) and sodium chlorate (I) (NaClO).

$$Cl_{2(g)} + 2NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + NaClO_{(aq)} + H_2O_{(l)}$$

Oxidation states of chlorine in the above reaction are given below:

Chlorine in Cl_2 = 0
Chlorine in NaCl = –1
Chlorine in NaClO = +1

Q.8 what happens when chlorine react with water?

Ans. When chlorine gas (Cl_2) is added to water, it undergoes hydrolysis to form a mixture of hydrochloric acid (HCl) and chloric (I) acid (HClO).

$$Cl_{2(g)} + H_2O_{(l)} \longrightarrow HCl_{(aq)} + HClO_{(aq)}$$

Chloric (I) acid (HOCl) is a weak acid and partially dissociate in water to form hydrogen ions (H^+) and chlorate (I) ion (OCl^-).

Q.9 How do pH and chlorine dose affect the disinfection?

Ans. **pH:**
At pH around 6-7.5, HOCl predominates and makes the disinfection process more effective.
At higher pH (above 7.5), OCl^- predominates, it is less effective but still provides disinfection.
Chorine Dose:
The higher the amount of chlorine, the more effective the disinfection. Sufficient chlorine must be added to get enough HOCl and OCl^- to kill bacteria.
Contact Time:
Contact time of water with chlorine must be long enough, to allow the disinfectants to penetrate and kill bacteria, viruses and protozoa.

Q.10 Write reaction of halides with conc. sulphuric acid.

Ans. Halides react differently with concentrated sulphuric acid (H_2SO_4) depending on their nature:

Fluoride (F^-) and Chloride (Cl^-):
Act as acids only — produce HF or HCl gas.
Example:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$$

Bromide (Br^-) and Iodide (I^-):
Act as reducing agents — reduce H_2SO_4 and are oxidized to Br_2 or I_2.
Example:

$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$$
$$8HI + H_2SO_4 \longrightarrow 4I_2 + H_2S + 4H_2O$$

Trend: Reducing ability increases from $Cl^- < Br^- < I^-$.

◈◈◈◈◈

SELF-ASSESSMENT Chapter # 13

Total Marks: 30

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) **Which halogen molecule has the strongest bond?**
A. F_2 B. Br_2 C. I_2 D. $C\ell_2$

(ii) **Which one of the following halogen molecules has strongest oxidizing power?**
A. Br_2 B. F_2 C. I_2 D. $C\ell_2$

(iii) **The decreasing thermal stability of the halogens down the group is primarily due to the:**
A. Increasing electronegativity of the atoms.
B. Decreasing bond length between the halogen atoms.
C. Increasing atomic radius, leading to a weaker covalent bond.
D. Increasing strength of van der Waals forces

(iv) **How does the acidic strength of hydrogen halides change as you move down the group?**
A. It remains constant. B. It decreases from HF to HI.
C. It increases from HF to HI. D. It fluctuates erratically

(v) **Why is fluorine the most reactive halogen?**
A. Bond length in the halogen molecule B. Bond strength in the halogen molecule
C. Electronegativity of the halogen D. Number of electrons in the halogen molecule

(vi) **When aqueous silver nitrate is added to a solution containing bromide ions, a cream precipitate forms. What is the solubility of this precipitate in ammonia solution?**
A. Soluble in dilute ammonia solution. B. Partially soluble in dilute ammonia solution.
C. Insoluble in dilute ammonia solution. D. Soluble only upon heating with ammonia.

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) Why chlorine is more volatile than bromine and iodine?
(ii) HF is the most thermally stable hydrogen halide. Give reasons.
(iii) Write down the equation for the reaction of KI with Ag^+ followed by NH_3. What would you observe at the completion of this reaction?
(iv) HI acts as strong reducing agent. Explain it with two chemical reactions.
(v) Which halogen is used as an antiseptic? How does it work?
(vi) Why HF is weaker acid than $HC\ell$?
(vii) Describe a simple chemical test that could be used to distinguish between aqueous solutions of potassium bromide and potassium iodide. Include the reagents and expected observations.
(viii) Explain the chemical principles behind the use of chlorine as a disinfectant in water purification. Include relevant chemical equations in your explanation.

Q.3 Extensive Questions. (2 × 4 = 8)

(a) Discuss reactions of halides with aqueous silver ion followed by aqueous ammonia.
(b) Describe the reactions that occur when chlorine is bubbled through
(i) Cold and (ii) Hot, aqueous sodium hydroxide (NaOH).

Chapter 14

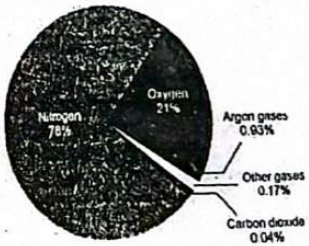
ATMOSPHERE

Student Learning Outcomes

After studying this chapter, students will be able to:

- Identify the properties and composition of the atmosphere. (Include the concept of 4 layers of atmosphere and their composition. **(Understanding)**
- Describe the sources and understand the effect of air pollution, (this can include both natural and human caused pollutants including Greenhouse gases (such as carbon dioxide, methane, and nitrous oxide), Chlorofluorocarbons (CFCs), and Ozone (O_3) and other ozone-depleting substances, Volatile organic compounds (VOCs), Polycyclic aromatic hydrocarbons (PAHs), Persistent organic pollutants (POPs), Heavy metals such Lead (Pb), Mercury (Hg), Cadmium (Cd). **(Understanding)**
- Describe the impact of human activities on the atmosphere including the effects of burning fossil fuels and deforestation. **(Understanding)**
- Identify the chemical reactions and processes that occur in the atmosphere (some examples include the formation of smog and acid rain). **(Understanding)**
- Identify the global scale problems of air pollution, such as global warming and the greenhouse effect. **(Understanding)**
- Describe the factors that affect air quality. **(Understanding)**
- Explain the link between air quality and human health. **(Understanding)**
- Evaluate the potential health risks associated with air pollution. **(Understanding)**
- Familiarize with use of methods and techniques to measure and monitor air quality. **(Understanding)**
- Design experiments and collect data to test hypotheses about air quality. **(Application)**
- Analyze data and interpret air quality measurements and trends. **(Understanding)**
- Explain the technologies and strategies used to reduce air pollution and improve air quality, such as emissions control and renewable energy sources. **(Understanding)**
- Identify the laws and regulations related to air quality and the measures used to control air pollution. **(Understanding)**
- Analyze the economic, social, and political issues related to air pollution and air quality management and demonstrate through answers. **(Understanding)**

The atmosphere is a sphere of different gases around the earth. The component of the atmospheres may be divided into major, minor and trace components. Major components are nitrogen (78.00 %) and oxygen (21 %). Minor components are argon (0.93 %), carbon dioxide (0.04 %). Trace components are methane, hydrogen, neon, helium, krypton, and xenon.



LAYERS OF THE ATMOSPHERE

The atmosphere has four distinct layers which are determined by the change in temperature that is observed with increasing altitude.

i) **Troposphere**

It is the lowest region of the atmosphere which extends up to 12 km. It includes all the major gases present in the atmosphere i.e., nitrogen, oxygen, and carbon-dioxide, etc. In this region, temperature decreases from 17°C to −58°C regularly. It is the densest layer of the atmosphere. It is the layer in which major events such as rain, lightening, and hurricanes occur.

ii) **Stratosphere**

Above the troposphere, the stratosphere lies which is at a distance of 12 – 50 km above the earth surface. Temperature increases from −58°C to −2°C. Stratosphere can also be divided into three regions according to the distribution of ultraviolet radiations from the Sun. Since ozone in the upper layer absorbs high energy ultraviolet radiations from the Sun. Ozone breaks down into monoatomic oxygen and diatomic oxygen.

$$O_{3(g)} \xrightarrow{h\nu} O_{2(g)} + O_{(g)}$$

The middle stratosphere has less ultraviolet radiations passing through it. Here, monoatomic oxygen and diatomic oxygen recombine to form ozone which is an exothermic reaction due to which formation of ozone layer takes place.

$$O_{2(g)} + O_{(g)} \longrightarrow O_{3(g)}$$

The lower stratosphere receives very low ultraviolet radiations, thus monoatomic oxygen is not found here and ozone is not formed here.

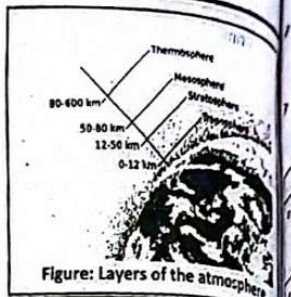


Figure: Layers of the atmosphere

Rack Your Mind!

1. Which layer of the atmosphere contains the ozone layer that protects life from harmful UV rays?
A) Troposphere B) Mesosphere
C) Thermosphere D) Stratosphere

Rack Your Mind!

2. What are the four main layers of the atmosphere and their key features?

iii) **Mesosphere**

It extends to a height of about 50 – 85 km from the ground. Here, the temperature decreases with altitude from −2°C to −93°C. The coldest region of the atmosphere is located in this layer.

iv) **Thermosphere**

It extends from 85 km to 600 km above the earth surface. This is the region where the temperature increases as the altitude increases. The increase in the temperature is caused due to the absorption of energetic ultra-violet (UV) and X-rays. Temperature in the upper thermosphere can range from 500°C to 2000°C or higher.

AIR POLLUTANTS

Pollutants are substances (gases, liquids and solids) that are harmful to the environment.

The most important pollutants are mentioned below:

- Oxides of Carbon (CO and CO_2)
- Oxides of Nitrogen (NO and NO_2) collectively known as NO_x
- Oxides of Sulphur (SO_2 and SO_3) collectively known as SO_x
- Hydrocarbons (Methane, Ethane)
- Low altitude Ozone (O_3)
- Chlorofluorocarbons (CFCs)
- Polycyclic Aromatic Hydrocarbon (PAHs)
- Persistent Organic Pollutant (POPs)
- Volatile Organic Compounds (VOCs)
- Particulate Matter (PM)
- Heavy Metals (Pb, Hg and Cd)

Air pollutants can be classified as primary and secondary.

Primary Pollutants:

Primary pollutants are substances directly produced or emitted, such as ash from a volcanic eruption or carbon monoxide gas from a motor vehicle exhaust.

Secondary Pollutants:

Secondary pollutants are formed due to chemical reactions of primary pollutants.

Differences between Primary and Secondary Pollutants

Primary Pollutants	Secondary Pollutants
• "The pollutants which are directly introduced into the environment from the sources are called primary pollutants."	• "The pollutants which are produced as a result of various reactions of primary pollutants in the environment are called secondary pollutants."
• They are emitted in the same form as they exist in the atmosphere.	• They are formed by transformation of primary pollutants.
• They formed instantly.	• They are formed overtime through chemical or photochemical reactions.
Examples: • Sulphur dioxide, sulphur trioxide, nitrogen oxides, carbon monoxide, hydrocarbons, ammonia, compounds of fluorine and radioactive materials.	Examples: • Sulphuric acid, nitrogen monoxide, carbonic acid, hydrofluoric acid peroxyacetyl-nitrate (PAN), ozone, aldehydes, ketones and peroxybenzol.

SOURCES OF AIR POLLUTION

There are broadly two main sources of air pollution:

(i) Natural sources (ii) Human-made sources

Natural Sources

- Naturally occurring particulate matter (PM) include dust from earth's surface, and biological materials in the form of pollens, spores and animal debris.
- Volcanic eruptions can introduce very large quantities of gases and particulate matter (PM) into the atmosphere.
- Thunderbolt produces significant quantities of oxides of nitrogen (NO_x).
- Other natural sources of air pollution are algae on the surface of the oceans, which gives out hydrogen sulphide (H_2S), wind erosion which introduces PM, and humid zones such as swamps, peat-bags or little deep lakes, which produce methane (CH_4).

Human-Made Sources

- Such sources can be classified as either mobile (cars, trucks, air planes, marine engines) or point sources (factories, electric power plants etc.).
- The combustion of fossil fuels (coal, fuel oils, and natural gas) in vehicle engines, factories and power plants produce carbon dioxide (CO_2) carbon-monoxide (CO), and hydrocarbons (CH_4).
- The burning of wood as a domestic fuel and coal in brick kilns are also the sources of air pollutants.

QUICK CHECK 14.1

1a) **Mention important air pollutants.**

Ans. **The most important pollutants are mentioned below:**

- Oxides of Carbon (CO and CO_2)
- Oxides of Nitrogen (NO and NO_2) collectively known as NO_x
- Oxides of Sulphur (SO_2 and SO_3) collectively known as SO_x
- Hydrocarbons (Methane, Ethane)

- Low altitude Ozone (O_3)
- Chlorofluorocarbons (CFCs)
- Polycyclic Aromatic Hydrocarbon (PAHs)
- Persistent Organic Pollutant (POPs)
- Volatile Organic Compounds (VOCs)
- Particulate Matter (PM)
- Heavy Metals (Pb, Hg and Cd)

b) Give the equations for the formation and depletion of ozone in the stratosphere.

Ans. Formation of Ozone:

The middle stratosphere has less ultraviolet radiations passing through it. Here, monoatomic oxygen and diatomic oxygen recombine to form ozone which is an exothermic reaction due to which formation of ozone layer takes place.

$$O_{2(g)} + O_{(g)} \longrightarrow O_{3(g)}$$

Depletion of Ozone

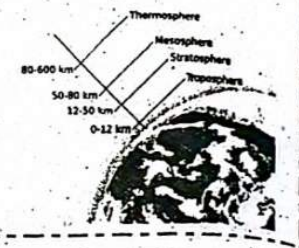
Since ozone in the upper layer absorbs high energy ultraviolet radiations from the Sun. It breaks down into monoatomic oxygen and diatomic oxygen.

$$O_{3(g)} \xrightarrow{h\nu} O_{2(g)} + O_{(g)}$$

c) Write down the names and approximate height of different layers of atmosphere.

Ans. The names and approximate height of different layers of atmosphere are given below;

- Troposphere – 0 to 12 km
- Stratosphere – 12 to 50 km
- Mesosphere – 50 to 80 km
- Thermosphere – 80 to 600 km



SOURCES OF AIR POLLUTANTS

Oxides of Carbon

There are two oxides of carbon i.e., carbon monoxide (CO) and carbon dioxide (CO_2).

Carbon Monoxide (CO):

Carbon monoxide (CO) Carbon monoxide (CO) is produced mainly due to incomplete combustion of fossil fuels.

$$2C_{(s)} + O_{2(g)} \longrightarrow 2CO_{(g)}$$

CO binds with haemoglobin approximately 200 to 250 times more strongly than O_2 does.

Did You Know?

Carbon monoxide is highly poisonous gas and cause suffocation if inhale. It binds blood hemoglobin more strongly than oxygen thus excluding oxygen from normal respiration. The CO poisonous can be reversed by giving high pressure oxygen.

Carbon Dioxide (CO_2):

Carbon dioxide is the key greenhouse gas emitted by human activities like combustion of fossil fuels. Carbon dioxide (CO_2) is a primary greenhouse gas that traps heat in the atmosphere, leading to global warming.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$$

Oxides of Nitrogen (NO_x)

- The gases like nitric oxide (NO) and nitrogen dioxide (NO_2) are represented by NO_x.
- These are generally produced from burning fossil fuels. NO_x is produced as a result of the following chemical reactions:

$$N_{2(g)} + O_{2(g)} \xrightarrow{\text{high temp}} 2NO_{(g)} \quad \text{(Nitric oxide)}$$

$$2NO_{(g)} + O_2 \longrightarrow 2NO_2 \quad \text{(Nitrogen-Dioxide)}$$

- Natural sources of N_2O include microbial processes in soil and oceans where bacteria break down nitrogen compounds.
- Human activities include agricultural activities (synthetic fertilizers) and industrial processes (combustion of fossil fuels). It depletes the ozone layer.
- The increased levels of N_2O contribute to climate change and can also affect air quality.

Oxides of Sulphur (SO_x)

- There are two oxides of sulphur i.e., sulphur dioxide (SO_2) and sulphur trioxide (SO_3) which are collectively called SO_x.
- These gases are emitted primarily by burning coal and oil. When SO_x combine water vapour, it causes acid rain that damages ecosystem. SO_2 is the major source of acid deposition in the air.

Hydrocarbons

- Hydrocarbons are produced naturally in various environmental processes like vegetation, wildfire, volcanoes, and seeps.
- Anthropogenic activities like incomplete burning of fossil fuels, oil spills, industrial and vehicle emission are sources of hydrocarbons.
- Automobiles are the major source of hydrocarbon emission.
- Methane is the most common hydrocarbon and air pollutant.

Low-Altitude Ozone (O_3)

- Ozone is a powerful oxidizing agent. It is non-toxic in small concentrations, but above 100 parts per million (ppm), it is toxic.
- It is harmful to humans, plants and other materials i.e., rubber, fabric dyes, and durability and appearance of paints.

Exercise LO 4.1

Q.4 Write short notes on the following:

i) CFCs and ozone layer depletion

Chlorofluorocarbons (CFCs) and Ozone Layer Depletion

- The decrease in the concentration of ozone in stratosphere is called depletion of ozone: This depleting of ozone has been caused by certain organic compounds called chlorofluorocarbons (CFCs).
- These compounds exist as gases or low boiling liquids at room temperature and are used as aerosols or refrigerants.
- Chlorofluorocarbons are known to diffuse into the stratosphere where they are broken down by UV radiation creating chloride free radical ($Cl^\bullet$). The chloride free radical breaks down the Ozone molecule as shown in the following reactions.

$$CFCl_3 \xrightarrow{UV} CFCl_2 + Cl^\bullet$$
$$Cl^\bullet + O_3 \longrightarrow ClO^\bullet + O_2$$
$$ClO^\bullet + O_2 \longrightarrow Cl^\bullet + O_2$$

- The formation of another chlorine free radical in the last step that can further break down another molecule of O_3. The 2nd and the 3rd steps are repeated many times.

Interesting Information!

Chlorofluorocarbons (CFCs) are used as propellants for aerosols and as coolant in refrigerators and air conditions. CFCs are 100,000 times more effective than CO_2 at preventing heat from especially from the earth's atmosphere. The decomposition of one molecule of CFCs can destroy up to 100,000 molecules of ozone.

Exercise L.O.2

Q. Discuss sources and effects of following air pollutants on environment:
i) Heavy metals ii) VOCs iii) PAHs iv) POPs

Polycyclic Aromatic Hydrocarbon (PAHs)

- Polycyclic aromatic hydrocarbon (PAHs), composed of fused multiple aromatic rings are common environmental pollutants. **e.g.,** Naphthalene, anthracene and phenanthrene.
- PAHs are generated primarily during the incomplete combustion of fossil fuels (coal, oil, petrol, and wood), vehicle emissions, industrial processes and even grilled foods.
- Some PAHs in the environment originate from the natural sources such as open burning, natural loss or seepage of petroleum and coal deposits. PAHs have potential toxicity and carcinogenic properties.

Persistent Organic Pollutants (POPs)

- POPs are organic compounds that are resistant to degradation through chemical, biological and photolytic processes.
- POPs are toxic and adversely affect human health and the environment, traveled by wind and water.
- Most POPs are generated in one country can affect people and wildlife far from where they are used and released.
- Because of their persistence, they accumulate in the environment and can have significant adverse effects on human health. Some POPs are given in Table below:

Table: Some POPs with their Uses

Names of POPs	Uses
Polychlorinated Biphenyls (PCBs)	Used in electrical equipment, surface coating ink, adhesives and paints
Dichlorobiphenyl tri-chloroethane (DDT)	Used as an insecticide in agriculture

Volatile Organic Compounds (VOCs)

- A large group of organic compounds that easily evaporates at room temperature.
- VOCs are emitted as gases from certain solids or liquids.
- Liquid fuels are major sources of VOCs that impact outdoor air quality.
- Vehicle exhaust and burning liquid fossil fuels, wood and garbage all release VOCs into the atmosphere.

Effect of VOCs:

- Exposure to VOCs can cause a variety of health effects including eye, nose and throat irritation, headache, nausea are short term exposures and damage to the liver, kidney and central nervous system are long term exposures
- They are significant air pollutants contributing to indoor and outdoor air pollution.

Examples:

- Some common VOCs are benzene, xylene, toluene, ethanol, formaldehyde, acetone etc.

Particulate Matter (PM)

The term "particulate matter (PM)" refers to the wide variety of tiny substances that float in the air in the form of either solid particles or liquid droplets or both.

- Particulate matter (PM) is all the dust, smoke, and haze particles suspended in ambient air.
- Particulate matter (PM) comprises acids, organic chemicals, metals, and soil or dust particles.
- **Sources of PM** are both natural and anthropogenic.

(i) **Natural sources** include volcanoes, fires, dust storms, and aerosolized sea salt.
(ii) **Man-made sources** of particulate matter PM include combustion in mechanical and industrial processes, vehicle emissions, and tobacco smoke.

Heavy Metals (Lead, Mercury and Cadmium)

- Heavy metal like lead, mercury and cadmium can indeed be significant air pollutants.
- They are released into the atmosphere from various industrial process, transportation and other human activities.
- Metallurgy, battery waste and incineration are their major sources.

IMPACT OF HUMAN ACTIVITIES ON THE ATMOSPHERE

Human activities have significant impact on the atmosphere, primarily through the burning fossil fuels and deforestation. These activities contribute to climate change, air pollution, poor air quality and other environmental issues.

In urban areas, most air pollution comes from human-made sources. Such sources can be classified as either mobile (cars, trucks, air planes, marine engines) or point sources (factories, electric power plants etc.)

Impact of Burning Fossil Fuels on the Atmosphere

The burning of fossil fuels is the primary cause of current climate change, altering the earth ecosystem and causing human and environment health problems. The burning of fossil fuels affects the earth system in a variety of ways. Some of these ways include greenhouse gas emission, air pollution, volatile organic compounds.

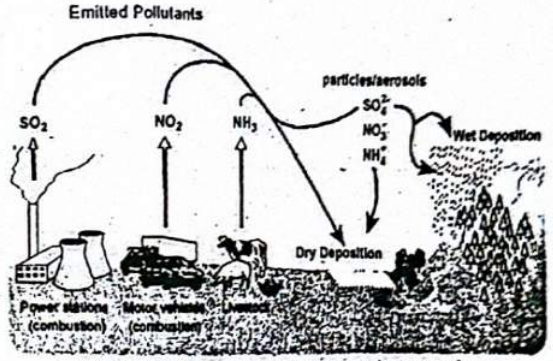


Figure: Impacts of air pollutants on the atmosphere

Impact of Deforestation on the Atmosphere

Deforestation is purposeful cleaning or thinning of forests by humans.

Causes:

(i) Agricultural expansion
(ii) Logging
(iii) Urbanization (Building roads, cities and infrastructures)
(iv) Mining

Deforestation represents one of the largest issues in global climate. Forests absorb GHGs like CO_2 and clean air for us.

Negative Effects of Deforestation:

Deforestation has a wide range of negative impact on the environment, including loss of biodiversity, climate change (trees absorb CO_2, without trees more CO_2 remains in the atmosphere), soil degradation (erosion), and water cycle disruption.

QUICK CHECK 14.2

a) **Mention man-made sources of air pollution.**

Ans. **Human-made sources**

Such sources can be classified as;

- Either mobile (cars, trucks, air planes, marine engines) or point sources (factories, electric power plants etc.).
- The combustion of fossil fuels (coal, fuel oils, and natural gas) in vehicle engines, factories and power plants produce carbon dioxide (CO_2) carbon-monoxide (CO), and hydrocarbons (CH_4).
- The burning of wood as a domestic fuel and coal in brick kilns are also the sources of air pollutants.

b) How do polycyclic aromatic hydrocarbons (PAHs) primarily enter the atmosphere?

Ans.

- They are generated primarily during the incomplete combustion of fossil fuels (coal, oil, petrol, and wood), vehicle emissions, industrial processes and even grilled foods.
- Some PAHs in the environment originate from the natural sources such as open burning, natural loss or seepage of petroleum and coal deposits.
- Naphthalene, anthracene and phenanthracene are examples of PAHs.
- They have potential toxicity and carcinogenic properties.

c) How do volatile organic compounds (VOCs) affect air quality?

Ans.

- Exposure to VOCs can cause a variety of health effects including eye, nose and throat irritation, headache, nausea are short term exposures and damage to the liver, kidney and central nervous system are long term exposures.
- They are significant air pollutants contributing to indoor and outdoor air pollution.
- Some common VOCs are benzene, xylene, toluene, ethanol, formaldehyde and acetone etc.

d) What are major sources of heavy metals in the atmosphere?

Ans. Heavy metal like lead, mercury and cadmium can indeed be significant air pollutants. They are released into the atmosphere from various industrial process, transportation and other human activities. Metallurgy, battery waste and incineration are their major sources.

EFFECTS OF AIR POLLUTANTS

The most important and commonly effects of air pollutants are formation of Smog and Acid Rain.

➲ Formation of Smog (Smoke + Fog)

Smog is a type of air pollution typically characterized by a thick haze. It primarily occurs in urban areas and is often caused by emissions from vehicle, industrial activities and other sources of pollution. It consists of fine dust or soot particles, condensed water vapor, poisonous gases like SO_2, NO_xO_3, CO, and CO_2, secondary pollutants like O_3, unburned hydrocarbons, VOCs and PM 10–2.5 micron.

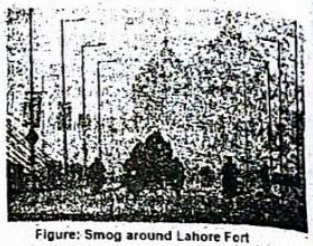


Figure: Smog around Lahore Fort

➲ Types of Smog

i) Industrial or Classical Smog (London Smog)
ii) Photochemical smog (Los Angeles Smog)

i) Classical or Sulphurous Smog

Sulfurous or Industrial smog also called as "Reducing smog or Classical Smog" usually results from high quantities of sulfur oxides (SO_x) being released into the air. It is also called **London smog.**

ii) Photochemical Smog

Photochemical smog is a type in which primary air pollutants like nitrogen oxides (NO_x), VOC and unburned hydrocarbons undergo photochemical reactions in the presence of sunlight and form secondary pollutants like ozone and peroxyacetyl nitrates (PAN). This type of smog is considered more dangerous as it can cause heart palpitations, pneumonia and even lung cancer. It is also called **Los Angeles smog.**

Rack Your Mind!

3. What is smog and how is it formed?

The term 'SMOG' was coined by Dr. Des Voeux.
Smog is a type of intense air pollution. The word "smog" was coined in the early 20th century, and is a contraction of the words smoke and fog to refer to smoky fog; its opacity and odour.

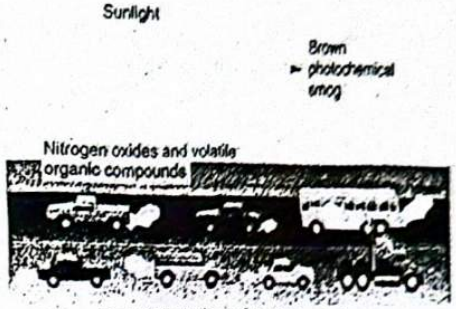


Figure: Illustration of Photochemical smog

Exercise Q.5

Q. How the fossil fuel burning causes acid rain? Discuss in detail with chemical reactions.

➲ Acid Rain

When rain water has pH less than 5-6, it is known as acid rain refers to precipitation (rain, snow sheet or hail). Burning of fossil fuels releases SO_x and NO_x into the atmosphere. These gases mix with the moisture in the air and form acids. Wind can carry these acidic droplets to huge distance. Finally, these droplets return to the ground as acid rain, acid hail, snow and even fog. Acid rain looks, feels and tastes like clean rain. Its corrosive nature causes widespread damage to the environment. The most important chemical reactions are following:

Rack Your Mind!

4. What causes acid rain?
A) Water vapor condensing into clouds
B) Sulfur dioxide and nitrogen oxides reacting with water
C) Ozone layer depletion
D) Deforestation

$$2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$$

$$SO_{3(g)} + H_2O_{(\ell)} \longrightarrow H_2SO_{4(aq)}$$

SO_2 from fossil fuels is oxidized to SO_3 which then reacts with water to form sulphuric acid.
Nitrogen oxide reacts with water to produce nitric acid and nitrous acid.

$$NO_{(g)} + H_2O_{(\ell)} \longrightarrow HNO_{3(aq)} + HNO_{2(aq)}$$

Effect of Acid Rain on Environment

(i) Acidification of the soil and rocks can leach metals like Aluminium, mercury, lead and calcium and discharges them into water bodies. These heavy metals are accumulated in the fishes and are health hazards for humans and birds as they eat these fishes. The elevated concentration of Aluminium is harmful for fish as it clogs the gills thus causing suffocation.
(ii) Acidification of the soil can also leach nutrients thus damaging leaves and plants and growth of forest.
(iii) It also damages building materials such as steel, paint, plastic, cement, masonry work and sculptural materials especially of marble and limestone.

GREENHOUSE EFFECT AND GLOBAL WARMING

Exercise Q.4 ii

Q.4 Write short notes on the following:
ii) Greenhouse effect and global warming

Global warming refers to the long-term rise in the Earth's average surface temperature due to human activities, primarily the emission of greenhouse gases (GHGs) released by burning fossil fuels. The progressive warming up of the earth's surface due to blanketing effect of greenhouse gases in the atmosphere is called the greenhouse effect.

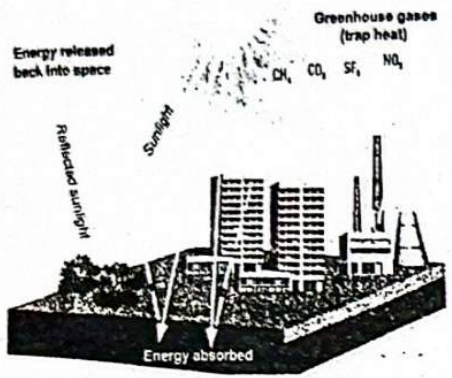


Figure: Mechanism of Global Warming

It is a global scale problem of air pollution. Carbon dioxide and water vapour in the atmosphere transmit short wavelength solar radiations but reflect back the longer wavelength heat radiation coming from warmed surface of the earth.

➤ **Greenhouse Effect:**

The greenhouse effect is a phenomenon which is based on the gases to absorb infrared radiations. In the day, heat from the sun (in the form of infrared) passes through the atmosphere heating up the earth. At night, the earth radiate heat to the outer space. Some atmospheric gases trap the heat from the sun, thus, preventing the loss of heat. Higher the concentration of carbon dioxide gas and other gases, greater will be the absorption of thermal radiations and greater will be the increase of global temperature.

Rack Your Mind!

5. Which of the following is a greenhouse gas that is also released by livestock and rice farming?
A) Oxygen B) Nitrogen
C) Methane D) CFC

Rack Your Mind!

6. What are greenhouse gases and how do they affect the Earth?

QUICK CHECK 14.3

a) **Differentiate classical and photochemical smog.**

Ans.

Feature	Classical Smog (London Smog)	Photochemical Smog (Los Angeles Smog)
Composition	Sulfur dioxide (SO_2), soot, and fog (sulfurous aerosols).	Ozone (O_3), NO_x, VOCs, PAN (Peroxyacyl nitrates).
Formation	Caused by burning coal (high sulfur content).	Forms due to sunlight-driven reactions of NO_x + VOCs.
Primary Pollutants	SO_2, particulate matter (PM), CO.	NO_x (NO, NO_2), hydrocarbons (VOCs).
Secondary Pollutants	Sulfuric acid (H_2SO_4), sulfate particles.	O_3, PAN, aldehydes.
Weather Conditions	Cold, humid climates (winter mornings).	Warm, sunny climates (summer afternoons).
Health Effects	Respiratory issues (bronchitis, asthma), reduced visibility.	Eye/nose irritation, lung damage, crop damage.
Geographical Association	Industrial cities (e.g., historic London).	Urban areas with high traffic (e.g., Los Angeles).
Key Chemical Process	Oxidation of $SO_2 \rightarrow H_2SO_4$.	NO_2 + sunlight → O_3 + other oxidants.

b) **Name greenhouse gases (GHGs). How do these gases cause global warming?**

Ans. **Greenhouse Gases (GHGs)**

(i) **Carbon Dioxide (CO_2):** Burning fossil fuels, deforestation.
(ii) **Methane (CH_4):** Agriculture (livestock), landfills, natural gas.
(iii) **Nitrous Oxide (N_2O):** Fertilizers, industrial processes.

(iv) **Water Vapor (H_2O):** Natural evaporation, amplified by warming.
(v) **Chlorofluorocarbons (CFCs):** Refrigerants (now regulated).
(vi) **Ozone (O_3):** Tropospheric pollution (not the protective stratospheric ozone).

How GHGs Cause Global Warming:

- **Natural Greenhouse Effect:** GHGs trap outgoing infrared (heat) radiation from Earth's surface, warming the planet to habitable levels.
- **Enhanced Effect (Anthropogenic):** Human activities increase GHG concentrations, causing excessive heat retention → rising global temperatures (global warming).

In short,

(i) Sunlight reaches Earth → Surface absorbs and re-emits heat as infrared radiation.
(ii) GHGs absorb this radiation → Re-radiate heat back to Earth (like a blanket).
(iii) **Result:** Disrupted energy balance → Climate change (melting ice, extreme weather).

c) **Write a balanced equation, including state symbols, showing the formation of sulfuric acid from atmospheric sulfur trioxide, SO_2.**

Ans. **Manufacturing of Sulphuric Acid:**

$$S_{(s)} + O_{2(g)} \xrightarrow[V_2O_5]{400\text{-}500^\circ C} SO_{2(g)} \quad \text{(Heterogeneous catalysis)}$$

$$2SO_{2(g)} + O_{2(g)} \xrightarrow[V_2O_5]{400\text{-}500^\circ C} 2SO_{3(g)} \quad \Delta H = -269.3 \text{ kJ mol}^{-1}$$

$$H_2SO_{4(aq)} + SO_{3(g)} \longrightarrow H_2S_2O_{7(l)}$$

$$H_2S_2O_{7(l)} + H_2O_{(l)} \longrightarrow 2H_2SO_{4(aq)}$$

d) **How HNO_3 is formed from NO in the atmosphere?**

Ans. Nitric acid (HNO_3) forms in the atmosphere through a series of reactions involving nitrogen oxides (NOx), which include nitric oxide (NO) and nitrogen dioxide (NO_2).

Key Steps:

i. **NO Emission:** NO is emitted into the atmosphere from sources like fossil fuel combustion, industrial processes, and lighting.
ii. **NO to NO_2:** NO reacts with ozone (O_3) or oxygen (O_2) to form NO_2.
iii. **NO_2 Reaction:** NO_2 reacts with hydroxyl radicals (OH) or ozone (O_3) to form nitric acid (HNO_3).

Equation:

i. $2NO + O_2 \rightarrow 2NO_2$
ii. $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

AIR QUALITY

Exercise L.Q.5

Q. What is meant by air quality AQI? Describe the factors affecting the air quality.

- Air quality is measured in terms of Air Quality Index (AQI).
- AQI is a measure of the concentrations of pollutants present in the air at a particular location.
- When the air quality is good, the air is clear and contains only small amount of solid particles and chemical pollutants.
- Poor air quality, which contain high level is often hazy and dangerous to health and the environment.
- An AQI value under 50 is considered good in quality. This means, it is safe for you to spend time outdoor without posing a risk to your health.
- An AQI over 300 is considered hazardous. Children under 18, adult over 65, people with chronic heart, and lung diseases are under high-risk.
- Outdoor workers are at higher risk because of the prolonged exposure.

Factors Affecting Air Quality

Air quality is influenced by several key factors or sources:

i) **Emission sources**

Burning of wood and fossil fuels can increase local pollution level. Factories and power plants use fossil fuels that release dangerous pollutants in air like SO_x and NO_x. Vehicles release CO, PM and VOCs.

Rack Your Mind!

7. How does deforestation impact air quality and the atmosphere?

ii) **Meteorological conditions**
Wind, temperature, and humidity affect pollutant dispersion and concentration. A layer of warm air trapping pollutants near the ground can lead to poor air quality.

iv) **Natural Events**
Wild fires can release large amounts of smoke and PM into the atmosphere. Natural dust storms can significantly lower air quality.

v) **Seasonal Changes**
Temperature variations, such as heating or cooling of buildings in different seasons can increase emissions of pollutants. Seasonal pollen concentration can contribute to poor air quality.

Rack Your Mind!
8. What are some methods used to improve air quality?

Table: AQI and level of health concern

Air Quality Index (AQI) Values	Levels of Health Concern	Colour
0 to 50	Good	Green
51 to 100	Moderate	Yellow
101 to 150	Unhealthy for Sensitive Groups	Orange
151 to 200	Unhealthy	Red
201 to 300	Very Unhealthy	Purple
301 to 500	Hazardous	Maroon

AIR QUALITY AND HUMAN HEALTH

The link between air quality and human health is well-documented and significant. Poor air quality can have immediate and long-term health impacts.

➲ Major Air Pollutants and their Health Effects

i) **Particulate matter (PM)**
Particular matter (PM) consists of tiny particles suspended in the air, including dust, dirt, soot and smoke ranging from diameter of 2.5 micrometer to 10.0 micrometer. Inhalation of these particulate matter (PM) can cause inflammation and irritation of airways, leading to conditions such as asthma and bronchitis.

ii) **Nitrogen Dioxide (NO_2) and Sulphur Dioxide (SO_2)**
The short-term exposures of NO_2 and SO_2 can irritate the respiratory system, while long term exposure can increase the risk of respiratory infection, asthma and bronchitis.

AIR POLLUTION AND HALTH RISK

Air pollution poses significant health risks to humans. The potential health effects can be acute or chronic and vary depending on the type and concentration of pollutants, duration of exposure and individual weakness.

➲ Main Health Risks Associated with Air Pollutions

i) **Respiratory Diseases**
Air pollutants such as ozone, particular matters (PM) and nitrogen dioxide (NO_2) can increase asthma symptoms and trigger asthma attack.
Long term exposure may lead to chronic cough and respiratory infections like pneumonia.

ii) **Cardio-Vascular Diseases**
Exposure to particular matters and other pollutants can increase the risk of heart attack by causing inflammation, blood vessel damage, high blood pressure and finally heart stroke.

Rack Your Mind!
9. Which harmful pollutants are classified as heavy metals found in air pollution?
A) Carbon dioxide and methane
B) Lead, mercury, and cadmium
C) Nitrogen and oxygen
D) Water vapour and argon

iii) **Cancer**
Prolonged exposure to certain air pollutants especially particulate matter (PM) and carcinogenic compounds (benzene formation) cause lung cancer.

iv) **Reproductive and Developmental Effects**
Exposure to air pollution may negatively impact reproductive health and fertility in both man and women. Premature birth and developmental problems in children may occur.

☑ QUICK CHECK 14.4

a) Explain the impact of particulate matter (PM) on the air quality.
Ans. **Impact of Particulate Matter (PM) on Air Quality:**
- **Health:** PM ($PM_{2.5}$, PM_{10}) causes respiratory/cardiovascular diseases.
- **Visibility:** Scatters light, reducing visibility (haze/smog).
- **Climate:** Alters radiation balance (cools or warms atmosphere).
- **Environment:** Acidifies soil/water, harms ecosystems.

b) What is AQI? How does it measure air quality?
Ans. AQI stands for Air Quality Index. AQI (Air Quality Index) is a numerical scale (0–500) that reports daily air pollution levels and associated health risks.
AQI Measures Air Quality:
Tracks Key Pollutants:
- $PM_{2.5}$, PM_{10}, O_3, CO, SO_2, NO_2.
- Converts Pollutant Concentrations into sub-indices (0–500) using standardized formulas.
- Highest Sub-Index determines the overall AQI value (e.g., if $PM_{2.5}$ is worst, it sets the AQI).

AQI Categories & Health Implications:
- 0–50 (Good): Minimal risk.
- 51–100 (Moderate): Acceptable; minor concern for sensitive groups.
- 101–150 (Unhealthy for Sensitive Groups): Children/asthmatics affected.
- 151+ (Unhealthy/Hazardous): Everyone faces health risks.

c) What are different levels of AQI? Mention the safest and the most hazardous ranges of AQI.
Ans. **AQI Levels & Ranges:**
1. 0–50 (Good) – Safest (minimal risk).
2. 51–100 (Moderate) – Acceptable.
3. 101–150 (Unhealthy for Sensitive Groups) – Mild risk (asthmatics, children).
4. 151–200 (Unhealthy) – Everyone affected.
5. 201–300 (Very Unhealthy) – Serious health effects.
6. 301–500 (Hazardous) – Most hazardous (emergency conditions).

In short, Safest = 0–50, Hazardous = 300+.

METHODS & TECHNIQUES TO MEASURE & MONITOR AIR QUALITY

Measuring and monitoring air quality involves a combination of methods and techniques to assess the concentration of various pollutants in the air. These pollutants can include particulates matter (PM), nitrogen dioxides (NO_2), sulphur dioxide (SO_2), carbon monoxide (CO), ozone (O_3) and volatile organic compounds (VOCs). There are various methods are techniques used by environmental engineers to measure air quality accurately. The instrument used to measure air quality index (AQI) is nephelometer. This is an instrument used to monitor PM such as dust, smoke, mist and fumes. Nephelometer, also known as photometer, detects particles by measuring the total amount of light they scatter.

➲ Direct Measurement Methods

i) **Continuous Emission Monitoring System (CEMS)**
Continuous emission monitoring system (CEMS) can usually monitor gas like CO, O_3, SO_2, NO_2, VOCs and PM at industrial sites.

ii) **Air Quality Monitoring Stations (AQMS)**
Fixed monitoring stations are equipped with various sensors and analyzers to measure pollutant level in real time located in urban areas and industrial zones.

iii) **Remote Sensing Techniques**
Satellites equipped with sensors can measure atmospheric pollutants over large areas, providing valuable data on regional and global air quality.

EXPERIMENTS AND DATA COLLECTION TO TEST HYPOTHESIS ABOUT AIR QUALITY

The design of experiments to test hypothesis about air quality involves careful planning, data collection and analysis. Following steps should be done about the air quality.

i) **Hypothesis**
As a first step, a hypothesis is developed to design an experiment. For example, the hypothesis, "The concentration of airborne particulate matters (PM 2.5) and nitrogen dioxide (NO_2) in urban areas is higher during peak traffic hours as compared to non-peak hours" can be tested by collecting air quality data at different time of the day.

ii) **Designing the experiment**
The detail of the experiment including the variables and method of data collection is planned. Busy roads sites and residential areas are selected for monitoring.

iii) **Data Collection**
The data on traffic volume during rush hours and non-rush hours is collected and finally compared. The reliable instruments and methods to collect air quality data are used.

ANALYZE DATA AND INTERPRET AIR QUALITY

The collected data is analyzed to confirm the truth or falseness of the hypothesis. The results of the analysis are interpreted and concluded.

Example Analyzing and Interpreting Air Quality Data: It involves understanding the concentration of various pollutants, identifying trends overtime and assessing the implications for public health and environmental Policy. General approach to analyze and interpret air quality measurements and trends are follows.

By carefully designing experiments, collecting and analyzing data, a hypothesis about air quality can be tested and the strategies for improving air quality can be made.

STRATEGIES USED TO REDUCE AIR POLLUTION

A variety of technologies is used to reduce air pollution and improve air quality. The following five types of technologies we can be used to control emission of air pollutants.

i) **Use of Catalytic convertor (CC) in Cars**
Oxides of nitrogen and other undesirable gases such as CO and various unburnt hydrocarbon are emitted by the vehicle engines. The most cars are equipped with catalytic convertors to convert the harmful pollutants to harmless substances. CO is oxidized to CO_2. NO_x are reduced to N_2. The unburnt hydrocarbon is converted to CO_2 and H_2O.

II **Diesel Particulate Filter (DPF) in Modern Diesel Engines**
Diesel particulate filter (DPF) is incorporated in modern diesel engines to reduce the emission of harmful particulate matter (PM) from the exhaust gases. The primary function of diesel particulate filter is to capture and store soot particles from the exhaust gases.

III) **Selective Catalytic Reduction (SCR)**
SCR is used in diesel engines to remove pollutants from the emission gases. It reduces NO_x to N_2 and oxidizes CO and hydrocarbons to CO_2 and water vapour using catalysts, such as TIO_2, zeolites, etc.

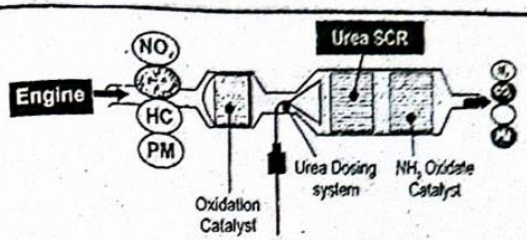


Figure: Selective Catalytic Reduction

iv **scrubbers**
Scrubbers can be used to control wide range of pollutants including particulate matters, SO_2, HCl, NH_3 and VOCs. Scrubbers use liquids (e.g., H_2O) to remove pollutants such as SO_2, PM from the industrial exhaust gases.

LAWS AND REGULATIONS RELATED TO ATMOSPHERE

Laws and Regulations

Common rules and regulations to control air pollution in Pakistan is given below:

i) Pakistan Environmental Protection Act (PEPA 1997)
ii) Natural Environmental Quality Standard (NEQS)
iii) Punjab Environmental Protection (Amendment) Act 2012

Measures to Control Air Pollutions

i. **Vehicle Emission Standard:** Enforcement of this standard is to reduce pollution from motor vehicles. The promotion of cleaner fuels such as compressed natural gas (CNG), liquid petroleum gas (LPG) and sticker regulation on fuel quality.

ii. **Industrial Emission Control:** To reduce emission from industrial resources and the encouragement of industries to adopt cleaner production techniques and pollution control technologies.

iii. **Public Awareness Campaigns:** Educating the public about the sources and effect of air pollution and ways to reduce personal contributions to air pollution also promote the use of public transport carpooling and non-motorized transport such as cycling and walking.

iv. **Urban Planning and Green Infrastructure:** Development of green belts and parks in urban / areas to improve air quality. Implementation of urban planning measures to reduce traffic congestion and promote sustainable transport options.

v. **Smog Control Measures:** Specific measures to control smog particularly during the winter months when air quality deteriorates significantly, Restrictions the burning of crop residues, which is a major contributes to smog and should use smog towers and other technologies to reduce particulates matter in the air.

vi. **Prohibition of the use of open fire:** for the disposal of domestic and industrial waste. Using open fire to bulk domestic and industrial waste can produce dust, smoke and significant amount of air pollutants.

vii. **Use of low-Sulphur Diesel:** Reduction of permissible level of sulphur in diesel.

Through these regulations and measures, Pakistan aims to improve air quality and minimize the adverse effects of air pollutions on public health and the environment.

ECONOMIC, SOCIAL & POLITICAL ISSUES

Air pollution and bad air quality is responsible for huge economic costs, social and potential issues.

Economic Issues

- Poor air quality can reduce worker productivity due to illness and absenteeism.
- Air pollution and air quality can damage crops reducing agricultural yield and increasing food prices.
- Air pollution leading to acid rain can degrade buildings, bridges and other infrastructure.

Social Issues

- Vulnerable populations, such as children, the elderly, and low-income communities are disproportionately affected by air pollution.
- Chronic exposure to polluted air reduces the overall quality of life. This affects social well-being and community health.
- Severe air pollution can force people to migrate from the unhealthy polluted areas to places with better air quality, leading to social displacement and associated challenges.

Rack Your Mind!

10. What is a key social issue related to air pollution?
A) Improved education
B) Poor communities often face higher pollution
C) More internet access
D) Increased rainfall

Political Issues

- Implementing effective air quality regulations can be challenging due to political and economic interests.
- Air pollution is not confined to borders and effective management requires international cooperation.
- Implementing air quality regulations requires strict governance, which might slow down industrial growth and economic development and leads to political conflicts.
- Addressing air pollution requires a multi-faceted approach, balancing socio-economic, and technological considerations.

Solution File — Rack Your Brain!

Sr. #	Option	Explanation
1.	D	The ozone layer is located in the stratosphere and absorbs most of the sun's ultraviolet radiation.
2.	S.Q	(i) **Troposphere:** Closest to Earth, weather occurs here (ii) **Stratosphere:** Contains the ozone layer (iii) **Mesosphere:** Coldest layer, where meteors burn (iv) **Thermosphere:** Hottest layer, contains auroras and satellites
3.	S.Q	Smog is a type of air pollution formed by the reaction of sunlight with pollutants like nitrogen oxides and VOCs. It causes breathing problems and eye irritation.
4.	B	These gases form sulfuric and nitric acids when they mix with water in the atmosphere, resulting in acid rain.
5.	C	Methane (CH_4) is a potent greenhouse gas emitted from natural sources and human activities like cattle digestion and wetland farming.
6.	S.Q	Greenhouse gases like CO_2, CH_4, and N_2O trap heat in the atmosphere, leading to global warming and climate change.
7.	S.Q	Deforestation reduces oxygen production, increases carbon dioxide levels, and contributes to the greenhouse effect and loss of biodiversity.
8.	S.Q	(i) Use of renewable energy (solar, wind) (ii) Emission control devices (e.g., catalytic converters) (iii) Air quality monitoring using sensors (iv) Laws and regulations like vehicle emission standards
9.	B	These heavy metals are toxic and can accumulate in the body, affecting organs and the nervous system.
10.	B	Disadvantaged groups often live in more polluted areas with fewer protections.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Four choices are given for each question. Select the correct choice.

i. Which gas causes yellow color in photochemical smog?
a) CO b) SO_3 c) NO_2 d) SO_2

ii. The depletion of Ozone in stratosphere region is mainly due to the reaction of O_3 with:
a) CO_2 b) SO_2 c) O_2 d) CFCs

iii. Which particulate matter size is considered the most harmful to human health?
a) PM 10.0 b) PM 5.0 c) PM 2.5 d) PM 1.0

iv. Which of the following is a natural factor that can improve air quality?
a) Wildfire b) Urbanization c) Rainfall d) Industrial emission

v. What is a common human activity that led to increased level of carbon monoxide in the atmosphere?
a) Tree planting b) Gasoline driven vehicles
c) Using electric appliances d) Solar panel installation

vi. Chlorofluorocarbons (CFCs) have been primarily used in:
a) Fertilizers b) Refrigerants and aerosol propellants
c) Pharmaceuticals d) Pesticides

vii. What are the primary chemical processes that removes carbon dioxide from the atmosphere?
a) Combustion b) Photosynthesis c) Respiration d) Volcanic activity

viii. An AQI value between 51 and 100 typically indicates which level of air quality?
a) Good b) Moderate c) Unhealthy d) Fatal

ix. Acid rain is primarily caused by the release of which of the following gases into the atmosphere?
a) Carbon dioxide (CO_2) and methane (CH_4)
b) Sulfur dioxide (SO_2) and nitrogen oxides (NO_x)
c) Chlorofluorocarbons (CFCs) and halons
d) Ozone (O_3) and carbon monoxide (CO)

x. In the presence of sunlight and nitrogen oxides (NO_x), VOCs can contribute to the formation of:
a) Acid rain b) Ozone depletion c) Photochemical smog d) Greenhouse gases

xi. Primary pollutants like nitrogen oxides (NO_x) and volatile organic compounds (VOCs) react in the presence of sunlight to form a key component of photochemical smog, which is a:
a) Primary pollutant. b) Secondary pollutant.
c) Naturally occurring atmospheric gas. d) Harmless byproduct of combustion.

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
i.	c	NO_2	• Nitrogen dioxide (NO_2) is a brown/yellow gas that contributes to the visible color of photochemical smog.
ii.	d	CFCs	• Chlorofluorocarbons (CFCs) react with ozone (O_3) in the stratosphere, breaking it down into O_2 (e.g., $Cl + O_3 \rightarrow ClO + O_2$).
iii.	c	PM 2.5	• PM 2.5 (particles ≤ 2.5 μm) penetrates deep into lungs and bloodstream, causing severe health issues (e.g., asthma, heart disease).
iv.	c	Rainfall	• Rainfall scrubs pollutants (e.g., PM, SO_2) from the air, improving air quality naturally.

V.	b	Gasoline driven vehicles	• Incomplete combustion in gasoline engines releases carbon monoxide (CO), a toxic gas.
VI.	b	Refrigerants and aerosol propellants	• CFCs were widely used in refrigerators, ACs, and spray cans before being phased out due to ozone depletion.
VII.	b	Photosynthesis	• Photosynthesis by plants/algae absorbs CO_2, converting it into oxygen and biomass.
VIII.	b	Moderate	• AQI 51–100 indicates "Moderate" air quality, acceptable but may affect sensitive groups.
IX.	b	SO_2 and NO_x	• SO_2 and NO_x react with water vapor to form sulfuric/nitric acid, causing acid rain (H_2SO_4/HNO_3).
X.	c	Photochemical smog	• VOCs + NO_x + sunlight form ozone (O_3) and PAN, key components of photochemical smog.
XI.	b	Secondary pollutant	• Ozone/PAN are secondary pollutants, formed by reactions of primary pollutants (NO_x/VOCs) in sunlight.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Identify and briefly explain three major natural sources of air pollutants.

Ans. The three major natural sources of air pollutants are given below;

1. **Volcanic eruptions:** Release sulfur dioxide (SO_2), ash, and gases into the atmosphere.
2. **Forest fires:** Emit carbon monoxide (CO), nitrogen oxides (NO_x), and particulate matter.
3. **Dust storms:** Spread large amounts of particulate matter (PM) into the air.

b. How can deforestation impact air quality?

Ans. Deforestation reduces the number of trees that absorb CO_2 and release oxygen, leading to increased carbon dioxide and particulate levels, thereby degrading air quality.

c. Explain the reasons for the temperature trends observed in the troposphere and the stratosphere.

Ans. In the **troposphere**, temperature decreases with height due to less heat from Earth's surface.
In this region, temperature decreases from 17°C to –58°C regularly.
In the **stratosphere**, temperature increases with height because of ozone absorption of ultraviolet (UV) radiation. Temperature increases from –58°C to –2°C.

d. Describe four significant anthropogenic (human-caused) activities that contribute to the deterioration of air quality. For each activity, name at least one major pollutant released.

Ans. Four significant anthropogenic (human-caused) activities that contribute to the deterioration of air quality are given below;

1. **Vehicle emissions:** Release nitrogen oxides (NO_x).
2. **Industrial activities:** Release sulfur dioxide (SO_2).
3. **Burning fossil fuels:** Produces carbon monoxide (CO).
4. **Agricultural practices:** Emit ammonia (NH_3) and methane (CH_4).

e. What are the environmental impacts of persistent organic pollutants (POPs)?

Ans. These are organic compounds that are resistant to degradation through chemical, biological and photolytic processes. These are toxic and adversely affect human health and the environment. POPs accumulate in the environment, harm wildlife, contaminate soil and water, and can travel long distances through air and water.

f. How does polycyclic aromatic hydrocarbon (PAHs) affect human health?

Ans. Polycyclic aromatic hydrocarbon PAHs can cause respiratory problems, skin irritation, and are known to be carcinogenic (cancer-causing).

g. What is photochemical smog? Under what conditions, it forms?

Ans. Photochemical smog is a type in which primary air pollutants like nitrogen oxides (NO_x), VOC and unburned hydrocarbons undergo photochemical reactions in the presence of sunlight and form secondary pollutants like ozone and peroxyacetyl nitrates (PAN).
This type of smog is considered more dangerous as it can cause heart palpitations, pneumonia and even lung cancer.
It forms in warm, sunny, and urban areas with heavy traffic.

h. What type of data do air quality index (AQI) system provide?

Ans. The AQI provides data on the concentration of major air pollutants like $PM_{2.5}$, PM_{10}, O_3, CO, SO_2, and NO_2, and indicates how polluted the air currently is or how polluted it is forecast to become.

i. Distinguish between PM_{10} and $PM_{2.5}$, specifying the size ranges and describing why $PM_{2.5}$ is generally considered more harmful to human health.

Ans. PM_{10} are particles ≤ 10 micrometers; $PM_{2.5}$ are particles ≤ 2.5 micrometers. $PM_{2.5}$ is more harmful as it can penetrate deep into the lungs and enter the bloodstream, causing heart and lung diseases.

j. What are the main chemical processes involved in the formation of acid rain?

Ans. Sulfur dioxide (SO_2) and nitrogen oxides (NO_x) react with water vapor in the atmosphere to form sulfuric acid (H_2SO_4) and nitric acid (HNO_3), which fall as acid rain.

k. What are the specific measures to control smog?

Ans. To control smog followings should be taken:

- Reducing vehicle emissions
- Using cleaner fuels
- Limiting industrial pollutants
- Planting trees
- Implementing air quality regulations.

l. How does a catalytic converter reduce harmful vehicle emissions?

Ans. Oxides of nitrogen and other undesirable gases such as CO and various unburnt hydrocarbon are emitted by the vehicle engines. The most cars are equipped with catalytic convertors to convert the harmful pollutants to harmless substances. CO is oxidized to CO_2. NO_x are reduced to N_2. The unburnt hydrocarbon is converted to CO_2 and H_2O.

m. Describe the sources of lead and mercury pollution.

Ans. Lead pollution comes from leaded gasoline, battery manufacturing, and paints.
Mercury pollution comes from coal burning, mining, and industrial waste.

DESCRIPTIVE QUESTIONS

Q.3 Discuss sources and effects of following air pollutants on environment:
i) Heavy metals ii) VOCs iii) PAHs iv) POPs

Ans. See Page No. (472)

Q.4 Write short notes on the following:
i) CFCs and ozone layer depletion ii) Greenhouse effect and global warming

Ans. See Page No. (471, 475)

Q.5 How the fossil fuel burning causes acid rain? Discuss in detail with chemical reactions.

Ans. See Page No. (475)

Q.6 What is meant by air quality AQI? Describe the factors affecting the air quality.

Ans. See Page No. (477)

ADDITIONAL SLOs BASED MCQs

1. **What is a primary source of air pollution?**
   A. Natural volcanic eruptions B. Industrial emissions
   C. Forest fires D. All of the above
2. **Which gas is primarily responsible for the greenhouse effect?**
   A. Oxygen (O_2) B. Carbon dioxide (CO_2) C. Nitrogen (N_2) D. Hydrogen (H_2)
3. **Which of the following is NOT a greenhouse gas?**
   A. Methane (CH_4) B. Nitrous oxide (N_2O) C. Sulfur dioxide (SO_2) D. Water vapor (H_2O)
4. **What is the main component of smog that poses health risks to humans?**
   A. Oxygen (O_2) B. Carbon monoxide (CO) C. Sulfur dioxide (SO_2) D. Nitrogen dioxide (NO_2)
5. **Acid rain is primarily caused by the emission of:**
   A. Carbon dioxide (CO_2) B. Ammonia (NH_3) C. Sulfur dioxide (SO_2) D. Oxygen (O_2)
6. **Which of the following is a short-term effect of air pollution on human health?**
   A. Increased cancer risk B. Respiratory problems C. Long-term memory loss D. None of the above
7. **What is the main consequence of global warming?**
   A. Rising sea levels B. Decreased carbon dioxide levels
   C. Increased ozone layer thickness D. Reduced rainfall
8. **Which of these is NOT an adverse effect of air pollution on the environment?**
   A. Disruption of ecosystem B. Increased agricultural productivity
   C. Damage to buildings and monuments D. Loss of biodiversity
9. **The ozone layer depletion is primarily caused by:**
   A. Greenhouse gases B. Volcanic eruptions
   C. Chlorofluorocarbons (CFCs) D. Deforestation
10. **What can individuals do to help reduce air pollution?**
    A. Drive gasoline-powered cars B. Use single-use plastics
    C. Reduce energy consumption D. Burn waste materials openly
11. **Air is polluted by:**
    A. toxic materials B. hydrocarbons C. harmful gases D. all of above
12. **Which of following gas is not pollution?**
    A. SO_2 B. CO C. CO_2 D. NO_2
13. **Oxides of sulfur and nitrogen react with oxygen to form:**
    A. bases B. acids C. salts D. all of above
14. **Oxidizing smog consists of high concentration of:**
    A. SO_2 B. Ozone C. NO_2 D. Cl_2
15. **Ozone is destroyed by:**
    A. SO_2 B. NO_2 C. Chlorofluorocarbons D. None of above

Answer Key with Explanations

Sr. #	Ans.	Explanations
1.	D	All listed sources, including natural volcanic eruptions, industrial emissions, and forest fires, contribute significantly to air pollution.
2.	B	Carbon dioxide (CO2) is a major greenhouse gas that traps heat in the atmosphere, contributing significantly to the greenhouse effect.
3.	C	While sulfur dioxide (SO_2) is an air pollutant, it is not classified as a greenhouse gas. Greenhouse gases include methane, nitrous oxide, carbon dioxide, and water vapor.
4.	D	Nitrogen dioxide (NO_2) is a key component of smog and can cause respiratory problems and other health issues.
5.	C	Sulfur dioxide (SO_2) and nitrogen oxides (NOx) are the primary contributors to acid rain, which forms when these gases react with water vapor in the atmosphere to produce acids.

6.	B	Short-term exposure to air pollution can cause respiratory problems such as coughing, shortness of breath, and exacerbation of asthma.
7.	A	Global warming leads to the melting of polar ice caps and glaciers, contributing to rising sea levels and potential flooding of coastal areas.
8.	B	Air pollution typically harms agriculture by damaging crops and reducing yields rather than increasing productivity.
9.	C	CFCs release chlorine atoms when they are broken down by UV radiation, which then deplete the ozone layer in the stratosphere.
10.	C	Reducing energy consumption helps decrease the demand for fossil fuels, thereby lowering the emissions of pollutants and greenhouse gases.
11.	D	Air polluted by harmful gases like CO, NO_x, SO_x, Ozone, Hydrocarbons and toxic material.
12.	C	CO_2 is not a pollutant gas as it is required for photosynthesis.
13.	B	In the atmosphere SO_2 and NO_x are transformed by reactions with oxygen and water into H_2SO_4 and HNO_3 respectively. These acids get mixed with rain. The acid deposition includes both wet (rain, snow, fog) and dry acidic deposition. $SO_2 + \frac{1}{2}O_2 + H_2O \xrightarrow{\text{Hydrocarbon, smoke, Metal oxide}} H_2SO_4$
14.	B	The photochemical smog consists of higher concentrations of oxidants like ozone and is also termed as oxidizing smog.
15.	C	Chlorofluorocarbons (CFCs) destroy ozone by releasing chlorine atoms that break down ozone molecules in the stratosphere.

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 What are the components of Environment?

Ans. Components of the Environment:

The environment consists of the following components.

- **Atmosphere:** The layer of gases which surrounds the earth.
- **Hydrosphere:** Concerned with all water bodies i.e. ocean, rivers, streams lakes, glaciers and ground water reservoirs.
- **Lithosphere:** Concerned with hard and rigid rocky earth crust.
- **Biosphere:** Area on earth which supports life i.e. air, lakes, etc.

Q.2 What is Troposphere?

Ans. Troposphere

It is the lowest region of the atmosphere which extends up to 12 km. It includes all the major gases present in the atmosphere i.e., nitrogen, oxygen, and carbon-dioxide; etc. In this region, temperature decreases from 17°C to −58°C regularly. It is the densest layer of the atmosphere. It is the layer in which major events such as rain, lightening, and hurricanes occur.

Q.3 What conditions are necessary for photochemical smog?

Ans. Conditions for Smog Formation:

The following conditions are required for the formation of smog.

i. There must be sufficient NO, hydrocarbons and volatile organic compounds (VOC) emitted by the vehicles.
ii. Sunlight, so that some of the chemical reactions may occur at a rapid rate.
iii. The movement of air mass must be little so that reactions are not disturbed.
iv. Temperature greater than 18°C.

Q.4 What are the effects of excess of CO_2 present in the atmosphere.

Ans. Effect of Excess of CO_2 Present in the Atmosphere:

If the atmosphere contains too much quantity of CO_2, the greenhouse effect is considerably increased i.e. the atmosphere; the temperature of the earth is increased too much. This too much high temperature melts all the glaciers (snow-mountains) floods the low-lying areas of the earth, changes the biological activity of oceans and the patterns of cropping etc. Thus we see that the presence of the excess of CO_2 in the atmosphere brings about climate changes.

Q.5 What is photochemical smog? Give its properties.

Ans. Smog:

"The word smog is a combination of smoke and fog".

It is formed from ground level upward to an altitude of few kilometers high.

Pollutants Causing Photochemical Smog:

- Due to having higher concentrations of oxidants like ozone, photochemical smog is also called **"oxidizing smog".**
- It is a yellowish brownish grey haze due to the presence of NO_2.
- It has unpleasant odour because of its gaseous components.

Reactants of Photochemical Smog:

- Nitric Oxide (NO) which main reactions of photochemical smog is oxidized to NO_2 within minutes to hours depending upon the concentration of pollutant gas.
- Unburnt hydrocarbons.

Q.6 What are greenhouse emissions?

Ans. Greenhouse gas emissions are gases released into the atmosphere that trap heat, contributing to global warming and climate change. The main greenhouse gases include:

- **Carbon dioxide (CO_2)** from burning fossil fuels like coal, oil, and natural gas.
- **Methane (CH_4)** from agriculture, landfills, and fossil fuel production.
- **Nitrous oxide (N_2O)** from fertilizers and industrial processes.
- **Fluorinated gases** synthetic gases used in refrigeration and manufacturing.

These gases create a "greenhouse effect" by trapping heat from the sun, leading to rising global temperatures and climate-related impacts.

Q.7 Relate greenhouse effect and global warming. Write some important points.

Ans. Here's how the greenhouse effect and global warming are related, explained point by point:

- **Greenhouse Effect is Natural:**
  It is a natural process where greenhouse gases trap some of the sun's heat in the Earth's atmosphere, keeping the planet warm enough to support life.
- **Human Activities Increase Greenhouse Gases:**
  Burning fossil fuels, deforestation, and industrial activities release excess greenhouse gases (like CO_2, CH_4, N_2O) into the atmosphere.
- **Enhanced Greenhouse Effect:**
  This build up of gases strengthens the natural greenhouse effect, trapping more heat than necessary.
- **Result: Global Warming:**
  The extra trapped heat leads to a gradual increase in Earth's average temperature—this is global warming.
- **Climate Change Link:**
  Global warming contributes to broader climate change, causing extreme weather, sea-level rise, and ecological disruptions.

In short, The greenhouse effect is the process; global warming is one of the harmful outcomes when this process is intensified by human actions.

Q.8 Write down the Impact of heavy metals like lead, Mercury and cadmium on environment and human health.

1. **Lead (Pb)**
   - **Environment:**
     - Contaminates soil and water.
     - Harms plants and animals by affecting growth and reproduction.
   - **Human Health:**
     - Damages the nervous system, especially in children.
     - Causes developmental delays, learning disabilities, and behavioral issues.
     - Long-term exposure may lead to kidney damage and high blood pressure.
2. **Mercury (Hg)**
   - **Environment:**
     - Bioaccumulates in aquatic ecosystems, especially in fish.
     - Highly toxic to wildlife, affecting reproduction and behavior.
   - **Human Health:**
     - Affects the brain and nervous system.
     - Particularly dangerous for pregnant women and young children—can cause developmental issues.
     - Inhalation or consumption (e.g., through contaminated fish) can lead to mercury poisoning.
3. **Cadmium (Cd)**
   - **Environment:**
     - Accumulates in soil and water, entering the food chain through plants.
     - Toxic to aquatic life and reduces crop productivity.
   - **Human Health:**
     - Damages kidneys and lungs.
     - Can cause bone weakness and pain.
     - Long-term exposure may lead to cancer.

Q.9 Discuss Air Quality Monitoring Stations (AQMS) as direct measurement method.

Ans. Air Quality Monitoring Stations (AQMS)-Direct Measurement Method

Air Quality Monitoring Stations (AQMS) are fixed installations used to directly measure air pollutants in the atmosphere. They play a crucial role in understanding and managing air pollution.

1. **Direct Measurement:**
   - AQMS use advanced sensors and instruments to continuously and accurately measure pollutant concentrations in real-time (e.g., PM 2.5, PM 10, CO, NO_2, SO_2, O_3).
2. **Stationary and Continuous Monitoring:**
   - These stations are usually located in urban, industrial, or sensitive ecological areas and provide 24/7 data on air quality.
3. **Data Collection and Analysis:**
   - Data from AQMS is used to generate Air Quality Index (AQI), track pollution trends, issue public health advisories, and support policymaking.
4. **High Accuracy:**
   - Compared to indirect or modeling methods, AQMS provide precise and reliable pollutant concentration levels.
5. **Regulatory Use:**
   - Governments and environmental agencies use AQMS data to enforce air quality standards and comply with environmental laws.

Advantages:

- Real-time and continuous data.
- Accurate and reliable results.
- Helps in early warning systems for pollution events.
- Supports long-term environmental planning and research.

Limitations:

- High installation and maintenance costs.
- Limited spatial coverage – fixed stations cannot cover wide areas.
- Requires skilled personnel for operation and calibration.

SELF-ASSESSMENT Chapter # 14

Total Mark: 30

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) **A key component that distinguishes photochemical smog from industrial smog is the presence of:**
A. High concentrations of sulfur dioxide.
B. A significant amount of ozone and other photochemical oxidants like PAN (peroxyacetyl nitrate).
C. Reduced visibility due to fog and smoke particles.
D. Formation primarily during the early morning hours.

(ii) **Primary pollutants like nitrogen oxides (NO_x) and volatile organic compounds (VOCs) react in the presence of sunlight to form a key component of photochemical smog, which is a:**
A. Primary pollutant. B. Secondary pollutant.
C. Naturally occurring atmospheric gas. D. Harmless byproduct of combustion.

(iii) **Acid rain is primarily caused by the release of which of the following gases into the atmosphere?**
A. Carbon dioxide (CO_2) and methane (CH_4)
B. Sulfur dioxide (SO_2) and nitrogen oxides (NO_x)
C. Chlorofluorocarbons (CFCs) and halons
D. Ozone (O_3) and carbon monoxide (CO)

(iv) **An AQI value between 51 and 100 typically indicates which level of air quality?**
A. Good B. Moderate C. Unhealthy D. Fatal

(v) **Which gas causes yellow color in photochemical smog?**
A. CO B. SO_3 C. NO_2 D. SO_2

(vi) **Which particulate matter size is considered the most harmful to human health?**
A. PM 10.0 B. PM 5.0 C. PM 2.5 D. PM 1.0

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) Discuss the use of Catalytic convertor (CC) in Cars.
(ii) Write down the differences between Primary and Secondary Pollutants
(iii) How do volatile organic compounds (VOCs) affect air quality?
(iv) How Chlorofluorocarbons (CFCs) effect ozone?
(v) Identify and briefly explain three major natural sources of air pollutants.
(vi) How can deforestation impact air quality?
(vii) Write two measures to control air pollutions
(viii) What is AQI? How does it measure air quality?

Q.3 Extensive Questions. (2 × 4 = 8)

(a) Discuss the four layers of atmosphere.
(b) Write a detailed note on smog and acid rain.

Chapter 15

BASIC SEPARATION TECHNIQUES

Student Learning Outcomes

After studying this chapter, students will be able to:
- Define important terms associated with creating chemical solutions: Solvent, Solute, Solution, Residue and Filtrate. **(Knowledge)**
- Explain methods of separation and purification: **(Understanding)**
  a) Filtration b) Crystallization
  c) Simple Distillation d) Fractional Distillation
- Identify substances and assess their purity using melting and boiling point information. **(Application)**
- Suggest suitable separation and purification techniques given information about the substances involved and their usage in daily life. **(Application)**
- Describe how paper chromatography is used to separate mixtures of soluble substances using suitable solvent. **(Understanding)**
- Describe use of locating agents when separating mixtures containing colorless substances. **(Understanding)**
- Interpret simple chromatograms to identify unknown substances by comparison with known substances pure and impure substances. **(Application)**
- State and use for R_f. **(Knowledge)**

Analytical Chemistry

- **Analytical chemistry is the science of chemical characterization.**
- A complete chemical characterization of a compound must include both qualitative and quantitative analyses.

Qualitative Analysis:
"In qualitative analysis, the chemist is concerned with the detection or identification of the elements present in a compound."

Quantitative Analysis:
"In quantitative analysis, the relative amounts of elements in compounds are determined."

Differences between Qualitative and Quantitative Analysis

Qualitative Analysis	Quantitative Analysis
The detection or identification of different elements present in the compound is called as qualitative analysis.	The analysis in which the exact amount of each element present in the compound is determined is called as quantitative analysis.
It is the initial analysis to detect the elements present in the compound.	By this analysis, the % age of element present in the compound can be calculated.
Example: Salt analysis, detection of elements and functional groups.	**Example:** Volumetric analysis, combustion analysis, gravimetric analysis.

Major Steps for Complete Chemical Characterization:
A complete quantitative determination generally consists of four major steps
(i) Obtaining a sample for analysis
(ii) Separation of the desired constituent
(iii) Measurement, and calculation of results
(iv) Drawing conclusion from the analysis.
Here, some basic separation techniques are discussed to practice in the lab.

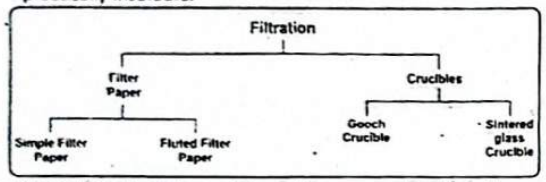
METHODS OF SEPARATION OF MIXTURES

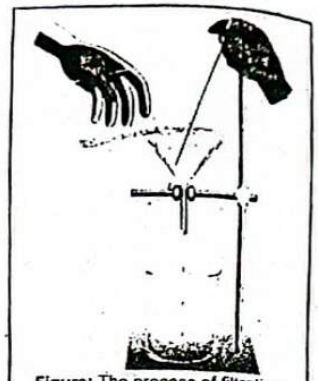
The components of a mixture can be separated by any of the following physical methods.

1. Filtration 2. Crystallization 3. Fractional distillation
4. Simple distillation 5. Paper Chromatography

Filtration

- Filtration process is used to separate one of the components of a two-component heterogeneous mixture from a solution.
- ***"The process in which suspended solid particles or insoluble particles are separated from a liquid through a filter medium is called filtration."***
- The first step is to select a suitable solvent in which one of the components dissolves completely while the other remains practically insoluble.




Figure: The process of filtration

- **Example:** Let us take a mixture of common salt and sand.
- Dissolve this mixture in distilled water. The common salt will distribute itself throughout water to give a homogeneous mixture. This homogenous mixture is called a **solution** of common salt in water.
- Common salt in this solution is called a solute while water is called a **solvent.**
- In a solution, the solvent is that component which is present in excess as compared to the solute.
- In this process, common salt disappears in water, the other component, sand remains undissolved and after some time settles down at the bottom of solution.
- The process of filtration is used to separate sand from the above solution.
- **Use of Filter media:** It can be performed with several types of filter media.
- Which filter medium will be used is decided on the basis of nature of the precipitate and other factors.
- The most convenient ways of filtration are either through a filter paper or through a filter crucible.

Rack Your Mind!
1. What is filtration?

Rack Your Mind!
2. What is the residue in filtration?
a) Liquid collected after filtration
b) Solid left on filter paper
c) Solvent
d) Solute

a) Filtration by using Filter Paper

Folding of filter paper is important and is done in two ways.

1. **Filtration by a Glass Funnel and Filter Paper:** It is usually a slow process. As the mixture is poured onto the filter paper, the solvent (water) passes through leaving behind the suspended particles on the filter paper. Filter papers are available in a variety of porosites (pore sizes). Which pore size is to be used, depends upon the size of particles in the precipitate. The size of filter paper should be large enough so that it is one-fourth to one-half full of precipitate at the end of filtration. In this way, the filtrate runs down the side of beaker without splashing. A complete filtration assembly is shown in Figure.

Rack Your Mind!
3. What is Porosite?

Rack Your Mind!
4. The word porosity means:
(A) Size of pores
(B) Number of pores
(C) Quality of pores
(D) Nature of pores

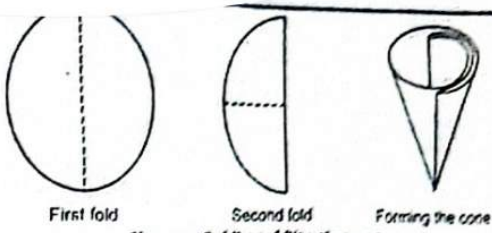


Figure a: Folding of filtration paper

The folded filter paper may then be inserted into 60° funnel, moistened with water and firmly pressed down.

Fluted Filter Paper: The rate of filtration through conical funnel can be considerably increased using a Fluted Filter Paper. For preparation of such a paper ordinary filter paper in folded in such a way that a fan like arrangement with alternate elevations and depressions at various folds is obtained Fig (b).

Rack Your Mind!
5. Why fluted filter paper is used for greater rate of filtration than ordinary cone filter paper?

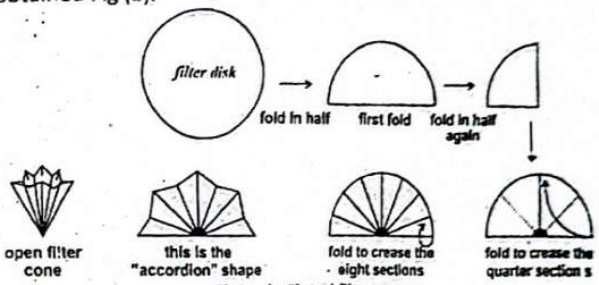


Figure b: Fluted filter paper

After filtration, the liquid which is obtained in the conical flask underneath the funnel is called the filtrate. The sand left behind on the funnel is called the residue.

Rack Your Mind!
6. Rate of filtration can be increased by using:
(A) Desiccator (B) Glass funnel
(C) Cold finger (D) Suction flask

b) Filtration by using Crucible

Another convenient way to filter a precipitate is by suction through a crucible. Two types of crucibles are generally used.

1. **Gooch crucible** is made of porcelain having a perforated bottom which is covered with paper pulp or a filter paper cut to its size (as shown in Figure). Quick filtration can be done by placing such crucible in a suction filtering apparatus. It is useful for the filtration of precipitates, which need to be ignited at high temperature. If its perforations are covered with asbestos mat, it may be used to filter solutions that react with paper e.g., concentrated HCl and $KMnO_4$ solutions.

Rack Your Mind!
7. Gooch crucible is made of:
(A) Glass (B) Paper
(C) Teflon (D) Porcelain


Figure: Gooch crucible


Figure: Sintered glass crucible

2. **Sintered glass** crucible is a glass crucible with a porous glass disc sealed into the bottom. It is very convenient to use because no preparation is needed as with the Gooch crucible as shown in Figure.

QUICK CHECK 15.1

a) Name different filter media used in filtration?

Ans. Here are the common filter media used in filtration:

1. **Filter Paper** (Qualitative/Quantitative)
2. **Sintered Glass Crucibles**
3. **Gooch Crucibles** (with asbestos/glass fiber mat)
4. **Charcoal** (Adsorptive filtration)
5. **Cotton or Wool Plugs**

b) What are the components of the filtration process?

Ans. The components of the filtration process are:

1. **Filter Medium** (e.g., paper, sintered glass).
2. **Slurry/Solution** (mixture to be filtered).
3. **Filtrate** (liquid that passes through).
4. **Residue/Precipitate** (solids retained).
5. **Driving Force** (gravity, vacuum, or pressure).

c) Differentiate gravity filtration and vacuum filtration.

Ans.

Feature	Gravity Filtration	Vacuum Filtration
Driving Force	Gravity (natural flow).	Pressure difference (vacuum pump/suction).
Speed	Slow (relies on gravity).	Fast (forced by vacuum).
Apparatus	Filter paper + funnel.	Büchner funnel, sintered crucible + vacuum flask.
Use Case	Coarse precipitates or small volumes.	Fine precipitates or large volumes.
Heat Compatibility	Suitable for hot solutions (no vacuum risk).	Unsuitable for very hot solutions (boiling under vacuum).
Precision	Less efficient for fine particles.	Better for fine/quantitative separations.

d) Differentiate between Gooch and sintered glass crucible.

Ans. Gooch Crucible:

- It is made up of porcelain.
- It has a perforated bottom which is covered with paper pulp or a filter paper cut to its size.
- Quick filtration can be done by placing the crucibles in a suction filtering apparatus.

Advantages:

- It is useful for the filtration of precipitates, which need to be ignited at higher temperature.
- If its perforations are covered with asbestos mat then it may be used to filter solutions that react with paper e.g. concentrated HCl, $KMnO_4$ (alkaline) solutions etc.

Sintered Glass Crucible:

- It is a glass crucible with a porous glass disc sealed into the bottom.

Advantages:

- There is no need to place any kind of filter paper in its bottom.
- There is no contamination of filter paper when we collect the residue. No preparation is needed as with the Gooch crucible.

CRYSTALLIZATION

(Exercise L.Q 4)

Q. Describe the criterion to choose the suitable solvent in the process of crystallization?

Definition:

The basic principle of crystallization is the fact that the solute should be soluble in a suitable solvent at high temperature and the excess amount of the solute is thrown out as crystals when it is cooled. The process of crystallization involves the following steps:

Rack Your Mind!

8. How is crystallization used for purification?

Choice of a Solvent

The solvent is chosen on hit and trial basis. It is necessary to try a number of solvents before arriving at a conclusion.

Properties or Characteristics of an Ideal Solvent

An ideal solvent should have the following features.

- It should dissolve a large amount of the substance at its boiling point and only a small amount at the room temperature.
- It should not react chemically with the solute.
- It should either not dissolve the impurities or the impurities should not crystallize from it along with the solute.
- On cooling, it should deposit well-formed crystals of the pure compound.
- It should be inexpensive, safe to use and easily removable.

Rack Your Mind!

9. Write down the main characteristics of a solvent selected for crystallization of a compound.

KEEP IN MIND

During crystallization, sometimes the crystals start to appear during the process of filtration. This result in choking the filter paper or the funnel. To avoid this a hot water funnel may be used.

Solvent Used: The solvents which are mostly used for crystallization are, water, absolute ethanol, chloroform, carbon tetrachloride and acetic acid.

If none of the solvents is found suitable for crystallization, a combination of two or more miscible solvents may be employed. If the solvent is inflammable, then precaution should be taken while heating the solution so that it does not catch fire. In such cases, water bath is used for heating purpose.

Steps of Crystallization

- Prepare a saturated solution of the substance in a suitable solvent at the temperature of the experiment.
- The insoluble impurities in the saturated solution are then removed by filtering the hot saturated solution. This avoids the premature crystallization of the solute on the filter paper or in the funnel stem. If necessary, hot water funnel should be used for this purpose.
- The hot filtered solution is then cooled at a moderate rate so that medium sized crystals are formed.

KEEP IN MIND

Sometimes during the preparation of a crude substance, the colouring matter or resinous products affect the appearance of product. Such impurities are conveniently removed by boiling the substance in the solvent with the sufficient quantity of finely powdered animal charcoal and then filtering the hot solution. The coloured impurities are adsorbed by animal charcoal and the pure decolourized substance crystallizes out from the filtrate on cooling.

- When the crystallization is complete, the mixture of crystals and the mother liquor is filtered through a Gooch crucible using a vacuum pump.

Drying the Crystals:

- The crystals may be dried in the following ways:

(i) **Air-dried:** The crystals may be air dried.

(ii) **Drying in an Oven:** The crystals are dried in an oven provided the substance does not melt or decompose on heating at 100°C.

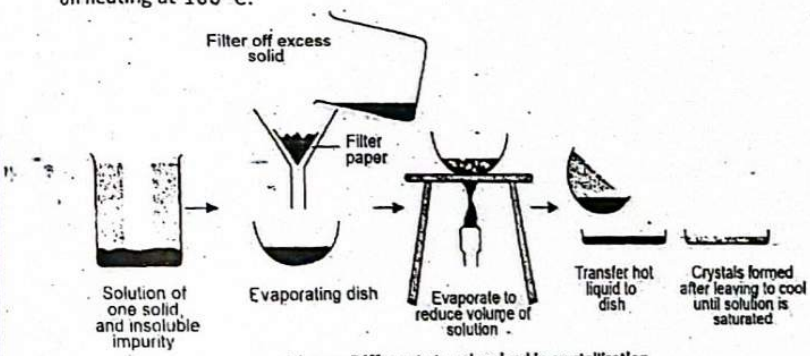


Figure: Different steps involved in crystallization

(iii) Drying through Vacuum Desiccator:

A safe and reliable method of drying crystals is through a vacuum desiccator. In this process the crystals are spread over a watch glass and kept in a vacuum desiccator for several hours.

Drying Agents: The drying agents used in a desiccator are $CaCl_2$, silica gel or phosphorus pentaoxide.



Figure: Vacuum Desiccator

Q. What is safe and reliable method of drying the crystals?

☑ QUICK CHECK 15.2

a) What is the basic principle of crystallization?

Ans. Basic Principle of Crystallization:

The basic principle of crystallization is that "the solute should be soluble in a suitable solvent at high temperature and excess amount of solute is thrown out as crystals when it is cooled."

b) How a suitable solvent is selected for the process of crystallization?

Ans. Choice of a Solvent

The solvent is chosen on hit and trial basis. It is necessary to try a number of solvents before arriving at a conclusion.

Properties or Characteristics of an Ideal Solvent

- It should dissolve a large amount of the substance i.e. solute at its boiling point and only a small amount at the room temperature.
- It should not react chemically with solute.
- It should either not dissolve the impurities or impurities should not be crystallized from it along with the solute.
- On cooling, it should deposit well-formed crystals of the pure compound.
- It should be inexpensive.
- It should be safe to use and should be easily removable.

c) Mention the important steps of crystallization.

Ans. Important Steps of Crystallization:

i. Prepare a saturated solutions of the substance in a suitable solvent at the temperature of the experiment.
ii. The insoluble impurities in the saturated solution are then removed by filtering the hot saturated solution. This avoids the premature crystallization of the solute on the filter paper or in the funnel stem. If necessary, hot water funnel should be used for this purpose.
iii. The hot filtered solution is then cooled at a moderate rate so that medium sized crystals are formed.
iv. When the crystallization is complete, the mixture of crystals and the mother liquor is filtered through a Gooch crucible using a vacuum pump.
v. The crystals may be air-dried are dried in an oven. The crystals are dried in an oven provided the substance does not melt or decompose on heating at 100°C.

SEPARATION THROUGH DISTILLATION

If a two-component mixture in a solution containing a solid compound dissolved in water or in any other suitable solvent, then that mixture can be separated by simple distillation. Sea water is not drinkable because it is a mixture of many soluble inorganic compounds in water. To get rid off these compounds, sea water is distilled to make it drinkable. **The process of fractional distillation is a type of distillation used to separate two liquids which are soluble or miscible with each other.** For example, a mixture of water and ethyl alcohol can be separated by heating the mixture in a distillation flask.

Distillation Process

1. Simple Distillation

Q. Differentiate between distillate and residue.

It is used to separate solvent from solution.

Example: Take 100 cm^3 sea water. Set up the apparatus as shown in the Figure. Add a few pieces of boiling chips to prevent bumping of the liquid in the flask. Make whole apparatus air tight to prevent vapors to escape.

Heat the flask gently with the help of a Bunsen burner. Turn on the tap to allow cold water to circulate slowly around the condenser. Water or alcohol will evaporate as its boiling point is reached, and its vapours will pass through the condenser. The water circulating around the condenser will condense these vapours back into the liquid form. This is called distillate and it will be collected in the receiving flask. The components left behind in the distillation flask are collectively called the residue.

2. Fractional Distillation

Separating the two miscible liquids in this way is called fractional distillation. The process of fractional distillation will be successful only if the difference in the boiling points of the two liquids being separated, is around 25° C. The distillation column is a glass equipment used in the distillation of mixture of liquids to separate it into its components depending upon their boiling points. The distillation column is filled with glass beads to increase the surface area available for condensing the vapor as shown in Figure.

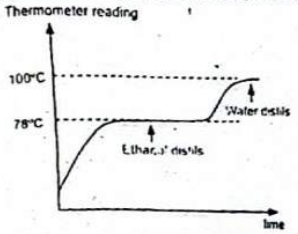


Figure: Fractional distillation of ethanol / water mixture

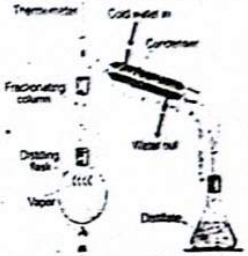


Figure: Fractional distillation setup

Separation of a Mixture of Ethyl Alcohol and Water:

Example:

- When a mixture of ethyl alcohol and water is heated, first ethyl alcohol will be distilled over because its boiling point is 78° C.
- Which is less than that of water whose boiling point is 100° C.
- As long as the alcohol is being distilled over, the temperature of the thermometer will remain at 78° C.
- As soon as the temperature starts rising above 78° C, replace the receiving flask with a new one as shown in Figure 15.7.
- Start heating again. When the temperature of the thermometer rises to 100° C, water will start boiling and is collected in the receiving flask after condensation as the second distillate.
- In this way both the components will be obtained in pure form.

Interesting Information!

Petroleum in natural form is a mixture of many compounds which are commonly used as fuels. Example of such fuels are petrol, diesel, kerosene oil and furnace oil. These components have boiling points not very different from one another. These components are separated as fractions by fractional distillation using a fractionating or distillation column.

☑ QUICK CHECK 15.3

a) What is the difference between simple distillation and fractional distillation?

Ans.

Feature	Simple Distillation	Fractional Distillation
Principle	Separates liquids with large boiling point differences (≥25°C).	Separates liquids with close boiling points (<25°C) using repeated vaporization-condensation cycles.
Apparatus	Distillation flask + condenser + receiver.	Includes a fractionating column (packed with beads/plates) for enhanced separation.
Purity	Lower purity (single evaporation step).	Higher purity (multiple condensation steps).
Efficiency	Less efficient for similar-boiling mixtures.	Highly efficient for complex mixtures (e.g., crude oil, ethanol-water).
Examples	Purifying seawater (water and salt).	Separating gasoline, kerosene, etc., from crude oil.

b) Give some daily-life applications of fractional filtration/distillation?

Ans. Applications:

1. **Petroleum Refining**
   - Separates crude oil into gasoline, diesel, kerosene, and lubricants.
   - Each fraction has different boiling points (e.g., gasoline evaporates first).
2. **Alcohol Separation**
   - Ethanol (78°C) and water (100°C) are close-boiling; fractional distillation achieves high purity.
3. **Essential Oils & Perfumes**
   - Extracts fragrant compounds from plants.
4. **Air Separation**
   - Produces liquid oxygen, nitrogen, and argon from air. Gases have slightly different boiling points (−183°C to −196°C).
5. **Water Purification**
   - Removes volatile contaminants in labs/industries.

CHROMATOGRAPHY

- Chromatography is a method used primarily for the separation of a sample of mixture.
- It involves the distribution of a solute (mixture) between two phases:
  (i) a stationary phase
  (ii) a mobile phase
- The stationary phase may be a solid or a liquid supported as a thin film on the surface of an inert solid. The mobile phase flowing over the surface of the stationary phase may be a gas or a liquid.
- Two types of Chromatography will be discussed here:
  (i) Partition Chromatography
  (ii) Adsorption Chromatography

Differences between Adsorption and Partition Chromatography

Partition Chromatography	Adsorption Chromatography
• The chromatography in which the stationary phase is a liquid is called partition chromatography.	• The chromatography in which the stationary phase is a solid is called adsorption chromatography."
• In this type, the substances being separated are distributed throughout both the stationary and mobile phases.	• In this type, a substance leaves the mobile phase to become adsorbed on the surface of solid stationary phase.
Examples • Paper chromatography • Gas liquid chromatography	**Examples** • Column chromatography • Thin layer chromatography • Gas solid chromatography

(Exercise L.Q.5)

Q. What is the basic principle of paper chromatography? Give its three practical life applications.

Paper Chromatography

- Paper chromatography is a type of partition chromatography.

Stationary and mobile phases in paper chromatography:

- The entrapped water in cellulose fibers of paper is stationary phase and mobile phase which passes over the paper are immiscible, the mobile phase is usually an organic liquid.

Types of Paper Chromatography:

- There are three common ways of carrying out paper chromatography namely:
  (i) ascending (ii) descending (iii) radial/circular.
- Only the ascending type will be discussed here. In this technique, the solvent travels upwards by capillary action.

Procedure of Ascending Paper Chromatography:

A solvent mixture, specially composed in accordance with the sample to be separated, is poured into the chromatographic tank Figure, cover the tank to homogenize its inner atmosphere. Take about 20 cm strip of Whatmann's chromatographic paper No. 1 and draw on it a thin pencil line about 2.5 cm from one end. Spot a point, on the pencil line, with the sample mixture solution. To facilitate identification of the components of the mixture, spots of the known compounds may also be placed along side.

When the spots have dried, suspend the paper with clips so that the impregnated end dips into solvent mixture to a depth of 5–6 mm. Cover the tank. As the solvent front passes the spots, the solutes begin to move upward. Different components of solute will move at different rates. This separates the mixture. When the solvent front has risen to about length of the paper, remove the strip, mark the solvent front with a pencil and allow the strip to dry.

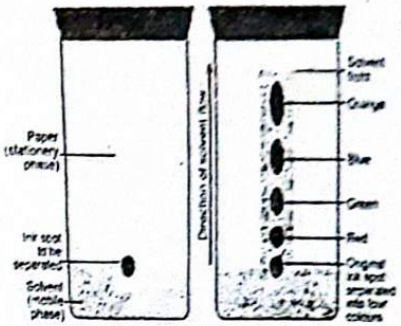


Figure: Paper Chromatography

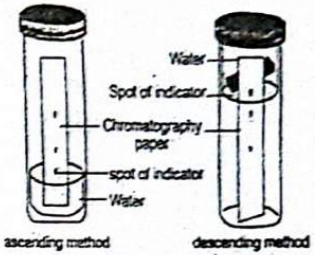


Figure: Ascending and Descending Paper Chromatography

Locating Agents for Colorless Substances

Once the paper is dried, the pattern on the paper is called a **chromatogram**. The different components of the mixture, if coloured, can visually be identified. If colourless, the chromatogram has to be developed by chemical methods or physical techniques used to identify the spots.

Use of a UV Lamp or Light: A very convenient way of visualizing the colourless chromatogram is to see it under the light of a UV lamp. The spots look coloured under UV light. Alternatively, a locating agent like ninhydrin can be used to locate the spots.

Locating Agent: A locating agent is generally a chemical that reacts with the colourless substances like amino acids to give coloured products that are visible for inspection.

Use of Retardation Factor

Each component has a specific retardation factor called R_f value. The R_f value is given by:

$$R_f = \frac{\text{Distance travelled by a component from the original spot}}{\text{Distance travelled by solvent from the original spot}}$$

With reference to Figure the chromatogram shows that the sample A contains both components B and C. The R_f values for B and C are given by:

$$R_f(B) = \frac{x}{y}$$

$$R_f(C) = \frac{x}{y}$$

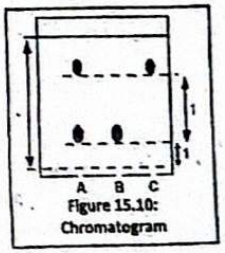


Figure 15.10: Chromatogram

Use/Significance of Paper Chromatography:

- Paper chromatography is a convenient way of checking if a substance formed in a chemical reaction is pure or impure using a suitable solvent in which the substance dissolves.

- A pure substance produces one spot on the chromatogram while an impure substance produces more than one spot.
- A paper chromatogram can also be used to identify substances by comparing them with known samples of pure substances.
- Two substances are likely to be identical have the same R_f values.

Explanation of Chromatogram:

In this chromatogram shown in Figure, the impure substance has two components present in it corresponding to two coloured spots it has shown. The spots in the impure substance have travelled the same distance as the reference's pure compounds. The R_f value is always the same for a particular substance if we use the same stationary phase and the same mobile phase.

Interesting Information!

Whatmann filter paper which are used in paper chromatography are made from specially selected cotton cellulose. Whatmann's filter paper No. 1 is used for routine applications and it has medium retention and medium flow rate. Its pore size is 11 µm.

Rack Your Mind!

10. Which of the following is used to identify unknown substances in paper chromatography?
a) Solvent front b) R_f value
c) Residue d) Filtrate

Applications of Paper Chromatography

i. The techniques of chromatography are very useful in organic synthesis for separation, isolation and purification of the products.
ii. They are equally important in qualitative and quantitative analyses and for determination of the purity of a substance.
iii. Chromatography is very useful for identifying complicated chemicals such as dyes, drugs and pesticides.

QUICK CHECK 15.4

a) On which basis the components of a mixture are separated from one another in paper chromatography?

Ans. In paper chromatography, components of a mixture are separated based on their differential affinities for the two phases involved:

1. **Stationary Phase:**
   - **Water molecules** bound to cellulose fibers in the paper (polar/hydrophilic).
   - **Polar compounds** interact strongly (slow movement).
2. **Mobile Phase:**
   - **Solvent** (e.g., ethanol, acetone) moving via capillary action.
   - **Non-polar compounds** dissolve better in the solvent (fast movement).

b) What are the stationary and mobile phases in paper chromatography?

Ans. In paper chromatography, the two phases are:

1. **Stationary Phase**
   - **Material:** Cellulose fibers in the filter paper + **adsorbed water** (from humidity or solvent).
   - **Role:** Acts as a **polar/hydrophilic** layer. Polar compounds bind to it (slow movement).
2. **Mobile Phase**
   - **Material:** Organic solvent or solvent mixture (e.g., ethanol, acetone, water-methanol).
   - **Role:** Moves via capillary action, carrying dissolved compounds. Non-polar compounds travel faster with it.

c) How the purity of a substance is determined by using paper chromatography?

Ans. Procedure to determine the **purity of a substance** using paper chromatography:

1. **Spot the Sample:**
   - Apply a small drop of the substance on the chromatography paper.
2. **Develop the Chromatogram:**
   - Immerse the paper in a solvent (mobile phase). Allow the solvent to rise via capil

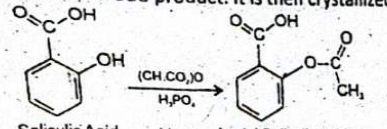
3. **Analyze the Results:**
   - **Pure Substance:** Forms **a single spot** (all molecules have identical R_f values).
   - **Impure Substance:** Shows **multiple spots** (each spot = a different component).
4. **Compare R_f Values:**
5. **Calculate**
   - R_f = Distance traveled by spot (Distance travelled by solvent).
   - **Pure compounds have a consistent R_f,** impurities show additional spots with different R_f.
   - **Single spot** = High purity.
   - **Multiple spots** = Contaminants present.
   - **Confirmation:** Repeat with different solvents for reliability.

HOW TO CHECK THE PURITY OF THE PRODUCT?

Purify Compounds:

Separate methods are applied to purify compounds if they exist in liquid or solid states under normal conditions. Liquids are generally purified by distilling them at normal pressure or under vacuum. Purity of liquids can be checked by comparing their boiling points with those mentioned in the literature.

Preparation of Aspirin: Aspirin is prepared by reacting salicylic acid with an excess of acetic anhydride in the presence of a few drops of concentrated H_2SO_4. Aspirin is a very important analgesic and antipyretic. After the reaction is over, water is added in the reaction mixture to precipitate out aspirin. The mixture is then filtered to get aspirin as a crude product. It is then crystallized in water as polar solvent.



Salicylic Acid → Acetyl Salicylic Acid (Aspirin)

Rack Your Mind!

11. What type of reaction is involved in the synthesis of Aspirin?

Aspirin obtained in the above process may be mixed with the unreacted starting material, salicylic acid.

To Check Whether the Product is Pure or Impure:

One way of assessing the purity is its melting point is determined. If the product melts sharply, e.g. Salicylic Acid melts at 136°C then the product is considered as pure. If the product shows a melting point which is not sharp i.e. it melts within a range of temperature, it means it is an impure product.

Other way of checking the purity of the product is to get the mixed melting point. In such a case the product is mixed with a pure sample of aspirin and the melting point is then determined. If it still shows a sharp melting point then it is a pure product.

Another way of checking the purity of aspirin is to run paper chromatography of this sample along with the pure samples of both aspirin and salicylic acid and matching their R_f value.

QUICK CHECK 15.5

a) How does melting point of a substance indicate its purity?

Ans. The melting point indicates purity as follows:

1. **Pure Substance:**
   Melts at a sharp, specific temperature (e.g., pure aspirin melts at 135°C).
2. **Impure Substance:**
   Melts over a broader, lower range (e.g., 120–130°C) due to disrupted crystal structure.

Which technique (filtration, crystallization and distillation) is suitable for the separation of the following mixtures?

i) …oleum and water ii) NaCl and $NaNO_3$
iii) …ated charcoal and sodium chloride iv) Methanol, ethanol and propanol

Ans.

i) Petroleum and water
- **Technique: Separating funnel** (immiscible liquids) or decantation.
- Petroleum (non-polar) and water (polar) form distinct layers.

ii) **NaCl and $NaNO_3$**
- **Technique:** Fractional crystallization.
- Differing solubilities in water allow selective crystallization (e.g., $NaNO_3$ crystallizes first on cooling).

iii) **Activated charcoal and sodium chloride**
- **Technique:** Filtration (charcoal is insoluble).
- Charcoal particles are trapped on filter paper; NaCl solution passes through.

iv) **Methanol, ethanol, and propanol**
- **Technique:** Fractional distillation.
- Their boiling points (methanol: 65°C, ethanol: 78°C, propanol: 97°C) are close but separable via a fractionating column.

Solution File — Rack Your Brain!

Sr. #	Option	Explanation
1.	S.Q	Filtration is a method used to separate an insoluble solid from a liquid by passing the mixture through filter paper. • The solid trapped on filter paper is called **residue.** • The liquid passing through is called **filtrate.**
2.	B	Residue is the insoluble solid particles trapped on the filter paper during filtration.
3.	S.Q	Porosites means pore sizes. It is related to porosity which is a measure of empty spaces within a solid material.
4.	A	Porosity is commonly used. Porosity is the measure of void spaces (pores) in a material.
5.	S.Q	The rate of filtration through conical funnel can be considerably increased by using fluted filter paper. For this an ordinary filter paper is folded in such a way that a fan like arrangement with alternate elevations and depressions at various folds is obtained. In this way, we increase the surface area of filter paper. As a result, the rate of filtration increases.
6.	D	Rate of filtration can be increased by using Suction flask an instrument used for vacuum filtration.
7.	D	Gooch crucible is made of porcelain having a perforated bottom which is covered with paper pulp or a filter paper cut to its size.
8.	S.Q	Crystallization separates pure solid crystals from impurities. The impure solid is dissolved in hot solvent; upon cooling, pure crystals form and can be collected by filtration.
9.	S.Q	See Topic Choice of a Solvent (Properties or Characteristics of an Ideal Solvent).
10.	B	R_f value helps compare the movement of an unknown substance with known substances for identification.
11.	S.Q	Esterification (See Reaction in synthesis of Aspirin).

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. After the crystals are formed, they are typically separated from the mother liquor by:
a) Evaporation b) Decantation or filtration
c) Sublimation d) Distillation

II. The comparative rates at which the solutes move in paper chromatography depend on:
a) The size of filter paper b) R_f values of solutes
c) Temperature d) Size of the chromatographic jar

III. The method that can be used to separate two solid compounds with different solubilities in a solvent is:
a) Distillation b) Isolation c) Crystallization d) Filtration

IV. It is suspected that a hand-written legal document has been changed by over writing some crucial figures. Which technique you will use to check the inks used at suspected places?
a) Distillation b) Chromatography c) Solvent Extraction d) Crystallization

V. In chromatography, the components of the mixture are separated based on:
a) Their molecular masses
b) The interaction of the components with stationary as well as mobile phone
c) The type of solvent used
d) The filter paper used

VI. 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

VII. 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.

VIII. The essential requirement for separating two liquids by simple distillation is that their boiling points should differ by at least:
a) 5°c b) 10°C c) 25°C d) 50°C

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	b	Decantation or filtration	• After crystallization, crystals are separated from the mother liquor (solution) by filtration (using filter paper) or decantation (pouring off the liquid).
II.	b	R_f values of solutes	• In paper chromatography, solute movement depends on R_f (retardation factor), which is specific to each compound's affinity for the stationary/mobile phases.
III.	c	Crystallization	• Crystallization exploits differences in solubility to separate solids. The less soluble compound crystallizes first, while the other remains in solution.
IV.	b	Chromatography	• Chromatography (e.g., TLC or HPLC) can distinguish between inks by separating their components based on differing chemical properties.
V.	b	The interaction of the components with stationary as well as mobile phone	• Separation occurs due to differential affinity of components for the stationary phase (e.g., filter paper) vs. the mobile phase (solvent).
	c	Filter medium	• The filter medium (e.g., filter paper, sintered glass) traps solids while allowing liquids (filtrate) to pass through.
	c	Fractionating column	• Fractional distillation uses a fractionating column to provide multiple vaporization condensation cycles, improving separation of liquids with close boiling points.
III.	c	25°C	• Simple distillation requires a minimum 25°C difference in boiling points for effective separation. Smaller differences need fractional distillation.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Why is there a need to crystallize a crude product?

Ans. The preparation of chemical compounds usually affords a crude product. The crude product may contain soluble and insoluble impurities. Insoluble impurities are removed by filtration while soluble impurities are removed by crystallization process. Crystallization also gives a definite geometrical shape to the crystals of the crude product. So in order to get pure product in the form of crystals there is a need to crystallize the crude product.

b. What is the function of fluted filter paper?

Ans. The function of fluted filter paper is to increase the filtration efficiency by providing a larger surface area and faster flow rate compared to flat filter paper.

Functions (Features):

1. Faster Filtration
   - The fluted (folded) design creates channels for the liquid to flow through, reducing clogging and speeding up the process.
2. Increased Surface Area
   - More folds = more contact points for solids to collect, preventing premature blockage.
3. Better Airflow
   - Gaps between folds allow air to escape, preventing pressure buildup that can slow filtration.

c. What is the difference between a Gooch crucible and sintered glass crucible?

Ans.

Feature	Gooch Crucible	Sintered Glass Crucible
Material	Porcelain or silica, lined with asbestos/glass fiber mat.	Made entirely of fused glass with porous frit.
Porosity	Adjustable (depends on mat used).	Fixed porosity.
Use Case	Filtering fine/gelatinous precipitates (e.g., $BaSO_4$).	Filtering fine to coarse precipitates (e.g., $AgCl$).
Heat Resistance	High (can be ignited/dried at high temps).	Moderate (may crack with rapid temp changes).
Chemical Resistance	Resists acids/bases (depends on mat).	Resists most acids (except HF) but not strong alkalis.
Cleaning	Mat must be replaced; crucible reused.	Reusable; cleaned with acids or solvents.
Typical Setup	Used with vacuum filtration.	Used with vacuum or gravity filtration.

d. What type of mixtures are filtered through a Gooch crucible?

Ans. Gooch crucibles are used to filter **precipitate-solid and liquid mixtures**, especially **gravimetric analysis** samples where the solid is dried and weighed.

e. What is function of fractionating column during fractional distillation?

Ans. The fractionating column in fractional distillation provides multiple vaporization-condensation cycles, enhancing separation of liquids with close boiling points by increasing surface area for selective condensation of higher-boiling components.

- **Improves purity** by allowing repeated condensation and re-vaporization.
- **Enables separation** of mixtures (e.g., crude oil into gasoline, kerosene, etc.).

f. What is the stationary phase in the paper chromatography?

Ans. In paper chromatography, the stationary phase is the water molecules adsorbed (bound) onto the cellulose fibers of the filter paper.

1. **Composition:**
   - Cellulose (paper) + bound water (from humidity or solvent).
   - Acts as a polar hydrophilic layer.
2. **Function:**
   - Interacts with analytes via hydrogen bonding and dipole forces.
   - Polar compounds bind more strongly, moving slower; non-polar compounds move faster.

g. What will happen during paper chromatography if the components of the mixture have a comparable attraction for the stationary phase?

Ans. If the components of a mixture have comparable attraction for the stationary phase in paper chromatography:

1. **Poor Separation:**
   - Components will travel at similar rates, staying close together on the paper.
2. **Overlapping Spots:**
   - Bands/spots may merge, making it difficult to distinguish individual compounds.
3. **Low Resolution:**
   - R_f values (retention factors) will be nearly identical.

Solution:

Use a different mobile phase or modify the stationary phase (e.g., polar/non-polar solvents) to alter affinities.

h. What is the meant by the term "developing the chromatogram" in paper chromatography?

Ans. **"Developing the chromatogram"** in paper chromatography refers to the process of **allowing the mobile phase (solvent) to migrate up the paper**, separating the mixture's components based on their differential affinities for the stationary (paper) and mobile phases.

Important Points:

- **Solvent Movement:** The mobile phase travels along the paper via capillary action.
- **Separation:** Components partition between the stationary (cellulose/water) and mobile phases, forming distinct spots/bands.
- **Completion:** The process stops when the solvent front nears the top of the paper.

i. What is the basic principle of paper chromatography?

Ans. The basic principle of paper chromatography is differential partitioning of components between two phases:

- **Stationary phase:** Water-bound cellulose fibers in the paper (polar/hydrophilic).
- **Mobile phase:** Solvent (e.g., ethanol, water) moving via capillary action.

j. Why water is not generally used as a solvent in paper chromatography?

Ans. Water is rarely used alone in paper chromatography because:

- **Slow Evaporation:** Prolongs drying time.
- **Poor Solubility:** Many organic compounds dissolve poorly in water.
- **Weak Separation:** Limited ability to differentiate components due to high polarity.

k. Differentiate between adsorption and partition chromatography.

Ans. **See** (Differences between Adsorption and Partition Chromatography) **(Already Answered above)**

l. How can you check the purity of a compound with the help of paper chromatography?

Ans. **To check the purity of a compound using paper chromatography:**

1. **Run the Sample:**
   - Spot the compound on chromatography paper and develop it with a suitable solvent.
2. **Analyze the Result:**
   - **Pure Compound:** Forms a single spot on the chromatogram.
   - **Impure Compound:** Shows multiple spots (each spot = a different component).
3. **Compare R_f Values:**
   - A single R_f (Retention Factor) value confirms purity; multiple values indicate impurities.

have prepared a solid sample of glucosazone in the laboratory. How will you proceed to check the ty of the sample?

ty of Glucosazone:

Melting Point Test:

Compare observed melting point with literature value (sharp range = pure).

TLC (Thin-Layer Chromatography):

Spot on silica plate, develop solvent → **single spot** confirms purity.

HPLC or NMR (if available):

Sharp peaks in HPLC/NMR spectra indicate purity.

DESCRIPTIVE QUESTIONS

Q.3 Differentiate simple distillation and fractional distillation in construction and applications.

Ans. See Answer in Quick Check 15.3 (a)

Q.4 Describe the criterion to choose the suitable solvent in the process of crystallization?

Ans. See Page No. (494)

Q.5 What is the basic principle of paper chromatography? Give its three practical life applications.

Ans. See Page No. (498)

ADDITIONAL SLOs BASED MCQs

1. **Branch of chemistry that deals with the complete qualitative and quantitative analysis of a substance is:**
   A. Stoichiometry B. Physical chemistry C. Analytical chemistry D. Quantum chemistry
2. **Identification of the components of a sample is:**
   A. Quantitative analysis B. Qualitative analysis C. Stoichiometry D. Physical chemistry
3. **Which of the following technique is used for the separation of insoluble particles from liquids?**
   A. Filtration B. Crystallization C. Solvent extraction D. Chromatography
4. **The technique used to separate components of mixture in solid phase.**
   A. Crystallization B. Filtration C. Sublimation D. Solvent extraction
5. **The solid which is left over the filter paper as a result of filtration:**
   A. Filtrate B. Residue C. Precipitate D. Mother Liquor
6. **Selection of filter paper depends on size of particles to be:**
   A. Filtered B. Dried C. Decolorized D. Decanted
7. **Fluted filter paper is used to:**
   A. Filter hot solution B. Avoid premature crystallization
   C. Increase the rate of filtration D. Decrease the area
8. **NaCl and sand can be separated by one of the following techniques:**
   A. Formation of solution and filtration
   B. Formation of solution and evaporation without filtration
   C. Sublimation D. Chromatography
9. **Size of filter paper is selected according to the amount of:**
   A. Solution B. Insoluble solute C. Soluble solute D. Solvent
10. **Without suction pump, filtration is:**
    A. Fast process B. Slow process C. Rapid process D. All are possible
11. **Rate of filtration can be increased by applying gentle suction:**
    A. Gooch crucible B. Filter paper C. Sintered crucible D. All of the above
12. **The solution remaining after the formation of crystals is called:**
    A. Mother liquor B. Dilute solution C. Residue D. both 'A' and 'B'
13. **Separation of a solid from its hot saturated solution by cooling is called:**
    A. Vapourization B. Solvent extraction C. Filtration D. Crystallization
14. **Safe and the most reliable method of drying crystals is through:**
    A. Filter paper B. Vacuum desiccators C. Oven D. None of these
15. **In order to have good crystals of a substance the temperature of the system at the time of preparation of solution should be:**
    A. Around 0°C B. Around room temperature
    C. Sufficiently more than room temperature D. Just above the room temperature

Answer Key

1. C	2. B	3. A	4. C	5. B	6. A	7. C	8. A	9. B	10. B	11. D	12.
13. D	14. B	15. C									

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 What is Chromatography?

Ans. The technique separation in which components of a mixture of substances, (coloured pigments and coloured metallic ions) are separated on the basis of their relative affinities for stationary and mobile phases is called chromatography.

Q.2 What do you understand by the term, "chromatogram"?

Ans. The finished dried paper with the coloured bands of various components of a mixture obtained in a chromatographic experiment, is called chromatogram.

Q.3 What is the locating agent?

Ans. A suitable chemical reagent which is sprayed on the chromatogram to locate the position of various colorless substances is called locating reagent, e.g., H_2S rubeanic acid etc.

Q.4 Define analytical chemistry.

Ans. Analytical Chemistry:
"The branch of chemistry which deals with the chemical characterization (qualitative and quantitative analysis) of a compound is called analytical chemistry."

Q.5 How chemical characterization of a compound is done?
OR Write down major steps involved in complete quantitative analysis.

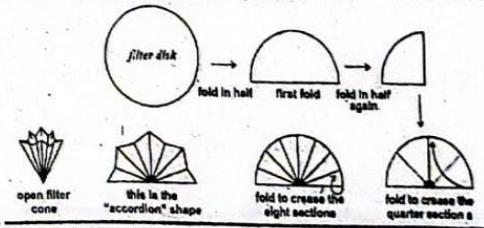
Ans. Four Major Steps:
Following major steps are necessary for complete quantitative analysis of a compound
(i) Obtaining a sample for analysis (ii) Separation of the desired constituent
(iii) Measurement and calculation of results (iv) Drawing conclusion from the analysis

Q.6 Why fluted filter paper is used for greater rate of filtration than ordinary cone filter paper?

Ans. Fluted Filter Paper:
The rate of filtration through conical funnel can be considerably increased by using fluted filter paper. For preparation of such a paper ordinary filter paper is folded in such a way that a fan like arrangement with alternate elevations and depressions at various folds is obtained. In this way, we increase the surface area of filter paper. As a result, the rate of filtration by fluted filter paper increases as compared to ordinary filter paper.

Q.7 Discuss folding of filter paper briefly.

Ans. Folding of Filter Paper:
The folding of filter paper is important and following points should be kept in mind:
- The paper should be folded twice. The first fold should be along the diameter of the paper. The second fold should be such that the edges do not quite match.
- The paper should be opened on the slightly larger section. This provides a cone with three-fold thickness halfway around and one thickness the other halfway around and an apex angle very slightly greater than 60°.
- The paper may then be inserted into 60° funnel, moistened with water and firmly pressed down.



Q.8 How saturated solution for crystallization can be prepared?

Ans. Preparation of the Saturated Solution:
After selecting a suitable solvent, the substance is then dissolved in a minimum amount of solvent and is heated directly or on a water bath with constant stirring.
...solvent to the boiling solution if necessary until all the solute has dissolved.

Q.9 Define filtration and crystallization.

Ans. **Filtration:** "The process in which insoluble particles (suspended particles or precipitates) are separated from liquids is called filtration."
Crystallization: "Crystallization is the removal of a solid from solution by increasing it concentration above the saturation point in such a manner that the excess solid separates out in the form of crystals."

Q.10 What is safe and reliable method for drying the crystals? Briefly explain.

Ans. **Vacuum Desiccator:**
A safe and reliable method of drying crystals is through a vacuum desiccator. In this process, crystals are spread over a watch glass and kept in vacuum desiccator for several hours. Drying agents used in a desiccator are $CaCl_2$, silica gel or phosphorous pentaoxide (P_2O_5).

◈◈◈◈◈

SELF-ASSESSMENT Chapter # 15

Total Mark: 30

Q.1 Encircle the correct option. **(1 × 6 = 6)**

(i) **After the crystals are formed, they are typically separated from the mother liquor by:**
a) Evaporation b) Decantation or filtration c) Sublimation d) Distillation

(ii) **The method that can be used to separate two solid compounds with different solubilities in a solvent is:**
a) Distillation b) Isolation c) Crystallization d) Filtration

(iii) **It is suspected that a hand-written legal document has been changed by over writing some crucial figures. Which technique you will use to check the inks used at suspected places?**
a) Distillation b) Chromatography c) Solvent Extraction d) Crystallization

(iv) **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

(v) **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.

(vi) **In chromatography, a locating agent is used to:**
a) Dissolve the sample for separation.
b) Carry the separated components along the stationary phase.
c) Make colorless separated components visible for identification.
d) Prevent the sample from interacting with the stationary phase.

Q.2 Write short answers of the following questions. **(2 × 8 = 16)**

(i) Differentiate gravity filtration and vacuum filtration.
(ii) Differentiate between adsorption and partition chromatography.
(iii) Why HF cannot be filtered through sintered glass crucible?
(iv) What is chromatography?
(v) Differentiate between stationary phase and mobile phase in chromatographic technique?
(vi) How does a Gooch crucible increases the rate of filtration?
(vii) Write down the uses/applications of chromatography.
(viii) What is the significance of distribution coefficient in chromatography?

Q.3 Extensive Questions. **(2**

(a) Differentiate simple distillation and fractional distillation in construction and applications.
(b) Write down the procedure of ascending paper chromatography with diagram.

Chapter 16

LAB SAFETY AND PRACTICAL SKILLS

Student Learning Outcomes

After studying this chapter, students will be able to:

- Identify the chemical hazards in the lab in the context of the experiment being conducted. **(Knowledge)**
- Test that the equipment is working properly without any potential risk of injury before conducting an experiment. **(Knowledge)**
- Ensure that work space for conducting the experiment is not crowded with apparatus as to be hazardous. **(Knowledge)**
- Ensure that safe distance space is kept at all times from other investigators who may handling lab apparatus. **(Knowledge)**
- Identify what bodily harm could occur from physical, chemical, biological and safety hazards in context of the experiment being conducted. **(Knowledge)**
- Recognize that it is always better to ask for help from the lab instructor when unaware of how to use new apparatus. **(Knowledge)**
- Identify the proper waste disposal system for chemicals being used. **(Knowledge)**
- Set up apparatus following instructions given in written or diagrammatic form. **(Understanding)**
- Use apparatus to collect an appropriate quantity of data. **(Understanding)**
- Make observations including subtle differences in colour, solubility or quantity of materials. **(Understanding)**
- Make measurements using pipettes, burettes, measuring cylinders, thermometers, and other common laboratory apparatus. **(Understanding)**
- Decide how many tests or observations to perform. **(Understanding)**
- Identify where repeated readings or observations are appropriate. **(Understanding)**
- Replicate readings or observations as necessary, including where an anomaly is suspected. **(Understanding)**
- Identify where confirmatory tests are appropriate and the nature of such tests. **(Understanding)**
- Select reagents to distinguish between given ions. **(Knowledge)**
- Carry out procedures using simple apparatus in situations where the method may not be familiar to the candidate. **(Application)**
- Describe acid base titration to include the use of a burette, volumetric pipette and suitable indicator. **(Understanding)**
- Describe how identify the end point of a titration using an indicator. **(Understanding)**
- Describe tests to identify the anions: (a) CO_3^{2-}, (b) Cl^{1-}, Br^{1-} and I^{1-} (c) NO_3^{1-} (d) SO_4^{2-} (e) SO_3^{2-} **(Understanding)**
- Describe tests using aqueous NaOH and aqueous NH_3 to identify the aqueous cations: (a) Al^{3+} (b) NH_4^+ (c) Ca^{2+} (d) Cr^{3+} (e) Cu^{2+} (f) Fe^{2+} (g) Fe^{3+} and (h) Zn^{2+} **(Understanding)**

A chemistry laboratory is a chemist workshop. It is a place where a student is trained to observe the physical and chemical characteristics of substances by following definite procedures. Before starting the laboratory work, a student should get himself familiarized with the layout of the laboratory and various fittings provided on the laboratory table as well as the side shelves.

GENERAL INSTRUCTIONS TO THE STUDENTS

i. Students are expected to conduct themselves in a responsible manner at all times in the lab.
ii. They are advised not to work alone in the lab. Experiments should be performed in the presence of lab instructor and other laboratory staff.
iii. Students should always wear lab coat and safety goggles while working in the lab. Girls must tie up their scarves and hair before start working in the lab.
iv. Determine the potential hazards related to any equipment or the experiment before beginning any work. Appropriate safety precautions must be observed at all cost.
v. There must not be any crowding in the lab and students should stick to their work places at a safe distance from each other.
vi. Don't bring any food items in the lab. Never taste or smell any compound or a gas.
vii. Any accident or breakage of glassware must be reported to the incharge of the laboratory immediately.
viii. If you cannot handle an instrument or an equipment properly then you must seek help from the instructor.
ix. Do not pour chemicals down the drains and do not utilize the sewer for chemical waste disposal.
x. Follow the warning sign displayed in the lab.

Rack Your Mind!

1. Before starting an experiment, what should you do to ensure safety?
   a) Wear casual clothes
   b) Test equipment for proper functioning
   c) Leave workspace crowded
   d) Work without supervision

COMMON TYPES OF HAZARDS IN A LABORATORY

(Exercise L.Q.3)

Q. Describe common types of the Chemistry lab hazards with two examples in each case.

Most hazards which we might face while working in the laboratory fall into three categories, physical, chemical and biological hazards.

Physical Hazards

The most common physical hazards are slips and falls when working on wet floor. A worker must take all types of precautions to avoid accidents related to physical hazards such as slipping, pulling, falling etc.

A worker should wear cut-resistant gloves while handling the broken glassware to prevent cuts, abrasions and skin damage. It should be mandatory for the laboratory staff to dispose off broken glassware in special container to prevent injury.

Rack Your Mind!

2. What safety precautions should be taken regarding workspace and distance?



Figure: Pictogram of chemical hazards

Chemical Hazards

A laboratory worker must use the chemicals according to the standard procedures keeping in view the particular hazards and precautions required for the safe use.

Biological Hazards

The most common biological hazards are allergens, infectious diseases which are transferred from animals to humans and viral diseases.

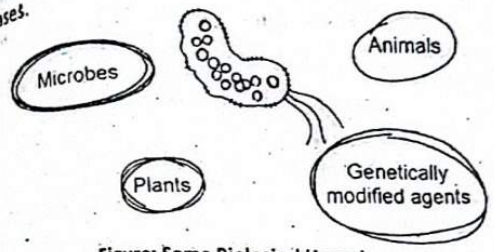


Figure: Some Biological Hazards

Rack Your Mind!

3. How can you identify chemical hazards in the laboratory?

Rack Your Mind!

4. What bodily harm can chemical hazards cause?
   a) Burns and poisoning
   b) Muscle strain
   c) Fractures
   d) Headache only

Rack Your Mind!

5. Why should you test equipment before starting an experiment?

WASTE DISPOSAL SYSTEM FOR CHEMICALS

Disposal of Chemical Waste:

Chemical waste cannot be disposed off in bins or sewer system. Most chemical wastes must be disposed off keeping in view the following rules and regulation of Environmental Protection Agency (EPA).

1. Store chemical wastes in proper containers.
2. Label the chemical waste containers with the types of wastes, the date of waste and place of origin.
3. These containers are then transferred to the allocated site where these are appropriately treated to dispose them off.
4. Chemical treatment of wastes involves:
   (i) neutralization (ii) precipitation (iii) ion exchange (iv) oxidation/reduction.

FIRST AID IN LABORATORY

(Exercise L.Q.4)

Q. What are common accidents in the Chemistry lab? How they are managed in first aid treatment.

Every laboratory must have a first aid box. Common accidents and their first aid treatments are given in the Table below:

Table: Accidents and their First Aid Treatment

	Type of Accident	First Aid Treatment
1.	Cuts Minor cuts Serious cuts	• Remove the glass piece if any, apply a little methylated spirit or tincture iodine with a piece of cotton. Both act as disinfectant. • Apply pressure on the cut for about 10 minutes to stop bleeding. Consult a doctor.
2.	Eye Injuries Acid in the eye Alkali in the eye Foreign particle in the eye Soreness in the eye	• Wash thoroughly with water and then with 1% sodium bicarbonate solution. • Wash with water followed by 1% boric acid solution. • Do not rub the eyes. Remove the particle carefully with soft handkerchief then wash with water. • Put a drop of olive oil in the eyes and keep them closed for some time.

3.	**Burns** Burns with dry heat (flame, hot object) Burns causing blisters Acid burns Alkali burns Bromine burns	• Apply burnol or mustard oil. • Wash freely with ice cold water. Then wash with a saturated solution of sodium bicarbonate and again with water. • Wash freely with water and then with 1% acetic acid solution and again with water, dry the skin and apply the burnol. • Wash fully with 2% ammonia solution and apply glycerin. Wipe off glycerin after sometime and apply burnol.
4.	**Poisons** Poisons swallowed Acid swallowed Caustic alkalies swallowed Salt of heavy metals swallowed.	• Spit immediately, wash mouth with water repeatedly. • Drink a lot of water or lime water or milk of magnesia. • Drink a lot of water; drink a glass of lemon or orange juice. • Take milk or white part of the egg.
5.	Fire i) Clothes catch fire ii) Beaker containing inflammable liquid. catches fire. iii) Spirit or oil catches fire. iv) Electric parts catcl fire.	• Do not run. Wrap with blanket or with dry cotton cloth. Lie down on the floor. • Cover the beaker with a duster or damp cloth. This will cut off the supply of oxygen. • Throw a mixture of sand and sodium bicarbonate. Do not throw water. It will simply spread the fire. • Switch off the electric supply immediately and throw sand. Do not throw water in such cases to extinguish fire.

☑ QUICK CHECK 16.1

a) Mention common types of hazard.

Ans. Most hazards which we might face while working in the laboratory fall into three categories, physical, chemical and biological hazards.

(i) Physical Hazards
(ii) Chemical Hazards
(iii) Biological Hazards

b) How chemical waste is disposed off?

Ans. Chemical Waste:

1. Store chemical wastes in proper containers.
2. Label the chemical waste containers with the types of wastes, the date of waste and place of origin.
3. These containers are then transferred to the allocated site where these are appropriately treated to dispose them off.
4. Chemical treatment of wastes involves neutralization, precipitation, ion exchange, oxidation or reduction.

c) How H_2SO_4 burn is treated in the lab?

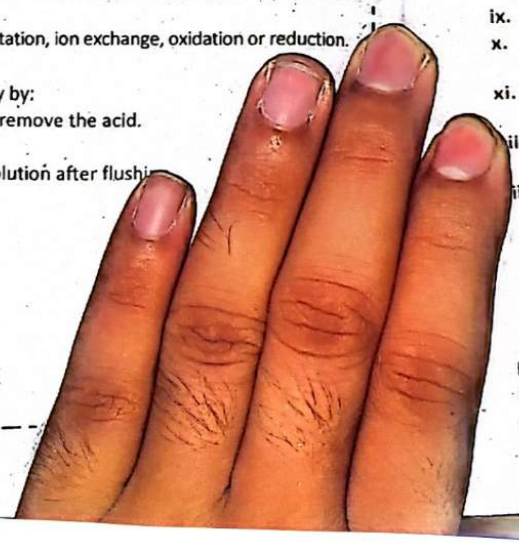
Ans. In the lab, an H_2SO_4 (sulfuric acid) burn is treated immediately by:

- Flush with water for at least 15–20 minutes to dilute and remove the acid.
- Remove contaminated clothing/jewelry carefully.
- Neutralize (optional) with a mild baking soda ($NaHCO_3$) solution after flushi
- Cover with a sterile, non-adhesive dressing.
- Seek medical attention, especially for severe burns.

d) What are different types of burns?

Ans. Types of Burns:

- Burns with dry heat (flame, hot object)
- Burns causing blisters
- Acid burns
- Alkali burns
- Bromine burns



ACID-BASE TITRATION

Volumetric Analysis:

- Volumetric analysis is used to find the concentrations of solutions by means of a technique known as titration.
- In acid-base tritration, a solution of unknown concentration is combined slowly and carefully with a known volume of a standard solution until a colour change shows the completion of the reaction.

Did You Know?

Phenolphthalein solution is prepared by adding one gram of the indicator in 500 cm^3 of 50% ethanol. Use only one to two drops in 10 cm^3 of the solution to be titrated. The color change is from pink to colorless as the pH decreases. The light pink color which marks the end point tends to fade gradually due to the interference of atmospheric carbon dioxide which slowly dissolves in the solution.

Indicator:

- The substance wnich indicates the completion of reaction by the change in its colour is called an indicator.

End Point:

- The moment at which the indicator changes colour is called the end point. Either solution can be taken in a burette with the other solution taken in a conical or a titration flask.

Materials Required

Burette, pipette, funnel, conical flask, HCl solution, NaOH solution, phenolphthalein.

Titrant: A Solution of known Concentration."
Analyte: Analyte (in titration) is the solution whose concentration is being determined. It is also called titrand.

Procedure of Titration

i. Rinse the pipette first with distilled water and then with the given NaOH solution.
ii. Rinse the conical flask with distilled water only.
iii. Pipette out 10 cm^3 of NaOH solution into a conical flask.
iv. Add one to two drops of **phenolphthalein** indicator into it. The solution turns pink.
v. Rinse the burette first with distilled water and then with the given HCl solution.
vi. Fix the burette on a clamp stand in an upright position.
vii. Fill it with the given HCl solution with the help of a funnel. Remove funnel from the burette.
viii. Using the tap at the base of the burette, allow the acid to flow into a beaker to remove any air bubble present in the nozzle.
ix. Note the burette reading as an initial reading using an anti-parallax card or a white paper.
x. During titration, place the conical flask on a white paper under the burette to see the colour change of the indicator clearly. Check that the burette does not leak.
xi. Carry out a rough titration by adding hydrochloric acid solution from the burette drop wise to the conical flask.
xii. The contents of the flask must be swirled adding of acid for thorough mixing.
xiii. Keep on adding acid till the colour of solution becomes light pink persistently. This will be the end point of the reaction.
Again, note down the burette reading, this will be the final reading. The difference of final and initial readings of burette will give the volume of the acid used.

Repeat the titration to get accurate and concordant readings. Take at least three concordant readings which agree with one another within 0.1 cm^3.

Rack Your Mind!

6. In acid-base titration, which apparatus is used to deliver the acid or base dropwise?
a) Pipette b) Burette
c) Measuring cylinder d) Beaker

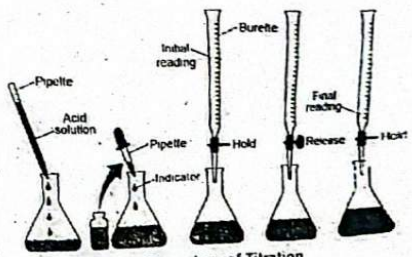


Figure: Procedure of Titration

Observations

Titration Number	Rough Reading	1	2	3
Final reading	x			
Initial reading	y			
Volume of acid used (cm^3)	(x − y)			

Volume of HCℓ solution used = _____ cm^3

Chemical Equation

$$NaOH_{(aq)} + HC\ell_{(aq)} \rightarrow NaC\ell_{(aq)} + H_2O_{(\ell)}$$

Calculation

Find out the molarity of NaOH solution by using the following molarity equation:

$$\frac{\text{Acid}}{\text{Base}} \quad \frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

M_1 = Molarity of acid solution
V_1 = Volume of the acid used
n_1 = No. of moles of the acid in the balanced chemical equation
M_2 = Molarity of base solution
V_2 = Volume of base solution used
n_2 = No. of moles of the base in the balanced chemical equation

$$M_2 = \frac{M_1V_1}{n_1} \times \frac{n_2}{V_2}$$

Molarity of the given base solution is _____ M.

Rack Your Mind!

7. How can you identify the end point in an acid-base titration?

QUICK CHECK 16.2

a) Define indicator and endpoint in a titration.

Ans. The substance which indicates the completion of reaction by the change in its colour is called an indicator. The moment at which the indicator changes colour is called the end point.

b) What is meant by concordant reading?

Ans. Concordant reading refers to multiple measurements (titres) that are in close agreement with each other usually with a minimal variability. In titration, one typically performs multiple trials to ensure accuracy. Concordant readings indicate that the process is consistent and reproducible, i.e., the results are likely reliable.

c) How the volume of the titrant used is calculated?

Ans. The volume of titrant used in titration is determined by reading the burette before and after the titration the difference between the initial and final burettte readings provides the volume of titrant added to reach the e quivalence point.

TESTS FOR IDENTIFICATION OF ANIONS

a) Identification of Carbonate CO_3^{2-} Radical

Experiment	Observation	Inference
Take about 2 g of solid carbonate sample in a clean test tube and then add about 5 cm^3 of dilute HCℓ solution. Pass the gas evolved in the above step through a solution of lime water.	Effervescence takes place during which a gas evolves briskly, that turns lime water milky.	Carbonate (CO_3^{2-}) are indicated ions.

Reactions involved in the above steps

$$CO_{3(aq)}^{2-} + 2H_{(aq)}^{+} \rightarrow H_2O_{(\ell)} + CO_{2(g)}$$

$$Ca(OH)_{2(aq)} + CO_{2(g)} \longrightarrow CaCO_{3(s)} + H_2O_{(\ell)}$$

lime water — white ppt

Rack Your Mind!

8. Which reagent can be used to test for carbonate ions (CO_3^{2-})?
a) HCℓ b) NaOH
c) $AgNO_3$ d) NH_3

Identification of Chloride ($C\ell^{-1}$), Bromide (Br^{-1}) and Iodide (I^{-1}) Radicals

Experiment	Observation	Inference
Take 2 g of solid sample in a test tube and add 5 cm^3 of distilled water to make the aqueous solution. Add a few drops of dil. HNO_3 solution to acidify the solution of the salt, finally add about 5 cm^3 of aqueous $AgNO_3$.	A thick white precipitate is formed which dissolves in aq. NH_3.	$C\ell^{-1}$ ions are indicated.
Take 2 g of solid sample in a test tube and add 5 cm^3 of distilled water to dissolve the salt. Add a few drops of dil. HNO_3 to acidify the above solution. Finally add 5 cm^3 of aqueous $AgNO_3$.	A thick cream-yellow precipitate is formed.	Br^{-1} ions are indicated.
Take 2 g of solid sample and dissolve it in 5 cm^3 of distilled waler. Add a few drops of dil. HNO_3 to make it acidic. Finally add 5 cm^3 aqueous $AgNO_3$.	A bright yellow precipitate is formed.	I^{-} ions are indicated.

Reactions involved in the above tests.

$$Ag_{(aq)}^{+} + C\ell_{(aq)}^{-} \longrightarrow \underset{\text{white ppt}}{AgC\ell_{(s)}}$$

$$Ag_{(aq)}^{+} + Br_{(aq)}^{-} \longrightarrow \underset{\text{cream yellow ppt}}{AgBr_{(s)}}$$

$$Ag_{(aq)}^{+} + I_{(aq)}^{-} \longrightarrow \underset{\text{bright yellow ppt}}{AgI_{(s)}}$$

Did You Know?

In the above tests for the detection of halide ions, dilute nitric acid is added to prevent the precipitation of carbonate ions along-with halide ions.

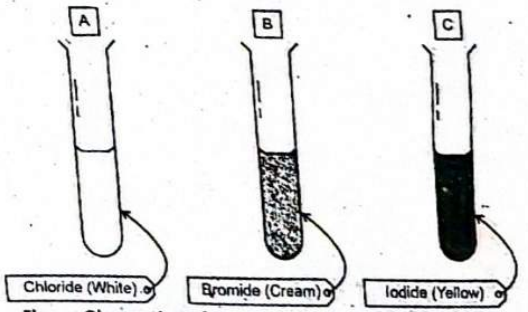


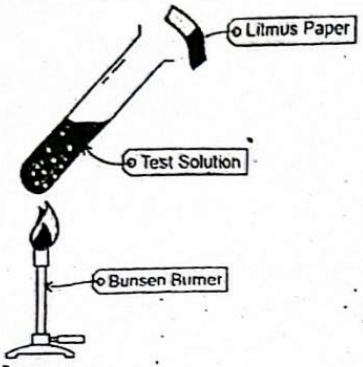
Figure: Observation of reactions of halide ions with $AgNO_3$

c) Identification of Nitrate (NO_3^{1-}) Radical

Experiment	Observation	Inference
Take 2 g of solid sample in a clean test tube and dissolve it in 5 cm^3 distilled water. Add to it 5 cm^3 of sodium hydroxide solution. Finally add 3 g of	A characteristic smell of NH_3 gas is felt near the mouth of test tube. This gas turns red litmus paper blue.	NO_3^{1-} ions are indicated.

Aluminium metal reduces nitrate ions to ammonium ions which then react with aqueous NaOH to evolve ammonia gas. The reduction of NO_3^{1-} with aluminium metal is a redox reaction in which Al metal acts as a cathode and reduces nitrate ions to ammonia gas.

$$3NO^{1-}_{3(aq)} + 8A\ell_{(s)} + 5OH_{(aq)} + 18H_2O_{(\ell)} \rightarrow 3NH_{3(g)} + 8[A\ell(OH)_{4(aq)}]^{1-}$$



(d) Identification of Sulphate (SO_4^{2-}) Radical

Experiment	Observation	Inference
Take 3 g of solid sample in a clean test tube. Dissolve it in 5 cm^3 of distilled water. Acidify the solution with a few drops of dil. HNO_3 and then add 5 cm^3 barium nitrate solution.	A heavy white precipitate of $BaSO_4$ is formed.	SO_4^{2-} ions are indicated.

$$SO^{2-}_{4(aq)} + Ba^{2+}_{(aq)} \longrightarrow \underset{\text{white ppt.}}{BaSO_{4(s)}}$$

Did You Know?

Dilute nitric acid is added to destroy any carbonate ions present in the solution as an impurity.

QUICK CHECK 16.3

a) Distinguish carbonate (CO_3^{2-}) and bicarbonate (HCO_3^{1-}) radicals.

Ans.

Experiment	Observation (CO_3^{2-})	Observation (HCO_3^-)	Inference
Add dilute HCℓ	Brisk effervescence (CO_2 gas)	Slower effervescence (CO_2 gas)	CO_3^{2-} reacts faster due to higher alkalinity.
$MgSO_4$ test	White ppt. ($MgCO_3$) forms immediately	No ppt. (unless heated)	CO_3^{2-} precipitates directly; HCO_3^- needs heating to form CO_3^{2-}.
Phenolphthalein test	Turns pink (strongly alkaline)	Remains colorless (weakly alkaline)	CO_3^{2-} shows higher pH.
Heat solid sample	No change (stable)	Releases CO_2, turns to CO_3^{2-} (loses $H_2O + CO_2$)	HCO_3^- decomposes on heating.

b) What is ring test? Give equation for this test.

Ans. The ring test is a qualitative chemical test used to detect the presence of nitrate ions (NO_3^-) in a solution.

Procedure & Observations:

Prepare the test solution containing nitrate (e.g., $NaNO_3$). Now, Add freshly prepared ferrous sulfate ($FeSO_4$) solution to it. Carefully add concentrated sulfuric acid (H_2SO_4) along the test tube walls without shaking.

Observation: A brown ring forms at the junction of the two layers.

Chemical Equation:

The brown ring is due to the formation of **Nitroso ferrous sulfate** complex:

$$NO_3^- + 3Fe^+_2 + 4H_2SO_4 \longrightarrow [Fe(NO)(H_2O)_5]SO_4 + 2SO_4^{2-} + 2H_2O$$

(Simplified: Brown ring = $[Fe(NO)]SO_4$ complex)

Inference:

- The brown ring confirms nitrate (NO_3^-) in the sample.

Give names and formulas of some water insoluble sulphates.

1. **Barium sulfate** – $BaSO_4$
2. **Lead(II) sulfate** – $PbSO_4$
3. **Calcium sulfate** (slightly soluble, but often considered insoluble) – $CaSO_4$
4. **Strontium sulfate** – $SrSO_4$
5. **Silver sulfate** (sparingly soluble, but mostly insoluble in dilute solutions) – Ag_2SO_4

TESTS FOR IDENTIFICATION OF BASIC RADICALS

a) Identification of Aluminium ($A\ell^{3+}$) radical

Take 4 g of solid sample in a clean test tube. Dissolve it in about 10 cm^3 distilled water. Divide this solution into two parts for further tests.

Experiment	Observation	Inference
To one part, add about 5 cm^3 NaOH solution.	A white gelatinous precipitate is formed.	$A\ell^{3+}$ ions are indicated.
To the second part of the above solution, add a few drops of aqueous ammonia.	A white precipitate is formed.	$A\ell^{3+}$ ions are indicated.

$$A\ell^{3+}_{(aq)} + 3OH^{1-}_{(aq)} \longrightarrow \underset{\text{white ppt}}{A\ell(OH)_{3(s)}}$$

Rack Your Mind!

9. How can aqueous NaOH and NH_3 help identify metal ions?

b) Identification of Ammonium (NH_4^{1+}) radical

Experiment	Observation	Inference
Take 4 g of sample in a clean test tube. Dissolve it in 10 cm^3 distilled water. Add NaOH solution and gently heat it.	Ammonia gas is evolved with a distinct smell. Ammonia gas turns moist red litmus blue.	NH_4^{1+} ions are indicated.

$$NH^{1+}_{4(aq)} + OH^{1-}_{(aq)} \longrightarrow NH_{3(g)} + H_2O_{(\ell)}$$

c) Identification of Calcium (Ca^{2+}) radical

Take 4 g solid sample in a clean test tube. Dissolve it in 10 cm^3 distilled water. Make two parts of this solution for further tests.

Experiment	Observation	Inference
To one part, add NaOH solution.	White precipitate is formed which does not dissolve in excess of NaOH solution.	Ca^{2+} ions are indicated.
To the second part of the above solution, add aqueous ammonia.	Only a slight turbidity appears or No precipitate is formed.	Ca^{2+} ions are indicated.

$$Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow \underset{\text{white ppt}}{Ca(OH)_{2(s)}}$$

d) Identification of Chromium radical (Cr^{3+})

Add 4 g sample in a clean test tube. Dissolve it in 10 cm^3 distilled water. Make two parts of the above solution for further tests.

Experiment	Observation	Inference
To one part, add NaOH solution.	A green precipitate appears which turns into green solution when excess of NaOH is added	Cr^{3+} ions are indicated.
To the second part of the above solution, add aqueous ammonia.	A green precipitate appears which is insoluble in excess of aqueous ammonia.	Cr^{3+} ions are indicated.

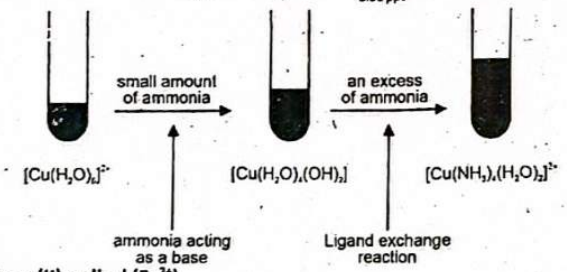
$$Cr^{3+}_{(aq)} + 3OH^-_{(aq)} \longrightarrow \underset{\text{Green ppt}}{Cr(OH)_{3_s}}$$

e) Identification of Copper radical (Cu^{2+})

Add 4 g solid sample in a clean test tube. Dissolve it in 10 cm^3 of distilled water. Make two parts of the above solution for further tests.

Experiment	Observation	Inference
To first part, add NaOH solution.	A light-blue precipitate is formed.	Cu^{2+} ions are indicated.
To the second part of the above solution, add aqueous ammonia.	Deep blue solution is formed.	Cu^{2+} ions are indicated.

$$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow \underset{\text{Blue ppt}}{Cu(OH)_{2s}}$$



f) Identification of Iron (II) radical (Fe^{2+})

Take 4 g sample in a clean test tube. Dissolve it in 10 cm^3 of distilled water. Make two portions of the solution for further tests.

Experiment	Observation	Inference
To one portion, add NaOH solution.	A green precipitate is formed which is turned into orange brown precipitate after some time.	Fe^{2+} ions are indicated.
To second portion of the above solution, add aqueous ammonia.	A white gelatinous precipitate of $Fe(OH)_2$ is formed which quickly oxidizes to form red brown precipitate of $Fe(OH)_3$.	Fe^{2+} ions are indicated.

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow \underset{\text{Green ppt}}{Fe(OH)_2}$$

g) Identification of Fe (III) radical (Fe^{3+})

Take 2 g $FeC\ell_3$ in a clean test tube. Dissolve it in 10 cm^3 of distilled water. Ma[illegible] solution for further tests.

Experiment	Observation	Inference
To one portion, add NaOH solution.	Orange brown precipitate is formed.	Fe^{3+} ions are indicated.
To the second portion of the above solution, add aqueous ammonia.	Orange brown precipitate is formed.	Fe^{3+} ions are indicated.

$$Fe^{3+}_{(aq)} + 3OH^-_{(aq)} \longrightarrow \underset{\text{Orange brown ppt}}{Fe(OH)_{3_s}}$$

h) Identification of Zinc radical (Zn^{2+})

Take 4 g solid sample in a clean test tube. Dissolve it in 10 cm^3 of distilled water. Make two portions of the above solution for further tests.

Experiment	Observation	Inference
To one portion add NaOH solution.	White precipitate is formed which is soluble in excess of NaOH solution.	Zn^{2+} ions are indicated.
To second portion of the above solution add aqueous ammonia.	White precipitate is formed which dissolves in excess of ammonia.	Zn^{2+} ions are indicated.

$$Zn^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow \underset{\text{white ppt}}{Zn(OH)_{2(s)}}$$

QUICK CHECK 16.4

a) What is lake test? Give equation.

Ans. Lake Test

Purpose: To detect aluminium ($A\ell^{3+}$) or other metal ions by forming a colored "lake" (adsorption complex) with an organic dye.

Experiment	Observation	Inference
O.S + few drops of $HC\ell$ + litmus solution + excess of NH_4OH.	A blue lake (blue ppt. in colourless solution) is formed.	$A\ell^{3+}$ is confirmed.

$$A\ell^+_3 + 3NH_4OH \longrightarrow A\ell(OH)_3\downarrow + 3NH^+_4$$

Inference:

- Blue colour floats over colourless solution.

b) How ammonium ion is indicated?

Ans. Identification of Ammonium (NH^{1+}_4) radical

Experiment	Observation	Inference
Take 4 g of sample in a clean test tube. Dissolve it in 10 cm^3 distilled water. Add NaOH solution and gently heat it.	Ammonia gas is evolved with a distinct smell. Ammonia gas turns moist red litmus blue.	NH^{1+}_4 ions are indicated.

$$NH^{1+}_{4(aq)} + OH^{1-}_{(aq)} \longrightarrow NH_{3(g)} + H_2O_{(\ell)}$$

c) How will you distinguish ferrous (Fe^{2+}) and ferric (Fe^{3+}) radicals?

Ans.

Test	Observation for Fe^{2+}	Observation for Fe^{3+}	Inference
Potassium ferricyanide ($K_3[Fe(CN)_6]$)	Deep blue precipitate (Turnbull's blue)	Brownish solution (no ppt)	Fe^{2+} confirmed by blue ppt.
[illegible]otassium [illegible]rrocyanide [illegible][Fe(CN)6])	White/blue ppt (if dilute)	Deep blue precipitate (Prussian blue)	Fe^{3+} confirmed by intense blue ppt.

NaOH solution	Dirty green precipitate ($Fe(OH)_2$)	Red-brown precipitate ($Fe(OH)_3$)	Fe^{3+} gives reddish-brown ppt.
NH_4SCN (Thiocyanate)	No colour change (pale green)	Blood-red colour $[Fe(SCN)]^{2+}$	Fe^{3+} confirmed by red complex.
$KMnO_4$ (in acid)	Decolourizes (oxidized to Fe^{3+})	No reaction (already Fe^{3+})	Fe^{2+} reduces $KMnO_4$.

d) What happens when e.g. NH_3 is added to Cu^{2+} solution in limited and excess quantities?

Ans. When aqueous NH_3 (ammonia) is added to a Cu^{2+} (copper(II)) solution in limited and excess amounts we observe:

1. Limited NH_3 (Pale Blue Precipitate)

Reaction: $Cu_2^+ + 2NH_3 + 2H_2O \longrightarrow Cu(OH)_2 \downarrow (\text{pale blue}) + 2NH_4^+$

Observation: A pale blue gelatinous precipitate of copper(II) hydroxide ($Cu(OH)_2$) forms.

2. Excess NH_3 (Deep Blue Solution)

Reaction: $Cu(OH)_2 + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2} + (\text{deep blue}) + 2OH^-$

Observation: The precipitate dissolves, forming a deep blue solution due to the tetraamminecopper (II) complex ion $[Cu(NH_3)_4]^{2+}$.

In short:

- **Limited NH_3:** Forms insoluble $Cu(OH)_2$.
- **Excess NH_3:** Forms soluble $[Cu(NH_3)_4]^{2+}$ complex (used in qualitative analysis).

Solution File — Rack Your Brain!

Sr. #	Option	Explanation
1.	B	Testing prevents accidents caused by faulty apparatus.
2.	S.Q	Keep the workspace organized and not overcrowded to avoid hazards, and maintain a safe distance from others handling apparatus to prevent accidents.
3.	S.Q	By understanding the properties of chemicals used, reading labels and safety data sheets, and knowing the risks associated with spills, fumes, and reactions during the experiment.
4.	A	Chemical hazards can cause burns, poisoning, respiratory issues, and skin irritation.
5.	S.Q	To ensure all apparatus works properly and safely, preventing accidents or injuries during th experiment.
6.	B	Burette allows precise delivery of titrant drop by drop to find the exact end point.
7.	S.Q	By observing a clear color change of the indicator, which signals that the titration re complete.
8.	A	Carbonate reacts with acid to produce CO_2 gas, confirming its presence.
9.	S.Q	They react with specific metal ions to form characteristic precipitates or solub helping to distinguish ions like $A\ell^{3+}$, Cu^{2+}, Fe^{2+}, etc.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. While taking a reading with a burette, why it is always advisable to read the lower meniscus for the colourless liquids and the upper meniscus for the coloured liquids?

a) because it is more convenient
b) because colourless liquids have more surface tension than coloured liquids
c) because lower meniscus does not exist for coloured liquids
d) because of the parallax effect

II. Why phenolphthalein indicator is more appropriate to use during the titrations which involve a strong acid and a strong base?

a) because it is itself weakly acidic
b) because the pH at the equivalence point as well as the pH over where the colour of phenolphthalein changes match each-other.
c) because the solution at the end of titration is acidic.
d) because the solution at the end of titration is basic.

III. Which cation gives a white gelatinous precipitate upon the addition of aqueous ammonia?

a) Cr^{3+} b) Cr^{2+} c) Zn^{2+} d) $A\ell^{3+}$

IV. Addition of NH_4OH to an aqueous solution of a cation gives a green precipitate which turns brown upon standing. Which basic radical is indicated?

a) Cu^{2+} b) Cr^{3+} c) Fe^{2+} d) Fe^{3+}

V. On dry heating test for salt analysis, the evolution of a colourless, odorless gas that turns limewater milky suggests the presence of:

a) Chloride ion ($C\ell^-$) b) Sulfate ion (SO_4^{2-}) c) Carbonate ion (CO_3^{2-}) d) Nitrate ion (NO_3^-)

VI. The chromyl chloride test is a specific confirmatory test for:

a) Bromide ions (Br^-) b) Iodide ions (I^-) c) Chloride ions ($C\ell^-$) d) Sulfate ions (SO_4^{2-})

VII. The brown ring test is a confirmatory test for which acid radical?

a) Chloride ($C\ell^-$) b) Nitrate (NO_3^-) c) Sulfate (SO_4^{2-}) d) Carbonate (CO_3^{2-})

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	a	because it is more convenient	• For colorless liquids, the lower meniscus is clearly visible. • For colored liquids, the upper meniscus is easier to see. • It is standard and convenient practice based on visibility, not surface tension or parallax.
II.	b	because the pH at the equivalence point as well as the pH over where the colour of phenolphthalein changes match each-other.	• Phenolphthalein changes color between pH 8.2–10, which matches the equivalence point pH of strong acid–strong base titrations.
III.	c	Zn^{2+}	• Zinc ions form a white gelatinous precipitate with aqueous ammonia, which is soluble in excess.
IV.	c	Fe^{2+}	• Fe^{2+} forms a green precipitate with NH_4OH, which oxidizes to Fe^{3+}, giving a brown colour on standing.

V.	c	Carbonate ion (CO_3^{2-})	• Heating carbonates produces CO_2 gas, which turns limewater milky due to formation of $CaCO_3$.
VI.	c	Chloride ions ($C\ell^-$)	• The chromyl chloride test gives red vapours of $CrO_2C\ell_2$ when chloride reacts with potassium dichromate and concentrated sulfuric acid.
VII.	d	Nitrate (NO_3^-)	• The brown ring test confirms nitrate ions by forming a brown ring of $[Fe(H_2O)_5(NO)]^{2+}$ complex.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. For which type of titration, methyl orange is used as an indicator?

Ans. Methyl orange is used as an indicator in strong acid–weak base titrations.
Methyl orange changes colour in the pH range of 3.1 to 4.4, making it ideal for titrations where the equivalence point is acidic, as is the case when a strong acid (e.g., $HC\ell$) is titrated against a weak base (e.g., NH_4OH).

b. Explain why phenolphthalein is a suitable indicator for the titration of a weak acid with a strong base but not for the titration of a strong acid with a weak base.

Ans. Phenolphthalein is suitable for weak acid–strong base titrations because the equivalence point is basic (pH ≈ 8.5), which falls within phenolphthalein's colour change range (pH 8.2–10).
It is not suitable for strong acid–weak base titrations because the equivalence point is acidic (pH < 7), outside phenolphthalein's range, so it would not show a clear endpoint.

c. Explain why different indicators change colour over different pH ranges.

Ans. Different indicators change colour over different pH ranges because each has a unique acid-base equilibrium and changes structure (and thus colour) at a specific pH range where its conjugate acid and base forms are present in comparable amounts.
Examples:
1. **Phenolphthalein:**
   - **Colour change range:** pH 8.2 – 10
   - **Colour:** Colourless in acid, pink in base
2. **Methyl Orange:**
   - **Colour change range:** pH 3.1 – 4.4
   - **Colour:** Red in acid, yellow in base

d. It is always advisable to use dilute solutions while performing experiments in volumetric analysis? Give a reason.

Ans. Yes, it is advisable to use dilute solutions in volumetric analysis because they reduce the risk of large heat changes and allow for more precise volume measurements, minimizing errors and improving the accuracy of the titration results.

e. White precipitates are formed when Ca^{2+}, $A\ell^{3+}$ and Zn^{2+} all react separately with NaOH solution. How will you detect which basic radical is present?

Ans. To distinguish between Ca^{2+}, $A\ell^{3+}$, and Zn^{2+} ions when all form white precipitates with NaOH, excess NaO can be used:
1. **Add excess NaOH to each white precipitate formed:**
   - **$Ca(OH)_2$:** Insoluble in excess NaOH → White ppt remains
   - **$A\ell(OH)_3$:** Dissolves in excess NaOH forming a colorless solution
   - **$Zn(OH)_2$:** Dissolves in excess NaOH forming a colorless solution
2. **Differentiate $A\ell^{3+}$ and Zn^{2+} using ammonium hydroxide (NH_4OH):**
   - **$A\ell(OH)_3$:** Insoluble in excess NH_4OH → White ppt remains
   - **$Zn(OH)_2$:** Soluble in excess NH_4OH → Colorless solution forms

f. How Fe^{2+} can be distinguished from Fe^{3+} chemically?

Ans. Identification of Iron (II) radical (Fe^{2+})

Take 4 g sample in a clean test tube. Dissolve it in 10 cm^3 of distilled water. Make two portions of the solution for further tests.

Experiment	Observation	Inference
To one portion, add NaOH solution.	A green precipitate is formed which is turned into orange brown precipitate after some time.	Fe^{2+} ions are indicated.
To second portion of the above solution, add aqueous ammonia.	A white gelatinous precipitate of $Fe(OH)_2$ is formed which quickly oxidizes to form red brown precipitate of $Fe(OH)_3$.	Fe^{2+} ions are indicated.

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow \underset{\text{Green ppt}}{Fe(OH)_2}$$

Identification of Fe(III) radical (Fe^{2+})

Take 2 g $FeC\ell_3$ in a clean test tube. Dissolve it in 10 cm^3 of distilled water. Make two portions of the solution for further tests.

Experiment	Observation	Inference
To one portion, add NaOH solution.	Orange brown precipitate is formed.	Fe^{3+} ions are indicated.
To the second portion of the above solution, add aqueous ammonia.	Orange brown precipitate is formed.	Fe^{3+} ions are indicated.

$$Fe^{3+}_{(aq)} + 3OH^-_{(aq)} \longrightarrow \underset{\text{Orange brown ppt}}{Fe(OH)_3}$$

g. Why does Ca^{2+} not give precipitate with aqueous ammonia?

Ans. Ca^{2+} does not give a precipitate with aqueous ammonia because calcium hydroxide ($Ca(OH)_2$), formed by the reaction of Ca^{2+} with ammonia, is sparingly soluble in water. The amount of hydroxide formed is insufficient to exceed the solubility product (K_{sp}) and produce a visible precipitate under normal conditions.
In contrast, other metal ions like $A\ell^{3+}$ and Zn^{2+} form insoluble hydroxides that precipitate in the presence of ammonia.

h. How will you find out the concentration of acetic acid in vinegar solution?

Ans. To find the concentration of acetic acid (CH_3COOH) in a vinegar solution, we can perform a titration using a strong base (such as NaOH) and an appropriate indicator (such as phenolphthalein).
Procedure:
1. **Prepare a Sample of Vinegar:** Measure a known volume (e.g., 10 cm^3) of the vinegar solution.
2. **Titration Setup:**
   - **Titrant:** Prepare a standard solution of **NaOH** of known concentration (e.g., 0.1 M).
   - **Indicator:** Add a few drops of **phenolphthalein** (which changes from colorless to pink as the solution goes from acidic to slightly basic).
3. **Perform the Titration:**
   - Slowly add the NaOH solution from the burette to the vinegar solution while stirring.
   - **End point:** The titration is complete when the solution turns light pink (indicating neutralization).
4. **Calculate the Concentration of Acetic Acid:**
   - Use the formula:

$$C_1V_1 = C_2V_2$$

where:

- C_1 = concentration of acetic acid (required),
- V_1 = volume of vinegar used,
- C_2 = concentration of NaOH,
- V_2 = volume of NaOH used to reach the endpoint.

5. **Final Calculation**: Solve for C_1, the concentration of acetic acid in vinegar.

Example Calculation:

- If 25 cm^3 of NaOH (0.1 M) neutralizes 10 cm^3 of vinegar, the calculation would be:

$$C_1 \times 10.0\ cm^3 = 0.1\ M \times 25\ cm^3$$
$$C_1 = 0.1 \times 25.0 / 10 = 0.25\ M$$

So, the concentration of acetic acid is **0.25 M**.
This gives the molarity of acetic acid in the vinegar.

i. What precautions you need to observe while diluting a concentrated acid?

Ans. Precautions to Observe while Diluting a Concentrated Acid:

(i) Always add acid to water, never water to acid — this prevents splashing due to the exothermic reaction.
(ii) Use protective gear — wear gloves, goggles, and a lab coat to prevent burns and injuries.
(iii) Perform the dilution slowly, while stirring continuously, to control heat release.
(iv) Use heat-resistant glassware — to prevent breakage from the heat generated.
(v) Work in a well-ventilated area or fume hood — to avoid inhaling harmful vapours.
(vi) Keep neutralizing agents (like baking soda) nearby in case of spills.

j. Why does an aqueous solution of Na_2CO_3 behave like a base?

Ans. An aqueous solution of Na_2CO_3 (sodium carbonate) behaves like a base because the carbonate ion (CO_3^{2-}) undergoes hydrolysis in water:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

This reaction produces hydroxide ions (OH^-), which increase the pH of the solution, making it basic in nature.
Na_2CO_3 is a salt of a strong base (NaOH) and a weak acid (H_2CO_3), so its solution is basic due to the weak conjugate acid (HCO_3^-) not fully neutralizing OH^- formation.

k. If an aqueous solution of NaOH is kept in an open container, what changes do you expect to take place with the passage of time?

Ans. If an aqueous solution of NaOH is kept in an open container, the following changes occur over time:

1. **Absorption of CO_2 from the air:**
   NaOH reacts with carbon dioxide in the atmosphere:
   $$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$
   This reaction forms sodium carbonate (Na_2CO_3) and water.
2. **Decrease in alkalinity:**
   As NaOH is gradually converted into Na_2CO_3, the concentration of OH^- ions decreases, reducing the solution's basic strength (pH).
3. **Formation of precipitates (if concentration is high):**
   If the solution becomes saturated, precipitates of sodium carbonate hydrate may form.

So, by the passage of time the NaOH solution becomes less basic and transforms into a carbonate solution.

DESCRIPTIVE QUESTIONS

Q.3 Describe common types of the Chemistry lab hazards with two examples in each case.

Ans. See Page No. (510)

Q.4 What are common accidents in the Chemistry lab? How they are managed in first aid tre

Ans. See Page No. (511)

Q.5 How the following acid radicals are indicated and confirmed in salt analysis:

i) CO_3^{2-} ii) Cl^- iii) NO_3^- iv) SO_4^{2-}

Ans. See above acid radicals in Theory.

Q.6 How the following basic radicals are indicated and confirmed in salt analysis:

i) Cu^{2+} ii) Al^{3+} iii) Fe^{3+} iv) Zn^{2+}

Ans. See above acid radicals in Theory.

ADDITIONAL SLOs BASED MCQs

1. **Which of the following is used as an indicator in the titration of a strong acid and a weak base?**
   A. Methyl orange B. Phenolphthalein C. Thymol blue D. Fluorescein

2. **The ideal indicator for the titration of strong acid and weak base should have a pH range between _____.**
   A. 3-5 B. 4-6 C. 6-8 D. 7-9

3. **Find the concentration of HCl, if 10 cm^3 of 0.5 M $Ca(OH)_2$ is required to titrate 50 cm^3 of HCl.**
   A. 1/10 M B. 1/5 M C. 5 M D. 10 M

4. **What is the concentration of the sulphuric acid solution, if 100 cm^3 of the solution is neutralized by 50 cm^3 of 0.5 M $Ba(OH)_2$ solution?**
   A. 0.25 M B. 0.5 M C. 25 M D. 50 m

5. **Which of the following is a buffer solution?**
   A. $CH_3COOH + CH_3COONH_4$ B. $H_2SO_4 + CuSO_4$
   C. $CH_3COONa + CH_3COOH$ D. NaCl + NaOH

6. **Which of the following is used as an indicator in the titration of a weak acid and a strong base?**
   A. Methyl orange (3 to 4.6) B. Bromothymol blue (6 to 7.5)
   C. Phenolphthalein (8 to 9.6) D. Methyl red (5 to 6.9)

7. **What is the molarity of the solution of barium hydroxide, if 35 cm^3 of 0.1 M HCl is used in the titration of 25 cm^3 of the barium hydroxide solution?**
   A. 0.28 B. 0.21 C. 0.14 D. 0.07

8. **A difference between strong and weak acid is _____.**
   A. proton donation and electron acceptance B. complete and partial ionization
   C. negative and positive pH D. presence and absence of halogen ions

9. **Which of the following titrations will have the equivalence point at a pH more than 8?**
   A. CH_3COOH and NaOH B. HCl and NaOH
   C. CH_3COOH and NH_3 D. HCl and NH_3

10. **What is the primary purpose of adding silver nitrate in the identification of non-metal anions?**
    A. To produce a gas B. To form precipitates C. To induce a colour change D. To neutralize acidity

11. **Which reagent is commonly used to test for the presence of chloride ions in a solution?**
    A. Iodine solution B. Silver nitrate C. Hydrochloric acid D. Sodium hydroxide

12. **What observation indicates the presence of sulphite ions in a solution during the identification of non-metal anions with $BaCl_2$ solution?**
    A. Formation of a white precipitate B. Evolution of a gas smelling like ammonia
    C. Formation of a yellow precipitate D. Absence of any visible change

13. **Which non-metal anion is typically identified through a starch-iodine reaction?**
    A. Chloride B. Bromide C. Iodide D. Sulphite

14. What safety measure is crucial when working with reagents during the identification of non-metal anions?
A. Wearing safety goggles B. using a fume hood C. Wearing gloves D. All of the above

15. Which cation gives a white gelatinous precipitate upon the addition of aqueous ammonia?
A. Cr^{3+} B. Cr^{2+} C. Zn^{2+} D. $A\ell^{3+}$

Answer Key

1. A	2. B	3. B	4. A	5. C	6. C	7. D	8. A	9. A	10. B	11. B	12. A
13. C	14. D	15. C									

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 What is meant by standardization?

Ans. Determination of exact concentration of a solution by titrating it against a solution of known strength is called standardization.

Q.2 What is the volumetric analysis?

Ans. A quantitative analysis based upon the measurement of volume is called as volumetric analysis.

Q.3 What is Titration?

Ans. The process of determination the exact volume of a solution which reacts completely with the definite volume of another solution.

Q.4 How carbonate (CO_3^{2-}) radicals are identified?

Ans.

Experiment	Observation	Inference
Take about 2 g of solid carbonate sample in a clean test tube and then add about 5 cm^3 of dilute $HC\ell$ solution. Pass the gas evolved in the above step through a solution of lime water.	Effervescence takes place during which a gas evolves briskly, that turns lime water milky.	Carbonate (CO_3^{2-}) are indicated ions.

Reactions involved in the above steps

$$CO_{3(aq)}^{2-} + 2H_{(aq)}^{+} \rightarrow H_2O_{(\ell)} + CO_{2(g)}$$

$$\underset{\text{Lime water}}{Ca(OH)_{2(aq)}} + CO_{2(g)} \rightarrow \underset{\text{(white ppt)}}{CaCO_{3(s)}} + H_2O_{(\ell)}$$

Confirmatory Test		
Original Solution + $MgSO_4$	White ppt. of $MgCO_3$	CO_3^{2-} is confirmed.

Q.5 How Chloride ($C\ell^{1-}$) radicals are identified?

Ans.

Experiment	Observation	Inference
Take 2 g of solid sample in a test tube and add 5 cm^3 of distilled water to make the aqueous solution. Add a few drops of dil. HNO_3 solution to acidify the solution of the salt, finally add about 5 cm^3 of aqueous $AgNO_3$.	A thick white precipitate is formed which dissolves in aq. NH_3. **In other words,** White ppt. ($AgC\ell$) soluble in dil. NH_4OH.	$C\ell^{-1}$ ions are indicated.
Confirmatory Test		
O.S + Silver Nitrate ($AgNO_3$) solution.	White ppt. ($AgC\ell$) soluble in dil. NH_4OH.	$C\ell^-$ is confirmed.

Result: Acid Radical = Chloride $C\ell^-$

Q.6 Give the chemistry of Chromyl Chloride test.

Ans. It is a confirmatory test of $C\ell^-$. In this test reddish brown chromyl fumes are evolved when solid salt, solid $K_2Cr_2O_7$ and Conc.H_2SO_4 are heated together.

$$4NaC\ell + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2CrO_2C\ell_2 + H_2O$$

Q.7 How Aluminium ($A\ell^{3+}$) radical is identified?

Ans. Take 4 g of solid sample in a clean test tube. Dissolve it in about 10 cm^3 distilled water. Divide this solution into two parts for further tests.

Experiment	Observation	Inference
To one part, add about 5 cm^3 NaOH solution.	A white gelatinous precipitate is formed.	$A\ell^{3+}$ ions are indicated
To the second part of the above solution, add a few drops of aqueous ammonia.	A white precipitate is formed.	$A\ell^{3+}$ ions are indicated

$$A\ell_{(aq)}^{3+} + 3OH_{(aq)}^{1-} \longrightarrow \underset{\text{white ppt}}{A\ell(OH)_{3(s)}}$$

Confirmatory Test (Lake Test):		
O.S + few drops of $HC\ell$ + litmus solution + excess of NH_4OH.	A blue lake (blue ppt. in colourless solution) is formed.	$A\ell^{3+}$ is confirmed.

Q.8 How Calcium (Ca^{2+}) radical is identified?

Ans. Take 4 g solid sample in a clean test tube. Dissolve it in 10 cm^3 distilled water. Make two parts of this solution for further tests.

Experiment	Observation	Inference
To one part, add NaOH solution.	White precipitate is formed which does not dissolve in excess of NaOH solution.	Ca^{2+} ions are indicated.
To the second part of the above solution, add aqueous ammonia.	Only a slight turbidity appears or No precipitate is formed.	Ca^{2+} ions are indicated.

$$Ca_{(aq)}^{2+} + 2OH_{(aq)}^{-} \longrightarrow \underset{\text{white ppt}}{Ca(OH)_{2(s)}}$$

Confirmatory Test:		
O.S + $NH_4C\ell$ + $K_4[Fe(CN)_6]$	White ppt. of $Ca_2[Fe(CN)_6]$ formed.	Ca^{2+} is confirmed.

Result: Basic Radical = Calcium (Ca^{2+})

Q.9 How Ammonium (NH_4^{1+}) radical is identified?

Ans.

Experiment	Observation	Inference
Take 4 g of sample in a clean test tube. Dissolve it in 10 cm^3 distilled water. Add NaOH solution and gently heat it.	Ammonia gas is evolved with a distinct smell. Ammonia gas turns moist red litmus blue.	NH_4^{1+} ions are indicated.

$$NH_{4(aq)}^{1+} + OH_{(aq)}^{1-} \longrightarrow NH_{3(g)} + H_2O_{(\ell)}$$

Confirmatory Test:		
To the O.S added Picric acid solution.	Yellow needle like crystals are obtained.	NH_4^+ is confirmed.

Result: Basic Radical = Ammonium NH_4^+

Q.10 How Chromium radical (Cr^{3+}) is identified?

Ans. Take 4 g sample in a clean test tube. Dissolve it in 10 cm^3 distilled water. Make two parts of the above solution for further tests.

Experiment	Observation	Inference
To one part, add NaOH solution.	A green precipitate appears which turns into green solution when excess of NaOH is added	Cr^{3+} ions are indicated.
To the second part of the above solution, add aqueous ammonia.	A green precipitate appears which is insoluble in excess of aqueous ammonia. $Cr^{3+}_{(aq)} + 3OH_{(aq)} \longrightarrow \underset{\text{Green ppt}}{Cr(OH)_3}$	Cr^{3+} ions are indicated.
Confirmatory Test: O.S + Na_3PO_4	Pale green ppt. of $CrPO_4$ formed.	Cr^{3+} is confirmed.

SELF-ASSESSMENT Chapter # 16

Total Mark: 30

Q.1 Encircle the correct option. **(1 × 6 = 6)**

(i) What color phenolphthalein turn in a basic solution:
a) Red b) Blue c) Pink d) Colourless

(ii) Which cation gives a white gelatinous precipitate upon the addition of aqueous ammonia?
a) Cr^{3+} b) Cr^{2+} c) Zn^{2+} d) $A\ell^{3+}$

(iii) Addition of NH_4OH to an aqueous solution of a cation gives a green precipitate which turns brown upon standing. Which basic radical is indicated?
a) Cu^{2+} b) Cr^{3+} c) Fe^{2+} d) Fe^{3+}

(iv) On dry heating test for salt analysis, the evolution of a colourless, odorless gas that turns limewater milky suggests the presence of:
a) Chloride ion ($C\ell^-$) b) Sulfate ion (SO_4^{2-}) c) Carbonate ion (CO^{2-}) d) Nitrate ion (NO_3^-)

(v) The chromyl chloride test is a specific confirmatory test for:
a) Bromide ions (Br^-) b) Iodide ions (I^-) c) Chloride ions ($C\ell^-$) d) Sulfate ions (SO_4^{2-})

(vi) The brown ring test is a confirmatory test for which acid radical?
a) Chloride ($C\ell^-$) b) Nitrate (NO_3^-) c) Sulfate (SO_4^{2-}) d) Carbonate (CO_3^{2-})

Q.2 Write short answers of the following questions. **(2 × 8 = 16)**

(i) What are different types of burns?
(ii) What is meant by concordant reading?
(iii) What is ring test? Give equation for this test.
(iv) If an aqueous solution of NaOH is kept in an open container, what changes do you expect to take place with the passage of time?
(v) What precautions you heed to observe while diluting a concentrated acid?
(vi) Why does an aqueous solution of Na_2CO_3 behave like a base?
(vii) Why Ca^{2+} does not give precipitate with aqueous ammonia?
(viii) Explain why different indicators change colour over different pH ranges.

Q.3 Extensive Questions. **(2 × 4 = 8)**

(a) How the following acid radicals are indicated and confirmed in salt analysis:
i) CO_3^{2-} ii) $C\ell^-$ iii) NO_3^- iv) SO_4^{2-}

(b) How the following basic radicals are indicated and confirmed in salt analysis:
i) Cu^{2+} ii) $A\ell^{3+}$ iii) Fe^{3+} iv) Zn^{2+}

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