1

PERIODIC TABLE AND PERIODIC PROPERTIES

STUDENT LEARNING OUTCOMES [C-11-B-01 to C-11-B-18]

- Explain the arrangement of elements in the periodic table. **(Understanding)**
- Identify the positions of metals, nonmetals 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 electron 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 behavior 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 behavior of the oxides and the hydroxides NaOH, $Mg(0H)_2$ 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 (NaCI, $MgCI_2$

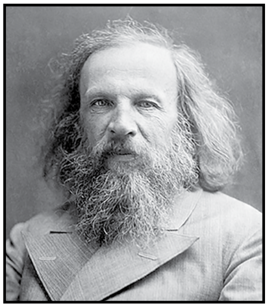
in terms of their outer shell (valence shell) electrons. **(Understanding)**

- 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)**

It is accurate to refer to the periodic table of elements 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. Elements are arranged in tabular form in the current periodic table based on their atomic number, electrical configuration, and recurrent chemical characteristics. It provides the foundation for comprehending 118 elements and their properties, making it a crucial tool in chemistry. The creation of the periodic table, which offers a framework for researching the periodic behaviors, is a significant accomplishment in scientific history.

1.1 HISTORICAL BACKGROUND

It is interesting to note that just three centuries ago, less than a dozen elements were known to humanity. By 1700 A.D., only 12 elements—Gold, Silver, Copper, Iron, Lead, Tin, Mercury, Phosphorus, Sulfur, Carbon, Zinc, and Arsenic—were recognized. Over time, more elements were discovered, prompting scientists to organize them systematically. Up to the end of 18th century, Antoine Lavoisier attempted to classify known elements as metals and nonmetals. In 1829, **Döbereiner** grouped the elements into **triads** (a group of three) with similar properties, noting 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 (^{7}Li^2,Na^3,^{7}K) .



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

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 element resembled the first element in properties.

In 1869, Russian chemist **Dmitri Mendeleev**, considered the father of the Periodic Table, arranged 63 elements into eight vertical columns by increasing atomic mass, aligning elements with similar properties into vertical groups. The success of his 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.

In the same year, **Lother Meyer** developed his famous curves by ploting a graph b/w the at weight and at volumes of elements. These curves also showed periodicity. In the same year Lother mayer developed his famous curves by plotting a graph between the atomic weights and atomic volumes of elements. These curves also showed periodic periodicity.

In 1913, Moseley determined the exact atomic numbers of known elements using X-ray emission, resolving flaws and discrepencies in Mendeleev's table by arranging the elements by atomic numbers instead of atomic masses. This significant breakthrough led Moseley to modify the Periodic Law to state that the properties of elements are periodic functions of their atomic numbers.

1.2 MODERN PERIODIC TABLE - FEATURES AND SIGNIFICANCE

The classification of elements in the modern periodic table helps in the easier understanding of their properties. Following are some of the main features of the modern periodic table:

- Presently, 118 elements are grouped in the table in ascending order of their respective atomic numbers.
- There are seven horizontal rows called **periods** and eighteen vertical columns called **groups**. (In older versions of the table, there were 8 vertical groups were divided into two types of groups: Eight A-Groups and Ten B-Groups.
- In the periodic table, elements within the same group exhibit similar chemical roperties ecause they have the same number of valence electrons. However, they show a gradual change in physical properties from top to bottom in a group.
- Elements in a period show a gradual change in properties moving from left to right in periods.

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

1.3 METALS, NON-METALS AND METALLOIDS

Elements can be broadly classified as metals, nonmetals and metalloids. Metals are elements which tend to lose electrons to form positive ions. Examples are iron, copper, gold and silver. On the other hand, non-metals are elements which tend to gain electrons to form negative ions. The examples are chlorine, sulfur and phosphorous. The metalloids separate 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 identifying the element groups. The line begins at boron (B) and extends down to polonium (Po) including Si, Ge, As, Sb and Te. Elements to the left of the line are considered metals. Elements just to the right of the line exhibit properties of both metals and nonmetals and are termed as metalloids or semimetals. Elements to the far right of the periodic table are nonmetals. The exception is hydrogen, the first element on the periodic table.

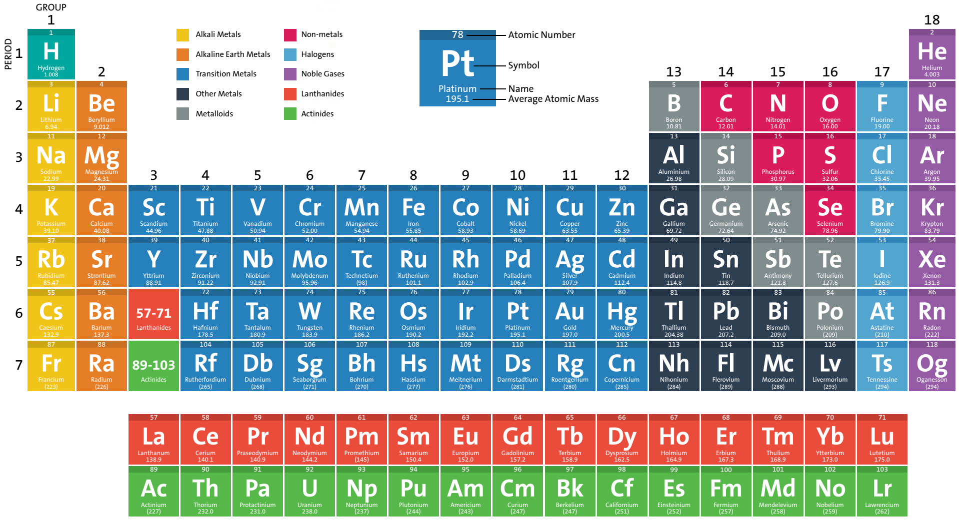


Fig 1.1: Modern periodic table

1.4 BLOCKS IN PERIODIC TABLE

Elements in the periodic table can be classified based on the subshells containing their valence electrons. For instance, the valence electrons of elements in the first two groups are in the **"s"** subshells, placing these elements in the s-block.

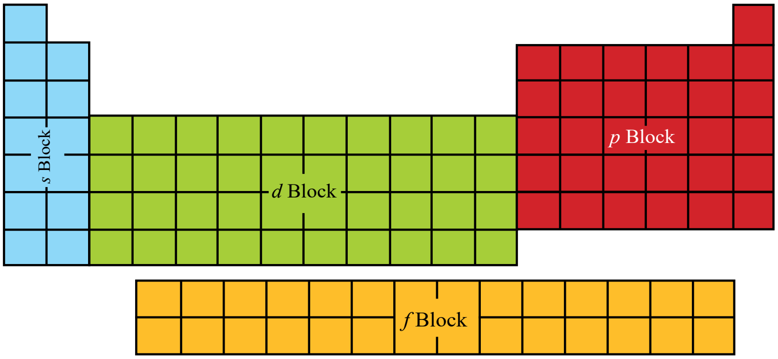


Figure 10.2: Blocks in periodic table

Similarly, 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, belong to the p-block. 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..

1.5 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 five famous families of elements in the periodic table:

- Alkali metals (Li, Na, K, Rb, Cs, Fr)
- Alkaline earth metals (Be, Mg, Ca, Ba, R.)
- Transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn)
- Chalcogens (O, S,Se, Te, Po)
- Halogens (F, Cl, Br, I, At, Ts)
- Noble gases (He, Ne, Ar, Kr, Xe, Rn, Og)

i) Alkali Metals

Elements in the group 1 of the periodic table are known as alkali metals because they produce alkalis when they react with water. Sodium and potassium are notable examples of these elements. Alkali metals are **characterized by** one valence electron, low densities, relatively low melting points, and low ionization energies. These are the most reactive metals.

ii) Alkaline Earth Metals

Group 2 elements are metals primarily found in the earth and form alkalis; hence they are referred to as alkaline earth metals. Examples include calcium and magnesium. These elements have two electrons in their valence shell, making them divalent. They are metallic solids that are harder and denser than alkali metals. Easily oxidized, with high thermal and electrical conductivities.

iii) Transition 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, as well as the lanthanides and actinides (f-block elements) 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

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

v) Halogens

Elements in group 17, known as halogens, are nonmetallic. The term "halogen" means "salt-former" because these elements easily react with alkali metals and alkaline earth metals to form stable halide salts. Examples are fluorine, chlorine, bromine. Halogens are highly reactive nonmetals with high electron affinities. Halogens can easily accept one electron to complete their outermost shell.

vi) Noble Gases

The noble gases are a group of unreactive elements present at the extreme right of the periodic table in Group 18. Examples include helium and argon. 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 compound. An example is compounds of xenon such as xenon hexafluoroplatinate ($XePtF_6$), 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?

b) Name the elements in the chalcogen family. Give their two characteristics.

1.6 PERIODIC ARRANGEMENT AND ELECTRONIC CONFIGURATION

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

- 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 3s subshell.
- Additionally, 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 3s subshell, which means that **X** would be magnesium (Mg).
- Here is another example to relate period number and group number with electronic configuration and position of element in period table.

X ⤵ belongs to group 13 and period 3

In above 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:

$$\begin{array}{ccc} 1s^2 & 2s^2\ 2p^6 & 3s^2\ 3p^1 \\ \downarrow & \downarrow & \downarrow \\ 1^{st}\text{ shell} & 2^{nd}\text{ shell} & 3^{rd}\text{ shell} \end{array}$$

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

Quick Check 1.2

a) X belongs to group 14 and period 2
   i. Write electronic configuration of the element X.
   ii. Identify block of the element. Identify this element from periodic table.

b) Identify an element that is in Period 4 and Group 17?

1.7 PERIODICTY OF PROPERTIES

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 instance, 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.

1.7.1 Variation in 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 It is half of the distance b/w two identical atoms bonded togather, (cova metalics & vander waals force) or 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).

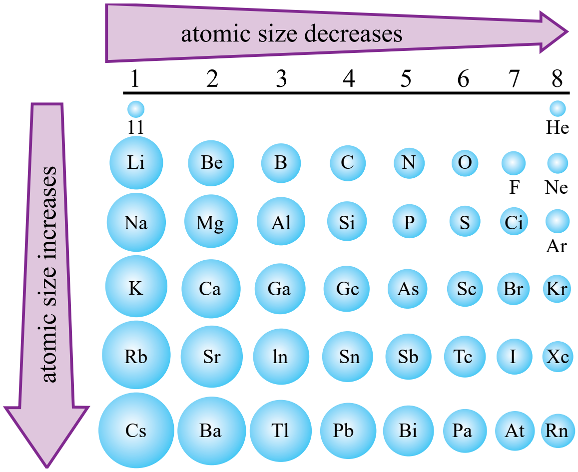


Fig 1.4: Variation in atomic radius across periods and down the groups

Periodic trends in atomic radius:

The factors affecting the atomic radius are: atomic number, effective nuclear charge and shielding effect of inner electrons. 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. Conversely, atomic radius increases **down a group** (from top to bottom) because additional electron shells are added, so more sheilding makes the atom larger despite the increase in nuclear charge (which is outweighed) .

1.7.2 Variation in Ionic Radius

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

As you move **across a period** from left to right, the ionic radius of **cations** decreases 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.

On the other hand, both cations and anions increase in size as we **move down a group**. This is because the principal quantum number (n) increases, leading to an increase in the number of electron shells. Consequently, 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.

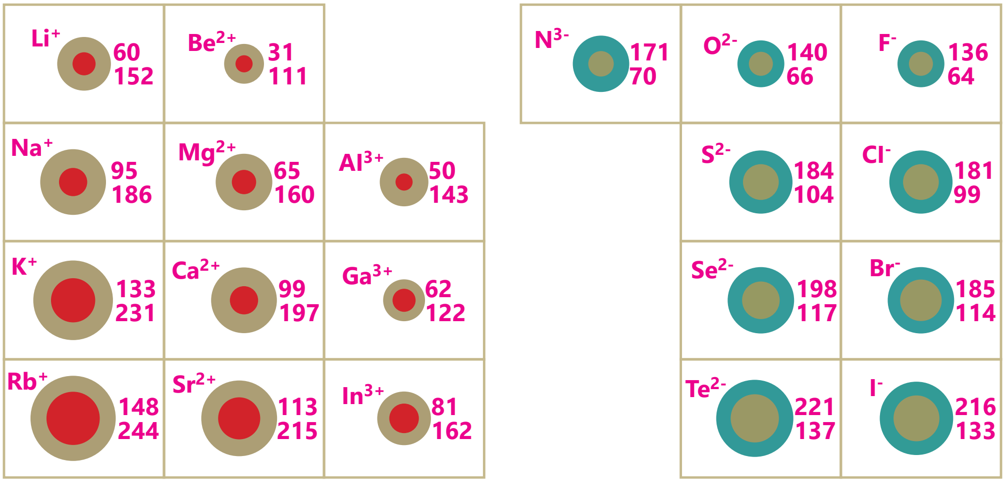


Fig. 1.5: Variation in Ionic Radius (Ions are coloured red and blue; parent atoms brown. Radii are in picometers)

Quick Check 1.5

a) Which factors affect atomic and ionic radii?

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

- i. the atomic radii of lithium and fluorine
- ii. a lithium atom and its ion, Li^+
- iii. an oxygen atom and its ion, O^{2-}
- iv. a nitride ion, N^{3-}, and a fluoride ion, F^-.

1.7.3 Variation in 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 (ΔHi1)."

$$Na_{(g)} \longrightarrow Na^{+}{}_{(g)} + e^{-} \quad \Delta H_{i1} = 494 \text{ kJ mol}^{-1}$$

$$Ca_{(g)} \longrightarrow Ca^{+}{}_{(g)} + e\text{–}^{o} \quad \Delta H_{i1} = 590 \text{ kJ mol}^{-1}$$

If a second electron is removed from each ion in a mole of gaseous 1+ ions, we call it the 2nd ionization energy, ΔHi2. Again, using calcium as an example:

$$Ca^{+}{}_{(g)} \longrightarrow Ca^{2+}{}_{(g)} + e\text{–}^{o} \qquad \Delta H_{i2} = 1150 \text{ kJ mol}^{-1}.$$

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

3rd ionisation energy:

$$Ca^{2+}{}_{(g)} \longrightarrow Ca^{3+}{}_{(g)} + e^{-} \quad \Delta H_{i3} = 4940 \text{ kJ mol–1}$$

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

Factors affecting the ionization energy

The magnitude of the ionisation 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, ionisation energy increases with an increase in the effective nuclear charge.

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 ionisation energy is higher when an electron is to be removed from a fully-filled or half-filled-shells.

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

(b) Oxygen has lower ionisation energy than nitrogen. The electronic configuration of oxygen and nitrogen are:

$_7N = 1s^2\ 2s^0\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$ $\Delta H_{i1} = 1403\ kJ\ mol^{-1}$

$_8O = 1s^2\ 2s^2\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 0}$ $\Delta H_{i1} = 1365\ kJ\ mol^{-1}$

Although, 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 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 2p 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 2p orbitals. Removing one of these unpaired electrons requires more energy due to the absence of spin-pairing repulsion.

Periodic trends in ionization energy

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.

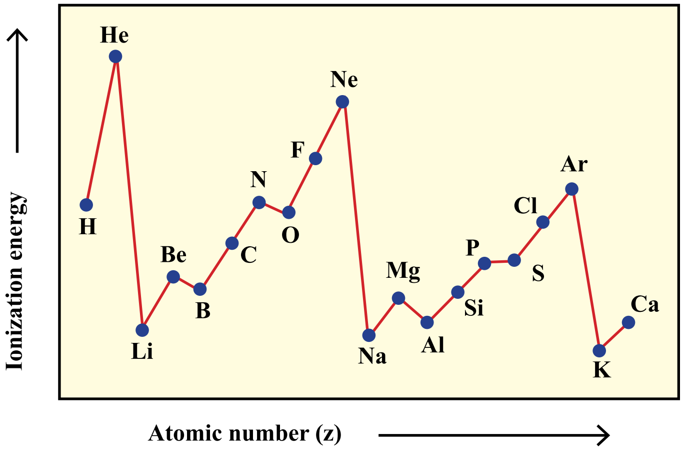


Figure 1.6 Variation in Ionization Energies across periods

As you 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 1.6** The figure also 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 1.6

a) Explain with reasoning following facts about ionization energy:

- i. 1st ionization energy of Boron is lesser than Beryllium.
- ii. 1st ionization energy of Aluminum is lower than Magnesium.

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

1.7.4 ELECTRON AFFINITY (ΔH°_{ea})

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.

$$Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)} \qquad \Delta H^\circ_{ea1} = -348.8\ kJ\ mol^{-1}$$

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.

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. For example, 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 (O2–) can be calculated by adding the first and second electron affinities

$$O_{(g)} + 2e^- \longrightarrow O^{2-}_{(g)}$$

$$\Delta H^\circ_{ea1} + \Delta H^\circ_{ea2} = (-141) + (+798) = +657\ kJ\ mol^{-1}$$

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. 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 ($N = 2s^2\ 2p^3$, $P = 3s^2\ 3p^3$). These half-filled p-subshells, being very stable, have very little tendency to accept any extra electron to be added to them. Noble gases group-18 (VIII-A) have stable $ns^2\ np^6$ configuration and hence the atoms of these gases, do not accept any extra electron, This is evident from their positive 1st electron affinities.

1.7.5 Periodic trends in electron affinity

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 < Cl). 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 1.1: 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 1.7

Explain with reasoning following facts about electron affinity:

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

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

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

1.7.6 Variation in 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.

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

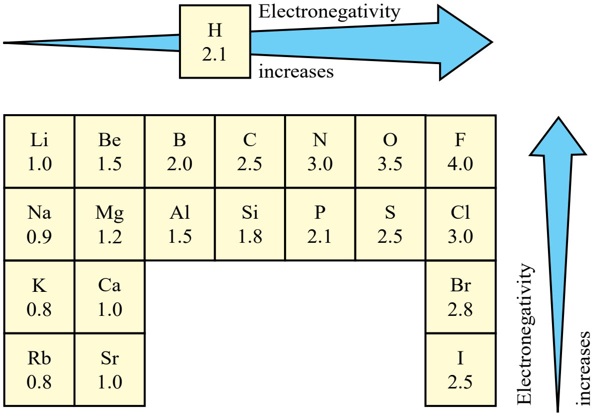
ii) Effective nuclear Charge

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.

1.7.7 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 decreaing size. In the groups, it decreases from top to bottom this is due to the increse 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 1.8.

Normally, **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.



H
2.1

Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0					Br 2.8
Rb 0.8	Sr 1.0					I 2.5

Fig 1.8: Variation of electronegativity in groups and periods

Figure 1.9 provides a summary of all the variation trends in various physical properties of elements in the periodic table.

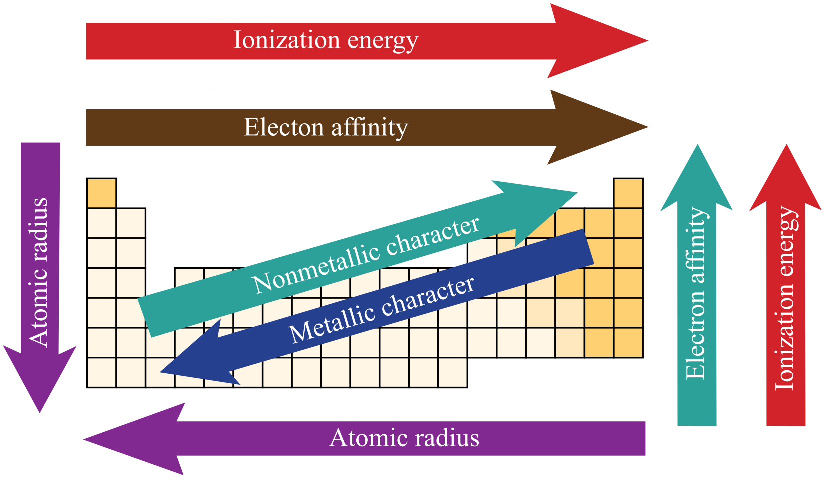


Fig. 1.9: Trends in various physical properties in the periodic table

1.7.8 Variation in Metallic Character

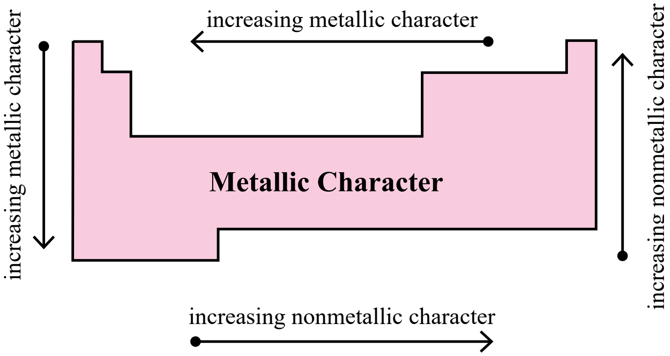


Fig 1.3: General trends for the metallic character of elements

The metallic character of elements is typically their tendency to lose electrons. We find that 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. Therefore, 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. Hence one can conclude that the metallic character of an element largely depends on its valence shell electronic configuration.

Consequently, 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, m.c decrees from left to right. Its metallic character. Thus, metallic character decreases across a period from left to right.

Contrarily 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. Hence Cesium is far more reactive and electropositive than sodium or lithium.

Quick Check 1.3

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

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

1.8 REACTIONS OF Na AND Mg WITH WATER, OXYGEN AND CHLORINE:

1.8.1 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.

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

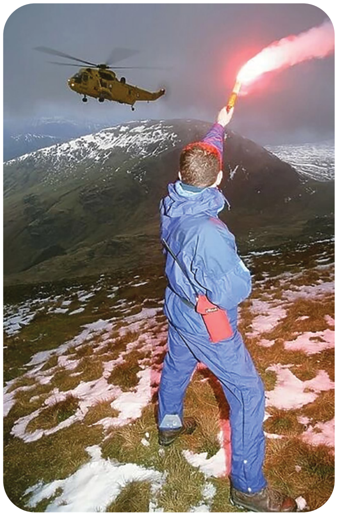
$$Mg_{(s)} + 2H_2O_{(l)} \longrightarrow Mg(OH)_{2(aq)} + H_{2(g)}$$

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

1.8.2 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.

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



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

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.

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

1.8.3 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.

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

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

Quick Check 1.4

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

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

1.9 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.

Similar to oxides, chlorides of group 1, 2 and 3 (e.g., NaCl) are predominately ionic. Chlorides of elements from group 4, 5, 6 and 7 (e.g., PCl_5) are covalent. The covalent character in chlorides increases due to decrease in difference of electronegativity between the halogen and the other atom.

1.9.1 Classification of Oxides

i) Oxides

Oxides are binary compounds formed by the reaction of oxygen with other elements. The classification of oxides is done 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. Group 1 and 2 form basic oxides when react with oxygen. Examples are: Na_2O, CaO, BaO. Group 2 hydroxides solubility increases down the group so alkalinity also increases down the group.

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

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

iii) Amphoteric Oxides

Amphoteric oxides are oxides that can react with both acids and bases. This means they have the ability to behave as either an acid or a base, depending on the conditions. **Aluminum oxide (Al_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.

$$Al_2O_{3(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(s)} + 3H_2O_{(l)}$$

$$Al_2O_{3(s)} + 2NaOH_{(aq)} \longrightarrow Na_2Al_2O_{4(s)} + H_2O_{(l)}$$

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 of acidic oxides in period 3 are: P_2O_3, P_2O_5, SO_3, SO_2

$$P_2O_{3(s)} + \mathbf{H_2}O_{(l)} \longrightarrow H_3PO_{3(aq)}$$

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

Reactions of theses oxides with bases are given below:

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

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

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

1.9.2 Classification of Chlorides

Chlorine forms compounds with other elements known as **chlorides.** These chlorides show characteristic behavior 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,

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

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

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

ii) Acidic Chlorides:

If we move in period 3, from alumium 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 casues a water molecule to lose an H^+ ion, this process is hydrolysis. This turns the solution acidic. The following reaction occurs:

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

Other examples of acidic chlorides are given below.

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

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

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?

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

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

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

1.10 VARIATION IN OXIDATION NUMBER IN OXIDES AND CHLORIDES

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 **(Table 1.2)** 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 sulfur exhibit several oxidation numbers because they can expand their octet by exciting electrons into empty 3d orbitals. For instance, in SO_2, sulfur has an oxidation number of +4 because only four electrons are used for bonding, while in SO_3, sulfur has an oxidation number of +6 because all six electrons are used for bonding.

Table 1.2: 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.

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

EXERCISE

MULTIPLE CHOICE QUESTIONS

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 one is the correct statement among the following?

a) Anionic radius is generally smaller than atomic radius.
b) Cationic radius is generally bigger than atomic radius.
c) Cationic ionic radius is generally smaller than atomic radius.
d) Both anionic and cationic radii are smaller than atomic radius.

V. Which property increases as you go down a group in the periodic table?

a) Atomic radius b) Electron Affinity
c) Electronegativity d) Ionization energy

VI. 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

VII. Which of the following atoms show more than one (variable) oxidation states?

a) Sodium b) Magnesium
c) Aluminum d) Phosphorous

VIII. 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.

IX. What is the oxidation state of sulfur in the sulfate ion (SO_4^{2-}).

a) + 4 b) + 2

c) + 6 d) 0

X. 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.

XI. The atomic radius generally…….. across a period in the periodic table.

a) Increases **b) Decreases**

c) Remains constant **d) First increases then decreases**

XII. Which one of the following elements has the highest ionization energy?

a) Sodium (Na) **b) Magnesium (Mg)**

c) Aluminium (Al) **d) Argon (Ar)**

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

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

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

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

d. What are the factors that affect electronegativity?

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

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

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

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

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

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.

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.

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

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 behavior when dissolved in water.

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.

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

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

Q.6 Describe the factors affecting and periodic trends of ionization energy.

2

ATOMIC STRUCTURE

STUDENT LEARNING OUTCOMES [C-11-A-01 to C-11-A-25]

- 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, sub-shells, 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, sub-shell 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)**

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

1n 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.

$$\sqrt{\text{frequency}}\ (\nu)\ \alpha\ Z$$

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

$$A = Z + N$$

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

$$N = A - Z$$

Let us consider ${}^{27}_{13}Al$,

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:

${}^{27}_{13}Al$ atom loses three electrons to form Al^{3+}, then;

No. of protons = 13

No. of neutrons =14

No of electrons = 13 – 3 = 10

Similarly, ${}^{35}_{17}Cl$ gains an electron to form Cl^{-} ion;

No. of protons = 17

No. of neutrons =18

No of electrons = 17+1 = 18

In case 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 2.1 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.

2.2 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.

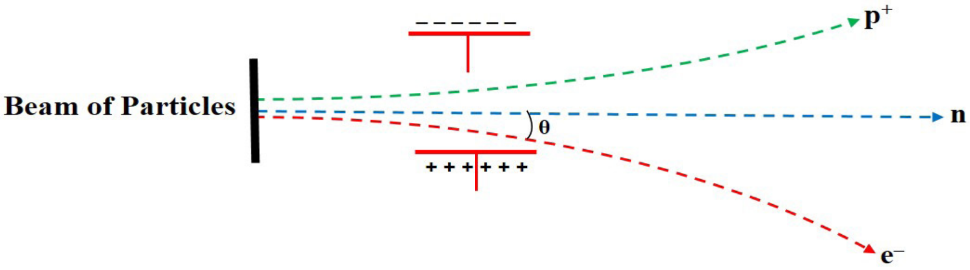


Figure 2.1 Behaviour of proton, electron and neutron in the electric field

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.

2.2.1 Properties of fundamental particles:

The **Table (2.2)** shows the properties of three fundamental particles electron, proton and neutron present in an atom.

Table 2.2 Properties of three fundamental particles

Particle	Charge (coulomb)	Relative charge	Mass (kg)	Mass (amu)
Proton	$+1.6022 \times 10^{-19}$	+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.

$^{39}_{19}\text{K}$, $^{35}_{17}\text{Cl}$, $^{40}_{18}\text{Ar}$

2.3 EXPERIMENTAL EVIDENCES FOR THE ELECTRONIC CONFIGURATION

The modern theory of electronic structure originates 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.

2.4.1 Atomic Spectra

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 2.2 (a).**

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 2.2 (b)**. The wavelengths of the dark lines in the absorption spectrum are exactly the same as those of coloured lines in the emission spectrum.

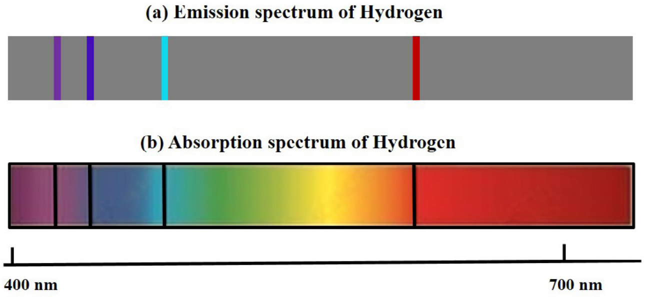


Figure 2.2 (a) atomic emission spectrum of hydrogen **(b)** atomic absorption spectrum of hydrogen

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. Hence, we can say that atomic spectra are the finger prints of the elements. **Figure 2.3** shows the emission spectra of some elements.

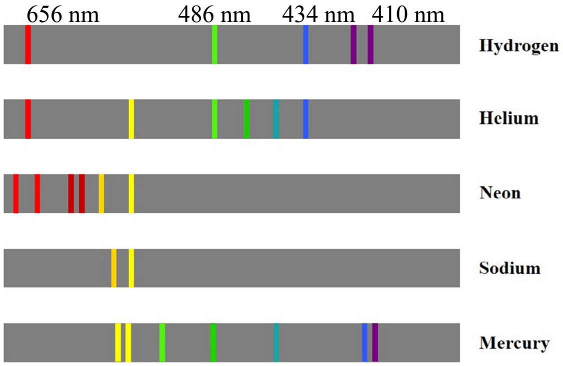


Figure 2.3 Spectral series of various elements as plotted by a spectrometer

2.3.2 Relation between 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 with in 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 element

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.

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

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.

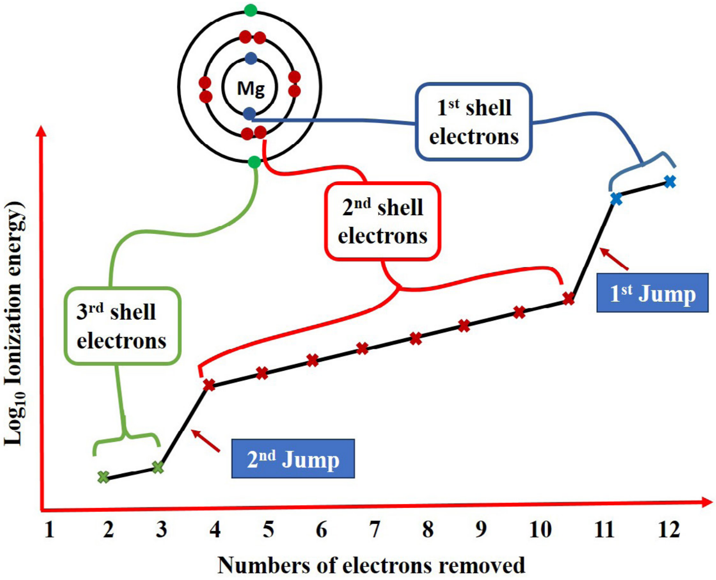


Figure 2.4 A plot of the successive ionization energies of Mg

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 2.4**. 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. But, a 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 Atoms

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 **Figure 2.5** shows a plot for the first 88 elements.

This graph tells us the following:

- All ionization energies are strongly endothermic; it takes energy to separate an electron from an atom.
- As we go down a particular group, for example, 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.
- 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.

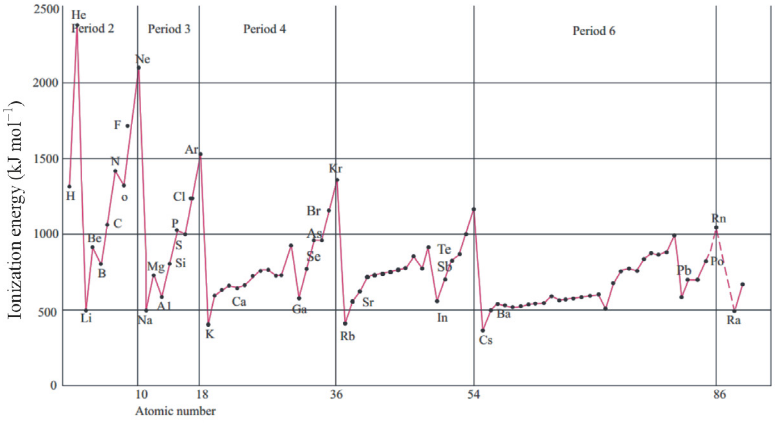


Figure 2.5 A plot of the ionization energies of first 88 elements against atomic number

Quick Check 2.2

a) Write equations that describe:
   - i. the 1st ionisation energy of calcium
   - ii. the 3rd ionisation energy of potassium
   - iii. the 2nd ionisation energy of lithium
   - iv. the 5th ionisation energy of sulfur.

b) For the element aluminium (Z = 13), draw a sketch graph between the log10 of the successive ionisation energies (y-axis) against the number of electrons removed (x-axis).

c) The first ΔH_{i1} and the second ΔH_{i2} ionisation energies (kJ / mol) of a few elements are given in table.

Element	ΔH_{i1}	ΔH_{i2}
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,
   - ii. a reactive non-metal,
   - iii. a noble gas
   - iv. a metal that forms a stable binary halide of the formula AX_2 (X = halogen).

e electron can be found.

2.5 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.

2.5.1 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.

2.5.2 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 ℓ. If n=3 there are, three values of 'ℓ' i.e 0,1 and 2. Similarly, if n=4, there are four values of 'ℓ', i.e. 0, 1, 2 and 3. 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.

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 2.3**.

Table 2.3 Shapes of orbital

Value of ℓ	0	1	2	3
Obital designation	s	p	d	f
shape of orbital	spherical	polar (dumb bell)	cloverleaf (double dumbbell)	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 2.4 Relationship between n, ℓ and subshells

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

2.5.3 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 ($2\ell + 1$) integral values of m as follows:

$-\ell$…………0………..$+\ell$

The values of m indicate the number of orbitals in a subshell. If $\ell = 0$, (s-subshell) there is only one possible value of m, i.e. 0. It means s-subshell has only 1 orbital. If $\ell=1$, (p-subshells) there are three values of m; -1,0 and +1. It means p-subshells has three orbitals.

Did you Know!

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

If $\ell=2$, (d-subshell), there are five values of m, namely, - 2, - 1, 0, + 1 and + 2. It means d-subshells have 5 orbitals.

If $\ell=3$, (f-subshell) there are seven values of m: i.e. -3, -2, -1, 0, +1, +2, +3. It means f-subshells have 7 orbitals.

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 2.5.**

Table 2.5 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 0 -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 2.8** 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 $-\frac{1}{2}$, as in **Figure 2.8.**

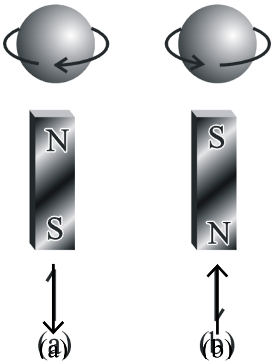


Figure 2.4 (a) clockwise **(b)** counterclockwise spins of an electron.

The 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.

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
   ii. Azimuthal quantum number
   iii. Magnetic quantum number
   iv. Spin quantum number

b) For an electron(s):
   i. If n=2 and $\ell = 1$, how many orientations in space are possible?
   ii. If n=3 and $\ell = 2$, which shell and subshell does the electron belong to?
   iii. If $\ell = 2$, find all possible values of m and maximum number of electrons for m.

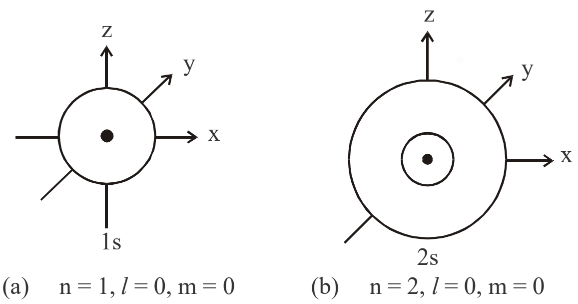
2.6 SHAPES OF ATOMIC ORBITALS

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.

2.6.1 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 2.5 The boundary surface for, (a) 1s (b) 2s.

2.6.2 *p*-orbitals

The distribution of electron density for a 2p orbital is shown in **Figure 2.6**. 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 exes.

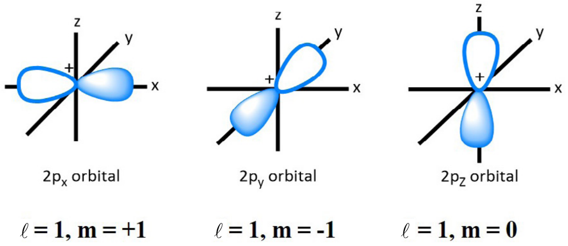


Figure 2.6 Thee 2p orbitals shapes of 2P orbitals

2.6.3 *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 2.7.**

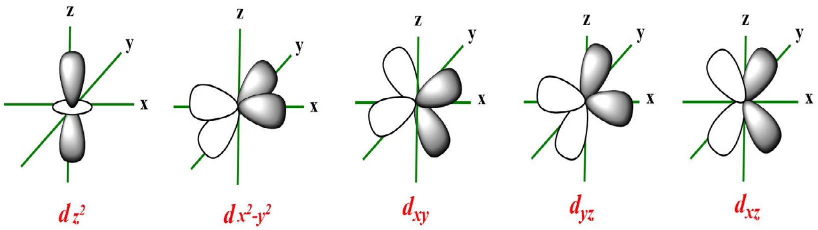


Fig. 2.7 The shapes of the five 3d orbitals

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

2.7 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 '1*s*' subshell and two electrons in the '2*s*' 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 = +½ and downward when s = −½. The orbital diagram of boron ($^{11}_{5}B$) is as follows

$$^{11}_{5}B = \overset{\upharpoonleft\downharpoonright}{1s}\ \overset{\upharpoonleft\downharpoonright}{2s}\ \overset{\upharpoonleft}{2p_x}\ \overset{0}{2p_y}\ \overset{0}{2p_z}$$

2.7.1 Electronic Configuration in Shells

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 (1s orbital)

L shell (n=2): 8 electrons maximum (2s and 2p orbitals)

M shell (n=3): 18 electrons maximum (3s, 3p, and 3d orbitals)

N shell (n=4): 32 electrons maximum (4s, 4p, 4d, and 4f 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)

2.7.2 Distribution of Electrons in sub shells orbitals

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.

Now, question arises that how to arrange the subshells energy wise.

Since, 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*), hence the order of filling subshells with electrons may be obtained from the summation (n + *l*). (n + *l*) values are given in **Table 2.6**.

Table 2.6 (n + ***l***) 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 + ℓ)** value has lower energy and is filled first. For example, 4s orbital has **(n + ℓ)** = 4 + 0 = 4 and 3d orbital has **(n + ℓ)** = 3+2 = 5. Since **(n + ℓ)** value of 4s orbital is lower than that of 3d, hence 4s subshell has lower energy than 3d and 4s will be filled first.

b) In case there are two subshells are having equal (n + ℓ) values, then the subshell with lower 'n' value will be filled first. For example, both 4p and 3d subshells have n+l 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

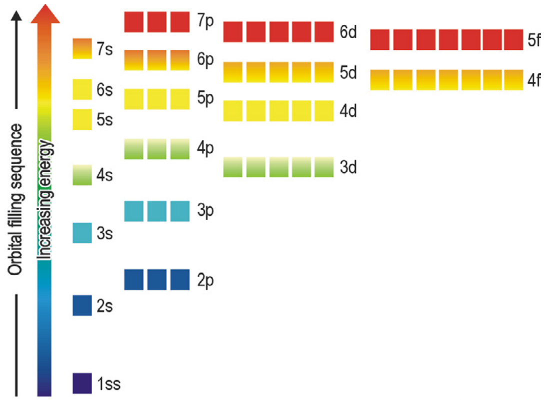


Fig 2.12 The diagram shows the energy of each subshell. Each box on the diagram represents an atomic orbital.

So, the order of filling of various subshells with electrons obtained by this rule is given below **Figure 2.12**.

2.7.2 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".

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

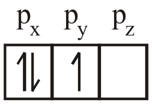
Table 2.6 values of quantum numbers of two electrons in the same orbital

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

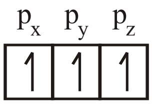
The two electrons having the same values of **'n'**, **'*l*'** and **'m'** can have different values of **'s'**. It means that their spins are in the opposite directions.

2.7.4 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)

Which of the two is correct? The answer is given by Hund's rule, which 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.

2.7.5 Filling the Orbitals

A useful way of representing electronic configurations is a diagram that places electrons in boxes **Figure 2.13**.

- 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.

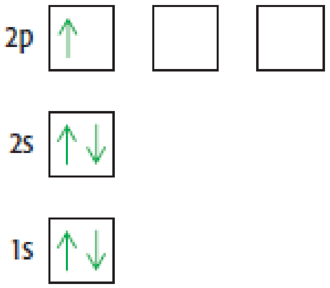


Figure 2.13 The electronic configuration of boron in

Figure 2.14 shows the electronic structures of carbon, nitrogen and oxygen to illustrate these points

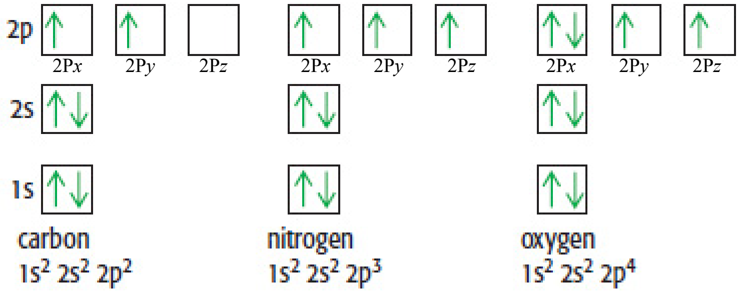


Figure 2.14 When adding electrons to a particular subshell, the electrons are only paired when no more empty orbitals are available.

The electron configurations of some elements of the periodic table in the light of the above-mentioned principles are given in **Table 2.7**

Table 2.7 Electronic configuration of ground states of elements Z = 1 –36.

Z	Element	Configuration	Z	Element	Configuration
1.	H	$1s^1$	19.	K	$1s^22s^22p^63s^23p^64s^1$
2.	He	$1s^2$	20.	Ca	$1s^22s^22p^63s^23p^64s^2$
3.	Li	$1s^22s^1$	21.	Sc	$1s^22s^22p^63s^23p^63d^14s^2$
4.	Be	$1s^22s^2$	22.	Ti	$1s^22s^22p^63s^23p^63d^24s^2$
5.	B	$1s^22s^22p^1$	23.	V	$1s^22s^22p^63s^23p^63d^34s^2$
6.	C	$1s^22s^22p^2$	24.	Cr	$1s^22s^22p^63s^23p^63d^54s^1$
7.	N	$1s^22s^22p^3$	25.	Mn	$1s^22s^22p^63s^23p^63d^54s^2$

8.	O	$1s^22s^22p^4$	26.	Fe	$1s^22s^22p^63s^23p^63d^64s^2$
9.	F	$1s^22s^22p^5$	27.	Co	$1s^22s^22p^63s^23p^63d^74s^2$
10.	Ne	$1s^22s^22p^6$	28.	Ni	$1s^22s^22p^63s^23p^63d^84s^2$
11.	Na	$1s^22s^22p^63s^1$	29.	Cu	$1s^22s^22p^63s^23p^63d^{10}4s^1$
12.	Mg	$1s^22s^22p^63s^2$	30.	Zn	$1s^22s^22p^63s^23p^63d^{10}4s^2$
13.	Al	$1s^22s^22p^63s^23p^1$	31.	Ga	$1s^22s^22p^63s^23p^63d^{10}4s^24p^1$
14.	Si	$1s^22s^22p^63s^23p^2$	32.	Ge	$1s^22s^22p^63s^23p^63d^{10}4s^24p^2$
15.	P	$1s^22s^22p^63s^23p^3$	33.	As	$1s^22s^22p^63s^23p^63d^{10}4s^24p^3$
16.	S	$1s^22s^22p^63s^23p^4$	34.	Se	$1s^22s^22p^63s^23p^63d^{10}4s^24p^4$
17.	Cl	$1s^22s^22p^63s^23p^5$	35.	Br	$1s^22s^22p^63s^23p^63d^{10}4s^24p^5$
18.	Ar	$1s^22s^22p^63s^23p^6$	36.	Kr	$1s^22s^22p^63s^23p^63d^{10}4s^24p^6$

2.8 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.

You can easily write the electron configuration of an element based on its location in the periodic table. The pattern is summarized in **Figure 2.15.** Notice that the elements can be grouped in terms of the type of orbital into which the electrons are placed.

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. 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.

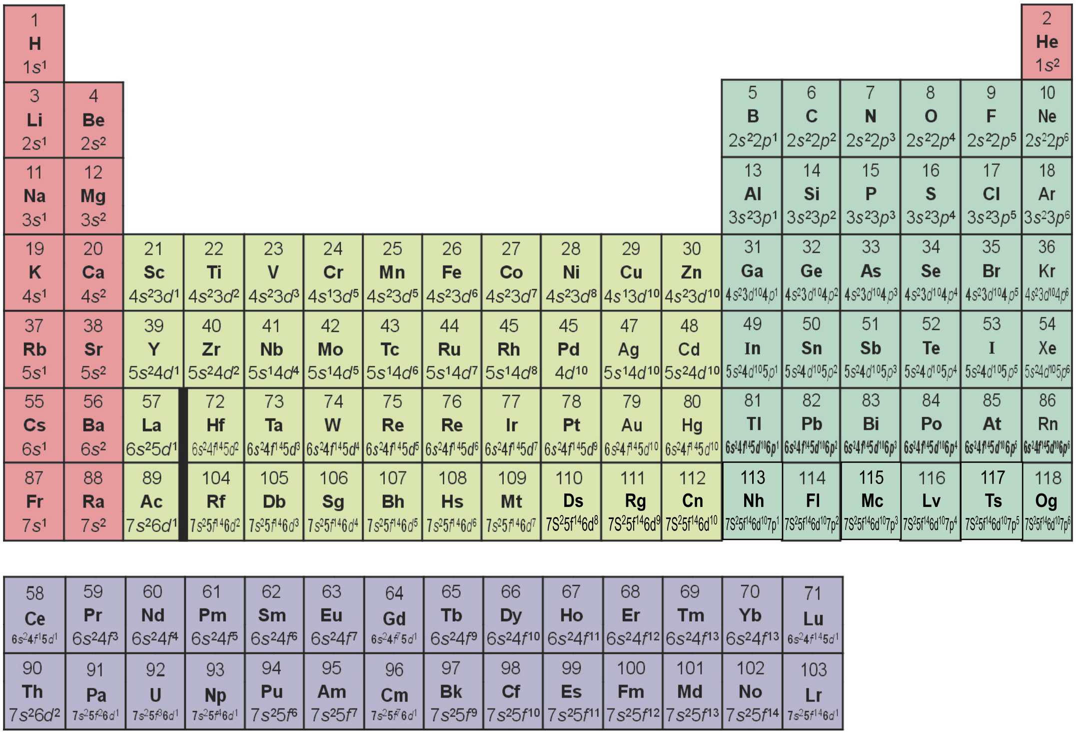
Quick Check 2.5

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.
b) Write the complete electron configuration for antimony (Sb) with atomic number 51.
c) How many unpaired electrons are there in each atom of $_{51}$Sb?

2.8.1 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 2.15 shows a periodic table which include the valence shell configurations included. Note the similarity in electron configuration within any group (column) of elements.



1 **H** $1s^1$																	2 **He** $1s^2$
3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^2 2p^1$	6 **C** $2s^2 2p^2$	7 **N** $2s^2 2p^3$	8 **O** $2s^2 2p^4$	9 **F** $2s^2 2p^5$	10 **Ne** $2s^2 2p^6$
11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^2 3p^1$	14 **Si** $3s^2 3p^2$	15 **P** $3s^2 3p^3$	16 **S** $3s^2 3p^4$	17 **Cl** $3s^2 3p^5$	18 **Ar** $3s^2 3p^6$
19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $4s^2 3d^1$	22 **Ti** $4s^2 3d^2$	23 **V** $4s^2 3d^3$	24 **Cr** $4s^1 3d^5$	25 **Mn** $4s^2 3d^5$	26 **Fe** $4s^2 3d^6$	27 **Co** $4s^2 3d^7$	28 **Ni** $4s^2 3d^8$	29 **Cu** $4s^1 3d^{10}$	30 **Zn** $4s^2 3d^{10}$	31 **Ga** $4s^2 3d^{10} 4p^1$	32 **Ge** $4s^2 3d^{10} 4p^2$	33 **As** $4s^2 3d^{10} 4p^3$	34 **Se** $4s^2 3d^{10} 4p^4$	35 **Br** $4s^2 3d^{10} 4p^5$	36 **Kr** $4s^2 3d^{10} 4p^6$
37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $5s^2 4d^1$	40 **Zr** $5s^2 4d^2$	41 **Nb** $5s^1 4d^4$	42 **Mo** $5s^1 4d^5$	43 **Tc** $5s^1 4d^6$	44 **Ru** $5s^1 4d^7$	45 **Rh** $5s^1 4d^8$	45 **Pd** $4d^{10}$	47 **Ag** $5s^1 4d^{10}$	48 **Cd** $5s^2 4d^{10}$	49 **In** $5s^2 4d^{10} 5p^1$	50 **Sn** $5s^2 4d^{10} 5p^2$	51 **Sb** $5s^2 4d^{10} 5p^3$	52 **Te** $5s^2 4d^{10} 5p^4$	53 **I** $5s^2 4d^{10} 5p^5$	54 **Xe** $5s^2 4d^{10} 5p^6$
55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La** $6s^2 5d^1$	72 **Hf** $6s^2 4f^{14} 5d^2$	73 **Ta** $6s^2 4f^{14} 5d^3$	74 **W** $6s^2 4f^{14} 5d^4$	75 **Re** $6s^2 4f^{14} 5d^5$	76 **Re** $6s^2 4f^{14} 5d^6$	77 **Ir** $6s^2 4f^{14} 5d^7$	78 **Pt** $6s^2 4f^{14} 5d^9$	79 **Au** $6s^2 4f^{14} 5d^{10}$	80 **Hg** $6s^2 4f^{14} 5d^{10}$	81 **Tl** $6s^2 4f^{14} 5d^{10} 6p^1$	82 **Pb** $6s^2 4f^{14} 5d^{10} 6p^2$	83 **Bi** $6s^2 4f^{14} 5d^{10} 6p^3$	84 **Po** $6s^2 4f^{14} 5d^{10} 6p^4$	85 **At** $6s^2 4f^{14} 5d^{10} 6p^5$	86 **Rn** $6s^2 4f^{14} 5d^{10} 6p^6$
87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac** $7s^2 6d^1$	104 **Rf** $7s^2 5f^{14} 6d^2$	105 **Db** $7s^2 5f^{14} 6d^3$	106 **Sg** $7s^2 5f^{14} 6d^4$	107 **Bh** $7s^2 5f^{14} 6d^5$	108 **Hs** $7s^2 5f^{14} 6d^6$	109 **Mt** $7s^2 5f^{14} 6d^7$	110 **Ds** $7S^2 5f^{14} 6d^8$	111 **Rg** $7S^2 5f^{14} 6d^9$	112 **Cn** $7S^2 5f^{14} 6d^{10}$	113 **Nh** $7S^2 5f^{14} 6d^{10} 7p^1$	114 **Fl** $7S^2 5f^{14} 6d^{10} 7p^2$	115 **Mc** $7S^2 5f^{14} 6d^{10} 7p^3$	116 **Lv** $7S^2 5f^{14} 6d^{10} 7p^4$	117 **Ts** $7S^2 5f^{14} 6d^{10} 7p^5$	118 **Og** $7S^2 5f^{14} 6d^{10} 7p^6$

58 **Ce** $6s^2 4f^1 5d^1$	59 **Pr** $6s^2 4f^3$	60 **Nd** $6s^2 4f^4$	61 **Pm** $6s^2 4f^5$	62 **Sm** $6s^2 4f^6$	63 **Eu** $6s^2 4f^7$	64 **Gd** $6s^2 4f^7 5d^1$	65 **Tb** $6s^2 4f^9$	66 **Dy** $6s^2 4f^{10}$	67 **Ho** $6s^2 4f^{11}$	68 **Er** $6s^2 4f^{12}$	69 **Tm** $6s^2 4f^{13}$	70 **Yb** $6s^2 4f^{13}$	71 **Lu** $6s^2 4f^{14} 5d^1$
90 **Th** $7s^2 6d^2$	91 **Pa** $7s^2 5f^2 6d^1$	92 **U** $7s^2 5f^3 6d^1$	93 **Np** $7s^2 5f^4 6d^1$	94 **Pu** $7s^2 5f^6$	95 **Am** $7s^2 5f^7$	96 **Cm** $7s^2 5f^7 6d^1$	97 **Bk** $7s^2 5f^9$	98 **Cf** $7s^2 5f^{10}$	99 **Es** $7s^2 5f^{11}$	100 **Fm** $7s^2 5f^{12}$	101 **Md** $7s^2 5f^{13}$	102 **No** $7s^2 5f^{14}$	103 **Lr** $7s^2 5f^{14} 6d^1$

Figure 2.15 The electronic distribution of elements of modern periodic table

2.8.2 Classification of elements of periodic table

The main-group or representative elements all have valence-shell configurations $ns^a np^b$. 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 2.16**. This shows the blocks of elements.

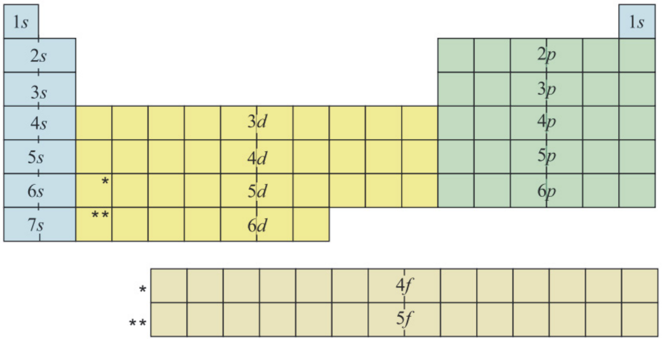


Figure 2.16 Modern periodic table showing s, p, d and f-block elements.

Figure 2.16 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 '1*s*' subshell is being filled. In the second period, we have '2*s*'; then staying in the same period but jumping across, we have '2*p*'. In the third period, we have '3*s*' and '3*p*'; in the fourth period, '4*s*', '3*d*' and then '4*p*'. 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?
   ii. Which group does it belong to?
   iii. Which period does it belong to?
   iv. Identify this element.

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?

2.9 ELECTRONIC CONFIGURATION OF IONS AND FREE RADICALS

2.9.1 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 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 4s subshell fills before the 3d subshell. But when atoms of a d-block element lose electrons to form ions, the 4s 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: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

2.9.2 Free radicals

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

An example of a simple free radical is free chlorine atom $:\overset{\bullet}{\underset{\bullet\bullet}{C\ell}}:$. 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. $Al^\bullet$ ($Z = 13$) **ii.** O^{2-} ($Z = 8$) **iii.** Fe3+ ($Z = 26$) **iv.** Cu^{2+} ($Z = 29$) **v.** $Cu^\bullet$ ($Z = 29$)

2.10 ELECTRONIC CONFIGURATION AND THE FORMATION OF SEMICONDUCTORS

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

Example of the elements that can act as semiconductors are silicon, germanium and arsenic etc. The formation of semiconductors is possible because of a unique electronic configuration of these elements. Let us 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.

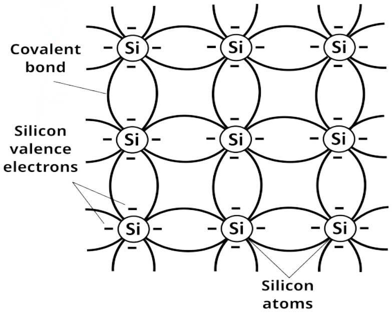


Figure 2.17 A crystal of pure silicon

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.

2.11.1 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 1.15**. 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.

2.11.2 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 1.15**. The result is an N-type semiconductor that can conduct electricity when connected to an external source.

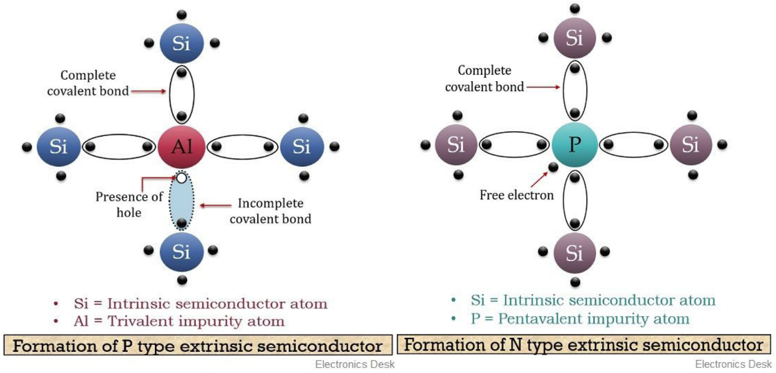


Figure 2.18 Dpoing and the formation of P-type and N-type semiconductor

EXERCISE

MULTIPLE CHOICE QUESTIONS

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) $n = 2, l = 1$
b) $n = 1, l = 2$
c) $n = 1, l = 0$
d) $n = 2, l = 0$

IV. An electron having the set of values: $n = 4, l = 0, m = 0$ and $s = +1/2$ lies in:

a) 2s
b) 3s
c) 4s
d) 5s

V. The quantum number values for the fourth electron of ${}_4^9Be$ 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. Which of the following species is predicted to have the highest bond order?

a) N_2	b) O_2
c) F_2	d) Ne_2

XI. 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

XII. Which of the following molecular geometries has bond angles of approximately 120°?

a) Tetrahedral	b) Trigonal planar
c) Bent (V-shaped)	d) Trigonal pyramidal

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.

b. Size of Mg is bigger than Al, but ionization energy of Mg is more than that of Al. Why?

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

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

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

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

g. (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.

h. 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.

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

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

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

   ii. How many electrons occupy 4d atomic orbitals?

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

iv. How many electrons have spin “up” ($s = -½$)?

k. 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?

l. 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.

m. (a) State the general order of filling orbitals up to the 4p subshell.

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

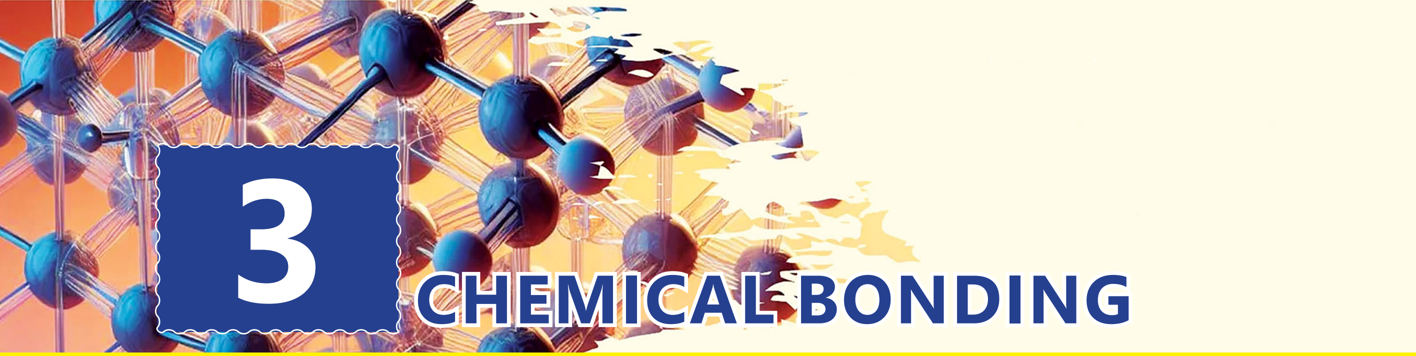
n. Draw the orbital box diagram for the valence electrons of a phosphorus atom (atomic number 15), ensuring that your diagram adheres to Hund’s rule and the Pauli Exclusion Principle.

DESCRIPTIVE QUESTIONS

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

Q4. Draw the shapes of s, p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

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?



3

CHEMICAL BONDING

STUDENT LEARNING OUTCOMES [C-11-A-26 to C-11-A-46]

- 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. (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)

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 inter-molecular forces, i.e. van der Waals forces. However, being weak enough, van der Waals forces are usually not termed as pure chemical bonds. In this chapter, 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

3.1 LEWIS CONCEPT 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.

3.1.1 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 electron 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 1and 2 metals and groups 16 and 17 elements.

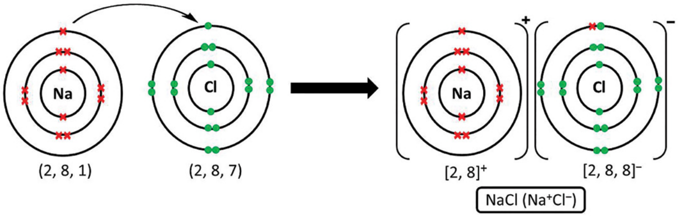


Figure 3.1: Ionic bond formation between Na and Cl

3.1.2 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. 3.2)**. A covalent bond may be non-polar or 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 are H–Cl, H-Br, H_2O, etc.

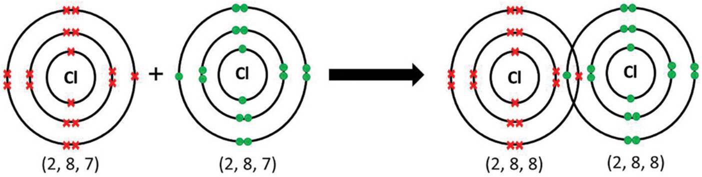


Figure 3.2: formation of a covalent bond between two Cl atoms

3.13 Dative bond (Coordinate Covalent Bond)

A **dative bond** is formed between two atoms when the shared pair of electrons is donated by one of the bonding atoms. 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 3.3(a)).

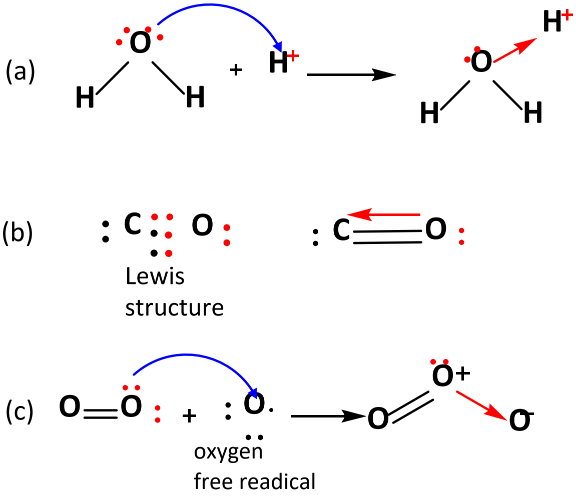


Figure 3.3: Dative bond formation (a) oxonium (hydronium) ion, (b) ozone molecule (c) carbon monoxide

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 a 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 3.3(b). The structure of ozone molecule is presented in Figure 3.3(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.

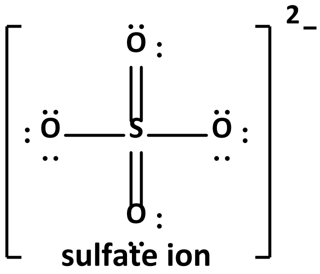
Quick Check 3.1

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

b) How many electrons are there in the valence shell of B in BF3? Does it have the ability to accept a lone pair of electrons?

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

3.1.4 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^{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**. Some prominent examples are SO_4^{2-}, ClO_4^-, PO_4^{3-}.

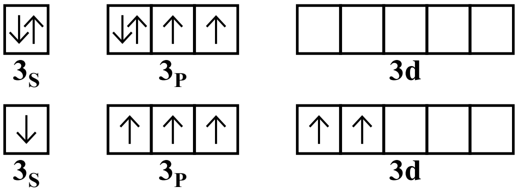
From the Lewis structures of SO_4^{2-}, we can calculate the number of electrons around the central S atom.

The number of electrons in the valence shell of S atom can be calculated as:

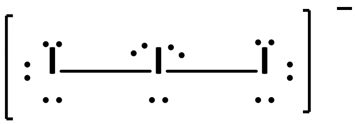
No of valence electrons = 2 × (double bond electrons) + 2 × (single bond electrons)

$$= 2\,(4) + 2(2) = 12$$

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 3p pair. It explains not only the variable oxidation states of S, but also the possibility of accepting extra electrons in its d orbital.



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 ion 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.

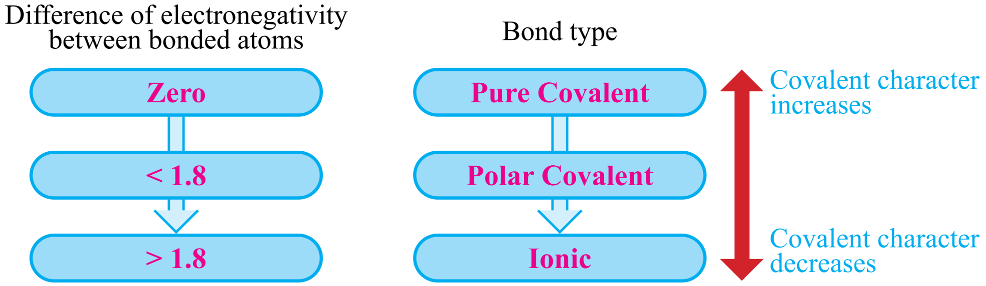
Quick Check 3.2

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

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

3.2 ELECTRONEGATIVITY AND THE TYPE OF BOND

The concept of electronegativity has been discussed in detail in chapter 1. Here we will discuss 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. 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. 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 (nonpolar), 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.

HF, KI, CaF_2, ICl, Br_2

Dipole Moment and Polarity of Molecules

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. 3.5**. Dipole moment is measured in Debye unit (D). Higher dipole moment indicates high polarity in a molecule.

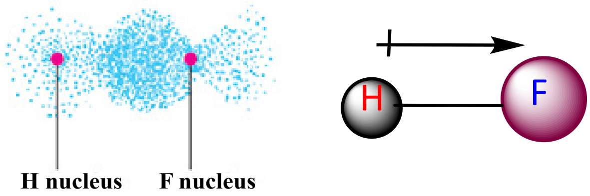
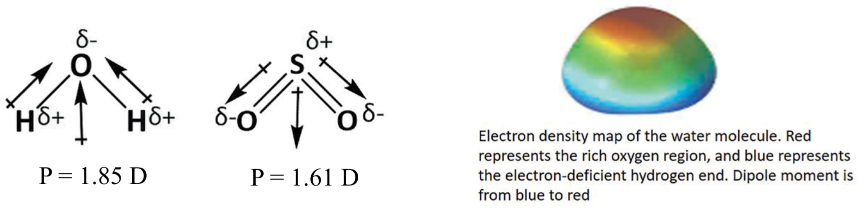


Figure 3.5: Electron density in HF is higher near the F atom and the dipole moment is directed from H to F

For compounds having more than two atoms, the dipole moment depends on the structure of the molecule. 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. 3.6**. 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. In contrast, SO_2 has a dipole moment of 1.61 D and in opposite direction to that in water. 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.



Electron density map of the water molecule. Red represents the rich oxygen region, and blue represents the electron-deficient hydrogen end. Dipole moment is from blue to red

Figure 3.6: Vector addition of individual bond moments in angular H_2O and SO_2 molecules

However, some molecules have zero dipole moments as the symmetry in their structures causes the cancellation of the individual bond moments. For example, $BeCl_2$ 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. Similarly, 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 CCl4 molecule is perfectly tetrahedral. Similarly, BF3 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.

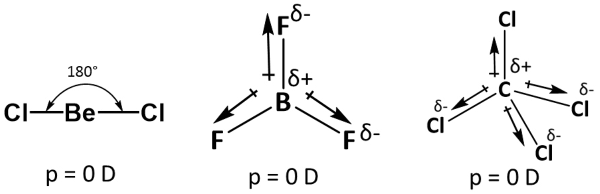


Figure 3.7: The individual bond moments in symmetrical molecules; $BeCl_2$, BF_3 and CH_4 are cancelled out to give zero net dipole moment.

Quick Check 3.4

a) Can you explain why CO has a dipole moment but CO_2 does not have any?

b) Do you think that individual bonds in CCl_4 are polar? Explain in terms of the electronegativity difference. What about the polarity of overall CCL_4 molecule?

c) Are these molecules polar or non-polar? Briefly give reasons. HF, CH_2Cl_2, O_2, H_2S

3.3.2 VALENCE SHELL ELECTRON PAIR REPULSION MODEL (VSEPR)

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 -bond pair (bp-bp)

An electron pair shared by two nuclei occupies less space thank 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.

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 (3.1) gives the possible shapes of different types of molecules having varying numbers of bond and lone pairs.

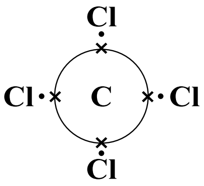
Table 3.1: Geometries and shapes of different systems of covalently bonded compounds

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, OF_2
5	0	Trigonal	Trigonal bipyramidal	120°, 90°	PCl_5, I_3^-
6	0	octahedral	octahedral	90°	SF_6

Steps to Determine the shapes of molecules.

The following steps are followed to predict the shape of a molecule.

- 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.
- 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.
- 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.



- Finally, the actual shape of the molecule is determined excluding the lone pairs (if any).

AB_2 **type Molecules** (Linear geometry)

In such molecules, two electrons pairs around the central atom are arranged at an angle of 180º to minimize repulsions between them. Thus, they form a linear geometry as shown in **Figure 3.9**. $BeCl_2$ molecule is of AB_2 type with Be as the central atom and two bond pairs around it, but no lone pair. .

Figure 3.9: Linear shape of the $BeCl_2$ molecule

AB_3 type (Trigonal planar geometry)

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. For example, BF_3 molecule has a trigonal planar shape with each F-B-F bond angle of 120° **Figure 3.10**. The similar geometries are expected in the hydrides of group 3 (III-A), i.e. AlH_3, GaH_3, BH_3, etc.

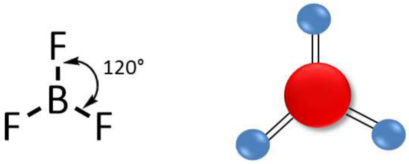


Figure 3.10: BF_3 is an AB_3 system having triangular planar geometry

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 3.11** 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.

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 3.12**.

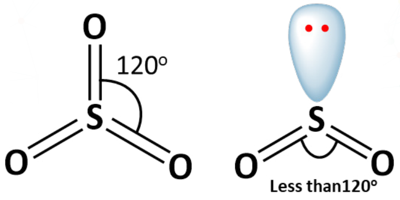


Figure 3.12: Shapes of multiply bonded SO_2 and SO_3

AB_4 Type (Tetrahedral geometry)

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°. For instance, each of the four valence electrons of carbon pair up with the sole 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 following **Fig 3.13** 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°. On the same grounds, SiH_4, GeH_4, CCl_4 possess the similar shape.

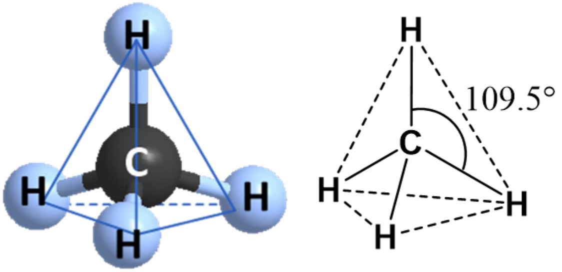


Figure 3.13: Regular tetrahedral shape of the CH_4 molecule

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.

In the ammonia molecule (NH_3), there are three atoms attached to the nitrogen atom having one lone pair. Due to a lone pairs the ideal angel 109.5° is reduce to 107° as in **Figure 3.14.** 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. Take the example of NF_3, which contains three highly electronegative F atoms bonded to the N atom. The bond angles are further compressed to 102.5°. 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.

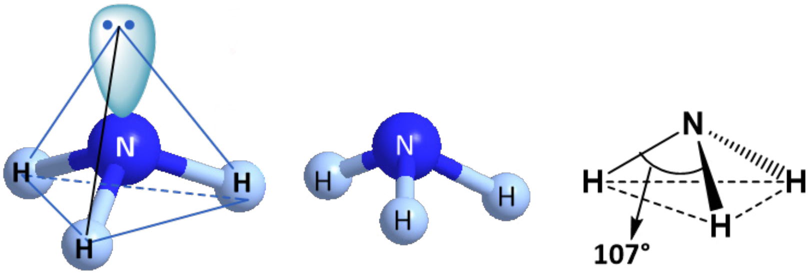
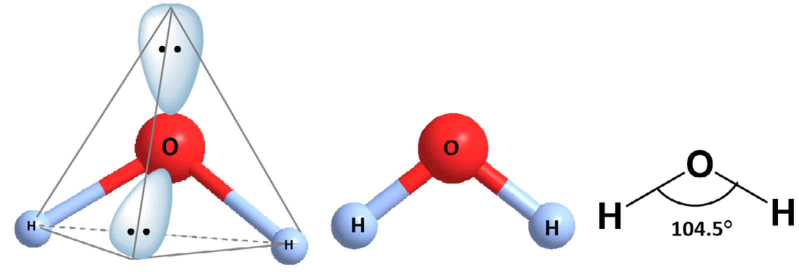


Figure 3.14: Distorted geometry and pyramidal shape of the NH_3 molecule

Experiments reveal 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 3.15**.

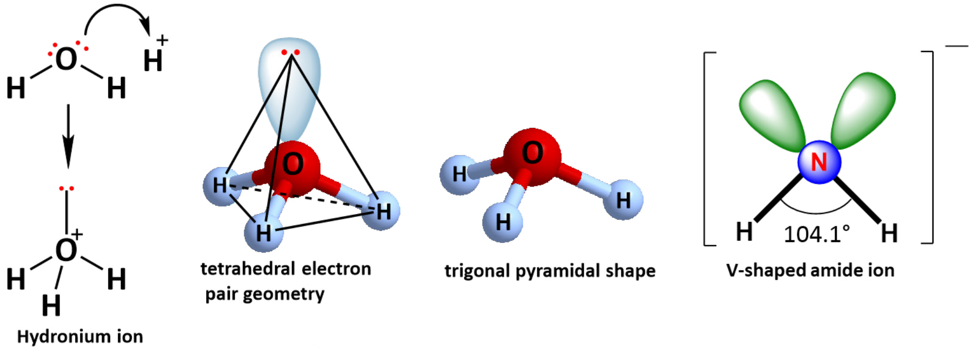


Tetrahedral geometry including lone pairs

Angular shape of water molecule excluding lone pairs

Figure 3.15: Water molecule has two lone pairs and is v-shaped with suppressed bond angle

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. 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 3.16).**



Hydronium ion

tetrahedral electron pair geometry

trigonal pyramidal shape

V-shaped amide ion

Figure 3.16: Shapes of hydronium (H_3O^+) and amide ions (NH_2^-)

Quick Check 3.5

a) Calculate the number of bond pairs and lone pairs in SiH_4, H_2Se, and PH_3.

b) Predict the shapes and angles in SiH_4, H_2Se, and PH_3.

c) Predict how the bond angle in H_2S would be different from that in H_2O.

AB_5 type (Trigonal Bipyramid Geometry)

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 3.17**. The angles within the plane are 120° and that between the axial atom and a planar atom is 90°.

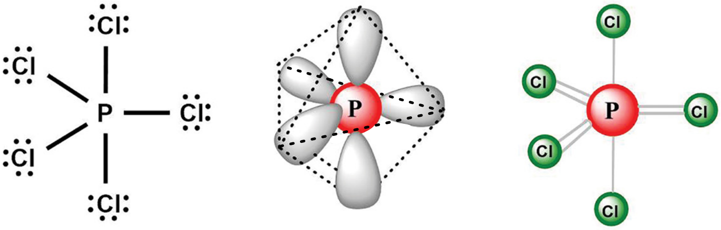


Figure 3.17 Lewis structure and shape of PCl_5 molecule

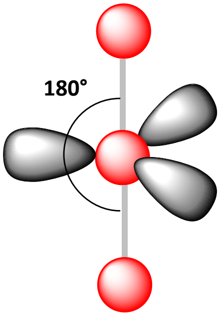


Figure 3.18: Shape of tri-iodide ion ([I_3])

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. 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 3.18.**

AB_6 type molecules (Octahedral Geometry)

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°. The Lewis structure of SF_6 is given in **Figure 3.19**, it shows that this is an AB_6 type molecule.

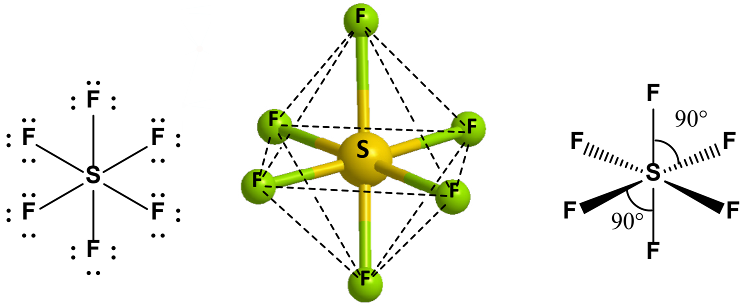


Figure 3.19: Lewis structure and octahedral shape of SF_6 with each angle of 90°

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°.

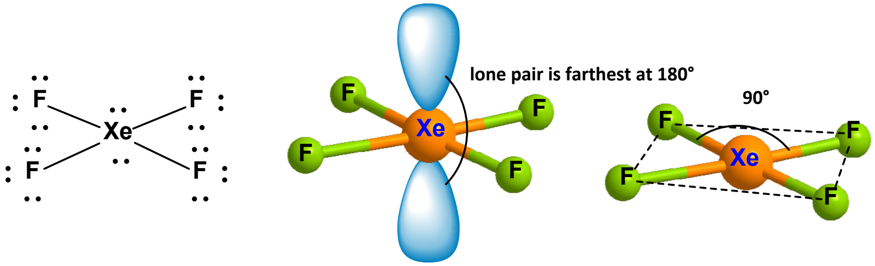
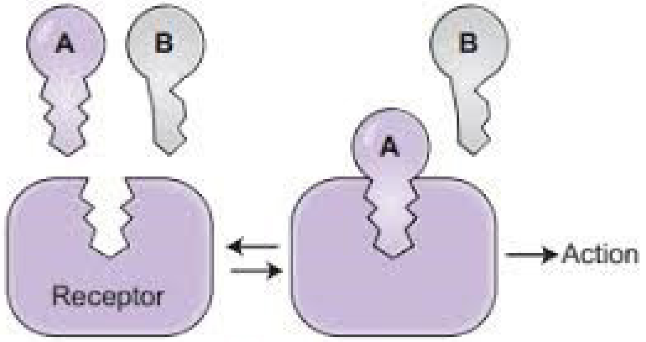


Figure 3.20: Lewis structure and square planar shape of XeF_4

Quick Check 3.6

Draw the Lewis structures for IF_3 and IF_5 and predict their geometry with reference to the VSEPR model.

3.3.3. Applications of VSEPR Model in Drug Designing



Drug **A** binds to receptor
Drug **B** cannot bind to receptor

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. 3.21 . Therefore, the binding is successful to block COX, which is a cause of the pain in the body.

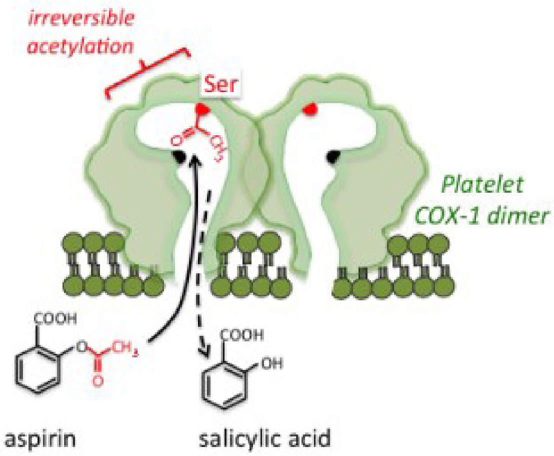


Figure 3.21: An interaction of Aspirin with COX (Published after permission from Tulane University Press)

3.4 VALENCE BOND THEORY (VBT)

The VSEPR model predicts and explains the shapes of molecules but does not give reasons for the formation of bonds. 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. 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.

3.4.1 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.

s-s Overlap

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 3.22.**

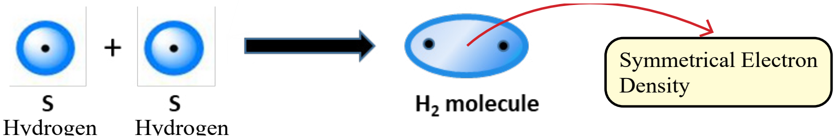


Figure 3.22: Overlap between s orbitals of two hydrogen atoms to form the H_2 molecule

s-p Overlap

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 half-filled p orbital of chlorine as shown in Figure 3.23. The electron density is higher close to the Cl atom due to its higher electronegativity value. This is why HCl is a polar molecule.

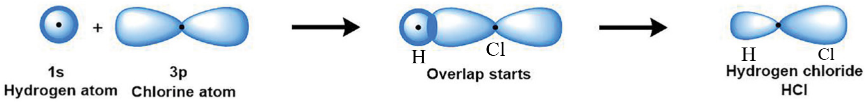


Fig. 3.23: Formation of σ bond by s-p overlap

p – p Overlap

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.

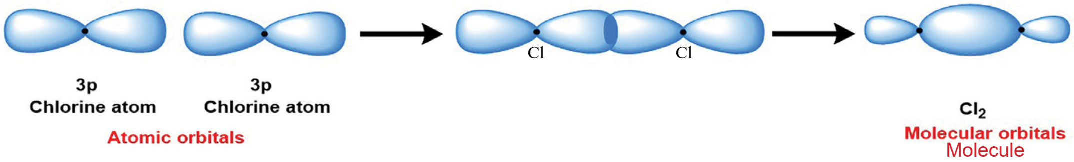


Figure 3.24: Overlap of p and p orbitals to form Cl_2 molecule according to VBT

The H_2S molecule is a non-linear molecule which is formed by the combination of one sulfur and two hydrogen atoms. The two 3p (say $3p_y$ and $3p_z$) orbitals of sulfur 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. 3.25.**

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.

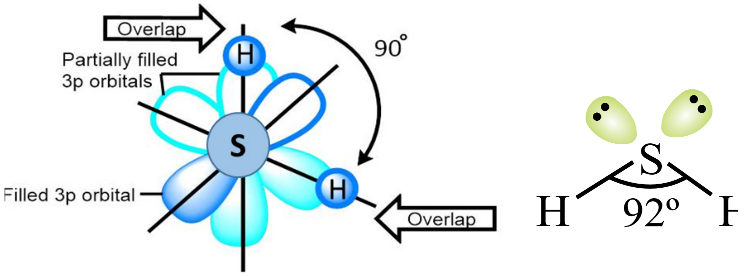


Fig. 3.25: The formation of H_2S molecule by H and S orbitals overlap

Formation of π bond:

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 3.26**. This results in the formation of **π** bond. the oxygen atoms are doubly bonded through σ and **π bonds**.

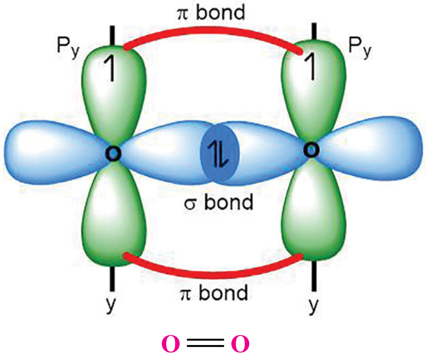


Figure 3.26: Formation of double bond (σ and π) between oxygen atoms

Quick Check 3.7

a) Draw the orbital structures of H_2O and N_2 molecules.
b) Draw the orbital overlap to show the formation of F_2 and HF molecules

3.5 ATOMIC ORBITAL HYBRIDIZATION AND SHAPES OF MOLECULES

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

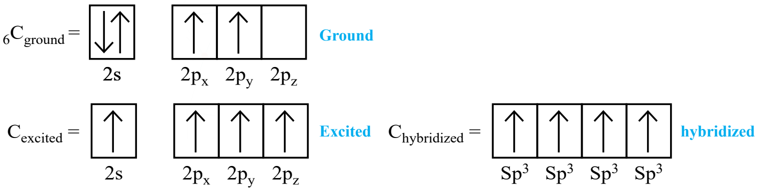
- Hybridization is a process of mixing of orbitals in a single atom (or ion).
- Only orbitals of comparable (relatively close) energies can be mixed to form hybrid orbitals.
- The number of mixing orbitals is always equal to the number of the resulting hybrid orbitals.

3.5.1 Types of Hybridization

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. These hybrid orbitals are arranged in the tetrahedral geometry as shown in the example of CH_4 as in **Fig. 3.27.**

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 3.27** shows the outermost four atomic orbitals of carbon mix up to give four hybrid orbitals of same energy and same shape.

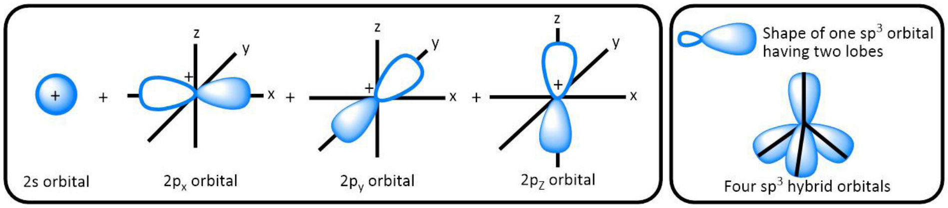


Figure 3.27: Formation of sp_3 hybrid orbitals of C in methane

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.

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.

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°.

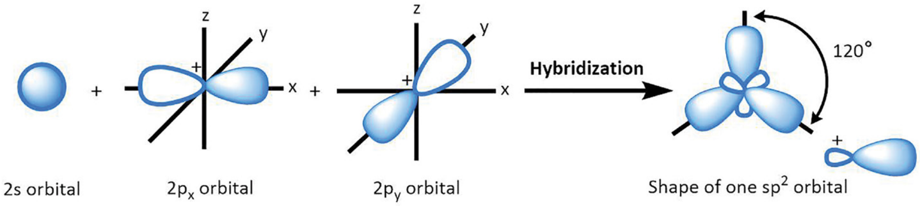
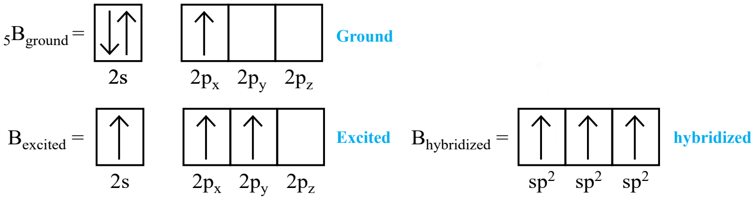


Figure 3.29: Formation of sp^2 hybrid orbitals from atomic orbitals

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.

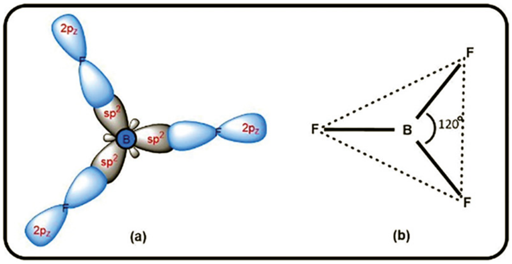
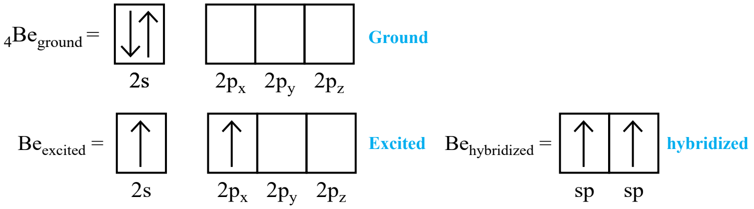


Figure 3.30: Formation of BF_3 molecule through sp^2-p overlap

sp Hybridization

In sp hybridization, one s (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 180º. 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. 3.32**. 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.

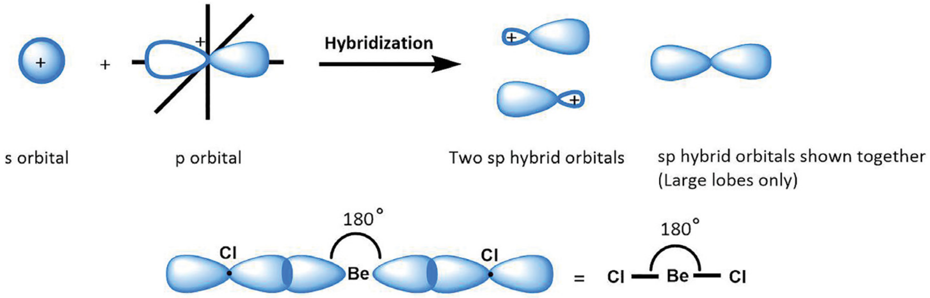


Figure 3.32: Mixing of s and p orbitals to give two hybrid sp orbitals and the formation of $BeCl_2$

3.6 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.
- 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 3.34**.

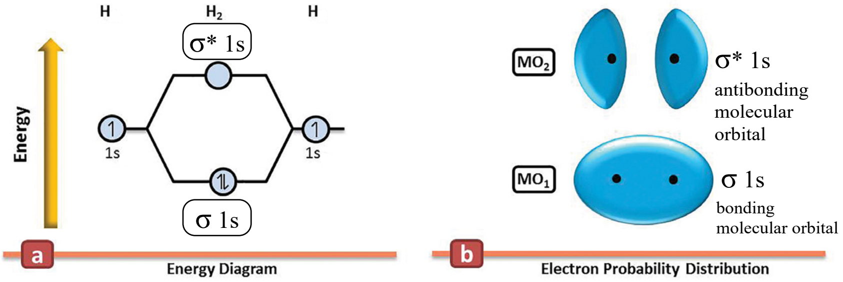


Figure 3.34: Formation of bonding and anti-bonding orbitals for the H_2 molecule

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 3.35**. This combination of atomic orbitals gives rise to σ (2px) bonding and σ* (2px) 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 3.35**. 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

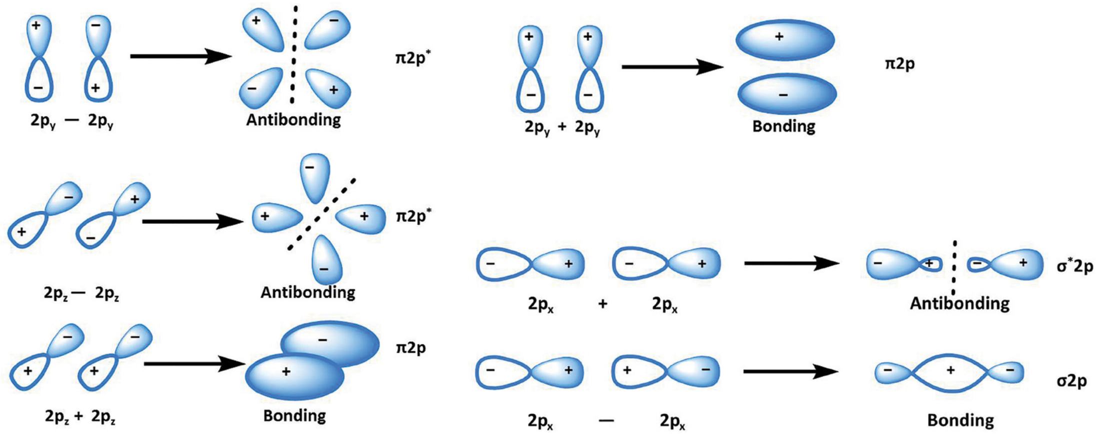


Figure 3.35: Formation of **δ and** π MOs from p_x, p_y and p_z orbitals

3.6.1 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 (δ1s) and anti-bonding (δ*1s) orbitals as shown in **Figure 3.36**. Out of four electrons, two enter the bonding molecular orbital δ (ls) and the remaining two occupy the antibonding δ*(1s) molecular orbital. But on calculation we discover that the bond order for He_2 is zero. Hence, He_2 molecule is not formed.

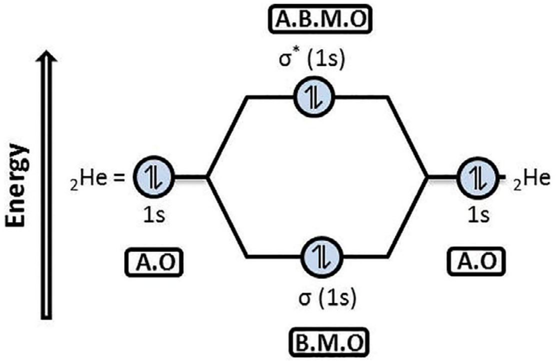


Figure 3.36: Molecular orbital diagram of He_2 molecule

$$\text{Bond order of } He_2 = \frac{2-2}{2} = \mathbf{0}$$

ii) Nitrogen (N_2)

Electronic configuration of N is,

$_7$**N:** $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

The molecular orbital diagram of N_2 based on this electron configuration is shown in the figure below (**Figure. 3.37**). The valence shell 2s on both N atoms give σ2s and σ* 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:

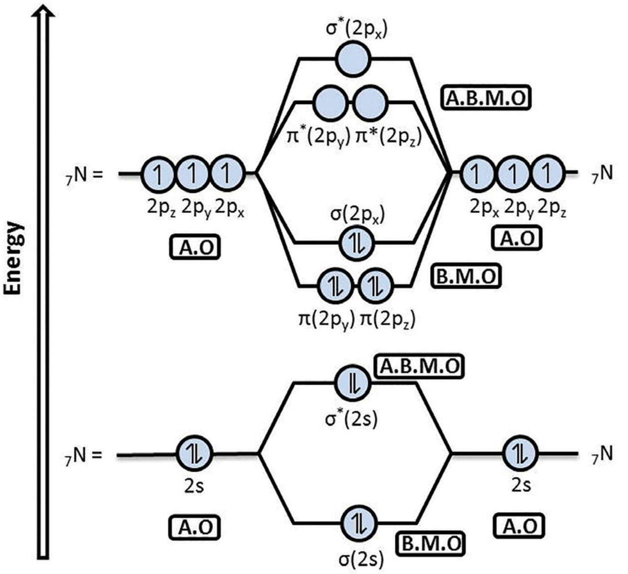


Fig 3.37: Molecular orbital diagram of N_2 molecule

$$\text{Bond order of } N_2 = \frac{6-0}{2} = 3$$

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.

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 $2(\frac{6-2}{2})$, 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.

Liquid oxygen is attracted and gets suspended between the poles of a strong magnet

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.

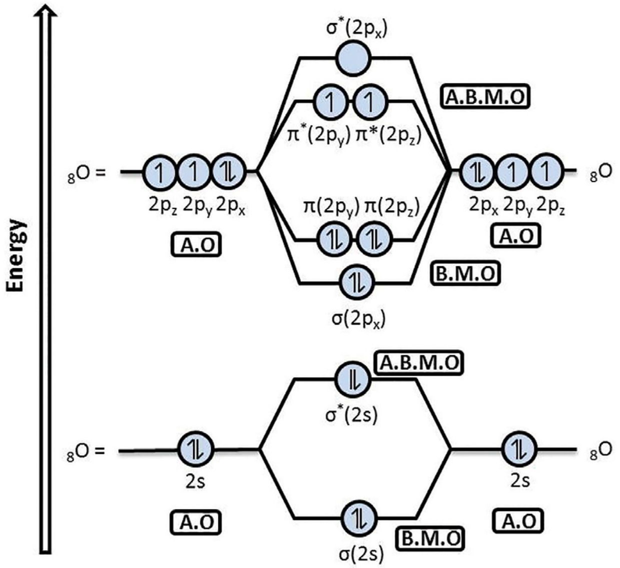


Figure 3.38: Molecular orbital diagram of O_2 molecule

3.7 INTERMOLECULAR FORCES

Intermolecular forces are also considered as 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

The detailed discussion on these forces will be made in the chapter on states and phases of matter

3.9 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.

- Electronegativity difference of bonded atoms
- Size of atoms.

The bond energies/enthalpies of some bonds are presented in Table 3.2.

Table 3.2 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	$C\equiv C$	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	$N\equiv N$	941
C-H	413	N-O	201	Si-Si	340	$C\equiv N$	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

$$C \equiv C > C=C > C-C$$

Bond length is the distance between the nuclei of two atoms forming a covalent bond. The bond lengths are experimentally determined by physical techniques, such as electron diffraction, X-ray diffraction, or spectral studies. The bond length of a bond is governed by many factors including electronegativity, size, and the nature of the covalent bond (single, double, or triple). Some selected bond lengths are given in **Table 3.3**.

Table 3.3 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
$C\equiv C$	120	C-I	214
C=O	122	B-F	130
Si-H	146	B-Cl	175

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=117 pm and F=64 pm) 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.

Quick Check 3.10

- HI is a stronger acid and a robust reducing agent, whereas HF is a weaker acid. Explain.
- Acetylene ($HC\equiv CH$) is more stable than ethene ($HC=CH$). Can you explain why?

3.10 A COMPARISON AMONG IONIC, COVALENT, METALLIC BONDS AND INTERMOLECULAR FORCES

Chemical bonds, i.e. ionic, covalent, and metallic bond are usually termed as true chemical bonds, as they affect the chemical properties of a substance. This is because of certain reasons. Firstly, 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. The distinctive feature of the chemical bonds and intermolecular forces is their bond strength. The strength of a force is measured by the bond energy. **Table 3.4** provides a comparison among different chemical bonds and intermolecular forces.

Table 3.4 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^{-}) is highest, followed by covalent bond (O-H = 464 kJ mol^{-}), and average hydrogen bond energy (20-25 kJ mol^{-}). 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^{-}) and London dispersion forces (1-20 kJ mol^{-}) 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^{-}. A satisfactory argument for the low strength of metallic bond is extensive delocalization of electrons within the metallic crystal.

EXERCISE

MULTIPLE CHOICE QUESTIONS

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) the ionization energy of A is high and electron affinity of B is low.

b) the 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) $CHCl_3$

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 ICl_3 according to the VSEPR model is:

a) Tetrahedral b) Trigonal planar

c) Trigonal bipyramidal d) T-shape

VII. Which of the following shows incorrect bond polarity?

a) $H^{\delta+}F^{\delta-}$ b) $Br^{\delta+}Br^{\delta-}$

c) $Cl^{\delta+}O^{\delta-}$ d) $C^{\delta+}O^{\delta-}$

VIII. Which of the following molecules has a dipole moment?

a) CO_2 b) CS_2

c) SO_2 d) CCl_4

IX. How many electrons are present in the valence shell of P in PO_4^{3-}?

a) 8 b) 10

c) 12 d) 14

X. 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

XI. 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

XII. Which type of hybridization of C occurs in CO_2?

a) sp^3 b) sp^2

c) sp d) dsp^2

XIII. 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

XIV. Which of the following species contains a dative bond?

a) CH_4 b) NaCl

c) NH_4^+ d) O_2

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Define the following:

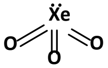
(i) Dipole (ii) Bond order (iii) Permanent dipole- permanent dipole force

(iv) London dispersion force

b. Draw the Lewis (electron dot) structures for the following species:

(i) HCN (ii) NCl_3 (iii) CO (iv) O_3 (v) NO_2

c. Xenon ist a noble gas (group 18); xenon trioxide has the following structure:

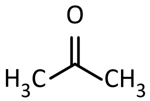


i. By counting electron pairs around the central atom, explain why xenon trioxide has this shape.

ii Draw a structure of xenon trioxide showing partial charges on the atoms and the direction of the dipole in the molecule.

d. Explain the difference between the formation of σ and π bonds.

e. The structure of propanone (acetone) is:



i. Show how the central carbon atom forms σ and π bonds through hybridization.

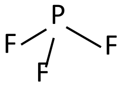
ii. Can propanone make a hydrogen bond with water when both are intermixed?

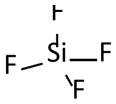
f. Predict the shapes of sulfate ($[SO_4]^{2-}$, borate ($[BH_4]^-$) and tri-iodide ions ($[I_3]^-$) according to the VSEPR model.

g. Sketch the molecular orbital pictures of π(2p) and π*(2p).

h. Sketch the hybrid orbitals and bond formation in PCl_3, $SiCl_4$, and NH_4^+.

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.





j. Draw the orbital structures of the CO_2 molecule in terms of VBT.

k. Draw the Lewis structures and tell whether these ions involve expanded octets?

i) ClO_4^- ii) ICl_4^- iii) NH_4^+ iv) I_3^-

l. The bond between K and Cl is ionic but that between Si and Cl is polar covalent. Explain why.

m. SO_2 is a polar molecule but SO_3 not. Justify.

n. Which of O_2^{2+}, and O_2^{2-} would be paramagnetic? Give reason in the light of MOT.

o. Which of the following bonds would be most polar?

i) C-Cl ii) Si-F iii) Se-F

p. What are necessary conditions for the hydrogen bond to form?

q. Compare the bond energies of single, double, and triple bonds between the same two atoms (e.g., H-H, O=O, O≡O). Explain the trend in terms of the number of shared electrons.

DESCRIPTIVE QUESTIONS

Q.3 **How the bonding in the following molecules can be explained with respect to valence bond theory?**

(i) Cl_2 (ii) O_2 (iii) N_2 (iv) HF (v) H_2S

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) PCl_5 (v) SO_2 (vi) SF_6

Q.5 **Explain the orbital hybridization for CH_4, NH_3, BF_3, and $BeCl_2$.**

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

Q.7 **Discuss the formation of F_2 molecule in the light of Lewis concept, VBT, and MOT.**

4

STOICHIOMETRY

STUDENT LEARNING OUTCOMES [C-11-A-47 to C-11-A-56]

- 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)**

Stoichiometry is derived from Greek words *stoicheion* means element and *metron* means measure. Collectively, stoichiometry means quantitative measure of reactants and products. 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.

Stoichiometric calculations obey law of conservation of mass and law of definite proportions. 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*. According to the law of definite proportions, a pure compound always contains the same element combined in the same ratio by mass.

4.1 CONCEPT OF MOLE

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?

Avogadro’s number is a physical constant representing the molar number of entities. The exact value of it is $6.02214179 \times 10^{23}$ mol^{-}. 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 NaCl contains 6.02×10^{23} formula units of NaCl.
- 1 mole of Na^+ contains 6.02×10^{23} ions of Na^+.

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.** The mass of one mole of a substance expressed in grams is called molar mass. The unit of molar mass is g/mol. The molar mass is the sum of the masses of the component atoms.

The mass of one mole of CCl_4 can be found by adding the masses of carbon and chlorine present.

$$\text{Molar mass of } CCl_4 = \text{Molar mass of one C} + \text{Molar mass of Cl} \times 4$$
$$= 12.0 \times 1 + 35.5 \times 4$$
$$\text{Molar mass of } CCl_4 = 12.0 + 142.0 = 154.0 \text{ g}$$

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.

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:

$$\text{Number of moles} = \frac{\text{Given mass}}{\text{Molar mass}}$$

$$\mathbf{n} = \frac{\mathbf{m}}{\mathbf{M}}$$

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 HCl.

Solution:

Mass of HCl = Number of moles x Molar mass

= 0.5 x 36.5 = 18.3 mol

Sample Problem 4.3

Calculate the mass of 10^{-3} mol of $MgSO_4$.

Solution:

Molar mass of $MgSO_4 = 24 + 96 = 120 \text{ g mol}^{-1}$

Number of moles of $MgSO_4 = 10^{-3}$

Mass of $MgSO_4 = 10^{-3} \text{ mol} \times 120 \text{ g mol}^{-1} = 120 \times 10^{-3} = 0.12 \text{ g}$

Quick Check 4.1

a. Calculate the molar mass of $KMnO_4$.
b. Calculate the number of moles in 0.23 g of sodium.
c. Calculate the mass of 1.5 moles of $Ca(OH)_2$.
d. The given mass of $KClO_3$ is 24.5 g. Calculate the number of moles of potassium chlorate.
e. How many molecules are present in 1.75 g of H_2O_2?
f. How many atoms are present in 15 g of gold ring?

4.2 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., 6.02 x 10^{23}.

It is interesting to know that different masses of elements have the same number of atoms.

1.0 g of hydrogen = 1 mol of hydrogen = 6.02 x 10^{23} atoms of H

23.0 g of sodium = 1 mol of Na = 6.02 x 10^{23} atoms of Na

238.0 g of uranium = 1 mol of U = 6.02 x 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 x 10^{23} molecules of water

180.0 g of glucose = 1 mol of glucose = 6.02 x 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 x 10^{23} ions of SO_4^{2-}

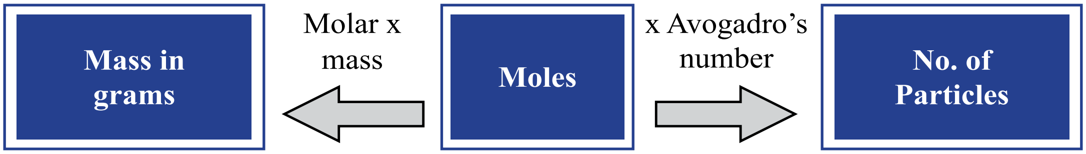
62.0 g of NO_3^{1-} = 1 mole of NO_3^{1-} = 6.02 x 10^{23} ions of NO_3^{1-}

One can calculate the number of moles by dividing the number of particles by Avogadro's number.

$$\textbf{Number of moles} = \frac{\textbf{No. of particles of a substance}}{\textbf{Avogadro's Number}}$$

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:

$$\textbf{Number of particles} = \frac{\textbf{Mass of subtance x } N_A}{\textbf{Molar Mass}}$$



Sample Problem 4.4

A sample of glucose, contains 3.76 x 10^{24} molecules of glucose. What is the number of moles in this quantity?

Solution: No. of moles of glucose = $\frac{3.76 \text{ x } 10^{24} \text{ molecules}}{6.02 \text{ x } 10^{23} \text{ molecules mol}^{-1}}$

= 6.25 moles

Sample Problem 4.5

How many atoms are there in a sodium metal that contains 2.3 g?

Solution:

$$\text{Number of moles of sodium} = \frac{2.3}{23.0} = 0.1 \text{ mol}$$

$$\begin{aligned}\text{Number of atoms of sodium} &= \text{Number of moles of sodium x } N_A \\ &= 0.1 \text{ x } 6.02 \text{ x } 10^{23} \\ &= 0.602 \text{ x } 10^{23} \text{ atoms}\end{aligned}$$

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) $C_{10}H_6O_3$

$10 \times A_r\,(C) + 6 \times 1.0\ A_r\,(H) + 3 \times A_r\,(O)$

$(10 \times 12.0) + (6 \times 1.0) + (3 \times 16.0)$

$120 + 6 + 48 = 174$ g/mol

Mass of 1 mol of $C_{10}H_6O_3 = 174$ g/mol

b) $$\text{Moles of juglone} = \frac{\text{Mass}}{\text{Molar Mass}} = \frac{0.87 \text{ g}}{174 \text{ g mol}^{-1}} = 0.005 \text{ mol}$$

Quick Check 4.2

a) A copper wire contains 27.10×10^{25} atoms of copper. Calculate the number of moles of copper.

b) Calculate the molecules of $1 \text{x} 10^{-6}$ 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?

Interesting Information!

Isopentyl acetate ($C_7H_{14}O_2$) is the compound responsible for the scent of bananas. Interestingly, bees release about 1 µg (1×10^{-6} g) of this compound when they sting. The resulting scent attracts other bees to join the attack.

4.3 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 $\mathbf{V_m}$. By using molar volume relationship, mass or mole of a gas at STP can be converted into volume, and vice versa.

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

- 22.4 dm^3 of CO_2 at STP = 44.0 g of CO_2 = 6.02×10^{23} molecules of CO_2 =1mole of CO_2
- 22.4 dm^3 of any gas at STP = molar mass in grams = 6.02×10^{23} molecules = 1mole
- 22.4 dm^3 of H_2 gas at STP = 2 g = 6.02×10^{23} molecules = 1mole
- 22.4 dm^3 of NH_3 gas at STP = 17 g = 6.02×10^{23} molecules= 1mole

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.

Volume of a gas = Number of moles x Molar volume

$$\mathbf{V = n \times V_m}$$

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 Cl_2 occupy a volume = 22.4 dm^3 x 2.5 = 56.0 dm^3

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 x 22.4 = 106.4 dm^3

4.4 MOLAR MASS AND DENSITY OF GASES

Density is defined as the mass per unit volume of a substance.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\mathbf{d = \frac{m}{V}}$$

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.

Sample Problem 4.9

Calculate the molar mass of a gas which has density of 1.97 g/dm^3 at STP.

Solution

$$m = d \times V$$

$$\text{Mass of gas at STP} = 1.97 \times 22.4 = 44.1\text{g mol}^{-1}$$

Quick Check 4.3

Calculate the molar mass of a gas which has density of 1.34 g/dm^3 at STP.

4.5 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

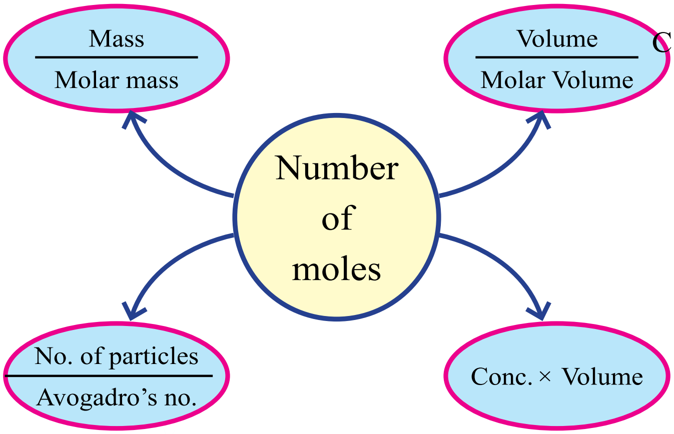
$$\mathbf{n = C \times V}$$

$$\mathbf{C = \frac{n}{V}}$$

where C is the molar concentration and V is the volume of the solution.

$$\text{Molar Concentration} = \frac{\text{Number of moles}}{\text{Volume in dm}^3}$$

$$C = \frac{0.2\text{ mol}}{1\text{ dm}^3} = 0.2\text{ mol dm}^{-3}$$



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}

$$\text{Number of moles} = \frac{\text{Given mass}}{\text{Molar mass}}$$

$$n = \frac{m}{M}$$

$$n = \frac{27.64}{138.2}$$

Volume of solution = 1 dm^3

$$\text{Molar Concentration} = \frac{\text{Number of moles}}{\text{Volume in dm}^3}$$

$$C = \frac{0.2\ \text{mol}}{1\ \text{dm}^3} = 0.2\ \text{mol dm}^{-3}$$

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}.

4.6 STOICHIOMETRY

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

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. 1 molecule of N_2 reacts with 3 molecules of H_2 to form 2 molecules of NH_3.

iii. 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

iv. 28.0 g of N_2 react with 6 g of H_2 to form 34.0 g of NH_3.

Keep in Mind!

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.
3) No side reaction occurs.

APPROACH TO DO STOICHIOMETRIC CALCULATIONS

Mass of known solid or volume of a known gas, or molar concentration of known solution

↓

Calculate number of moles of known solid or volume of a known gas, or molar concentration of known solution using the relevant formula

↓

Find the ratio of the known and the unknow reactant or product from the balanced chemical equation

↓

Calculate the number of moles of the unknown reactant or product using the relevant formula

↓

Convert the number of moles of the unknown to mass, volume, or concentration of the substance

Sample Problem 4.11 (Mole-Mole Conversion)

When 3.3 mole 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 $NH_3 = \frac{3}{1} = 3\text{mol}$

3.6 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:

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O(l)$$

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:

$$2Al_{(s)} + Fe_2O_{3(s)} \longrightarrow Al_2O_{3(s)} + 2Fe_{(s)}.$$

Solution:

Molar mass of Fe_2O_3, M $= 159.6 \text{ g mol}^{-1}$

Number of moles of Fe_2O_3 (n) $= \dfrac{m}{M}$

$$= \frac{32.0 \text{ g}}{159.6 \text{ g mol}^{-1}}$$

$$= 0.02 \text{ mol}$$

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 x 0.02 = 0.04 mol

Mass of Aℓ $= n \times M$

$= 0.04 \text{ mol} \times 27 \text{ g mol}^{-1}$

$= 1.08$ 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?

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 = ?

67.2 dm^3 (3 mol) of H_2 produce ammonia = 44.8 dm^3 (2 mol)

1 dm^3 of H_2 produce ammonia $= \frac{44.8}{67.2} = \frac{2}{3}$

100 dm^3 of H_2 produce ammonia $= \frac{2}{3} \times 100 = 66.7\ dm^3$

So, the volume of ammonia produced by the reaction of 100 dm^3 of H_2 with excess nitrogen is 66.7 dm^3.

Quick Check 4.7

Calculate the volume of carbon dioxide produced at STP when 4.5 dm^3 of methane is burnt by a person. The oxygen is in excess. The equation for the reaction is:

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

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.

$$2LiOH_{(s)} + CO_{2(g)} \longrightarrow Li_2CO_{3(s)} + H_2O(l)$$

Solution:

According to the given balanced chemical equation,

2 moles of LiOH produces = 1 mole Li_2CO_3

20.0 moles of LiOH produces $= \frac{1}{2} \times 20.0 = 10.0$ mol Li_2CO_3

Mass of Li_2CO_3 produced = No. of mole × Molar mass

Mass of Li_2CO_3 produced $= 10.0\ mol \times 73.9\ g\ mol^{-1} = 739.0\ g$

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 $2\ NaOH_{(aq)} + Cl_{2(g)} \longrightarrow NaOCl_{(aq)} + NaCl_{(aq)} + H_2O_{(\ell)}$.

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.

$$NaHCO_{3\,(g)} + HCl(aq) \longrightarrow NaCl(aq) + H_2O_{(l)} + CO_{2(aq)}$$

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}

Moles of $NaHCO_3 = \dfrac{2.1\text{ g}}{84.0\text{ g mol}^{-1}} = 0.025$ 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.

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) $= \dfrac{m}{M}$

$$= \frac{7.0\text{ g}}{55.8\text{ gmol}^{-1}}$$

$$= 0.125 \text{ mol}$$

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

$$= 22.4\ dm^3\ mol^{-1} \times 0.125\ mol$$

$$= 2.8\ dm^3$$

4.7 LIMITING AND EXCESS REACTANT

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. 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. 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.

4.7.1 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.

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.

Following numerical problem will make the idea clear.

Sample Problem 4.17 (Limiting Reactant)

Calculate the mass of N_2 produced from 1.81 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/ 17.0gmol^{-1} = 1.06 mol

Moles of CuO = 90.4g of CuO/79.5gmol^{-1} = 1.14 mol

In balanced equation, CuO : N_2

3 : 1

$$1.14 : \frac{1}{3} \times 1.14 = 0.38 \text{ mol}$$

$$NH_3 : N_2$$

$$2 : 1$$

$$1 : \frac{1}{2}$$

$$1.06 : \frac{1}{2} \times 1.06 = 0.53 \text{ mol}$$

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 x M

$$= 0.38 \text{ mol x } 17.0 \text{ g mol}^{-1}$$

$$= 9.0 \text{ g}$$

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

$$Pb^{+2}_{(aq)} + SO_4{}^{-2}{}_{(aq)} \longrightarrow PbSO_{4(s)}$$

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}) x Volume (dm^3)

$$n = CV$$

moles of Pb^{2+} ions = 0.05 mol $dm^{-3} \times$ 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 $dm^{-3} \times$ 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}):

$$\text{Mass of } PbSO_4 = 0.05 \text{ mol} \times 303.3 \text{ g mol}^{-1} = 15.2 \text{ g}$$

4.7.2 Maximum Amount of Product and Amount of Any Unreacted Excess Reagent

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). “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.

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$$

- 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. Actually, we will get 2 moles (36 g) of water 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, ½ mole of O_2 is required. The remaining $\frac{1}{2}$ mole will be excess.

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.

$$\text{Moles of } CH_4 = \frac{\text{given mass of } CH_4}{\text{molar mass of } CH_4} = \frac{30\text{g}}{16\text{gmol}^{-1}} = 1.875\,\text{mol}$$

$$\text{Moles of } O_2 = \frac{\text{given mass of } O_2}{\text{molar mass of } O_2} = \frac{50\text{g}}{32\text{gmol}^{-1}} = 1.563\,\text{mol}$$

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 = 1mol

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 $CO_2 = 0.5 \times 1.563$ 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

$$= 0.7815 \text{ moles} \times 44 \text{ g mol}^{-1} = 34.39 \text{ g}$$

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 $CH_4 = \frac{1}{2} \times 1.563\text{mol} = 0.7815$ 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

b) 2 moles of N_2 and 3 moles of H_2

c) 1 mole of N_2 and 5 moles of H_2

d) 3 moles of N_2 and 3 moles of H_2

e) Each produces the same amount of product.

4.8 THEORETICAL YIELD, ACTUAL YIELD, AND PERCENTAGE YIELD

The amount of the products obtained in a chemical reaction is called the actual yield of that reaction. 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.

In most chemical reactions the amount of the product obtained is less than the theoretical yield.

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.

$$\% \text{ Yield} = \frac{\textbf{Actual yield}}{\textbf{Theoretical yield}} \times 100$$

Greater the % age yield, higher will be the efficiency of reaction and vice versa.

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 gmol^{-1}) and acetic anhydride, $C_4H_6O_3$ (molar mass 163.93 gmol^{-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 gmol^{-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:

$C_7H_6O_3$	+	$C_4H_6O_3$	$\longrightarrow$	$C_9H_8O_4$	+	CH_3COOH
Salicylic acid		Acetic anhydride		Aspirin		
1 mol		1 mol		1 mol		
138.12 g		163.93 g		180.16 g		

1mole 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 gmol^{-1} = 0.022 mol

Mass of Salicylic acid = 6.00 g

Number of moles of Salicylic acid = 6.00 g/ 163.93 gmol^{-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

= 3.00/138.12 = 0.022 mol

0.022 mol Salicylic acid produces Aspirin =0.022 mol

Mass of Aspirin = 0.021 mol x 180.16 g mol^{-1} = 3.96 g

Theoretical yield = 3.96

Actual yield = 2.85

% age yield = 2.85/3.96 x 100 = 71.97 %

Quick Check 4.10

When limestone ($CaCO_3$) is roasted, quicklime (CaO) is produced according to the following equation.

$$CaCO_3 \longrightarrow CaO + CO_2$$

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?

4.9 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.

4.9.1 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. Paracetamol is used as a pain killer and to decrease fever. An overdose may result a blood thinning, organ damage and severe liver damage.

EXERCISE

MULTIPLE CHOICE QUESTIONS

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 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

III. Which one of the following gases will have maximum 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 atoms 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) 28 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}

SHORT-ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. How is the concept of mole derived from Avogadro's number?

b. Define the following terms with one example in each case.

(a) Molar mass (b) Molar volume (c) Molar concentration

c. What do you mean by molar volume of a gas? How Avogadro's number is related with molar volume?

d. 39 g of potassium and 56 g of iron have equal number of atoms in them. Justify.

e. 4 g of H_e, 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.

f. Do you think that 1 mole of H2 and 1 mole of NH3 at 0 ^{o}C and 1 atm will have Avogadro's number of particles?

g. What is stoichiometry? Give the basic assumptions of stoichiometric calculations.

h. What is a limiting reactant? How does it control the quantity of the product formed?

i. Differentiate theoretical and actual yields. How is the percentage yield of a reaction calculated?

j. What are the factors which are mostly responsible for the low yield of the products in chemical reactions?

DESCRIPTIVE QUESTIONS

Q. 3 Differentiate limiting and non-limiting reactants. How a limiting reactant is determined from a balanced chemical equation and given data?

Q4. Differentiate actual and theoretical yields. Why the theoretical yield is always greater than actual yield?

(NUMERICAL PROBLEMS)

Q.5A 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 500 cm^3, what would be the concentration now?

Q.6 Ammonia gas (NH_3) reacts with oxygen gas (O_2) according to the following balanced equation:

$$4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(g)}$$

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)

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:

$$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

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)

Q.8 $PbSO_4$ is precipitated when aqueous solutions of Na_2SO_4 and $Pb(NO_3)_2$ are mixed. Calculate the mass of $PbSO_4$ formed when 1.25 dm^3 of 0.05 M $Pb(NO_3)_2$ and 2 dm^3 of 0.025 M Na_2SO_4 are mixed.

5

STATES AND PHASES OF MATTER

STUDENT LEARNING OUTCOMES [C-11-A-79 to C-11-A-92]

- 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, vapor 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 vapor pressure, high heat of vaporization, and high boiling point). (Application)
- Define molar heat of fusion and molar heat of vaporization. (Knowledge)
- Describe how heat of fusion and heat of vaporization 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.e., solid, liquid, gas and plasma. The simplest form of matter is the gaseous state and 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 look at the general properties of gases, liquids, and solids. Kinetic molecular theory of gases can help us to understand their properties.

5.1 PROPERTIES OF GASES

i. Gases do not have a definite shape and volume. The volume of a 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 negligible intermolecular forces in ideal gases.

5.2 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. According to Boyle's law.

$$V \propto \frac{1}{P} \quad \text{(when 'n' and 'T' are held constant)} \ldots\ldots (1)$$

According to Charles' law

$$V \propto T \quad \text{(when 'n' and 'P' are held constant)} \ldots\ldots\ldots (2)$$

According to Avogadro's law volume of the given gas at constant temperature and pressure is directly proportional to the number of moles.

$$V \propto n \quad \text{(when P and T are held constant)} \ldots\ldots (3)$$

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}.

$$\text{Hence } V = R\frac{nT}{P}$$

$$PV = nRT \quad \text{………} \ (4)$$

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:

$$M = \frac{mRT}{PV}$$

$$M = \frac{(134\ g)(0.0821\ atm\ dm^3\ mol^{-1}\ K^{-1})(200\ K)}{(10\ atm)(5\ dm^3)}$$

$$M = 44\ g\ mol^{-1}$$

Therefore, the relative molecular mass of the gas is 44 amu.

Quick Check 5.1

a) Explain why gases can be compressed easily?

b) What is Joule-Thomson effect

c) The volume of 21g a gas is 8 dm^3 at -90 ºC under 7 atm pressure. Calculate the relative molecular mass of the gas.

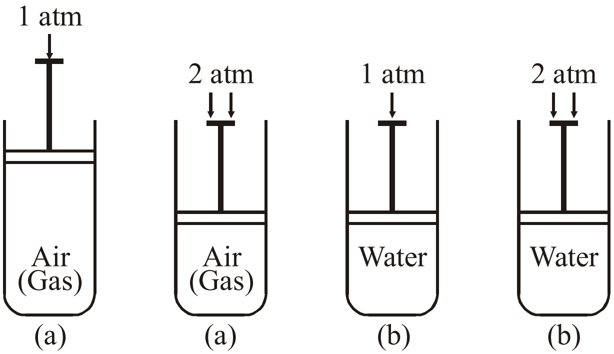
5.3 PROPERTIES OF LIQUIDS

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 5.1 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 KE 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)

5.4 INTERMOLECULAR 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

5.4.1 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 polarisation is relatively easier. This factor operates in the halogen and noble gas families. 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 Cl_2) are gases, but bromine is a liquid and iodine a solid (b.p. = 458 K). The boiling points of noble gases in group 18 also increase from helium (He) to xenon (Xe) as in **Table 5.1**.

Table 5.1 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
Cl_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

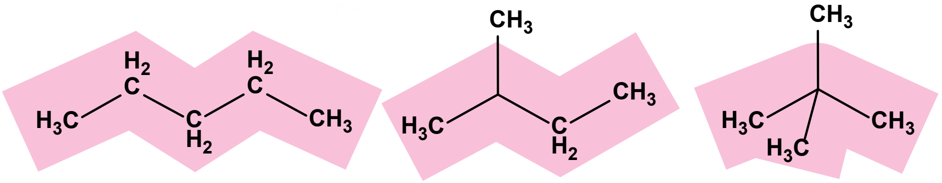
ii. Surface area (shape of molecule)

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. Consider saturated hydrocarbons. These have chains of carbon atoms linked with hydrogen atoms. 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 5.2**.

Table 5.2 Boiling points and physical states of some hydrocarbons

Name	B.P. °C (1 atm)	Physical state at S.T.P.	Name	B.P. °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 5.2**.



pentane
(n-pentane)
36.2 °C

2-Methylbutane
(iso-pentane)
28 °C

2,2-Dimethylpropane
(neo-pentane)
9.5 °C

Figure 5.2 The three isomers of pentane have different structures, surface areas and intermolecular forces

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?

b) Which forces are present among the molecules of the following substances? CCl_4, SiF_4

c) Differentiate id-id and pd-pd forces with examples.

5.4.2 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-permanent dipole force**. Whenever the HCl molecules are close to each other (as in liquid state), they tend to line up as in **Figure 5.3**. Similar type of forces is present among the molecules of chloroform ($CHCl_3$).

The molecule of chloroform has a positive center at the H atom and the negative center on the end with Cl atoms.

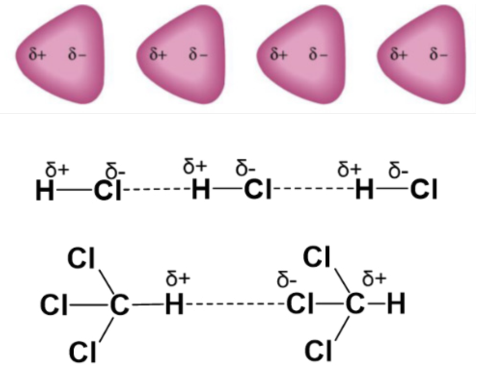


Figure 5.3 Permanent dipole-permanent dipole forces in HCl and chloroform

5.4.3 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. 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

A water molecule contains two hydrogen atoms and two lone pairs on oxygen. Therefore, it can form two bonds 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. 42. This bonding acts as a bridge between two electronegative oxygen atoms.

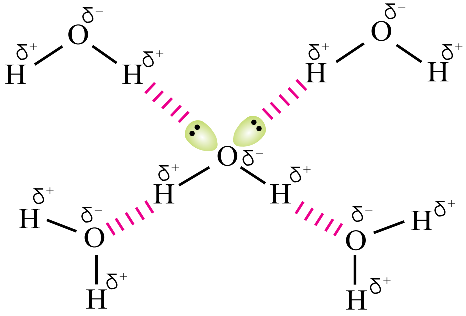


Figure 5.4 Hydrogen bonding in water

On the other hand, ammonia can form only one hydrogen bond per molecule despite having three hydrogen atoms. This is due to the availability of only one lone pair on the N atom as shown in **Figure 5.4.** The hydrogen bonding in liquid ammonia is much weaker than water. This is why its boiling point is much lower (-33°C). 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. Nevertheless, its hydrogen bond is strong enough compared to NH_3, which owes to its high electronegativity. Thus, its b.p (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 solid form due to the presence of the hydrogen bonds. 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 5.5**).

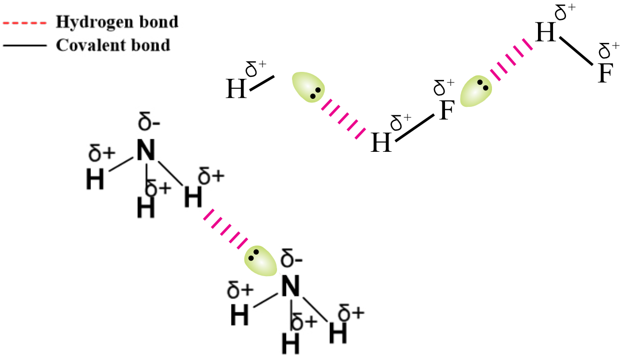


Figure 5.5: Hydrogen bonding in NH_3 and HF

5.4.4 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 5.6**). This is why, when water freezes, it occupies 9% more space and its density decreases. For this reason, ice floats on water. Due to this so called anomalous behavior 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.

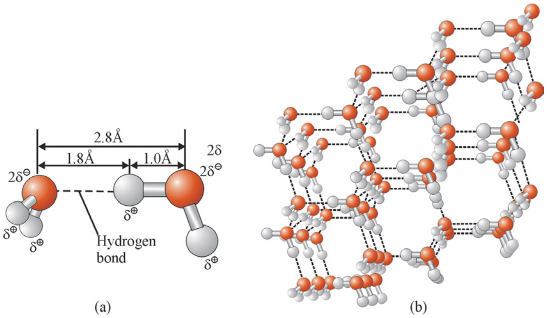


Figure 5.6: Extensive hydrogen bonding in ice and spaces among molecules

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 5.7**). This is because the molecules of these compounds are bound by weak London dispersion forces.

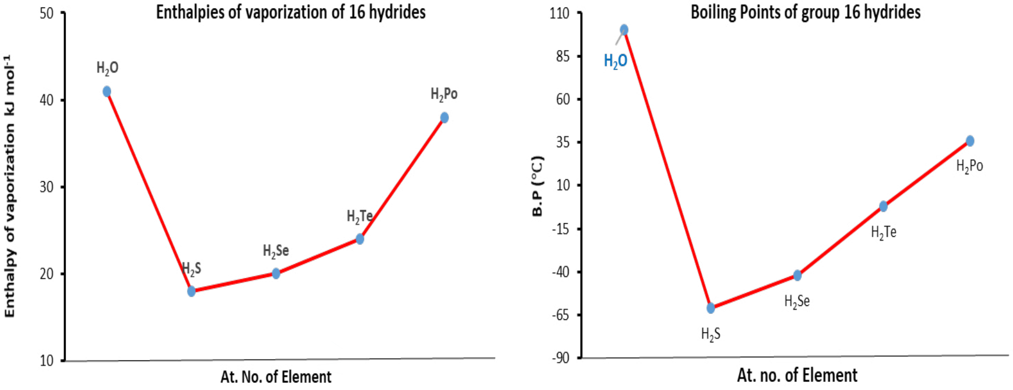


Figure 5.7: A graphical expression of variation in enthalpy of vaporization and B.Ps of group 16 hydrides

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. However, water has the highest enthalpy change of vaporization (41 $kJ\ mol^-$) 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 vapor.

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.

Quick Check 5.4

a) Can the CHF_3 molecule make a hydrogen bond? Explain why or why not?

b) Show a hydrogen bond between two molecules of ethanol

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

d) The boiling point difference in each of the following pairs is given

i. CH_3CH_3 (-89 °C) and CH3OH (65 °C), difference = 154 °C

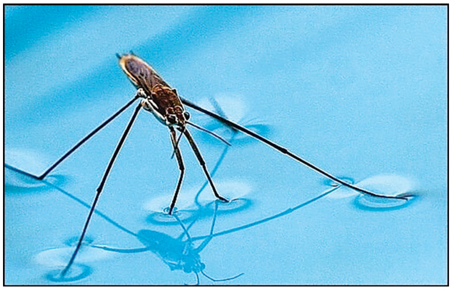
ii. $CH_3CH_2CH_2CH_4$ (0 °C) and $CH_3CH_2CH_2OH$ (97 °C), difference = 97 °C

e) Explain why the difference decreases as the size of the molecules increases.

f) 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?

5.5 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.



Mosquitos can float on surface on water due to high surface tension

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 and formation of droplets and bubbles.

Factors Affecting Surface Tension

i) **Temperature:** Surface tension typically decreases with increasing temperature.

ii) **Intermolecular forces:** Stronger intermolecular forces lead to higher surface tension.

Table 5.3 Surface tension of some liquids at 20 °C in Nm^{-1}

Sr. No.	Liquid	γ (10^{-3} Nm^{-1})	Sr. No.	Liquid	γ (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 CCl_4	26.95

'γ' are values multiple of $10^{-3} = 1/1000$. It means 'γ' value of the water (H_2O) at 20°C = 72.75×10^{-3} Nm^{-1} or 72.75 dynes cm^{-1}.

5.6 VISCOSITY OF LIQUIDS

In order to understand the term viscosity, let us 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. Now, observe this process carefully, you will see 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 concluded 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. **This resistance to the flow of a liquid is termed as viscosity.**

In international system (SI), unit of viscosity is in kg m^{-1} s^{-1}. In CGS system, the unit of viscosity is poise (P).

5.6.1 Factors affecting viscosity:

The factors affecting viscosity are as follows:

i. 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. 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 5.5

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)

b) Why do you think tetracholro methane (carbon tetrachloride, CCl_4) has higher viscosity than chlroform ($CHCl_3$) but less than ethanol (C_2H_5OH)?

c) Drugs with higher viscosity are not oxidized easily, justify.

d) The viscosity of honey is higher than water, explain why.

e) Which of the following is more viscous: glycerine ($CH_2OHCH_2OHCH_2OH$) or hexane (C_6H_6)? Why?

5.7 EVAPORATION

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.

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.

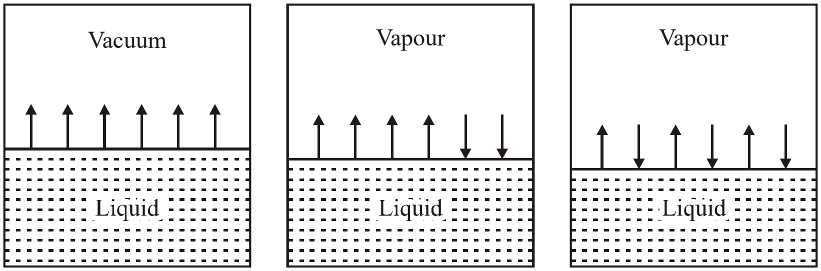
5.8 VAPOUR PRESSURE:

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 (5.11).

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. It does not depend on surface area of a liquid. The larger surface area presents a larger target for returning the molecules, so the rate of condensation also increases.



(a) (b) (c)

Figure. 5.8 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 5.6

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?

b) Which one in each of the following pairs is more viscous: Glycerine, kerosene?

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.

d) Why evaporation gets faster at higher temperatures?

5.9 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

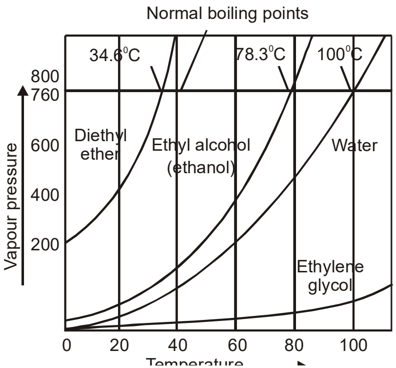


Figure 5.9 Vapour pressures (torr) of four common liquids shown as a function of temperature.

come out of the liquid and burst at the surface. A constant stream of bubbles comes out at the boiling point of the liquid.

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 one atmospheric pressure are shown in the Table (5.9).

The **Figure 5.9** 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.

5.9.1 Factors affecting boiling points of liquids

The boiling point of a liquid is affected by the factors given below.

1) Strength of intermolecular forces

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 5.4**.

Table 5.4 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

As already explained that 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.

For example, water shows B.P of 120°C at 1489 torr pressure and boils at 25°C at 23.7 torr. Water boils at 98°C at Murree hills due to external pressure of 700 torr while at the top of Mount Everest water boils at only 69ºC at 323 torr.

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 5.7

a) Why food cooking is difficult in the areas with high altitudes?
b) The food cooks fatser in the pressure cooker, explain.
c) Why the boiling point of water (100 °C) is higher than that of ethanol (78 °C), although oth have hydrogen bonds?

5.10 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.

$$H_2O_{(s)} \longrightarrow H_2O_{(l)} \quad \Delta H_f = 4.6 \text{ kJ mol}^{-1}$$

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 100ºC, then heat absorbed is **40.6 kJ mol^{-1}**.

$$H_2O_{(l)} \longrightarrow H_2O_{(g)} \quad \Delta H_v = 40.6 \text{ kJ mol}^{-1}$$

NH_3 and HCl 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 vaporization and fusion on matter particles

The molar heat of fusion and vaporization affect the particles that make up matter by providing them with enough energy. Due to this, the particle 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.

5.11 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.

5.12 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.

5.12.1 Crystalline Solids

Crystal Lattice

The regular arrangement of ions, atoms, or molecules in three dimensional space is called the crystall lattice.

The solids which have definite regular and three dimensional geometric shapes are called crystalline solids. For example, diamond, sodium chloride, ice, etc.

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.

ii. Melting points

Crystalline solids have sharp melting points. They can be identified from their definite melting points.

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.

For example, the solubility of sodium thiosulphate ($Na_2S_2O_3$) in water at 100°C is 231g/100 cm^3. At room temperature solubility is 50 g / 100 cm^3. In case, 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.

5.12.2 Amorphous solids

Amorphous solids, contrary to the crystalline solids, do not possess regular three dimensional geometrical shapes. The examples of amorphous solids are 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 5.5 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.

Quick Check 5.8

a) Why solids have very low compressibility and expansion?

b) What is meant by habit of a crystal.

c) Why solids do not undergo translatory motion?

d) Why most of solids can not be compressed easily?

5.13 LIQUID CRYSTALS

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.

5.13.1 General properties of liquid crystals:

The general properties of liquid crystals are as follows:

Liquid crystals

i. have parallel ordered arrangement.
ii. are elongated, rod-like and linear.
iii. flow like liquids
iv. show viscosity like liquids.
v. show optical properties like crystals.
vi. are somewhat rigid.
vii. are always anisotropic.

5.13.2 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.

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 5.9

a) Name the properties of liquid crystals in which they resemble solids.
b) Mention the properties of liquid crystals in which they resemble liquids.
c) Which property of liquid crystals make it possible to use them in temperature sensing devices?

EXERCISE

MULTIPLE CHOICE QUESTIONS

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 ^{o}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 the following options is wrong about hydrides of groups 14, 15, 16, and 17 elements?

a) All the hydrides show H-bonding.
b) Only H_2O, NH_3 and HF show H-bonding.
c) The molecules of CH_4 are non-polar.
d) H_2S is a gas at room temperature but H_2O is liquid.

V. 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) $H_2O > F_2 > NH_3$

VI. 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

VII. Amorphous solids:

a) have sharp melting points

b) undergo clean cleavage when cut with knife

c) have perfect arrangement of atoms

d) do not have definite geometric shape

VIII. Which change of state involves overcoming only London dispersion forces?

a) Melting of ice ($H_2O_{(s)} \rightarrow H_2O_{(l)}$)

b) Boiling of ethanol ($CH_3CH_2OH_{(l)} \rightarrow CH_3CH_2OH_{(g)}$)

c) Sublimation of iodine ($I_{2(s)} \rightarrow I_{2(g)}$)

d) Dissolving sodium chloride in water

IX. 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)

X. 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.

XI. 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 ($CH_2(OH)CH(OH)CH_2(OH)$)

XII. 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

XIII. Liquid crystals exhibit properties:

a) Only like solids. b) Only like liquids.

c) Between solids and liquids. d) Unlike solids or liquids.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Explain, at a molecular level, why evaporation leads to a cooling effect.

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.

c. One feels sense of cooling under the fan after bath.

d. Dynamic equilibrium is established during evaporation of a liquid in a closed vessel at constant temperature.

e. The boiling point of water is different at Lahore and Murree hills.

f. Discuss two significant consequences of the lower density of ice compared to liquid water in natural environments.?

g. Why B.P of a liquid increases when the external pressure rises?

h. Mention four items in which liquid crystals are used.

i. How do you differentiate between crystalline solids and amorphous solids?

j. Propanone(CH_3COCH_3),propanol($CH_3CH_2CH_2OH$)andbutane($CH_3CH_2CH_2CH_3$) have very similar relative molecular masses. List them in the expected order of increasing boiling points. Explain your answer.

k. Discuss how hydrogen bonding is responsible for the relatively high surface tension of water.

l. What type of intermolecular forces will dominate in the following liquids?

(i) NH_3 (ii) Ar (iii) CH_3COCH_3 (iv) CH_3OH

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	109	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.

DESCRIPTIVE QUESTIONS

Q.3. What are London dispersion forces? Give examples, and discuss the factors affecting these forces.

Q.4 Hydrogen bonding is present in H_2O, NH_3, HF, $(CH_3)_2CO$ and $CHCl_3$ molecules. Sketch structures and discuss briefly.

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^oC and lower density of ice.

Q.6 How liquid crystals resemble liquids and solids? Give their uses in daily life.

Q.7 Describe the following properties of crystalline solids.

i) Geometrical shape
ii) Melting point
iii) Cleavage plan
iv) Habit of a crystal

NUMERICAL PROBLEMS

Q8. 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, $R=8.31JK^{-1}mol^{-1}$)

Q9. 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 vapor was found to be 0.495 g. Determine the molecular mass of the liquid ($R = 8.314\ J\ K^{-1}\ mol^{-1}$).

6

CHEMICAL ENERGETICS

STUDENT LEARNING OUTCOMES [C-11-A-93 to C-11-A-123]

- 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 $q = mcdT$ and $\Delta H^\circ = - mcdT/n$. **(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 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' law, a special case of Ist 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.

6.1 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.

Mathematically,

$$\Delta H = (\text{Heat content of products, } H_P) - (\text{Heat content of reactants, } H_R)$$

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**."

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**."

Following **Figure 6.1** shows the **enthalpy diagram** of exothermic and endothermic reactions.

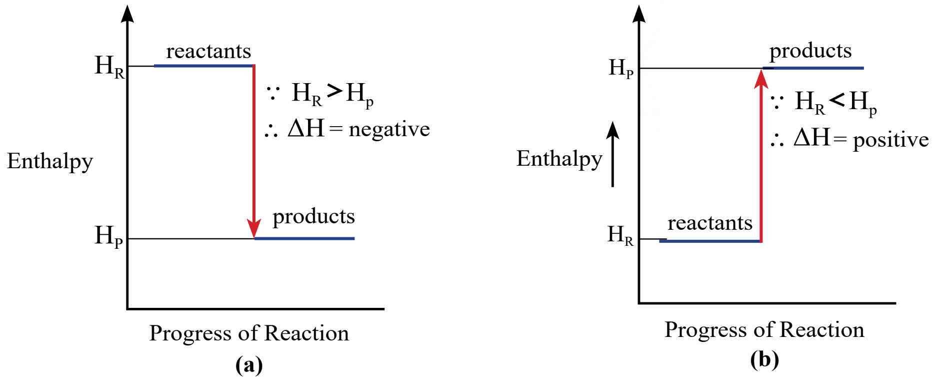


Figure 6.1: Enthalpy diagram of (a) Exothermic Reaction and (b) Endothermic Reaction

For example, combustion of carbon in oxygen is an exothermic reaction.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -393.7 \text{ kJ mol}^{-1}$$

The dissolution of ammonium chloride (NH_4Cl) in water is an endothermic process.

$$NH_4Cl_{(s)} \xrightarrow{H_2O_{(\ell)}} NH_4{}^+{}_{(aq)} + Cl^-{}_{(aq)} \qquad \Delta H = +16.2 \text{ kJ mol}^{-1}$$

Interesting information

The dissolution of ammonium chloride (NH_4Cl) 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_4Cl crystals mix and energy is absorbed from the surroundings, producing a cooling sensation.

6.2 ENERGY PROFILE DIAGRAM:

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. The energy profile diagram of exothermic and endothermic reactions are given in **Figure 6.2**.

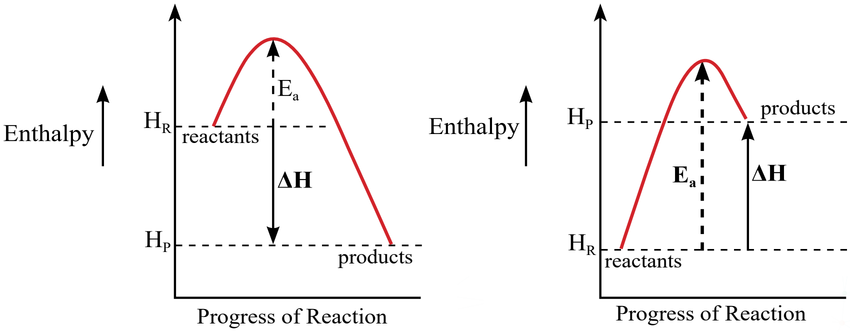


Figure 6.2 Energy profile diagram in terms of ΔH and E_a

Quick Check 6.1

Draw the energy profile diagrams for the following reactions:

i. $CH_{4(g)} + 2\,O_{2(g)} \longrightarrow CO_{2(g)} + 2\,H_2O_{(\ell)}$ $\Delta H = -890.3$ kJ mol^{-1}

ii. $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$ $\Delta H = +572$ kJ mol^{-1}

6.3 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 1atm 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**.

6.3.1 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.

For example, consider the reaction between hydrogen and oxygen gases to form 1 mole of water:

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)} \qquad \mathbf{\Delta H_r} = -286 \text{ kJ mol}^{-1}$$

6.3.2 Enthalpy Change of Combustion (ΔH^o_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**.** For example, standard enthalpy of combustion $\mathbf{\Delta H^o_C}$ of ethanol is −1368 kJ mol^{-1}.

$$C_2H_5OH_{(\ell)} + 3\,O_{2(g)} \longrightarrow 2\,CO_{2(g)} + 3\,H_2O_{(\ell)} \qquad \mathbf{\Delta H^o_C} = -1368 \text{ kJ mol}^{-1}$$

Enthalpy change of combustion is useful in calculating calorie content of foods and fuels.

6.3.3 Enthalpy Change of Formation (ΔH^o_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. For instance, ΔH°_f for methane is given below.

$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)} \qquad \Delta H^\circ_f = -74.8 \text{ kJ mol}^{-1}$$

6.3.4 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."

$$H_{2(g)} \longrightarrow 2H_{(g)} \qquad E_{H\text{-}H} = +436 \text{ kJ mol}^{-1}$$

$$\tfrac{1}{2} H_{2(g)} \longrightarrow H_{(g)} \qquad \Delta H^o_{at} = +218 \text{ kJ mol}^{-1}$$

6.3.5 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. For 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:

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(\ell)} \qquad \Delta H^o_n = -57.1 \text{ kJ mol}^{-1}$$

For all strong acid-base reactions ΔH^o_n is always near -57.1 kJ mol^{-1}.

6.3.6 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.

Electron affinity of chlorine atom.

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

Since, energy is released, so first electron affinity carries negative sign.

Note: A detailed discussion of electron affinity is given in chapter 1.

Quick Check 6.2

a) Write equations, including state symbols, that represent the enthalpy change of atomization of: **(i)** Oxygen **(ii)** Barium **(iii)** Bromine

b) Classify the enthalpy change in each of the following reactions:

i) $C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)}$
ii) $HCl_{(g)} + NH_{3(g)} \longrightarrow NH_4Cl_{(s)}$
iii) $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(\ell)}$

c) The first electron affinity of sulfur is –200 kJ mol^{-1} and the second electron affinity +640 kJ mol^{-1}. Calculate the value for the enthalpy change of the following reaction:

$$S_{(g)} + 2e^- \longrightarrow S^{2-}{}_{(g)}$$

6.4 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* which is defined as, "The average amount of energy required to break (dissociate) one mole of a particular bond in a substance."

Table 6.1. 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

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 B.E. values, in all of their compounds. Actually, B.E. is affected by other atoms in a molecule. For example, C–C bonds usually have B.E. values of approximately 350 to 380 kJ/mol.

In ethane: $[H_3C—CH_3]$; $E_{C\text{-}C} = 376$ kJ mol^{-1}

In propane: $[H_3C—CH_2—CH_3]$; $E_{C\text{-}C} = 356$ kJ mol^{-1}

In butane: $[H_3C—CH_2—CH_2—CH_3]$; $E_{C\text{-}C} = 352\ \text{kJ mol}^{-1}$

In these examples, $E_{c\text{-}c}$ for ethane is exact bond energy. Similarly for propane and butane, $E_{c\text{-}c}$ are exact bond in the change. When we take average of all $E_{c\text{-}c}$ 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 6.1**.

6.5 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 (ΔH = +ve) while bond formation releases it (ΔH = −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.

For example, 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,

$$2\,H_{2(g)} + O_{2(g)} \longrightarrow 2\,H_2O_{(g)} \quad \Delta H_r = \text{-ve}$$

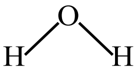
Sample Problem 6.1

With the help of the following bond energy data; calculate the enthalpy change of the following reaction:

$E_{H\text{–}H} = 436\ \text{kJ mol}^{-1}$; $E_{O=O} = 495\ \text{kJ mol}^{-1}$ and $E_{H\text{–}O} = 463\ \text{kJ mol}^{-1}$

$$H_{2(g)} + \tfrac{1}{2}\,O_{2(g)} \longrightarrow H_2O_{(g)}$$

Solution: $\underbrace{H{-}H + \tfrac{1}{2}\,O{=}O}_{436\ +\ \frac{1}{2}(495)} \longrightarrow$



$2 \times (463)$

(bond breaking energy) (bond forming energy)

$$\because\ \Delta H^o_r = \sum E_R - \sum E_P$$

$$= [E_{H\text{-}H} + E_{O=O}] - [2\,E_{H\text{-}O}]$$

$$= [436 + 247.5] - [2(463)]$$

$$\mathbf{\Delta H^o_r = -242.5\ kJ\ mol^{-1}}$$

6.6 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".

Calorimetry relies on the fact that it takes 4.18J of energy to increase temperature of 1g of the water by 1°C. The amount of heat energy required to raise the temperature of a substance of mass 1kg through 1K (or 1°C) is known as specific heat capacity, c, of the liquid. So the specific heat capacity of water is 4.18 $J\ g^{-1}\ K^{-1}$(or $J\ g^{-1}$ $\mathbf{°C^{-1}}$).

The energy is transferred as heat and is shown by relationship

$$\mathbf{q = c \times m \times \Delta T}$$

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, ($\mathbf{\Delta T}$ = $T_f - T_i$)

6.6.1 Glass Calorimeter

A glass calorimeter is suitable for measuring heat-flow for reactions in solutions. However, 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.

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. 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.

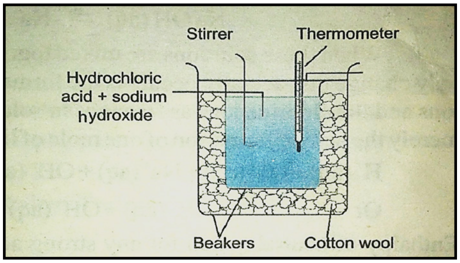


Figure 6.3 Glass calorimeter to measure enthalpy change of reactions

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:

$\Delta H = -q/n\ kJmol^{-1}$ (for exothermic reaction)

or $= -mc\Delta T/n\ kJmol^{-1}$ (n = no. of moles)

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 (Δ) as explained in the following example.

Sample Problem 6.2

Neutralization of 100 cm^3 of 0.5 $moldm^{-3}$ NaOH at 25°C with 100 cm^3 of 0.5 $moldm^{-3}$ 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 J $g^{-1}K^{-1}$

Solution

Density of H_2O is around 1gcm^{-3}, so total volume of solution which is 200 $cm^3 \approx$ 200 g

Rise in temperature, $\Delta T = 28.5 - 25.0 = 3.5°C = 3.5$ K

∵ Amount of total heat evolved, $q = m \times c \times \Delta T$

$= 200 \times 4.2 \times 3.5 = 2940$ J

$= 2.94$ kJ

Quick Check 6.3

Calculate ΔH^o_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,

Calculation of n (no. of moles of H_2O formed)

Using mole = Concentration(mol/dm^3) x Volume (dm^3)

$n_{(HCl)} = n_{(NaOH)} = 0.5 \times 100/1000 = 0.05$ mol

Using equation, Number of moles of water formed, $n_{(H2O)} = 0.05$ mol

Heat evolved in the formation of 0.05 mole of water, $q = -2.94$ kJ

$\Delta H^o_n = q/n = -2.94$ kJ / 0.05 mol

So, Enthalpy of neutralization, $\Delta H^o_n = -58.8$ kJ mol^{-1}

6.7 ENTHALPY CHANGE AND CALORIE CONTENT OF FOOD

In this section, we will look at 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. This energy is typically expressed in units of kilocalories (k cal) or joules (J).

6.7.1 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.

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(\ell)} \qquad \Delta H° = -2803\ \text{kJ mol}^{-1}$$

The calorie content of glucose can be calculated as follows: First, we find ΔH per gram of glucose. Molar mass of glucose is 180gmol^{-1}. Above equation shows that;

mol (180.0 g) of glucose burns to produce energy = 2803 kJ

$$1.0\ \text{g of Glucose} = \frac{2803\ \text{kJ/g}}{180\ \text{g/mol}}$$

$$= 15.57\ \text{kJ/g}$$

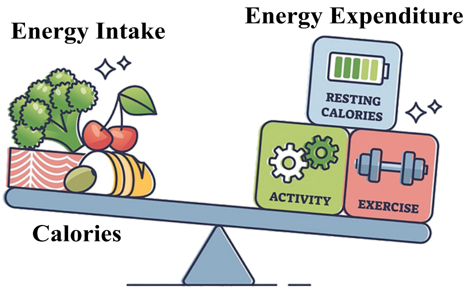
Using the relation,

$$\mathbf{\Delta H\ (kJ/g)} = -4.184 \times \text{calorie content}$$

$$\text{calorie content} = -\frac{\Delta H\ (\text{kJ/g})}{4.184\ (\text{kJ/kcal})}$$

$$= -\frac{15.57\ \text{kJ/g}}{4.184\ (\text{kJ/kcal})}$$

calorie content = – 3.72 kcal/g



Negative Energy Balance

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

6.8 HESS' LAW OF HEAT SUMMATION

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. It states:

"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."

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 6.8. The products formed in these routes (M, N and X, Y, Z) are called reaction intermediates.

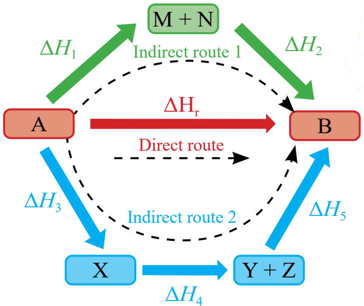


Figure 6.4 Hess' cycle

Then according to Hess' law,

For the indirect route 1, we can write: $\mathbf{\Delta H_r} = \Delta H_1 + \Delta H_2$

For the indirect route 2, we can write: $\mathbf{\Delta H_r} = \Delta H_3 + \Delta H_4 + \Delta H_5$

Below are few examples of it.

i) Calculating Enthalpy of Formation (ΔH^o_f) using Enthalpy of Combustion (ΔH^o_c)

Sample problem 6.3

Calculate the enthalpy change of formation of CO using Hess cycle with the help of following combustion data.

$$C(graphite) + O_{2(g)} \longrightarrow CO_{2(g)} \quad \mathbf{\Delta H} = -393.5\ kJ\ mol^{-1}$$

$$CO_{(g)} + \tfrac{1}{2} O_{2(g)} \longrightarrow CO_{2(g)} \quad \mathbf{\Delta H_2} = -283\ kJ\ mol^{-1}$$

$$C(graphite) + \tfrac{1}{2} O_{2(g)} \qquad CO_{(g)} \quad \mathbf{\Delta H_1} = ?$$

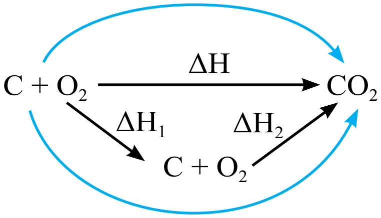
Solution: Applying Hess' law, we can write

$\Delta H = \Delta H1 + \Delta H2$

$\Delta H_1 = \Delta H - \Delta H_2$

$= -393.5 - (-283)$

$= -110.5\ kJ\ mol^{-1}$



ii) Calculating Enthalpy Change of Reaction (ΔH^o_r) using Enthalpies of formation (ΔH^o_f)

Sample Problem 6.4 Calculate the enthalpy change of reaction of

$$C_2H_4 + HCl \longrightarrow C_2H_5Cl$$

Using Hess cycle with the help of following combustion data.

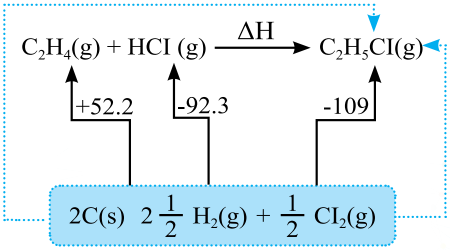
ΔH^o_f of $C_2H_4 = +52.2\ KJ\ mol^{-1}$

ΔH^o_f of $HCl = -92.3\ KJ\ mol^{-1}$

ΔH^o_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:

$$6C_{(s)} + 3H_{2(g)} \longrightarrow C_6H_{6(l)} \qquad \Delta H_f^\circ = ?$$

The standard enthalpies of combustion of $C_{(s)}$, $H_{2(g)}$ and $C_6H_{6(l)}$ are -394 kJ mol^{-1}, -286 kJ mol^{-1} and -3267 kJ mol^{-1} respectively.

iv) Calculating Enthalpy Change of Formation of a substance (ΔH_f°) using Enthalpy of Combustion and Enthalpies of Formation of other substances

Sample problem 6.6 Propane ($C_3H_{8(g)}$) burns in oxygen according to the equation:

$$C_3H_{8(g)} + 5\,O_{2(g)} \longrightarrow 3\,CO_{2(g)} + 4\,H_2O_{(g)}$$

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 $H_2O_{(g)}$ 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' law:

$$\Delta H_r = [3 \times \Delta H^o{}_f\,(CO_2) + 4 \times \Delta H^o{}_f(H_2O)] - [1 \times \Delta H^o{}_c\,(C_3H_8) + 5 \times \Delta H^o{}_c\,(O_2)]$$

$$-2044\text{ kJ} = [3\times(-393.51) + 4\times(-241.82)] - [1 \times \Delta H^o{}_f\,(C_3H_8) + 5\times(0)]$$

Taking the heat of combustion of $O_{2(g)}$ to be zero and solving this equation for $\Delta H^o{}_f\,(C_3H_8)$ gives,

$$\Delta H^o{}_f\,(C_3H_8) = -104\text{ kJ mol}^{-1}$$

Quick Check 6.5

Draw enthalpy cycle of sample problem 6.6 according to Hess' law to validate above calculation.

v) Calculating Enthalpy Change of Reactions (ΔH_r) using Bond Energies

A special case of Hess' law involves the use of bond energies to estimate heats of reaction for gas-phase reactions. 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 6.1. In the second step, the product molecules are formed. The enthalpy change for this step can again be estimated from the bond enthalpies of Table 6.1, 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' law:

$$\begin{tikzcd}
\text{Reactants} \arrow[rr, "\Delta H^o_{rxn}"] \arrow[dr, "E_{(R)}"'] & & \text{Products} \\
& \text{Atoms} \arrow[ur, "E_{(P)}"'] &
\end{tikzcd}$$

Figure 6.4 Hess Cycle; showing the relationship between B.E.'s and ΔH_r. $= \sum n\, E_R - \sum n\, E_P$

Sample problem 6.7 In the case of formation of $HCl_{(g)}$ from $H_{2(g)}$ and $Cl_{2(g)}$, use B.E. data from Table 6.1 to estimate ΔH for the reaction:

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2\,HCl_{(g)}$$

And finally calculate the heat of formation of HCl.

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:

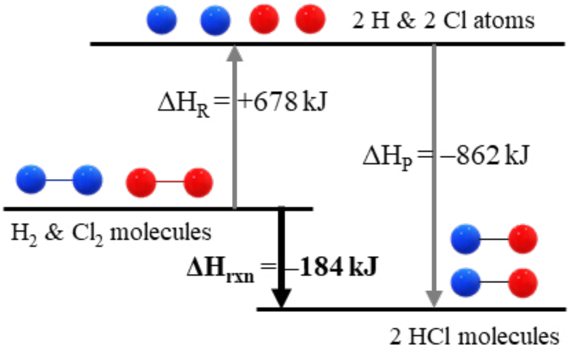
$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2\,H + 2\,Cl_{(g)}$$

$E_{H\text{-}H} = 436\ \text{kJ mol}^{-1}$; $E_{Cl\text{-}Cl} = 242\ \text{kJ mol}^{-1}$

$$E_R = \left(1\ \cancel{\text{mol}} \times 436\ \frac{\text{kJ}}{\cancel{\text{mol}}}\right) + \left(1\ \cancel{\text{mol}} \times 242\ \frac{\text{kJ}}{\cancel{\text{mol}}}\right)$$

$= 436\ \text{kJ} + 242\ \text{kJ}$

$= 478\ \text{kJ}$



Hess' Cycle; showing the relationship between B.E.'s and ΔH.

Second Step:

$$2\,H_{(g)} + 2\,Cl_{(g)} \longrightarrow 2\,HCl_{(g)}$$

$E_{H\text{-}Cl} = 431\ \text{kJ mol}^{-1}$

$E_P = \cancel{2}\ \text{mol} \times 431\ \text{kJ mol}^{-1} = 862\ \text{kJ}$

The standard enthalpy change in the reaction is obtained by the following formula:

$\Delta H_r^\circ = \sum E_R - \sum E_P$

$\Delta H_r^\circ = 678 - 862$

$\Delta H_r^\circ = -184$ kJ (for 2 mol of HCl)

$$\begin{tikzcd}
H_{2(g)} + Cl_{2(g)} \arrow[rr, "\Delta H_r^\circ"] \arrow[dr] & & 2HCl_{(g)} \\
& 2H_{(g)} + 2Cl_{(g)} \arrow[ur] &
\end{tikzcd}$$

Enthalpy of formation of HCl, $= -184/2\ \text{kJ} =$ **-92 kJ mol^{-1}**

The energy cycle is shown below:

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:

$E_{N\equiv N} = 945\ kJ\ mol^{-1}$, $E_{H\text{-}H} = 436\ kJ\ mol^{-1}$, $E_{N\text{-}H} = 391\ kJ\ mol^{-1}$.

Calculate the enthalpy change of the above reaction.

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 kJ mol^{-1}) are given below:

$E_{C\text{-}C} = +347$, $E_{C\text{-}H} = +410$, $E_{C\text{-}O} = +336$, $E_{O=O} = +496$, $E_{C=O} = +805$, $E_{O\text{-}H} = +465$

6.9 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^o_{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^o_{sol} and it may be exothermic or endothermic. The enthalpy changes of solution of sodium carbonate and ammonium chloride are described by the equations below:

$$Na_2CO_{3(s)} + aq \longrightarrow 2\,Na^+_{(aq)} + CO_3{}^{2-}{}_{(aq)} \qquad \Delta H^o_{sol} = -25\ kJ\ mol^{-1}$$

$$NH_4Cl_{(s)} + aq \longrightarrow NH_4{}^+{}_{(aq)} + Cl^-_{(aq)} \qquad \Delta H^o_{sol} = +16.2\ kJ\ mol^{-1}$$

In Table 6.2 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. Two factors govern the process of dissolution

Table 6.2 Heats of solution of some important ionic solids (kJ mol^{-1})

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)

6.9.1 Hydration

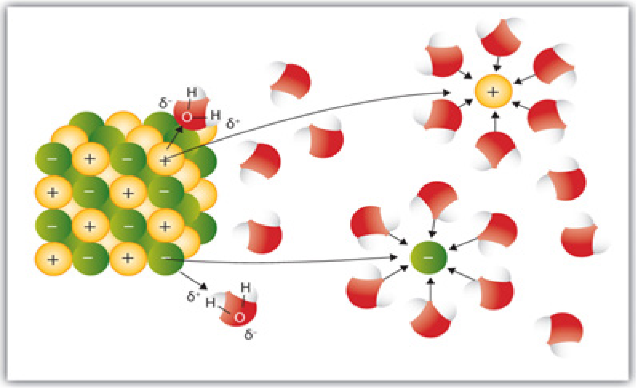


Figure 6.5 Dissolution of an ionic compound through the process of hydration.

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 6.5.** 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:

"The enthalpy change involved when one mole of a solute is dissolved in excess of water to make infinitely dilute solution under standard conditions."

It is denoted by ΔH_{hyd}. This energy is always released as it is formation of *ion-dipole bond*.

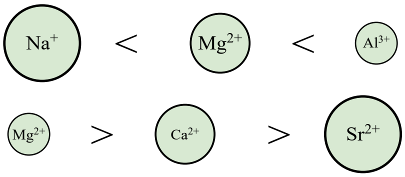
Factors Affecting the magnitude of Hydration Energy

The heat of hydration depends on following factors:

i. Charge on the ion

ii. Size of the ion

We use a combined term for these two factors i.e., "charge density" 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 following ions are in the order:



On the same basis we can explain the hydration energy of anions.

6.9.2 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."

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H^o_{latt} = -787 \text{ kJ mol}^{-1}$$

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 6.6 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.

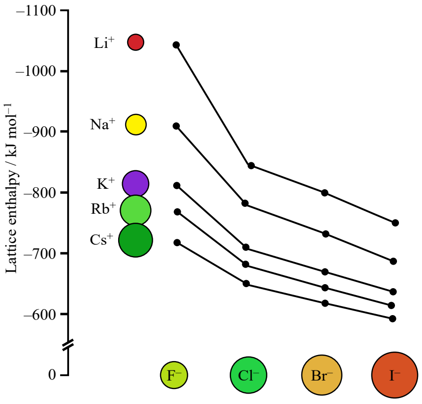


Figure 6.6 Lattice energies of alkali metal halides

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. 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.
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. $\mathbf{\Delta H^{\circ}_{sol}}$ becomes more exothermic so solubility increase.

- Now look at the solubility trends of group II metal sulphates. Because 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 $BaSO_4$. $\mathbf{\Delta H^{\circ}_{sol}}$ becomes more endothermic so solubility increase.

6.9.3 Calculating Enthalpy Change of Solution (ΔH^o_{sol})

We can calculate the enthalpy change of solution or the enthalpy change of hydration by constructing an enthalpy cycle and using Hess' law (**Figure 6.7).**

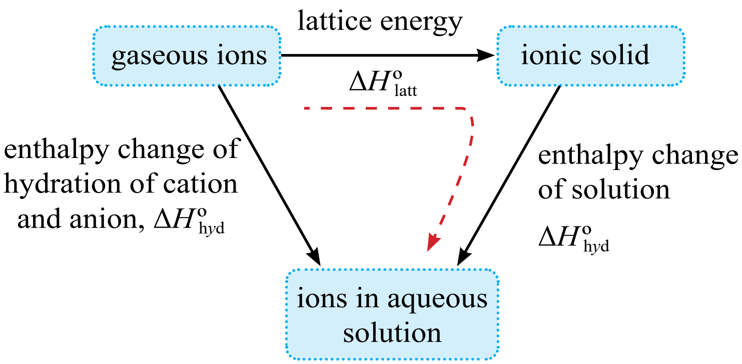


Figure 6.7 Energy cycle of formation of an aqueous solution of an ionic solid using Hess' law

We can see from this enthalpy cycle that:

$$\Delta H^o_{latt} + \Delta H^o_{sol} = \Delta H^o_{hyd}$$

We can use this energy cycle to calculate:

Sample problem 6.8

Determine the enthalpy change of solution (ΔH^o_{hyd} of sodium fluoride (NaF) using the following data:

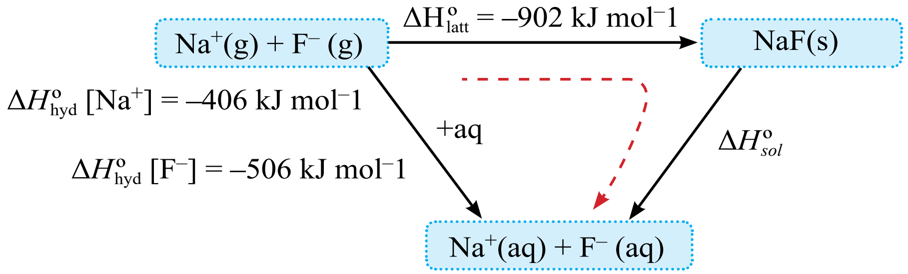
Lattice energy of sodium fluoride (NaF) = –902 kJ mol^{-1}

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

$\Delta H^{o}_{latt} + \Delta H^{o}_{sol} = \Delta H^{o}_{hyd}$

$\Delta H^{o}_{sol} = (-406) + (-506) - (-902)$

ΔH^{o}_{hyd} [NaF] = –10 kJ mol^{-1}

6.10 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^{o}_{latt} using several experimental data and an energy cycle called the Born–Haber cycle. Born-Haber cycle is an application of Hess' law. Let us consider calculation of lattice energy of sodium Chloride using hess's law and Born-Haber cycle.

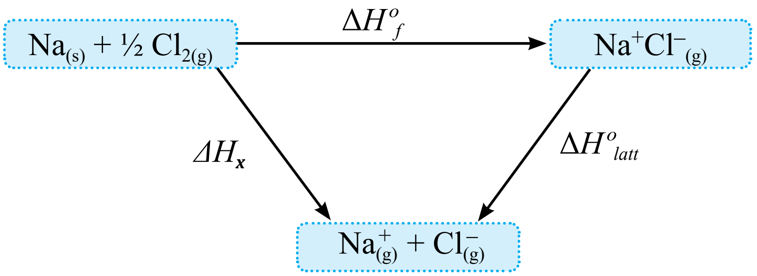


Figure 6.8 Enthalpy cycle of sodium chloride

where,

ΔH^{o}_{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' law on the above energy cycle, we can write

$$\Delta H_x + \Delta H^{o}_{latt} = \Delta H^{o}_{f}$$

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 6.9**.

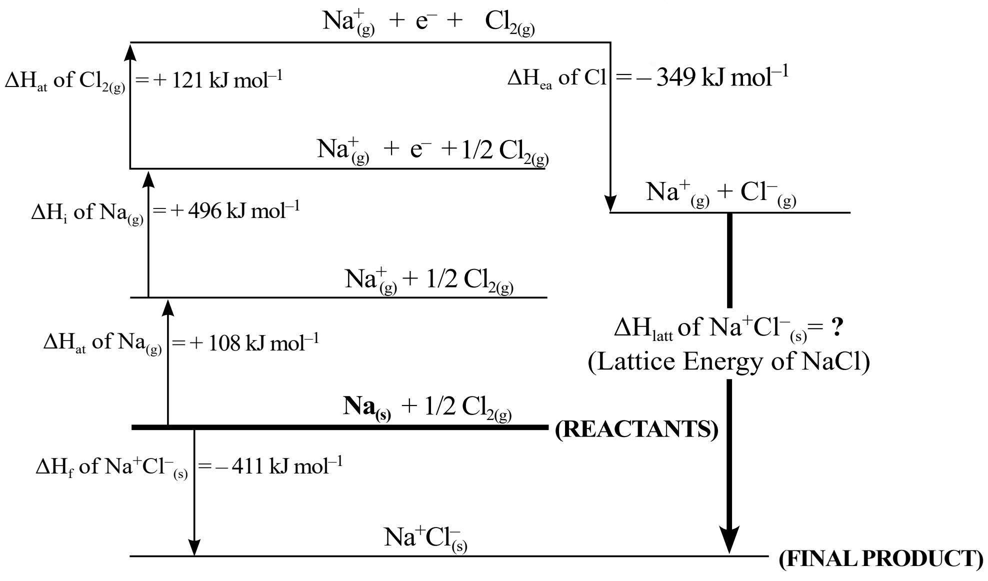


Figure 6.9 Born Haber cycle of sodium chloride (not according to scale)

Calculation of ΔH_x

From above cycle we have,

$$\Delta H_x = \Delta H_{at\ (Na)} + \Delta H_{i1\ (Na)} + \Delta H_{at\ (Cl2)} + \Delta H_{ea1\ (Cl2)}$$

$$\Delta H_x = 376\ \text{kJ mol}^{-1} \text{--------------(ii)}$$

Using, $\mathbf{\Delta H^o_{latt} = \Delta H^o_f - \Delta H_x}$

$$\mathbf{\Delta H^o_{latt} = -787\ kJ\ mol^{-1}}$$

Sample problem 6.9 Calculate the heat of formation of sodium fluoride, which crystallizes in the sodium chloride lattice. The heat of atomization of $Na_{(s)}$ is 109 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' law:

$$\mathbf{\Delta H^o_f = \Delta H^o_{latt}} + \Delta H^o_{at\ (Na)} + \Delta H^o_{1i\ (Na)} + \Delta H^o_{at\ (F2)} + \Delta H^o_{1ea\ (F)}$$

$$= (-939 + 109 + 494 + 79 - 328)\ \text{kJ mol}^{-1}$$

$$\mathbf{\Delta = -585\ kJ\ mol^{-1}}$$

Quick Check 6.7

a) Draw Born-Haber cycle for sample problem 6.8.

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.

6.11 ENTROPY

Entropy is a measure of the number of ways energy can be distributed within a system at a specific temperature. When the energy is distributed in more ways, a system is more stable. Entropy can also be thought of as 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.

6.11.1 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 6.10** below.

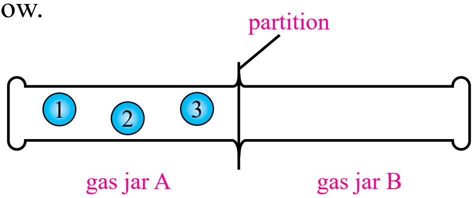


Figure 6.10 Diffusion and number of possible arrangements

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.

6.11.2 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. $Br_{2(\ell)}$ S^O = 151.6 J K^{-1} mol^{-1} and $I_{2(s)}$ S^O = 116.8 J K^{-1} mol^{-1}

ii. $H_{2(g)}$ S^O = 130.6 J K^{-1} mol^{-1} and $CH_{4(g)}$ S^O = 186.2 J K^{-1} mol^{-1}

iii. $Hg_{(\ell)}$ S^O = 76.00 J K^{-1} mol^{-1} and $Na_{(s)}$ S^O = 51.20 J K^{-1} mol^{-1}

iv. $SO_{2(g)}$ S^O = 248.1 J K^{-1} mol^{-1} and $SO_{3(\ell)}$ S^O = 95.60 J K^{-1} mol^{-1}

6.11. 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. 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:

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

There is an increase in entropy of the above system because the a gas is being produced (high entropy) but the reactant, calcium carbonate, is a solid (low entropy). Such reactions are spontaneous.

Also, consider the reaction:

$$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$$

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 (**ΔS^o** = +ve) means a spontaneous process

A negative entropy change value(**ΔS^o** = -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.

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) $N_{2(g)} + 3H_{2(g)} 2NH_3(g)$ ii) $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$

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
- ii. Water turning to ice at -10 °c iii. Ethanol vaporising at 20 °c
- iv. Water mixing completely with salt
- v. Limestone (calcium carbonate) decomposing at room temperature

6.11.4 Calculating the Entropy Change of the System (Reaction)

In order to calculate the entropy, change of the system we use the relationship:

$$\Delta S^O_{\text{system}} = S^O_{\text{products}} - S^O_{\text{reactants}}$$

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:

$$S^O_{[Ca(s)]} = 41.40 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$S^O_{[O2(g)]} = 205.0 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$S^O_{[CaO(s)]} = 39.70 \text{ J K}^{-1} \text{ mol}^{-1},$$

As $\Delta S^O_{\text{system}} = S^O_{\text{products}} - S^O_{\text{reactants}}$

$$= 2 \times S^O_{[CaO(s)]} - \{2 \times S^O_{[Ca(s)]} + S^O_{[O2(g)]}\}$$
$$= 2 \times 39.70 - \{(2 \times 41.40) + 205.0\}$$
$$= 79.40 - 287.8$$
$$\Delta S^O_{\text{system}} = -208.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

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.

6.12 FREE ENERGY (G)

The heat content, or enthalpy (H) of any system is a combination of the following:

i. That, which is free to be converted to other forms of energy and is called Gibbs free energy, G.

ii. That, which is necessary to **maintain the system** at the specified temperature, and this is unavailable for conversion (T x S).

This can be expressed as,

$$H = G + TS$$

It follows from the equation that all of the enthalpy of a system would be available only if the system were at zero kelvin temperature.

The following equations can be written to express the enthalpies of two different states:

$$\Delta H = \Delta G + \Delta(TS)$$

For a process occurring at constant temperature,

$$\Delta H = \Delta G + T\Delta S \quad \text{(at constant T)}$$

$$\text{or} \quad \Delta G = \Delta H - T\Delta S \quad \text{(constant T)}$$

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

6.12.1 Calculating ΔG° for a Reaction

Sample Problem 6.12

For the reaction:

$$CaSO_{4(s)} \xrightarrow{\hspace{3em}} Ca^{2+}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

Calculate ΔH°, ΔS° and ΔG° at 25 °C using the following data; and discuss its spontaneity.

Heat of Formation:

$\Delta H^\circ_f\,[CaSO_{4(s)}] = -1432.7$ kJ, $\Delta H^\circ_f[Ca^{2+}_{(aq)}] = -543.0$ kJ, $\Delta H^\circ_f[SO_4{}^{2-}{}_{(aq)}] = -907.5$ kJ

Standard entropy:

$S^\circ[CaSO_{4(s)}] = 106.7$ J/K, $S^\circ[Ca^{2+}_{(aq)}] = -55.2$ J/K , $S^\circ[SO_4{}^{2-}{}_{(aq)}] = +17.2$ J/K

Solution

$$\Delta H^\circ = \sum \Delta H_{f\,(products)} - \sum \Delta H_{f\,(reactants)} = [-543.0 - 907.5] - [-1432.7] = \mathbf{-17.8\ kJ}$$

$$\Delta S^\circ = \sum S^\circ_{(products)} - \sum S^\circ_{(reactants)} = [(-55.2 + 17.2) - (106.7)]\ \text{J/K} = -1447\ \text{J/K}$$

$$\Delta S^\circ = \mathbf{-0.1447\ kJ/K}$$

$\Delta G° = \Delta H° - T\,\Delta S° = (-17.8\ \text{kJ}) - (298\ \text{K}) \times (-0.1447\ \text{kJ/K}) = \mathbf{+\ 25.3\ kJ}$

Result: We conclude that this process is nonspontaneous at standard conditions at 25 °C

Sample Problem 6.13

What is the standard free-energy, ΔG° for the following reaction (Haber's process) at 25°C?

$$N_{2(g)} + 3\ H_{2(g)} \longrightarrow 2\ NH_{3(g)}$$

Also discuss its spontaneity.

Heat of Formation: $\Delta H°_f\,[N_{2(g)}] = 0$ kJ, $\Delta H°_f[H_{2(g)}] = 0$ kJ, $\Delta H°_f[NH_{3(g)}] = -45.9$ kJ

Standard entropy: $S°[\ N_{2(g)}] = 191.5$ J/K, $S°[H_{2(g)}] = 130.6$ J/K , $S°[\ NH_{3(g)}] = +193$ J/K

Solution

$\Delta H° = \sum \Delta H_{f\,(products)} - \sum \Delta H_{f\,(reactants)} = [2 \times (-45.9)] - [0 + 0] = \mathbf{-91.8\ kJ}$

$\Delta S° = \sum nS°_{(products)} - \sum mS°_{(reactants)} = [2 \times (193)] - [191.5 + 3 \times 130.6]\ \text{J/K} = -197\ \text{J/K}$

$\Delta S° = \mathbf{-0.197\ kJ/K}$

$\Delta G° = \Delta H° - T\,\Delta S° = (-91.88\ \text{kJ}) - (298\ \text{K}) \times (-0.197\ \text{kJ/K}) = -33.1\ \mathbf{kJ}$

Result

Since ΔG° is a negative value, thus it is concluded that Haber's process is spontaneous at standard conditions , i.e. at 25 °C.

EXERCISE

MULTIPLE CHOICE QUESTIONS

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 (diamond) + $2H_{2(g)}$ $C_2H_{4(g)}$

b) 2C (graphite) + $2H_{2(g)}$ $C_2H_{4(g)}$

c) C (graphite) + $H_{2(g)}$ **½** $C_2H_{4(g)}$

d) 2C (diamond) + $4H_{(g)}$ $C_2H_{4(g)}$

II. Which of the following equations correctly defines lattice energy of $MgCl_2$?

a) $Mg_{(s)} + Cl_{2(g)}$ $MgCl_2$

b) $Mg^{2+}_{(g)} + 2Cl^-_{(g)}$ $MgCl_{2(g)}$

c) $Mg^{2+}_{(s)} + 2Cl^-_{(g)}$ $MgCl_{2(s)}$

d) $Mg^{2+}_{(g)} + 2Cl^-_{(g)}$ $MgCl_{2(s)}$

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)
c) Enthalpy change (ΔH)
d) Specific heat capacity (c)

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) $\Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}$
b) $\Delta H_{\text{lattice}} - \Delta H_{\text{hydration}}$
c) $-\Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}$
d) $-\Delta H_{\text{lattice}} - \Delta H_{\text{hydration}}$

IX. Which of the following reactions has an enthalpy change that is equal to the standard enthalpy of formation of water, $\Delta H^\circ_f[H_2O_{(l)}]$?

a) $2H_{(g)} + O_{(g)} \rightarrow H_2O_{(l)}$
b) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$
c) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$
d) $2H^+_{(aq)} + O^{2-}_{(aq)} \rightarrow H_2O_{(l)}$

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 ΔH>0 and ΔS<0. This reaction will be:

a) Spontaneous at all temperatures b) Non-spontaneous at all temperatures

c) Spontaneous only at high temperaturesd) Spontaneous only at low temperatures

SHORT-ANSWER QUESTIONS

Q.2Attempt the following short-answer questions:

a. Differentiate between exothermic and endothermic reactions.

b. What do you understand by the enthalpy of a system?

c. Differentiate clearly between entropy (S) and Gibbs free energy (G).

d. Distinguish clearly between standard enthalpy of reaction and standard enthalpy of formation.

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

f. Explain why the lattice enthalpy of an ionic compound is typically a large negative value.

g. What factors influence the magnitude of the lattice enthalpy?

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?

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.

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?

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.

l. 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.

DESCRIPTIVE QUESTIONS

Q.3 State and explain Hess' law. Give its two applications.

Q.4 What is lattice energy? How does Born-Haber cycle help to calculate the lattice energy of NaCl?

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

Q.6 By applying Hess' 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) $NH_{3(g)} + aq \quad NH_{3(aq)} \longrightarrow \Delta H = -35.16\ kJ\ mol^{-1}$

(ii) $HCl_{(g)} + aq \quad HCl_{(aq)} \longrightarrow \Delta H = -72.41\ kJ\ mol^{-1}$

(iii) $NH_{3(aq)} + HCl_{(aq)}\ NH_4Cl_{(aq)} \longrightarrow \Delta H = -51.48\ kJ\ mol^{-1}$

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 $-285.8\ kJ\ mol^{-1}$

Q8 Using the information given in the table below, calculate the lattice energy of potassium bromide.

Reactions	ΔH/ kJ mol^{-1}
$K_{(s)} + \frac{1}{2} Br_{2(l)} \longrightarrow K^+Br^-$	−392
$K_{(s)} \longrightarrow K_{(g)}$	+90
$K_{(s)} \longrightarrow K^+_{(g)} + e^-$	+420
$\frac{1}{2} Br_{2(l)} \longrightarrow Br_{(g)}$	+112
$Br + e^- \longrightarrow Br^-$	−342

Q.9 Calculate the entropy change of the surroundings $\Delta S°_{surrounding}$ for the reaction at 298K :

$$2Ca_{(s)} + O_{2(g)} \longrightarrow 2CaO_{(s)} \quad \Delta H^O_{reaction} = -1270.2\ kJ\ mol^{-1}$$

Q.10 For the reaction: $CaSO_{4(s)} \qquad Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

Calculate ΔH°, ΔS° and ΔG° at 25 °C using the following data; and discuss its spontaneity.

Enthalpy of Formation:

$\Delta H°_{f\ (CaSO4(s))} = -1432.7$ kJ, $\Delta H°_{f\ (Ca^{2+}{}_{(aq)})} = -543.0$ kJ, $\Delta H°_{f\ (SO4^{2-}{}_{(aq)})} = -907.5$ kJ

[Standard entropy: $S°_{(CaSO4(s))} = 106.7$ J/K, $S°_{(Ca^{2+}{}_{(aq)})} = -55.2$ J/K, $S°_{(SO4^{2-}{}_{(aq)})} = +17.2$ J/K]

7

REACTION KINETICS

STUDENT LEARNING OUTCOMES [C-11-A-124 to C-11-A-134]

- 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 hydrolysic of ester proceeds at a moderate rate. Whereas, rusting of iron is a slow process.

Reaction kinetics is the study of the rates of chemical reactions. 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 occuring 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.

7.1 COLLISION THEORY

Collision theory explains how reactions occur. 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. 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. 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.

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) The collision frequency and the orientation of molecules are necessary conditions a reaction to occur. Justify the statement.

b) What role does the activation energy play in chemical reactions?

c) How does the activation energy affect the rate of reaction?

7.2 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. 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.

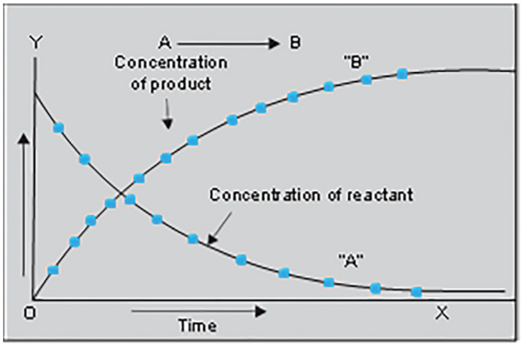


Figure 7.1 Change in the concentration of reactants and products with time for the reaction A → B

$$\textit{Rate of reaction} = \frac{\textit{change in concentration of the substance}}{\textit{time taken for the change}}$$

$$\textit{Rate of reaction} = \frac{\Delta x}{\Delta t}$$

Where Δx is a very small change in the concentration of a reactant or a product in a very small time interval Δt.

The situation is explained graphically in **Figure 7.1.** for the reactant A which is changing irreversibly to the product B.

$$\mathbf{A} \longrightarrow \mathbf{B}$$

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.

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 $dm^{-3}s^{-1}$.

$$\text{Rate of reaction} = \frac{mol.dm^{-3}}{seconds} = mol.dm^{-3}\,s^{-1}$$

However, 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.

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.

7.2.1 Instantaneous and Average Rate

The rate at any one instant during the interval is called the instantaneous rate. Whereas 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.

Sample Problem 7.1

The reaction for the formation of ammonia in Haber process is:

$$N_{2(aq)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$

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

$\Delta C = \Delta[NH_3] = (6.2\text{-}3.5)\ \text{mol.dm}^{-3}$; $\Delta c = 2.7\ \text{mol. dm}^{-3}$

$\Delta t = (4.0 - 1.0)$; $\Delta t = 3.0$ min

$$\text{Rate of formation of } NH_3 = \frac{\Delta C}{\Delta t} = \frac{\Delta[NH_3]}{\Delta t} = \frac{2.7\ \text{mol.dm}^{-3}}{3\ \text{min}} = \mathbf{0.90\ mol\ dm^{-3}min^{-1}}$$

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?

7.2.2 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.

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. 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 (7.3). 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

Table 7.1 Change in concentration of HI with regular intervals $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$

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

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.

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 7.2** shows that in 100 sec, the change in concentration is 0.04 mol.dm^{-3}. The rate is then calculated by using the following expression.

$$Rate\ of\ reaction = \frac{\Delta C}{\Delta T}$$

$$rate = \frac{0.04\ mol.dm^{-3}}{100\ sec} = 4 \times 10^{-4}\ mol\ dm^{-3}\ s^{-1}$$

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.

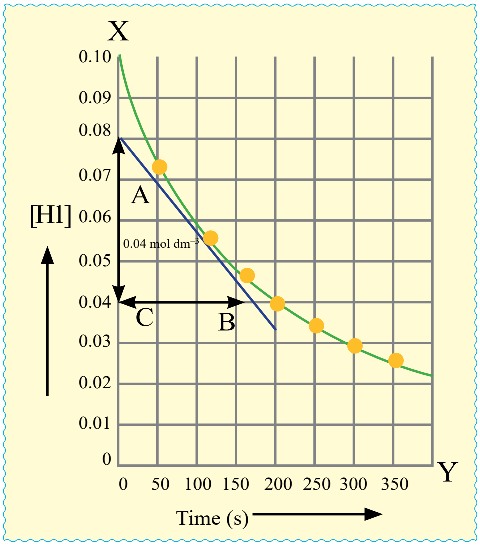


Figure 7.2 The change in the HI concentration with time to the reaction $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$ at 508ºC

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 4x10^{-4} mol dm^{-3} s^{-1}.

Quick Check 7.3

a) Plot the data in Table 7.1 for HI.

b) Calculate the rate after 300 sec (when the concentration is 0.03 mol dm^{-3}) by drawing a tangent.

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.

d) What do you deduce about the rate of the reaction with time from these calculations?

e) At which concentration, the rate is highest, and lowest?

7.2.3 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. The acid hydrolysis of an ester (ethyl acetate) in the presence of a small amount of an acid is one of the best examples.

$$CH_3COO_2H_{5(\ell)} + H_2O_{(\ell)} \xrightarrow{H^+} CH_3COOH_{(\ell)} + C_2H_5OH_{(\ell)}$$

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.

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 7.3**, the concentration can be measured using the colorimetry.

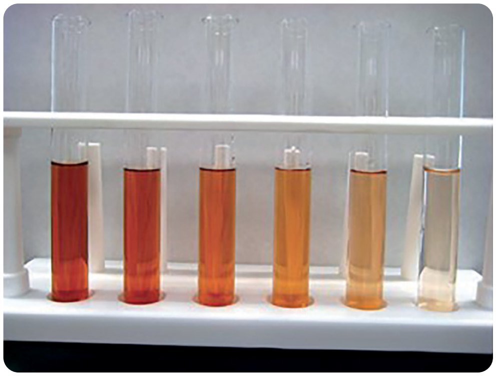


Figure 7.3 The concentration change for this reaction can be determined using colorimetry.

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.

iii) Volume change method

This method is useful for those reactions, which involve changes in volumes of gases as shown in **Figure 7.4.** The volume change is directly proportional to the extent of reaction, and changes in concentration.

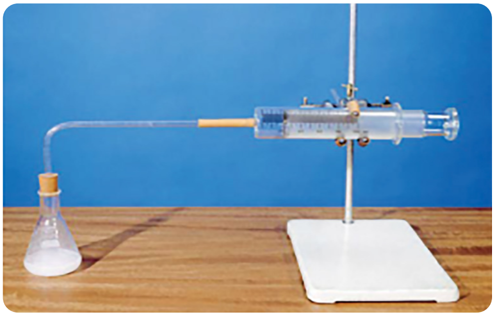


Figure 7.4 Rate of reaction can be followed by measuring the change in volume of a gas given off in a reaction.

Interesting Information

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.

7.3 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?

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.

7.3.1 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.

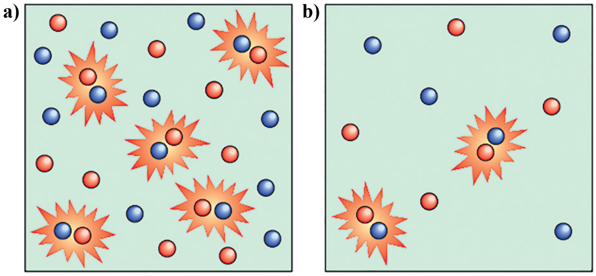


Figure 7.5 The reaction in box **a)** will occur faster than that in, **b)** due to the higher concentration.

7.3.2 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.

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

Figure7.6, this is called the **Boltzmann distribution.** As you know that 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 7.6** 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.

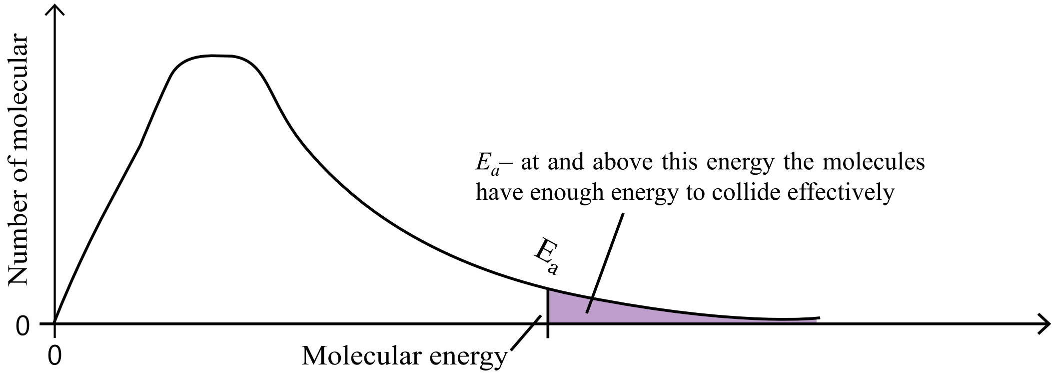


Figure 7.6 The Boltzmann distribution of molecular energies showing the activation energy

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 7.8**. 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.

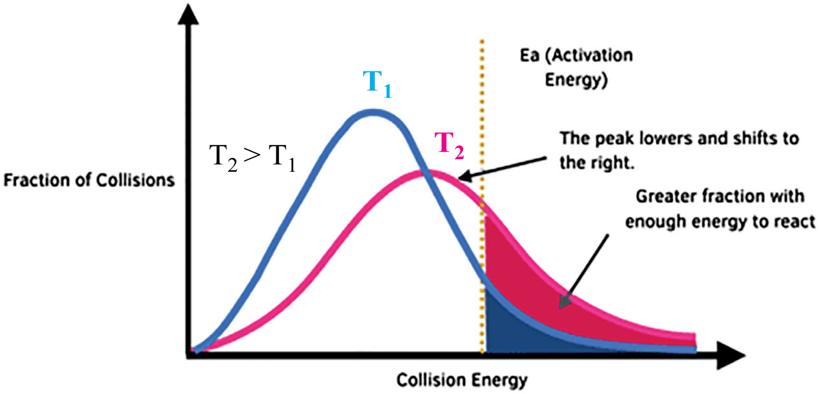


Figure 7.7 The Boltzmann distribution of molecular energies at temperatures T_1 and T_2

Quick Check 7.4

a) What is the Boltzmann distribution curve?

b) Explain why a 10 °C rise in temperature approximately doubles the rate of a reaction.

7.3.3 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. For 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. A catalyst provides a new reaction path with a low activation energy barrier, as shown in **Figure 7.8**. A greater number of molecules are now able to get over the new energy barrier and reaction rate increases.

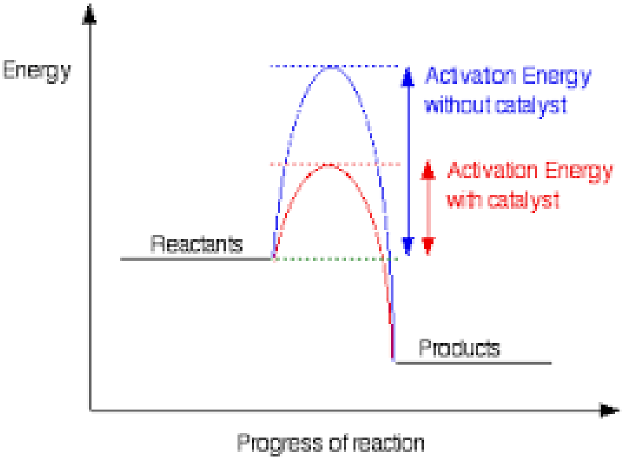


Figure 7.8 The energy path diagram for an uncatalyzed and a catalyzed reaction

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:

i. 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.

$$2SO_{2\,(g)} + O_{2\,(g)} \xrightarrow{NO} 2SO_{3(g)}$$

ii. Esters are hydrolyzed in the presence of H_2SO_4. Both the reactants and the catalyst are in the solution state.

$$CH_3COOCH_2CH_{3(\ell)} + H_2O_{(\ell)} \xrightarrow{H^+} CH_3COOH_{(\ell)} + CH_3CH_2OH_{(\ell)}$$

Ethyl ethanoate Ethanoic acid Ethanol

Did you Know!

Biochemical catalysts, commonly known as enzymes (nature's catalyst) are essential molecules in living organisms' function by lowering 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.

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.

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{Pt,\ 800^oc} 4NO_{(g)} + 6H_2O_{(g)}$$

Hydrogenation of unsaturated organic compounds are catalysed by finely divided Ni, Pd or Pt.

$$C_2H_{4(g)} + H_{2(g)} \xrightarrow{Ni,\ 150^oC} C_2H_{6(g)}$$

Interesting Information

Vitamins are organic compounds that act as catalysts in biochemical reactions, especially when they function as 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.

Quick Check 7.5

a) Can a catalyst be consumed in a chemical reaction? Why or why not?

b) Explain whether the reaction below is an example of heterogeneous or homogeneous catalysis:

$$2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$$

c) Draw an energy profile diagram to show a typical uncatalysed reaction and an enzyme-catalysed reaction.

On your diagram show:

i) the activation energy for the catalysed and

ii) uncatalysed reactions

7.4 RATE LAW, RATE CONSTANT AND ORDER OF REACTION

7.4.1 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. The representation of rate of a reaction in terms of concentration of the reactants is known as **rate law**. 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.

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 and the proportionality constant k is called rate constant for the reaction.

If $[A] = 1\ \text{mol dm}^{-3}$ and $[B] = 1\ \text{mol dm}^{-3}$

$$\text{Rate of reaction} = k \times 1^x \times 1^y = k$$

The rate constant 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.

7.4.2 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”. Thus, the reaction is of order ‘x’ with respect to A and of order ‘y’ with respect to B. The overall order of reaction is (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.

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

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?

b) Explain what is meant by the specific rate (rate constant) of a reaction and how it is represented in rate equation.

7.4.3 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.

For the general reaction: $A \longrightarrow \text{Product}$

$$\text{Rate} = k\,[A]^0$$

Examples:

i) $H_2(g) + Cl_2 \xrightarrow{\qquad} 2HCl(g)$

$$\text{Rate} = k\,[H_2]^0[Cl_2]^0 = k$$

ii) $2NH_3 \xrightarrow{\qquad} N_2 + 3H_2$

$$\text{Rate} = k\,[NH_3]^0 = k$$

Photochemical reactions are usually zero order.

First Order Reaction

In these reactions, there may be multiple reactants present, but concentration of only one reactant will change during the reaction. Examples of a first order reaction is:

Decomposition of nitrogen pentoxide involves the following equation.

$$2N_2O_{5(g)} \xrightarrow{\qquad} 2N_2O_{4(g)} + O_{2(g)}$$

The experimentally determined rate equation for this reaction is as follows:

$$\text{Rate} = k[N_2O_5] \quad (n = 1)$$

This equation suggests that the reaction is first order with respect to the concentration of N_2O_5.

Second Order Reaction

A reaction for which sum of the exponents of the concentrations in the rate equation is 2. 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.

$$\text{Rate} = k[A]^2 \quad (n = 2)$$

$$\text{Rate} = k\,[A]^1[B]^1 \quad (n = 1+1 = 2)$$

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.

$$NO(g) + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)} \qquad \text{Rate} = k[NO][O_3]$$

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.

$\text{Rate} = k[A]^3 \quad (n = 3)$

or $\text{Rate} = k\,[A]^2[B]^1 \quad (n = 2+1 = 3)$

or $\text{Rate} = k\,[A]^1[B]^1[C]^1 \quad (n = 1+1+1 = 3)$

$$2FeCl_{3(aq)} + 6KI_{(aq)} \longrightarrow 2FeI_{2\,(aq)} + 6KCI_{(aq)} + I_2$$

This reaction involves eight reactant molecules but experimentally it has been found to be a third order reaction.

$$\text{Rate} = k[FeCl_3][KI]^2$$

also, the following reaction is third order

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)} \qquad \text{Rate} = k[NO]^2[O_2]^1$$

Fractional Order Reaction

A reaction in which the sum of exponents of rate equation is in fraction, is called the fractional order reaction. For example, consider the formation of carbon tetrachloride from chloroform.

$$CHCl_{3(l)} + Cl_{2(g)} \longrightarrow CCl4_{(l)} + HCl_{(g)}$$

$$\text{Rate} = k[CHCl_3]\,[Cl_2]^{1/2} \qquad n = 1 + 1/2 = 1.5$$

Reactions involving free radicals frequently exhibit fractional orders.

7.4.4 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:

$$\text{Rate} = k[\text{Reactants}]^n \qquad \text{where } n = \text{order of reaction}$$

$$k = \frac{\text{Rate}}{(\text{Rectants})^n} = \frac{(\text{mol dm}^{-3})\ s^{-1}}{(\text{mol dm}^{-3})^n}$$

$$\text{or } k = (\text{mol.dm}^{-3})^{1-n}\ s^{-1}$$

$$\text{or } k = (\text{concentration})^{1-n}\ s^{-1}$$

This equation can be used to determine units of any order of reaction.

For a **zero order reaction** (n = 0),

$$k = (\text{mol.dm}^{-3})^{1-0}\ s^{-1}$$

$$k = \text{mol.dm}^{-3}\ s^{-1}$$

For a first order reaction (n = 1), the rate is directly proportional to the concentration of one reactant.

$$k = (\text{mol.dm}^{-3})^{1-1}\ s^{-1}$$

$$k = (\text{mol.dm}^{-3})^{0}\ s^{-1}$$

$$k = s^{-1}$$

Therefore, the units of k for a first order rate constant are s^{-1}.

For a second order reaction (n = 2),

$$k = (\text{mol dm}^{-3})^{1-2}\ s^{-1}$$

$$k = \text{mol}^{-1}\ \text{dm}^{3}\ s^{-1}$$

$$k = \text{dm}^{3}\ \text{mol}^{-1}\ s^{-1}$$

The units of k for a second order rate constant are $dm^3\ mol^{-1}\ s^{-1}$.

For a third order reaction (n = 3),

$$k = (\text{mol dm}^{-3})^{1-3}\ s^{-1}$$

$$k = \text{mol}^{-2}\ \text{dm}^{6}\ s^{-1}$$

$$k = \text{dm}^{6}\ \text{mol}^{-2}\ s^{-1}$$

Therefore, the units of k for a third order rate constant are $dm^6\ mol^{-2}\ s^{-1}$.

Quick Check 7.7

a) Calculate the overall order of reactions which have the rate expressions:

   i) rate = $k[NO]^2\ [NH_3]^0$

   ii) rate = $k[BrO_3][Br^-][H^+]^2$

b) Why do you think chemists want to know the order of a reaction and the rate constant for a reaction?

c) Why the sum of the coefficients of a balanced chemical equation is not necessarily important to give the order of a reaction?

7.5 DETERMINATION OF RATE CONSTANT

The rate constant (k) of a reaction can be calculated using the following two methods:

7.5.1 Initial Concentration Method

In the presence of hydrogen ions, hydrogen peroxide, H_2O_2, reacts with iodide ions to form water and iodine:

$$H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \longrightarrow 2H_2O_{(l)} + I_{2(aq)}$$

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 7.2** 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

$$k = \frac{3.50 \times 10^{-6} \times (0.0100)}{(0.0200)}$$

$$k = 1.75 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

Table 7.2: Effect of change in concentrations of reactants on the rate of reaction

Experiment	$[H_2O_2]$/ moldm^{-3}	$[I^-]$/ moldm^{-3}	$[H^+]$/ moldm^{-3}	Initial rate of reaction/moldm^{-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 $[H^+]$.

7.5.2 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". 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:

$$k = 0.693/t_{1/2}$$

Here is an example to help you understand how the process is done. 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:

$$2 \times 60 \times 60 = 7200 \text{ s}$$

We then simply substitute this value into the equation:

$$k = \frac{0.693}{7200 \text{ s}}$$

$$k = 9.6 \times 10^{-5} \text{ s}^{-1}$$

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:

$$k = \frac{0.693}{t_{1/2}}$$

$$k = \frac{0.693}{17 \times 60\ s}$$

$$= 6.79 \times 10^{-4}\ dm^3\ mol^{-1}\ s^{-1}$$

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.

7.6 REACTION MECHANISM

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. The number of reactant molecules involved in an elementary step is called its molecularity.

A unimolecular elementary reaction involves only a single reactant molecule. The example of a unimolecular reactions is the 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 **termolecular** 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 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. So 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.

Lets consider the following reaction:

$$2NO_{(g)} + 2H_{2(g)} \longrightarrow 2H_2O_{(g)} + N_{2(g)}$$

Table 7.2 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 reactionis directly proportional to the first power of concentration of H_2.

$$\text{Rate} \propto [H_2]$$

Table 7.3: Effect of change in concentrations of reactants on the rate of reaction

[NO] in (mol dm$^-$)	[H_2] in (mol dm$^-$)	Initial rate (atm min-)
0.006^3	0.001^3	0.025^1
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

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.

$$\text{Rate} \propto [NO]^2$$

The overall rate equation of reaction is,

$$\text{Rate} \propto [H_2][NO]^2$$

$$\text{or} \quad \text{Rate} = k[H_2]^1[NO]^2$$

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.

$$\text{Step 1: } 2NO_{(g)} + H_{2(g)} \xrightarrow{\text{Slow}} N_{2(g)} + H_2O_{2(g)} \text{ (rate determining step)}$$

$$\text{Step 2: } H_2O_{2\,(g)} + H_{2(g)} \xrightarrow{\text{Fast}} 2H_2O_{(g)}$$

The step 1 is slow and rate determining.

Another example is 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. The experimental rate law is first order in NO_2 and in F_2:

$$\text{Rate} = k\,[NO_2][F_2] \qquad \text{(Observed)}$$

The accepted mechanism for the reaction is:

Step 1: $NO_{2(g)} + F_2 \xrightarrow{\text{Slow}} NO_2F_{(g)} + F^{\cdot}_{(g)}$ Rate = $k_1[NO_2][F_2]$

Step 2: $NO_{2(g)} + F^{\cdot}_{(g)} \xrightarrow{\text{Fast}} NO_2F_{(g)}$ Rate = $k_2[NO_2][F^{\cdot}]$

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

An acidified solution of hydrogen peroxide reacts with iodide ions.

$$H_2O_{2(aq)} + 2H^+_{(aq)} + 2I_{-(aq)}\ 2H_2O_{(l)} + I_{2(aq)}$$

The rate equation for this reaction is

rate = $[H_2O_2]\ [I^-]$

The mechanism below has been proposed for this reaction.

$H_2O_2 + I^- \xrightarrow{\text{Slow}} H_2O + IO^-$

$H+ + IO^- \xrightarrow{\text{Fast}} HIO$

$HIO + H^+ + I^- \xrightarrow{\text{Fast}} I_2 + H_2O$

Explain why this mechanism is consistent with the rate equation.

EXERCISE

MULTIPLE CHOICE QUESTIONS

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?

$$2NO_2 \rightarrow NO + NO_3 \quad (k_1) \quad \text{slow}$$

$$NO_3 + CO \rightarrow CO_2 + NO_2 \quad (k_2) \quad \text{fast}$$

a) $R = k_1 [NO_2]^3$ b) $R = k_2 [NO_3][CO]$

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 (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}

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. What do you understand by the rate of a reaction?

b. Give the difference between enthalpy change of reaction and energy of activation of reaction

c. Differentiate clearly between order and molecularity of a reaction.

d. Why the instantaneous rate changes during a reaction?

e. Briefly summarize the effects of temperature and surface area on the rates of reactions.

f. Justify that the radioactive decay is always a first order reaction.

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?

h. What is meant by half-life and what is it used for?

i. Why does wood burn more rapidly in pure oxygen than in air?

j. A catalyst lowers the activation energy of a chemical reaction. Illustrate it.

k. The rate constant for a certain reaction is $3.5\times10^{-4}\ s^{-1}$ at 25°C.

l. What is the order of the reaction.? Explain based on the units of the rate constant.

m. If the initial concentration of the reactant is $0.50\ mol\ dm^{-3}$, calculate the initial rate of the reaction.

n. How would the rate of this reaction change if the concentration of the reactant were doubled?

o. 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.

p. 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}.

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?

Q.4 How do you find the numerical value of a rate constant by initial and half-life methods?

Q.5 How does the activation energy profile of an uncatalyzed reaction compare with that of the catalyzed reaction?

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.

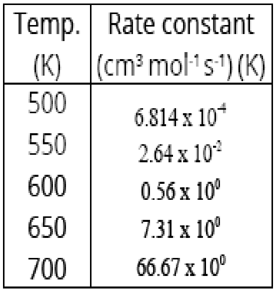
iii) What is the rate-determining step?

iv) Write the rate equation for the reaction, expressing it in terms of the reactants in the overall reaction.

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 $4.0M^{-2}s^{-1}$. Given the rate law for a reaction: Rate = $k[A][B]^2$.

Q.7 A first order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14}\ s^{-1}$. 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}

Q.8 Three experiments that have identical conditions were performed to measure the initial rate of the reaction. $2HI(g) \rightarrow H_2(g) + I_2(g)$ __________

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.

8

CHEMICAL EQUILIBRIUM

STUDENT LEARNING OUTCOMES [C-11-A-135 to C-11-A-148]

- 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)**

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. However, some reactions 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 this point, the concentrations of reactants and products become constant and the rates of the forward and reverse reactions become equal.

This chapter will deal with the equilibria of reversible processes, both physical and chemical changes. Examples of some reversible reactions are given below :

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

$$PCl_{5(g)} \rightleftharpoons PCI_{3(g)} + Cl_{2(g)}$$

The double arrow tells that the reaction is reversible.

8.1 MACROSCOPIC EVENTS AND MICROSCOPIC EVENTS

8.1.1 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. 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.

8.1.2 Microscopic Events

Microscopic events refer to the phenomena that cannot be observed with the naked eye. The collisions between molecules, breaking and forming bonds, rearrangement of atoms in molecules, loss. or gain of electrons are examples of microscopic events.

8.2 REVERSIBLE REACTIONS, MICROSCOPIC EVENTS AND DYNAMIC EQUILIBRIUM

When a 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.

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. When steam and carbon monoxide are mixed, a maximum number of collisions per second between them will occur as 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.

$$H_2O_{(g)} + CO_{(g)} \longrightarrow H_{2(g)} + CO_{2(g)}$$

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.

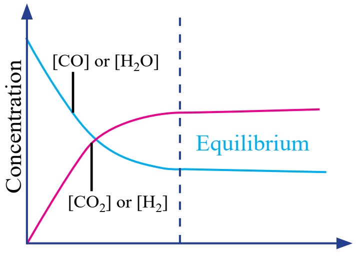


Figure 8.1 Plot of concentration vs time

$$H_{2(g)} + CO_{2(g)} \longrightarrow H_2O_{(g)} + CO_{(g)}$$

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. 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**.

The plots of the concentrations of reactants and products versus time for a general reaction are shown in **Figure 8.1**. 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 8.1 (a)**, or the amount of reactant may be lower or greater than that of the product as shown in **Figure 8.1 (b and c)**. However, for all of these graphs, it is clear that after the equilibrium is established, the concentrations become constant.

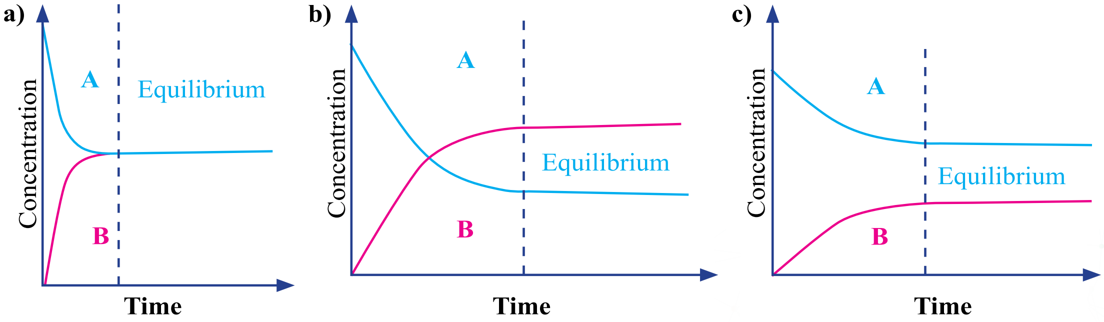


Figure 8.1 Plot of concentration vs time **(a)** Reactant = Product **(b)** Reactant < Product

(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.

8.3 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

b) The equilibrium is dynamic in nature, explain in terms of microscopic events.

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 and time.

ii. Plot a graph between rate of the reaction with respect to time.

8.4 DYNAMIC EQUILIBRIUM BETWEEN TWO PHYSICAL STATES

Dynamic equilibrium 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. For example, at 0 °C, ice and water coexist in equilibrium. Water changes into ice whereas ice converts back into water at the same rate.

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**.

$$\textbf{Liquid} \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \textbf{Gas}$$

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.

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.

b) Do you think that dynamic equilibrium exists between ice and water at 0°C? If yes, explain.

8.5 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. The equilibrium can be established only if the reaction vessel is closed. No part of the reactants and products is allowed to escape out.

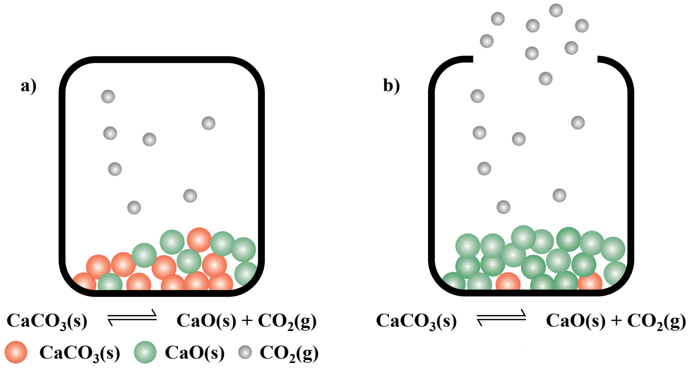


Figure 8.2 (a) Equilibrium is established when the system is closed
(b) Equilibrium can not be established in the open system.

8.6 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.

8.7 TYPES OF EQUILIBRIUM

With respect to the physical states of reactants and products, there are two types of chemical equilibrium.

8.7.1 Homogeneous Equilibrium

An equilibrium system in which all of the reactants and products are in the same phase. 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. 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

i. Condition for this equilibrium requires the closed cap of the bottle. Why?

ii. When the cap of the bottle is removed, to which direction the equilibrium shifts?

b) Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

c) In soda water bottles, gaseous CO_2 is in equilibrium with the aqueous CO_2 (HCO_3^- and H^+).

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons HCO^{3-}_{(aq)} + H^+_{(aq)}$$

8.8 EQUILIBRIUM CONSTANT AND POSITION OF EQUILIBRIUM

The position of equilibrium refers to the relative amounts of products and reactants present in an equilibrium mixture.

In 1864, the Norwegian chemists C. Guldberg (1836–1902) and P. Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. 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.

Consider the 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.

$$K_c = \frac{[C]^c\ [D]^d}{[A]^n\ [B]^b}$$

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. By the term active mass, we mean 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 α [A][B]

$$= k_f [A][B]$$

'k_f' is the proportionality constant, and is known as forward rate constant.

Rate of reverse reaction α [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,

$$k_f[A][B] = k_r[C][D]$$

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

The left side of this equation is the ratio of two rate constants, so it gives another constant called the equilibrium constant (K_c).

$$K_c = \frac{k_f}{k_r}$$

$$\text{So,} \quad K_c = \frac{[C][D]}{[A][B]}$$

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.

$$\text{Then} \quad K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

8.8.1 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) $2N_2O_{5\,(g)} \rightleftharpoons 4NO_{2\,(g)} + O_{2\,(g)}$

$$K_c = \frac{[NO_2]^4\,[O_2]}{[N_2O_5]^2}$$

Sample Problem 8.1

Ethanol reacts with ethanoic acid to form ethyl ethanoate and water.

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

Ethanoic acid **Ethanol** **Ethyl Ethanoate** **Water**

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.

$$\begin{array}{ccccccc} CH_3COOH_{(l)} & + & C_2H_5OH_{(l)} & \rightleftharpoons & CH_3COOC_2H_{5(l)} & + & H_2O_{(l)} \\ \dfrac{0.235\text{ mol}}{0.5\text{ dm}^3} & & \dfrac{0.0350\text{ mol}}{0.5\text{ dm}^3} & & \dfrac{0.182\text{ mol}}{0.5\text{ dm}^3} & & \dfrac{0.182\text{ mol}}{0.5\text{ dm}^3} \\ 0.470\text{ mol dm}^{-3} & & 0.070\text{ mol dm}^{-3} & & 0.364\text{ mol dm}^{-3} & & 0.364\text{ mol dm}^{-3} \end{array}$$

Step 2 Write the equilibrium constant for this reaction in terms of concentrations.

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]} = \frac{(0.364\text{ mol dm}^{-3})\ \ (0.0364\text{ mol dm}^{-3})}{(0.470\text{ mol dm}^{-3})\ \ (0.070\text{ mol dm}^{-3})}$$

Step 3 Substitute the equilibrium concentrations into the expression

$$K_c = 4.03 \text{ (to 3 significant figures)}$$

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:

$$\begin{array}{ccccc} CH_3COCH_{3\ (l)} & + & HCN_{\ (g)} & \rightleftharpoons & CH_3C(OH)(CN)CH_{3\ (l)} \\ \textbf{Propanone} & & \textbf{Hydrogen cyanide} & & \textbf{Product} \end{array}$$

A mixture of 0.0500 mol dm^{-3} propanone and 0.0500 mol dm^{-3} hydrogen cyanide is left to reach equilibrium at room temperature. At equilibrium the concentration of the product is 0.0233 mol dm^{-3}. Calculate K_c for this reaction.

Solution:

Step 1 Write out the balanced chemical equation with all the data underneath:

	$CH_3COCH_{3\ (l)}$	+	$HCN_{\ (g)}$	$\rightleftharpoons$	$CH_3C(OH)(CN)CH_{3\ (l)}$
Initial conc.	0.0500 mol dm^{-3}		0.0500 mol dm^{-3}		0 mol dm^{-3}
Equil. conc.	?		?		0.0233 mol dm^{-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:

$$CH_3COCH_3;\ 0.0500 - 0.0233 = 0.0267\text{ mol dm}^{-3}$$

$$HCN;\ 0.0500 - 0.0233 = 0.0267\text{ mol dm}^{-3}$$

Step 3 Write the equilibrium constant for this reaction in terms of concentrations:

$$K_c = \frac{[CH_3C(OH)(CN)CH_3]}{[CH_3COH_3]\,[HCN]} = \frac{(0.0233\text{ mol dm}^{-3})}{(0.05\text{ mol dm}^{-3})\ \ \ (0.05\text{ mol dm}^{-3})}$$

Step 4 Substitute the equilibrium concentrations into the expression

$$K_c = 32.7 \text{ mol dm}^{-3}$$

Quick Check 8.4

a) Write K_c for the following reactions:

i. $Sn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} \rightleftharpoons Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)}$

ii. $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

iii. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

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 mol dm^{-3}.
Initial conc. of $CO_{2(g)}$ = 10.00 mol dm^{-3}.
Equilibrium conc. of $CO_{(g)}$ = 9.47 mol dm^{-3}.

8.8.2 Units of Equilibrium Constants

- 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.

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.

$$CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \rightleftharpoons CH_3COOC_2H_{5(aq)} + H_2O_{(l)}$$

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH_{(aq)}]\,[C_2H_5OH_{(aq)}]} = \frac{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}} = \text{no umits}$$

- 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.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$K_c = \frac{[NH_{3(g)}]^2}{[N_{2(g)}]\;[H_{2(g)}]^3} = \frac{[\text{mols dm}^{-3}]^2}{[\text{mol dm}^{-3}]\,[\text{mol dm}^{-3}]^3}$$

$$= \frac{1}{[\text{mol dm}^{-3}]^2}$$

$$= \text{mol}^{-2}\text{ dm}^6$$

8.9 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,

$$aA + bB \rightleftharpoons cC + dD$$

(1) When the concentrations of reactants and products are in mole dm^{-3}, then equilibrium constant is written as:

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \qquad (1)$$

Square brackets [ ] are used for mole dm^{-3}.

(2) When the concentrations are expressed in terms of partial pressures (p) for gaseous reactants and products, then

$$K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} \qquad (2)$$

(3) When the concentrations are expressed in terms of number of moles, then

$$K_n = \frac{n_C^c \cdot n_D^d}{n_A^a \cdot n_B^b} \qquad (3)$$

(4) When the concentrations are expressed in terms of mole fractions, (X) then

$$K_x = \frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b} \qquad (4)$$

The relationships between these equilibrium constants are as follows:

$$K_p = K_c\,(RT)^{\Delta n} \qquad (5)$$

$$K_p = K_x\,(P)^{\Delta n} \qquad (6)$$

$$K_p = K_n\,(N)^{\Delta n} \qquad (7)$$

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,

$$\Delta n = 0 \text{ then } K_p = K_c = K_x = K_n$$

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

$$K_p = 6.0 \times 10^{-2}\ (0.0821\ dm^3\ atm\ K^{-1}\ mol^{-1} \times 773\ K)^{-2}$$

$$= 6.0 \times 10^{-2}\ (63.5\ dm^3\ atm\ mol^{-1})^{-2}$$

$$K_p = \frac{6.0 \times 10^{-2}}{(63.5)^2} = \frac{0.06}{4032.25}$$

$$K_p = 1.4 \times 10^{-5}$$

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) Decide the comparative magnitudes of K_c and K_p, for the following reversible reactions.

i) Ammonia synthesis b) Dissociation of PCl_5

(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 x 10^7 Pa. Under these conditions, the partial pressure of nitrogen is 1.5 x 10^7 Pa and the partial pressure of hydrogen is 0.4 x 10^7 Pa. Calculate the value of K_p for this reaction.

8.10 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.

8.11 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.

8.11.1 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.

Henry-Louis Le Chatelier

(1850-1936)

A French chemist of the late 19th and early 20th centuries. He proposed the Le-Chatlier Principle, a significant achievement in chemistry

8.12 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.

(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 ofBiOCl. At equilibrium, a certain amount of BiOCl and HCl has been produced and certain number of moles of $BiCl_3$ are left behind. 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.

8.13 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.

$$n_{\text{reactants}} = n_{\text{products}}$$

This effect can only be discussed if the gaseous moles of reactants and products are unequal.

$$n_{\text{reactants}} \neq n_{\text{products}}$$

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.

$2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$ (Increasing P)

$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$ (Increasing V)

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ (Increasing P)

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ (Increasing V)

8.14 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).

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:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H° = -198\ kJ$$

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.

$$2SO_{2(g)} + O_{2(g)} \overset{\longrightarrow}{\leftharpoondown} 2SO_{3(g)}$$

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, 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:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \quad \Delta H° = +57.2\ kJ$$

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.

8.15 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. It 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.**

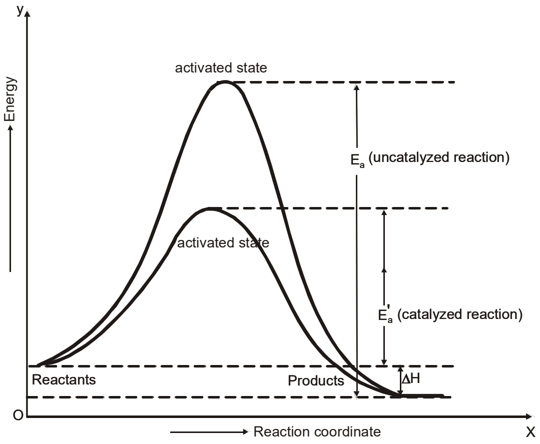


Figure 8.3 Effect of a catalyst on Reversible Reactions.

8.16 INDUSTRIAL APPLICATIONS OF CHEMICAL EQUILIBRIUM

8.16.1 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.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -46.11 \text{ kJ mol}^{-1}$$

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 8.2** given below and the **Figure 8.3**, 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 (8.1): 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}

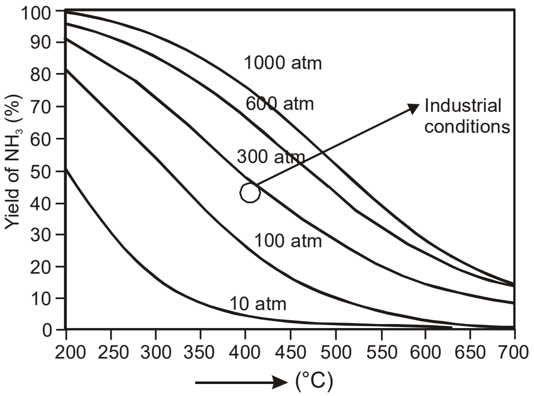


Fig (8.4) : Percent yield of ammonia vs. Temperature(°C) at five different operating pressures. At very high pressure and low temperature (top left), the yield is high, but the rate of formation is low. Industrial conditions (circle) are between 200 and 300 atm at about 400°C

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 ºC 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, Al_2O_3 and SiO_2, as catalyst

8.16.2 PREPARATION OF SULPHUR TRIOXIDE

To manufacture H_2SO_4, sulphur trioxide gas is produced from SO_2 and O_2, in a reversible process.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H = -97.9 \text{ kJ mol}^{-1}$$

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 8.2** helps us to understand the parameters, when pressure is maintained at 1 atmosphere.

Table 8.2 Effect of temperature on equilibrium position of SO_3 formation

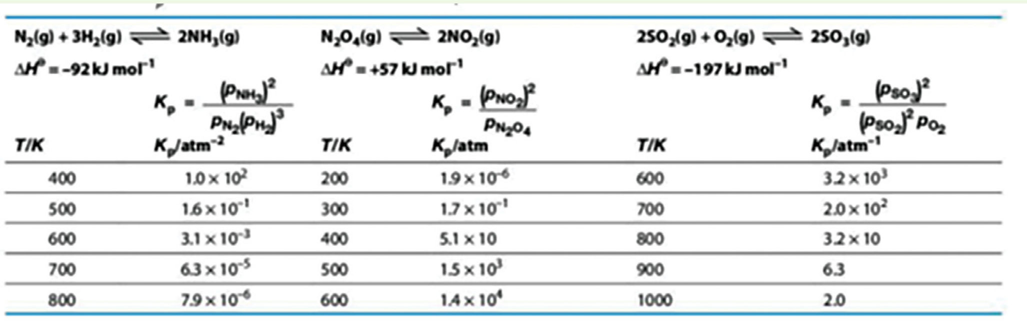
1. Temperature (°C)	200	300	400	500	600	700
2. K_c	5500	690	160	55	25	13
3. Mole % of SO_3	98	91	75	61	46	31

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 600 °C. The equilibrium mixture is recycled at low temperature of 400-500 °C to increase the yield of $SO_{3(g)}$.

Quick Check 8.6

Look at the information given in the table below:



$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$		$N_2O_4(g) \rightleftharpoons 2NO_2(g)$		$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	
$\Delta H^\circ = -92\ kJ\ mol^{-1}$		$\Delta H^\circ = +57\ kJ\ mol^{-1}$		$\Delta H^\circ = -197\ kJ\ mol^{-1}$	
	$K_p = \frac{(p_{NH_3})^2}{p_{N_2}(p_{H_2})^3}$		$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}}$		$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2 p_{O_2}}$
T/K	K_p/atm^{-2}	T/K	K_p/atm	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 ammonia in the $N_2/H_2/NH_3$ system change as the temperature increases?

ii) What is the value of ΔH^o for this reactions

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

What is the value of K_p for the raection at 400 K?

iii) Use *Le Chatelier's principle* to predict the effect of increasing temperature on K_p for the reaction in part ii.

EXERCISE

MULTIPLE CHOICE QUESTIONS

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 (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?

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -197.9\ kJmol^{-1}$$

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 for the reaction given below at 450 °C:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Evaluate K_p for the reaction at 450 °C.

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.

XI. 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

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. What is meant by the state of chemical equilibrium?

b. Define reversible reaction. Give an example.

c. Decide the comparative magnitudes of K_c and K_p, for the following reversible reactions.

(i) Ammonia synthesis (ii) Dissociation of PCl_5

d. The change of volume disturbs the equilibrium position for some of the gas phase reactions but not the equilibrium constant.

e. Mention the characteristics of chemical equilibrium.

f. Reversible reaction attains the position of equilibrium which is dynamic in nature and not static. Explain it.

g. Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

h. Why ice at 0 °C can be melted by applying pressure without supply of heat from outside?

i. Write two conditions of equilibrium constant.

j. At 445 °C, K_c for the following reaction is ٠٫٠٢٠.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

A mixture of H_2, I_2, and HI in a vessel at 445 °C has the following concentrations:

[HI] = 2.0 M, $[H_2]$ = 0.50 M and $[I_2]$ = 0.10 M. Which one of the following statements concerning the reaction quotient, Q_c, is TRUE for the above system?

i) $Q_c = K_c$; the system is at equilibrium.

ii) Q_c is less than K_c; more H_2 and I_2 will be produced.

iii) Q_c is less than K_c; more HI will be produced.

iv) Q_c is greater than K_c; more H_2 and I_2 will be produced.

k. 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/dm^3 of SO_2 and 0.050 mol/dm^3 of O_2. After equilibrium is reached, the concentration of SO_3 is 0.040 mol/ dm^3. What is the equilibrium concentration of O_2?

9

ACID-BASE CHEMISTRY

STUDENT LEARNING OUTCOMES [C-11-A-149 to C-11-A-165]

- 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 pKa and use them in calculations. **(Application)** (K_b and the equation $K_w = K_a \times K_b$ will not be tested).
- 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 (pK_a values will not be used). **(Understanding)**
- Perform acid-base titration to calculate molarity and strength of given sample solutions. **(Application)**

From the earliest days of experimental chemistry, scientists have recognized acids and bases that have distinct characteristic properties. Acids have a sour taste; bases are bitter. Also, acids and bases change the color of certain dyes called indicators, such as litmus and phenolphthalein. Acids change litmus from blue to red and basic phenolphthalein from pink to colorless. Bases change litmus from red to blue and phenolphthalein from colorless to pink. As you can see from these color changes, acids and bases neutralize each other. During

Interesting Information

Acidity in our stomachs is due to excess HCl. It is treated by taking mild bases such as, baking soda neutralization, acids and bases react with each other to produce ionic substances called salts.

9.1 BRONSTED-LOWRY CONCEPT

In 1923, the Danish chemist J.N. Bronsted and the English chemist T.M. Lowry independently expanded the Arrhenius theory of acid-base. The limitations of Arhenius 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. According to the Bronsted–Lowry concept, an **acid** is the species donating a proton in a proton-transfer reaction and a **base** is the species accepting the proton.

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 effect, HCl (the acid) has donated the H^+ and H_2O (the base) has accepted it.

$$\underset{\text{Proton donor}}{HCl_{(g)}} + \underset{\text{Proton acceptor}}{H_2O_{(\ell)}} \rightleftharpoons \underset{\text{Conjugate acid}}{H_3O^+_{(aq)}} + \underset{\text{Conjugate base}}{Cl^-_{(aq)}}$$

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 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.

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:

$$\underset{\text{Base}}{NH_{3(g)}} + \underset{\text{Acid}}{H_2O_{(\ell)}} \rightleftharpoons \underset{\text{Conjugate base}}{OH^-_{(aq)}} + \underset{\text{Conjugate base}}{NH_4^+{}_{(aq)}}$$

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.

The above examples show that H_2O is amphoteric in nature because it acts as a base in one case and as an acid in the other. 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.

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.

Table 9.1 Conjugate Acid-Base Pairs of Common Species

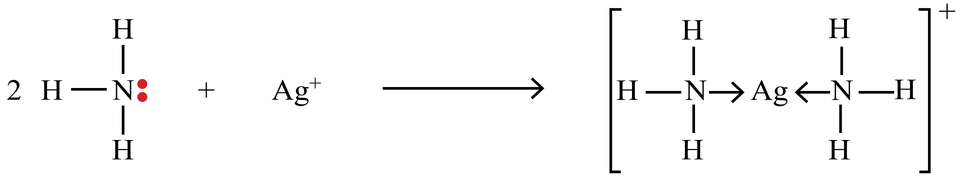
Acid		Base		Conjugate Acid		Conjugate Base
HNO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NO_3^-
H_2SO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HSO_4^-
H_2O	+	CO_3^{2-}	$\rightleftharpoons$	HCO_3^-	+	OH^-

9.2 LEWIS CONCEPT OF ACIDS AND BASES

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.

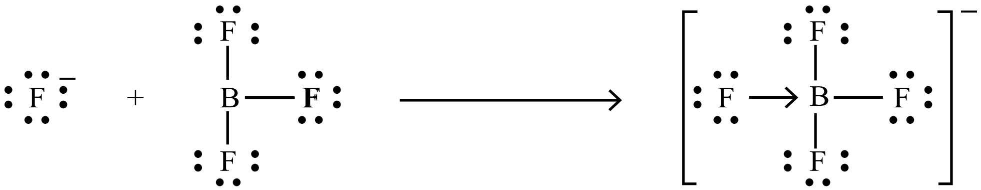
A Lewis acid is any species (molecule or ion) that can accept a pair of electrons, and a Lewis base is any species (molecule or ion) that can donate a pair of electrons. A Lewis acid-base reaction occurs when a base donates a pair of electrons to an acid.

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** **Alcid base adduct**

The boron atom in boron trifluoride, BF_3, has only six electrons in its valence shell. Since the boron atom has an incomplete octet, it can behave as an electron pair acceptor. As a result, BF_3 is a very good Lewis acid and reacts with many Lewis bases; a fluoride ion is the Lewis base in this reaction, donating 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.

Quick Check 9.1

a) Identify the conjugate acid-base pairs in the following reactions:

i. $HCN_{(g)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CN^-_{(aq)}$

ii. $CH_3COOH_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

iii. $H_2S_{(g)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HS^-_{(aq)}$

iv. $HCl_{(g)} + HCO_3^-{}_{(aq)} \rightleftharpoons H_2CO_{3\,(aq)} + Cl_{(aq)}^-$

b) Identify the Lewis acid and Lewis base in the reaction between:

i. SO_3 and O^{2-}

ii. HCl and H_2O

iii. BF_3 and NH_3

Also write down the balanced chemical equation for the reaction and explain.

9.3 IONIC PRODUCT OF WATER

Pure water is a poor conductor of electricity but its conductance is measurable. Water undergoes self-ionization reversibly as follows,

$$H_2O_{(\ell)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

Net reaction $$H_2O_{(\ell)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant for this reaction can be written as follows:

$$K_c = \frac{[H^+]\,[OH^-]}{[H_2O]} = 1.8 \times 10^{-16}\ \text{mol dm}^{-3}$$

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 mol dm^{-3}. Since, 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 $$1.8 \times 10^{-16} \times 55.5 = 1.01 \times 10^{-14} = [H^+]\,[OH^-]$$

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. 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 $$[H^+][H^+] = 10^{-14}$$

$$[H^+]^2 = 10^{-14} \quad \text{(at 25 °C)}$$

$[H^+] = 10^{-7} mol\, dm^{-3}$

and $[OH^-] = 10^{-7} mol\, dm^{-3}$

The effect of temperature on K_w is shown in **Table 9.2.** 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.

Table 9.2 K_w at various temperature.

Temp. (°C)	**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}

9.4 pH AND pOH

In all the aqueous solutions, the concentration of H^+ and OH^- are too low to be conveniently expressed and used in calculations. In 1909, Sorenson, a Danish biochemist, introduced the term pH and pOH. So, the scales of pH and pOH were developed. These two quantities can be calculated as:

$pH = -\log[H^+]$

$pOH = -\log[OH^-]$

For neutral water, $pH = -\log[10^{-7}] = 7$

$pOH = -\log[10^{-7}] = 7$

Also, $pH + pOH = 14$

The value of pH normally varies between 0 →14 at 25°C.

Interesting Information!

Solutions of negative pH and having values more than 14 are also known.

The pH values of some familiar aqueous solutions are shown in **Figure 9.1**. This table can help you to understand the acidic or basic nature of commonly used solutions.

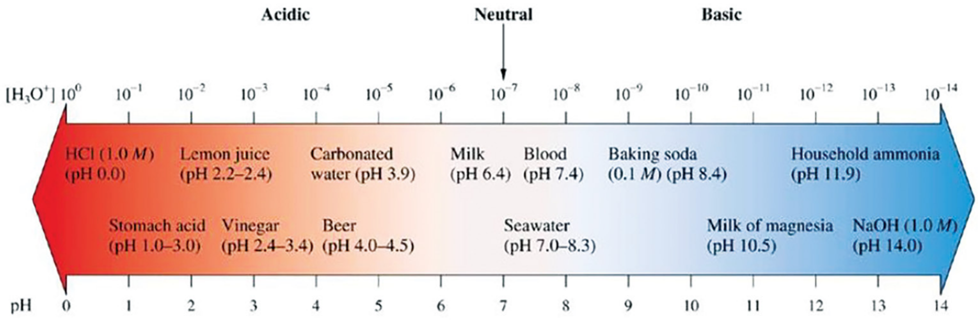


Figure 9.1 pH Values of some common substances

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 p^{OH}

antilog pH = antilog (9.2)

$$[OH^-] = 10\text{-}^{pH}$$

$$[H^+] = 10^{-9.2}$$

$$[OH^-] \approx 6.3 \times 10^{-10}\ M$$

Similarly, antilog pOH = antilog (4.8)

$$[OH^-] = 10\text{-}^{pOH}$$

$$[OH^-] = 10^{-4.8}$$

$$[OH^-] \approx 1.6 \times 10^{-5}\ M$$

Sample Problem 9.2

The ionic product of water at a certain temperature is $K_w = 1.0 \times 10^{-14}$ at 25 ºC. If the concentration of H^+ ions in a solution is $1.0 \times 10^{-7}M$.

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^+:

$$1.0 \times 10^{-14} = (1.0 \times 10^{-7})\ [OH^-]$$

Solve for the concentration of OH^-

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-14}$$

Calculate the pH:

$$pH = -\log[H^+]$$

$$pH = -\log(1.0 \times 10^{-7}) = 7$$

Calculate the pOH:

$$pOH = -\log[OH-]$$

$$pOH = -\log(1.0\times10-7)$$

$$pOH = 7$$

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.

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.

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 ºC.

9.5 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. Suppose we have an acid HA dissolved in water,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

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 $K_a = \dfrac{[H_3O^+]\ [A^-]}{[HA]}$

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.

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 9.3**.

Table 9.3 The values of K_a for some acids

Acid	Dissociation	K_a	Relative strength
HCI	$HCI \rightleftharpoons H^+ + CI^-$	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_4^1	$NH_4 \rightleftharpoons H^+ + NH_5$	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

9.5.1 Calculating H_3O^+ ions from k_a and Molar Concentration of Weak Acid

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^+:

$$H^+_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)}$$

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:

$$[H_3O^+] = x; \qquad [A^-] = x \text{ and } [HA] = C - x$$

The expression for the acid dissociation constant (K_a) is:

$$K_a = \frac{[H_3O^+]\ [A^-]}{[HA]}$$

Substitute the equilibrium concentrations into this expression:

$$K_a = \frac{x \times x}{C - x} = \frac{x^2}{C -}$$

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 (mol dm^{-3}) solution of acetic acid $[CH_3COOH]$, given that the acid dissociation constant K_a is 1.8×10^{-5}.

Solution

$$[H_3O^+] \approx \sqrt{K_a \times C}$$
$$[H_3O^+] \approx \sqrt{1.8 \times 10^{-5} \times 0.1}$$
$$[H_3O^+] \approx \sqrt{0.18 \times 10^{-6}}$$
$$[H_3O^+] \approx 1.34 \times 10^{-3}\ \text{M (mol dm}^{-3}\text{)}$$

The concentration $[H_3O^+]$ in the solution is approximately $\mathbf{1.34 \times 10^{-3}}$ mol dm^{-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.

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}.

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.

9.6 COMMON ION EFFECT

The suppression of ionization of a weak electrolyte by adding a common ion to it is called **common ion effect**. We are familiar with purification of sodium chloride by passing hydrogen chloride gas through brine (saturated solution of NaCl). 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:

$$HCl_{(g)\,(s)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

On passing HCl gas, concentration of Cl^- ion is increased, therefore NaCl crystallizes out of the solution to maintain the constant value of the equilibrium constant. This type of effect is called the common ion effect. The addition of a common ion to the solution of a less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitate.

$$Na^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons NaCl_{(s)}$$

More Examples of Common Ion Effect

i. 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.

$$KClO_{3(s)} \rightleftharpoons K^+_{(aq)} + ClO^-_{(aq)}$$

$$KCl_{(s)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$$

ii. 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-} ion is produced.

$$H_2S_{(g)} \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$$

This low concentration of S^{2-} ions helps to do the precipitation of radicals of second group basic radicals during salt analysis.

$$HCl_{(aq)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

iii. An addition of NH_4Cl in NH_3 solution suppresses the concentration of OH^- 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 a group reagent in third group basic radicals for salt analysis.

$$NH_4Cl_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

$$NH_3 + H_2O_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

Common ion effect finds extensive applications in the qualitative analysis and the preparation of buffers.

9.7 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 and their pH values do not change on dilution and on keeping for a long time.

Buffer solutions are mostly prepared by mixing two substances.

i. 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. 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.

Let us take the example of 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 9.4** 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 9.4 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.

9.7.1 Calculating the pH of a Buffer

Let us try to learn, how a buffer of definite pH can be prepared. 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:

$$HA \rightleftharpoons H^+ + A^-$$

$$NaA \rightleftharpoons Na^+ + A^-$$

pH of a buffer solution can be calculated by using Henderson equation as given below:

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

Interchanging the numerator and denominator, the sign of log changes.

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

Interesting Information!

The body's blood buffering system, involving bicarbonates, helps maintain a

This relationship is called **Henderson's equation**. This equation shows that two factors evidently govern the pH of a buffer solution. First is the pK_a of the acid used and the second is 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. For example, for acetic acid – sodium acetate buffer, if

$$[CH_3COOH] = [CH_3COONa]$$

Then $$pH = pK_a + \log \frac{[CH_3\ COONa]}{[CH_3\ COOH]}$$

$$pH = pK_a + \log (1)$$

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.

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.
   ii. Explain your answer with respect to the common ion effect.

c) How does a buffer maintain pH stability?

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 (Ka of HF = 6.8×10^{-4}).

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}

9.8 SOLUBILITY PRODUCT

(For slightly soluble ionic compounds)

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. For example, when $PbSO_4$ 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 $\quad K_c\,[PbSO_4] = K_{sp}$

then $\quad K_{sp} = [Pb^{2+}][SO_4^{2-}] = 1.6 \times 10^{-8}$ 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.

Similarly, for another sparingly soluble salt, $PbCl_2$. $\quad K_{sp} = [Pb^{2+}][Cl^-]^2$

K_{sp} is usually a very small quantity at room temperature. The value of K_{sp} is temperature dependent. So, the solubility product is the product of the concentrations of ions raised to an exponent equal to the co-efficient of the balanced equation. The value of K_{sp} is a measure of the dissociation of sparingly soluble salt.

The following **Table 9.5** shows the K_{sp} values of some slightly soluble ionic compounds.

Table 9.5 K_{sp} values for some ionic compounds

Salt	Ion Product	K_{sp}	Salt	Ion Product	K_{sp}
AgBr	$[Ag^+]\ [Br^-]$	$5.0 x 10^{-13}$	CuS	$[Cu^{2+}]\ [S^{2+}]$	$8 x 10^{-34}$
AgCl	$[Ag^+]\ [Cl^-]$	$1.8 x 10^{-10}$	Fe_2S_3	$[Fe^{3+}]^2\ [S^{2-}]^3$	$1.4 x 10^{-85}$
$AI(OH)_3$	$[AI^{3+}]\ [OH^-]^3$	$3 x 10^{-34}$	$MgCO_3$	$[Mg^{2+}][CO_3{}^{2-}]$	$3.5 x 10^{-8}$
$BaSO_4$	$[Ba]\ [CO_4{}^{2-}]$	$1.1 x 10^{-10}$	MnS	$[Mn^{2+}]\ [S^{2-}]$	$3 x 10^{-11}$
$CaCO_3$	$[Ca^{2+}]\ [Ca_3{}^{2-}]$	$3.3 x 10^{-9}$	$PbCrO_4$	$[Pb^{2+}][CrO_4{}^{2-}]$	$2.3 x 10^{-13}$
CaF_2	$[Ca^{2+}]\ [F^-]^2$	$3.2 x 10^{-11}$	$PbSO_4$	$[Pb^{2+}][SO_4{}^{2-}]$	$1.6 x 10^{-8}$

9.8.1 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 9.6** shows the relationship between the K_{sp} values and the solubility of some sparingly soluble compounds.

Table 9.6 The relation between solubility and solubility products of some salts

Formula	No. of ions	KSP	Solubility gdm^{-3}
$PbSO_4$	2	$1.69 x 10^{-4}$	$1.3 x 10^{-4}$
$Ca(OH)_2$	3	$6.5 x 10^{-6}$	$1.175 x 10^{-2}$
CaF_2	3	$3.2 x 10^{-11}$	$2.0 x 10^{-4}$
Ag_2CrO_4	3	$2.6 x 10^{-12}$	$8.7 x 10^{-5}$

Sample Problem

$Ca(OH)_2$ is a sparingly soluble compound. Its solubility product is $6.5 x 10^{-6}$. 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:

$$Ca(OH)_{2(aq)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2OH^-{}_{(aq)}$$

$$Ca(OH)_{2(aq)} \rightleftharpoons 0 \quad + \quad 0 \qquad \text{Initial stage}$$

$$Ca(OH)_2 \rightleftharpoons S \quad + \quad S \qquad \text{Equilibrium stage}$$

The concentration of OH^- is double than the concentration of Ca^{2+}, so

$$K_{sp} = [Ca^{2+}][OH^-]^2 = S \text{ x } (2S)^2$$

$$4S^3 = 6.5 \text{ x } 10^{-6}$$

$$S^3 = \frac{6.5 \text{ x } 10^{-6}}{4}$$

$$S = (1.625)^{1/3} \text{ x}10^{-2}$$

$$S = \mathbf{1.18 \text{ x}10^{-2} \text{ mol dm}^{-3}}$$

Hence, at equilibrium stage $1.18 \text{ x}10^{-2}$ mol dm^{-3} mol dm^{-3} of Ca^{2+} and $2 \text{ x } 1.18 \text{ x}10^{-2}$ mol dm^{-3} = $2.36 \text{ x } 10^{-2}$ 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.

$$PbCrO_{4\,(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)}$$

Now add Na_2CrO_4 which is a soluble salt. 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 can also help in predicting whether the precipitation of a salt will occur or not. For example, the solubility product of $CaSO_4$ is $2 \text{ x } 10^{-5}$. If we add 10^{-2} mol dm^{-3} solution Ca^{2+} to10^{-2} mol dm^{-3} solution of SO_4^{2-} ions at 25 °C. The concentrations of each ionic species can be calculated as

$$[Ca^{2+}]=[\,SO_4^{2-}] = \frac{10^{-2}}{2} = \; 5.0 \text{ x } 10^{-3} \text{ mol dm}^{-3}$$

$$[Ca^{2+}][\,SO_4^{2-}] = 5.0 \text{ x } 10^{-3} \text{ mol dm}^{-3} \text{ x } 5.0 \text{ x } 10^{-3} \text{ mol dm}^{-3}$$

$$= 2.5 \text{ x } 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$$

$$= \; 2.5 \text{ x } 10^{-5} \text{ mol}^2 \text{ dm}^{-6} > K_{sp} \text{ of } CaSO_4$$

As the product of concentrations is greater than K_{sp}, therefore $CaSO_4$ will precipitate out.

Ionic Product	Type of Solution	Precipitation
$> K_{sp}$	Supersaturated	Yes
$= K_{sp}$	Saturated	No
$< K_{sp}$	Unsaturated	No

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.

b) Predict whether $CaSO_4$ will be precipitated or not when 10^{-3} mol dm^{-3} of each of Ca^{2+} and SO_4^{2-} is mixed together.

c) Will the aqueous solution of ammonium oxalate be acidic or basic? Explain your answer by giving equation.

d) Solution of potassium carbonate is basic.

i. Explain why the solution is alkaline.

ii. Also give the equation for the hydrolysis of the above salt.

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.

9.8 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.

9.8.1 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.

9.8.2 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:

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(g)} + H_3O^+{}_{(aq)}$$

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.

9.8.3 Salts of Weak Acids and Strong Bases

The example of salt of weak acid and strong base is sodium acetate.

$$CH_3COONa_{(s)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-{}_{(aq)} + Na^+{}_{(aq)}$$

CH_3COO^- is the conjugate base of CH_3COOH (a weak acid) and reacts with water:

$$CH_3COO^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-{}_{(aq)}$$

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.

9.8.4 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^+.

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+{}_{(aq)}$$

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.

9.9 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 Brønsted 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.

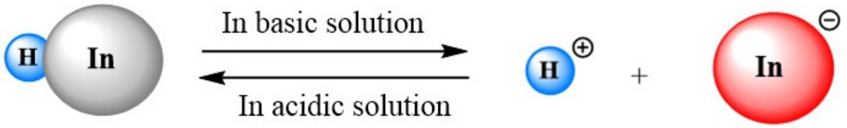


Figure 9.1 Unionized acid-base indicators and their ionised forms exist in an **equilibrium**

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.

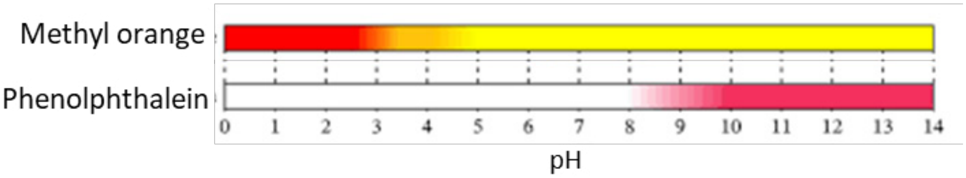


Figure 9.2 Range and color changes of some common Acid-Base indicators

9.9.1 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.

9.9.2 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

As an example of a strong acid–strong base titration, let's 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.

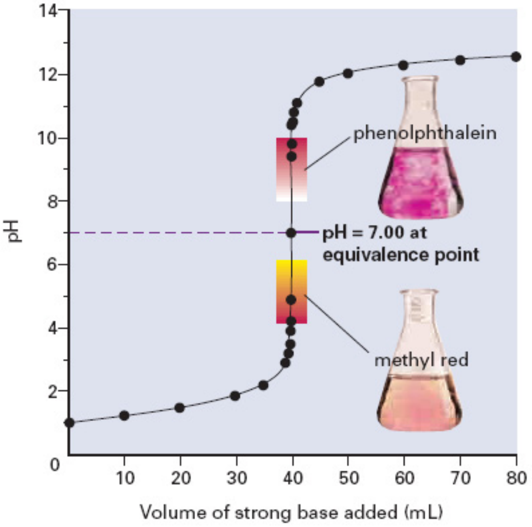


Figure 9.3 Strong acid-strong base titration curve

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.

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.

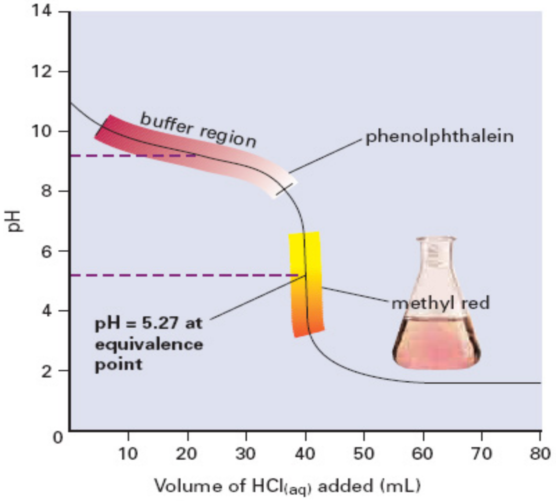


Figure 9.4 strong acid-weak base titration curve

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 ($NH_4^+ \rightarrow NH_3 + H^+$).

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.

Table 9.7 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.

b) Explain how an indicator changes its colour in acidic and basic solution.

c) Suggest a suitable indicator for weak acid and strong base titration.

d) Suggest a suitable indicator for weak acid and weak base titration.

EXERCISE

MULTIPLE CHOICE QUESTIONS

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

I. Given the following reaction:

$$NH_{3\,(g)} + H_2O_{\,(l)} \rightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

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} 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) 1.0×10^{-10} mol dm^{-3}
d) 4.0×10^{-20} mol dm^{-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?

$OH^-_{(aq)}$ b. $H^+_{(aq)}$ c. $H_2O_{(l)}$ d. $H_3O^+_{(aq)}$

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

VI. 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.

VII. 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

VIII. 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

IX. 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

X. Which of the following pairs forms a buffer solution?

a) Hydrochloric acid (HCl) and sodium chloride (NaCl)

b) Sodium acetate (CH_3COONa) and acetic acid (CH_3COOH)

c) Sodium hydroxide (NaOH) and hydrochloric acid (HCl)

d) Ammonia (NH_3) and sodium sulfate (Na_2SO_4

XI. What is the purpose of a titration acid-base curve?

a) To measure the volume of acid or base used

b) To determine the pH at various points during the titration

c) To calculate the concentration of the titrant

d) To identify the endpoint of the titration

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

ii) Common ion effect iv) Acid-base Indicator

b. Differentiate between:

i) Hydrolysis and dissolution ii) Acidic and basic buffer solutions

c. Explain the concept of conjugate acid-base pairs. How are they related in terms of proton transfer?

d. What is the relationship between the strength of an acid and the strength of its conjugate base?

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) $NaOH_{(s)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$ i) $HF_{(aq)} + H_2O_{(l)} \longrightarrow F^-_{(aq)} + H_3O^+_{(aq)}$

ii) $H^+_{(aq)} + NH_{3(aq)} \longrightarrow NH_4{}^+{}_{(aq)}$

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) $H_2O + HCl \rightarrow H_3O^+ + Cl^-$ ii) $NH_3 + H_2O \rightarrow NH_4{}^+ + OH^-$

iii) $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$ iv) $CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$

g. Which salt would you expect to dissolve more readily in acidic solution: Barium sulfate or Barium fluoride? Explain.

h. Why does common ion effect decrease solubility of a less soluble salt?

i. State the basic principle of solubility product. Mention factors affecting solubility product.

j. What is the main reason that titration of weak acids with weak bases are not performed for volumetric analysis?

k. Prove by equations what happens when Na_2CrO_4 is added to saturated solution of $PbCrO_4$.

l. According to the Lewis acid-base concept, Boron trifluoride (BF_3) can act as an acid. Is this statement correct?

m. If the concentration of hydrogen ions in a solution is 1 x 10^{-5} M, what is the pH of the solution?

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.

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.

Q.5 Discuss applications and implications of the common ion effect in various fields.

Q.6 What is the solubility product for sparingly soluble salts. Give its two applications.

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 a titration curve for a strong acid-strong base titration?

NUMERICAL PROBLEMS

Q.8 A buffer solution has a pH of 5.0. It is made from a weak acid HA with a pKa 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?

Q.9 Calculate the solubility of a sparingly salt lead (II) iodide (PbI_2) in water. It has $K_{sp} = 1.4 \times 10^{-8}$.

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 Ksp of silver chromate at this temperature.

10

ELECTROCHEMISTRY

STUDENT LEARNING OUTCOMES [C-11-A-56 to C-11-B-78]

- 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.

10.1 OXIDATION, REDUCTION, AND REDOX REACTIONS

Oxidation is a process involving loss of electron or electrons.

$$Fe^{+2} \rightarrow Fe^{+3} + e^{-}$$

$$Zn^{\circ} \rightarrow Zn^{+2} + e^{-}$$

Here Fe^{+2} and Zn^{0} have lost electrons, therefore they are oxidized.

Reduction is a process involving gain of electron or electrons.

$$Cl^{0} + e^{-} \rightarrow Cl^{-1}$$

$$Cu^{+2} + 2e^{-} \rightarrow Cu^{0}$$

In these examples, Cl^{0} and Cu^{+2} have gained electrons; therefore, they are reduced.

Oxidation and reduction always take place together. The reactions in which this happens is called **redox reactions**.

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.

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

10.2 OXIDATION NUMBER AND ITS SIGNIFICANCE

The oxidation numbers are also called oxidation states. An oxidation number is a number given to each atom or ion in a compound that shows us its degree of oxidation. Oxidation numbers can be positive, negative or zero. The + or – sign must always be included. It is the apparent charge on an atom (per atom) of an element in a molecule or an ion. 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.

10.2.1 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, Cl_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, Cl^- 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. HCl and NaCl.

vi. In ions, the algebraic sum of oxidation number equals the charge on the ion. For examples CO_3^{-2} and SO_4^{-2}.

While applying the oxidation number rules in the following examples, 'Ox. No.' as an abbreviation for oxidation number is used.

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.

10.2.2 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, $Na_2\underline{S}$:

$$2(+1) + S = 0$$
$$+2 + S = 0$$
$$S = -2$$

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,

$$S + 2(-2) = 0$$
$$S - 4 = 0$$
$$S = +4$$
$$\text{Ox. No. of S} = +4$$

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

$$[\text{Ox. No. of S}] + 4\,[\text{Ox. No. of O}] = -2$$
$$S + 4(-2) = -2$$
$$S = +6$$

Thus, the oxidation number of sulphur in SO_4^{2-} is +6.

Sample Problem 10.3

Calculate the oxidation number (Ox. No.) of manganese in $KMnO_4$.

Solution

$$(\text{Ox. No. of K}) + (\text{Ox. No. of Mn}) + 4\,(\text{Ox. No. of O}) = 0$$

$$+1 + Mn + 4\,(-2) = 0$$

$$(+1) + Mn - 8 = 0$$

$$\text{Or } Mn = +7$$

Thus, the oxidation number (Ox. No.) of Mn in $KMnO_4$ is + 7.

Quick Check 10.1

- a) Define oxidation and reduction in terms of electron transfer with examples.
- b) Define oxidation and reduction in terms of change in oxidation number with examples.
- c) Determine Ox. No. of:
  - i) Oxygen (N) in Na_2O
  - ii) Iodine (I) in ICl_3
  - iii) Nitrogen (N) in NO_3^{1-}
  - iv) Chromium (Cr) in $K_2Cr_2O_7$

10.3 DISPROPORTIONATION REACTION

A disproportionation reaction is a chemical reaction where a single substance 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.

For example, the decomposition of hydrogen peroxide (H_2O_2) to form water (H_2O) and oxygen (O_2) is a disproportionation reaction:

$$2H_2O_2 \rightarrow H_2O_2^{-1} + O_2^{0}$$

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)

Similarly

$$6NaOH_{(aq)} + 3Cl_2^{0}(g) \rightarrow 5NaCl^{-1}{}_{(aq)} + NaCl^{+5}O_{3\,(aq)} + 3H_2O$$

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)

Disproportionation reactions can occur where ions or molecules can exist in multiple oxidation states in a reaction.

10.4 OXIDIZING AGENT (OXIDANT) AND REDUCING AGENT (REDUCTANT)

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, while, 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, $Cl + e^- \longrightarrow Cl^-$

On other hand, 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 Ox. No.) (Higher Ox. No.)

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. $Fe_2O_{3(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$ ii. $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

b) Identify the species in the following reaction which undergoes both oxidation and reduction.

i. $3HNO_{2(aq)} \rightleftharpoons HNO_{3(aq)} + 2NO_{(g)} + H_2O_{(l)}$

ii. $P_{4(s)} + 3OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow PH_{3(g)} + 3H_2PO_2{}^-_{(aq)}$

10.5 BALANCING OF REDOX EQUATIONS BY OXIDATION NUMBER METHOD

Carry out the following steps 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. It 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.

$$Zn_{(s)} + HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2\,(g)}$$

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.

$$Cl_2 + NaOH + Cl_2 \longrightarrow NaCl + H_2O + NaOCl$$

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.

$$HNO_3 + Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O + NO_2$$

$$HCl + K_2Cr_2O_7 + HCl \longrightarrow Cl_2 + KCl + CrCl_3 + H_2O$$

Sample Problem 10.4

Balance the following equation by oxidation number method.

$$K_2Cr_2O_7 + HCl \rightarrow KCl + CrCl_3 + Cl_2 + H_2O$$

Solution:

1- Write down the skeleton of chemical equation.

$$K_2Cr_2O_7 + HCl \longrightarrow Cl_2 + KCl + CrCl_3 + H_2O$$

2- Write down the oxidation number of each element.

$$K^{1+}{}_2Cr^{6+}{}_2O^{2-}{}_7 + H^{1+}Cl^{1-} \rightarrow Cl^0{}_2 + K^{1+}Cl^{1-} + Cr^{3+}Cl^{1-}{}_3 + H^{1+}{}_2O^{2-}$$

3- Identify the elements that show change in oxidation number on both sides.

$$K_2^{1+}\ \overbrace{Cr_2^{6+}\ O_7^{2-}\ +\ H^{1+}\underbrace{Cl^{1-} \rightarrow Cl_2^0}_{2e^-}\ + K^{1+}Cl^{1-} + Cr}^{6e^-}{}^{3+}Cl_3^{1-} + H_2^{1+}O^{2-} \text{ .... (i)}$$

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

$$K_2Cr^{6+}{}_2O_7 \longrightarrow 2Cr^{3+}Cl_3 \quad \text{Half reduction reaction .... (ii)}$$

$$2HCl^{1-} \longrightarrow Cl^0{}_2 \quad \text{Half oxidation reaction .... (iii)}$$

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.

$$3 \text{ x } 2HCl \longrightarrow 3Cl_2$$

$$6HCl \longrightarrow 3Cl_2 \text{ .... (iv)}$$

Now eq. (i) becomes:

$$K_2Cr_2O_7 + 6HCl \longrightarrow 3Cl_2 + KCl + 2CrCl_3 + H_2O$$

5. Rest of the following equation is balanced by inspection method:

$$K_2Cr_2O_7 + 6HCl \longrightarrow 3Cl_2 + 2KCl + 2CrCl_3 + H_2O$$

To balance Cl and K, 14 molecules of HCl and 2 KCl molecules are required, therefore, we add 8 HCl to left hand side

$$8HCl + K_2Cr_2O_7 + 6HCl \longrightarrow 2CrCl_3 + 3Cl_2 + 2KCl + H_2O$$

To balance hydrogen and oxygen, $6H_2O$ are added to RHS.

Hence, the balanced equation is,

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

Quick Check 10.3

Balance the given equations by oxidation number method.

i. $Fe_2O_{3(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$

ii. $MnO_2 + HCl \rightarrow MnCl_2 + H_2O + Cl_2$

iii. $Fe^{2+}_{(aq)} + MnO^{4-}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)}$

iv. $K_2Cr_2O_{7\,(aq)} + FeSO_{4\,(aq)} + H_2SO_{4\,(aq)} \rightarrow Cr_2(SO_4)_{3\,(aq)} + Fe_2(SO_4)_{3(aq)} + K_2SO_{4(aq)} + H_2O_{(l)}$

10.6 ELECTROLYTIC CELL

An electrolytic cell is a device that converts electrical energy into chemical energy through a process called **electrolysis**. 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.

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.

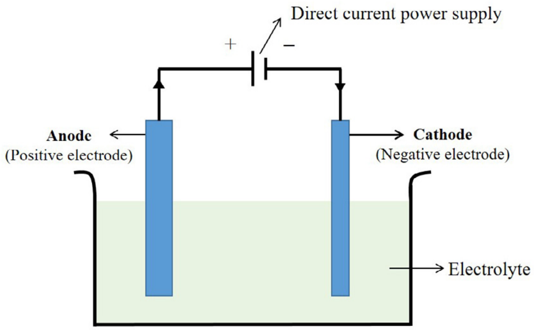


Figure 10.1 Main parts of an electrolytic cell

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 10.1**.

In the electrolysis cell,

- the electrolyte is the compound that is decomposed; it is either a molten ionic compound or a concentrated aqueous solution of ions
- 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
- the power supply must be direct current.

The actual structure of the cell will vary according to the element extracted.

10.7 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:

$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^-$$

$$4OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-$$

Electrolysis is a redox reaction. For example, when molten zinc chloride ($ZnCl_2$) is electrolyzed, the electrode reactions are:

Cathode: $Zn^{2+}_{(l)} + 2e^- \longrightarrow Zn_{(s)}$ (Reduction)

Anode: $2Cl^-_{(l)} \longrightarrow Cl_{2(s)} + 2e^-$ (Oxidation)

The electron loss at the anode balances the electron gain at the cathode. The overall reaction is $ZnCl_{2(l)} \longrightarrow Zn_{(s)} + Cl_{2(g)}$

Quick Check 10.4

Molten copper (II) bromide ($CuBr_2$) is electrolyzed using inert electrodes.

i. Which ions are present in this solution?
ii. Name the electrode on which the formation of copper metal occurs?
iii. Give the half-equation that represents the formation of copper metal.
iv. Write the half-equation for the formation of bromine on the other electrode.

10.8 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.

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}.

During the electrolysis of silver nitrate solution, silver is deposited at the cathode.

$$\begin{array}{lll} Ag^{+}_{(aq)} + e^{-} & \longrightarrow & Ag_{(s)} \\ 1\text{ mol} \quad 1\text{ mol} & & 1\text{ mol} \end{array}$$

1 Faraday of electricity (96500 C) is required to deposit 1 mole of silver. During the electrolysis of copper(II) sulfate solution, copper is deposited at the cathode.

$$\begin{array}{lll} Cu^{2+}_{(aq)} + 2e^{-} & \longrightarrow & Cu_{(s)} \\ 1\text{ mol} \quad 2\text{ mol} & & 1\text{ mol} \end{array}$$

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

10.9 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.

$$\begin{aligned} Q &= I \times t \\ &= 1.50 \times 20 \times 60 \\ &= 1800\ C \end{aligned}$$

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 = 1.93 g Pb

10.10 AVOGADRO'S CONSTANT BY THE ELECTROLYTIC METHOD

The Avogadro 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 constant by calculating the charge associated with 1 mole of electrons.

$$L = \frac{\text{Charge on 1 mole of electrons}}{\text{Charge on 1 electron}}$$

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.

10.10.1 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 10.2**.

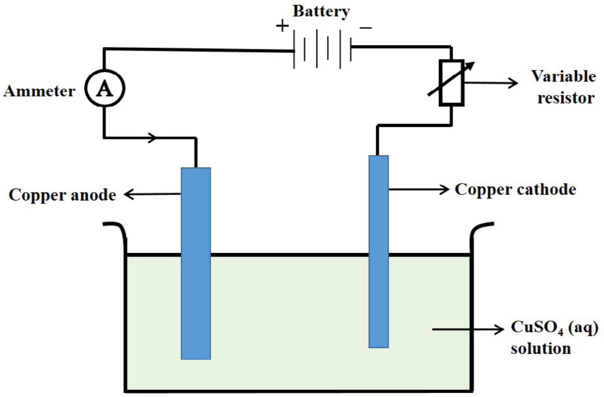


Figure 10.2 Apparatus for calculating the mass of copper deposited

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 10.2.** 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.

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.

10.10.2 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	$= I \times t$
	$= 0.20 \times 34 \times 60$
	= 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 $= \dfrac{408}{0.13}$

63.5 g of copper requires $= \dfrac{408}{0.13} \times 63.5$

$= 99646$ 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 $= \dfrac{63.5}{0.13} \times 408\text{ C} = 99646\text{ C}$

If the charge on one electron is 1.60×10^{-19} C,

$$L = \frac{99646}{1.60} \times 10^{-19} = 6.2 \times 10^{23}\ \text{mol}^{-1}$$

This is in good agreement with the accurate value of $6.02 \times 10^{23}\ \text{mol}^{-1}$.

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 = 96 500 C mol^{-1})

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?

   ii. How many coulombs of charge are required to liberate 1 mole of hydrogen gas? (F = 96 500 C mol^{-1})

10.11 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. 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 and it indicates the ease of oxidation or reduction of a substance. For example, when a copper rod is placed in contact with an aqueous solution of its ions, the following equilibrium exists:

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$$

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.

$$V^{2+}_{(aq)} + 2e^- \longleftarrow V_{(s)}$$

$V^{2+}_{(aq)}$ 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.

10.11.1 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. For example, 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.

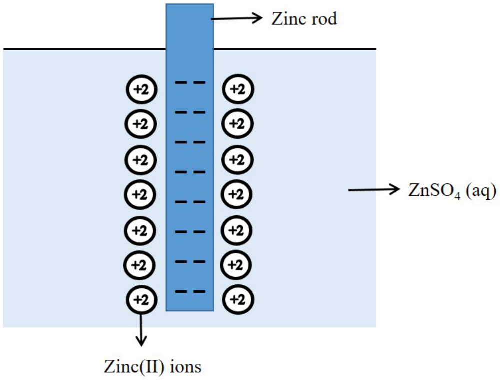


Figure 10.3 Formation of electrical double layer

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. But 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)**.

10.12 STANDARD HYDROGEN ELECTRODE

The standard hydrogen electrode is one of several types of half-cell that can be used as reference electrode. **Figure 10.4** shows a standard hydrogen electrode.

This electrode consists of:

- Hydrogen gas at 101 kPa 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^O 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:

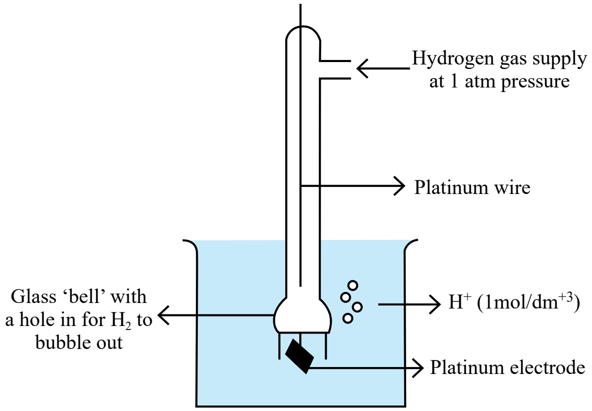


Figure 10.4 Standard hydrogen electrode (SHE)

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)} \qquad E^\circ = 0.00\text{ V}$$

or

$$2H^+_{(aq)} + 2e^- \longleftarrow H_{2(g)} \qquad E^\circ = 0.00\text{ V}$$

The way that the half-equation is balanced makes no difference to the value of E^O. The equation does not affect the tendency for the element to gain electrons. Its voltage is arbitrarily fixed at 0.00 V.

10.13 STANDARD ELECTRODE POTENTIAL

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.

These are:

- 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 kPa)
- 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^O. 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".

10.14 MEASURING STANDARD ELECTRODE POTENTIALS

There are three main types of half-cell whose E^O value can be obtained when connected to a standard hydrogen electrode (SHE):

- metal/metal ion half-cell (Cu^{2+}/Cu^0)
- non-metal/non-metal ion half-cell (Cl^{1-}/Cl_2)
- ion/ion half-cell. (Fe^{2+}/Fe^{3+})

Figure 10.5 shows how to measure the E^O 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:

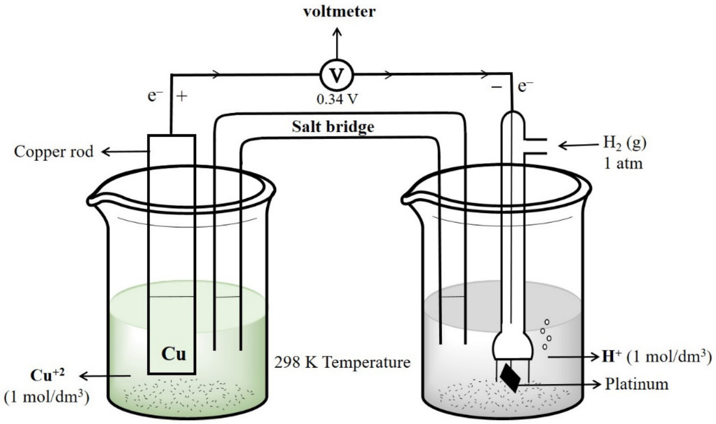


Figure 10.5 Measuring the standard electrode potential of a Cu^{2+}/Cu half-cell

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \qquad E^O = +0.34\ V$$

$$H^+_{(aq)} + e^- \longrightarrow 1/2\ H_{2(g)} \qquad E^O = 0.00\ V$$

The E^O values show us that Cu^{2+} ions are easier to reduce than H^+ ions (they have a more positive E^O 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.

Figure 10.6 shows how to measure the E^O 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:

$$H^{+}_{(aq)} + e^{-} \longrightarrow 1/2\ H_{2(g)} \qquad E^{O} = 0.00\ V$$

$$Zn^{2+}_{(aq)} + 2e^{-} \longrightarrow Zn_{(s)} \qquad E^{O} = -0.76\ V$$

The E^{O} values show us that Zn^{2+} ions are more difficult to reduce than H^{+} ions (they have a more negative E^{O} 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.

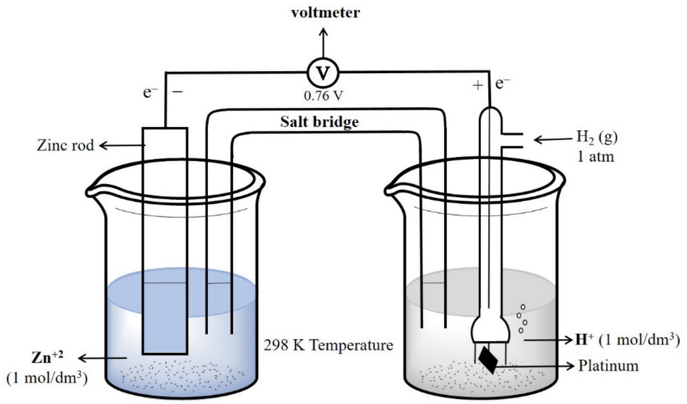


Figure 10.6 Measuring the standard electrode potential of a Zn^{2+}/Zn half-cell

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:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{-}$$

Quick Check 10.6

a) Explain the following keeping in view the standard electrode potential values ($E^{o}\ Cl_2/2Cl^{-} = +1.36\ V$ $E^{o}Br_2/2Br^{-} = +1.07\ V$, $E^{o}\ I_2/2I^{-} = +0.54\ V$)

i. The aqueous solution of iodine can be oxidized with bromine of iodide ions.

ii. Why bromine does not react with chloride ions.

b) Give answers using E° values ($E^{o}_{Ag^{+}/Ag} = + 0.80\ V$, $E^{o}_{Cr^{2+}/Cr} = - 0.91\ V$, $E^{o}_{Fe^{2+}/Fe} = - 0.44\ V$

i. Which of Ag^{+}, Cr_2+ and Fe^{+}_{2}, is the strongest oxidizing agent? Which is the least oxidizing?

Explain with reason.

ii. Arrange Ag, Cr and Fe in increasing order of their reducing powers.

10.15 ELECTROCHEMICAL 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. A galvanic cell is designed to take advantage of spontaneous transfer of electrons. A **Galvanic Cell**, is also known as a **Voltaic Cell**. For example: Daniel cell and 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
- 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 10.7** can be

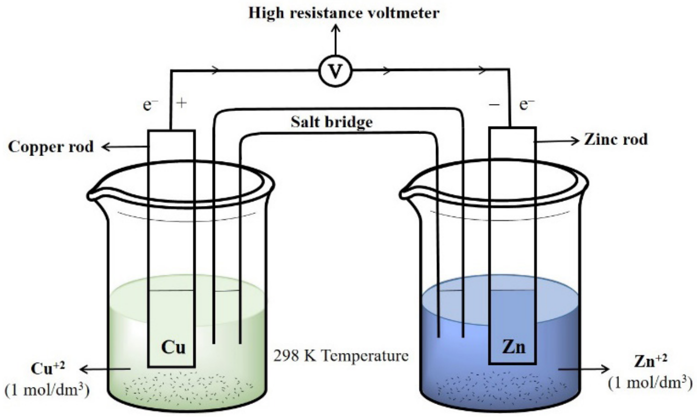


Figure 10.7 An electrochemical cell, made by connecting a Cu^{2+}/Cu half-cell to a Zn^{2+}/Zn half-cell.

represented by the following half-equations:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \qquad E^\circ = +0.34\ V$$

$$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)} \qquad E^\circ = -0.76\ V$$

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. The voltage generated by this cell is +1.10 V.

$$E^\circ_{cell} = E^\circ_{red} + E^\circ_{oxi} = +0.34 - (-0.76) = +1.10$$

In a Cu-Zn galvanic cell, zinc (Zn) serves as the anode, and copper ions (Cu^{2+}) in solution serve as the cathode.

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:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

This process effectively converts the chemical energy of the redox reaction into electrical energy, which can be connected to perform work.

10.16 CALCULATION OF STANDARD POTENTIAL (E^o_{Cell})

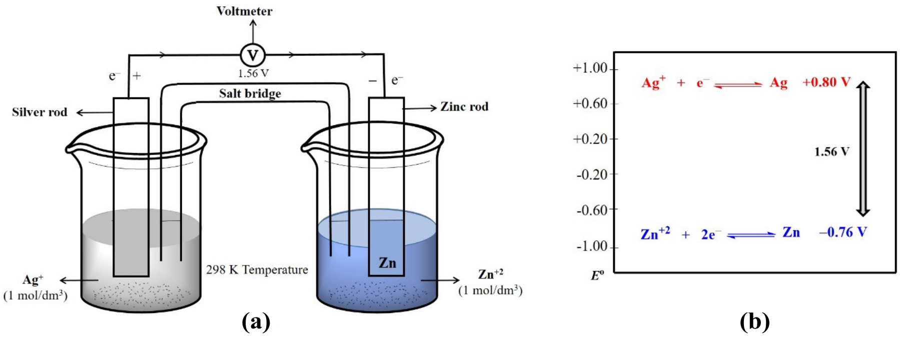
We can use E^O values to calculate the voltage of an electrochemical cell made up of two half-cells, even when neither of them is a standard hydrogen electrode. The voltage measured is the difference between the E^O values of the two half-cells. we call this value the **standard cell potential (E^o_{Cell}).**

For the electrochemical cell shown in **Figure 10.8 (a)**, the two relevant half-equations are:

$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)} \qquad E^O = +0.80\ V$$

$$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)} \qquad E^O = -0.76\ V$$

The voltage of this cell is +0.80 – (–0.76) = +1.56 V as in **Figure 10.8 (b)**.



(a) (b)

Figure 10.8 (a) An Ag^+/Ag, Zn^{2+}/Zn electrochemical cell, **(b)** The difference between +0.80 V and –0.76 V is +1.56 V.

Quick Check 10.7

i) What is the function of salt bridge in the voltaic cell?

ii) Calculate the voltage of a cell having iron and copper electrodes.

$$Fe_{(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2e^- \quad E^o = -0.44\ V$$

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \quad E^o = -0.44\ V$$

The E^O 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.

10.17 APPLICATIONS OF E° VALUES

10.17.1 Direction of Electron Flow

We can deduce the direction of electron flow in the wires in the external circuit by comparing the E^O values for the two half-cells which make up the electrochemical cell. For example, in **Figure 10.9** these voltages are:

$$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)} \qquad E^O = +0.80\ V$$

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \qquad E^O = -0.76\ V$$

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.

10.17.2 Feasibility of A Reaction Using E° Values

Standard electrode potential values, E^O, give us a measure of how easy or difficult it is to oxidize or reduce a species. The E^O 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^O, 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^O, the greater the tendency for the half-equation 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

$$Mg^{2+} + Ag \qquad ?$$

We need half cell equations and E° values

$$Mg^{2+} + 2e^- \rightleftharpoons Mg \qquad E° = -2.32\ V$$

$$Ag^+ + 1e^- \rightleftharpoons Ag \qquad E° = +0.80\ V$$

Mg^{2+} are supposed to be reduced here and Ag is supposed to get oxidized, So calculating E° cell gives us

$E°_{cell} = E°_{red} - E°_{ox}$

$= (-2.32) - (+0.80)$

$= -1.52V$

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.

$E°_{cell} = E°_{red} - E°_{ox}$

$= (-0.80) - (-2.32)$

$= +1.52V$

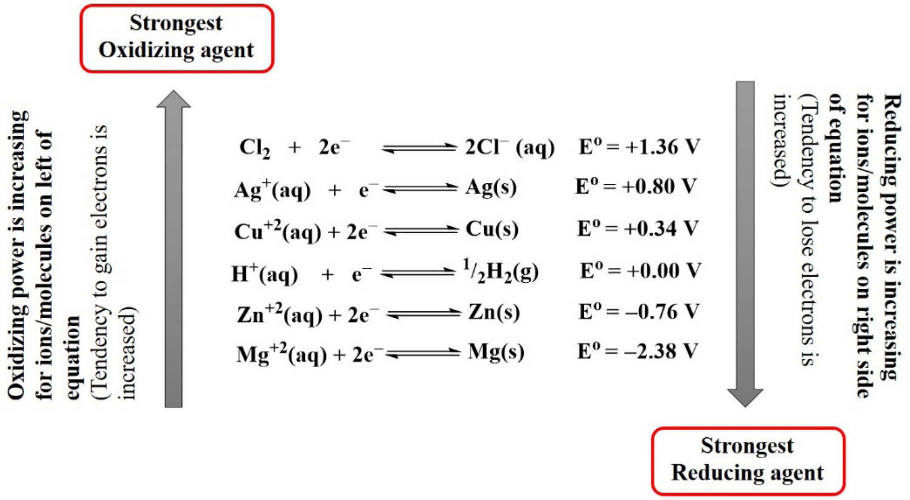


Figure 10.9 Standard electrode potentials for some oxidizing and reducing agents

Zn has a greater tendency to lose electrons than Cu, so the chemical reaction that proceeds in this half-cell is in the reverse direction:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

We can combine these two half-equations to show the direction of the reaction in the electrochemical cell as a whole.

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

This is the reaction taking place in the electrochemical cell. The reaction between zinc metal and copper ions is feasible. If the forward reaction is feasible, the reverse reaction (between Cu metal and zinc ions) is not feasible.

If a piece of copper metal is placed directly into a 1.00 mol dm^{-3} solution of Zn^{2+} ions, no reaction takes place. The half-equations, the direction of the reaction is given by a clockwise pattern reactant, product, reactant, product) starting from the top left as shown in **Figure 10.10** for the cell made from the two half-cells Cu^{2+}/Cu and Zn^{2+}/Zn.

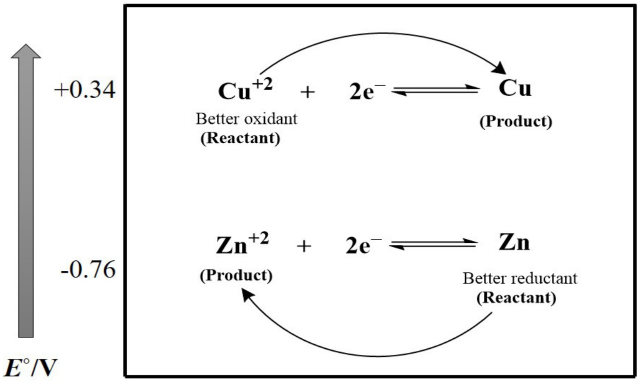


Figure 10.10 A reaction occurs in a direction so that the stronger oxidizing agent reacts with the stronger reducing agent.

Quick Check 10.8

a) Explain the following keeping in view the standard electrode potential values (Eo Cl2/2Cl- = +1.36 V Eo ($Br_2/2Br^-$) = +1.07 V, Eo ($I_2/2I^-$) = +0.54 V)

i. The aqueous solution of iodine can be oxidized with bromide or iodide ions.

ii. Why bromine does not react with chloride ions?

10.17.3 Oxidising and Reducing Agents Using E° Values

Look back at **Figure 10.11**. Note the following as the values of E^O 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^O value more negative than the E^O value for Zn^{2+}/Zn. In Figure 10.13 we see that the half-equation Mg^{2+}/Mg has a more negative E^O value. So, Mg is a suitable reducing agent.

$$Zn^{2+}_{(aq)} + e^- \longrightarrow Zn_{(s)} \qquad E^O = -0.76\text{ V}$$

$$Mg^{2+}_{(aq)} + 2e^- \longrightarrow Mg_{(s)} \qquad E^O = -2.38\text{ V}$$

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 $KMnO_4$ (+0.54V) $K_2Cr_2O_7$ (+1.33V) are oxidizing agent because of there 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 has oxidizing as well as reducing agents.

10.18 VARIATION OF E^O 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 non-standard conditions we use the symbol E for the electrode potential. Let us take an example of a metal/metal ion equilibrium:

Table 10.1 Variation of Potential with Ion Concentration

$[Fe^{3+}]$ (mol dm $^{-3}$)	$[Fe^{2+}]$ (mol dm $^{-3}$)	E^O (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

$$Zn^{2+}_{(aq)} + e^- \longrightarrow Zn_{(s)} \qquad E^O = -0.76\ V$$

- 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.

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad E^O = +0.77\ V$$

$$1.00\ mol\ dm^{-3} \qquad 1.00\ mol\ dm^{-3}$$

10.19 NERNST EQUATION

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:

$$Cu_{(s)} + 2Ag^{+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)} \qquad E^{O} = +0.46\ V$$

When E^{o}_{cell} is ploted against concentration we obtain a graph as shown in **Figure 10.11.**

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.

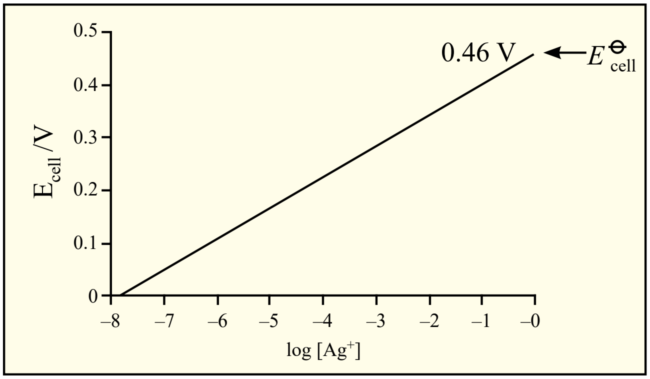


Figure 10.11 Increasing the concentration of silver ions in the cell reaction

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:

$$E = E^{o} + \frac{RT}{zF}\,\ell n\,\frac{[\text{oxidized form}]}{[\text{reduced form}]}$$

where,

E is the electrode potential under non-standard conditions

E^{O} 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.

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

  $\ln x = 2.303 \log_{10} x$

- At standard temperature the values of R, T and F are constant

  The equation then becomes

$$E = E^{o} + \frac{0.059}{z}\,\ell og\,\frac{[\text{oxidized form}]}{[\text{reduced form}]}$$

Sample problem

What is the eloectrode potential of a Zn electrode dept in a solution containing Zn^{2+} ions (0.1M), The e° value of Zn^{2+} / ZnO is -0.76V

Using Half equation and E°,

$$Zn^{2+} + 2e^- \longrightarrow Zn \qquad E° = -0.76V$$

$$E = (-0.76) + \frac{8.31 \times 298}{2 \times 96500} \ell n\,(0.1)$$

$$E = -0.76 + (-0.029) = -0.78\ V$$

Since, Concentration of Zn^{2+} is decreased to shift equilibrium backward and electrode potential decreases to -0.78 V

10.20 ACTIVITY SERIES OF METALS AND EASE OF OXIDATION

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 10.2**.

Table 10.2 Activity Series of Metals

Metals	Ions	E^0 (V)	Reaction Occurring	Trend
Li	Li^{1+}	-3.05	React with cold water, replacing hydrogen $2M_{(s)} + 2H_2O_{(l)} \longrightarrow 2MOH_{(aq)} + H_{2(g)}$	↓ decreasing ease of oxidation, reactivity and acting as 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	React with steam, but not cold water, replacing hydrogen. $M_{(s)} + H_2O_{(l)} \longrightarrow MO_{(aq)} + H_{2(g)}$	
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		

10.21 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.

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, the reaction is possible if 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 ovelall 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**.

Consider another example:

From the activity series of metals, we have

$$Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)} \qquad E^\circ_{(red)} = -1.66\ V$$

$$Ag^{+}_{(aq)} + 1e^- \rightleftharpoons Ag_{(s)} \qquad E^\circ_{(ox)} = +0.080\ V$$

$$Al^{3+}_{(aq)} + Ag_{(s)} \longrightarrow Al_{(s)} + Ag^{+}_{(aq)} \qquad E^\circ_{(red)} = -1.66 + 0.080 = -0.86\ V$$

The sum of E^O values of the two half-cell reactions is **negative**. Hence the reaction is **not feasible**.

Quick Check 10.9

a) State the Nernst equation, why is it significant in electrochemistry.

b) What is the effect of variation in ion concentration on the standard electrode potential of a half reaction?

c) Give answers using Eo values (EoAg+/Ag = + 0.80 V, EoCr2+/Cr = - 0.91 V, EoFe2+/Fe = - 0.44 V

i. Which of Ag+, Cr2+ and Fe2+, is the strongest oxidizing agent? Which is the least oxidizing? Explain with reason.

ii. Arrange Ag, Cr and Fe in increasing order of their reducing powers.

d) What is the electrode potential of a Cu electrode dipped in a solution containing Cu2+ ions (0.01 M), The Eo value of Cu2+/Cu0 is +0.34 V.

10.22 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.

10.22.1 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.

10.22.2 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.

10.27 WINKLER METHOD, BOD AND DO

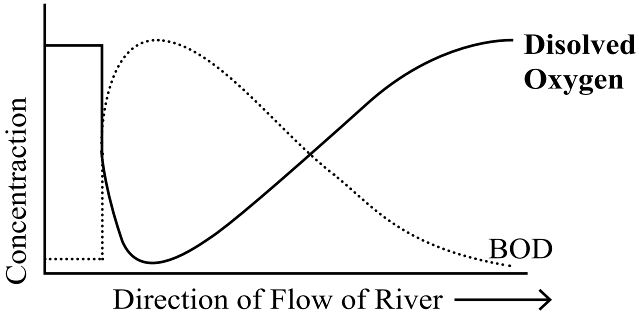


Figure 10.12 Inverse relationship between BOD and DO

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.

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 8 mg/dm^3. The minimum level of DO should be 5 mg/dm^3. Below 5 mg/dm^3, the water supposed to be polluted.

Dissolved Oxygen (DO) and Biochemical Oxygen Demand (BOD) have an inverse relationship as shown in **Figure 10.12**. 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.

EXERCISE

MULTIPLE CHOICE QUESTIONS

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) $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$
b) $Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^-$
c) $Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$
d) $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

f. 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

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. How and why electrical double layer is formed?

b. Why electrode potential of Cu is called reduction potential?

c. What are the advantages of salt bridge in a galvanic cell?

d. How can we predict the feasibility of a chemical reaction using the cell voltage?

e. During electrolysis of aqueous NaCl, why Na is not liberated at the cathode?

f. Calculate the Ox. No. of chromium (Cr) in the following compounds:

(i) $CrCl_3$ (ii) $Cr_2(SO_4)_3$ (iii) $Cr_2O_7^{2-}$

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 sulfate.

ii) Iron is added to a dilute solution of hydrochloric acid.

h. Explain why some metals higher in the activity series can displace hydrogen from acids, while others lower in the series cannot.

i. Calculate Number of Faradays required to deposit 108 g of Ag^{1+}, 63.5 g of Cu^{2+} and 27 g of Al^{3+}.

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.

k. A cell is set up with a standard nickel electrode ($Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni(s)$ $E^0 = -0.25$ V) and a standard cobalt electrode ($Co^{2+}_{(aq)} + 2e^- \rightleftharpoons Co(s)$, $E^0 = -0.28$ 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 ($E°_{cell}$).

DESCRIPTIVE QUESTIONS

Q.3. How electrode potential varies with concentration of an aqueous solution? Use the NERST equation to explain this variation.

Q.4. How Avogadro's number can be derived using an electrolytic cell?

Q.5. Describe the construction and working principle of the Zn-Cu Galvanic cell.

Q.6 What is meant by Standard Hydrogen Electrode (SHE)? How it is used to measure the electrode potential of another electrode?

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})**

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})**

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.

11

HYDROCARBONS

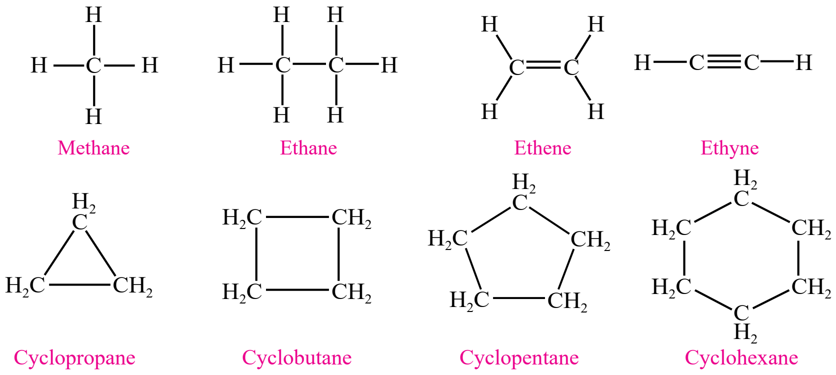
STUDENT LEARNING OUTCOMES [C-11-D-01 to C-11-D-17]

- 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. 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. Hydrocarbons are broadly divided into two classes that is aliphatic and aromatic hydrocarbons.

11.1 ALIPHATIC AND AROMATIC 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 11.1** shows some examples of aliphatic hydrocarbons.

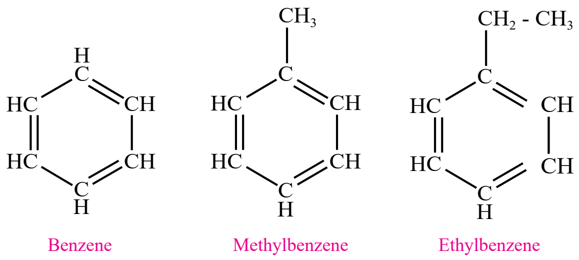


Methane Ethane Ethene Ethyne

Cyclopropane Cyclobutane Cyclopentane Cyclohexane

Figure 11.1: Aliphatic 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 11.2** presents the structures of some aromatic hydrocarbons.



Benzene Methylbenzene Ethylbenzene

Figure: 11.2 Some aromatic hydrocarbons

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**.

11.2 NOMENCLATURE

11.2.1 Alkanes or Paraffins

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 11.1**.

Did You Know?

Butane is a fuel used in lighters. Isobutane is used as a propellant in products such as shaving gel.

Table 11.1 Condensed structural formulae and molecular formulae of alkanes

IUPAC Name	Molecular formula	Condensed structure
Methane	CH_4	CH_4
Ethane	C_2H_6	$CH_3\ CH_3$
Propane	C_3H_8	$CH_3\ CH_2\ CH_3$
Butana	C_4H_{10}	$CH_3\ CH_2\ CH_2\ CH_3$
Pentane	C_5H_{12}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_3$
Hexane	C_6H_{14}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$
Heptane	C_7H_{10}	$CH_3\ \ CH_2\ CH_3\ CH_2\ CH_2\ CH_2\ CH_3$
Octane	C_8H_{18}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$
Nonane	C_9H_{20}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$
Decane	$C_{10}H_{22}$	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$

What we obtain 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 **Table 11.2 & Table 11.3.**

Table 11.2 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.

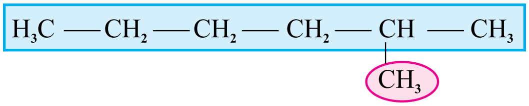
Table 11.3 alkyl groups, straight chain and branched and their names

Alkane	Possible Alkyl Groups			
$CH_3CH_2CH_3$ Propane	$CH_3CH_2CH_2$ —— n-Propyl group (Propyl)	$CH3\overset{|}{C}HCH3$ iso-Propul group (1-Methylethyl)		
$H_3CH_0CH_2CH_3$	$CH_3CH_2CH_2CH_2$ — n-Butyl group (Butyl)	$CH_3\overset{|}{C}H_2CHCH_3$ sec-Butyl group (1-Methylpropyl)	$\underset{CH_3}{CH_3}CHCH_2$— Iso-Butyle group (2-Methylpropyl)	$\underset{CH_3}{\overset{|}{CH_3}}CCH_3$ tert-Butyl group (1,1-Dimethylpropyl)

11.2.2 Nomenclature of alkanes

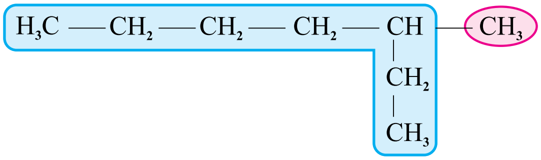
Branched chain alkanes are named according to the following rules.

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, that is, a bent change.



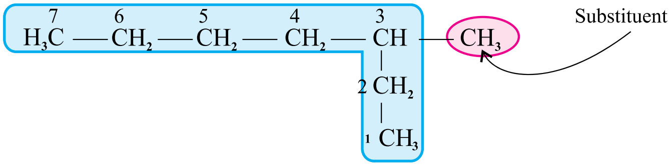
$$H_3C—CH_2—CH_2—CH_2—\underset{CH_3}{CH}—CH_3$$

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.

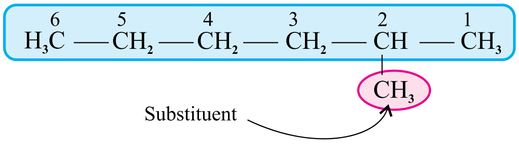


$$H_3C—CH_2—CH_2—CH_2—\underset{\underset{CH_3}{|}}{\underset{CH_2}{|}}{CH}—CH_3$$

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.

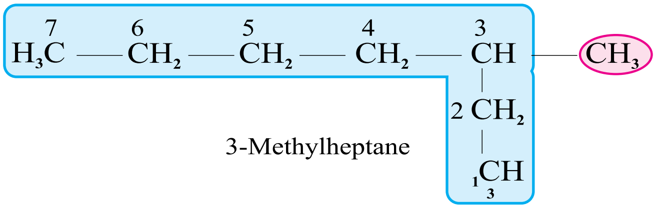


$$\overset{7}{H_3C}—\overset{6}{CH_2}—\overset{5}{CH_2}—\overset{4}{CH_2}—\underset{\underset{{}^1CH_3}{|}}{\underset{{}^2CH_2}{|}}{\overset{3}{CH}}—CH_3$$



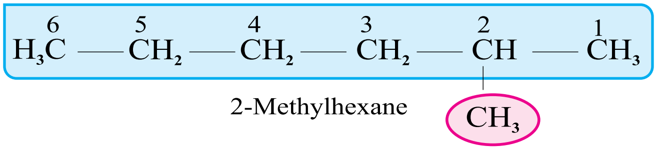
$$\overset{6}{H_3C}—\overset{5}{CH_2}—\overset{4}{CH_2}—\overset{3}{CH_2}—\underset{CH_3}{\overset{2}{CH}}—\overset{1}{CH_3}$$

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:



$H_3C-CH_2-CH_2-CH_2-CH(CH_3)-CH_2-CH_3$

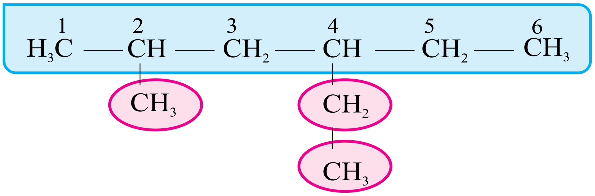
3-Methylheptane



$H_3C-CH_2-CH_2-CH_2-CH(CH_3)-CH_3$

2-Methylhexane

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.

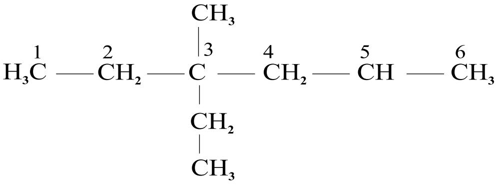


$H_3C-CH(CH_3)-CH_2-CH(CH_2CH_3)-CH_2-CH_3$

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”.

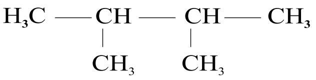
5. When two substituents are present on the same carbon atom, use that number twice.



$H_3C-CH_2-C(CH_3)(CH_2CH_3)-CH_2-CH_2-CH_3$

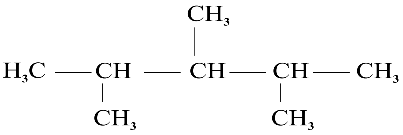
3-Ethyl-3-methylhexane

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.



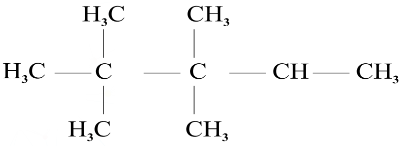
$H_3C-CH(CH_3)-CH(CH_3)-CH_3$

2, 3-Dimethylbutane



$H_3C-CH(CH_3)-CH(CH_3)-CH(CH_3)-CH_3$

2,3,4 Trimethyl butane

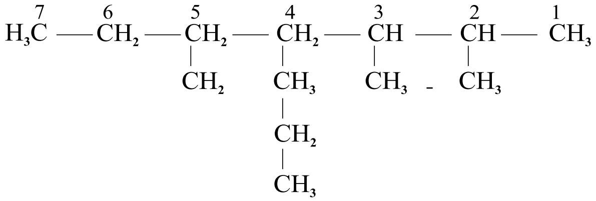


$H_3C-C(CH_3)_2-C(CH_3)_2-CH-CH_3$

2, 2, 3, 3-Tetramethyl butane

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.

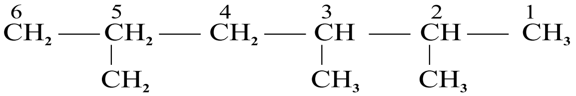
7. When two chains of equal length compete for selection as the parent chain, choose the chain with the greater number of substituents.



$$\overset{7}{H_3C}-\overset{6}{CH_2}-\underset{\begin{array}{c}|\\CH_2\end{array}}{\overset{5}{CH_2}}-\underset{\begin{array}{c}|\\CH_3\\|\\CH_2\\|\\CH_3\end{array}}{\overset{4}{CH_2}}-\underset{\begin{array}{c}|\\CH_3\end{array}}{\overset{3}{CH}}-\underset{\begin{array}{c}|\\CH_3\end{array}}{\overset{2}{CH}}-\overset{1}{CH_3}$$

2, 3, 5-Trimethyl-4-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.

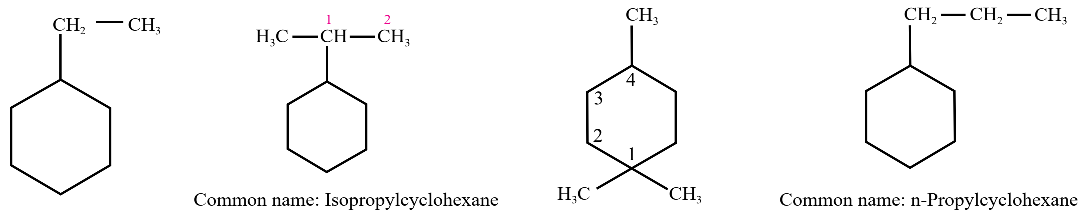


$$\overset{6}{CH_2}-\underset{\begin{array}{c}|\\CH_2\end{array}}{\overset{5}{CH_2}}-\overset{4}{CH_2}-\underset{\begin{array}{c}|\\CH_3\end{array}}{\overset{3}{CH}}-\underset{\begin{array}{c}|\\CH_3\end{array}}{\overset{2}{CH}}-\overset{1}{CH_3}$$

2, 3, 5-Trimethyl-hexane (not-2,4,5 trimethyl hexane)

11.2.3 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**



Ethylcyclohexane

Common name: Isopropylcyclohexane
IUPAC name: 1-Methylethylcyclohexane

1,1,4-Trimethylcyclohexane

Common name: n-Propylcyclohexane
IUPAC name: Propyclcyclohexane

Figure 11.3 Naming cycloalkanes

Quick Check 11.1

a) Write down the structural formulas for 2-methylbutane and 2,2-dimethylpropane.

b) Write down displayed formula of 2,3,3-trimethylhexane and methylcyclohexane.

c) Give two differences between molecules of cyclopentane and pentane?c)

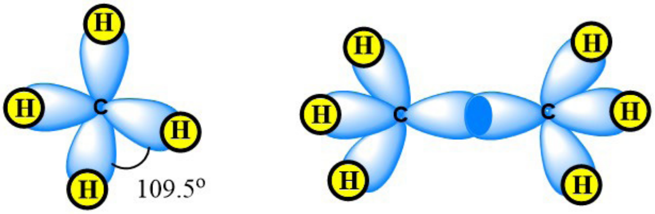
d) Eicosane is a straight chain alkane whose molecules contain 20 carbon atoms. What is the molecular formula of eicosane?

11.2.3 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 11.4**. 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 are shown **(Table 11.4)**.

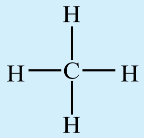
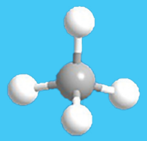
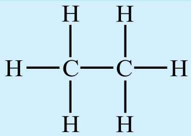
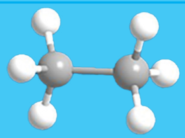
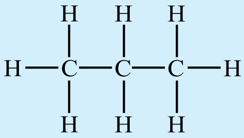
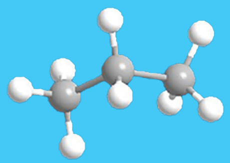
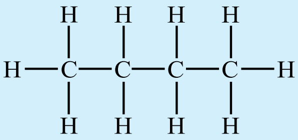
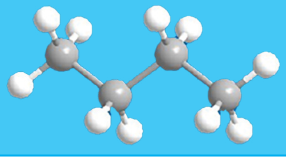


Methane
sp^3 hybrid tetrahedral

Ethane

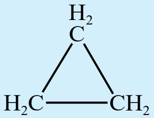
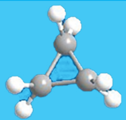
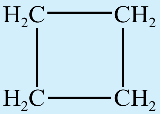
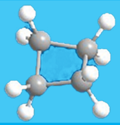
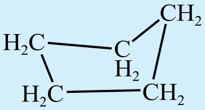
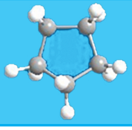
Figure 11.4 Sp^3 hybridised methane and ethane

Table 11.4 Shapes of some straight chain alkanes

IUPAC name & Molecular formula	Structural formula	3D Structure
Methane CH_4	 $\mathrm{H-\overset{H}{\underset{H}{C}}-H}$	
Ethane C_2H_6	 $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$	
Propane C_3H_8	 $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$	
Butane C_4H_{10}	 $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$	

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 11.5)**

Table 11.5 Shapes of few cycloalkanes

IUPAC name & Molecular formula	Structural formula	3D Structure
Cyclopropane C_3H_6		
Cyclobutane C_4H_8		
Cyclopentane C_4H_{10}		

11.2.4 Physical Properties of Alkanes

1. 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. 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. 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, e.g. straight change butane has a higher boiling point -0.50 ºC 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?
b) Explain why alkanes have a tetrahedral shape.
c) Draw the shapes of cyclopropane and cyclopentane.

11.3 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

Homolytic fission occurs when the covalent bond breaks evenly to produce free radicals. Free Radical is a 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.

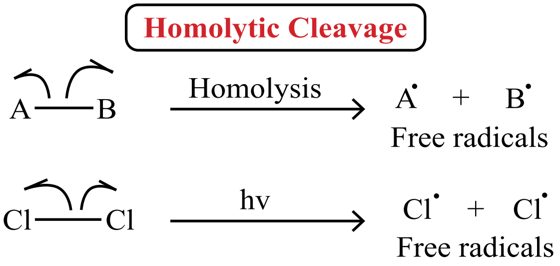


Figure 11.5 Homolytic fission and free radical formation

(b) Heterolytic Fission

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.

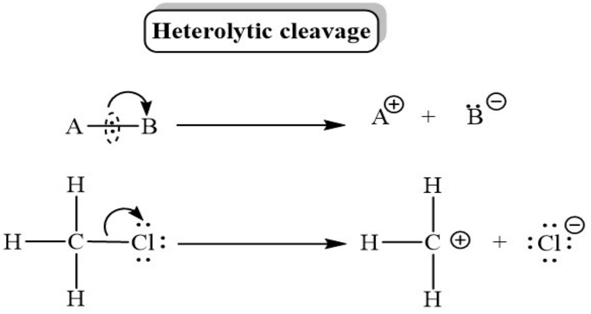


Figure 11.6 Heterolytic fission and formation of radical ions

11.4 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. 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.

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.

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.

11.5 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.

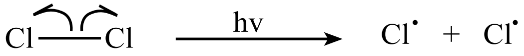
11.5.1 Free radical Substitution Reactions

Substitution reactions of alkanes take place in the presence of light energy through the formation of highly reactive free radicals. An example is the substitution of a halogen atom with a hydrogen of an alkane, called **halogenation**. Alkanes react with chlorine and bromine in the presence of sunlight or UV light resulting in the successive replacement of hydrogen atoms with halogens. The extent of halogenation depends upon the amount of halogen used. Reaction of alkanes with fluorine is highly violent and results in a mixture of carbon, fluorinated alkanes and hydrofluoric acid. Iodine does not substitute directly because the reaction is too slow and reversible. The order of reactivity of halogens is:

$$\mathbf{F_2 > Cl_2 > Br_2 > I_2}$$

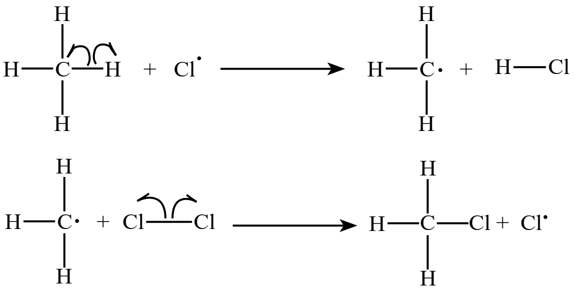
Halogenation involves the following three steps.

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.



$$Cl-Cl \xrightarrow{hv} Cl^{\bullet} + Cl^{\bullet}$$

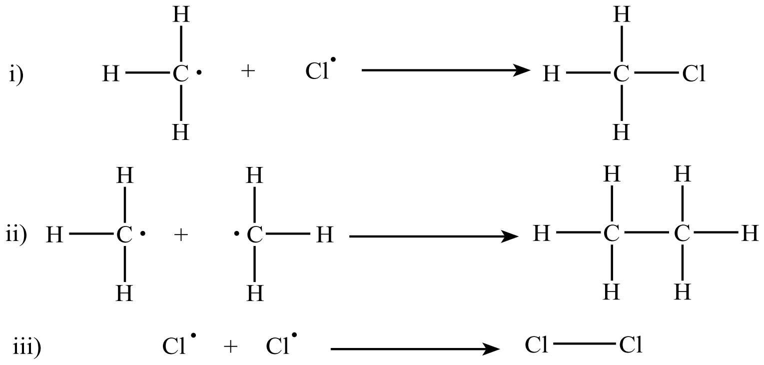
ii) Propagation step is the second step in the free radical substitution in which the initially formed radicals attack the alkane molecule generating more free radicals.



$$CH_4 + Cl^{\bullet} \longrightarrow CH_3^{\bullet} + H-Cl$$

$$CH_3^{\bullet} + Cl-Cl \longrightarrow CH_3-Cl + Cl^{\bullet}$$

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 may take place in different ways. The chloride and alkyl radicals may combine to form an 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.

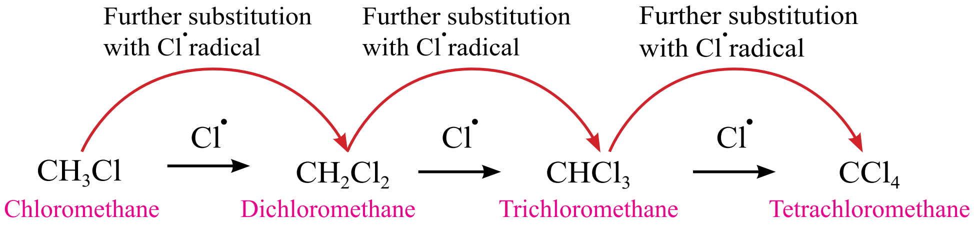


By repetition of step (ii), propagation step, a mixture of halogen substituted products (chloroalkanes) is obtained. The more the chlorine gas in reaction mixture to start with, the greater the proportions of chlorine atoms in the chloroalkane molecules formed.

Trichloromethane is also known as chloroform and tetrachloromethane is also known as carbon tetrachloride.

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?
b) What are major types of reactions that alkanes undergo?
c) How the termination step occurs in the halogenation of alkenes?
d) State the conditions under which a mixture of halogenoalkanes is obtained from the halogenation of alkanes.
e) Predict the products of the free radical chlorination of ethane.

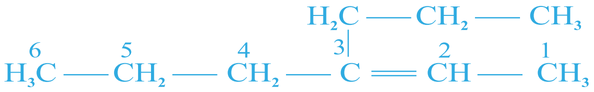
11.6 ALKENES

11.6.1 Nomenclature of 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.

The IUPAC rules for naming alkenes are similar in many respects to those for naming alkanes.

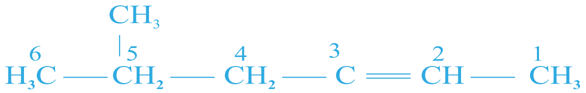
1. Select the longest continuous chain that contains the C = C as the parent chain. Change the ending of the name of the alkane of identical length from — ane to — ene, e.g.,



$$\overset{6}{\mathrm{H_3C}}-\overset{5}{\mathrm{CH_2}}-\overset{4}{\mathrm{CH_2}}-\overset{\overset{\mathrm{H_2C-CH_2-CH_3}}{|\,3}}{\mathrm{C}}=\overset{2}{\mathrm{CH}}-\overset{1}{\mathrm{CH_3}}$$

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.



$$\overset{6}{\mathrm{H_3C}}-\overset{\overset{\mathrm{CH_3}}{|\,5}}{\mathrm{CH_2}}-\overset{4}{\mathrm{CH_2}}-\overset{3}{\mathrm{C}}=\overset{2}{\mathrm{CH}}-\overset{1}{\mathrm{CH_3}}$$

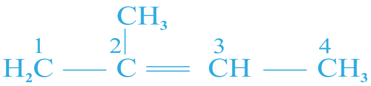
5-Methyl 2-hexene

3. Designate the location of the double bond by using the number of the first atom of the double bond as a prefix.

$\overset{1}{\mathrm{H_2C}}=\overset{2}{\mathrm{CH_2}}-\overset{3}{\ }-\overset{4}{\mathrm{CH_3}}$ 1-butene

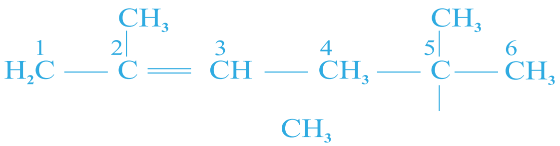
$\overset{1}{\mathrm{H_2C}}=\overset{2}{\mathrm{CH}}\ \mathrm{CH_2}\overset{3}{\ }-\overset{4}{\mathrm{CH_2}}-\overset{5}{\mathrm{CH_3}}$ 1-pentene

4. Indicate the locations of the substituent groups by the numbers of the carbon atoms to which they are attached.



$$\overset{1}{\mathrm{H_2C}}-\overset{\overset{\mathrm{CH_3}}{2|}}{\mathrm{C}}=\overset{3}{\mathrm{CH}}-\overset{4}{\mathrm{CH_3}}$$

2-Methyl-2-butene



$$\overset{1}{\mathrm{H_2C}}-\overset{\overset{\mathrm{CH_3}}{2|}}{\mathrm{C}}=\overset{3}{\mathrm{CH}}-\overset{4}{\mathrm{CH_3}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{\overset{\mathrm{CH_3}}{5|}}{\mathrm{C}}}-\overset{6}{\mathrm{CH_3}}$$

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.

11.6.2 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.

$$CH_3{-}CH_2OH + H_2SO_4 \xrightarrow{180^{\circ}C} CH_3{-}CH_2{-}OSO_3H + H_2O$$

$$CH_3{-}CH_2OSO_3H \xrightarrow{\text{heat}} H_2C{=}CH_2 + H_2SO_4$$

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.

$$H_3C{-}CH_2{-}Br + KOH_{(\text{alcoholic})} \xrightarrow{\text{heat}} H_2C{=}CH_2 + KBr + H_2O$$

11.6.2 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, they show weakly polar properties because of sp^2 hybridization

Quick Check 11.4

a) Give the reactions of propanol with H_2SO_4, wright down all the reaction involved.

b) Name the following alkenes

i) $CH_3C(CH_3){=}CH{-}CH_3$ ii) $CH_2{=}CHCH(CH_3)_2$

c) Draw the structural formulas of the following alkenes.

i) 3-Methyl-2-butene ii) 2-Methyl-4-ethyl-2-pentene

d) Give the dehydrohalogenation reaction of bromopropane?

e) Can propanaol undergo dehydration? If yes give reactions involving dehydration.

11.7 STRUCTURE AND REACTIVITY OF ALKENES

11.7.1 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 11.8**.

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 11.9**.

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 ethane so they could ripen in short time.

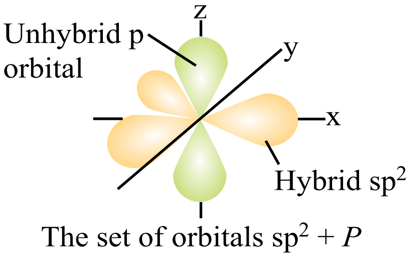


Fig.11.8: sp^2 hybrid & unhybrid orbitals of C

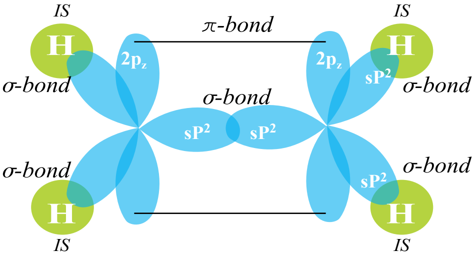


Fig.11.9: Bond formation of carbons in ethene

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 11.10.**

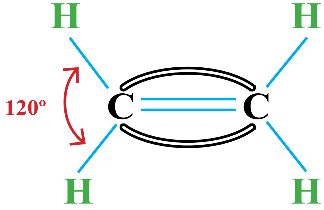


Figure 11.10 Structure of ethene

11.7.1 Reactivity of π bond

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.

Did You Know?

Electrophile is a species that can act as electron pair acceptor, it is represented by $\mathbf{E^+}$. 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 $\mathbf{Nu}^{\cdot\cdot -}$.

Quick Check 11.5

a) How does an alkane differ from an alkene in stability?

b) Which of the following species is likely to act as a nucleophile?

i) H_2 ii) H^+ iii) OH^-

c) Explain your answer to (d).

d) Which of the following species is likely to act as an electrophile?

i) H_2 ii) H^+ iii) OH^-

e) Explain your answer to (f).

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.

11.7.2 Carbocation Stability and Inductive effect of Alkyl group

Carbocation is an alkyl group with a single positive charge on one of its carbon atoms. Carbocations are classified into following types.

i. Carbocation which is bonded to H only is named as methyl carbocation.

ii. If carbocation is bonded to one C or alkyl substituent then it is named as primary 1° carbocation.

iii. If it is bonded to 2 carbons (alkyl substituent) directly, then it is named as secondary 2° carbocation.

iv. If it is named as tertiary 3° carbocation if it is directly bonded to 3 carbons (alkyl substituent).

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. 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.

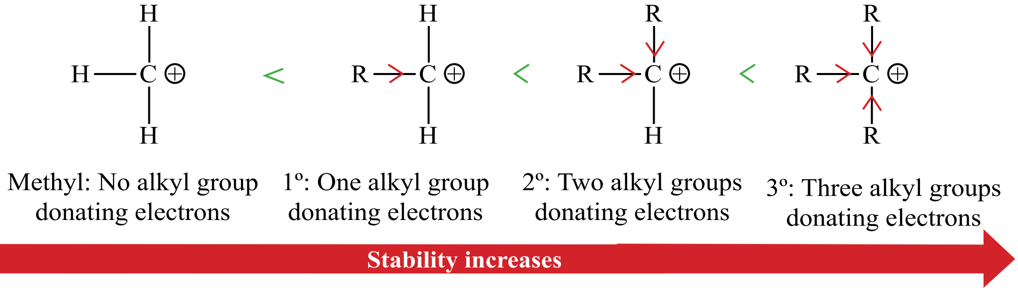


Fig. 11.11 Inductive effect & Stability of carbocation

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 11.11**.

11.7.3 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 11.12**.

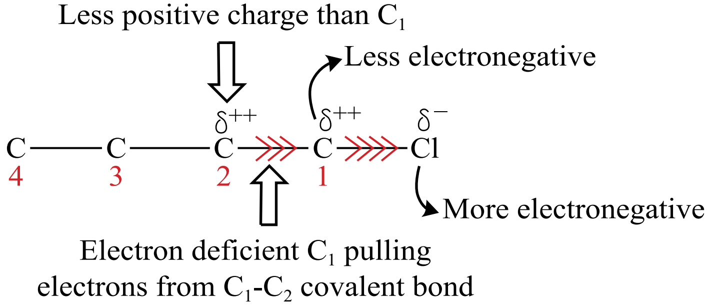


Figure 11.12 Inductive effect: Polarization of sigma bond

11.8 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.

11.8.1 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 11.13**, X^+ represents an electrophile and Y^- represents a nucleophile.

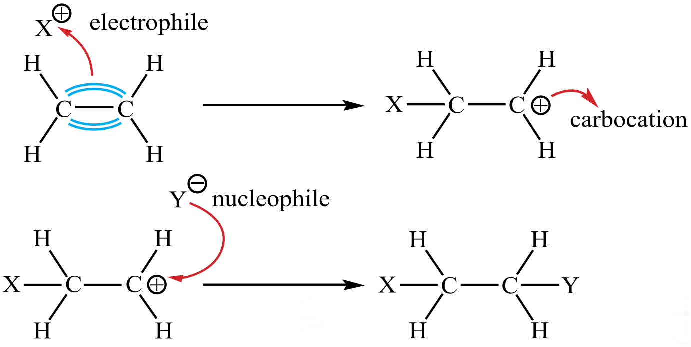


Figure 11.13 Generalized mechanism of electrophilic addition

Quick Check 11.6

a) How do alkenes react with an electrophile?
b) Why the order of stability of carbocation is 3° > 2° > 1°?

In this chapter, only the mechanism of halogen addition and hydrogen halide addition will be learnt.

1. Halogenation

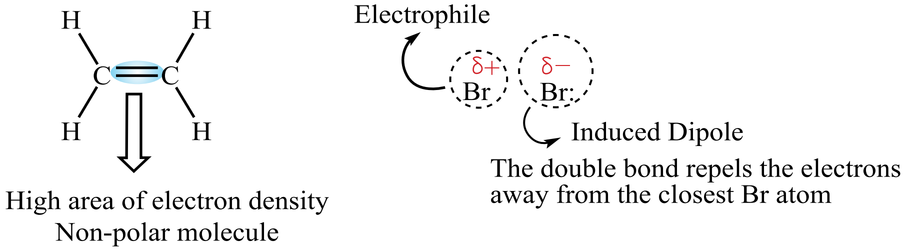
Halogenation means addition of halogens like chlorine or bromine. When bromine water (a solution of bromine in water having red-brown colour) is added to ethene in an inert solvent like carbon tetrachloride, its reddish brown colour is discharged at once. This reaction is used to identify the unsaturation of an organic compound.

$$CH_2=CH_2 + Br_2 \rightarrow Br\text{-}CH_2\text{-}CH_2\text{-}Br$$

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 11.14.**

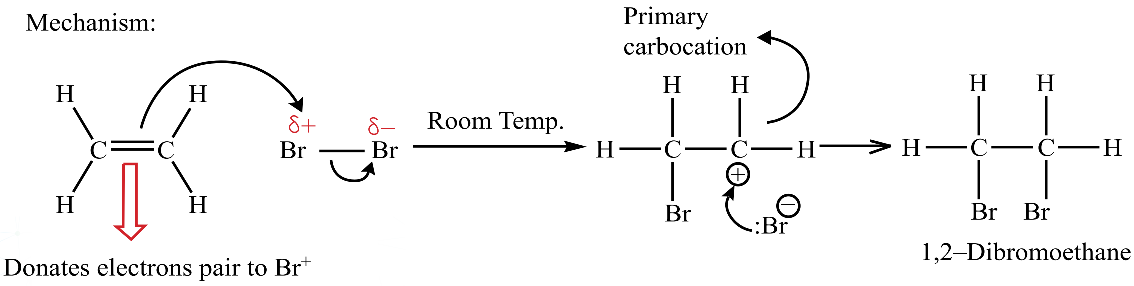


Figure 11.14 Electrophilic addition mechanism of ethene and Br_2

2. Hydrohalogenation

When an alkene reacts with dry gaseous hydrogen halide at room temperature, the product is a halogenoalkane.

$$\underset{\text{Ethene}}{CH_2=CH_2} + HBr \longrightarrow \underset{\text{Bromoethane}}{CH_3\text{–}CH_2\text{–}Br}$$

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.

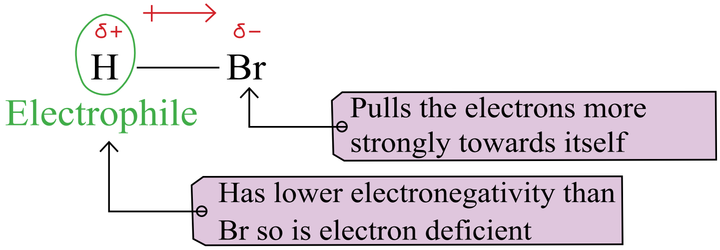


Figure 11.15 HBr molecule polarity

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 11.16**.

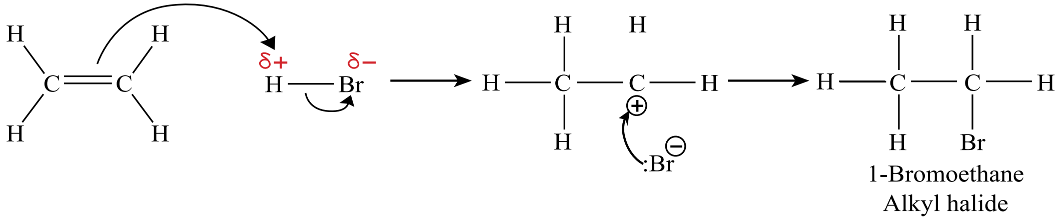


Figure 11.16 Electrophilic addition mechanism of HBr to ethene

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 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^o 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 11.17**.

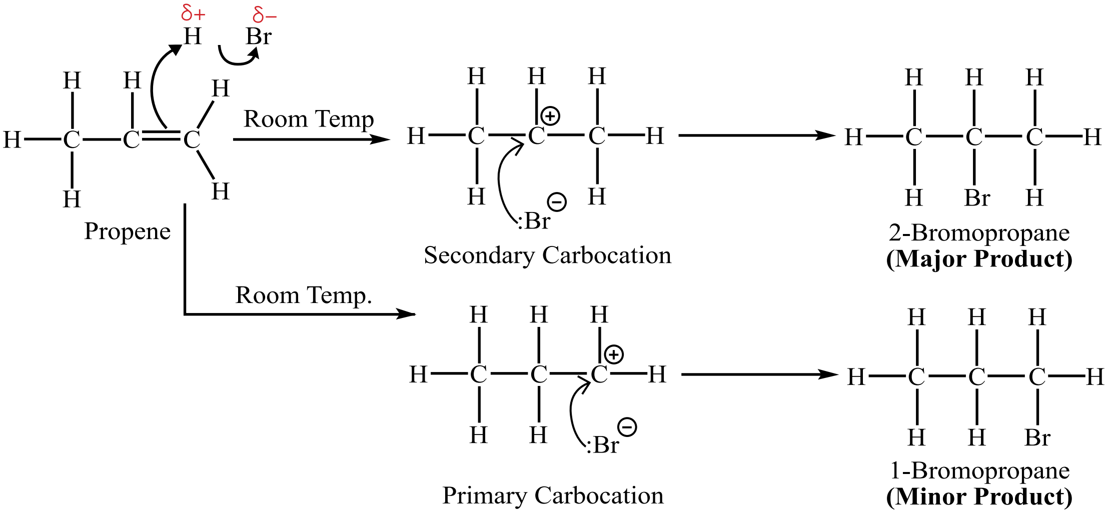


Figure 11.17 Electrophilic addition mechanism of HBr to propene

Quick Check 11.7

a) Compare and explain the relative rates of addition to alkenes (reactivities) of HCl, HBr and HI

b) Explain the difference between an addition reaction and an elimination reaction?

c) How alkene react with an electrophile?

d) Explain how Markovnikove's rule is applied in addition of HBr to 2-pentene.

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 ^{0}C.

$$H_2C=CH_2 + H_2 \xrightarrow[250-300\ ^oC]{Ni} H_3C-CH_3$$

On industrial scale, this reaction is used to convert vegetable oil into margarine (Banaspati ghee).

$$\text{Oil} + H_2 \xrightarrow{Ni} \text{Margarine (Banaspati ghee)}$$

4. Hydration

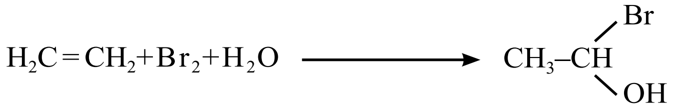
Gaseous alkenes react with steam at high temperature and pressure in the presence of concentrated acid (H_2SO_4) as the catalyst to form alcohols.

$$H_2C=CH_2 + H_2O \xrightarrow{H_2SO_4} C_2H_5OH$$

Similar to hydrohalogenation, the alkene forms a carbocation intermediate, which is then attacked by OH^-.

5. Halohydration

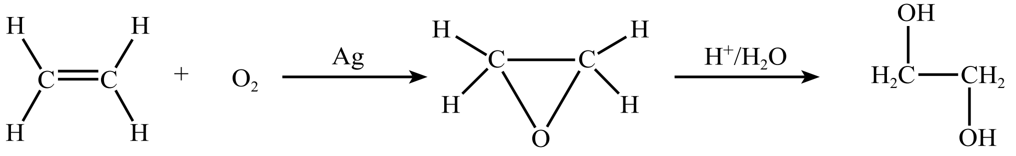
Halohydration is a reaction where an alkene reacts with a halogen (such as bromine or chlorine) in the presence of water to form a halohydrin. For **ethene (C_2H_4),** the reaction specifically produces a bromohydrin or chlorohydrin, depending on the halogen used.



1-Bromo-2-ethanol

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. 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. The epoxides can be converted in to diols by acid hydrolysis.



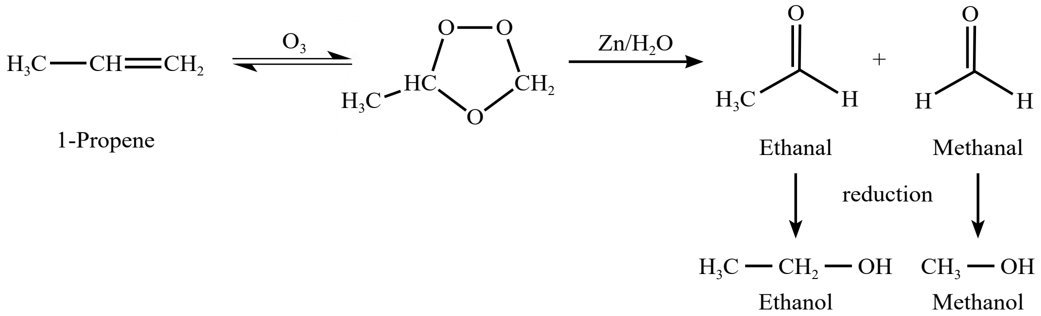
Epoxide

Ethane-1,2-diol

7. Ozonolysis

Ozonolysis is a method of oxidatively cleaving alkenes using ozone (O_3), a reactive allotrope of oxygen. This reaction is often used to identify the structure of unknown alkenes by breaking them down into smaller, more easily identifiable pieces. Alkenes react with ozone (O_3) to form ozonides, which can be further reduced to carbonyl compounds (aldehydes or ketones), and ultimately to alcohols.

$$\mathbf{C_2H_4+O_3 \longrightarrow C_2H_4O_3 \longrightarrow 2CH_2O}$$



Quick Check 11.8

a) Write the equation for the ozonolysis of ethene.

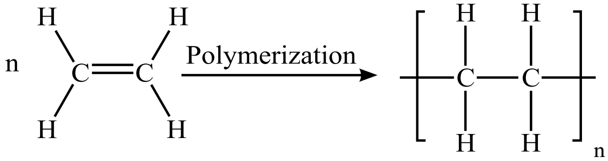
b) Give the epoxidation reaction of 2-Butene.

c) How ozonolysis can indicate the position of a double bond in an alkene? Explain with the help of an example.

8. Polymerization

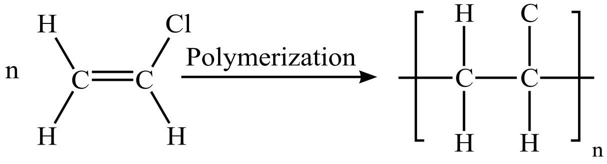
Polymerization is the formation of extremely long molecules (polymers) from small reactive molecules that join together (monomers). Addition polymerization is one of the most important addition reactions of alkenes which form the basis of the plastics industry. Addition polymerization is the reaction 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.



Ethene
Monomer

Poly (ethene)
Polymer



Chloroethene
Monomer

Poly(chloroethene) (PVC)
Polymer

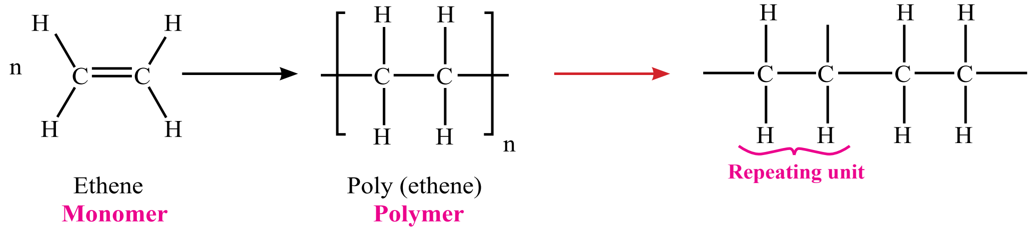
Interesting Information!

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

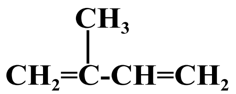
i. Ethene is a monomer used in the polymerization process to create polyethylene.
  (a) Discuss how the chemical structure of ethene makes it suitable for polymerization.
  (b) Discuss the change in hybridization and bond angle during this reaction.
ii. Explain why an addition reaction increases the saturation of a molecule.

11.9 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.

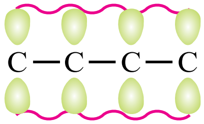
$CH_2=CH-CH=CH_2$

But-1,3-diene



$$CH_2=\overset{\overset{CH_3}{|}}{C}-CH=CH_2$$

2-Methylbut-1,3-diene (Isoprene)



Delocalization of pie electrons of the conjugated bonds

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 Buta-1,3-diene.
b) Illustrate the delocalization of electrons in conjugated dienes.

11.10 ISOMERISM

The concept of isomerism is an important feature of organic compounds. 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. For example, chlorobutane molecule can have two different arrangements as represented by the following structural formulas:

$CH_3CH_2CH_2CH_2Cl$ and **$CH_3CHClCH_2CH_3$**

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_9Cl. 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.

11.10.1 Types of Isomerism

A. Structural Isomerism

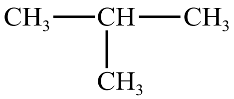
The structural isomerism is not confined to hydrocarbons only. In fact, all classes of organic compounds and their derivatives show the phenomenon of structural isomerism. The structural isomerism arises due to the difference in the arrangement of atoms within the molecule. The structural isomerism can be exhibited in five different ways.

1. The Chain 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.

$$CH_3-CH_2-CH_2-CH_3$$

Butane

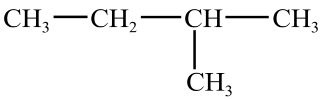


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

2-Methylpropane
(Isobutane)

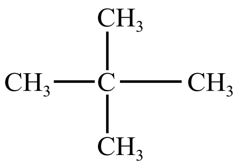
$$CH_3-CH_2-CH_2-CH_2-CH_3$$

Pentane



$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

2-Methylbutane
(Isopentane)



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

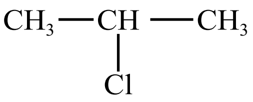
2,2-Dimethylpropane
(Neopentane)

2. Position Isomerism

This type of isomerism arises due to the difference in the position of the same functional group on the carbon chain. The arrangement of carbon atoms remains the same. For example: chloropropane and butene (C_4H_8) can have two positional isomers.

$$CH_3{-}CH_2{-}CH_2{-}Cl$$

1-Chloropropane



$$CH_3{-}\underset{\underset{Cl}{|}}{CH}{-}CH_3$$

2-Chloropropane

$$CH_3{-}CH_2{-}CH{=}CH_2$$

But-1-ene

$$CH_3{-}CH{-}CH{=}CH_3$$

But-2-ene

3. Functional Group Isomerism

The compounds having the same molecular formula but different functional groups are said to exhibit functional group isomerism. For example, thereare two compounds having the same molecular formula C_2H_6O , but different arrangement of atoms.

$$H_3C{-}O{-}CH_3$$

Methoxy methane

$$H_3C{-}CH_2{-}OH$$

Ethanol

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. For example, diethyl ether and methoxy methane.

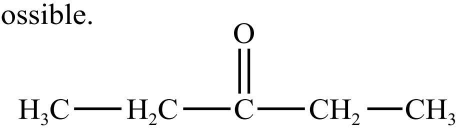
$$H_3C{-}H_2C{-}O{-}CH_2{-}CH_3$$

Ethoxy ethane

$$H_3C{-}O{-}CH_2{-}CH_2{-}CH_3$$

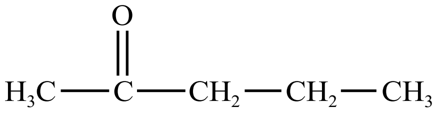
Methoxy propane

For a ketonic compound having the molecular formula $C_5H_{10}O$, the following two metamers are possible.



$$H_3C{-}H_2C{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_3$$

3-Pentanonone

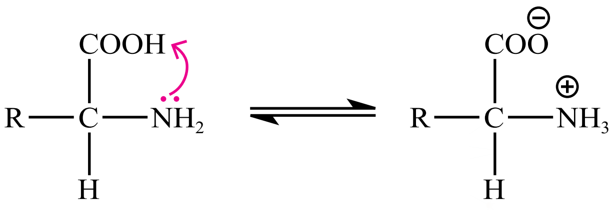


$$H_3C{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_2{-}CH_3$$

2-Pentanone

5. Tautomerism

This type of isomerism arises due to shifting of proton from one atom to another in the same molecule. This is commonly seen in amino acids. They exist as zwitterions which are formed when a proton is shifted from the carboxylic acid end of amino acid molecule to the amine group.



$$R{-}\overset{\overset{COOH}{|}}{\underset{\underset{H}{|}}{C}}{-}\ddot{N}H_2 \rightleftharpoons R{-}\overset{\overset{COO^{\ominus}}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\oplus}{N}H_3$$

Amino acid Zwitterion

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. It is part of class 12 syllabus and will be covered there.

There are two types of stereoisomerism;

i. Geometrical or cis trans isomerism

ii. Optical isomerism

11.11 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:

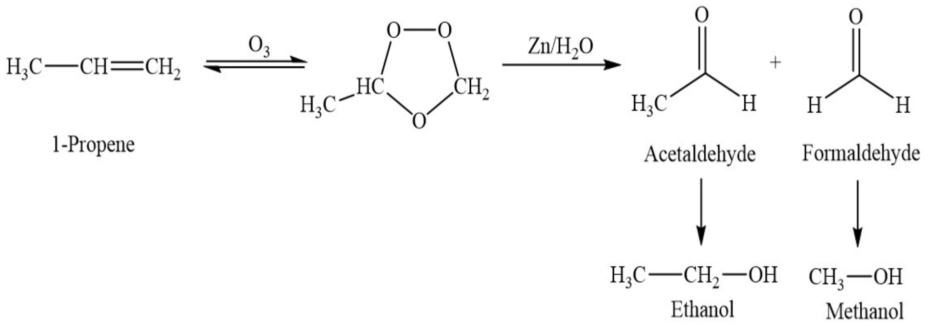
11.11.1 Oxidation

Oxidation of organic compounds involving reaction with oxygen is usually the combustion reaction:

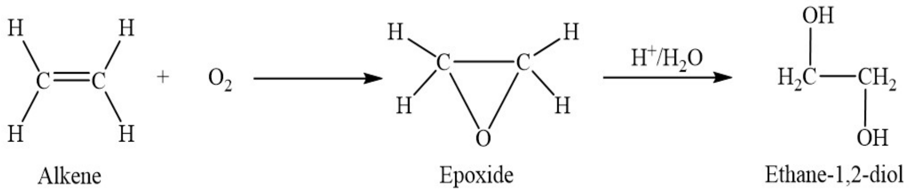
$$C_2H_6 + 2O_2 \longrightarrow 2CO_2 + 3H_2$$

Reactions of organic compounds with oxidizing agents.e.g.

i) Ozonolysis is a method of oxidatively cleaving 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.

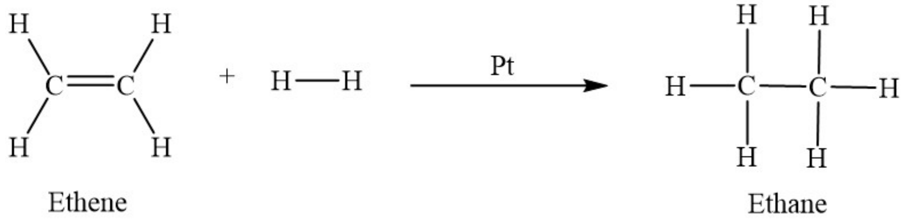


iv) Reaction of primary alcohols with acidified $K_2Cr_2O_7$ to make carboxylic acids, detail will be discussed in class 12 syllabus.

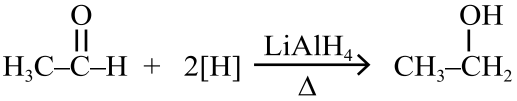
$$C_2H_5OH + 2[O] \longrightarrow CH_3COOH + H_2O$$

a) Reduction

Addition of hydrogen to carbon-carbon double bond to form alkane is an example of organic reduction reaction.



Various reducing agents are used in Organic synthesis. e.g; $LiAlH_4$, $NaBH_4$, Sn + conc.HCl. 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.



$$H_3C\text{–}\overset{\overset{O}{||}}{C}\text{–}H + 2[H] \xrightarrow[\Delta]{LiAlH_4} CH_3\text{–}\overset{\overset{OH}{|}}{C}H_2$$

Quick Check 11.9

a) Draw the displayed formula and name an isomer of C_4H_8 that could be an example of positional isomerism?

b) What type of isomers are ethoxy methane ether and propanol?

c) What are the different types of structural isomerism in alkenes?

d) Write down different isomers of the compound $C_4H_9NH_2$.

EXERCISE

MULTIPLE CHOICE QUESTIONS

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) $(CH_3)_2 — C = CH_2$

IX. What intermediate is formed during the electrophilic addition of HBr to an alkene?

a) Carbocation b) Carbanion

c) Radical d) Epoxide

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) $-CH(CH_3)CH_2-$

XIII. Which type of structural isomerism involves differences in the arrangement of the carbon skeleton?

a) Chain isomerism b) Positional isomerism

c) Metamerism d) Stereoisomerism

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

b. Differentiate between:

i) Aliphatic and Aromatic hydrocarbons

ii) Homolytic and Heterolytic Fission

iii) Electrophile and Nucleophile

c. Explain why alkanes do not undergo addition reactions.

d. How elimination reaction is considered the opposite of an addition reaction.

e. Compare the carbocation stability in propene and 2-butene.

f. Given the molecular formula C_5H_{10}, list all possible structural isomers that are alkenes.

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.

h. Explain why conjugated alkenes may show different reactivity compared to isolated alkenes.

i. Explain how inductive effects from alkyl groups stabilize carbocations in alkenes.

j. Write the equation for each reaction.

i. $CH_3CH_2CH{=}CH_2$ with H_2 (Ni catalyst)

ii. $CH_3CH{=}CH_2$ with Cl_2

iii. $CH_3CH_2CH{=}CHCH_2CH_3$ with H_2O (H_2SO_4 catalyst)

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

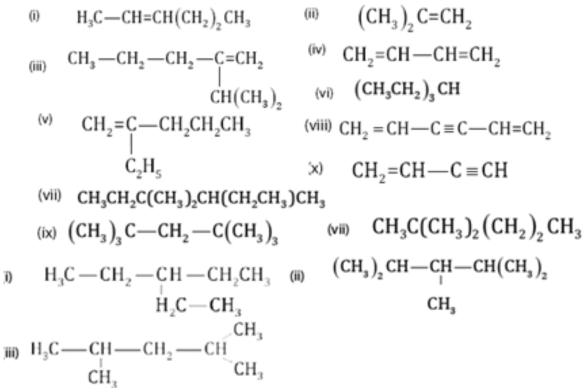
v) Vinylacetylene vi) 1,3-Pentadiene

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) $CH_3{-}CH_2{-}CH_2{-}\underset{\underset{\displaystyle CH(CH_3)_2}{|}}{C}{=}CH_2$ (iv) $CH_2{=}CH{-}CH{=}CH_2$

(vi) $(CH_3CH_2)_3CH$

(v) $CH_2{=}\underset{\underset{\displaystyle C_2H_5}{|}}{C}{-}CH_2CH_2CH_3$ (viii) $CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2$

x) $CH_2{=}CH{-}C{\equiv}CH$

(vii) $CH_3CH_2C(CH_3)_2CH(CH_2CH_3)CH_3$

(ix) $(CH_3)_3C{-}CH_2{-}C(CH_3)_3$ (vii) $CH_3C(CH_3)_2(CH_2)_2CH_3$

i) $H_3C{-}CH_2{-}\underset{\underset{\displaystyle H_2C{-}CH_3}{|}}{CH}{-}CH_2CH_3$ (ii) $(CH_3)_2CH{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH(CH_3)_2$

iii) $H_3C{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_2{-}CH(CH_3)_2$

DESCRIPTIVE QUESTIONS

Q.3Describe the free radical halogenation of methane using Cl_2 as an example.

Q.4Describe the following methods for the preparation of alkenes:

i) Dehydrohalogenation of alkyl halides

ii) Dehydration of alcohols

Q.5Describe the mechanism of electrophilic addition of hydrogen halides to alkenes. Discuss Markovnikov's Rule in the context of hydrogen halide addition.

Q.6Explain the following reactions of alkenes with examples:

a) Halogenation **b) Ozonolysis**

c) Epoxidation **d) Polymerization**

12

NOTROGEN AND SULFUR

STUDENT LEARNING OUTCOMES [C-11-B-30 to C-11-B-41]

- 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 the reaction 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

Nitrogen belongs to group 15 of the periodic table. In industrial processes, nitrogen is typically obtained by cooling air until it becomes a liquid. Liquid nitrogen is commonly used for rapid cooling purposes. In laboratory settings, nitrogen can be generated by slowly heating a solution of ammonium nitrite.

$$NH_4\,NO_{2(aq)} \xrightarrow{\Delta} N_{2(g)} + H_2O_{(l)}$$

Table 12.1 Physical properties of nitrogen

Atomic number	7
Relative atomic mass	14.007 Da
Physical appearance	Colourless Gas
Electronic configuration	[He] $2s^2$ $2p^3$
Melting point	-210 °C
Boiling point	-195.8 °C
Covalent radius	74 pm

Ionic radius (3-)	171 pm
1st Ionization energy	1402 kJ/mol
Electronegativity	3.0
Electron affinity	-8.0 kJ/mol
Density	0.001145 g/cm^3
Principal oxidation states	3+ and 5+

12.1 REACTIVITY OF NITROGEN (N_2)

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. With an electronic configuration of $1s^2$ $2s^2$ $2p^3$, nitrogen requires three electrons to complete its octet, forming a triple bond by sharing three electrons with another nitrogen atom as shown in **Figure 12.1**. This bond has a bond enthalpy of +944 $kJmol^{-1}$. High energy is required to break this bond to form new bonds, making N_2 very unreactive. The second reason for its lack of reactivity is the non-polarity of its bond. 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.

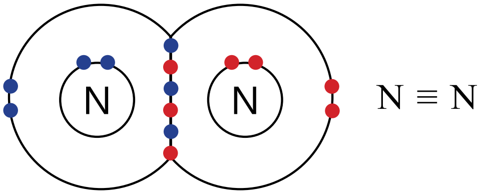


Figure 12.1 Bonding in N_2 molecule

Interesting Information!

The high concentration of nitrogen in the air serves to dilute oxygen, preventing every spark in our atmosphere from igniting a massive fire. 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. It is also used in laboratory to carry out the reactions which require inert atmosphere.

12.2 AMMONIA (NH_3)

Ammonia (NH_3) is an important industrial compound of nitrogen, which is mainly used as a fertilizer. zzIt is prepared industrially by Haber-Bosch process.

$$N_{2(g)} + 3H_{2(g)} \overset{\Delta}{\rightleftharpoons} 2NH_{3(g)}$$

12.2.1 Basicity of Ammonia

Ammonia behaves as a Lowry-Brønsted base by accepting a proton (H^+) from an acid to form ammonium:

$$NH_{3(aq)} + H^{+1}_{(aq)} \rightleftharpoons NH_4{}^{1+}{}_{(aq)}$$

It dissolves in water to form ammonium hydroxide (NH_4OH) and equilibrium is established between ammonia molecules and ammonium ions in the solution.

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH^{1+}_{4(aq)} + OH^{1-}_{(aq)} \qquad K_b{=}1.8\times10^{-5}$$

Ammonia solution is a weak base due to the low basicity constant (K_b) and the equilibrium position being towards the far left side.

12.2.2 Structure of Ammonium ($NH_4{}^{1+}$)

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, this ion adopts a tetrahedral shape in which all the bonds are of equal length and strength, as depicted in **Figure 12.2**.

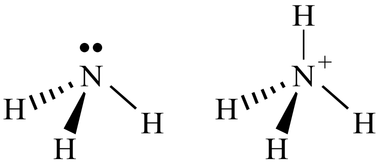


Figure 12.2 Pyramidal and tetrahedral shapes of ammonia and ammonium

12.2.3 Synthesis of Ammonia from Ammonium salts

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 12.3.**

$$NH_4Cl_{(s)} + Ca(OH)_{2(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)} + NH_{3(g)}$$

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. It is commonly used to identify ammonium in salt analysis. If a gas with a pungent smell is released and turns moistend red litmus paper blue, it indicates the presence of ammonium in the compound.

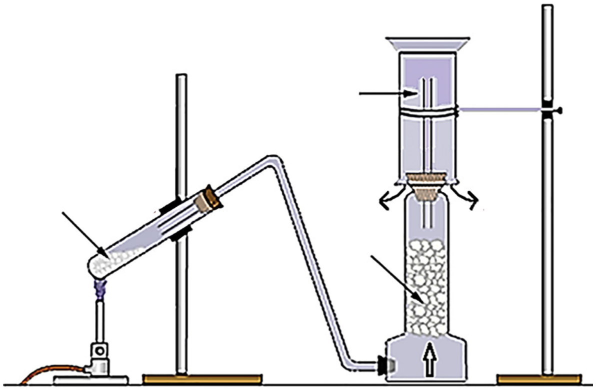


Figure 12.3 Synthesis of ammonia gas

Quick Check 12.1

a) Why N_2 gas is used in food packaging?

b) Both CO and N_2 have triple bonds in their molecules. Why do you think CO is more reactive than N_2?

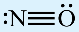
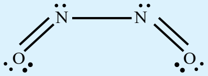
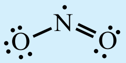
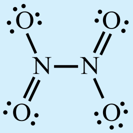
c) Ammonium salts such as $(NH_4)_2SO_4$ or $(NH_4)_2NO_3$ are commonly used as fertilizers. Why a farmer wouldn't treat a field with an ammonium fertilizer at the same time as using lime? What would be the chemical reactions?

d) If magnesium ribbon is ignited and placed in a jar containing N_2O, it continues to burn brightly. Explain this observation with reason.

12.3 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 I+ 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 12.2**.

Table 12.2 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, oxidising 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 $\underset{Brown}{2NO_2} \underset{Heat}{\overset{Cool}{\rightleftharpoons}} \underset{Colourless}{N_2O_4}$	 	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?

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).

12.4 SOURCES OF OXIDES OF NITROGEN

Here are the main categories of NO_x sources.

12.4.1 Natural Sources

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.

12.4.2 Anthropogenic (Man-made) Sources

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.

12.5 ROLE OF NO & NO_2 IN SMOG & PAN FORMATION

NO_x is responsible for numerous harmful effects on living organisms.

12.5.1 Photochemical Smog

Photochemical smog (Los Angeles smog) forms in the atmosphere from NO_x and volatile organic compounds (VOCs) in the sunlight. It is oxidising 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.

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$$

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

$$NO_{2(g)} \xrightarrow{h\upsilon} NO_{(g)} + O_{(g)}$$

$$O_{(g)} + O_{2(g)} \longrightarrow O_{3(g)}$$

Did you know?

Lahore smog consists of volatile organic compounds (VOCs), NOx, ground level ozone (O_3), particulate matter PM2.5, CO and SO_2.

$$RCH{=}RCH_{(g)} + O_{3(g)} \longrightarrow RCO^{\bullet}_{3(g)} + RCH^{\bullet}_{2(g)} \rightarrow\rightarrow\rightarrow RC(O)OONO_2$$

12.5.2 Formation of Peroxyacyl Nitrates (PANs)

NOx 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 nitratesas shown in **Figure 12.4**.

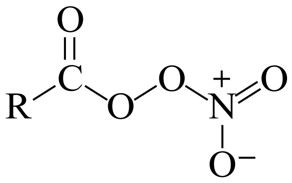


Figure 12.4 General structure of PANs

The R group in peroxyacetyl nitrate is CH_3, but other hydrocarbon chains may also be present.

The formation of PAN is illustrated in **Figure 12.5.** 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.

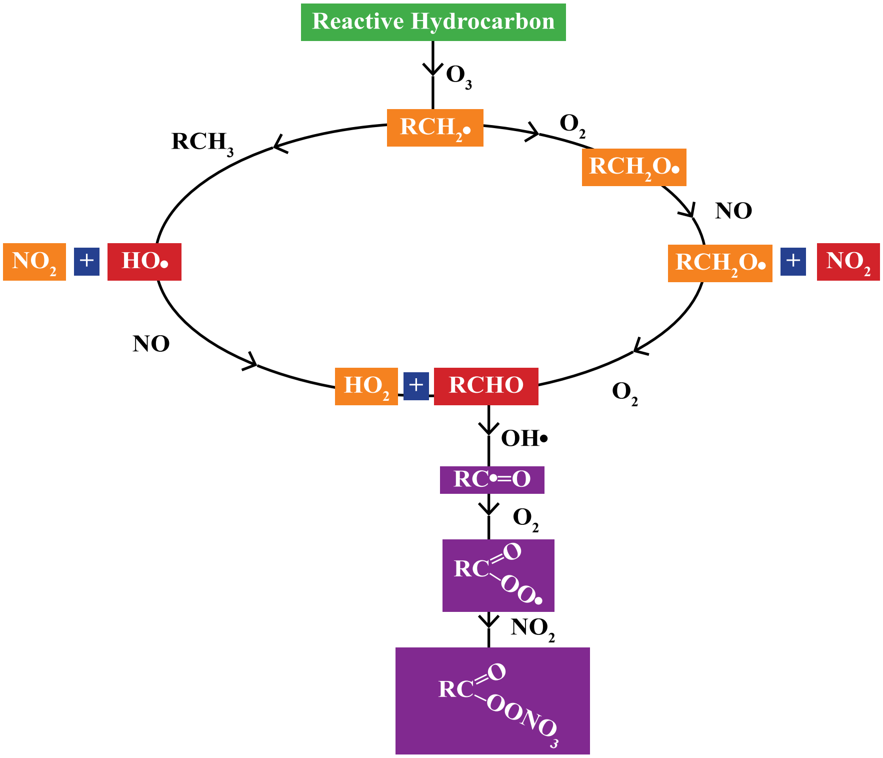


Figure 12.5 Mechanism of PAN formation

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

b) What does PAN stand for? Give its general formula.

c) Write down the formulas of the compounds responsible for the formation of PAN.

d) 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?

12.6 CATALYTIC CONVERTER

A catalytic converter is a ceramic or metallic monolith with a honeycomb-like structure, as shown in **Figure 12.6**. 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.

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.

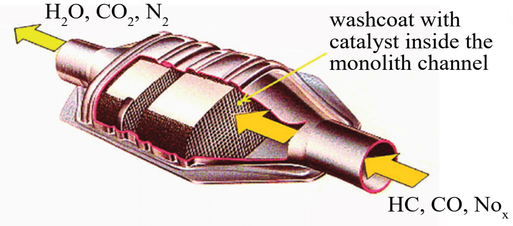


Figure 12.6 Three-way catalytic converter

Reduction

$$2NO_{(g)} + 2CO_{(g)} \xrightarrow{Pt / Rd} N_{2(g)} + 2CO_{2(g)}$$

Oxidation

$$2CO_{(g)} + O_{2(g)} \xrightarrow{Pt/Rh} 2CO_{2(g)}$$

$$2C_2H_4 + 6O_{2(g)} \xrightarrow{Pt/Rd} 4CO_{2(g)} + 4H_2O_{(g)}$$

12.7 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 12.2.**

Table 12.3 Differences between nitrification and denitrification

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.
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 $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$ $2NH_{4(aq)}^{1+} + 3O_{2(aq)} \rightarrow 2NO_{2(aq)}^{1-} + 4H_{(aq)}^{+} + 2H_2O_{(l)}$ $2NO_{2(aq)}^{1-} + O_{2(aq)} \rightarrow 2NO_{3(aq)}^{1-}$	**Reduction of nitrogen** $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$ $2NO_{3(aq)}^{1-} + 10e^- + 12H_{(aq)}^{+} \rightarrow N_{2(g)} + 6H_2O_{(l)}$

Quick Check 12.3

a) Write down the reduction and oxidation reactions that occur in the catalytic converter in the vehicle exhausts.
b) What is the basic principle of catalytic converter? Describe the role of catalyst in the catalytic converter.
c) Do hybrid and electric cars have catalytic converters? Explain why or why not.

12.8 SULFUR

Sulfur is a member of group 16 which is also called the *Chalcogen* family. Some physical properties of sulfur are listed in **Table 12.3.**

Table 12.4 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] $3s^2\ 3p^4$	**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

12.8.1 Reactivity of Sulfur

Sulfur usually forms single bonds with other sulfur 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**.

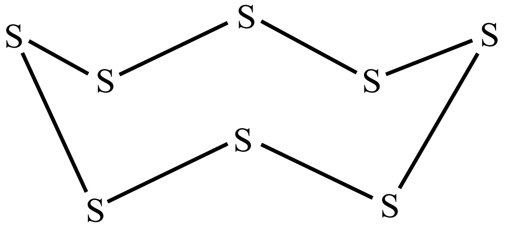


Figure 12.7 Cyclo-octasulfur, (S_8) crown molecule

12.8.2 Oxidation States of Sulfur

Sulfur exhibits oxidation states of −2, 0, +2, +4, and +6. The electronic configuration of sulfur is depicted in **Figure 12.8**, where the oxidation state is determined by the number of unpaired electrons. Under standard conditions, sulfur and oxygen react to produce sulfur dioxide (SO_2) in which sulphur has an oxidation state of +4. However, to form sulfur trioxide (SO_3) with an oxidation state of +6, high energy is required.

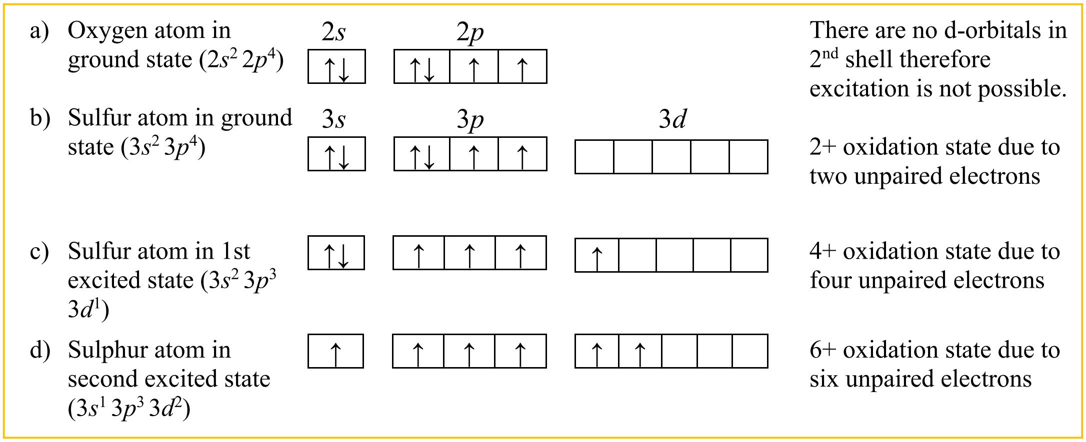


Figure 12.8 Electronic configurations of sulfur for attaining different oxidation states

12.9 STABILITY OF OXIDATION STATES OF SULPHUR

The Stability of oxidation states of sulphur is explained by Frost diagram in which an element X is a plot of nE⁰ vs oxidation state (n) for the redox couple X(n)/X(0) as shown in **Figure 12.9**. It tells about the relative stabilities of different oxidation states of an element at two extreme pH values (pH=0 and pH=14) i.e. acidic and basic conditions. It can also be regarded as a plot between standard reaction Gibb's free energy (ΔG°) versus oxidation state (n) because oxidation state(n) is directly proportional to ΔG° as shown below.

$$-\Delta G^\circ = nFE^0$$

$$\text{or}\ \frac{-\Delta G^\circ}{F} = nE^0$$

Here **E⁰** is the standard reduction potential, **F** is the Faraday constant and **n** is the number of transferred electrons in a redox half reaction.

The more stable oxidation state has a lower nE⁰ value or more negative Gibb's free energy. Therefore, the more stable oxidation state is at the lowest position in the diagram. Further, a couple with a more positive slope is a good oxidising agent, while a couple with a more negative slope is a good reducing agent.

In the diagram for sulfur, +6 (SO_4^{2-}) is the most thermodynamically stable oxidation state, completely non-oxidising under extreme basic conditions, while under extreme acidic conditions, it is shown to be very unstable.

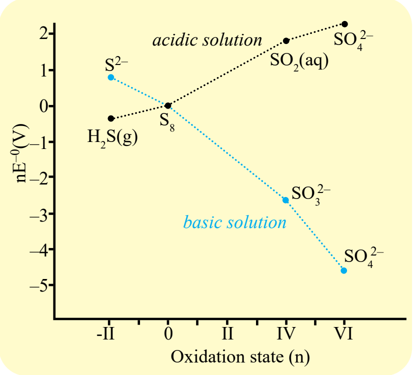


Figure 12.9 Frost diagram for oxidation states of sulfur

It can be seen that in basic environments, the oxidized sulfur states are all more stable than the elemental form but under acidic conditions all the oxidized sulfur states are less stable than the elemental form.

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. $S_2O_3^{2-}$

b) Which oxidation states of sulphur are the most common? Explain your answer with reason.

c) Explain the involvement of d orbital in variable oxidation states of S in its compounds.

12.10 REACTIONS OF SULFUR

Sulfur 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-oxidising acids, and noble gases. Its ability to catenate allows it to form ring structures and linear chains. Here are some important reactions of sulfur:

i. Sulfur 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.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

$$2SO_{2(g)} + O_{2(g)} \xrightarrow[Pt]{\Delta} 2SO_{3(g)}$$

Sulfur can be oxidised by nitric acid to produce NO_2 and H_2SO_4.

$$S_{(s)} + 6HNO_{3(l)} \longrightarrow H_2SO_{4(l)} + 6NO_{2(g)} + 2H_2O_{(l)}$$

ii. When sulfur 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. Sulfur does not react with Au and Pt.

$$2Ag_{(s)} + S_{(s)} \longrightarrow Ag_2S_{(s)}$$

$$Hg_{(l)} + S_{(s)} \longrightarrow HgS_{(s)}$$

$$2Cu_{(s)} + S_{(s)} \longrightarrow Cu_2S_{(s)}$$

iii. Sulfur converts cyanide into thiocyanate which is also known as pseudohalide. It is used to analyse Fe^{3+}.

$$KCN_{(s)} + S_{(s)} \xrightarrow{\Delta} KSCN_{(s)}$$

iv. 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).

$$S_{(s)} + 3F_{2(g)} \longrightarrow SF_{6(g)}$$

$$2S_{(s)} + Cl_{2(g)} \longrightarrow S_2Cl_{2(l)}$$

12.11 USES OF SULFUR AND ITS COMPOUNDS

12.11.1 Vulcanisation

Sulphur is used as a cross linker for the rubber molecular chains. This is called vulcanisation and it improves the strength of rubber as shown in **Figure 12.10**.

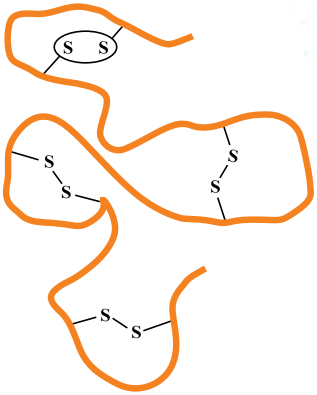


Figure 12.10 S-S cross-linkages between polymer chains

12.11.2 Fertilizer

Sulfur is an essential nutrient for plant growth. When soils become depleted in sulfate, sulfur can be restored in soil by applying sulfur containing N/P fertilizers, or sulfur-coated fertilizers such as sulfur-coated urea. Soil components and microbes convert elemental sulfur into soluble forms for the use of plants. Gypsum ($CaSO_4 \cdot 5H_2O$) is also used as a fertilizer.

12.11.3 Gun powder

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:

$$10KNO_{3(s)} + 3S_{(s)} + 8C_{(s)} \longrightarrow 2K_2CO_{3(s)} + 3K_2SO_{4(s)} + 6CO_{2(g)} + 5N_{2(g)}$$

Quick Check 12.5

a) What is the function of SO_2 and sulfite (SO_3^{2-}) salt in preserving the food?

b) Give the reaction of S with HCl acid and NaOH.

12.12 ROLE OF SULFUR IN ORGANIC SYNTHESIS OF DRUGS, DYES AND FRAGRANCES

Carbon-Sulfur bonds are prevalent 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.

12.12.1 Drugs

Sulfa drugs are the antibacterial sulfonamides such as penicillins and cephalosporins contain sulfur. The common drug omeprazole, used in GERD (Gastroesophageal reflux disease) contains sulfoxide group.

12.12.2 Dyes

Sulfur dyes are synthesised by the process of thionation or sulfurization of organic compounds that contain nitro or amino groups. These compounds contain sulfur linkages. They generally give black, brown, khaki, blue, and green colours.

Some examples are sulfur black 1, sulfur blue and sulfur brilliant green.

12.12.3 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. cis-glabanum 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.

12.13 SULPHURIC ACID (H_2SO_4)

The major portion of sulfur, 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 12.11**.

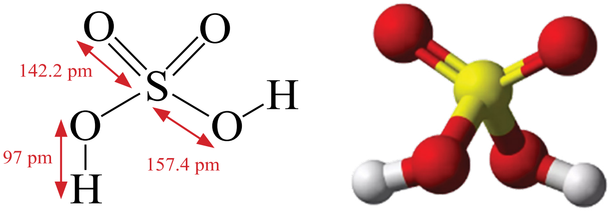


Figure 12.11 Structure of H_2SO_4

12.13.1 THE CONTACT PROCESS

Sulphuric acid is produced by the contact process. A flow sheet diagram of the contact process is shown in **Figure 12.12.**

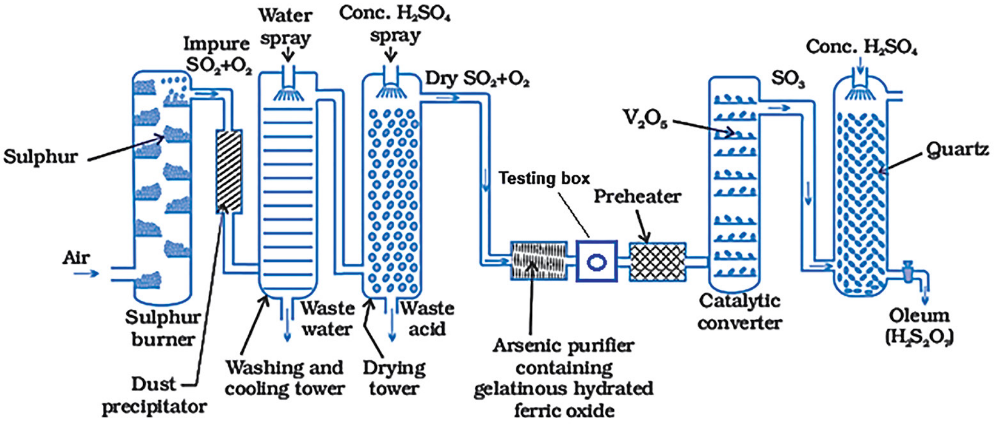


Figure 12.12 Contact process for the industrial production of sulphuric acid

The Contact process can be divided into the following stages.

Sulfur/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 sulfur dioxide SO_2.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)} \qquad \Delta H = -297.03\ \text{kJ/mol}$$

$$4FeS_{(s)} + 6O_{2(g)} \longrightarrow 2Fe_2O_{3(s)} + 4SO_{2(g)}$$

Purification Unit

If pyrite ore is used as a sulfur 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.

$$As_2O_{3(g)} + 2Fe(OH)_{3(l)} \longrightarrow 2FeAsO_{3(l)} + 3H_2O_{(l)}$$

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.

$$SO_{2(g)} + \frac{1}{2} O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad \Delta H = -98.98\ \text{kJmol}^{-1}$$

The catalyst works in two steps:

Oxidation of SO_2 into SO_3 by V^{5+}:

$$SO_{2(g)} + V_2O_{5(s)} \longrightarrow SO_{3(g)} + 4V_2O_{4(s)}$$

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?

b) Write down dehydration reactions of conc. H_2SO_4 with starch and oxalic acid

c) How does the catalyst V_2O_5 function in the conversion of SO_2 to SO_3.

Absorption Tower

Sulfur trioxide is cooled and can be converted to sulphuric acid by reacting with water.

$$H_2O_{(l)} + SO_{3(g)} \longrightarrow H_2SO_{4(l)} \qquad \Delta H = -176.6\ \text{kJ/mol}$$

Mixing SO_3 with water is not feasible because the reaction is extremely exothermic and acidic vapour or mist is produced rather than a liquid solution. Mainly, sulfur trioxide is dissolved in recirculating hot 98.5% sulphuric acid. The term fuming sulphuric acid or oleum is used for the mixtures of sulfur 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.

$$H_2SO_{4(l)} + SO_{3(g)} \longrightarrow H_2S_2O_{7(l)}$$

$$H_2S_2O_{7(l)} + H_2O_{(l)} \longrightarrow 2\ H_2SO_{4(l)}$$

12.13.2 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 12.4.**

Table 12.5 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.	

12.13.3 CHEMICAL PROPERTIES

i. It self-ionizes or undergoes autoprotolysis as follows.

$$H_2SO_{4(l)} + H_2SO_{4(l)} \rightleftharpoons H_3SO_{4\,(aq)}^{1+} + HSO_{4\,(aq)}^{1-} \qquad K = 2.7 \times 10^{-4}$$

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:

$$H_2SO_{4(aq)} \rightleftharpoons H_3O^+_{(aq)} + HSO_{4(aq)}^{1-} \quad (pK_{a1} = -2)$$

But hydrogensulfate (HSO_4^{1-}) is a far weaker acid due to a positive pK_{a2} value:

$$HSO_{4(aq)}^{1-} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + SO_{4(aq)}^{2-} \quad (pK_{a2} = 1.92)$$

ii. 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.

Interesting Information!

A common laboratory demonstration is the dehydration of table sugar, where a black porous carbon mass called carbon snake protrudes out of the apparatus.

$$C_{12}H_{22}O_{11(s)} + H_2\ SO_{4(l)} \longrightarrow 12C_{(s)} + 11H_2O_{(g)} + H_2SO_{4(aq)}$$

It also dehydrates ethyl alcohol to ethene or ethoxyethane depending upon the reaction conditions.

$$C_2H_5OH_{(l)} + H_2SO_{4(l)} \longrightarrow C_2H_{4(s)} + H_2O_{(l)} + H_2SO_{4(aq)}$$

iii. Hydrochloric acid (HCl) gas, is formed when sulphuric acid reacts with sodium chloride

$$NaCl_{(s)} + H_2SO_{4(l)} \longrightarrow NaHSO_{4(s)} + HCl_{(g)}$$

iv. 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 formsulfates.

$$Zn_{(s)} + H_2SO_{4(aq)} \longrightarrow H_{2(g)} + Zn^{2+}_{(aq)} + SO^{2-}_{4\,(aq)}$$

$$Zn_{(s)} + H_2SO_{4(l)} \longrightarrow SO_{2(g)} + Fe^{2+}_{(aq)} + SO^{2-}_{4\,(aq)} + 2H_2O_{(l)}$$

v. 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 oxidising agent due to the stability of SO_4^{2-} anion. This anion is weakly oxidising. However hot concentrated sulphuric acid is a moderately strong oxidising agent due to high temperature, high concentration of protons (H^+), and formation of nascent oxygen. Hot concentrated sulphuric acid oxidises Cu, as given below:

$$Cu_{(s)} + 2H_2SO_{4(l)} \longrightarrow SO_{2(g)} + 2H_2O_{(l)} + SO_4^{2-}{}_{(aq} + Cu^{2+}_{(aq)}$$

Quick Check 12.7

a) Write down dehydration reactions of conc. H_2SO_4 with starch and oxalic acid.
b) How does conc. H_2SO_4 react with NaCl? What is the importance of this reaction?
c) What is the difference between the oxidizing power of cold and hot sulphuric acid?

12.13.4 Uses and Industrial Applications

Sulphuric acid is considered a king of chemicals and its consumption is an indicator of the industrial progress of a country.

1. A major portion of the acid is used in making fertilizers, normally 77.67 % is used to digest the phosphate rock containing calcium phosphate ($Ca_3(PO_4)_2$.
2. It is used in the extraction of metals from ores such as Cu, Ni, steel etc.
3. It is utilized as a catalyst in oil and coal refining, polymers, synthetic rubber, and plastic industries.

4. It is used in the pulp and paper industry and involved in the production of pesticides, insecticides, herbicides, varnishes, dyes, pharmaceuticals, soaps and detergents.
5. It is used for nitration in making explosives such as trinitrotoluene (TNT), nitroglycerine, picric acid, nitrocellulose, etc.
6. It is involved in the food industry for making sugar, starch, and corn syrup.
7. It is used in the paint industry for making titanium dioxide (TiO_2) pigment.
8. It is used to dry gases in industrial processes.
9. 35.67% acid is used in lead storage batteries.
10. 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.

EXERCISE

MULTIPLE CHOICE QUESTIONS

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 $N\equiv N$ 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) Sulfur dioxide (SO_2)

III. The shape of ammonium is

a) pyramidal
b) triangular planar
c) tetrahedral
d) linear

IV. In a catalytic converter, the conversion of nitrogen oxides (NOx) 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) $HO^{\bullet}$

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 sulfur in H_2SO_4 is

a) +1 b) +2

c) +4 d) +6

X. In a Frost diagram, a species that lies above the line connecting its neighbors is:

a) Thermodynamically stable. b) A strong oxidizing agent.

c) Prone to disproportionation. d) A poor reducing agent.

XI. Sulfur dioxide (SO_2) produced from the combustion of sulfur can be further oxidized to sulfur 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. Sulfur trioxide (SO3) is not directly dissolved in water to produce sulfuric 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 sulfuric acid.

d) Requires very high pressures.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. List two reasons for the inertness of N_2.

b. How is nitrogen isolated from air?

c. Why ammonia (NH_3) is a weak base?

d. How does NO_2 catalyze the formation of SO_3?

e. Write down the reactions of photochemical smog formation.

f. What is the construction and function of a catalytic converter?

g. Why sulfur is quite unreactive at room temperature?

h. Which are the most stable oxidation states of sulphur in water at pH=0 and pH=14?

i. How does sulfur react with halogens?

j. Draw the structures of cyclo-octasulfur (S_8) and sulfuric acid.

k. What is the role of sulfur in the vulcanization of rubber?

l. What is the composition and the chemical reaction of gunpowder combustion?

m. What is the importance of disulfide bridges?

n. Write down self-ionization equation of sulfuric acid and its ionization in water.

o. Give two examples where sulfuric acid acts as a dehydrating agent.

p. How does V_2O_5 catalyze the formation of SO_3?

q. What is purpose of formation of oleum?

DESCRIPTIVE QUESTIONS

Q.3 Explain the preparation and basicity of ammonia.

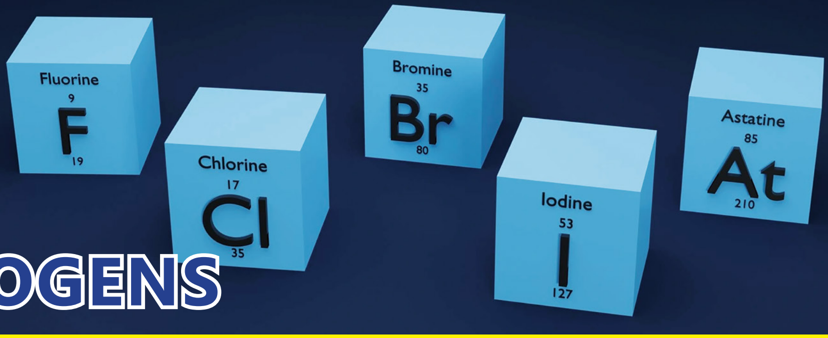
Q.4 How oxides of nitrogen (NO_x) cause the formation of photochemical smog and PAN? Give its mechanism.

Q.5 Frost diagram explains the stabilities of different oxidation states of sulfur. Which oxidation states of sulphur are the most stable at acidic and basic conditions?

Q.6 Discuss sulfuric acid as an oxidizing agent and a dehydrating agent with three reactions for each.

13

HALOGENS



STUDENT LEARNING OUTCOMES [C-11-B-19 to C-11-B-41]

- 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.

Halogens exist as diatomic molecules 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 vapor. The colors of halogens (X_2) darken progressively from chlorine to iodine. 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 13.1 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 13.1 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	$2s^22p^5$	$3s^23p^5$	$4s^24p^5$	$5s^25p^5$
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 vaporisation /kJ mol^{-1}	+3.3	+10.2	+15	+30
Solubility/g per 100g of water at 20°C	reacts readily with water	0.59 (reacts slightly)	3.6	0.018

13.1 VOLATILITY OF CHLORINE, BROMINE AND IODINE

Chlorine being a liquid is very volatile at room temperature and it disperses quickly in the air. 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.

Interesting Information

Bromine liquid evaporates easily at room temperatures emitting an orange vapor. Bromine has a very strong and bad odor. It gets its name from the Greek word “bromos” which means “stench.”

13.2 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. 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 13.2.**

Table 13.2 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?
b) What is the reason behind the different colours of halogens?
c) Why chlorine is more volatile than bromine and iodine?

13.3 THE BOND STRENGTH OF HALOGEN MOLECULES

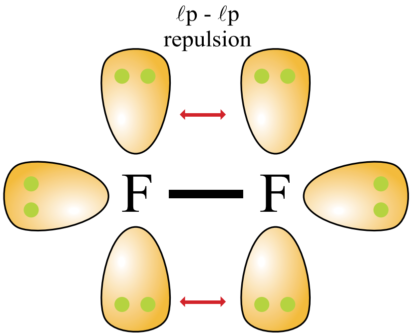


Figure. 13.1 F_2 molecule with lone pairs of electrons

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. However, 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 13.3.**

Table 13.3 Bond energies of halogen molecules

Halogen Molecule	Bond Energy ($kJmol^{-1}$)
F_2	156
Cl_2	243
Br_2	193
I_2	151

13.4 RELATIVE REACTIVITIES OF THE HALOGENS AS OXIDIZING AGENTS

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.

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

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:

$$F_2 > Cl_2 > Br_2 > I_2.$$

The reactivity of halogens is directly related to their ability to acquire an electron and form halide ions (F^-, Cl^-, 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 (Cl^-, Br^- and I^-) to free halogens.

$$F_{2(g)} + Cl^{1-}_{(aq)} \longrightarrow F^{1-}_{(aq)} + Cl_{2(g)}$$

$$F_{2(g)} + Br^{1-}_{(aq)} \longrightarrow F^{1-}_{(aq)} + Br_{2(g)}$$

$$F_{2(g)} + I^{1-}_{(aq)} \longrightarrow F^{1-}_{(aq)} + I_{2(g)}$$

Similarly, chlorine can oxidize and displace Br^- and I^-. Bromine can oxidize and displace I^-. Iodine cannot oxidize any halide ion.

Table 13.4 Standard electrode potential E°(X_2/X^-)

Halogen Molecule (X_2)	Standard Reduction Potential, E°(V)
F_2	+ 2.87
Cl_2	+1.36
Br_2	+1.07
I_2	+0.54

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°(X_2/X^-) for halogens shown in **Table 13.4** become less positive from fluorine to iodine. This reflects the decreasing oxidizing power. 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 Cl-Cl bond although fluorine is the most electronegative element, Explain.

b) Is the reaction between $NaCl_{aq}$ and F_2 gas possible?

   i) Give reason whether yes or no.

   ii) If yes, write the equation for this reaction.

c) What is the relationship between the oxidizing power of halogens and their standard reduction potential values?

13.5 REACTIONS OF THE HALOGENS WITH HYDROGEN

When halogen elements react with hydrogen, they produce hydrogen halides.

$$H_2 + X_2 \longrightarrow 2HX \qquad \text{Where } X_2 = F_2, Cl_2, Br_2 \text{ and } I_2$$

Hydrogen halides are colourless gases that dissolve in water to form hydrohalic acid. When we move down the group from fluorine to iodine, the reactivity of halogens with hydrogen decreases.

$$F_2 > Cl_2 > Br_2 > I_2$$

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 HCl gas which forms hydrochloric acid in water.

$$H_{2(g)} + CI_{2(g)} \xrightarrow{hv} 2HCI_{(g)}$$

Hydrogen bromide (HBr) gas is produced when bromine reacts with the hydrogen upon heating. HBr gas is less reactive than HCl and HF. It forms a strong hydrobromic acid in water. This is an exothermic 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 iodide (HI) gas, which forms hydroiodic acid in water.

$$H_{2(g)} + I_{2(g)} \overset{catalyst}{\rightleftharpoons} 2HI_{(g)}$$

This is a reversible reaction and occurs very slowly.

13.6 RELATIVE THERMAL STABILITIES OF HYDROGEN HALIDES IN TERMS OF THEIR BOND STRENGTH

As we move down the halogen group from fluorine to iodine, the thermal stabilities of hydrogen halides (H-X) decrease due to decrease in bond dissociation energies as given in **Table 13.5**. The order of thermal stability of HX is as follows:

$$HF > HCl > HBr > HI$$

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 (HCI) is less thermally stable than hydrogen fluoride but more stable than other hydrogen halides. Due to the larger atomic radius of chlorine than fluorine H-CI bond is weaker than H-F bond. Its bond dissociation energy is less than that of H-F. 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 13.5 Bond dissociation energy of H-X bonds

Hydrogen halide (HX)	Bond dissociation energy ($kJmol^{-1}$)
H-F	569
H-Cl	431
H-Br	366
H-I	299

Quick Check 13.3

a) What is the relationship between the oxidizing power of halogens and their standard reduction potential values?

b) The reaction between H_2 and F_2 is explosive but that between H_2 and I_2 is slow and reversible. Explain why.

c) Refer to Table 13.4 and 13.5 to predict which of the following reactions would be more exothermic. Explain your answer.

$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$ and $H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr_{(g)}$

d) How thermal stability of hydrogen halides is related to their bond dissociation energies?

e) HF is the most thermally stable hydrogen halide. Give reasons.

13.7 RELATIVE REACTIVITY OF HALIDE IONS AS REDUCING AGENTS

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 **$I^- > Br^- > Cl^- > F^-$**. 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 (Cl^-) 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.

13.8 REACTIONS OF HALIDES WITH AQUEOUS SILVER ION FOLLOWED BY AQUEOUS AMMONIA

13.8.1 Reactions of halides with aqueous silver ion

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:

$$X^{1-}_{(aq)} + Ag^{1-}_{(aq)} \longrightarrow 2AgX_{(s)}$$

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.

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.

$$Ag^{1+}_{(aq)} + Cl^{1-}_{(aq)} \longrightarrow AgCl_{(s)}$$

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.

$$Ag^{1+}_{(aq)} + Br^{1-}_{(aq)} \longrightarrow AgBr_{(s)}$$

A yellow precipitate of silver iodide forms on mixing aqueous silver Ion with aqueous halide solution. The product AgI is insoluble in ammonia.

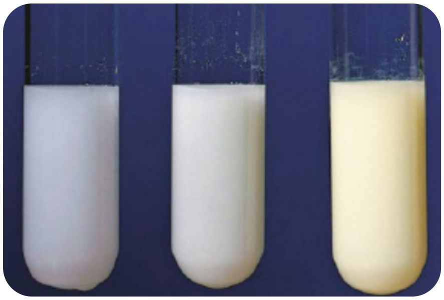


Figure 13.2 Colours of the silver halide precipitates: silver chloride (left), silver bromide (middle) and silver iodide (right).

$$Ag^{1+}_{(aq)} + I^{1-}_{(aq)} \longrightarrow AgI_{(s)}$$

This type of reactions is used to identify halide ions and is called **silver nitrate test**.

13.8.2 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.

$$AgCl_{(s)} + 2NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]^+_{(aq)} + Cl^{1-}_{(aq)}$$

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 13.6** 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 Cl^-. Explain why.
b) What is the cause of the different solubilities of silver halides in ammonia?
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?

Table 13.6 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 (Cl^-)	White precipitate (AgCl)	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(Agl)	Insoluble in aq. NH_3

13.9 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.

$$NaCl_{(s)} + H_2SO_{4(\ell)} \longrightarrow NaHSO_{4(\ell)} + HCl_{(g)}$$

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.

$$NaBr + H_2SO_{4(\ell)} \longrightarrow NaHSO_{4(l)} + HBr_{(g)}$$

$$2HBr_{(s)} + H_2SO_{4(\ell)} \longrightarrow Br_{2(g)} + 2SO_{2(g)} + 2H_2O_{(\ell)}$$

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.

13.10 REACTIONS OF CHLORINE WITH COLD AND HOT AQUEOUS SODIUM HYDROXIDE

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.

13.10.1 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).

$$Cl_{2(g)} + 2NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + NaClO_{(aq)} + H_2O_{(l)}$$

Oxidation states of chlorine in the above reaction are given below:

Chlorine in Cl_2 = 0
Chlorine in NaCl = -1
Chlorine in NaClO = +1

Keep in Mind!

Sodium chlorate (I) is previously called sodium hypochlorite.

Chlorine in Cl_2 is oxidized from 0 to +1 in NaOCl. Chlorine in Cl_2 is reduced from 0 to 1 in NaCl.

The above reaction shows the simultaneous oxidation and reduction of chlorine and is example of disproportionation reaction.

13.10.2 Reaction with hot aqueous sodium hydroxide

When chlorine reacts with hot aqueous sodium hydroxide (NaOH), it forms sodium chloride (NaCl) and sodium chlorate (V) ($NaClO_3$). It is another example of **disproportionation** reaction.

$$3Cl_{2(g)} + 6NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + NaClO_{3(aq)} + 3H_2O_{(l)}$$

Chlorine in Cl_2 = 0

Chlorine in NaCl = -1

Chlorine in $NaClO_3$ = +5

Chlorine is oxidized from 0 to +5 in $NaClO_3$. 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?

b) Show that the reaction of Cl_2 with cold and hot aqueous KOH is a disproportionation reaction.

c) HI acts as strong reducing agent. Explain it with chemical reactions.

13.11 USE OF CHLORINE IN WATER PURIFICATION

Chlorine gas is very poisonous. However, in small quantities, they are harmless to humans but poisonous to the 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 concentrations 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 (HOCI) and the chlorate (I) or hypochlorite ions (OCl^-). Chlorination is a relatively inexpensive method of water disinfections.

13.11.1 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 (HCIO).

$$Cl_{2(g)} + H_2O_{(l)} \longrightarrow HCl_{(aq)} + HClO_{(aq)}$$

Chloric (I) acid (HOCI) is a weak acid and partially dissociate in water to form hydrogen ions (H^+) and chlorate (I) ion (OCl^-).

13.11.2 Disinfection Activity

HOCl and OCI^- 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 OCI^-, which disrupt the cell function leading to cell death. HOCI and OCI 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 HOCI and OCl^- and thus preventing bacteria from replicating and vital cellular functions.

13.11.3 Factors affecting disinfection

pH

1. At pH around 6-7.5, HOCI predominates and makes the disinfection process more effective.

2. At higher pH (above 7.5), OCl^- predominates, its 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 HOCI and OCI^- 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?
b) What are the factors that affect disinfection of bacteria in water?
c) What are the primary active species in the chlorination of water? Give equation that shows their production.

EXERCISE

MULTIPLE CHOICE QUESTIONS

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.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Which halogen is the least reactive, which is the most? Why?

b. The ionic equation for a reaction is:

$$Br_2 + 2I^- \rightarrow Br^- + I_{2.}$$

c. Explain which species is oxidized in this reaction. Why?

d. What is role of London dispersion forces in the trend of volatility of halogens?

e. How does the reactivity of halogens with hydrogen vary?

f. Which halogen is used as an antiseptic? How does it work?

g. What is the colour change when chlorine displaces bromine?

h. How the halogen acids are ionized in water?

i. Why HF is weaker acid than HCl?

j. 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.

k. Explain the chemical principles behind the use of chlorine as a disinfectant in water purification. Include relevant chemical equations in your explanation.

l. Describe one significant disadvantage associated with the use of chlorine in water purification.

m. What is disproportionation reaction? Give an example.

n. Chlorine gas reacts differently with sodium hydroxide solution depending on the temperature and concentration.

o. Write balanced chemical equations for the reaction of chlorine (Cl_2) with:

   i) Cold, dilute sodium hydroxide (NaOH).

   ii) Hot, concentrated sodium hydroxide (NaOH).

p. For each reaction in question l), 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 dispropo**rtionation reactions.**

DESCRIPTIVE QUESTIONS

Q.3 Describe and explain the relative thermal stabilities of the halogen hydrides in terms of bonds strength.

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.

Q 5. Describe the reactions that occur when chlorine is bubbled through

(i) Cold and (ii) Hot, aqueous sodium hydroxide (NaOH).

Q.6 Discuss the reducing power of halide ions with relevant reactions. Also explain the factors affecting it.

14

ATMOSPHERE

STUDENT LEARNING OUTCOMES [C-11-C-01 to C-11-B-14]

- 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 on 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 (21.01%). **Minor components** are argon (0.93%), carbon dioxide (0.04%). **Trace components** are methane, hydrogen, neon, helium, krypton, and xenon.

14.1 LAYERS OF THE ATMOSPHERES

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.

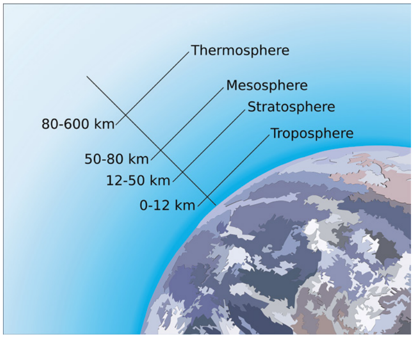


Figure 14.1 Layers of the atmosphere

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. It breaks down into monoatomic oxygen and diatomic oxygen.

$$O_{3\,(g)} \xrightarrow{h\upsilon} O_{2\,(g)} + O_{\,(g)}$$

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.

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.

14.2 AIR POLLUTANTS

Pollutants are substances (gases, liquids and solids) that are harmful to the environment. Air pollutants can be classified as primary and secondary. **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** are formed due to chemical reactions of primary pollutants.

The most important pollutants are mentioned below:

1. Oxides of Carbon (CO and CO_2)
2. Oxides of Nitrogen (NO and NO_2) collectively known as NO_x
3. Oxides of Sulphur (SO_2 and SO_3) collectively known as SO_x
4. Hydrocarbons (Methane, Ethane)
5. Low altitude Ozone (O_3)
6. Chlorofluorocarbons (CFCs)
7. Polycyclic Aromatic Hydrocarbon (PAHs)
8. Persistent Organic Pollutant (POPs)
9. Volatile Organic Compounds (VOCs)
10. Particulate Matter (PM)
11. Heavy Metals (Pb, Hg and Cd)

14.3 SOURCES OF AIR POLLUTION

There are broadly two main sources of air pollution.

14.3.1 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).

14.3.2 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

a) Mention important air pollutants.
b) Give the equations for the formation and depletion of ozone in the stratosphere.
c) Write down the names and approximate height of different layers of atmosphere.

14.4 SOURCES OF AIR POLLUTANTS

14.4.1 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) is produced mainly due to incomplete combustion of fossil fuels.

$$2C_{(S)} + O_{2(g)} \longrightarrow 2CO_{(g)}$$

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.

$$C_{(S)} + O_{2(g)} \longrightarrow CO_{2(g)}$$

14.4.2 Oxides of Nitrogen (NO_x)

The gases like nitric oxide (NO) and nitrogen dioxide (NO_2) are represented by NO_x. It is generally produced from burning fossil fuels. NO_x is produced as a result of the following chemical reactions:

$$N_{2(g)} + O_{2(g)} \xrightarrow{\text{high temp}} 2NO_{(g)} \text{(Nitric oxide)}$$

$$2NO_{(g)} + O_2 \rightarrow 2NO_2 \text{(Nitrogen-Dioxide)}$$

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.

14.4.3 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.

14.4.4 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.

14.4.5 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.

14.4.6 Chlorofluorocarbons (CFCs)

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 ($C\ell^{\cdot}$). The chloride free radical breaks down the Ozone molecule as shown in the following reactions.

$$CFC\ell_3 \xrightarrow{UV} CFC\ell_2 + C\ell^{\cdot}$$

$$C\ell^{\cdot} + O_3 \longrightarrow C\ell^{\cdot}O + O_2$$

$$C\ell^{\cdot}O + O_2 \longrightarrow C\ell^{\cdot} + O_2$$

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 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.

14.4.7 Polycyclic Aromatic Hydrocarbon (PAHs)

Polycyclic aromatic hydrocarbon (PAHs), composed of fused multiple aromatic rings are common environmental pollutants. Naphthalene, anthracene and phenanthracene are examples of PAHs. 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.

14.4.8 Persistent Organic Pollutants (POPs)

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, 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.

Owing to their persistence, they accumulate in the environment and can have significant adverse effects on human health. Some POPs are given in Table 14.1 below:

Table 14.1 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

14.4.9 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.

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,.

14.4.10 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. Natural sources include volcanoes, fires, dust storms, and aerosolized sea salt. Man-made sources of particulate matter PM include combustion in mechanical and industrial processes, vehicle emissions, and tobacco smoke.

14.4.11 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.

14.5 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.)

14.5.1 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.

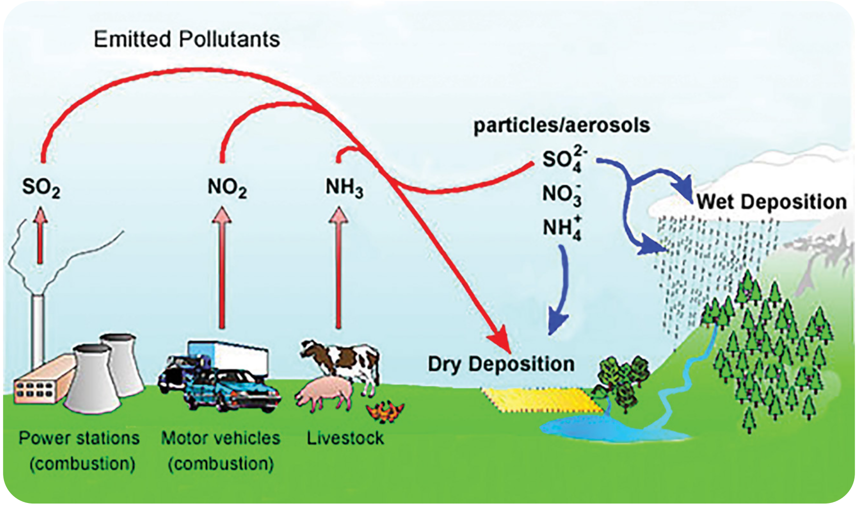


Figure 14.2 Impacts of air pollutants on the atmosphere

14.5.2 Impact of Deforestation on the Atmosphere

Deforestation is purposeful cleaning or thinning of forests by humans. Deforestation represents one of the largest issues in global climate. Forests absorb GHGs like CO_2 and clean air for us. In short, deforestation has a wide range of negative impact on the environment, including loss of biodiversity climate change, soil degradation, and water cycle disruption.

Quick Check 14.2

a) Mention man-made sources of air pollution.
b) How do polycyclic aromatic hydrocarbons (PAHs) primarily enter the atmosphere?
c) How do volatile organic compounds (VOCs) affect air quality?
d) What are major sources of heavy metals in the atmosphere?

14.6 EFFECTS OF AIR POLLUTANTS

The most important and commonly effects of air pollutants are formation of Smog and Acid Rain.

14.6.1 Formation of Smog

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_x, O_3, CO and CO_2, secondary pollutants like O_3, unburned hydrocarbons, VOCs and PM 10-2.5 micron.

Figure 14.3 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.

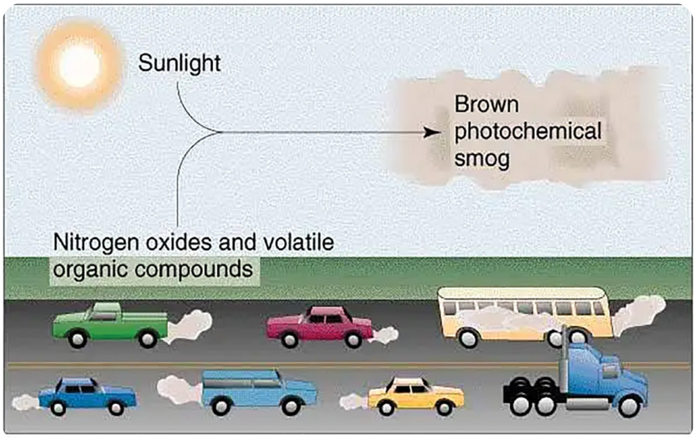


Figure 14.4 Illustration of Photochemical smog

14.6.2 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:

$$2SO_{2_{(g)}} + O_{2_{(g)}} \rightarrow 2SO_{3_{(g)}}$$

$$SO_{3_{(g)}} + H_2O_{(l)} \rightarrow H_2SO_{4_{(aq)}}$$

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.

$$\mathrm{NO_{(g)} + H_2O_{(\ell)} \longrightarrow HNO_{3(aq)} + HNO_{2(aq)}}$$

14.7 GREENHOUSE EFFECT AND GLOBAL WARNING

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**.

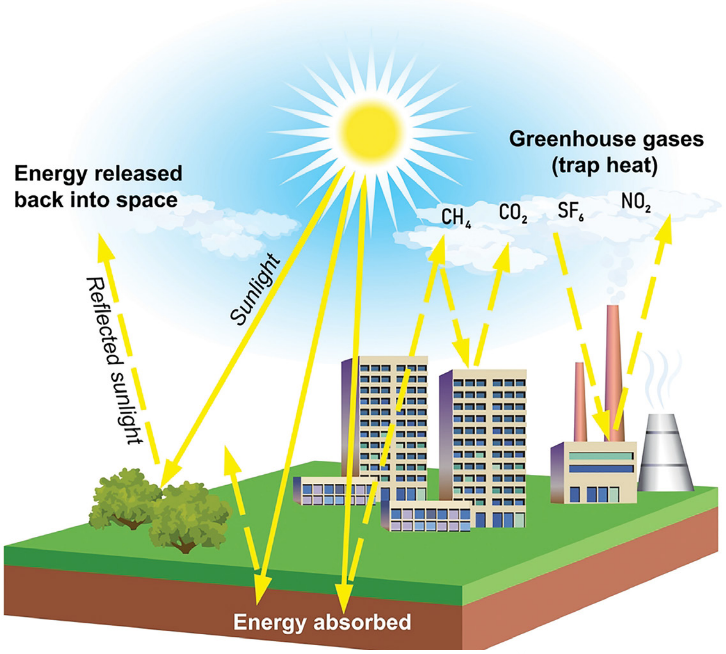


Figure 14.5 Mechanism of Global Warming

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.

The greenhouse effect is a phenomenon which is based on the gases to absorb infra-red 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.

Quick Check 14.3

a) Differentiate classical and photochemical smog.

b) Name greenhouse gases (GHGs). How do these gases cause global warming?

c) Write a balanced equation, including state symbols, showing the formation of sulfuric acid from atmospheric sulfur trioxide, SO_2.

14.8 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.

14.8.1 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.

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.

Table 14.2 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

14.9 LINK BETWEEN 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.

14.9.1 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.

14.10 POTENTIAL HEALTH RISK ASSOCIATED WITH AIR POLLUTION

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.

14.10.1 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.

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.
b) What is AQI? How does it measure air quality?
c) What are different levels of AQI. Mention the safest and the most hazardous ranges of AQI.

14.11 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.

14.11.1 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.

14.12 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.

14.13 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.

Analyzing and interpreting air quality data 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.

14.14 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) Catalytic convertor (CC)

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)

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.

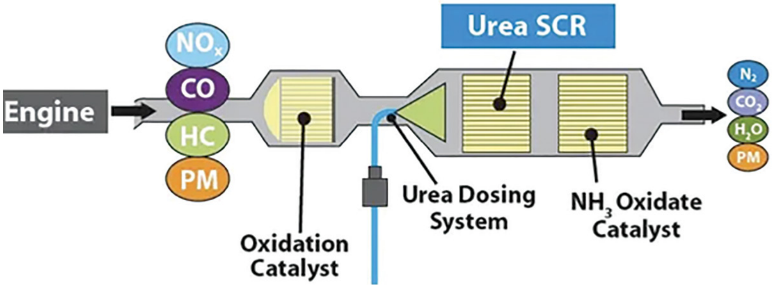


Figure 14.6 Selective Catalytic Reduction

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.

14.15 LAWS AND REGULATIONS RELATED TO ATMOSPHERE

14.15.1 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

14.15.2 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.

14.16 ECONOMIC, SOCIAL & POLITICAL ISSUES

Air pollution and bad air quality is responsible for huge economic costs, social and potential issues.

14.16.1 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.

14.16.2 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.

14.16.3 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 corporation.
- 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.

EXERCISE

MULTIPLE CHOICE QUESTIONS

Q.1 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 (NOx) 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.

XII. 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.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Identify and briefly explain three major natural sources of air pollutants.

b. How can deforestation impact air quality?

c. Explain the reasons for the temperature trends observed in the troposphere and the stratosphere.

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.

e. What are the environmental impacts of persistent organic pollutants (POPs)?

f. How does polycyclic aromatic hydrocarbon (PAHs) affect human health?

g. What is photochemical smog? Under what conditions, it forms?

h. What type of data do air quality index (AQI) system provide?

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.

j. What are the main chemical processes involved in the formation of acid rain?

k. What are the specific measures to control smog?

l. How does a catalytic converter reduce harmful vehicle emissions?

m. Describe the sources of lead and mercury pollution.

DESCRIPTIVE QUESTIONS

Q.3 Discuss sources and effects of following air pollutants on environment:

i) Heavy metals ii) VOCs iii) PAHs iv) POPs

Q.4 Write short notes on the following:

i) CFCs and ozone layer depletion ii) Greenhouse effect and global warming

Q.5 How the fossil fuel burning causes acid rain? Discuss in detail with chemical reactions.

Q.6 What is meant by air quality AQI? Describe the factors affecting the air quality.

15

BASIC SEPARATION TECHNIQUES

STUDENT LEARNING OUTCOMES [C-11-E-01 to C-11-E-08]

- 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 Rf. **(Knowledge)**

Analytical chemistry is the science of chemical characterization. A complete chemical characterization of a compound must include both qualitative and quantitative analyses. In **qualitative analysis**, the chemist is concerned with the detection or identification of the elements present in a compound, whereas in **quantitative analysis**, the relative amounts of elements in compounds are determined.

A complete quantitative determination generally consists of four major steps

1. Obtaining a sample for analysis
2. Separation of the desired constituent
3. Measurement, and calculation of results
4. Drawing conclusion from the analysis.

In this chapter, some basic separation techniques are discussed here to practice in the lab.

15.1 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. **Simple distillation**
4. **Fractional distillation**
5. **Paper Chromatography**

15.1 Filtration

This process is used to separate one of the components of a two-component heterogeneous mixture from a solution. The first step is to select a suitable solvent in which one of the components dissolves completely while the other remains practically insoluble. For example, let us take a mixture of common salt and sand.

Dissolve this mixture in distilled water. The common salt will distribute itself through out water to give a homogeneous mixture. This homogenous mixture is called a **solution** of common salt in water.

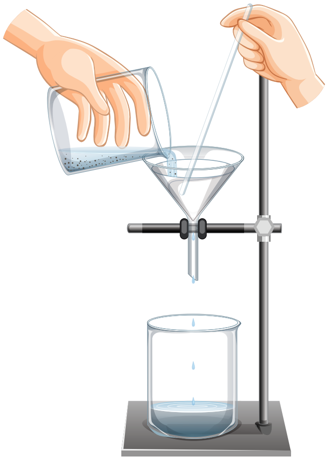


Figure 15.1 The process of filtration

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 co-mpared to the solute. While 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. It can be performed with several types of filter media. Nature of the precipitate and other factors dictate which filter medium must be used. The most convenient ways of filtration are either through a filter paper or through a filter crucible.

a) 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 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 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 15.1**.

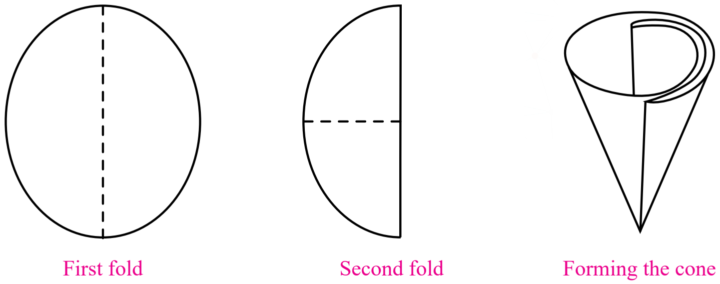


Fig 15.2 a Folding of filtration paper

The folded filter paper may then be inserted into 60-degree funnel, moistened with water and firmly pressed down.

2. 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 (15.2 b)**.

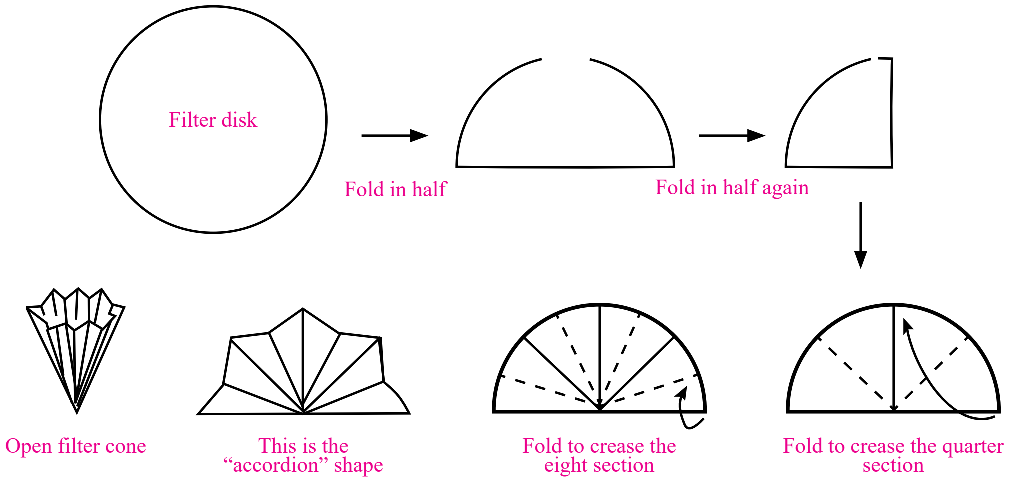


Fig 15.2 b Fluttled filter paper

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**.

b) 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 15.3**. 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.

Figure 15.3 Gooch crucible

Fig 15.4 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 15.4**.

Quick Check 15.1

a) Name different filter media used in filtration?
b) What are the components of the filtration process?
c) Differentiate gravity filtration and vacuum filtration.
d) Different shade Gooch and sintered glass crucible.

15.2 CRYSTALLIZATION

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.

Choice of a Solvent

An ideal solvent should have the following features.

i. It should dissolve a large amount of the substance at its boiling point and only a small amount at the room temperature.
ii. It should not react chemically with the solute.
iii. It should either not dissolve the impurities or the impurities should not crystallize from it along with the solute.
iv. On cooling, it should deposit well-formed crystals of the pure compound.
v. It should be inexpensive, safe to use and easily removable.

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.

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.

15.4.1. 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.

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.

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.

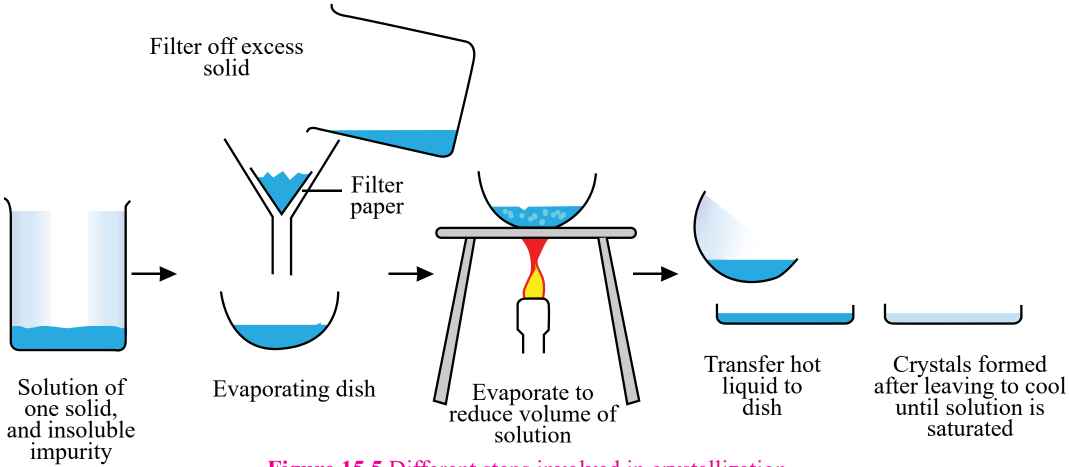


Figure 15.5 Different steps involved in crystallization

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. The drying agents used in a desiccator are $CaCl_2$, silica gel or phosphorus pentaoxide **Figure 15.9**.

Quick Check 15.2

a) What is the basic principle of crystallization?
b) How a suitable solvent is selected for the process of crystallization?
c) Mention the important steps of crystallization.

15.3 SEPARATION THROUGH DISTILLATION

If a two-component mixture is 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 of these compounds, sea water is distilled to make it drinkable.

The process of **fractional distillation** is another 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.

15.2.1 Distillation Process

1. Simple distillation

It is used to separate solvent from solution. For example, take 100 cm^3 sea water. Set up the apparatus as shown in the **Figure 15.5**. 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 15.7**.

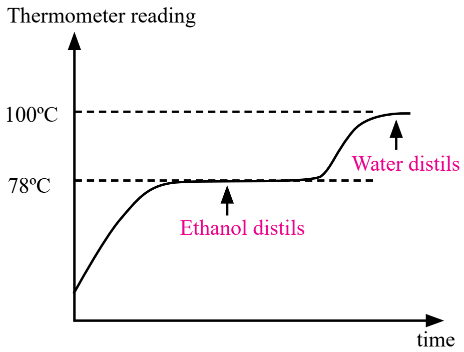


Figure. 15.6 Fractional distillation of ethanol / water mixture

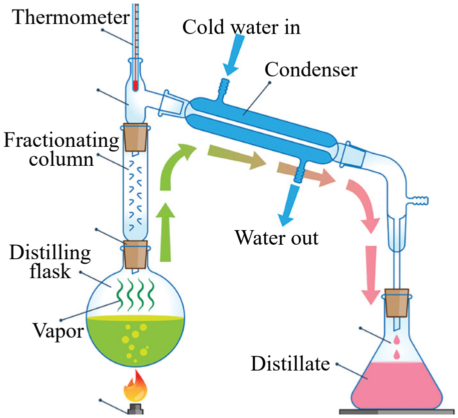


Figure 15.7 Fractional distillation setup

For 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 less than that of water whose boiling point is 100 ºC. As long as the alcohol is being distilled over, the temperature of the thermometer will remain at 78 ºC. As soon as the temperature starts rising above 78 ºC, 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 ºC, 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?

b) Give some daily-life applications of fractional filtration?

15.3. CHROMATOGRAPHY

Chromatography is a method used primarily for the separation of a sample of mixture. It involves the distribution of a solute (mixture) between a stationary phase and 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.

Chromatography in which the stationary phase is a solid, is classified as **adsorption chromatography**. In this type, a substance leaves the mobile phase to become adsorbed on the surface of the solid phase. Examples of adsorption chromatography are thin layer chromatography (TLC) and column chromatography.

Chromatography in which the stationary phase is a liquid, is called **partition chromatography**. In this type, the substances being separated are distributed throughout both the stationary and mobile phases. Examples of partition chromatography are paper chromatography and gas liquid chromatography.

15.3.1. PAPER CHROMATOGRAPHY

It is a type of partition chromatography. The entrapped water in cellulose fibers of paper and mobile phase which passes over the paper are immiscible, The mobile phase is usually an organic liquid.

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.

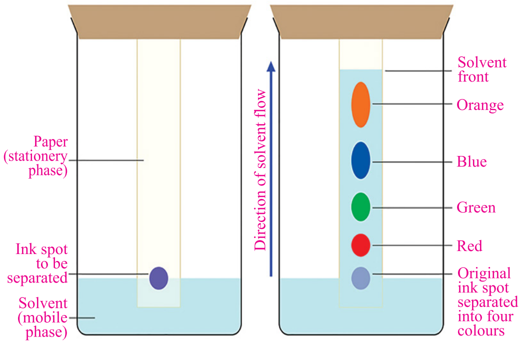
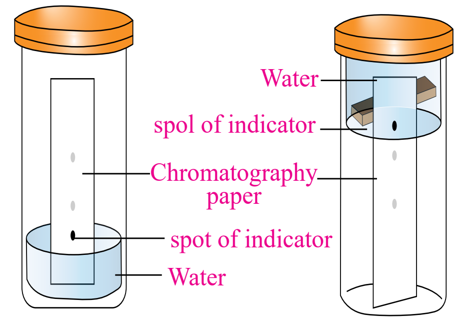


Figure 15.8 Paper chromatagraphy

A solvent mixture, specially composed in accordance with the sample to be separated, is poured into the chromatographic tank **Figure 15.7**, 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 alongside.

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.



ascending method descending method

Figure 15.9 Ascending and descending paper chromotography

15.3.2 Locating agents 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.

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 locale the spots. 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.

15.3.3 Use of Retardation Factor

Each component has a specific retardation factor called R_r 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 15.10** the chromatogram shows that the sample A contains both components B and C. The R_f values for B and Care given by:

$$R_f(B) = \frac{x}{y}$$

$$R_f(C) = \frac{x}{y}$$

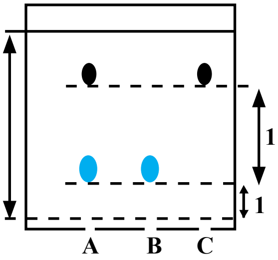


Figure 15.10 Chromatogram

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.

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.

In this chromatogram shown in **Figure 15.10**, 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.

15.3.4 Applications of Paper Chromatography

i. The techniques of chromatography are very useful in organic synthesis for separation, isolation and purification of the products. They are equally important in qualitative and quantitative analyses and for determination of the purity of a substance.

ii. 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?

b) What are the stationary and mobile phases in paper chromatography?

c) How the purity of a substance is determined by using paper chromatography?

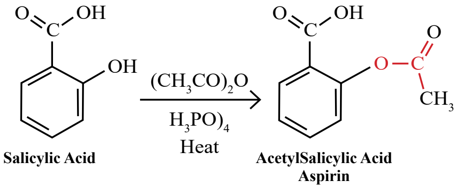
15.4 HOW TO CHECK THE PURITY OF THE PRODUCT?

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.

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.

i. 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, its melting point is determined. If the product melts sharply, in this case at exactly 136°C then the product is considered as pure. If the product shows a melting point which is not sharp rather it melts within a range of temperature, it is considered as an impure product.



ii. Another way of assessing 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.

iii. 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 the R_f value.

Quick Check 15.5

a) How does melting point of a substance indicate its purity?

b) Which technique (filtration, crystallization and distillation) is suitable for the separation of the following mixtures?

i) Petroleum and water
ii) NaCl and $NaNO_3$
iii) activated charcoal and sodium chloride
iv) Methanol, ethanol and propanol

EXERCISE

MULTIPLE CHOICE QUESTIONS

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 phones
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

IX. 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.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Why is there a need to crystallize a crude product?

b. What is the function of fluted filter paper?

c. What is the difference between a Gooch crucible and sintered glass crucible?

d. What type of mixtures are filtered through a Gooch crucible?

e. What is function of fractionating column during fractional distillation?

f. What is the stationary phase in the paper chromatography?

g. What will happen during paper chromatography if the components of the mixture have a comparable attraction for the stationary phase?

h. What is the meant by the term “developing the chromatogram” in paper chromatography?

i. What is the basic principle of paper chromatography?

j. Why water is not generally used as a solvent in paper chromatography?

k. Differentiate between adsorption and partition chromatography.

l. How can you check the purity of a compound with the help of paper chromatography?

m. You have prepared a solid sample of glucosazone in the laboratory. How will you proceed to check the purity of the sample?

DESCRIPTIVE QUESTIONS

Q.3 Differentiate simple distillation and fractional distillation in construction and applications.

Q.4 Describe the criterion to choose the suitable solvent in the process of crystallization?

Q.5 What is the basic principle of paper chromatography? Give its three practical life applications.

16

LAB SAFETY AND PRACTICAL SKILLS

STUDENT LEARNING OUTCOMES [C-11-F-01 to C-11-F-21]

- 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.

16.1. 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.

16.2 COMMON TYPES OF HAZARDS IN A LABORATORY

Most hazards which we might face while working in the laboratory fall into three categories, physical, chemical and biological hazards.

16.2.1 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.

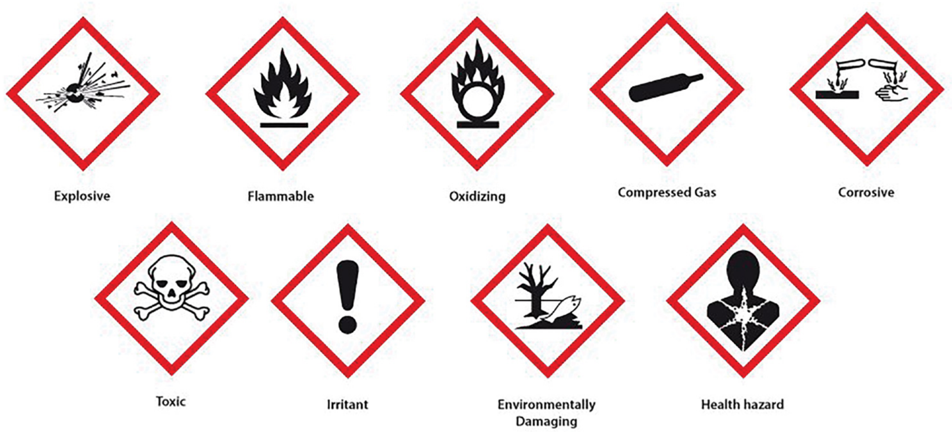


Figure 16.2 Pictogram of chemical hazards

16.2.2 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.

16.2.3 Biological Hazards

The most common biological hazards arc allergens, infectious diseases which are transferred from animals to humans and viral diseases.

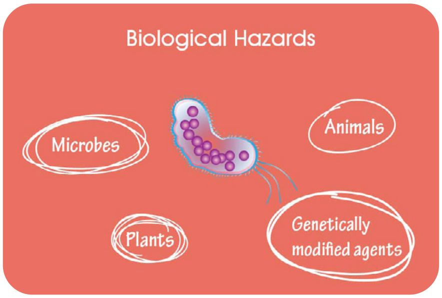


Figure 16.3 Some biological hazards

16.3 WASTE DISPOSAL SYSTEM FOR CHEMICALS

Chemical waste cannot be disposed of in bins or sewer system. Most chemical wastes must be disposed of 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.

i. Chemical treatment of wastes involves neutralization, precipitation, ion exchange, oxidation or reduction.

16.4 FIRST AID IN LABORATORY

Every laboratory must have a first aid box. Common accidents and their first aid treatments are given in the **Table 16.1** below:

Table 16.1 Accidents and their First Aid treatment

	Type of Accident	First Aid Treatment
1	**Cuts**	
	Minor cuts	• Remove the glass piece if any, apply a little methylated spirit or tincture iodine with a piece of cotton. Both act as disinfectant.
	Serious cuts	• Apply pressure on the cut for about 10 minutes to stop bleeding. Consult a doctor.
2	**Eye Injuries**	
	Acid in the eye	• Wash thoroughly with water and then with 1% sodium bicarbonate solution.
	Alkali in the eye	• Wash with water followed by 1% boric acid solution.
	Foreign particle in the eye	• Do not rub the eyes. Remove the particle carefully with soft handkerchief then wash with water.
	Soreness in the eye	• 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)	• Apply burnol or mustard oil.
	Burns causing blisters	• Wash freely with ice cold water. Then wash with a saturated solution of sodium bicarbonate and again with water.
	Acid burns	• Wash freely with water and then with 1% acetic acid solution and again with water, dry the skin and apply the burnol.
	Alkali burns	• Wash fully with 2% ammonia solution and apply glycerin. Wipe off glycerin after sometime and apply burnol.
	Bromine burns	
4	**Poisons**	
	Poisons swallowed	Spit immediately, wash mouth with water repeatedly.
	Acid swallowed	• Drink a lot of water or lime water or milk of magnesia.
	Caustic alkalies swallowed	• Drink a lot of water; drink a glass of lemon or orange juice.
	Salt of heavy metals swallowed.	• Take milk or white part of the egg.

5	**Fire**	
	i) Clothes catch fire	• Do not run. Wrap with blanket or with dry cotton cloth. Lie down on the floor.
	ii) Beaker containing inflammable liquid. catches fire.	• Cover the beaker with a duster or damp cloth. This will cut off the supply of oxygen.
	iii) Spirit or oil catches fire.	• Throw a mixture of sand and sodium bicarbonate. Do not throw water. It will simply spread the fire.
	iv) Electric parts catch 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.
b) How chemical waste is disposed off?
c) How H_2SO_4 burn is treated in the lab?
d) What are different types of burns?

16.5 ACID-BASE TITRATION

Volumetric analysis is used to find the concentrations of solutions by means of a technique known as titration. In this technique 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. 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**. Either solution can be taken in a burette with the other solution taken in a conical or a titration flask.

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.

Materials Required

Burette, pipette, funnel, conical flask, HCI solution, NaOH solution, phenolphthalein.

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 color 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.

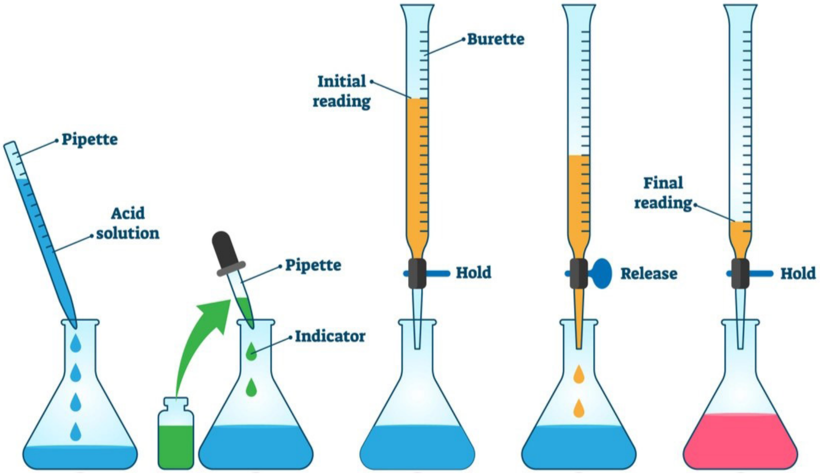


Figure 16.6 Procedure of titration

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.

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

$$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

Calculation

Find out the molarity of NaOH solution by using the following molarity equation:

$$\begin{array}{ccc} Acid & & Base \\ \frac{M_1V_1}{n_1} & = & \frac{M_2V_2}{n_2} \end{array}$$

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.

Quick Check 16.2

a) Define indicator and endpoint in a titration.
b) What is meant by concordant reading?
c)
d)

16.6 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 turns milky.	Carbonate (CO_3^{2-}) are indicated ions.

Reactions involved in the above steps

$$CO_{3(aq)}^{2-} + 2H_{(aq)}^{+} \rightarrow H_2O_{(\ell)} + CO_{2(g)}$$

$$\underset{\text{Lime water}}{Ca(OH)_{2(aq)}} + CO_{2(g)} \rightarrow \underset{\text{(white ppt)}}{CaCO_{3(s)}} + H_2O_{(l)}$$

(b) Identification of chloride (Cl^{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 Ag NO_3.	A thick white precipitate is formed which dissolves in aq.NH_3.	Cl^{-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^{1-} ions are indicated.

Reactions involved in the above tests

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow \underset{\text{white ppt}}{AgCl_{(s)}}$$

$$Ag^+_{(aq)} + Br^-_{(aq)} \rightarrow \underset{\text{cream yellow ppt}}{AgBr_{(s)}}$$

$$Ag^+_{(aq)} + I^-_{(aq)} \rightarrow \underset{\text{bright yellow ppt}}{AgI_{(s)}}$$

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.

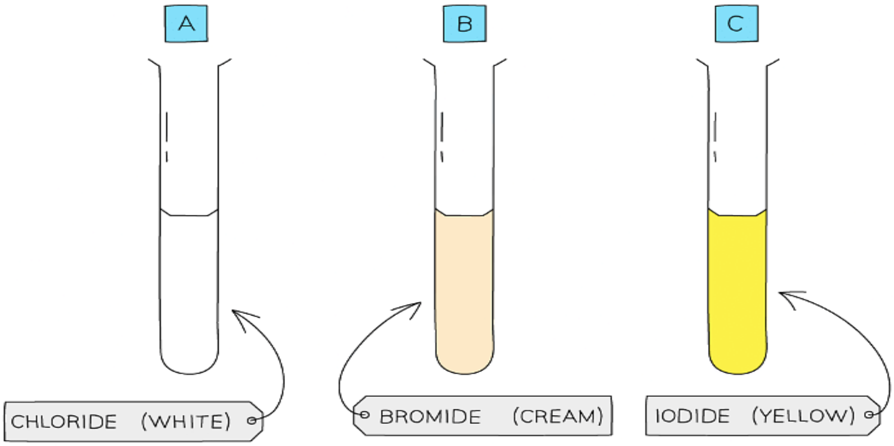
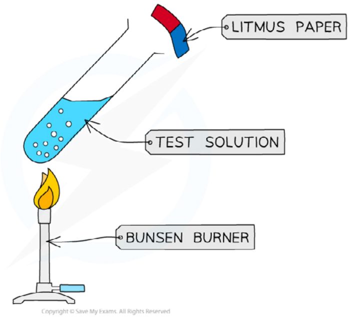


Figure 16.7 Observation of reactions of halide ions with $AgNO_3$

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 powdered aluminium metal.	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.



$$3NO^{1-}_{3(aq)} + 8Al_{(s)} + 5\overset{-}{O}H_{(aq)} + 18H_2O_{(\ell)} \rightarrow 3NH_{3(g)} + 8\left[Al(OH)_{4(aq)}\right]^{1-}$$

(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.
b) What is ring test? Give equation for this test.
c) Give names and formulas of some water insoluble sulphates.

16.7 TESTS FOR IDENTIFICATION OF BASIC RADICALS

a) Identification of Aluminium (Al^{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.	Al^{3+} ions are indicated.
To the second part of the above solution, add a few drops of aqueous ammonia.	A white precipitate is formed.	Al^{3+} ions are indicated

$$Al^{3+}_{(aq)} + 3OH^{1-}_{(aq)} \rightarrow \underset{\text{white ppt}}{Al(OH)_{3(s)}}$$

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.

$$NH^{1+}_{4(aq)} + OH^{1-}_{(aq)} \rightarrow NH_{3(g)} + H_2O_{(\ell)}$$

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.

$$Ca^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow \underset{\text{white ppt}}{Ca(OH)_{2(s)}}$$

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.

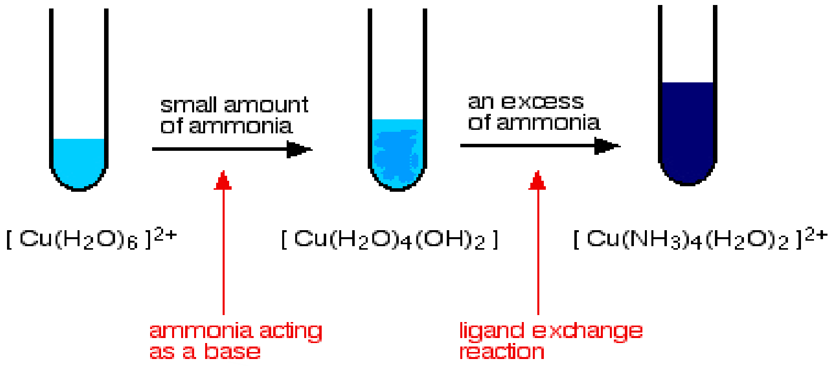
$$Cr^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow \underset{\text{Green ppt}}{Cr(OH)_{3(s)}}$$

e) Identification of Copper radical (Cu^{2+})

Add 4g solid sample in a clean test tube. Dissolve it in 10cm^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.

$$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow \underset{\text{Blue ppt}}{Cu(OH)_{2(s)}}$$



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.

$$Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow \underset{\text{Green ppt}}{Fe(OH)_2}$$

f) Identification of Fe(III) radical (Fe^{3+})

Take 2 g $FeCl_3$ 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.

$$Fe^{3+}_{(aq)} + 3OH^{-}_{(aq)} \rightarrow \underset{\text{Orange brown ppt}}{Fe(OH)_{3(s)}}$$

g) 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.

$$Zn^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow \underset{\text{white ppt}}{Zn(OH)_{2(s)}}$$

Quick Check 16.4

a) What is lake test? Give equation.

b) How ammonium ion is indicated?

c) How will you distinguish ferrous (Fe^{2+}) and ferric (Fe^{3+}) radicals?

d) What happens when aq. NH_3 is added to Cu^{2+} solution in limited and excess quantities?

EXERCISE

MULTIPLE CHOICE QUESTIONS

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 colorless liquids and the upper meniscus for the coloured liquids?

a) because it is more convenient

b) because colorless liquids have more surface tension than colored liquids

c) because lower meniscus does not exist for colored 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) Al^{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 colorless, odorless gas that turns limewater milky suggests the presence of:

a) Chloride ion (Cl^-) b) Sulfate ion (SO_4^{2-})

c) Carbonate ion (CO_3^{2-}) d) Nitrate ion (NO_3^-)

VI. The chromyl chloride test is a specific confirmatory test for:

a) Bromide ions (Br^-) b) Iodide ions (I^-)

c) Chloride ions (Cl^-) d) Sulfate ions (SO_4^{2-})

VII. The brown ring test is a confirmatory test for which acid radical?

a) Chloride (Cl^-) b) Nitrate (NO_3^-)

c) Sulfate (SO_4^{2-}) d) Carbonate (CO_3^{2-})

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. For which type of titration, methyl orange is used as an indicator?

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.

c. Explain why different indicators change color over different pH ranges.

d. It is always advisable to use dilute solutions while performing experiments in volumetric analysis? Give a reason.

e. White precipitates are formed when Ca^{2+}, Al^{3+} and Zn^{2+} all react separately with NaOH solution. How will you detect which basic radical is present?

f. How Fe^{2+} can be distinguished from Fe^{3+} chemically?

g. Why Ca^{2+} does not give precipitate with aqueous ammonia?

h. How will you find out the concentration of acetic acid in vinegar solution?

i. What precautions you need to observe while diluting a concentrated acid?

j. Why does an aqueous solution of Na_2CO_3 behave like a base?

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?

DESCRIPTIVE QUESTIONS

Q.3 Describe common types of the Chemistry lab hazards with two examples in each case.

Q.4 What are common accidents in the Chemistry lab? How they are managed in first aid treatment.

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-}

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+}