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 ($NaCl$, $MgCl_2$

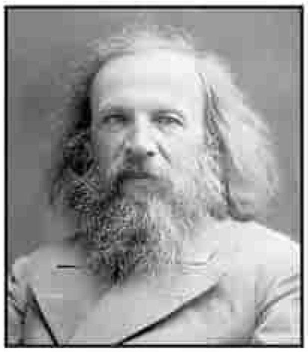
in terms of their outer shell (valence shell) electrons. **(Understanding)**

- Write equations for the reactions of Na and Mg with oxygen, chlorine and water. **(Application)**
- Explain the variations and trends in terms of bonding and electronegativity. **(Understanding)**

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.

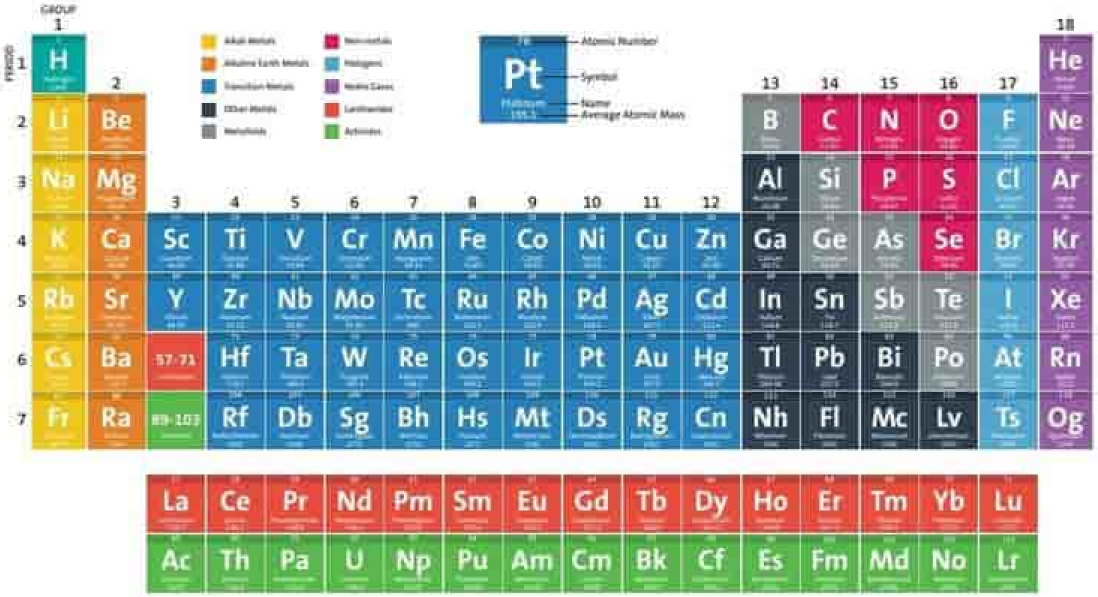


Fig 1.1: Modern periodic table

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.

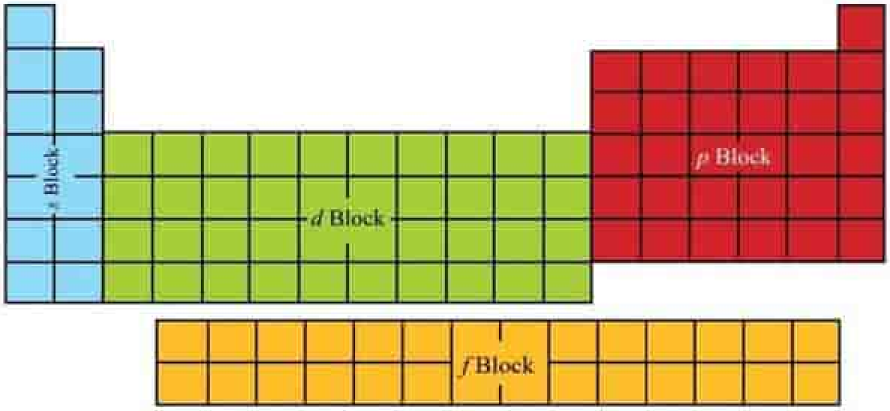


Figure 10.2: Blocks in periodic table

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) $\overset{\curvearrowright}{X}$ 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).

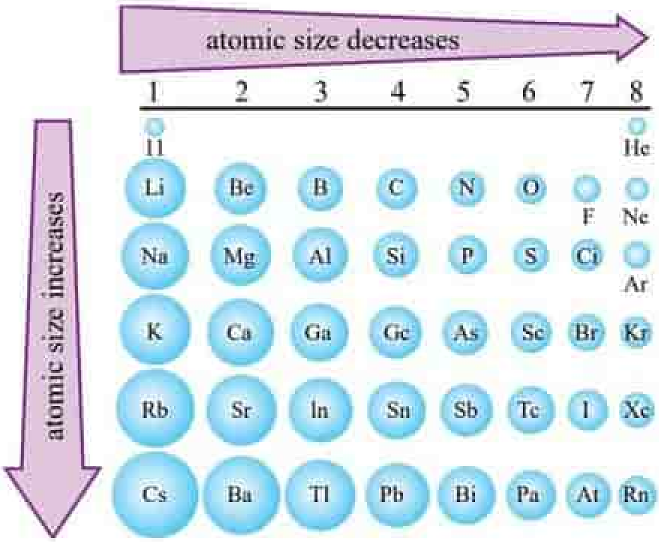


Fig 1.4: Variation in atomic radius across periods and down the groups

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.

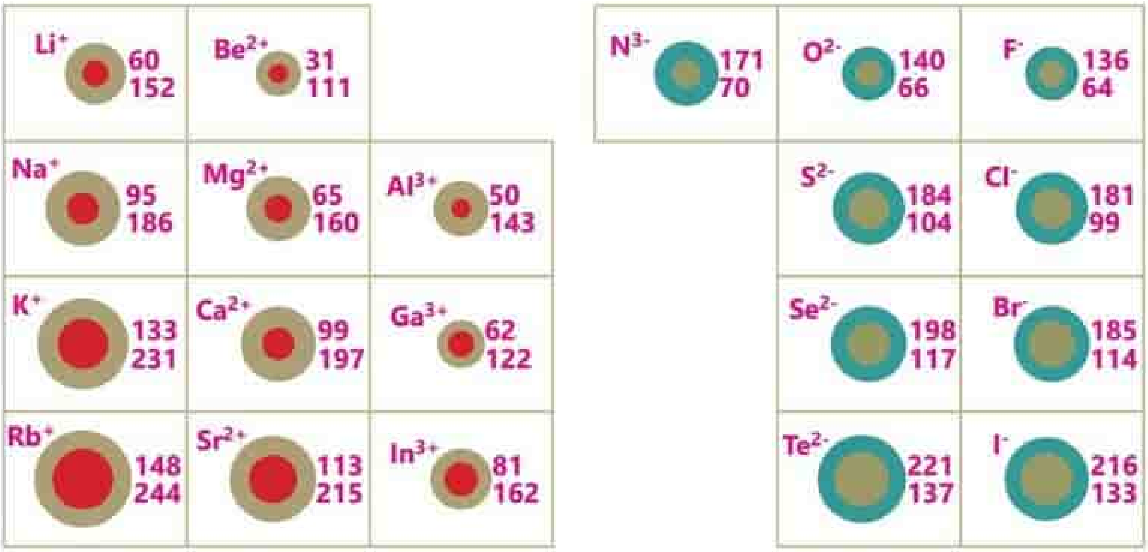


Fig. 1.5: Variation in Ionic Radius (Ions are coloured red and blue; parent atoms brown. Radii are in picometers)

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)."

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

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

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:

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

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:

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

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.

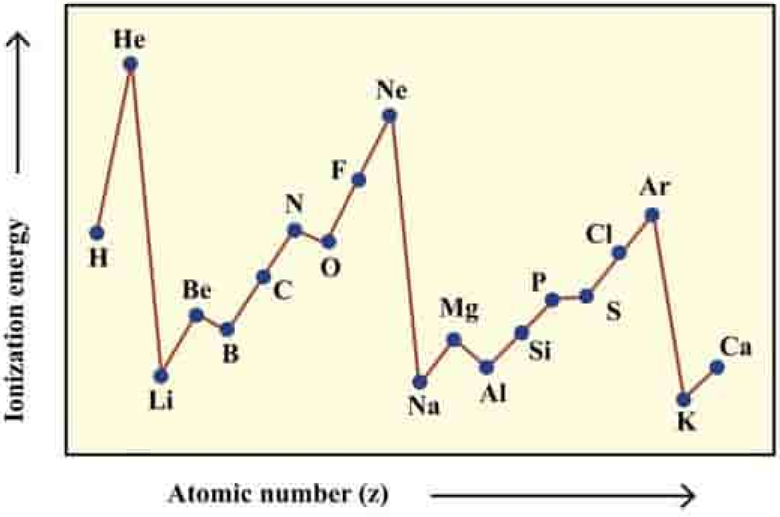


Figure 1.6 Variation in Ionization Energies across periods

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.

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

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.

$$O_{(g)} + e^- \longrightarrow O^-_{(g)} \qquad \Delta H^\circ_{ea1} = -141 \text{ kJ mol}^{-1}$$

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

$$O^-_{(g)} + e^- \longrightarrow O^{2-}_{(g)} \qquad \Delta H^\circ_{ea2} = +798 \text{ kJ mol}^{-1}$$

The net enthalpy change for the formation of the oxide ion (O2–) can be calculated by adding the first and second electron affinities

$$O_{(g)} + 2e^- \longrightarrow O^{2-}_{(g)}$$
$$\Delta H^\circ_{ea1} + \Delta H^\circ_{ea2} = (-141) + (+798) = +657 \text{ kJ mol}^{-1}$$

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:

$$F > Cl > Br > I$$

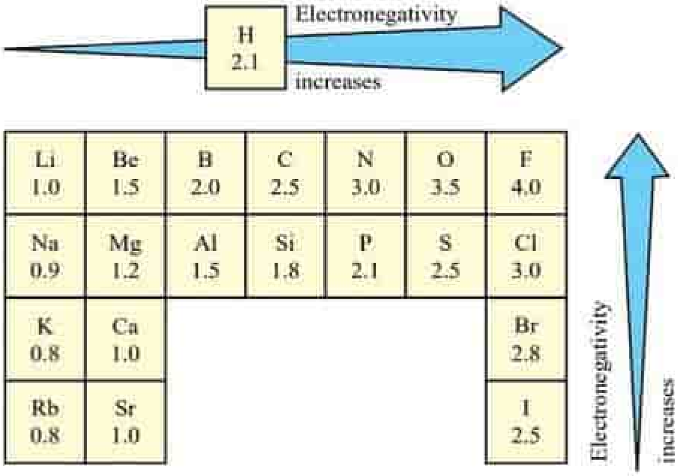
ii) Effective nuclear Charge

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.



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.

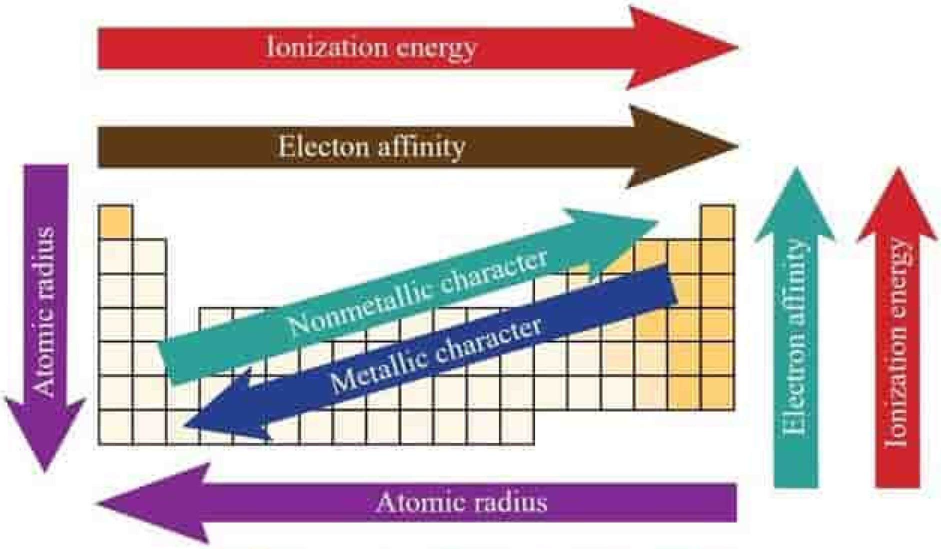


Fig. 1.9: Trends in various physical properties in the periodic table

1.7.8 Variation in Metallic Character

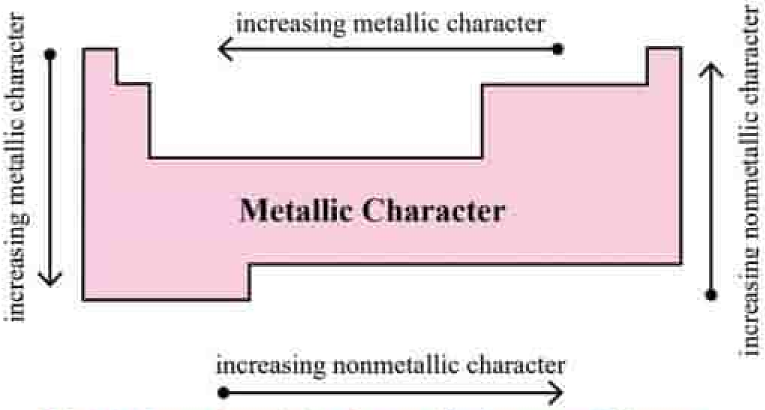


Fig 1.3: General trends for the metallic character of elements

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.

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

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

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

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

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.

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

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.

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

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,

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

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

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.

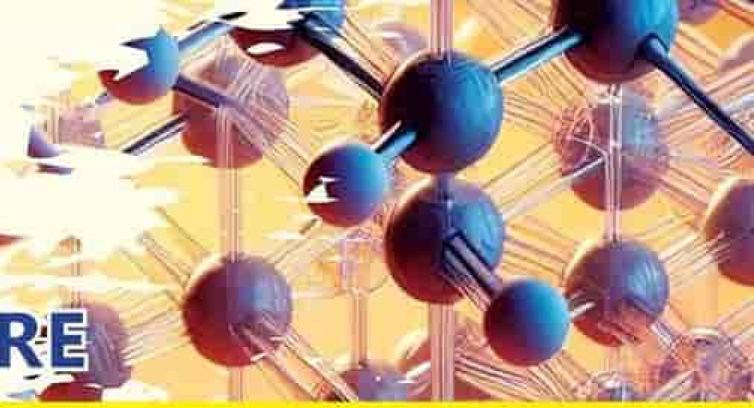
Q.4 Explain with the help of equations acidic and basic behavior of oxides and chlorides.

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.

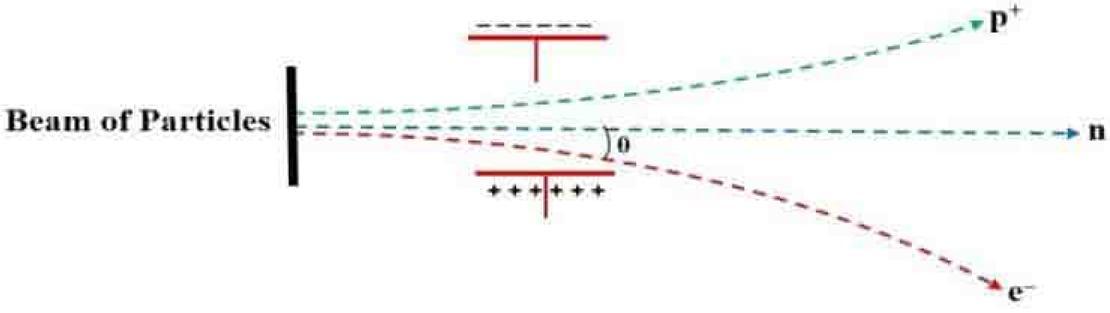


Figure 2.1 Behaviour of proton, electron and neutron in the electric field

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.

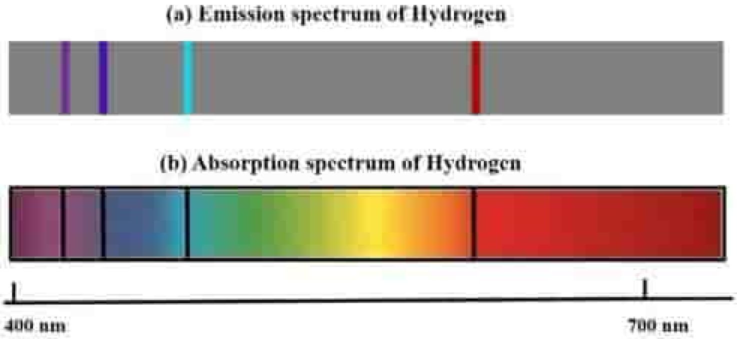


Figure 2.2 (a) atomic emission spectrum of hydrogen **(b)** atomic absorption spectrum of hydrogen

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.

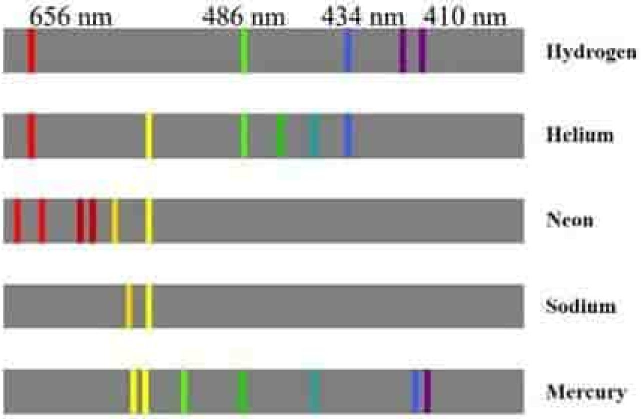


Figure 2.3 Spectral series of various elements as plotted by a spectrometer

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.

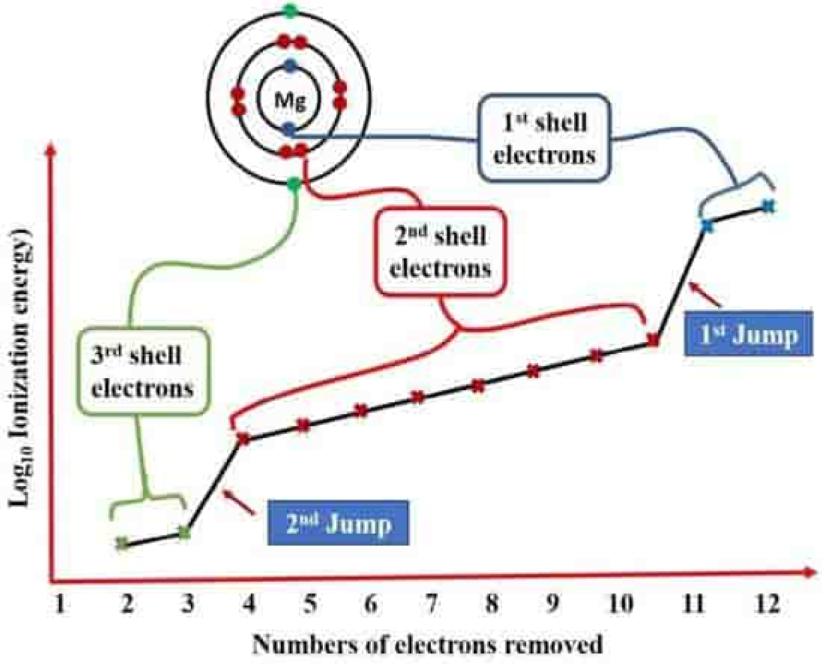


Figure 2.4 A plot of the successive ionization energies of Mg

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.

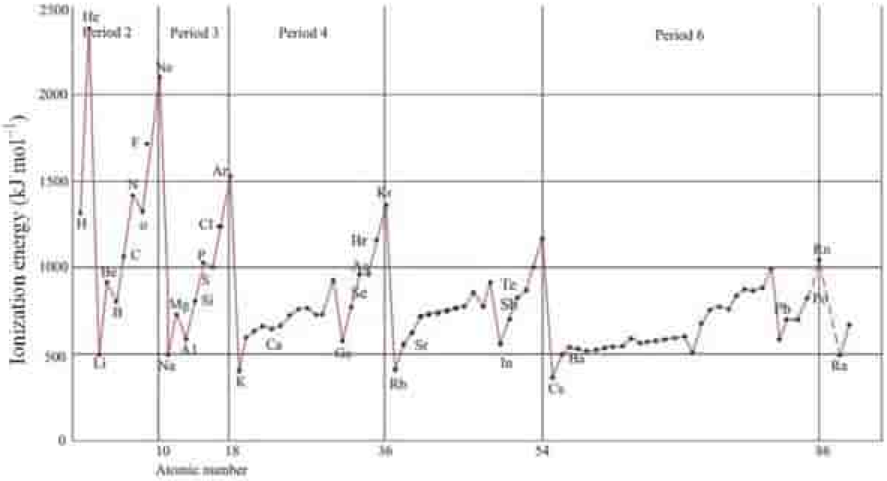


Figure 2.5 A plot of the ionization energies of first 88 elements against atomic number

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.**

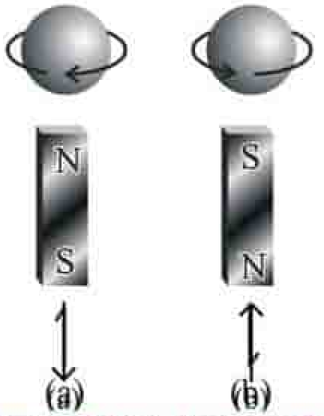


Figure 2.4 (a) clockwise **(b)** counterclockwise spins of an electron.

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.

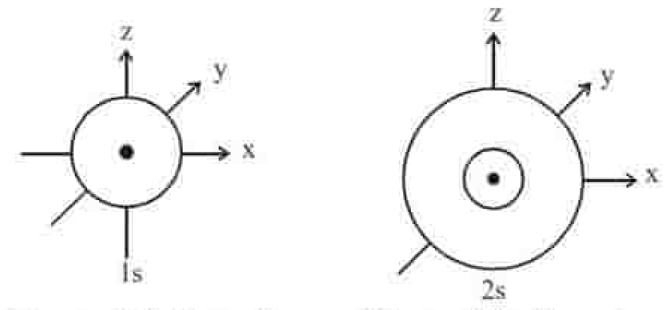
2.6 SHAPES OF ATOMIC ORBITALS

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.

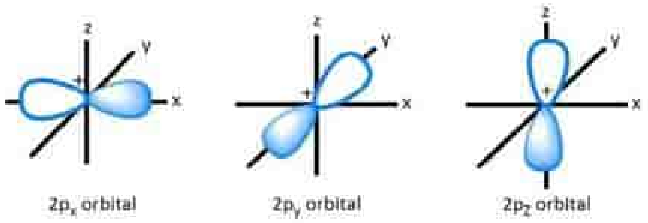


(a) $n = 1, l = 0, m = 0$ (b) $n = 2, l = 0, m = 0$

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.



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

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.**

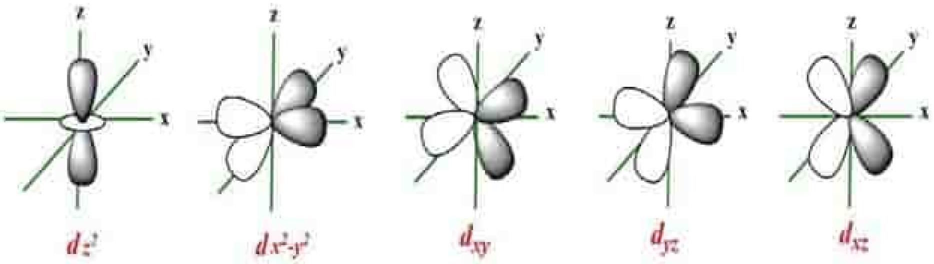


Fig. 2.7 The shapes of the five 3d orbitals

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

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

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	2s	$(2 + 0) = 2$
	1	2p	$(2 + 1) = 3$
3	0	3s	$(3 + 0) = 3$
	1	3p	$(3 + 1) = 4$
	2	3d	$(3 + 2) = 5$
4	0	4s	$(4 + 0) = 4$
	1	4p	$(4 + 1) = 5$
	2	4d	$(4 + 2) = 6$
	3	4f	$(4 + 3) = 7$

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

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

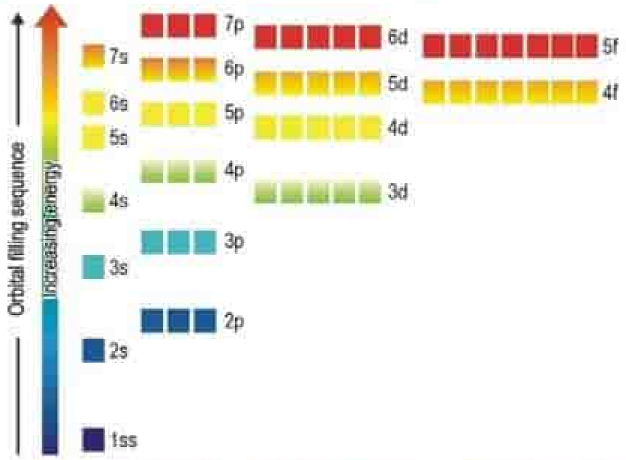


Fig 2.12 The diagram shows the energy of each subshell. Each box on the diagram represents an atomic orbital.

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:**

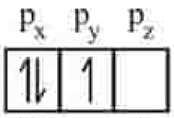
Table 2.6 values of quantum numbers of two electrons in the same orbital

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

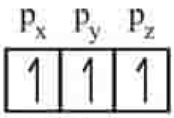
The two electrons having the same values of **'n'**, **'*l*'** and **'m'** can have different values of **'s'**. It means that their spins are in the opposite directions.

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.

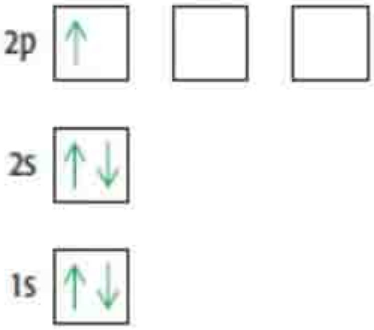


Figure 2.13 The electronic configuration of boron in

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

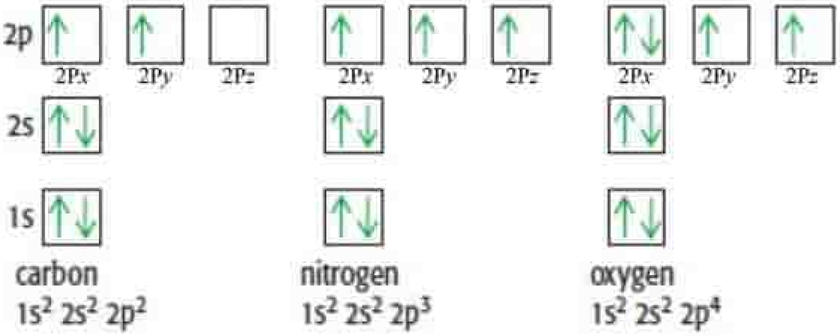


Figure 2.14 When adding electrons to a particular subshell, the electrons are only paired when no more empty orbitals are available.

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.

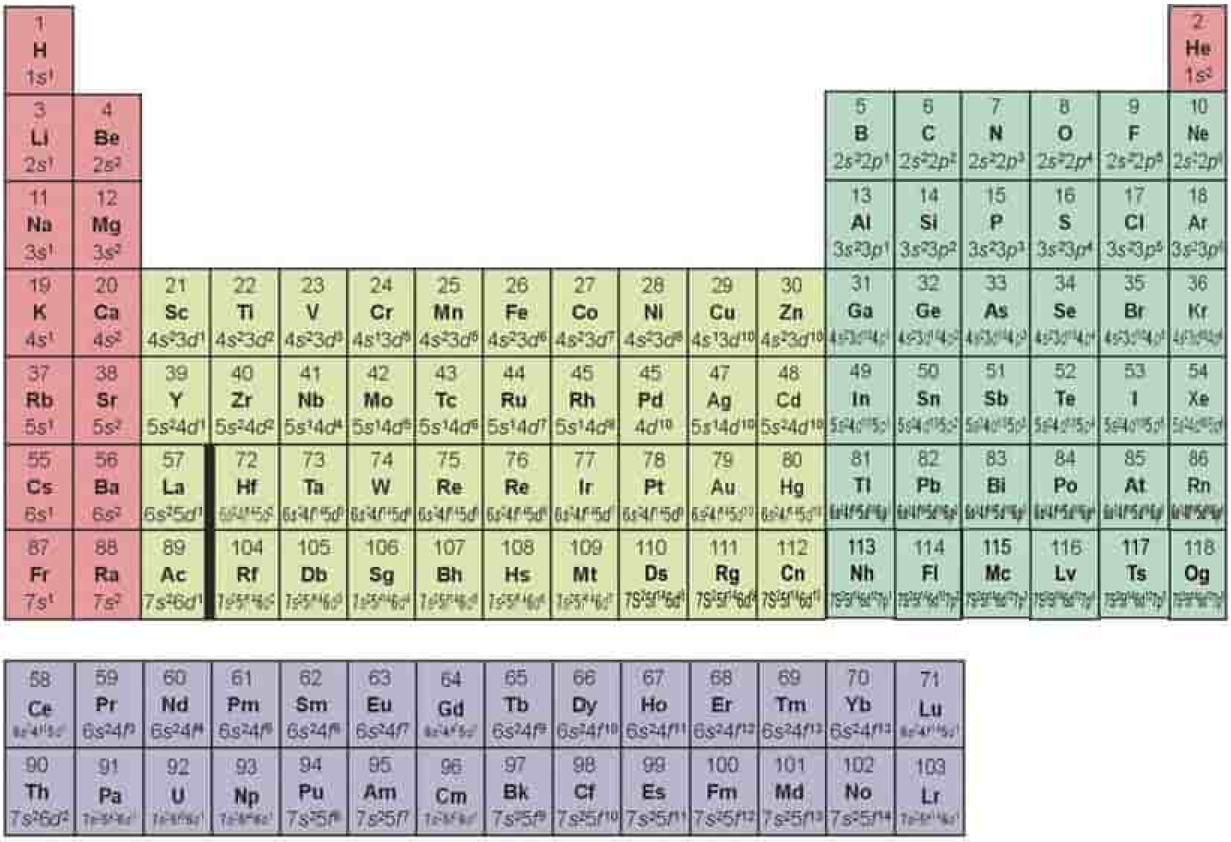
Quick Check 2.5

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** [illegible]	32 **Ge** [illegible]	33 **As** [illegible]	34 **Se** [illegible]	35 **Br** [illegible]	36 **Kr** [illegible]
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** [illegible]	50 **Sn** [illegible]	51 **Sb** [illegible]	52 **Te** [illegible]	53 **I** [illegible]	54 **Xe** [illegible]
55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La** $6s^2 5d^1$	72 **Hf** [illegible]	73 **Ta** [illegible]	74 **W** [illegible]	75 **Re** [illegible]	76 **Re** [illegible]	77 **Ir** [illegible]	78 **Pt** [illegible]	79 **Au** [illegible]	80 **Hg** [illegible]	81 **Tl** [illegible]	82 **Pb** [illegible]	83 **Bi** [illegible]	84 **Po** [illegible]	85 **At** [illegible]	86 **Rn** [illegible]
87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac** $7s^2 6d^1$	104 **Rf** [illegible]	105 **Db** [illegible]	106 **Sg** [illegible]	107 **Bh** [illegible]	108 **Hs** [illegible]	109 **Mt** [illegible]	110 **Ds** [illegible]	111 **Rg** [illegible]	112 **Cn** [illegible]	113 **Nh** [illegible]	114 **Fl** [illegible]	115 **Mc** [illegible]	116 **Lv** [illegible]	117 **Ts** [illegible]	118 **Og** [illegible]

58 **Ce** [illegible]	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** [illegible]	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** [illegible]
90 **Th** $7s^2 6d^2$	91 **Pa** [illegible]	92 **U** [illegible]	93 **Np** [illegible]	94 **Pu** $7s^2 5f^6$	95 **Am** $7s^2 5f^7$	96 **Cm** [illegible]	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** [illegible]

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.

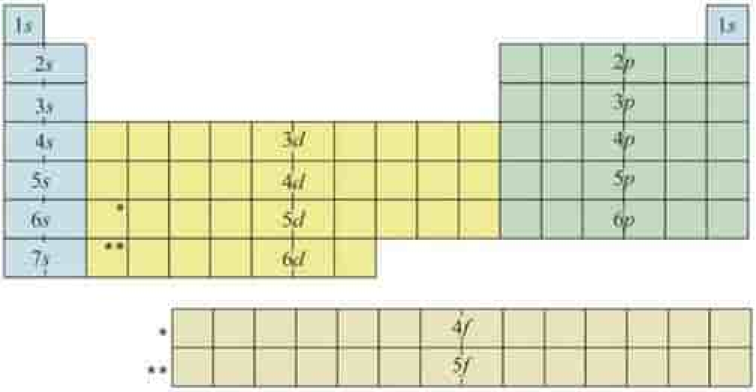


Figure 2.16 Modern periodic table showing s, p, d and f-block elements.

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

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1 \text{ belong to?}$$

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 $:\underset{\cdot\cdot}{\overset{\cdot}{C\ell}}:$. 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 $Cl^{\cdot}$. Apart from single atoms, groups of atoms can also be free radicals. For example, $OH^{\cdot}$, $CH_3^{\cdot}$, etc.

Quick Check 2.7

Write electronic configurations for the following ions and free radicals:

i. $Al^{\cdot}$ ($Z = 13$) **ii.** O^{2-} ($Z = 8$) **iii.** Fe3+ ($Z = 26$) **iv.** Cu^{2+} ($Z = 29$) **v.** $Cu^{\cdot}$ ($Z = 29$)

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.

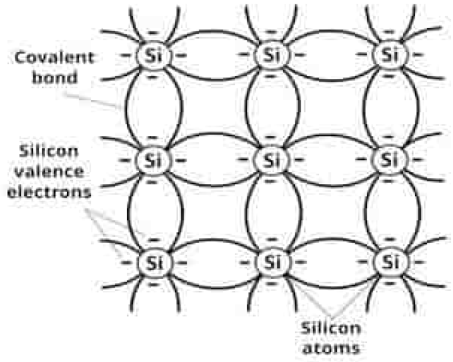


Figure 2.17 A crystal of pure silicon

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.

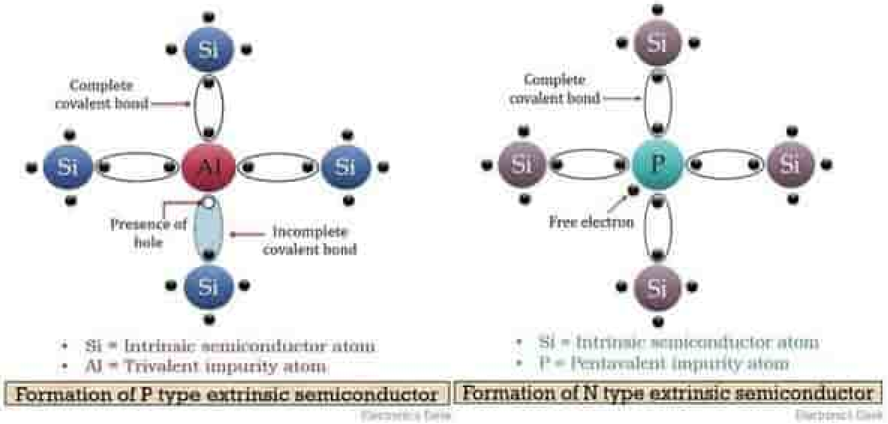


Figure 2.18 Dpoing and the formation of P-type and N-type semiconductor

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) $n = l, l = 2$

c) $n = l, l = 0$

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 intermolecular 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.

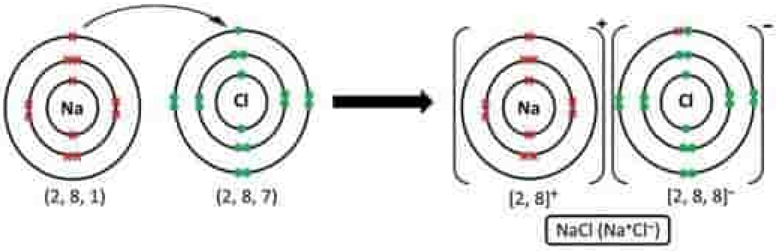


Figure 3.1: Ionic bond formation between Na and Cl

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.

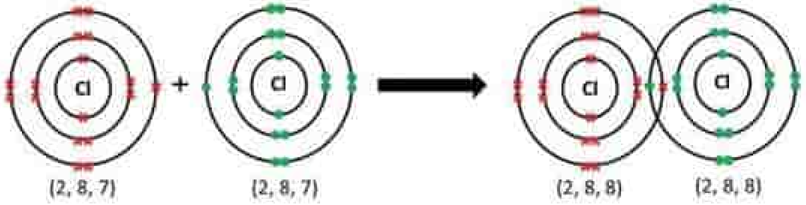


Figure 3.2: formation of a covalent bond between two Cl atoms

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)).

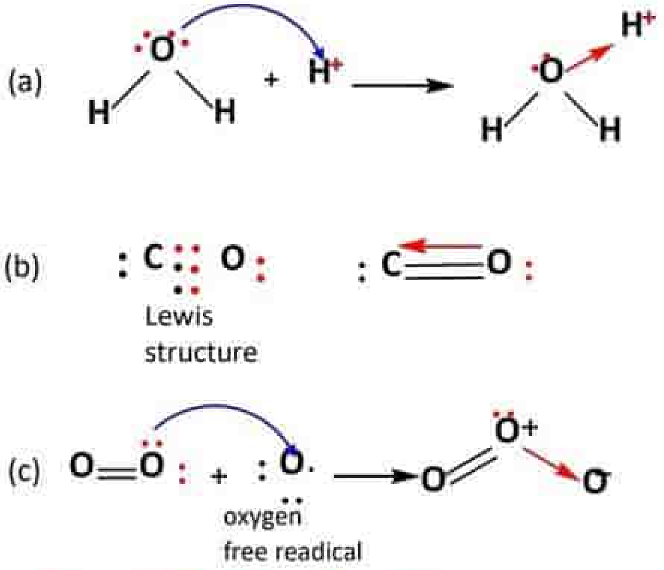


Figure 3.3: Dative bond formation (a) oxonium (hydronium) ion, (b) ozone molecule (c) carbon monoxide

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

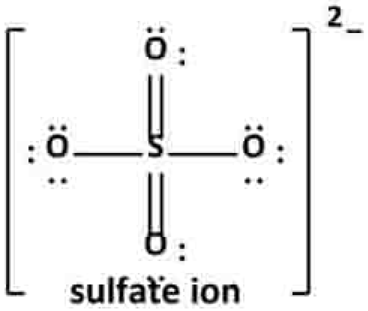
a) Draw the Lewis structures of N_2 and CS_2 molecules?

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-}.


sulfate ion

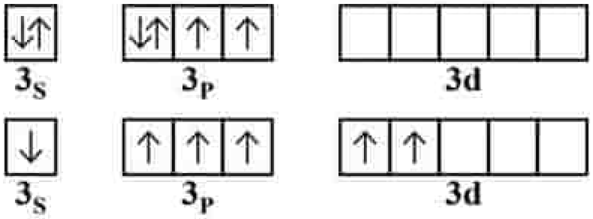
From the Lewis structures of SO_4^{2-}, we can calculate the number of electrons around the central S atom.

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

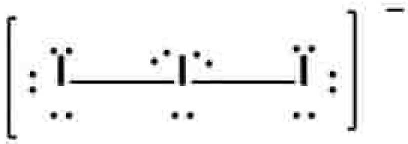
No of valence electrons = 2 × (double bond electrons) + 2 × (single bond electrons)

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

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.

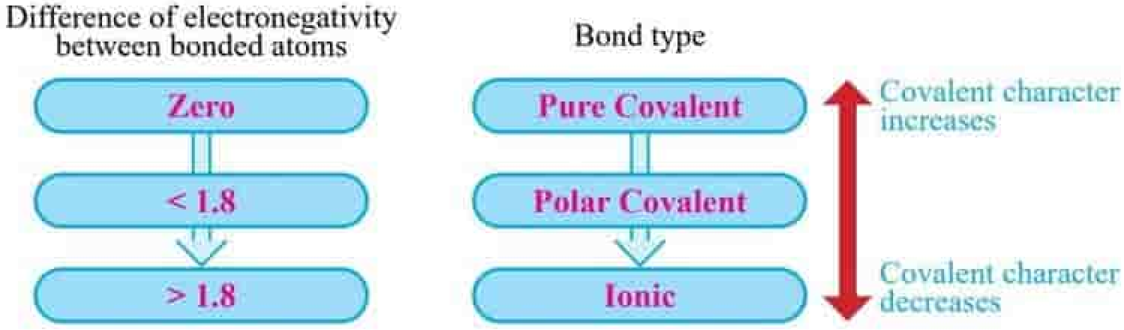
Quick Check 3.2

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.

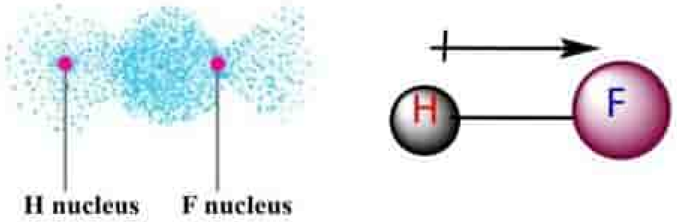
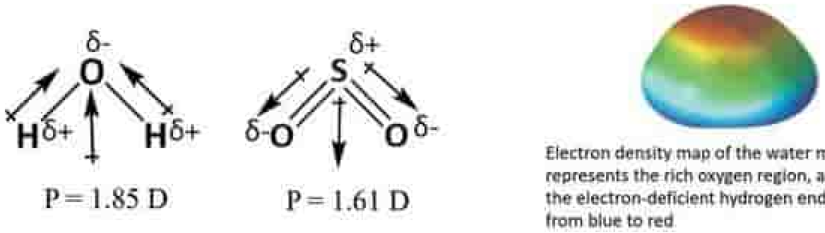


Figure 3.5: Electron density in HF is higher near the F atom and the dipole moment is directed from H to F

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.

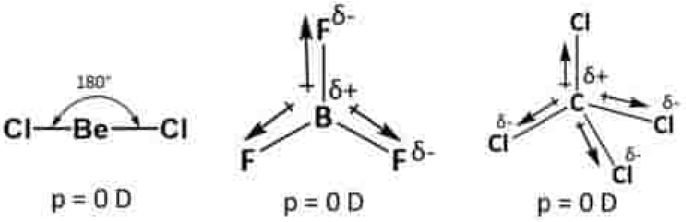


Figure 3.7: The individual bond moments in symmetrical molecules; $BeCl_2$, BF_3 and CH_4 are cancelled out to give zero net dipole moment.

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.

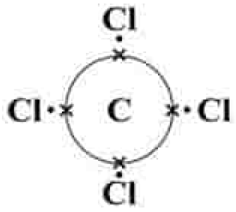
Table 3.1: Geometries and shapes of different systems of covalently bonded compounds

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 180° 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.

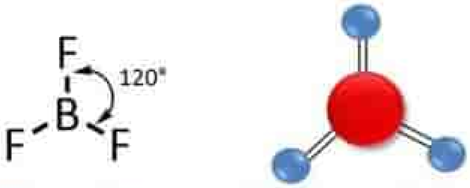


Figure 3.10: BF_3 is an AB_3 system having triangular planar geometry

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**.

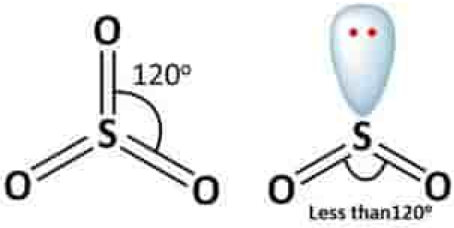


Figure 3.12: Shapes of multiply bonded SO_2 and SO_3

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.

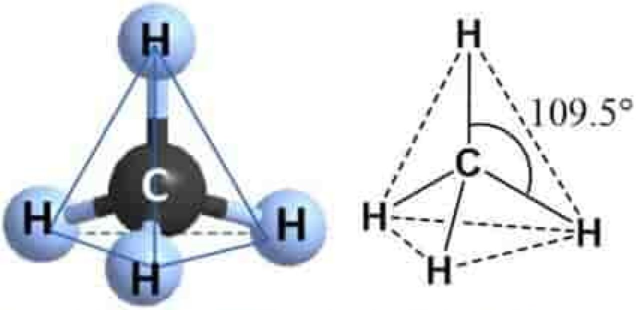


Figure 3.13: Regular tetrahedral shape of the CH_4 molecule

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.

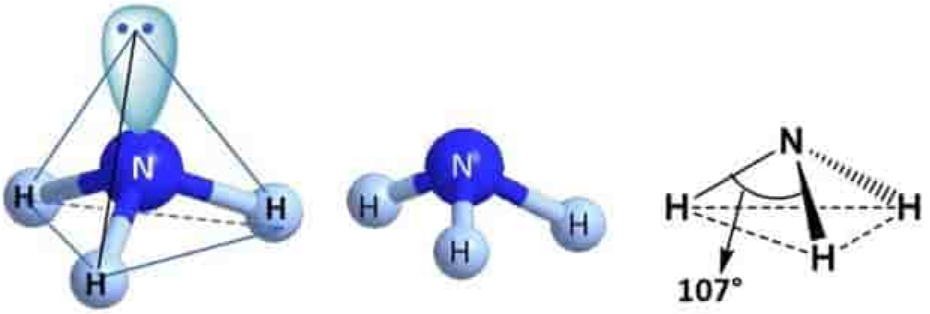
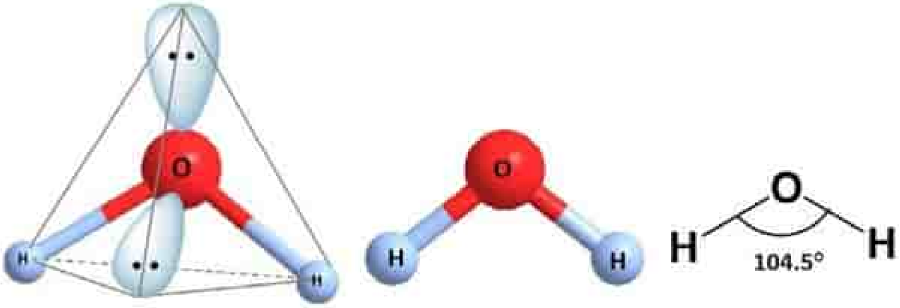


Figure 3.14: Distorted geometry and pyramidal shape of the NH_3 molecule

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).**

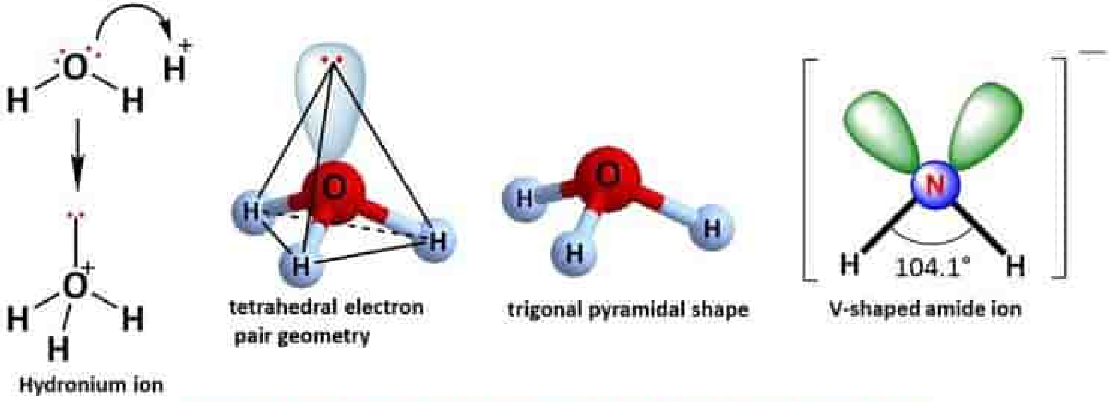


Figure 3.16: Shapes of hydronium (H_3O^+) and amide ions (NH_2^-)

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°.

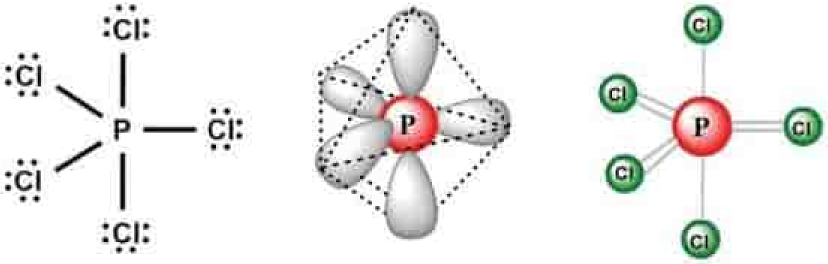


Figure 3.17 Lewis structure and shape of PCl_5 molecule

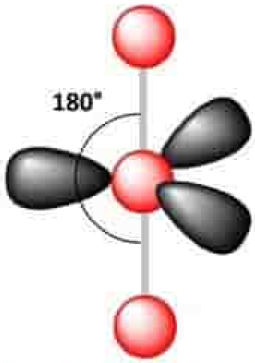


Figure 3.18: Shape of tri-iodide ion ($[I_3]^-$)

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.

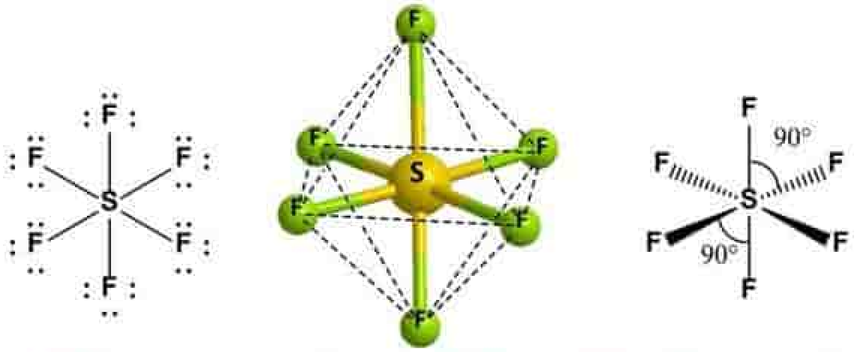


Figure 3.19: Lewis structure and octahedral shape of SF_6 with each angle of 90°

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°.

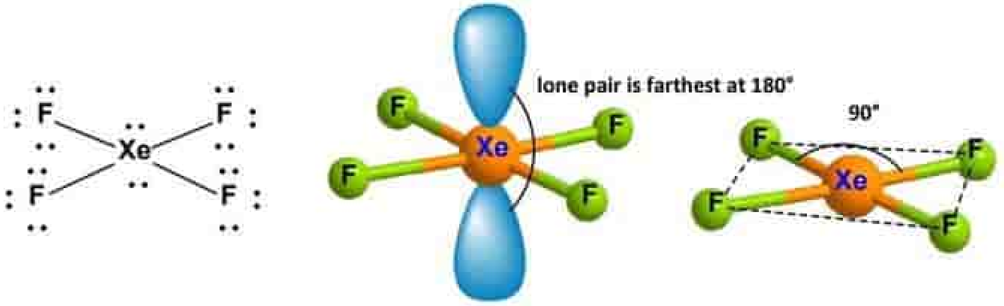


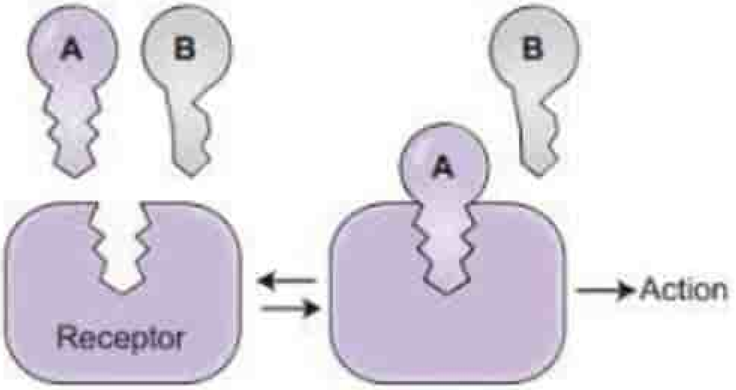
Figure 3.20: Lewis structure and square planar shape of XeF_4

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

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.



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

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.

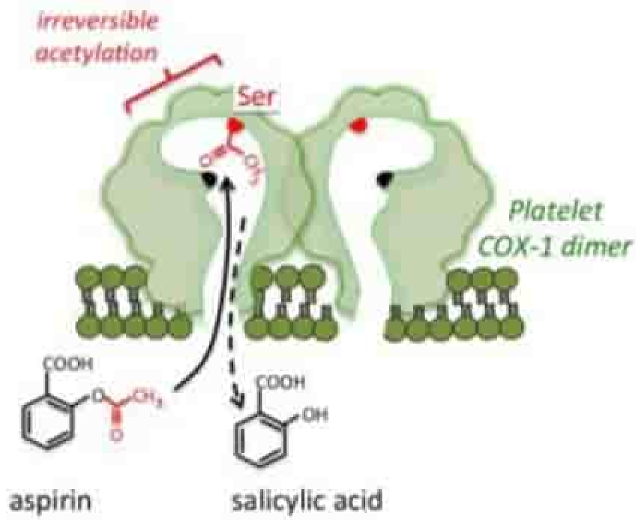


Figure 3.21: An interaction of Aspirin with COX (Published after permission from Tulane University Press)

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.**

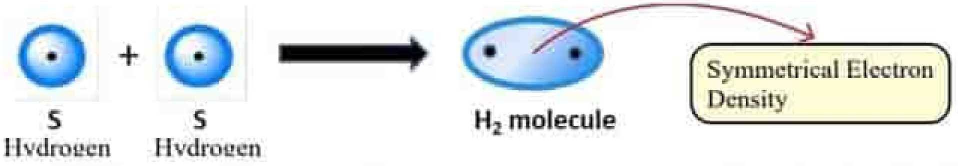


Figure 3.22: Overlap between s orbitals of two hydrogen atoms to form the H_2 molecule

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.

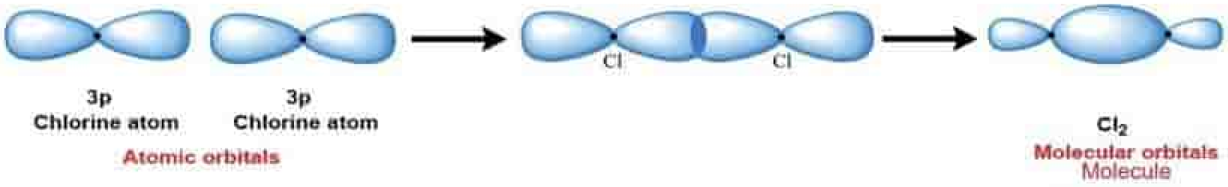


Figure 3.24: Overlap of p and p orbitals to form Cl_2 molecule according to VBT

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.

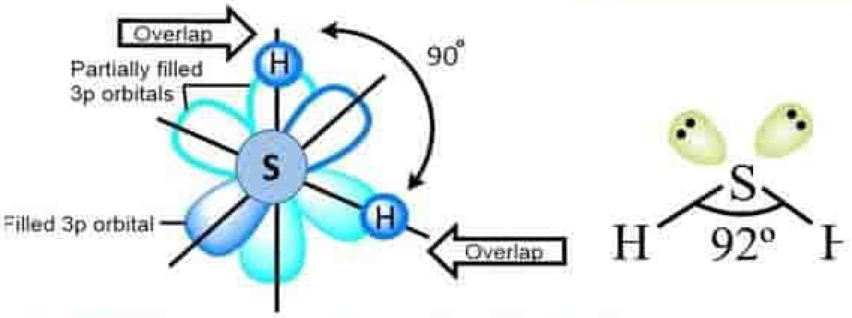


Fig. 3.25: The formation of H_2S molecule by H and S orbitals overlap

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**.

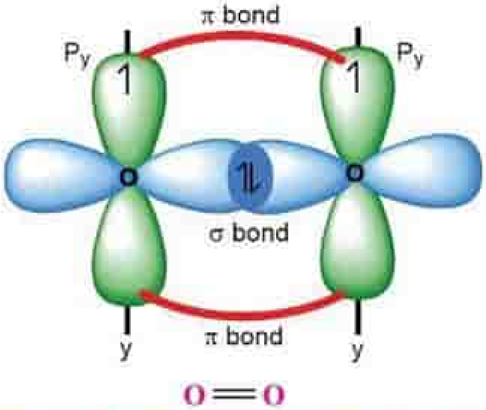


Figure 3.26: Formation of double bond (σ and π) between oxygen atoms

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

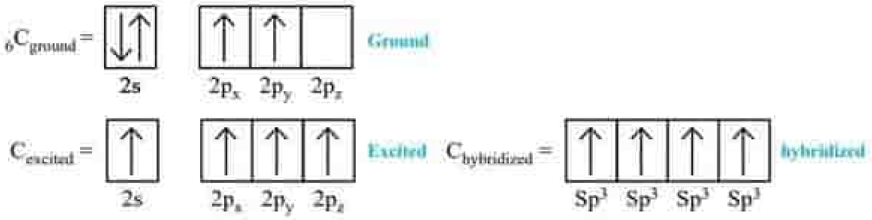
- Hybridization is a process of mixing of orbitals in a single atom (or ion).
- Only orbitals of comparable (relatively close) energies can be mixed to form hybrid orbitals.
- The number of mixing orbitals is always equal to the number of the resulting hybrid orbitals.

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.

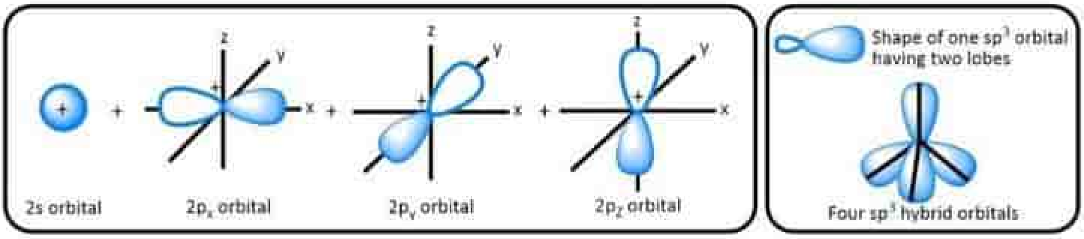


Figure 3.27: Formation of sp_3 hybrid orbitals of C in methane

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°.

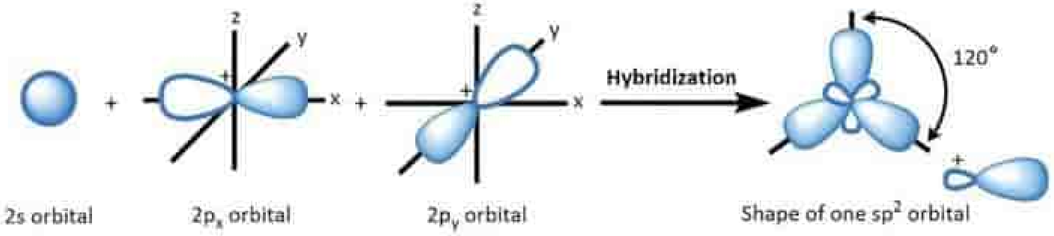
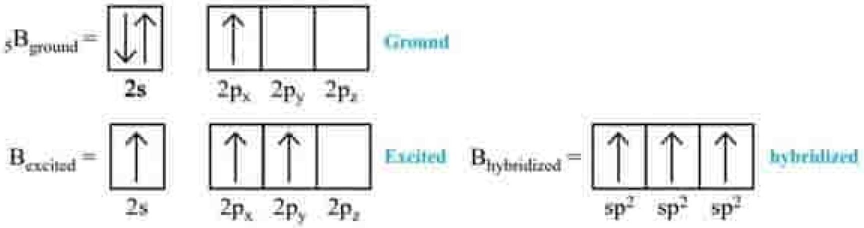


Figure 3.29: Formation of sp^2 hybrid orbitals from atomic orbitals

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.

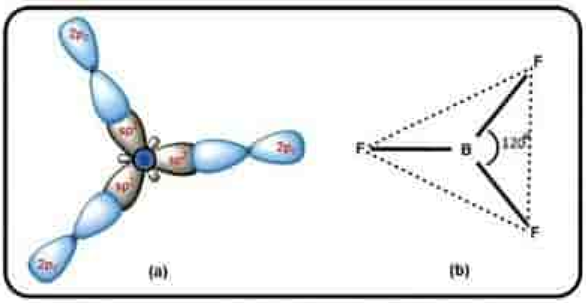
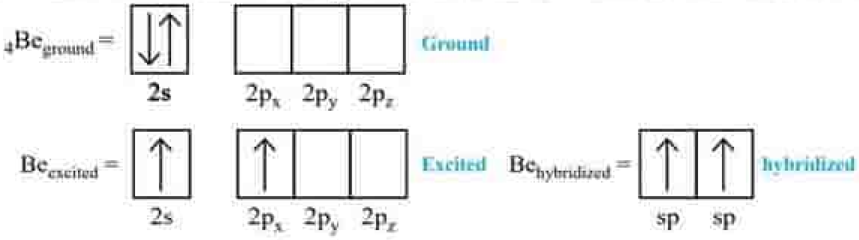


Figure 3.30: Formation of BF_3 molecule through sp^2-p overlap

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.

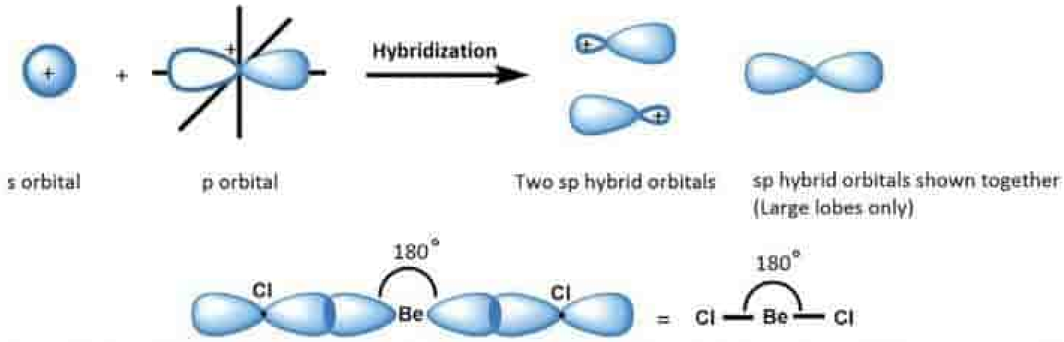


Figure 3.32: Mixing of s and p orbitals to give two hybrid sp orbitals and the formation of $BeCl_2$

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**.

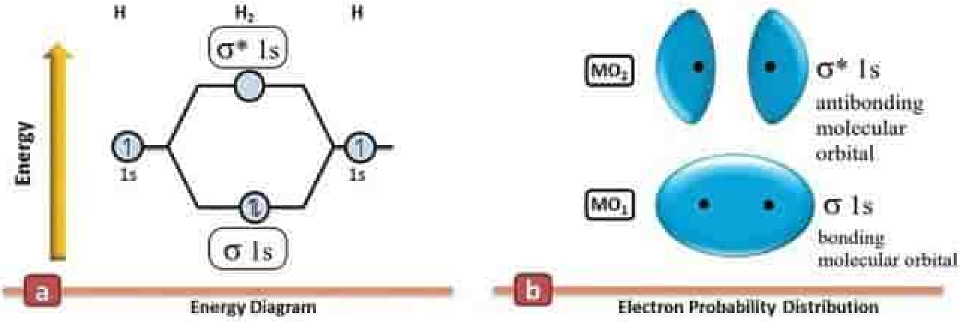


Figure 3.34: Formation of bonding and anti-bonding orbitals for the H_2 molecule

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

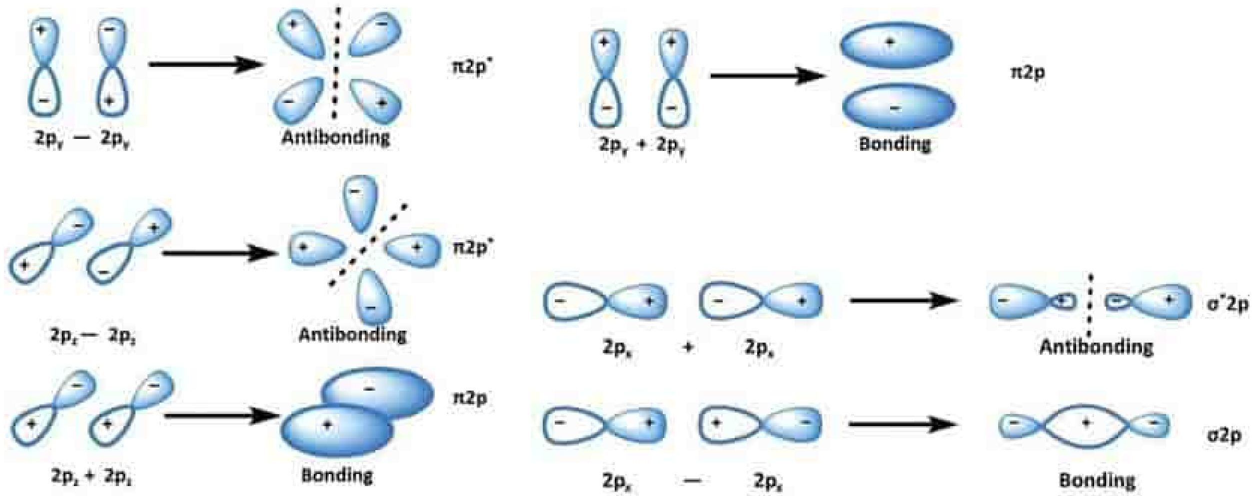


Figure 3.35: Formation of **δ and** π MOs from p_x, p_y and p_z orbitals

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.

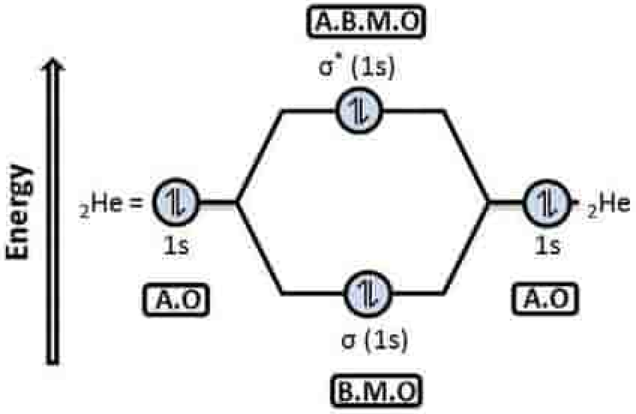


Figure 3.36: Molecular orbital diagram of He_2 molecule

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

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:

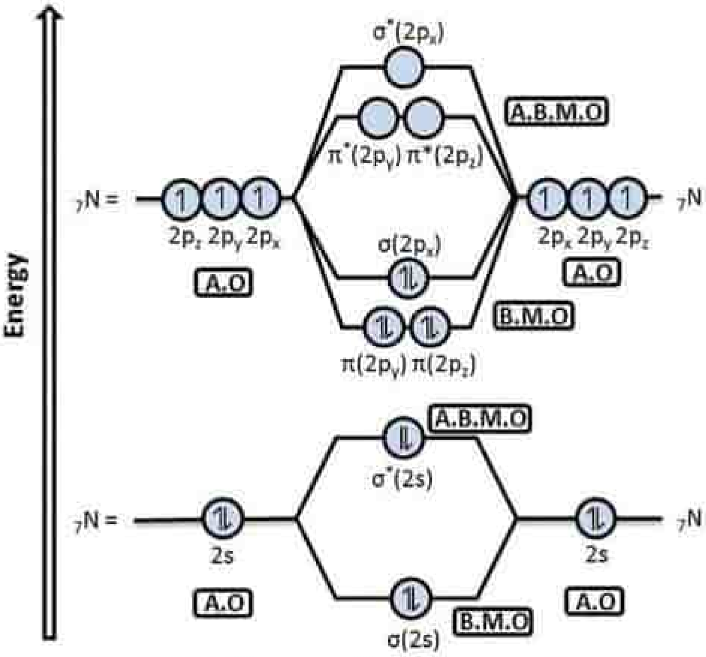


Fig 3.37: Molecular orbital diagram of N_2 molecule

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

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.

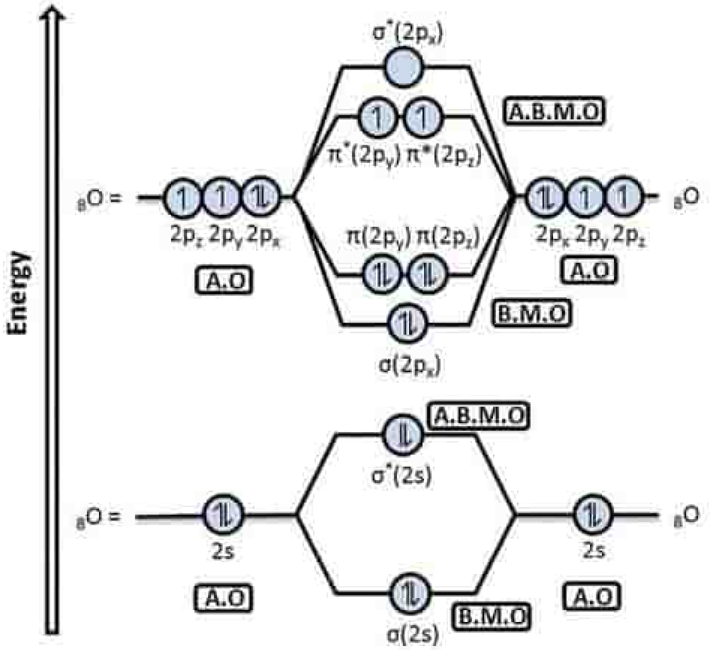


Figure 3.38: Molecular orbital diagram of O_2 molecule

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≡C	839
H-Cl	427	C-N	305	Br-Br	193	O=O	495
H-Br	363	C-O	358	I-I	149	C=O	745
H-I	295	N-H	391	S-S	266	N≡N	941
C-H	413	N-O	201	Si-Si	340	C≡N	615
C-C	347	O-H	467	Si-O	452	N=O	607

Let us consider the role played by electronegativity difference. Look at the bond energies of H-X type of compounds, where X=F, Cl, Br, I. The data show that the bond energy of a bond rises with the increasing electronegativity difference between the bonded atoms. As the difference in electronegativity increases, the bond polarity also becomes greater and this gives rise to additional attractive force for binding the atoms. This is why the bond energy for HF is higher (565 kJ mol^{-1}) than for HI (295 kJ mol^{-1}). It may be noted that energies of multiple bonds are greater than those of single bonds

$$C \equiv C > C{=}C > C{-}C$$

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≡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≡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:

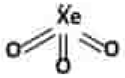
(i) Dipole (ii) Bond order (iii) Permanent dipole- permanent dipole force

(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:

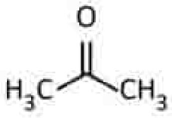


i. By counting electron pairs around the central atom, explain why xenon trioxide has this shape.

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.

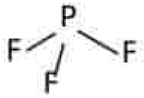
ii. Can propanone make a hydrogen bond with water when both are intermixed?

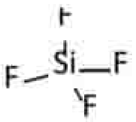
f. Predict the shapes of sulfate ($[SO_4]^{2-}$, borate ($[BH_4]^-$) and tri-iodide ions ($[I_3]^-$) according to the VSEPR model.

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., 6.02×10^{23}.
It is interesting to know that different masses of elements have the same number of atoms.

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

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

Sample Problem 4.1

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Calculate the mass of 0.5 moles of HCl.

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= 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 $MgSO_4 = 24 + 96 = 120$ g mol^{-1}

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

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

Quick Check 4.1

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b. Calculate the number of moles in 0.23 g of sodium.
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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., 6.02×10^{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 = 6.02×10^{23} atoms of H

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

238.0 g of uranium = 1 mol of U = 6.02×10^{23} atoms of U

An atom of sodium is 23 times heavier than an atom of hydrogen. In order to have equal number of atoms, sodium should be taken 23 times greater in mass than hydrogen.

18.0 g of H_2O = 1 mol of water = 6.02×10^{23} molecules of water

180.0 g of glucose = 1 mol of glucose = 6.02×10^{23} molecules of glucose

Hence, one mole of different compounds has different masses but the same number of molecules.

Similarly, the number of ions in one mole of different ionic species is always the same, i.e Avogadro's number.

96.1 g of SO_4^{2-} = 1 mole of SO_4^{2-} = 6.02×10^{23} ions of SO_4^{2-}

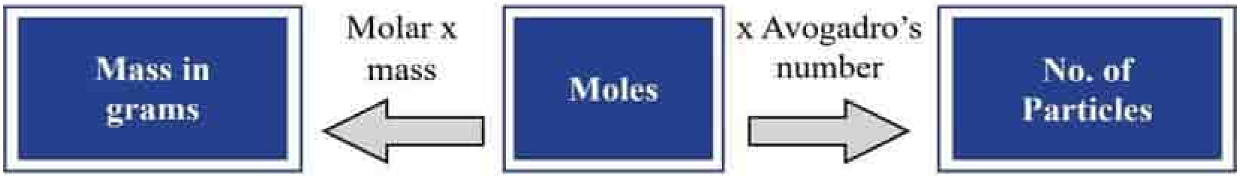
62.0 g of NO_3^{1-} = 1 mole of NO_3^{1-} = 6.02×10^{23} ions of NO_3^{1-}

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

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

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 3.76×10^{24} molecules of glucose. What is the number of moles in this quantity?

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

$= 6.25$ moles

Sample Problem 4.5

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

Solution:

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

Number of atoms of sodium = Number of moles of sodium x N_A

$= 0.1 \times 6.02 \times 10^{23}$

$= 0.602 \times 10^{23}$ atoms

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) Moles of juglone = $\dfrac{\text{Mass}}{\text{Molar Mass}} = \dfrac{0.87\text{ g}}{174\text{ g mol}^{-1}} = 0.005$ 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 1×10^{-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 =$6.02 \text{ x } 10^{23}$ particles of a gas= 1 mole of a gas

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

$$\text{Volume of a gas} = \text{Number of moles x Molar volume}$$

$$\mathbf{V = n \text{ x } V_m}$$

Sample Problem 4.7

Determine the volume of 2.5 moles of chlorine molecules at STP.

Solution:

The formula for volume determination at STP

$$V= n \text{ x } V_m$$

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

$$V= n \text{ x } V_m$$

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.

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

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

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

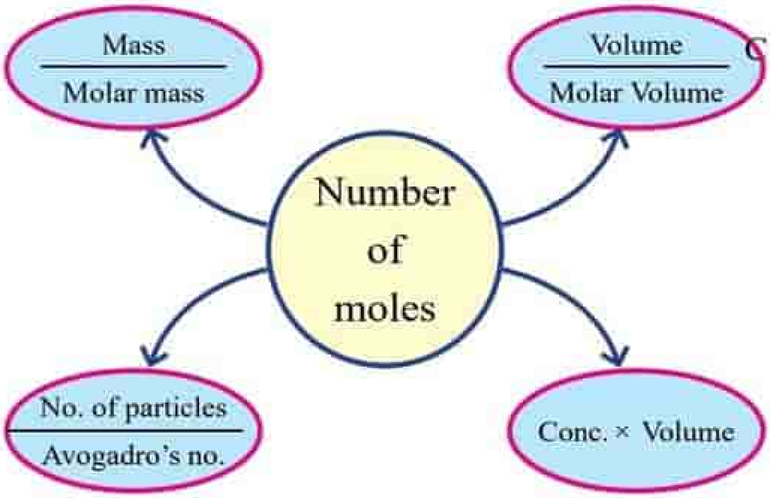
$$\mathbf{n = C \times V}$$

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

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

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

$$= 0.02 \text{ mol}$$

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 $Fe_2O_3 = 2 \times 0.02 = 0.04$ mol

Mass of Aℓ $= n \times M$

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

$$= 1.08 \text{ g}$$

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 $= \frac{2}{3} \text{ x } 100 = 66.7\ dm^3$

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 $NaHCO_3 = \dfrac{2.1\ g}{84.0\ g\ mol^{-1}} = 0.025$ 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) $= \dfrac{m}{M}$

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

$= 0.125$ mol

From the balanced equation, 1 mol of iron produces 1 mole of hydrogen.

So, number of moles of $H_2 = 0.125$ mol

Volume of H_2 in dm^3 = molar volume x moles of H_2

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

$= 2.8\ dm^3$

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 mol x 17.0 g mol^{-1}

= 9.0 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} × 1.25 dm^3 = 0.0625 mol

Thus, 0.025 mol dm^{-3} Na_2SO_4 solution contains 0.025 mol dm^{-3} SO_4^{-2} ions.

moles of SO_4^{-2} ions = 0.025 mol dm^{-3} × 2.00 dm^3 = 0.05 mol

As Pb^{2+} and SO_4^{-2} react in a 1 : 1 ratio, here, SO_4^{2-} (0.05 mol) will be consumed earlier than Pb^{2+} (0.0625 mol). The amount of SO_4^{-2} will be limiting. The reason is that 0.05 mole of SO_4^{-2} is less than 0.0625 mole of Pb^{2+}. Since the Pb^{2+} ions are present in excess, only 0.05 mole of solid $PbSO_4$ will be formed. The mass of $PbSO_4$ formed can be calculated using the molar mass of $PbSO_4$ (303.3 g mol^{-1}):

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

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 $CO_2 = 1\text{mol}$

1.875 mole of methane produces $CO_2 = 1 \times 1.875$ 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.

$$CaCO_3 \xrightarrow{} CaO + CO_2$$

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 H_2 and 1 mole of NH_3 at 0 ^oC 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.

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

According to Charles' law

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

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

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

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}.

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

$$PV = nRT \quad \ldots\ldots\ldots (4)$$

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

$$PV = \frac{mRT}{M} \quad \ldots\ldots\ldots (5)$$

Now rearranging equation (5)

$$M = \frac{mRT}{PV} \quad \ldots\ldots (6)$$

At molecular level, the molar mass becomes relative molecular mass of a compound, therefore, we can write

$$M_r = \frac{mRT}{PV} \quad \ldots\ldots\ldots (7)$$

Sample Problem 5.1

The volume of 134 g of a gas at -73 °C under 10 atm pressure is 5 dm^3. Determine the relative molecular mass of the gas.

Solution: The molecular mass of the gas can be calculated by using the formula:

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

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

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

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

Quick Check 5.1

a) Explain why gases can be compressed easily?

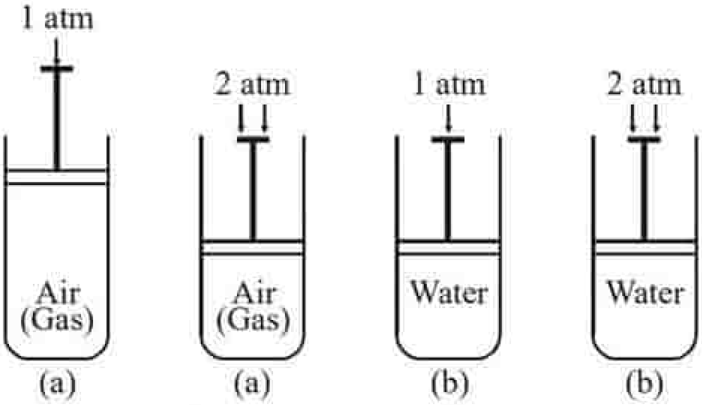
b) What is Joule-Thomson effect

c) The volume of 21g a gas is 8 dm^3 at -90 °C 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.



(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.

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.

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

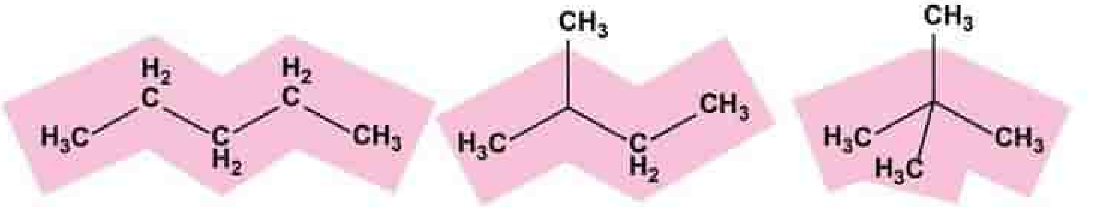
ii. Surface area (shape of molecule)

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.

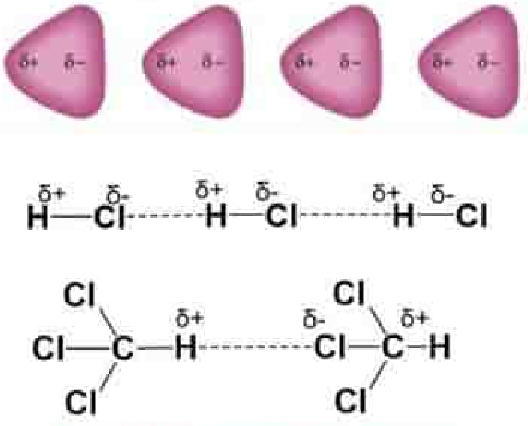


Figure 5.3 Permanent dipole-permanent dipole forces in HCl and chloroform

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.

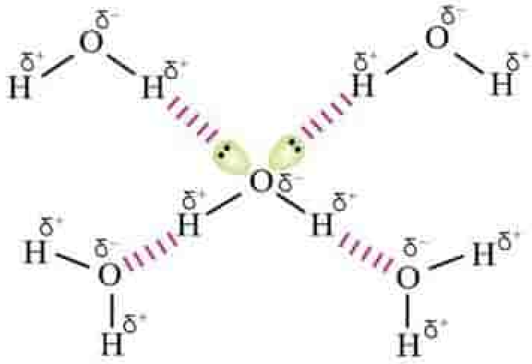


Figure 5.4 Hydrogen bonding in water

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**).

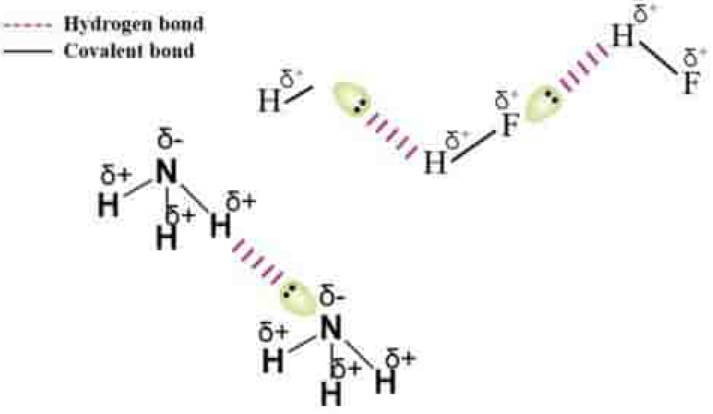


Figure 5.5: Hydrogen bonding in NH_3 and HF

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.

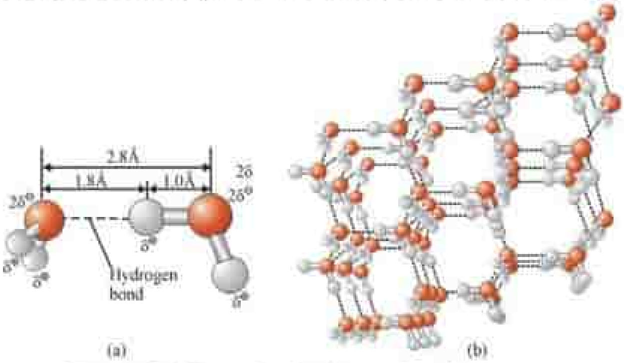


Figure 5.6: Extensive hydrogen bonding in ice and spaces among molecules

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.

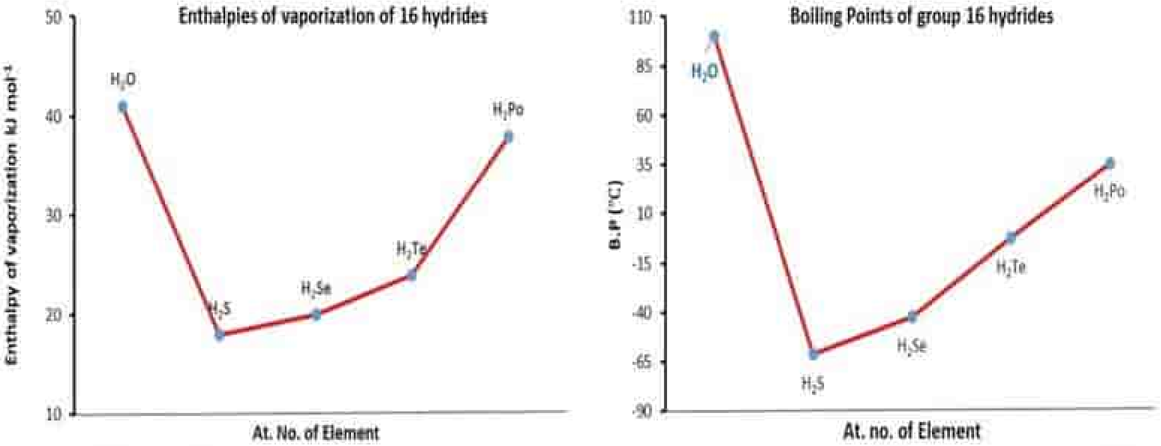


Figure 5.7: A graphical expression of variation in enthalpy of vaporization and B.Ps of group 16 hydrides

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

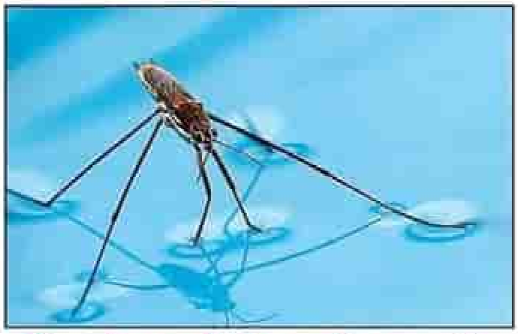
ii. $CH_3CH_2CH_2CH_4$ (0 °C) and $CH_3CH_2CH_2OH$ (97 °C), difference = 97 °C

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.

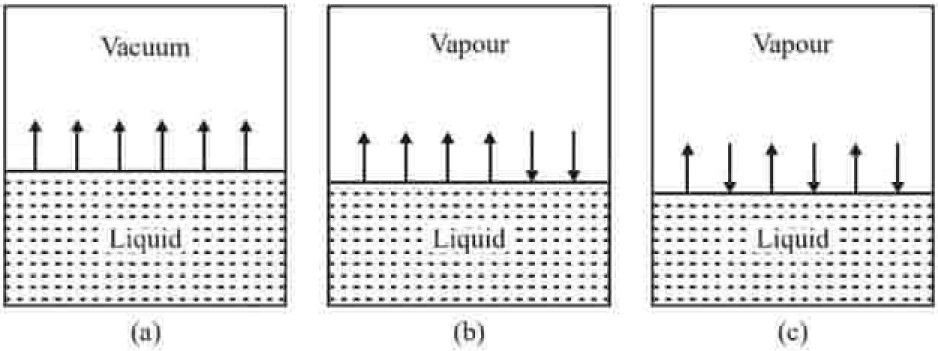


Figure. 5.8 Attainment of equilibrium when the evaporation of liquid is carried out in an evacuated closed vessel. (a) Initial state, with evacuated space above the liquid, (b) intermediate state, and (c) equilibrium state, when the rate of evaporation is equal to the rate of condensation.

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

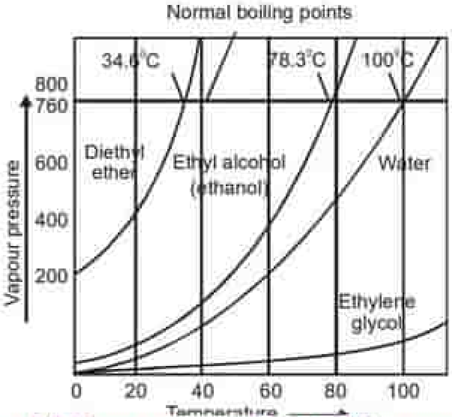


Figure 5.9 Vapour pressures (torr) of four common liquids shown as a function of temperature.

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 69°C 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 100°C, 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 ^{0}C, its density decreases due to:

a) cubic structure of ice
b) empty spaces present in the structure of ice
c) decrease in volume
d) decrease in viscosity

IV. Which of 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 4^0C 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} m³ 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 cm³ 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.

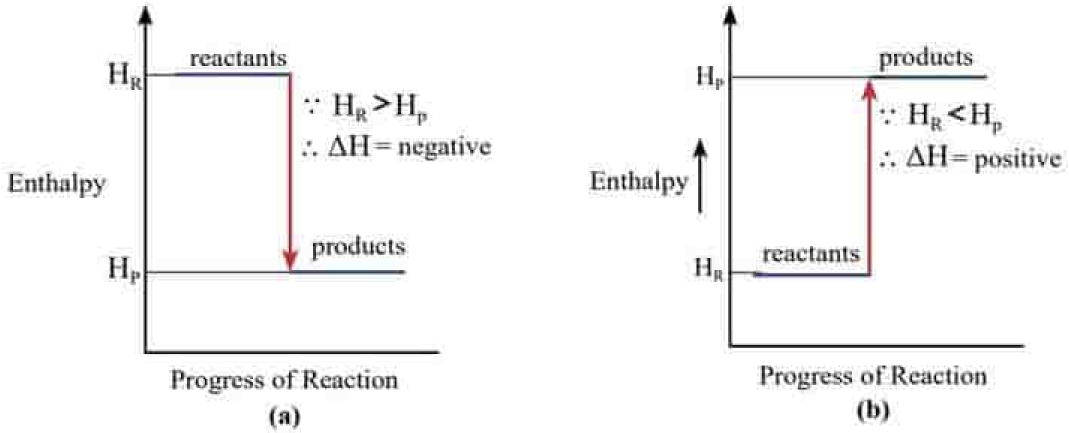


Figure 6.1: Enthalpy diagram of (a) Exothermic Reaction and (b) Endothermic Reaction

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.

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

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**.

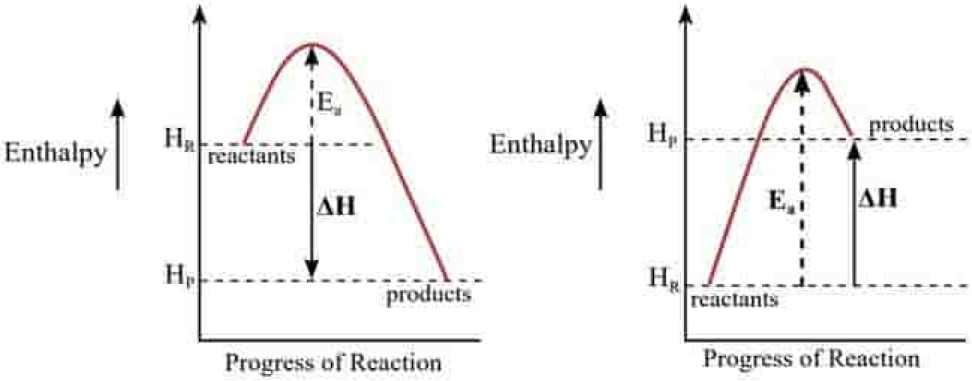


Figure 6.2 Energy profile diagram in terms of ΔH and E_a

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:

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

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 $-1368\ kJ\ mol^{-1}$.

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

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:

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

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) $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)}$

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

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 ($\Delta H = +ve$) while bond formation releases it ($\Delta H = -ve$) and their difference will decide the overall sign of ΔH. That is whether a reaction is exothermic or endothermic is determined by the net change.

Overall reaction is exothermic if the energy released in making of new bonds is greater than that absorbed in bond breaking. The reverse is true for an endothermic reaction.

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,

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

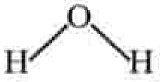
Sample Problem 6.1

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

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

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

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 $J\ g^{-1}\ {}^{\circ}C^{-1}$).

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

$\mathbf{\Delta T}$ 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.

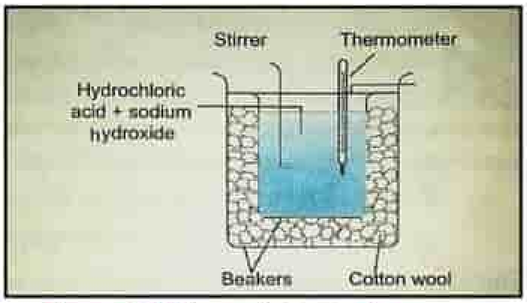


Figure 6.3 Glass calorimeter to measure enthalpy change of reactions

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 ≈ 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.

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

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

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

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

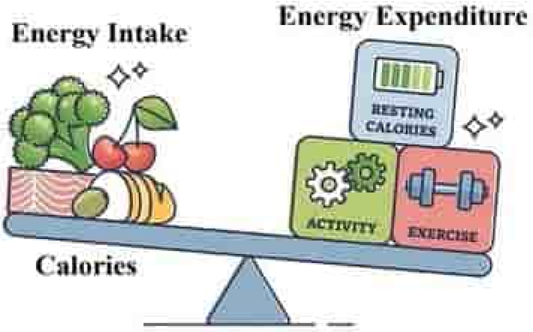
Using the relation,

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

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

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

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.

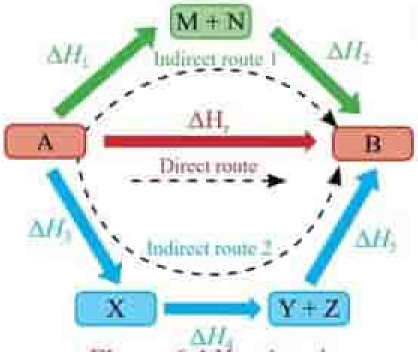


Figure 6.4 Hess' cycle

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.

$$C(\text{graphite}) + O_{2(g)} \longrightarrow CO_{2(g)} \quad \mathbf{\Delta H} = -393.5 \text{ kJ mol}^{-1}$$
$$CO_{(g)} + \tfrac{1}{2} O_{2(g)} \longrightarrow CO_{2(g)} \quad \mathbf{\Delta H_2} = -283 \text{ kJ mol}^{-1}$$
$$C(\text{graphite}) + \tfrac{1}{2} O_{2(g)} \qquad CO_{(g)} \quad \mathbf{\Delta H_1} = ?$$

Solution: Applying Hess' law, we can write

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

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

$= -393.5 - (-283)$

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

$$\begin{tikzcd} C + O_2 \arrow[rr, "\Delta H"] \arrow[rr, bend left] \arrow[dr, "\Delta H_1"] \arrow[rr, bend right=80] & & CO_2 \\ & C + O_2 \arrow[ur, "\Delta H_2"] & \end{tikzcd}$$

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.

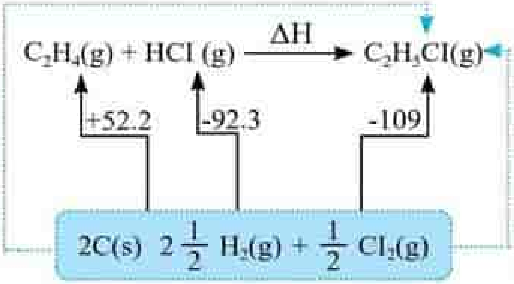
ΔH^o_f of $C_2H_4 = +52.2$ KJ mol^{-1}

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:

$$\Delta H_r = [3 \times \Delta H^o_f(CO_2) + 4 \times \Delta H^o_f(H_2O)] - [1 \times \Delta H^o_c(C_3H_8) + 5 \times \Delta H^o_c(O_2)]$$

$$-2044\ kJ = [3\times(-393.51) + 4\times(-241.82)] - [1 \times \Delta H^o_f(C_3H_8) + 5\times(0)]$$

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,

$$\Delta H^o_f(C_3H_8) = -104\ kJ\ mol^{-1}$$

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:

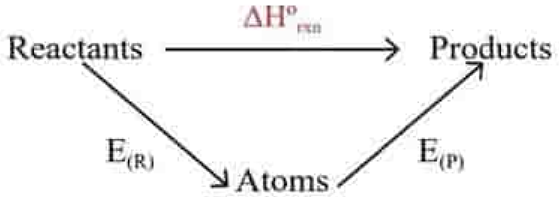


Figure 6.4 Hess Cycle; showing the relationship between B.E.'s and $\Delta H_r = \sum n\ E_R - \sum n\ E_P$

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:

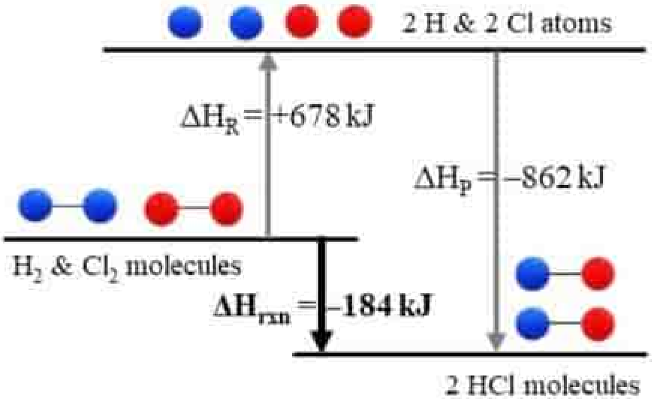
$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2\ H + 2\ Cl_{(g)}$$

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

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

$= 436\ kJ + 242\ kJ$

$= 478\ kJ$



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

Second Step:

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

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

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

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

$\Delta H^\circ_r = \sum E_R - \sum E_P$

$\Delta H^\circ_r = 678 - 862$

$\Delta H^\circ_r = -184\ kJ$ (for 2 mol of HCl)

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

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

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:

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

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:

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

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:

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

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

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

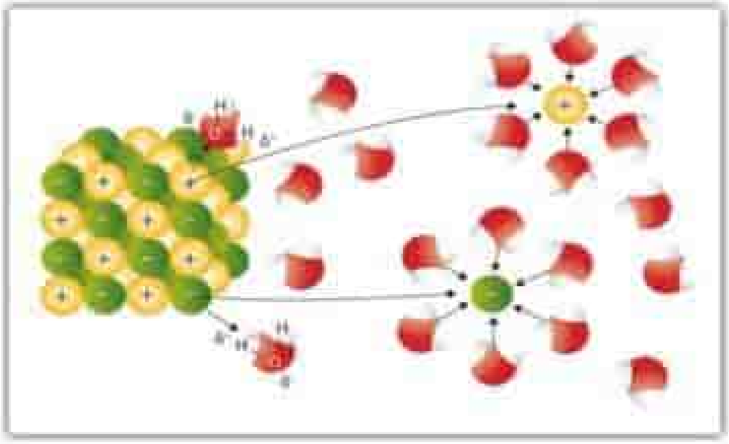


Figure 6.5 Dissolution of an ionic compound through the process of hydration.

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:

$Na^+ < Mg^{2+} < Al^{3+}$

$Mg^{2+} > Ca^{2+} > Sr^{2+}$

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."

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

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.

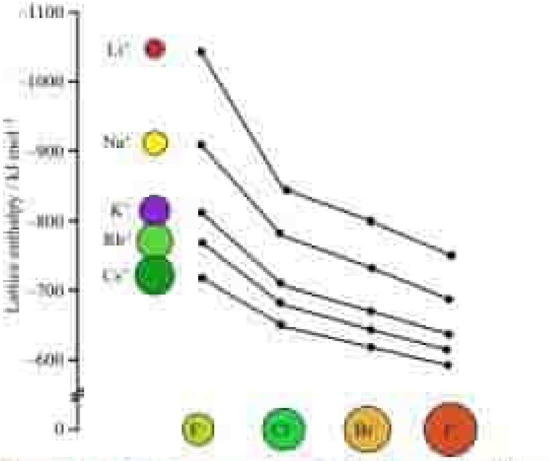


Figure 6.6 Lattice energies of alkali metal halides

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 $\Delta H_{latt\ [MgO]} = -3923\ kJ\ mol^{-1}$ is a greater than lithium fluoride $\Delta H_{latt\ [LiF]} = -1049\ kJ\ mol^{-1}$

The doubly-charged Mg^{2+} and O^{2-} ions in MgO attract each other more strongly than the singly-charged ions of the same size in LiF. For ions of similar size, the greater the ionic charge, the higher the charge density. This results in stronger ionic bonds being formed.

Solubility trends of Group II hydroxides and sulphates:

ΔH°_{sol} depends on both lattice energy and hydration enthalpy.

- Look at the solubility trends of group II metal hydroxides. Both hydration energy and lattice enthalpy decreases down the group due to decrease in charge density of group 2 cations. But it is observed that the lattice energy decreases more rapidly in the series $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ than does the energy of hydration in ions

Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}. For this reason, the lattice energy factor dominates this solubility trend. **ΔH°_{sol}** becomes more exothermic so solubility increase.

- 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 $BaSO_4$. **ΔH°_{sol}** becomes more endothermic so solubility increase.

6.9.3 Calculating Enthalpy Change of Solution (ΔH°_{sol})

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

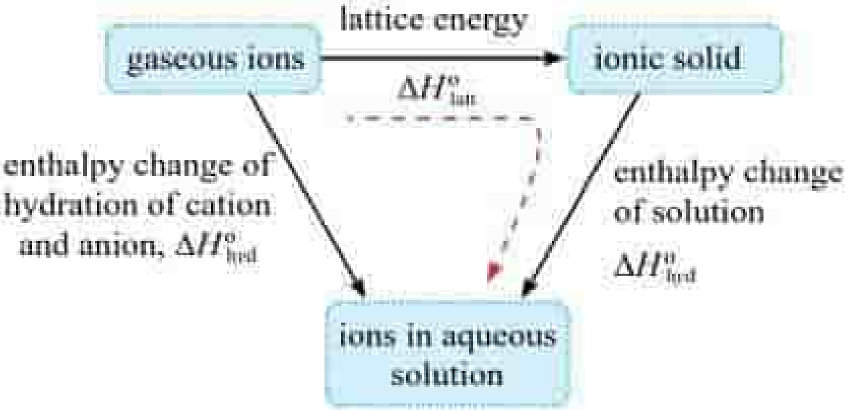


Figure 6.7 Energy cycle of formation of an aqueous solution of an ionic solid using Hess' law

We can see from this enthalpy cycle that:

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

We can use this energy cycle to calculate:

Sample problem 6.8

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

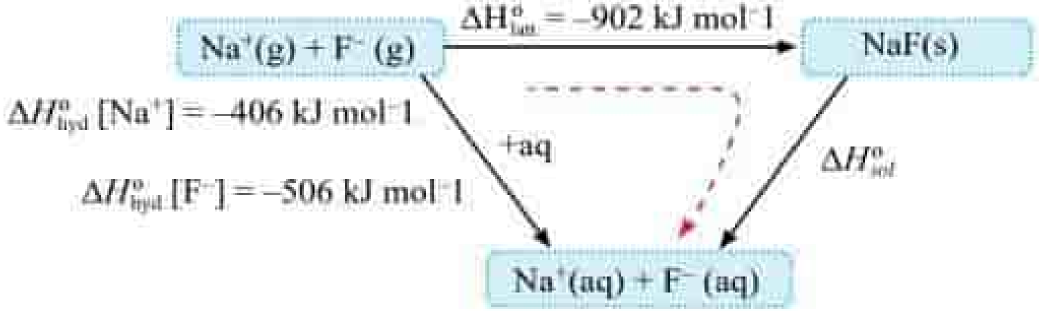
Lattice energy of sodium fluoride (NaF) = –902 kJ mol^{-1}

Heat of hydration of sodium ions (Na^+) = –406 kJ mol^{-1}

Heat of hydration of fluoride ions (F^-) = –506 kJ mol^{-1}

Solution:

Step 1: Draw the enthalpy cycle



Step 2: Rearrange the equation and substitute the values to find Δ

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

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

$$\Delta H^o_{hyd}\ [NaF] = -10\ kJ\ mol^{-1}$$

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.

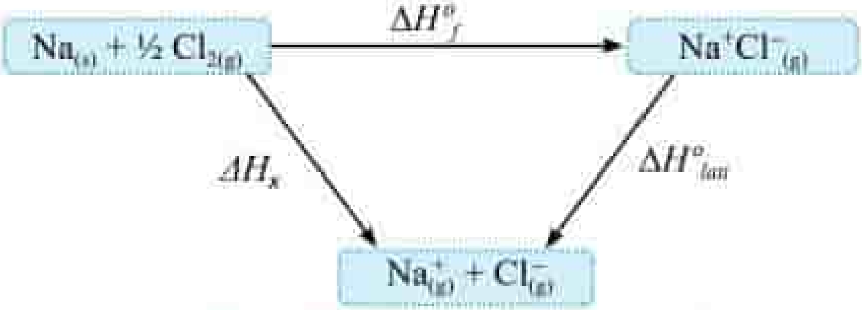


Figure 6.8 Enthalpy cycle of sodium chloride

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**.

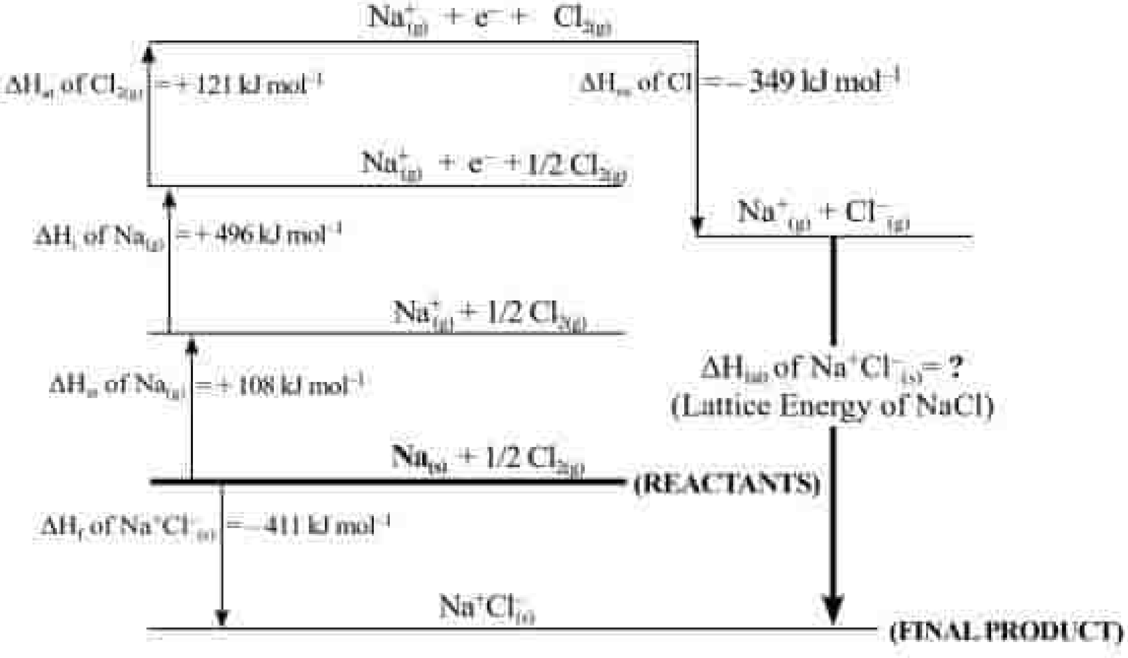


Figure 6.9 Born Haber cycle of sodium chloride (not according to scale)

Calculation of ΔH_x

From above cycle we have,

$$\Delta H_x = \Delta H_{at\,(Na)} + \Delta H_{I1\,(Na)} + \Delta H_{at\,(Cl2)} + \Delta H_{ea1\,(Cl2)}$$

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

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

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

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:

$$\Delta H^o_f = \Delta H^o_{latt} + \Delta H^o_{at\,(Na)} + \Delta H^o_{I1\,(Na)} + \Delta H^o_{at\,(F2)} + \Delta H^o_{1ea\,(F)}$$

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

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

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.

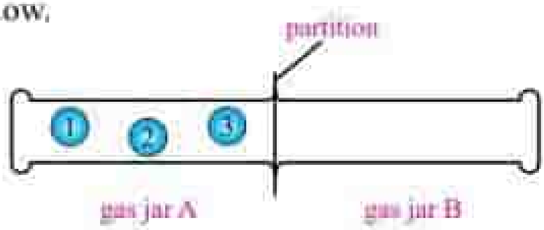


Figure 6.10 Diffusion and number of possible arrangements

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. $Br_{2(l)}$ 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. $Hg_{(l)}$ 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 $SO_{3(l)}$ 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:

$$\Delta S^{O}_{system} = S^{O}_{products} - S^{O}_{reactants}$$

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:

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

As $\Delta S^{O}_{system} = S^{O}_{products} - S^{O}_{reactants}$

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

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,

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

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

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:

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

Calculate $\Delta H°$, $\Delta S°$ and $\Delta G°$ at 25 °C using the following data; and discuss its spontaneity.

Heat of Formation:

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

Standard entropy:

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

Solution

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

$$\Delta S° = \sum S°_{(products)} - \sum S°_{(reactants)} = [(-55.2 + 17.2) - (106.7)]\ J/K = -1447\ J/K$$

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

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

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: $\Delta H^\circ_f\,[N_{2(g)}] = 0$ kJ, $\Delta H^\circ_f\,[H_{2(g)}] = 0$ kJ, $\Delta H^\circ_f\,[NH_{3(g)}] = -45.9$ kJ

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

Solution

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

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

$\Delta S^\circ = \mathbf{-0.197\ kJ/K}$

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

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) $2C\ (\text{diamond}) + 2H_{2(g)} \qquad C_2H_{4(g)}$

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

c) $C\ (\text{graphite}) + H_{2(g)} \qquad \tfrac{1}{2}\,C_2H_{4(g)}$

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

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

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

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

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

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

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 $\Delta H>0$ and $\Delta S<0$. This reaction will be:

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

c) Spontaneous only at high 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
$K_{(g)} \longrightarrow K^+_{(g)} + e^-$	+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 $\Delta S^\circ_{surrounding}$ 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:

$\Delta H^\circ_{f\,(CaSO4(s))} = -1432.7$ kJ, $\Delta H^\circ_{f(Ca^{2+}(aq))} = -543.0$ kJ, $\Delta H^\circ_{f(SO4^{2-}(aq))} = -907.5$ kJ

[Standard entropy: $S^\circ_{(CaSO4(s))} = 106.7$ J/K, $S^\circ_{(Ca^{2+}(aq))} = -55.2$ J/K, $S^\circ_{(SO4^{2-}(aq))} = +17.2$ 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.

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.

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.

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.

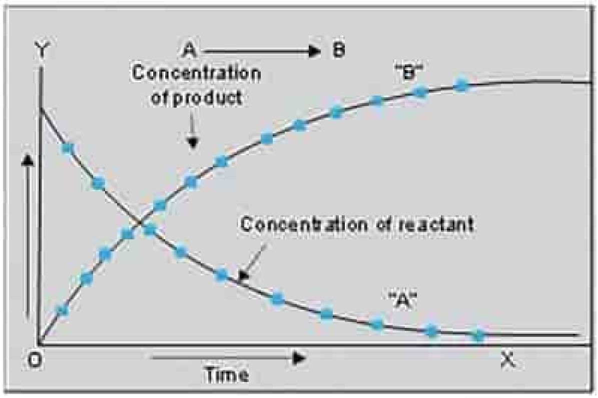


Figure 7.1 Change in the concentration of reactants and products with time for the reaction A → B

$$\text{Rate of reaction} = \frac{\text{change in concentration of the substance}}{\text{time taken for the change}}$$

$$\text{Rate of reaction} = \frac{\Delta x}{\Delta t}$$

Where Δx is a very small change in the concentration of a reactant or a product in a very small time interval Δt.

The situation is explained graphically in **Figure 7.1.** for the reactant A which is changing irreversibly to the product B.

$$\mathbf{A \longrightarrow B}$$

The slope of the graph for the reactant or the product is steepest at the beginning. This shows a rapid decrease in the concentration of the reactant and consequently, a rapid increase in the concentration of the product. As the reaction proceeds, the slope becomes less steep indicating that the reaction is slowing down with time, ultimately both the curves become parallel. It means that the rate of a reaction is changing every moment. This is the stage of completion of reaction.

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

$\Delta C = \Delta[NH_3] = (6.2\text{-}3.5)$ mol.dm^{-3} ; $\Delta c = 2.7$ 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.

$$Rate\ of\ reaction = \frac{\Delta C}{\Delta T}$$

$$rate = \frac{0.04\ mol.dm^{-3}}{100\ sec} = 4\times10^{-4}\ mol\ dm^{-3}\ s^{-1}$$

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.

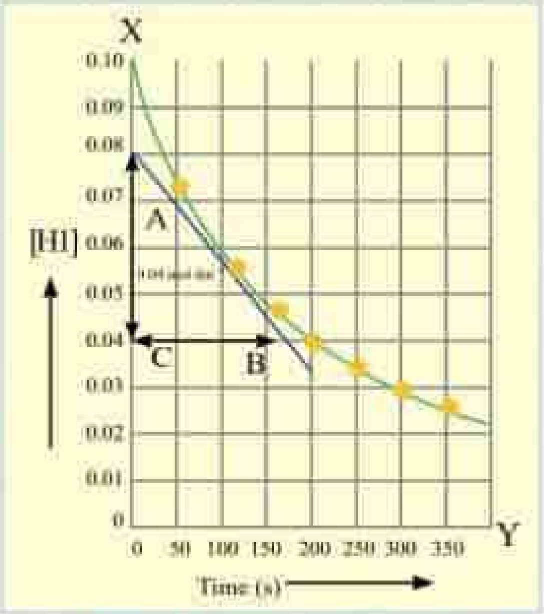


Figure 7.2 The change in the HI concentration with time to the reaction $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$ at 508°C

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.

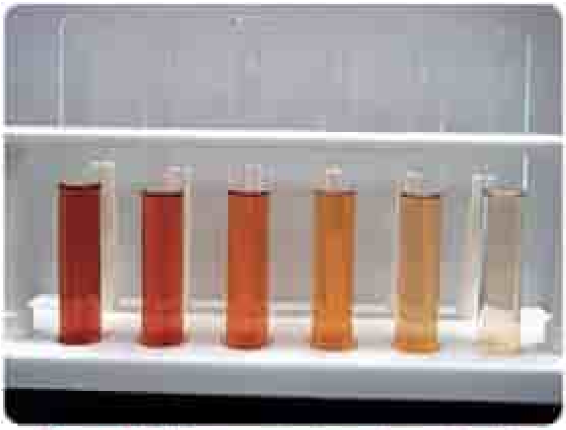


Figure 7.3 The concentration change for this reaction can be determined using colorimetry.

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.

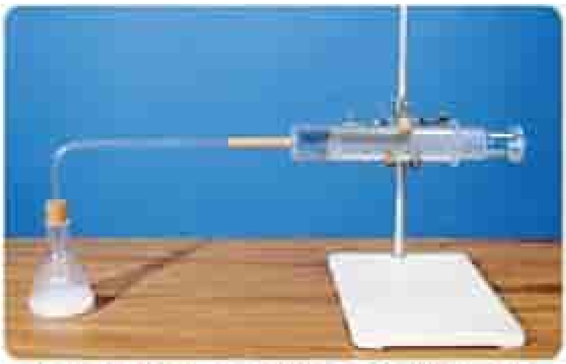


Figure 7.4 Rate of reaction can be followed by measuring the change in volume of a gas given off in a reaction.

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.

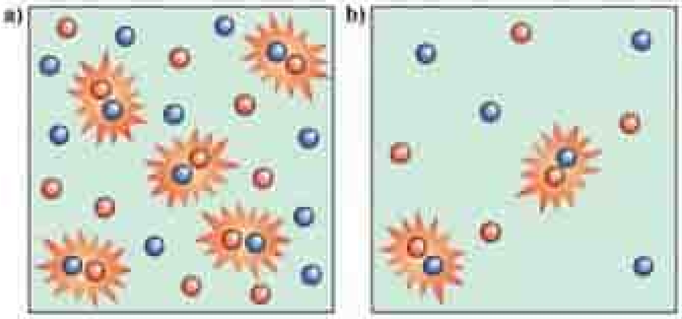


Figure 7.5 The reaction in box a) will occur faster than that in, b) due to the higher concentration.

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.

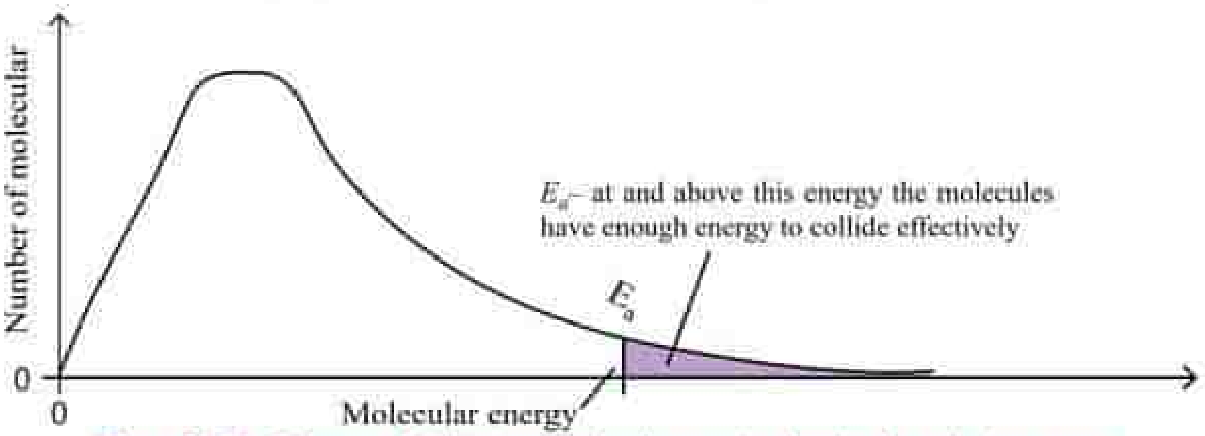


Figure 7.6 The Boltzmann distribution of molecular energies showing the activation energy

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.

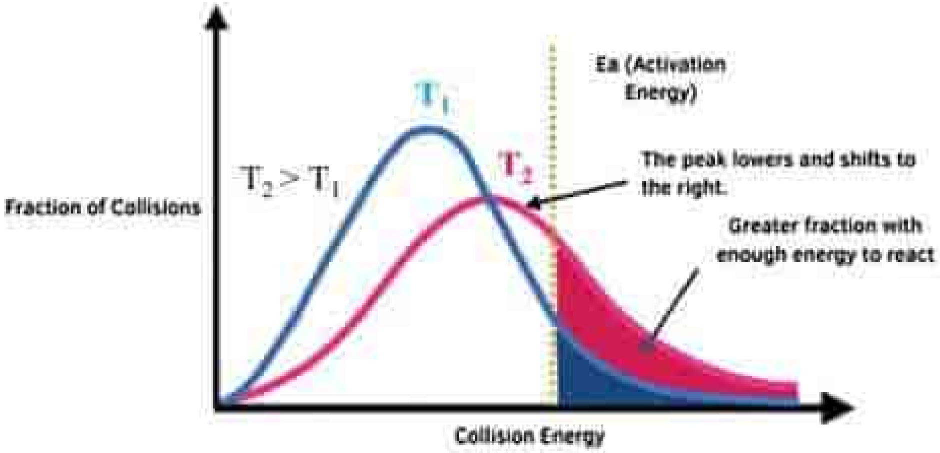


Figure 7.7 The Boltzmann distribution of molecular energies at temperatures T_1 and T_2

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.

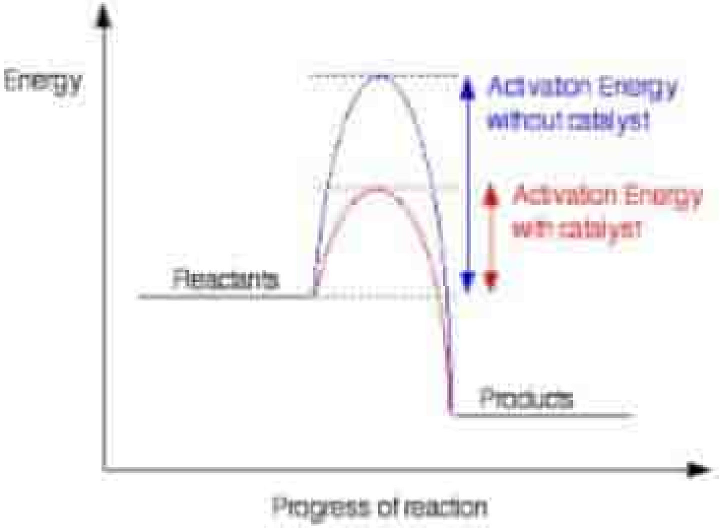


Figure 7.8 The energy path diagram for an uncatalyzed and a catalyzed reaction

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.

$$\underset{\text{Ethyl ethanoate}}{CH_3COOCH_2CH_{3(\ell)}} + H_2O_{(\ell)} \xrightarrow{H^+} \underset{\text{Ethanoic acid}}{CH_3COOH_{(\ell)}} + \underset{\text{Ethanol}}{CH_3CH_2OH_{(\ell)}}$$

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 $[B] = 1\ \text{mol dm}^{-3}$

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: $A \rightarrow \text{Product}$

$$\text{Rate} = k\,[A]^0$$

Examples:

i) $H_2(g) + Cl_2 \longrightarrow 2HCl(g)$

$$\text{Rate} = k\,[H_2]^0[Cl_2]^0 = k$$

ii) $2NH_3 \longrightarrow N_2 + 3H_2$

$$\text{Rate} = k\,[NH_3]^0 = k$$

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.

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

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.

$$NO(g) + O_{3(g)} \xrightarrow{\quad\quad} NO_{2(g)} + O_{2(g)} \qquad \text{Rate} = k[NO][O_3]$$

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 $\text{Rate} = k\,[A]^1[B]^1[C]^1 \quad (n = 1+1+1 = 3)$

$$2FeCl_{3(aq)} + 6KI_{(aq)} \xrightarrow{\quad\quad} 2FeI_{2\,(aq)} + 6KCl_{(aq)} + I_2$$

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

$$2NO_{(g)} + O_{2(g)} \xrightarrow{\quad\quad} 2NO_{2(g)} \qquad \text{Rate} = k[NO]^2[O_2]^1$$

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.

$$CHCl_{3(l)} + Cl_{2(g)} \xrightarrow{\quad\quad} CCl4_{(l)} + HCl_{(g)}$$

$$\text{Rate} = k[CHCl_3]\,[Cl_2]^{1/2} \qquad n = 1 + 1/2 = 1.5$$

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:

Rate = k[Reactants]^n where n = 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:

$$H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \xrightarrow{\hspace{3em}} 2H_2O_{(l)} + I_{2(aq)}$$

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:

$$k = \frac{0.693}{t_{1/2}}$$

$$k = \frac{0.693}{17 \times 60 \text{ s}}$$

$$= 6.79 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

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;

$$CO_{(g)} + NO_{(g)} \longrightarrow NO_{2(g)} + CO_{2(g)}$$

$$NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$$

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 reaction is directly proportional to the first power of concentration of H_2.

$$\text{Rate} \propto [H_2]$$

In the next three experiments, the concentration of H_2 is kept constant. By doubling the concentration of NO, the rate increases four times and by tripling the concentration of NO the rate is increased nine times. So, the rate is proportional to the square of concentration of NO.

$$\text{Rate} \propto [NO]^2$$

The overall rate equation of reaction is,

$$\text{Rate} \propto [H_2][NO]^2$$

$$\text{or} \quad \text{Rate} = k[H_2]^1[NO]^2$$

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

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:

$$\text{Step 1: } NO_{2(g)} + F_2 \xrightarrow{\text{Slow}} NO_2F_{(g)} + F^{\cdot}_{(g)} \quad \text{Rate} = k_1[NO_2][F_2]$$

$$\text{Step 2: } NO_{2(g)} + F^{\cdot}_{(g)} \xrightarrow{\text{Fast}} NO_2F_{(g)} \quad \text{Rate} = k_2[NO_2][F^{\cdot}]$$

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, $k = 5.5\times10^{-14}\ s^{-1}$. Find the half-life of the reaction.

Temp. (K)	Rate constant $(cm^3\,mol^{-1}s^{-1})$ (K)
500	6.814×10^{-4}
550	2.64×10^{-2}
600	0.56×10^{0}
650	7.31×10^{0}
700	66.67×10^{0}

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 :

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

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

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.

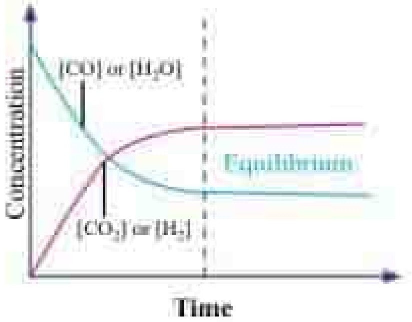


Figure 8.1 Plot of concentration vs time

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

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.

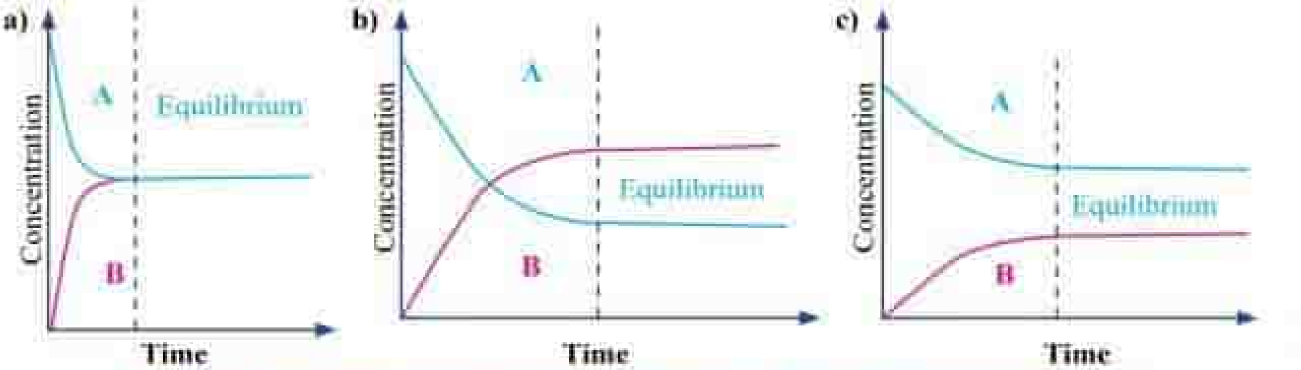


Figure 8.1 Plot of concentration vs time **(a)** Reactant = Product **(b)** Reactant < Product

(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.

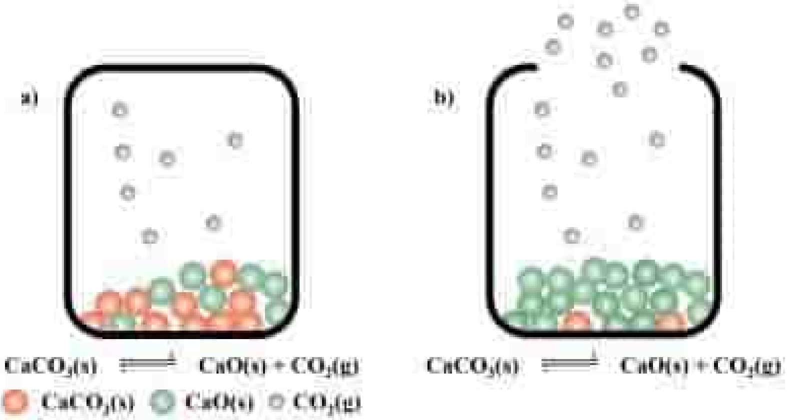


Figure 8.2 (a) Equilibrium is established when the system is closed
(b) Equilibrium can not be established in the open system.

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^+).

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons HCO^{1-}_{(aq)} + H^+_{(aq)}$$

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.

$$K_c = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

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.

$$\underset{\textbf{Ethanoic acid}}{CH_3COOH_{(l)}} + \underset{\textbf{Ethanol}}{C_2H_5OH_{(l)}} \rightleftharpoons \underset{\textbf{Ethyl Ethanoate}}{CH_3COOC_2H_{5(l)}} + \underset{\textbf{Water}}{H_2O_{(l)}}$$

500 cm^3 of the reaction mixture at equilibrium contained 0.235 mol of ethanoic acid and 0.0350 mol of ethanol together with 0.182 mol of ethyl ethanoate and 0.182 mol of water. Use this data to calculate a value of K_c for this reaction.

Step 1 Write out the balanced chemical equation with the concentrations beneath each substance.

$$\begin{array}{cccccc} CH_3COOH_{(l)} & + & C_2H_5OH_{(l)} & \rightleftharpoons & CH_3COOC_2H_{5(l)} & + & H_2O_{(l)} \\ \frac{0.235\ \text{mol}}{0.5\ \text{dm}^3} & & \frac{0.0350\ \text{mol}}{0.5\ \text{dm}^3} & & \frac{0.182\ \text{mol}}{0.5\ \text{dm}^3} & & \frac{0.182\ \text{mol}}{0.5\ \text{dm}^3} \\ 0.470\ \text{mol dm}^{-3} & & 0.070\ \text{mol dm}^{-3} & & 0.364\ \text{mol dm}^{-3} & & 0.364\ \text{mol dm}^{-3} \end{array}$$

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:

$$\begin{array}{lccccc} & CH_3COCH_{3\,(l)} & + & HCN_{(g)} & \rightleftharpoons & CH_3C(OH)(CN)CH_{3\,(l)} \\ \text{Initial conc.} & 0.0500\ \text{mol dm}^{-3} & & 0.0500\ \text{mol dm}^{-3} & & 0\ \text{mol dm}^{-3} \\ \text{Equil. conc.} & ? & & ? & & 0.0233\ \text{mol dm}^{-3} \end{array}$$

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 $H_{2(g)} = 10.00 \text{ mol dm}^{-3}$.
Initial conc. of $CO_{2(g)} = 10.00 \text{ mol dm}^{-3}$.
Equilibrium conc. of $CO_{(g)} = 9.47 \text{ mol dm}^{-3}$.

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 2.0×10^7 Pa. Under these conditions, the partial pressure of nitrogen is 1.5×10^7 Pa and the partial pressure of hydrogen is 0.4×10^7 Pa. Calculate the value of K_p for this reaction.

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.

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

8.11.1 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.

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:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H^\circ = -198\ kJ$$

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.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

Due to this change, the concentration of SO_3 will increase and concentrations of SO_2 and O_2 will decrease. Therefore, the value of the equilibrium constant will increase.

The equilibrium will shift towards right. The increase in temperature will favour the reverse reaction and the formation of the reactants. The production of SO_3 is not favoured at a higher temperature. K_c for this reaction is 2.8×10^2 at 1000 K; whereas, at 298 K the value of K_c is 1×10^{26}.

For an endothermic reaction, 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:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \quad \Delta H^\circ = +57.2\ kJ$$

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.**

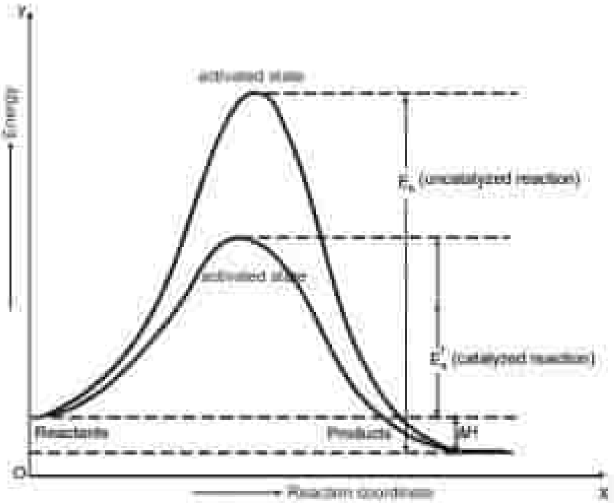


Figure 8.3 Effect of a catalyst on Reversible Reactions

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}

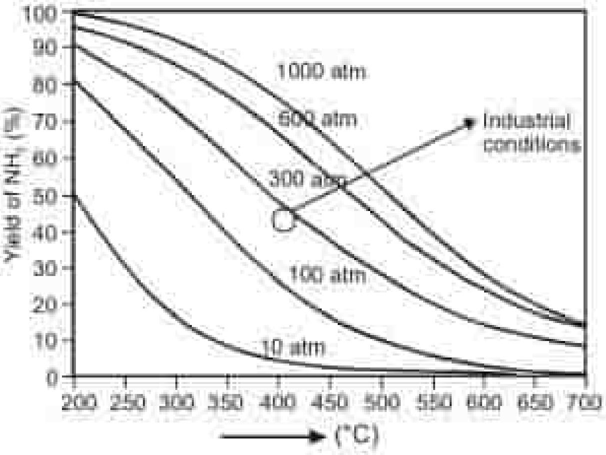


Fig (8.4) : Percent yield of ammonia vs. Temperature(°C) at five different operating pressures. At very high pressure and low temperature (top left), the yield is high, but the rate of formation is low. Industrial conditions (circle) are between 200 and 300 atm at about 400°C

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 °C and a catalyst is used to increase the rate. If we want to achieve the same rate without a catalyst then we require much higher temperature, which lowers the yield.

Optimum conditions to get best yield of ammonia

The most suitable conditions to get maximum yield of ammonia are:

a) Pressure between 200-300 atmospheres

b) Temperature around 673 K (400°C)

c) Pieces of iron crystals present in a fused mixture of MgO, 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:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H^\circ = -92\ kJ\ mol^{-1}$	$K_p = \frac{(p_{NH_3})^2}{p_{N_2}(p_{H_2})^3}$	$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H^\circ = +57\ kJ\ mol^{-1}$	$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}}$	$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H^\circ = -197\ kJ\ mol^{-1}$	$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2 p_{O_2}}$
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° 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^-

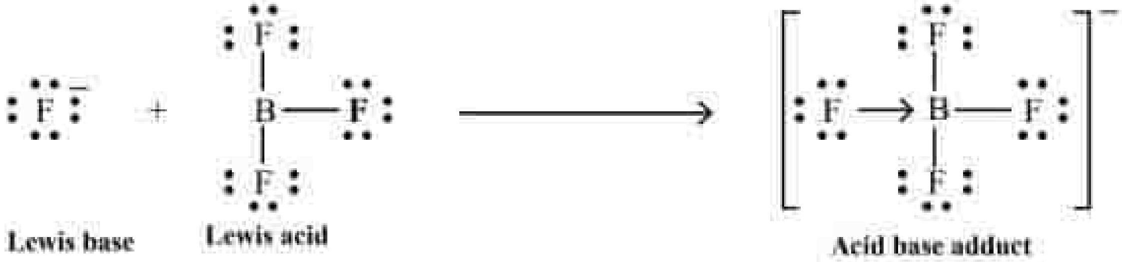
9.2 LEWIS CONCEPT OF ACIDS AND BASES

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:

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:



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.

$$[OH^-] > [H^+]$$

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}

During both of these additions, the values of K_w will remain the same, i.e. 10^{-14} at 25 °C.

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, $pH + pOH = 14$

Interesting Information!

Solutions of negative pH and having values more than 14 are also known.

The value of pH normally varies between $0 \rightarrow 14$ at $25^\circ C$.

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.

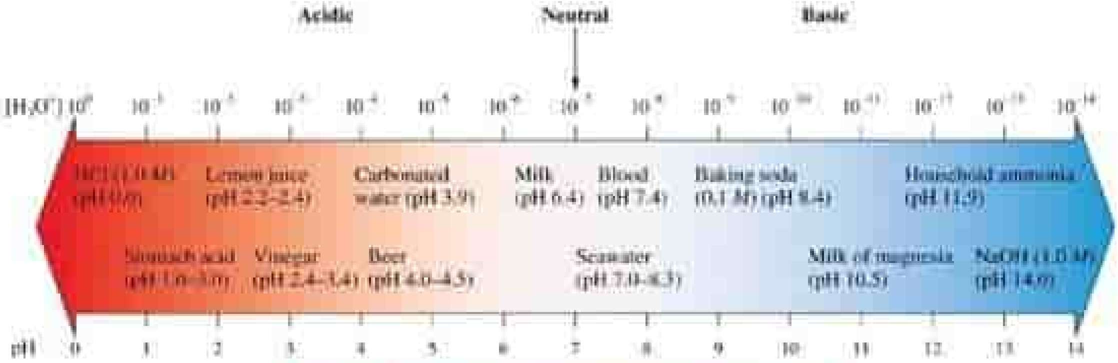


Figure 9.1 pH Values of some common substances

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)

$$[OH^-] = 10^{-pH}$$
$$[H^+] = 10^{-9.2}$$
$$[OH^-] \approx 6.3 \times 10^{-10}\ M$$

Similarly, antilog pOH = antilog (4.8)

$$[OH^-] = 10^{-pOH}$$
$$[OH^-] = 10^{-4.8}$$
$$[OH^-] \approx 1.6 \times 10^{-5}\ M$$

Sample Problem 9.2

The ionic product of water at a certain temperature is $K_w = 1.0 \times 10^{-14}$ at 25 °C. If the concentration of H^+ ions in a solution is 1.0×10^{-7}M.

Calculate the concentration of OH^- ions, the pH and pOH of the solution.

Solution

Use the expression for K_w:

$$K_w = [H^+][OH^-]$$

Substitute the known values of K_w and the concentration of H^+:

$$1.0 \times 10^{-14} = (1.0 \times 10^{-7})\,[OH^-]$$

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 °C.

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
HCl	$HCl \rightleftharpoons H^+ + Cl^-$	very large (10^{-2})	Very strong
HNO_3	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	very large (10^{-5})	Very strong
H_2SO_4	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	Large (10^{-2})	Very strong
HSO^-_4	$HSO_4 \rightleftharpoons H^+ + SO_4^{2-}$	1.3×10^{-4}	Strong
HF	$HF \rightleftharpoons H^+ + F^-$	6.7×10^{-5}	Week
CH_3COOH	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.85×10^{-5}	Week
H_2CO_3	$H_2CO_3 \rightleftharpoons H^+ + HS^-$	4.4×10^{-7}	Week
H_2S	$H_2S \rightleftharpoons H^+ + HS^-$	1.0×10^{-7}	Week
$NH_4^!$	$NH_4 \rightleftharpoons H^+ + NH_3$	5.7×10^{-10}	Week
HCO_3^-	$HCO_3 \rightleftharpoons H^+ + CO_3^2$	4.7×10^{-12}	Week
H_2O	$H_2O \rightleftharpoons H^+ + OH^-$	1.8×10^{-15}	Very week

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

$$[H_3O^+] \approx \sqrt{K_a \times C}$$
$$[H_3O^+] \approx \sqrt{1.8 \times 10^{-5} \times 0.1}$$
$$[H_3O^+] \approx \sqrt{0.18 \times 10^{-6}}$$
$$[H_3O^+] \approx 1.34 \times 10^{-3}\ M\ (mol\ dm^{-3})$$

The concentration $[H_3O^+]$ in the solution is approximately **1.34×10^{-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 $$pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$pH = pK_a + \log (1)$$

So, $$pH = pK_a + 0 = pK_a$$

$$pH = 4.74.$$

It means that the pH of this buffer is just equal to the pK_a of the acid.

Quick Check 9.4

a) Explain the impact of common ion effect on solubility.

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 $PbCl_2$.

$$PbSO_{4(s)} \underset{}{\overset{H_2O}{\rightleftharpoons}} Pb^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

$$K_c = \frac{[Pb^{2+}][SO_4^{2-}]}{[PbSO_4]}$$

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, $PbCl_2$: $K_{sp} = [Pb^{2+}][Cl^-]^2$

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	$[Ag^+][Br^-]$	5.0×10^{-13}	CuS	$[Cu^{2+}][S^{2+}]$	8×10^{-34}
AgCl	$[Ag^+][Cl^-]$	1.8×10^{-10}	Fe_2S_3	$[Fe^{3+}]^2[S^{2-}]^3$	1.4×10^{-85}
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	3×10^{-34}	$MgCO_3$	$[Mg^{2+}][CO_3^{2-}]$	3.5×10^{-8}
$BaSO_4$	$[Ba][CO_4^{2-}]$	1.1×10^{-10}	MnS	$[Mn^{2+}][S^{2-}]$	3×10^{-11}
$CaCO_3$	$[Ca^{2+}][Ca_3^{2-}]$	3.3×10^{-9}	$PbCrO_4$	$[Pb^{2+}][CrO_4^{2-}]$	2.3×10^{-13}
CaF_2	$[Ca^{2+}][F^-]^2$	3.2×10^{-11}	$PbSO_4$	$[Pb^{2+}][SO_4^{2-}]$	1.6×10^{-8}

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	1.69×10^{-4}	1.3×10^{-4}
$Ca(OH)_2$	3	6.5×10^{-6}	1.175×10^{-2}
CaF_2	3	3.2×10^{-11}	2.0×10^{-4}
Ag_2CrO_4	3	2.6×10^{-12}	8.7×10^{-5}

Sample Problem

$Ca(OH)_2$ is a sparingly soluble compound. Its solubility product is 6.5×10^{-6}. Calculate the solubility of $Ca(OH)_2$.

Solution

Let the solubility be represented by S in terms of mol dm^{-3}.

The balanced equation is:

$$Ca(OH)_{2(aq)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

$$Ca(OH)_{2(aq)} \rightleftharpoons 0 \quad + \quad 0 \qquad \text{Initial stage}$$

$$Ca(OH)_2 \rightleftharpoons S \quad + \quad S \qquad \text{Equilibrium stage}$$

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.

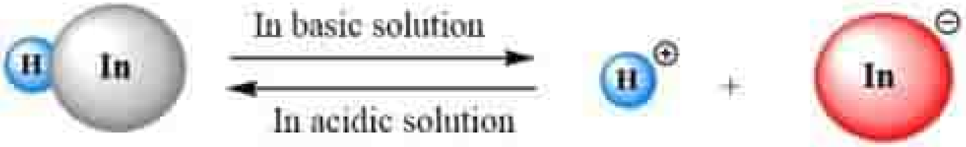


Figure 9.1 Unionized acid-base indicators and their ionised forms exist in an **equilibrium**

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.

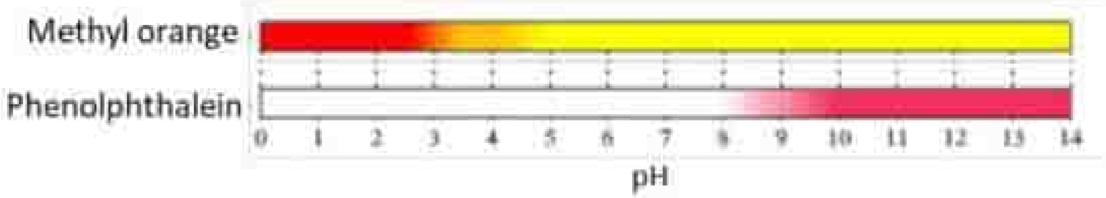


Figure 9.2 Range and color changes of some common Acid-Base indicators

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.

The equivalence point is reached when the amount of OH^- added is stoichiometrically equal to the amount of H^+ originally present in the acid. The pH at the equivalence point in a strong acid-strong base titration is 7.0. The titration curve at this stage shows a steep rise in pH, changing quickly from acidic to neutral. The pH value at the endpoint changes about from 4.0 to 10.0. These titrations have a pH of 7.0 at equivalence, so, such phenolphthalein as indicator can be used as they show different colours in this range.

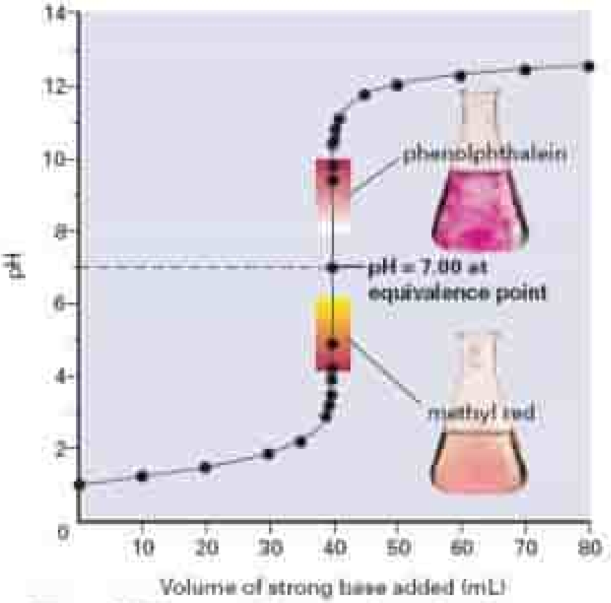


Figure 9.3 Strong acid-strong base titration curve

2. Strong Acid-Weak Base Titration Curve

Consider the titration of aqueous NH_3 with HCl. Initially, the solution contains only the weak base and it only partially dissociates, with a lower concentration of OH^- ions compared to a strong base. The initial pH will be greater than 7 but lower than the pH of a strong base. As HCl is added, the concentration of OH^- decreases, causing a further decrease in pH.

Before reaching the equivalence point, the solution is in a buffer-like region where the pH changes more gradually. The presence of the weak base and its conjugate acid (from the salt formed) creates a buffering effect, which helps to moderate the pH change as the base is added.

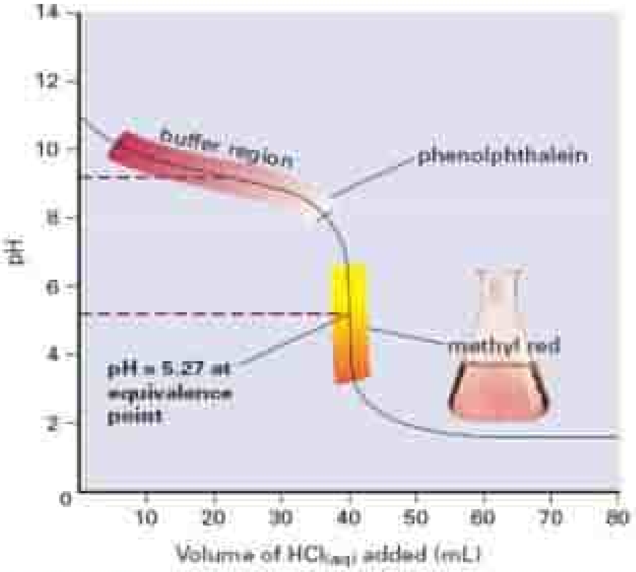


Figure 9.4 strong acid-weak base titration curve

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) $CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3$
O^+

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 1×10^{-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.