THE GOVERNMENT OF THE REPUBLIC OF THE UNION OF MYANMAR
MINISTRY OF EDUCATION

CHEMISTRY

GRADE 10

BASIC EDUCATION CURRICULUM, SYLLABUS AND
TEXTBOOK COMMITTEE

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INTRODUCTION TO NEW EDITION

Chemistry may be generally defined as that branch of science which is concerned with the study of the composition, properties and structure of matter and the ways in which substances can change from one form to another or react with one another. Matter is anything which has mass and occupies space. It is present all over, and in the far corners, of the universe. The study of chemistry, therefore, implies the study of all processes which are going on all around us and even inside us.

The past decade has witnessed spectacular developments in chemistry and the related fields of scientific studies. Well over 3 million different substances or compounds are now known, a good number of them having been produced or synthesized by chemists in the laboratories. Thousands more are turned out synthetically every year in various parts of the world. All these new substances are being produced with the expectation that at least a number of them will benefit us and make our lives more comfortable. Most of the new substances used in medicine, agriculture and the textile and plastic industries, to mention a few, had their beginnings in the laboratory.

It would be an impossible task to learn the properties and reactions of each and every one of these substances. For a meaningful study of chemistry, the various component substances of the natural world are observed, measured and classified into appropriate categories. Scientific laws are then formulated to summarize the results of these numerous observations. Once the formulation of a scientific law is achieved, theories or models are devised to explain the law.. Only those theories tested and proven by the entire scientific community survive to provide the basic foundations for the study of the science of chemistry. In the course of time a great many of the old established theories have been forced to the background by new developments resulting from a better understanding of the chemical processes and phenomena. Such new insights into the science of chemistry and the related scientific fields, coupled with the mountains of facts accumulated especially during the past decade or so, have had a profound effect on the study of chemistry.

Old ideas are revised or reformulated to blend in with the new. Still newer ideas are generated, developed and applied at a pace never before known in the history of chemistry.

These developments have prompted major changes in the way chemistry is studied and taught throughout the world. This is reflected not only in the new chemistry course contents but also in the course organizations and the methods of teaching and examining the subject. The modern day emphasis on practical work is one such prominent aspect of the new approach to the teaching of chemistry.

Fully aware of the new developments in the teaching of high school chemistry and taking cognizance of the fact that some of the students will need to have professional orientations on completion, the authors have undertaken the task of preparing two textbooks, one for the grade 9 and the other for the grade 10 of the Basic Education High School, in conformity with the revised high school chemistry syllabus. The course contents of these two textbooks taken together comprise the requirements for the Basic Education High School Chemistry Course.

Grade-10 chemistry text is based on the knowledge the student has acquired from the study of the (Grade- 9) chemistry text. Any student preparing for the Basic Education High School Examination should be familiar and proficient with the theoretical portions included in the grade 9 and the grade 10 chemistry texts as also with the experimental chemistry texts which accompany these books.

In this new edition, most of the chapters have been revised, summary and relevant questions for all chapters are added and updated. For the benefit of the students, four appendices are added and enhanced.: Appendix 1: Periodic table of the elements (updated 2003), Appendix 2: Table of the relative atomic numbers and relative atomic masses of the elements (including the new discovered web-elements), Appendix 3 Vapour pressure of water and Appendix 4 The Activity series

The authors should like to acknowledge their gratitude to the Ministry of Education and to the Directorates of Basic Education and Higher Education for their help and encouragement during the writing of this book.

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CONTENTS

CHAPTER 1

THE ELECTRONIC STRUCTURES OF ATOMS, PERIODIC TABLE AND CHEMICAL BONDS

1.1 Arrangement of Fundamental Particles of Matter

Fundamental Particles

All matter is made up of atoms. In turn, atoms consist of three main fundamental particles. They are protons, neutrons and electrons. The masses and charges of these particles are shown in Table. 1.1

Table 1.1 Fundamental particles of matter

Particle	Mass	Charge
Proton (p)	1 amu	Positive (+1)
Neutron (n)	1 amu	Neutral
Electron (e)	$\frac{1}{1840}$ amu	Negative (-1)

Arrangement of the Fundamental Particles in the Atom

Figure 1.1 represents the models of the hydrogen and helium atoms.

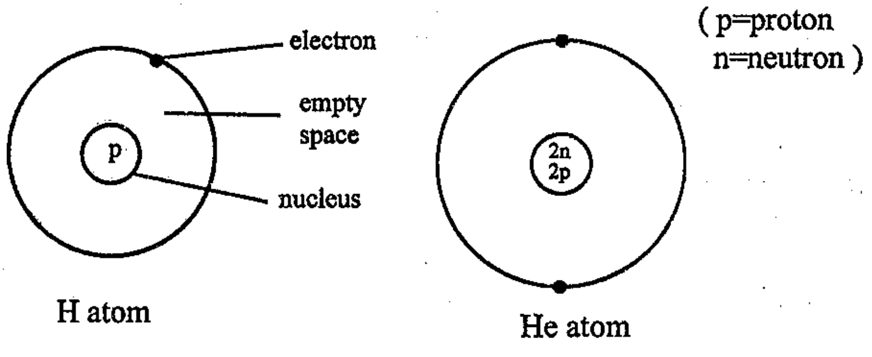


Fig. 1.1 Models of the hydrogen and helium atoms

The atom may be pictured as follows.

The atom has a small, dense, positively charged centre called the nucleus. This nucleus contains protons and neutrons. Outside and around the nucleus, electrons move in circular or near circular orbits. The negative charge of the electrons balances the positive charge of the nucleus. The atom as a whole is neutral. Most of an atom is empty space that separates the tiny nucleus from the distant electrons. Most of the mass of the atom is concentrated in the nucleus since the mass of the electrons is so small that it can be considered negligible.

Atomic Number

Atoms are electrically neutral. Therefore, in an atom, the number of protons must be equal to the number of electrons.

The number of protons in the nucleus of an atom is known as the atomic number of an element. Since an atom contains an equivalent number of protons and electrons, the atomic number of an element represents the number of protons as well as electrons present in the atom of the element.

Table 1.2 Atomic structure of selected elements

Element	Symbol	Atomic number	Number of electrons, protons and neutrons in each atom.		
			Electrons	Protons	Neutrons
Hydrogen	H	1	1	1	-
Helium	He	2	2	2	2
Lithium	Li	3	3	3	4
Beryllium	Be	4	4	4	5
Chlorine	Cl	17	17	17	18
Zinc	Zn	30	30	30	34
Lead	Pb	82	82	82	124
Uranium	U	92	92	92	146

Mass Number and Isotopes

The mass number of the element is the sum of the numbers of protons and neutrons in the nucleus of an atom of that element.

The atomic number of an element never changes. This means that all atoms of the same element contain the same number of protons. However, this is not the case with the number of neutrons. Atoms of the same element can have different numbers of neutrons.

Atoms of the same element that have the same number of protons but different numbers of neutrons are called **isotopes.** In other words, isotopes are the atoms of the same element with different masses.

The atomic number of Cl is 17. The two isotopes of chlorine are represented as $^{35}_{17}Cl$ and $^{37}_{17}Cl$. In $^{35}_{17}Cl$ one atom of chlorine contains 17 protons and 35-17=18 neutrons whereas one atom of $^{37}_{17}Cl$ contains 17 electrons, 17 protons and 20 neutrons. Note that both isotopes of chlorine contain the same number of protons (17) and electrons (also 17).

Notation for Isotopes

The isotope of any element X is usually represented as $^{A}_{Z}X$ where A is the mass number of the isotope and Z is the atomic number of the element X. Isotopes of the same element have the same atomic number Z, but the mass number A may be different.

1.2 The Electronic Structures of Atoms

Electrons move round the nucleus in definite orbits or shells. The first shell is known as K shell, the second as L shell, the third as M shell, the fourth as N shell, the fifth as O shell and so on. The first shell is also given the number 1, the second the number 2, the third number 3 etc. See Figure 1.2.

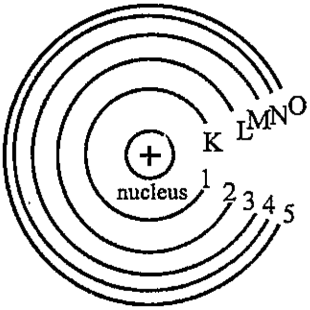


Fig. 1.2 Diagrammatic representation of the nucleus and the electron shells in an atom (not to scale)

Each shell or energy level can contain a limited number of electrons. The maximum number of electrons which each shell could contain can be calculated by the formula $2n^2$, where n is the shell number. For number 1 shell the maximum number of electrons it could contain is $(2 \times 1^2) = 2$ electrons, for number 2 shell $(2 \times 2^2) = 8$ electrons, for number 3 shell $(2 \times 3^2) = 18$ electrons, for number 4 shell $(2 \times 4^2) = 32$ electrons and so on.

Here we shall concern ourselves only with the elements having atomic number up to 10.

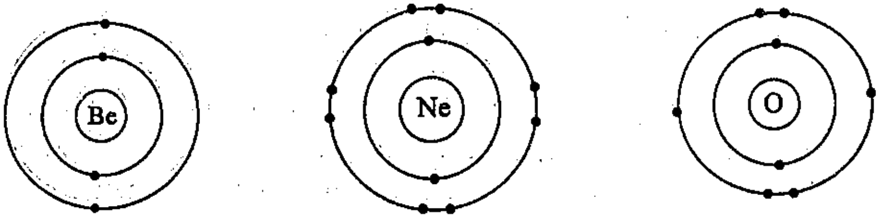
Table 1.3 The electronic structure of the atoms of the elements

Symbol	Atomic number	Electrons in		Electronic Structure
		1st shell	2nd shell	
H	1	1	-	1
He	2	2	-	2
Li	3	2	1	2.1
Be	4	2	2	2.2
B	5	2	3	2.3
C	6	2	4	2.4
N	7	2	5	2.5
O	8	2	6	2.6
F	9	2	7	2.7
Ne	10	2	8	2.8

The distribution of electrons in an atom of an element is known as the electronic structure of that element. The electronic structures of elements of atomic number 1to 10 are given in Table 1.3.

The electronic structures of an element, for example; fluorine is written as F 2.7. Then the first integer 2 indicates there are 2 electrons in the first shell. The second integer 7 indicates there are 7 electrons in the second shell.

The electronic structure of an element can also be represented diagrammatically as in Figure 1.3. The small circle at the centre with the symbol of the element represents the nucleus of the atom of that element. The electrons surrounding the nucleus are shown as dots.



Be atom
(2.2)

Ne atom
(2.8)

O atom
(2.6)

Fig 1.3 Electronic structure of Be, Ne and O

Sub-shells

Each shell is again divided into a number of sub-shells, which are known as s,p,d and f. The letters used for sub-shells notations are the initial letters of the names given to certain spectral lines, s stands for sharp; p for principal; d for diffuse and f for fundamental.

s sub- shell can have the maximum number of 2 electrons; p sub-shell can at the maximum accommodate 6 electrons, d can have 10 and f 14 electrons. Thus in a shell which have 8 electrons, 2 would be in sub-shell s and 6 in the sub-shell p. The shell which has 32 electrons will have 2 in s sub-shell (written as s^2), 6 in the p sub-shell (written as p^6), 10 in the d sub-shell (written as d^{10}) and 14 in the f sub-shell (written as f^{14}).

Order of filling up sub-shells with electrons

The shell nearest to the nucleus has the lowest energy. In general the closer the shell is to the nucleus, the lower is its energy.

The order in which the sub-shells are filled is shown in Figure 1.4.

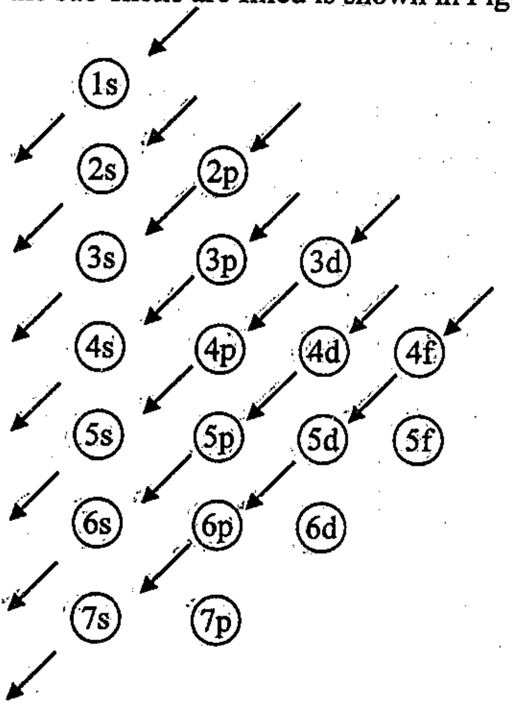


Fig 1.4 Order of occupancy of sub-shells

The complete electronic structures of elements with atomic numbers 1 to 32 are shown in Table 1.4.

Table 1.4 The complete electronic structures of some elements

Symbol of element	**Atomic number**	**Complete Electronic structure**
H	1	$1s^{1}$
He	2	$1s^{2}$
Li	3	$1s^{2}\ 2s^{1}$
Be	4	$1s^{2}\ 2s^{2}$
B	5	$1s^{2}\ 2s^{2}\ 2p^{1}$
C	6	$1s^{2}\ 2s^{2}\ 2p^{2}$
N	7	$1s^{2}\ 2s^{2}\ 2p^{3}$
O	8	$1s^{2}\ 2s^{2}\ 2p^{4}$
F	9	$1s^{2}\ 2s^{2}\ 2p^{5}$
Ne	10	$1s^{2}\ 2s^{2}\ 2p^{6}$
Na	11	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{1}$
Mg	12	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}$
Al	13	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{1}$
Si	14	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{2}$
P	15	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{3}$
S	16	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{4}$
Cl	17	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{5}$
Ar	18	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}$
K	19	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{1}$
Ca	20	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{2}$
Sc	21	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{2}\ 3d^{1}$
Ti	22	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{2}\ 3d^{2}$
V	23	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{2}\ 3d^{3}$
Cr	24	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{1}\ 3d^{5}$
Mn	25	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{2}\ 3d^{5}$
Fe	26	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{2}\ 3d^{6}$
Co	27	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{2}\ 3d^{7}$
Ni	28	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{2}\ 3d^{8}$
Cu	29	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{1}\ 3d^{10}$
Zn	30	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{2}\ 3d^{10}$
Ga	31	$1s^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{2}\ 3d^{10}\ 4p^{1}$
Ge	32	$Is^{2}\ 2s^{2}\ 2p^{6}\ 3s^{2}\ 3p^{6}\ 4s^{2}\ 3d^{10}\ 4p^{2}$

Complete and Essential Electronic Structures

The arrangement of all the electrons of an atom of the element in appropriate sub-shells is sometimes known as the complete electronic structure of that element. For example, the complete electronic structure of potassium is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$.

The representation of the arrangement of valence electrons of an atom of the element in appropriate sub-shells is called the essential electronic structure of that element. For example, the essential electronic structure of potassium is $4s^1$.

Valence of the Elements

From the electronic structure of an element, the valence of the element may be determined. When the number of electrons in the outermost shell of the atom of the element is 4 or less than 4, then the valence of that element is equal to the number of electrons in that outermost shell. When the number of electrons in the outermost shell of the atom of the element is greater than 4, the valence of the element becomes 8 minus the number of electrons in that outermost shell.

1.3 The Periodic Table

The elements may be arranged in a table in order of their atomic numbers, so that elements with similar electronic structures or similar properties fall under one another in a column. In this arrangement, elements with similar electronic structures or similar properties occur at certain periodic intervals, i.e., the electronic structures of the atom of the elements vary periodically with their atomic numbers. Hence the table is named the "Periodic Table" (Appendix 1). The Periodic Table with elements of atomic number 1 to 118 is given in Appendix 2.

The Groups and the Periods

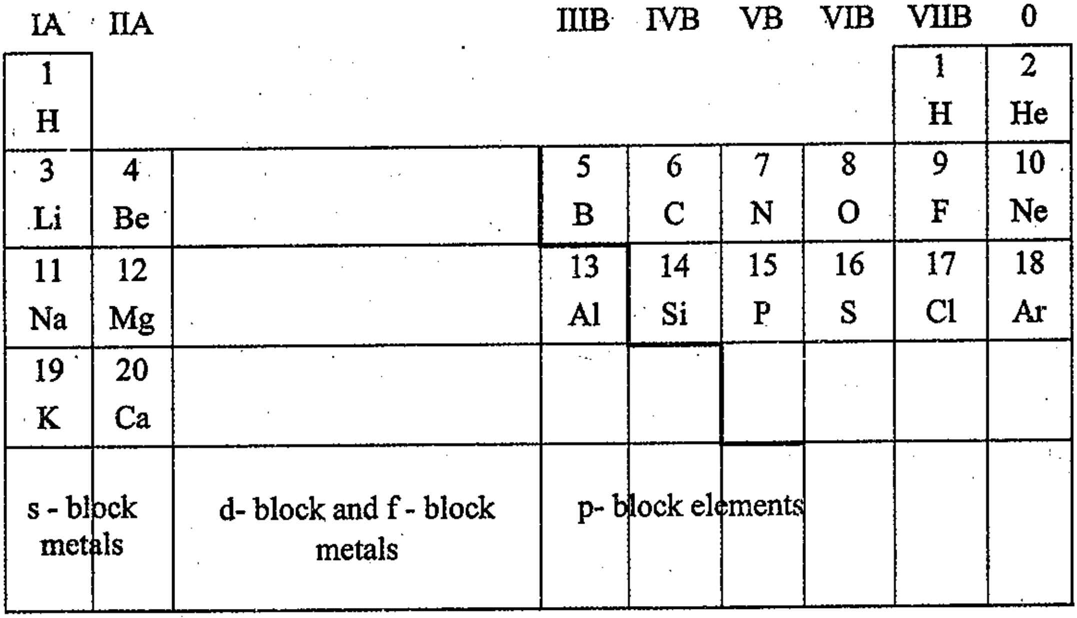
In the modern periodic table, there are 18 vertical columns and 7 horizontal rows.

The vertical columns are called groups. Elements in the same group have the same number of electrons in the outermost shell of their atoms, i.e., they have the same number of valence electrons.

The horizontal rows are called periods. All elements in the same period have the same number of electron shells, i.e., elements of period 2 have 2 electron shells, while those of period 3 have 3 electron shells and so on.

The elements in the Group I A with the exception of hydrogen, are called the alkali metals. Beryllium, magnesium and calcium in the Group IIA are known as the alkaline earth metals. The elements in the Group VIIB again with the exception of hydrogen, are called the halogens. The elements in the Group 0 are known as the noble gases or inert gases (Figure 1.5).

The elements in the central section of the periodic table are known as the transition elements.



IA	IIA		IIIB	IVB	VB	VIB	VIIB	0
1 H							1 H	2 He
3 Li	4 Be		5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg		13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca							
s - block metals		d- block and f - block metals	p- block elements					

Fig. 1.5 The three blocks in the periodic table

1.4 Periodic Properties

Metals and Non-Metals in the Periodic Table

As we go from left to right across the periodic table, the elements change in properties from metals to non-metals. The division of metals and non-metals in the periodic table is indicated by the dark line. The elements to the left of this dark line are metals and those to the right are non metals. For along each side of the dark line are elements that have properties of both metals and non-metals. These elements except Al are called metalloids.

Electropositive and Electronegative Elements

In general, metals are the electropositive elements. This means that they tend to lose electrons and form positive ions. However, the electropositivity of the elements decreases on going from left to right across a period, because the greater the number of electrons that has to be lost, the more difficult it becomes for the element to lose electrons.

Generally, it is considered that non-metals are the electronegative elements. In other words, these elements have the tendency to gain electrons. On going across a period from left to right, the electronegativity increases, i.e., the elements have an increasing tendency to gain electrons.

The noble gases or inert gases, are neither electropositive nor electronegative, because they have very stable electronic structure and have little tendency to gain or lose electrons.

When the eletropositive elements combine with the electronegative elements, i.e., when metals combine with non-metals, ionic compounds are usually formed. When electronegative elements, or non-metals, combine with one another, covalent compounds are formed.

Atomic Sizes

The size of an individual atom is difficult to determine. However, one can estimate the approximate radii of atoms by knowing the distances between atoms in molecules. Atomic size is generally described by the radius of an atom.

Table 1.5 Atomic radii of elements in second period

Atomic number	3	4	5	6	7	8	9
Element	Li	Be	B	C	N	O	F
Atomic radius (nm)	0.123	0.089	0.080	0.077	0.074	0.074	0.072

Table 1.6 Atomic radii of alkali metals

Atomic number	Element	Atomic radius(nm)
3	Li	0.123
11	Na	0.157
19	K	0.203
37	Rb	0.216
55	Cs	0.235

Tables 1.5 and 1.6 show the atomic radii for some elements. Note the periodic trends for atomic radii.

1. Atomic radii decrease from left to right across a period in the periodic table.
2. Atomic radii increase from top to bottom in a group.

The trends in atomic radii can be explained as follows:

As you know the higher the atomic number, the greater the number of protons in the nucleus. The charge on the nucleus increases with increasing atomic number. The attraction between the nucleus and any electron around the nucleus also increases. As you move left to right across a period in the periodic table, the nuclear charge (atomic number) increases while the added electrons enter the same shell, the outermost shell. The increased nuclear charge attracts the electrons in the outermost shell closer to the nucleus. Hence the shell contracts, resulting in smaller atoms.

Down a group in the periodic table, atomic radii increase because of two reasons. First, the number of electrons increases. These additional electrons are in the larger **electron shells** farther and farther from the nucleus. Second, there is the repulsion between individual electrons. Hence, the shell expands, resulting in larger atoms.

Although the nuclear charge increases down a group, its effect will be little compared to the effect of the change in distance between the electrons and the nucleus.

Ionic Sizes

When one or more electrons are removed from a metal atom, a positive ion is formed. Both a positive ion and the parent neutral atom have same nuclear charges but there is a lesser number of electrons in the positive ion. Hence, the repulsion between electrons is reduced in the positive ion. For this reason a positive ion is always smaller than its parent atom.

When one or more electrons are added to a neutral atom, a negative ion is formed. Increasing the number of electrons cause an increase in the repulsion between electrons. Thus, a negative ion is always larger than its parent atom.

Ionization Energy

Energy is required to remove electrons from atoms because they are held strongly within the atom by the attraction of the nucleus. The amount of energy required to remove an electron from a gaseous atom to form a gaseous ion is called the ionization energy. The ionization process can be expressed in an equation.

$$\text{element}_{(g)} + \text{ionization energy} \longrightarrow \text{ion}^{+}_{(g)} + \text{electron}$$

We can represent this for sodium:

$$Na_{(g)} \quad + \quad \text{energy} \quad \longrightarrow \quad Na^{+}_{(g)} \quad + \breve{e}$$

Successive removal of other electrons give the second, third and subsequent ionization energies. The ionization energies become progressively higher.

Ionization energies measure how tightly electrons are bound to atoms. Low ionization energies indicate ease of removal of electrons, and hence ease of positive ion (cation) formation. Figure 1.6 shows a plot of first ionization energy versus atomic number for several elements.

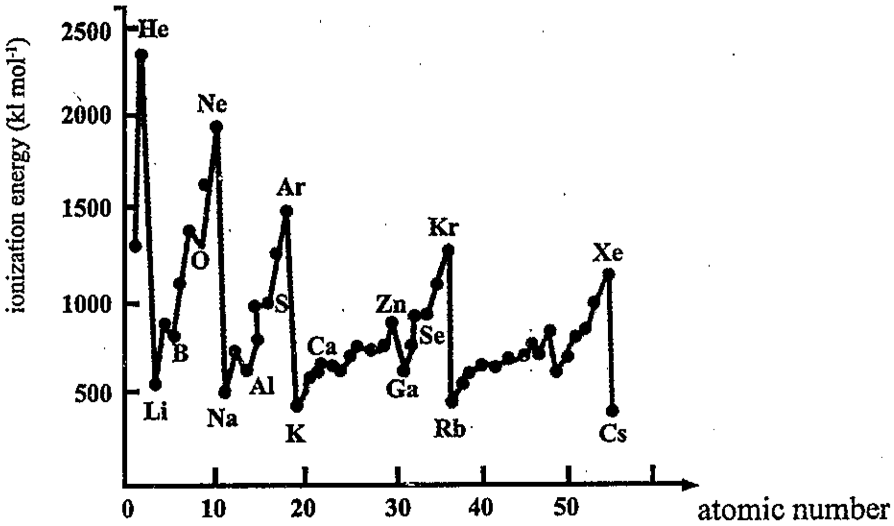


Fig. 1.6 Variation in first ionization energies with atomic number

We see also that in each period of Figure 1.6, the noble gases have the highest first ionization energies and the alkali metals have the lowest first ionization energies. This should not be surprising, because the noble gases are known to have the closed electronic structures (the octet) which resist the removal of electrons, whereas the alkali metals have only one electron outside of a noble gas structure, which is very easy to remove.

The ionization energies of the elements depend on the electronic structures. Let us examine the periodic trends in the ionization energy to learn about the stability of the various electronic structures. Table 1.7 provides a list of the ionization energies of the elements in the second period.

Table 1.7 Ionization energies of the elements in the second period

Atomic number	3	4	5	6	7	8	9	10
Element	Li	Be	B	C	N	O	F	Ne
IE (kJ mol^{-1})	520	900	800	1086	1403	1314	1681	2081
Essential electronic structure	$2s^1$	$2s^2$	$2s^22p^1$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2s^22p^5$	$2s^22p^6$

In general, as one moves from left to right across a period, ionization energies increase. For example, ionization energies generally increase from Li to Ne (Table 1.7). This is because, the nuclear charge increases across a period and the electrons are more strongly held by the force of attraction between the nucleus and the electrons. Another approach to this trend is to look at the relative sizes of the atoms.

The size of the atoms decreases from left to right across a period. The nuclear attractive force is greater in the smaller atoms. Therefore, more energy is required to remove an electron from the element as you go across the period.

The trend in ionization energy within a group is shown in Table 1.8. In general, ionization energies decrease down a group. This is consistent with the trend in atomic sizes. As we go down the group, the atomic size increases and the outermost electron is farther from the nucleus making it easier to remove it.

Table 1.8 Ionization energies of alkali metals

Atomic number	Element	IE (kJ mol^{-1})
3	Li	520
11	Na	495
19	K	418
37	Rb	403
55	Cs	374

Electron Affinity

The electron affinity of an element is the energy released when an electron is added to a gaseous atom to form a gaseous ion.

e.g., $\text{element}_{(g)} + \text{electron} \longrightarrow \text{ion}^-_{(g)} + \text{energy}$

$Cl_{(g)} + \bar{e} \longrightarrow Cl^-_{(g)} + \text{energy}$

The halogens have the highest electron affinities. This is because, they form stable anions with noble gas electronic structures, $ns^2\ np^6$, by gaining one electron. On the other hand, the alkali metals have very low electron affinities since they do not bind their outermost electron very strongly.

Electron affinity values for halogens (Group VIIB elements) are given in Table 1.9.

Table 1.9 Electron affinities of halogens

Atomic Number	Element	Electron affinity (kJ mol^{-1})
9	F	333
17	Cl	348
35	Br	340
53	I	297

The decreasing trend in electron affinity on moving down a group arises because the size of the atom increases and the electron being added goes to higher shells. The anomalous behaviour of fluorine may be due to the fact that the fluorine atom is so small that the incoming electron is affected by comparatively strong repulsion from the nine electrons already around the nucleus, so diminishing the overall amount of energy released by the process.

For many reasons, the variations in electron affinities are not regular across a period. The electron affinities generally increase from left to right across a period.

It is interesting that non-metals generally have higher electron affinities than metals. Metals, on the other hand, have lower ionization energies. Since non-metals characteristically gain electrons to become negative ions, the word electronegative is used to describe them. Similarly, since metals characteristically lose electrons to become positive ions, the word electropositive is often used to describe them.

1.5 Types of Bonds

Generally speaking there are three main types of chemical bonds, such as (1) ionic bond, (2) covalent bond and (3) metallic bond.

The coordinate bond, which is a special type of covalent bond is another common chemical bond.

Ionic Bond (Electrovalent Bond)

An ionic bond is formed when there is complete transfer of an electron or electrons from one atom to another resulting in the formation of cations and anions. These oppositely charged ions are held together by an electrostatic attraction known as ionic bond.

The most typical ionic compounds are formed when a metal element from Group IA or Group IIA reacts with a non-metal from Group VIB or Group VIIB. When the reaction occurs, electrons are transferred from the metal to the non-metal until the outer electron shells are identical to those of the nearest noble gases. This electron transfer process produces charged particles called ions.

An ion is an atom (or group of atoms) that is electrically charged as the result of the loss or gain of electrons.

Atoms or groups of atoms lose valence electrons to form positive ions (cations), or gain valence electrons (from other atoms) to form negative ions (anions). The charge on an ion is directly correlated with the number of electrons lost or gained. The ions are stable because they obtain the electronic structure of a noble gas.

An ionic bond results from the electrostatic attraction between positively charged cations and negatively charged anions.

For example, when sodium and chlorine combine to form sodium chloride, one electron from the sodium atom is transferred to the chlorine atom, resulting in the cation Na^+ and the anion Cl^-.

	$\overset{\bullet}{\mathrm{Na}}$	+	$\overset{\times\times}{\underset{\times\times}{{}_{\times}\mathrm{Cl}^{\times}_{\times}}}$	$\longrightarrow$	Na^+	+	$\overset{\times\times}{\underset{\times\times}{{}^{\bullet}_{\times}\mathrm{Cl}^{\times}_{\times}}}^{-}$
electronic structure	2.8.1		2.8.7		2.8		2.8.8

Both Na^+ and Cl^- ions now possess stable electronic structures of the noble gases. The sodium and chloride ions are held together by the strong electrostatic force of attraction which is known as the ionic bond.

Characteristic Properties of Ionic Compounds

Ionic compounds do not contain molecules. They consist of aggregates of oppositely charged ions. Consequently, if they are melted or dissolved in water, the ions become more mobile. They conduct electricity and are, therefore, electrolytes.

Ionic compounds are solids and do not vaporize easily.

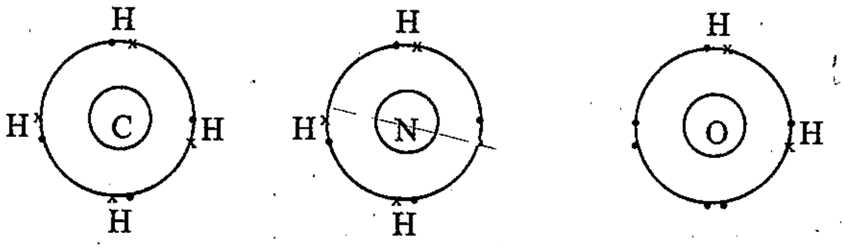
Ionic compounds will not usually dissolve in organic solvents such as toluene, ether, benzene, etc.

Covalent Bond

In a covalent bond between two atoms, the electrons are not actually gained or lost by the atoms concerned. The two electrons forming a covalent bond are shared between the two atoms.

Covalent compounds are formed when non-metals react with one another. In covalent bonding actual molecules are produced, not ions. Each electron of the "shared pair " passes from an orbit controlled by the nucleus of one atom into an orbit controlled by the nuclei of both atoms.

Examples of molecules formed by covalent bonding are shown in Figure 1.7.



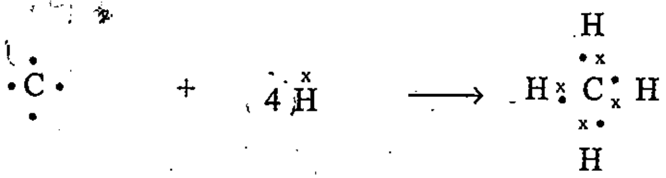
methane **ammonia** **water**

x electron of H

- electron of other element

Fig 1.7 Covalent molecules of methane, ammonia and water (only valence electrons are shown in this figure)

Each shared electron pair is made up of one electron from each of the atoms concerned. All the atoms share the resulting octet or duplet of electrons. The formation of four covalent bonds in methane can be represented by the electron dot-cross structure as:



Characteristic Properties of Covalent Compounds

Covalent compounds consist of molecules. They contain no ions, are unable to conduct electricity and so are non-electrolytes.

Simple covalent compounds are gases or volatile liquids (e.g., ammonia, carbon dioxide, ethanol) because their molecules are electrically neutral and the forces of attraction between them are very small. As the molecules come closer together, the atomic nuclei of one molecule and the electrons of another molecule attract each other while at the same time there is repulsion between their electrons. The forces of attraction and repulsion are balanced in the formation of crystal. These van der Waals forces are, however, rather weak and the crystals have low melting points. (e.g., naphthalene has melting point of 81 °C compared to that of the ionic crystal such as sodium chloride of melting point, 804 °C).Covalent compounds are usually soluble in covalent organic solvents, such as benzene or carbon disulphide.

Coordinate Bond or Dative Bond

Coordinate bond or dative bond is a special type of covalent bond This bond is characterized by the fact that the two shared electrons are both supplied by one of the participating atoms. This is quite different from an ordinary covalent bond, where the two bonded atoms contribute an electron each towards the formation of the bond. A coordinate bond is formed when one of the participant atoms possesses a lone pair of electrons. This lone pair is donated to an atom needing them to build up, or complete, an electron octet or duplet of great stability.

The formation of NH_4^+ is an example of a dative covalent combination. The ammonia molecule possesses a lone pair of electrons; it can be donated to a hydrogen ion from an acid to produce the ammonium ion NH_4^+, forming a coordinate bond. This bonding supplies an electron duplet to the hydrogen nucleus while still maintaining the stable electron octet structure of the nitrogen atom in ammonia.

As a result of the combination, the positive charge on the hydrogen ion is carried over to give the positively charged ammonium ion, NH_4^+ (Figure 1.8).

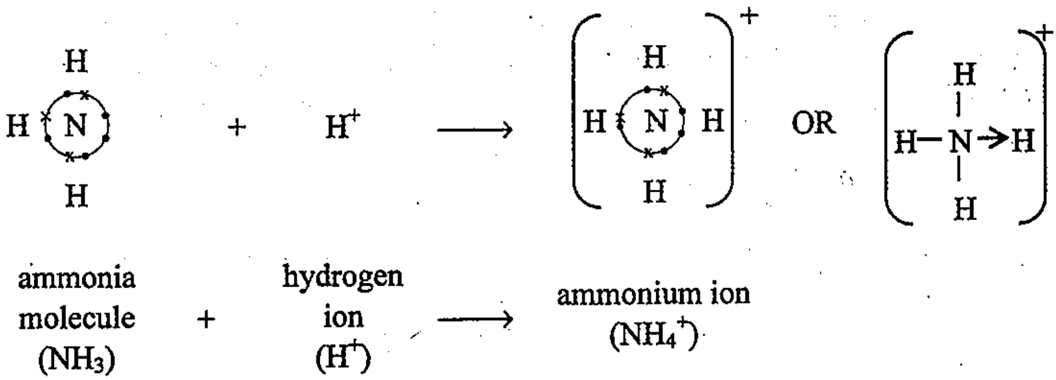


Fig. 1.8 Formation of ammonium ion

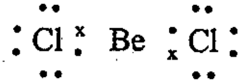
The Octet Rule

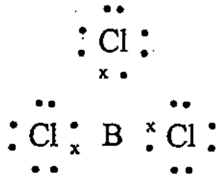
The noble gas stable electronic structures have in common that the outermost s and p sub-shells are completely filled. In general, there are eight outer shell electrons. Atoms of many electrons that lack the very stable outer-shell electronic structure of the noble gas tend to attain it in chemical reactions that result in compound formation.

Studies of the chemical bond have led to the fact that in forming a chemical bond, atoms gain, lose or share electrons in such a way to attain the stable electronic structures of the noble gases, i.e., to have eight electrons in the outermost shell. This is known as the octet rule.

Exceptions to the Octet Rule

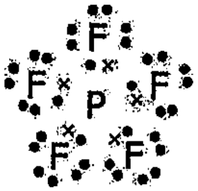
There are some exceptions to the octet rule which the student should know. Such exceptions, are found with the elements of the second period of the periodic table, e.g., $BeCl_2$ and BCl_3.

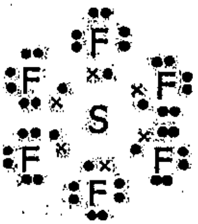




In $BeCl_2$, the beryllium atom is surrounded by 4 valence electrons and in BCl_3, the boron atom is surrounded by 6 valence electrons.

Also there are exceptions in the third period of the periodic table, e.g., PF_5, ClF_3 and SF_6.





In PF_5 and ClF_3, the phosphorus and the chlorine atoms are surrounded by 10 valence electrons. In SF_6, the sulphur atom is surrounded by 12 valence electrons.

Metallic Bond

Most of the metals are solids at room temperature and therefore, there must be some sort of bonding between these metal atoms. These metal atoms are held together in solid crystalline form by what is known as metallic bonding.

In metallic solids, atoms of metals are present. They form metallic bonds. In a metallic bond, valence electrons of the atoms are very loosely held, forming a common electron cloud. Electrons move freely within this electron cloud. These electrons are often described as a sea of electrons. The positively charged metallic ions resulting by loss of valence electrons, repel each other, but they are surrounded by free-moving electrons. Hence, they are held together by the attractive force of the electron cloud. Each metal atom is bonded to all the atoms around it by a surrounding sea of electrons.

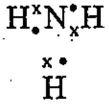
The sea of mobile electrons in a metallic crystal accounts for many of the properties of metals. Metals are malleable and ductile. The flexibility of metals results from the fact that the metal ion can slide by each other and the electrons are free to flow. The ability of the electrons to flow freely also accounts for the high electric conductivity of metals. Electricity flows easily through metals.

SUMMARY

In this chapter, the fundamental particles of atoms such as protons, electrons and neutrons have been introduced first, followed by the electronic structure of the atoms of elements including complete and essential electronic structures of the various types of elements. The definitions of atomic number, mass number, isotopes of the elements in the periodic table have been presented. The group number, period number, periodic properties such as metals and non-metals, electropositive and electronegative elements, atomic sizes, ionic sizes, ionization energy, electron affinities of the elements have been elaborated. The octet rule and the exception to the octet rule have been depicted with suitable examples. The types of bonds such as ionic or electrovalent bond, covalent bond, coordinate (dative) bond and metallic bonds have been illustrated with appropriate examples.

Questions and Problems

1. Write only TRUE or FALSE for each of the following statements.
   - (a) A metallic bonding is observed in metals.
   - (b) Noble gas elements are neither electropositive nor electronegative.
   - (c) The essential electronic structure of $_{14}Si$ is $3p^2$.
   - (d) The electron dot-cross structure of ammonia is



$$\begin{matrix} H\,{}^{\times}_{\bullet}\,N\,{}^{\bullet}_{\times}\,H \\ {\times}\,{\bullet} \\ H \end{matrix}$$

   - (e) $_6C$ and $_7N$ are both in period 2. Therefore, the size of C is larger than that of N.
2. Fill in the blanks with the correct word(s), phrase, term etc., as necessary.
   - (a) Atoms of the same element that have same atomic number but different atomic masses are..............
   - (b) Elements that are found within the same................ of the periodic table have similar properties.
   - (c) From top to bottom in a given group, the atomic number increases and the size of the atom............
   - (d) A charged particle is a (an) ....
   - (e) Compounds formed between metals and non-metals will have.......... bonds.
3. Select the correct word (s),notation, terms etc., given in the brackets.
   - (a) The atom without neutron (s) is [hydrogen, helium, caesium]
   - (b) The atom with the duplet structure is [hydrogen, helium, neon].

(c) The element at the group VII B and the period 3 in the periodic table is [X(2.7), Y(2.8.3), Z (2.8.7)]

(d) The ionic (electrovalent) compounds have [low, medium, high] melting points.

(e) [Cl^-, Cl^+, Cl)] is stabilized by electron octet.

4. Match each of the items given in List A with the appropriate correct item shown in List B.

	List A		**List B**
(a)	proton	(i)	increases down the group
(b)	alkali metals	(ii)	covalent bond
(c)	sharing electrons	(iii)	2 x n^2(n=shell number)
(d)	number of electrons in the main n^{th} shells	(iv)	in the nucleus
(e)	atomic size	(v)	lowest electron affinity

5. Answer the following:

(a) In a neutral atom of an element, the number of a certain particle or particles is equal to the atomic number. Name the particle or particles.

(b) Select the isotopes from the following and give reasons for your answer.

$$^{40}_{18}Ar,\ ^{35}_{17}Cl,\ ^{40}_{20}Ca,\ ^{37}_{17}Cl$$

(c) Determine the number of neutrons, protons and electrons in the atom of $^{32}_{16}S$.

(d) What elements are most likely to form covalent bonds?

(e) What type of bond exists in the solid metals?

6. (a) Write down

(i) the complete electronic structure (ii) the essential electronic structure

(iii) the group number (iv) the period number

(v) the chief valence of the following elements.

$_{11}Na$, $_9F$, $_{12}Mg$, $_{13}Al$, $_{17}Cl$, $_{18}Ar$

(b) Classify the above elements as alkali metal, alkaline earth metal, halogen, noble gas and give reasons for your classification.

7. (a) Generally, the elements of the same group have similar electronic structures. Arrange the following elements in their appropriate group.

$_3Li$,$_{12}Mg$, $_{20}Ca$, $_8O$,$_{11}Na$,$_{19}K$,$_{16}S$

(b) What is meant by the term
   (i) electropositive element
   (ii) electronegative element?

(c) Arrange the following elements in order of their increasing electronegativity.

   oxygen, carbon, fluorine, nitrogen

8. The following information regarding elements I to IV are provided.

Element	Atomic number	Mass number	Complete electronic structure
I	4	9	$1s^2\ 2s^2$
II	18	40	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
III	17	35	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
IV	12	24	$1s^2\ 2s^2\ 2p^6\ 3s^2$

Answer the following questions.
(a) Which of the above elements are in the same group of the periodic table?
(b) Which element is a noble gas?
(c) Which element has the highest electron affinity?
(d) Which element has 18 neutrons in each atom?
(e) Which of the elements have a valence of 2?

9. Complete the following table and answer the following questions.

	Element X	Element Y	Element Z
Atomic number	11	6	-
Number of protons	-	-	16
Number of neutrons	12	6	16
Mass number	-	12	32
Electronic structure	2.8.1	-	-

(a) Which of the above elements X, Y and Z is a metal?
(b) What type of bonding exist between X and Z?
(c) Write down the most likely formula of this compound using the symbol X and Z.

10. Give the difference between ionic compounds and covalent compounds based on
   (a) volatility
   (b) solubility
   (c) electrical conductivity.

11. (a) A compound is formed between $_{5}$A and $_{17}$B. Name the type of bonding exists between A and B . Write down the electron dot-cross formula of the compound formed.

(b) What type of bond is formed between the above compound and :NH_3? Draw the electron dot-cross structure.

12. (a) From the following group of elements, select the one which has the largest radius. Give reasons.

(i) Fe^{2+}, Fe^{3+} (ii) Cl, Cl^- (iii) Li, Na, K (iv) C, N, O

(b) Explain which of the following group has the largest ionization energy.

(i) 2.8.1 (ii) 2.8.5 (iii) 2.8.7

(c) Explain (i) why Be has higher ionization energy than that of B and

(ii) why N has higher ionization energy than that of O.

(iii) why fluorine has lower electron affinity than that of chlorine.

13. Answer the following questions.

(a) What is the charge and mass of a proton ?

(b) From the following , calculate the number of protons, neutrons, and electrons in each of these atoms.

$^{40}_{18}Ar$, $^{35}_{17}Cl$, $^{41}_{20}Ca$, $^{39}_{19}K$, $^{31}_{15}P$

(c) Which two elements would form a covalent compound ?

(d) Which two elements would form an electrovalent compound ?

(e) Which particle contains 20 neutrons, 19 protons and 19 electrons ?

(f) Explain the meaning of the atomic number of the element.

(g) How are the elements arranged in the periodic table ?

14. Answer the following questions.

(a) How many electrons does a potassium atom lose in forming the K^+ ion ?

(b) How many electrons does a chlorine atom gain in forming the Cl^- ion ?

(c) Explain the formation of ionic compounds . Give three examples.

(d) Describe the differences between covalent compounds and ionic compounds.

(e) What do we call bonding which involves electron transfer ?

(f) What do we call bonding which involves electron sharing ?

(g) What type of bonding do we find in molecules ?

(h) Why the noble gases or inert gases are neither electropositive nor electronegative ?

****

CHAPTER 2

THE GASEOUS STATE AND GAS LAWS

2.1 Measurable Quantities of Gases

A gaseous substance consists of very small particles as other states of matter-solids and liquids. The particles of the gas are widely spaced and free to move in any direction. It spreads itself uniformly throughout any container.

Before dealing with the theory of gases, we should consider the properties (mass, volume, pressure and temperature) that can be measured.

Volume of the Gas

Suppose that a sample of gas is enclosed in a container of 1 dm^3. The particles of gas are freely moving within the whole space of container. Thus, the volume of enclosed gas is 1 dm^3. If the gas is transferred into another container of 2 dm^3, the available space occupied by the gas will be 2 dm^3.

Pressure of the Gas

During the motion, the particles of a gas collide with each other and also with the walls of the container. Hitting the walls of the container by the particles is actually the force on it. The force acting on the unit area is what we know as; the gas pressure.

$$\text{Pressure of gas} = \frac{\text{Force}}{\text{Area}}$$

Temperature of the Gas

At any low temperature, the particles of a gas are moving with a slow speed. If the temperature is increased, they move faster resulting in the more frequent collisions on the container. Variation of temperatures can affect the pressure and volume of the gas.

2.2 Gas Laws

Pressure- Volume Behaviour

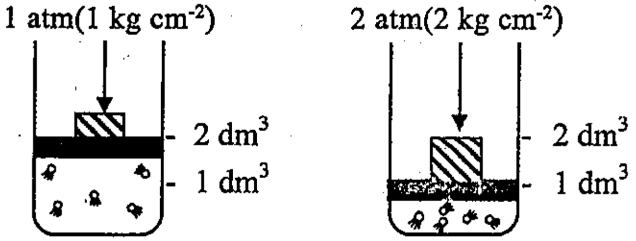


Fig. 2.1 Pressure-volume behaviour of a gas at constant temperature

Figure 2.1 shows that when a pressure of 1 atmosphere is applied on a volume of gas, the volume of the gas supports against this external pressure. The pressure of the gas is 1 atmosphere which corresponds to 2 dm^3. When a pressure of 2 atmospheres is applied, the volume of the gas reduces to half of its original volume.

∴ The decrease of gas volume accompanies the increase of gas pressure.

Boyle's Law

Boyle's law shows the relation of gas volume (V) and pressure (P). It can be expressed in mathematical form as:

$$V \propto \frac{1}{P} \text{(mass and temperature are kept constant)}$$

$$V = \text{constant} \times \frac{1}{P}$$

$$PV = \text{constant}$$

$$P_1V_1 = P_2V_2$$

Thus, Boyle's law can be stated as follows:

When the temperature of a given mass of gas is kept constant, the volume of the gas is inversely proportional to its pressure.

Example: A volume of a certain mass of gas occupies 952 cm^3 at 561 mmHg. What is the volume under 760 mmHg at the same temperature?

Initial state	Final state
$P_1 = 561$ mmHg	$P_2 = 760$ mmHg
$V_1 = 952\ cm^3$	$V_2 = ?$

According to Boyle's law:

$$P_1 V_1 = P_2 V_2$$

$$V_2 = \frac{P_1 V_1}{P_2}$$

$$V_2 = \frac{561 \text{ mmHg} \times 952 \text{cm}^3}{760 \text{ mmHg}}$$

$$V_2 = 702.8 \text{ cm}^3$$

Volume-Temperature Behaviour

When a given mass of gas is heated at a constant external pressure, the gas particles begin to move with greater speed. Therefore, they hit the walls with greater impact making the gas to expand to a new volume. Hence when a given mass of gas is heated at constant pressure the volume will expand with respect to the increase in temperature. This means that the volume of a given mass of gas varies with temperature.

Similarly the volume of the gas decreases regularly with regular decrease of temperature. If the constant contraction rate is continued, the volume of the gas will become zero at – 273 °C. This temperature is taken as the zero point of a new scale of temperature, (Kelvin temperature scale) and also known as absolute zero temperature.

Absolute zero temperature= -273 °C or 0 K.

Relation of Kelvin temperature and Celsius temperature

$$T\,K = t\,°C + 273$$

Charles' Law

Charles' law shows the relation of volume (V) and Kelvin temperature (T). It can be stated in mathematical form as:

$$V \propto T \text{ (mass and pressure are kept constant)}$$

$$\therefore V = \text{constant} \times T$$

$$\therefore \frac{V}{T} = \text{constant}$$

$$\therefore \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

This relation may also be expressed as;

When the pressure of a given mass of gas is kept constant, the volume of the gas is directly proportional to its temperature on the Kelvin scale.

Example: A certain mass of gas occupies 617 cm^3 at 9 °C. What is the volume at 0 °C under the same pressure?

Initial state

$V_1 = 617\,cm^3$

$T_1 = 9\,°C + 273$

$= 282\,K$

Final state

$V_2 = ?$

$T_2 = 0\,°C + 273$

$= 273K$

According to Charles' law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 \times T_2}{T_1}$$

$$V_2 = \frac{617\ cm^3 \times 273\ K}{282\ K}$$

$$V_2 = 597.3\ cm^3$$

Relationship between Temperature and Pressure of Gases

As mentioned in the above section, the increase in the temperature makes the particles to move with greater speed and greater force or pressure on the walls of the container. Therefore, when a volume of given mass of gas is heated, the pressure of the gas increases with the increase of temperature.

A mathematical expression of this statement can be written as:

$P \propto T$ (mass and volume are kept constant)

$$\therefore P = \text{constant} \times T$$

$$\therefore \frac{P}{T} = \text{constant}$$

$$\therefore \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

This relation can also be expressed as:

When a volume of a given mass of gas is kept constant, the pressure of the gas is directly proportional to its temperature on the Kelvin scale.

Example: The pressure of a gas at 27 °C is 760 mmHg. What is the pressure of the gas at 87 °C at constant volume?

Initial state	Final state
$P_1 = 760\ cm^3$	$P_2 = ?$
$T_1 = 27\ °C + 273$	$T_2 = 87\ °C + 273$
$= 300\ K$	$= 360\ K$

$$\frac{P_2}{T_2} = \frac{P_1}{T_1}$$

$$P_2 = \frac{P_1 \times T_2}{T_1} = \frac{760\ \text{mmHg} \times 360\ \text{K}}{300\ \text{K}}$$

$$= 912.\ \text{mmHg}$$

Combination of Boyle's Law and Charles' Law

Boyle's law, $V \propto \frac{1}{P}$ (mass and temperature are kept constant).

Charles' law, $V \propto T$ (mass and pressure are kept constant).

By the combination of these laws

$$V \propto \frac{T}{P} \text{ (mass is constant)}$$

$$\therefore\ V = \text{constant} \times \frac{T}{P}$$

$$\therefore\ \frac{PV}{T} = \text{constant}$$

$$\therefore\ \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

This equation is known as combined gas law equation.

Standard Temperature and Pressure, STP

STP means standard temperature and pressure.

Standard temperature = 0 °C or 273 K

Standard pressure = 760 mmHg or 1 atmosphere (atm)

Example: At 27 °C and 750 mmHg a gas occupies 380 cm^3. What is the volume of the gas at STP?

		Initial state			Final state
P_1	=	750 mmHg	P_2	=	760 mmHg
T_1	=	27 °C + 273	T_2	=	0 °C + 273
	=	300 K		=	273 K
V_1	=	380 cm^3	V_2	=	?

According to the combined gas law equation,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

$$V_2 = \frac{750\ \text{mmHg} \times 380\ \text{cm}^3 \times 273\ \text{K}}{300\ \text{K} \times 760\ \text{mmHg}}$$

$$V_2 = 341.3\ \text{cm}^3$$

Molar Volume of Gases

One mole of every gas occupies 22.4 dm^3 at STP.

The amount of the gas expressed as relative molecular mass in gram is equivalent to one mole and occupies 22.4 dm^3 at STP.

Example: What is the mass of hydrogen gas enclosed in 5.6 dm^3 at STP? (H=1)

22.4 dm^3 of the gas at STP = 1 mol.

5.6 dm^3 .... $= \frac{5.6\ dm^3}{22.4\ dm^3} \times 1\ \text{mol}$

$= 0.25$ mol

1 mol of hydrogen = 2 g

0.25 mol = 2 x 0.25 g = 0.5 g

Gay-Lussac's Law of Combining Volumes of Gases

At the same temperature and pressure, the volume of reacting gases and gaseous products are in simple ratios of small whole numbers.

$$\begin{array}{lcll} \text{hydrogen} & + & \text{nitrogen} & \longrightarrow \text{ammonia} \\ 3H_2(g) & + & N_2(g) & \longrightarrow 2NH_3(g) \\ \text{3 volumes} & + & \text{1 volume} & \longrightarrow \text{2 volumes} \end{array}$$

volume ratio of $H_2 : N_2 : NH_3 = 3 : 1 : 2$

Avogadro's Theory

At the same temperature and pressure, equal volumes of all gases contain the same number of molecules.

(OR)

For a given mass of an ideal gas, the volume and amount (moles) of the gas are directly proportional if the temperature and pressure are constant.

$V \propto n$ (at the same temperature and pressure)

n = number of molecules

V = volume of gas

Relative Density of Gas

Relative density of a gas can be defined as the ratio of the mass of a volume of gas at a certain temperature and pressure to the mass of equal volume of hydrogen at the same temperature and pressure.

According to Avogadro's theory,

$$\text{Relative density of a gas} = \frac{\text{mass of n molecules of the gas}}{\text{mass of n molecules of hydrogen}}$$

$$\text{Relative density of a gas} = \frac{\text{mass of a volume of the gas}}{\text{mass of an equal volume of hydrogen}}$$

(both gases are measured at the same temperature and pressure.)

$$= \frac{\text{mass of n molecules of the gas}}{\text{mass of n molecules of hydrogen}}$$

$$= \frac{\text{mass of one molecule of the gas}}{\text{mass of one molecule of hydrogen}}$$

$$= \frac{\text{mass of one molecule of the gas}}{\text{mass of two atoms of hydrogen}}$$

$$= \frac{\text{mass of one molecule of the gas}}{2\times\text{mass of one atom of hydrogen}}$$

$$= \frac{1}{2} \times \frac{\text{mass of one molecule of the gas}}{\text{mass of one atom of hydrogen}}$$

$$= \frac{1}{2} \times \frac{\text{mass of one molecule of the gas}}{\frac{1}{12}\times\text{mass of a } ^{12}\text{C atom}}$$

$$= \frac{1}{2} \text{ relative molecular mass of the gas}$$

Relative density of a gas is equivalent to half of the relative molecular mass of the gas.

Example: What is the relative density of CO_2 ? (C = 12, O = 16)

Relative molecular mass of CO_2 $= 12 + 2 \times 16$

$= 44$

Relative density of CO_2 $= \frac{1}{2} \times$ relative molecular mass of CO_2

$= \frac{1}{2} \times 44$

$= 22$

Pressure Behaviour in a Gas Mixture

It is obvious that the total pressure of a gas mixture is related to the partial pressure of each gas if the individual gas is inert to one another.

When a mixture of oxygen and nitrogen gas is enclosed in a container with the capacity of 1 dm^3, the pressure shown in the pressure gauge is the total pressure of the gas mixture.

If each gas is separately stored in the container with the same size as the volume of the gas mixture (i.e. in 1 dm^3), the pressure exerted by each gas at the same temperature is the partial pressure of each gas.

Dalton's Law of Partial Pressures

The phenomenon of gas pressure in a gas mixture can be summarized as follows:

$$P_{total} = p_1 + p_2 + p_3 + \ldots \quad \text{(temperature is kept constant)}$$

P_{total} = total pressure of gas mixture

p_1, p_2, p_3 = partial pressures of different gases

Hence, when the temperature is kept constant, the total pressure of a gas mixture is the sum of the partial pressures of different gases.

Example: The pressure of hydrogen collected over water at 27 °C is 776.7 mmHg. The vapour pressure of water at 27 °C is 26.7 mmHg. What is the pressure of dry hydrogen?

$$\begin{aligned} P_{total} &= p_{H_2} + p_{H_2O} \\ p_{H_2} &= P_{total} - p_{H_2O} \\ &= 776.7\ \text{mmHg} - 26.7\ \text{mmHg} \\ &= 750\ \text{mmHg} \end{aligned}$$

Diffusion of Gases

Particles of gases are always in constant and rapid motion. Therefore when two gases are in contact with each other one gas travels through another gas. The process by which the molecules of one gas spreads through the spaces created between the molecules of another gas is known as diffusion. In general, the lighter gas diffuses faster than the heavier one.

Graham's Law of Gaseous Diffusion

$$r \propto \frac{1}{\sqrt{d}} \quad \text{(at the same temperature and pressure)}$$

$$r = \text{constant} \times \frac{1}{\sqrt{d}}$$

$$r\sqrt{d} = \text{constant}$$

$$r_1\sqrt{d_1} = r_2\sqrt{d_2} \quad \text{or} \quad r_1\sqrt{M_1} = r_2\sqrt{M_2}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad \text{or} \quad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

r = rate of diffusion of gas ($cm^3 s^{-1}$)

d = density of gas ($g\ dm^{-3}$)

M = molar mass ($g\ mol^{-1}$)

This relation can be expressed as:

At the same temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of the density of the gas.

Example: What is the relative molecular mass of the gas that diffuses 4 times as fast as oxygen? What is the molar mass of that gas? (O = 16)

$$M_{O_2} = 2 \times 16 = 32 \text{ g mol}^{-1}$$

$$\frac{r_x}{r_{o_2}} = \sqrt{\frac{M_{o_2}}{M_x}}$$

$$4 = \sqrt{\frac{32}{M_x}}$$

$$16 = \frac{32}{M_x}$$

$$M_x = \frac{32}{16}$$

$$M_x = 2 \text{ g mol}^{-1}$$

$$\text{Molar mass} = 2 \text{ g mol}^{-1}$$

$$\text{Relative molecular mass} = 2$$

2. 3 Chemical Calculations Involving Gas Laws and Theories

Expressing measurable quantities of gases in various terms (i.e., dm^3, mole, mmol, g and amu)

1. You are provided with 11.2 dm^3 of hydrogen gas at STP. Find the amount of hydrogen in (i) moles (ii) molecules (iii) gram (ix) amu.(H= 1)

(i) 22.4 dm^3 at STP = 1 mol of H_2

$$11.2 \text{ dm}^3 = \frac{11.2 \text{ dm}^3}{22.4 \text{ dm}^3} \text{ mol}$$

$$= 0.5 \text{ mol of } H_2$$

(ii) 1 mol of H_2 = 6.02×10^{23} molecules

0.5 mol = 6.02×10^{23} molecules $mol^{-1} \times 0.5$ mol

= 3.01×10^{23} molecules

(iii) 1 mol of H_2 weighs = 2 g

0.5 mol = 2 g $mol^{-1} \times 0.5$ mol

= 1 g

(iv) 1 molecule of H_2 weighs = 2 amu

3.01×10^{23} molecules = 2 amu $molecule^{-1} \times 3.01 \times 10^{23}$ molecules

= 6.02×10^{23} amu

2. 8 g of oxygen gas is given. Calculate the following: (i) moles (ii) molecules (iii) volume in dm^3 at STP (iv) density of oxygen gas at STP (v) relative density of oxygen.

(i) 32 g of oxygen = 1 mol

$$8\ \text{g} = \frac{8\ \text{g}}{32\ \text{g mol}^{-1}}$$

$$= 0.25\ \text{mol}$$

(ii) molecules = $0.25\ \text{mol} \times 6.02 \times 10^{23}$ molecules mol^{-1}

$= 1.505 \times 10^{23}$ molecules

(iii) volume at STP = $0.25\ \text{mol} \times 22.4\ \text{dm}^3\ \text{mol}^{-1}$

$= 5.6\ \text{dm}^3$

(iv) density at STP

$$= \frac{\text{mass}}{\text{volume at STP}}$$

$$= \frac{8\ \text{g}}{5.6\ \text{dm}^3}$$

$$= 1.428\ \text{gdm}^{-3}$$

(v) relative density of oxygen

$$= \frac{1}{2} \times \text{relative molecular mass of the gas}$$

$$= \frac{1}{2} \times 32$$

$$= 16$$

Change of Volumes with Temperatures and Pressures

3. The volume of a certain mass of gas collected over water is 227 cm^3 at 12 °C and 762 mmHg. Vapour pressure of water at 12 °C is 10.5 mmHg. What would be the volume of dry gas at 15 °C and 757 mmHg?

$$P_{\text{total}} = p_{\text{dry gas}} + p_{H_2O}$$

$$p_{\text{dry gas}} = P_{\text{total}} - p_{H_2O}$$

$$= 762\ \text{mmHg} - 10.5\ \text{mmHg}$$

$$= 751.5\ \text{mmHg}$$

Initial state	Final state
P_1 = 751.5 mmHg	P_2 = 757 mmHg
T_1 = 12 °C + 273	T_2 = 15 °C + 273
= 285 K	= 288 K
V_1 = 227 cm^3	V_2 = ?

According to the combined gas law equation,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

$$V_2 = \frac{751.5\ \text{mmHg} \times 227\ \text{cm}^3 \times 288\text{K}}{285\ \text{K} \times 757\ \text{mmHg}}$$

$$V_2 = 227.7\ \text{cm}^3$$

Application of Gas Law to Problems Involving Chemical Reactions

4. 10 g of calcium carbonate is treated with dilute hydrochloric acid. The liberated gas measured at 27 °C and 750 mmHg is 1.85 dm^3. Find the percentage purity of calcium carbonate. (C= 12,O=16, H= 1, Ca= 40)

Change the volume to STP.

	Initial state		Final state
P_1	$= 750$ mmHg	P_2	$= 760$ mmHg
T_1	$= 27$ °C $+ 273$	T_2	$= 0$ °C $+ 273$
	$= 300$ K		$= 273$ K
V_1	$= 1.85\ \text{cm}^3$	V_2	$= ?$

According to the combined gas law equation,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

$$V_2 = \frac{750\ \text{mmHg} \times 1.85\ \text{cm}^3 \times 273\text{K}}{300\ \text{K} \times 760\ \text{mmHg}}$$

$$V_2 = 1.661\ \text{dm}^3 \text{ at STP}$$

$CaCO_3(s)$	+	$2HC1(aq)$	$\rightarrow$	$CaCl_2(aq)$	+	$H_2O(l)$	+	$CO_2\ (g)$
1 mol								1mol
(40 +12 + 48)								(12+32)
100 g								44 g or 22.4 dm^3 at STP

At STP 22.4 dm^3 of CO_2 is obtained from 100 g of $CaCO_3$.

$$1.661 dm^3 \dots\dots\dots \quad = \quad \frac{1.661\ dm^3}{22.4\ dm^3} \times 100\ g$$

$$= \quad 7.415\ g$$

$$\therefore \text{Percentage purity of } CaCO_3 \quad = \quad \frac{7.415}{10} \times 100$$

$$= \quad 74.15\ \%$$

Problems of Gaseous Diffusion

5. What is the relative rate of diffusion of hydrogen and oxygen? (H=1, O=16)

$M_{O2} = 2 \times 16 = 32\ g\ mol^{-1}$
$M_{H2} = 2 \times 1 = 2\ g\ mol^{-1}$

$$\frac{r_{H_2}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}}$$

$$\frac{r_{H_2}}{r_{O_2}} = \sqrt{\frac{32}{2}}$$

$$\frac{r_{H_2}}{r_{O_2}} = 4$$

Hydrogen diffuses 4 times faster than oxygen.

6. Helium gas diffuses 4 times as fast as an unknown gas. What is the relative molecular mass of the gas ? (He = 4)

$$\frac{r_{He}}{r_x} = \sqrt{\frac{M_x}{M_{He}}}$$

$$4 = \sqrt{\frac{M_x}{4}}$$

$$16 = \frac{M_x}{4}$$

$$M_X = 64\ g\ mol^{-1}$$

Relative molecular mass = 64

Problems of Dalton's Law of Partial Pressures

7. A gas occupies 500 cm^3 at 17 °C and 785 mmHg when it is collected over water. The vapour pressure of water at this temperature is 15 mmHg. What is the pressure of the dry gas at 17 °C?

$$\begin{aligned} P_{\text{total}} &= P_{\text{dry gas}} + P_{H_2O} \\ P_{\text{dry gas}} &= P_{\text{total}} - P_{H_2O} \\ &= 785 \text{ mmHg} - 15 \text{ mmHg} \\ &= 770 \text{ mmHg} \end{aligned}$$

8. Total pressure of oxygen and acetylene gas storage tank is 7520 mmHg. The partial pressure of oxygen is 3400 mmHg. What is the pressure of acetylene?

$$\begin{aligned} P_{\text{total}} &= p_{O_2} + p_{C_2H_2} \\ \therefore p_{C_2H_2} &= P_{\text{total}} - p_{O_2} \\ &= 7520 \text{ mmHg} - 3400 \text{ mmHg} \\ &= 4120 \text{ mmHg} \end{aligned}$$

SUMMARY

This chapter is concerned with the gaseous states of matter and the laws governing their behaviour. The fundamental properties of gases include mass, volume, pressure, and temperature. The gas laws include ; Boyle's law, Charles' law , Combination of Boyle's law and Charles' law, Gay-Lussac's law of combining volumes of gases, Avogadro's theory, Graham's law of gaseous diffusion, and Dalton's law of partial pressures. Standard temperature and pressure (STP) is defined as 0 °C or 273 K of temperature and 760 mm Hg or 1 atmosphere (1 atm) of pressure. One mole of every gas occupies 22.4 dm^3 at STP and is regarded as molar volume . Relative density of a gas is equivalent to half of the relative molecular mass of the gas.

Questions and Problems

1. Fill in the blanks with suitable word, phrase of numerical figure.
   - (a) STP means .... The standard conditions chosen are.......... and.........
   - (b) 100 °C is equivalent to ....K.
   - (c) One mole of any gas occupies .... at.......... .
   - (d) One gram of hydrogen gas occupies .... at STP. (H= 1)
   - (e) The combined gas law equation is ....
2. Choose the correct term or terms given in the brackets.
   - (a) Boyle's law can be expressed as($V= 1/P$,$PV=$ constant, $P/V=$ constant).
   - (b) Graham's law of gaseous diffusion can be symbolized as .

     ($r\sqrt{d}$ = constant, $r_1\sqrt{d_1} = r_2\sqrt{d_2}$, $r = 1/\sqrt{d}$)

(c) Dalton's law of partial pressures can be used to the gas mixture of (Cl_2 and H_2, He and Ne, NH_3 and HCl).

(d) One molecule of hydrogen gas weighs (1 g, 2 g, 2 amu).

(e) 100 cm^3 of CO_2 diffuses through a porous pot in 50 s. The same volume of propane gas C_3H_8 would take (10s, 50s, 60s) to diffuse through the same pot. (C=12, H=1, O=16)

3. Which Law represents each of the following statements?

(a) A volume of gas expands when it is heated.

(b) When the volume of a gas is compressed at the same temperature, the pressure of the gas will increase.

(c) The same volume of different gases at constant temperature and pressure contains the same number of molecules.

(d) A lighter gas diffuses faster than the heavier one.

4. State TRUE or FALSE for the following statements.

(a) Equal amount of moles of the gases occupies the same volume at the same temperature and pressure.

(b) The pressure of the gas in a closed container will increase when it is heated.

(c) 18 g of liquid water occupies 22.4 dm^3 at STP. (H = 1, O=16)

(d) The relative density of the gas is directly proportional to its relative molecular mass.

(e) One molecule of hydrogen weighs 2 g. (H=1)

5. Give a short answer for each of the following questions.

(a) Which one diffuses faster in each of the following pairs under comparable condition? (i) He and Ne (ii) $^{235}UF_6$ and $^{238}UF_6$ (iii) N_2 and CO

(b) What will be the volume of hydrogen chloride gas when 100 cm^3 of hydrogen and 50 cm^3 of chlorine are mixed? (All gases are measured at the same conditions).

(c) How many molecules are there in 5.6 dm^3 of hydrogen at STP?

(d) 7 g of nitrogen gas occupies 5.6 dm^3 at STP. What is the relative molecular mass of the nitrogen?

(e) What is the mass of CO_2 enclosed in 5.6 dm^3 at STP?

6. A gas with the relative density of 22 is given.

(a) Find the relative molecular mass.

(b) What is the mass of one mole of the gas in g?

(c) What volume at STP would the gas occupy by 22 g of that gas?

7. A certain mass of gas occupies 942 cm^3 at 22 °C. At what temperature in °C will the gas occupy 311 cm^3 under the same pressure?

8. 0.21 g of a gas occupies a volume of 186 cm^3 measured over water at 766 mmHg and 23 °C. Vapour pressure of water at 23 °C is 21.1 mmHg. What is the approximate molecular mass of the gas?

9. If it takes 1minute for 50 cm^3 of oxygen to diffuse through a pinhole, how long will it take for the same volume of hydrogen to diffuse through the same hole?

10. Match each of the items given in **List A** with the appropriate correct item shown in **List B**

List A	**List B**
(a) Gas pressure	(i) Avogadro's theory
(b) One mole of substance	(ii) ½ Relative Molecular Mass
(c) One mole of gas	(iii) 0 K
(d) $V \propto n$ (at P, T = constant)	(iv) 22.4 dm^3 at STP
(e) Relative density of a gas	(v) force per unit area
(f) Absolute zero temperature	(vi) 6.02×10^{23} particles

11. Which law represents relationship between temperature and volume?

12. What do you think, a volume of given mass of gas when heated, pressure of the gas increases with the increase of temperature ?

13. How many grams are there in

(a) 5 moles of carbon dioxide , CO_2 ? (C = 12, O = 16)

(b) 0.1 mole of calcium carbonate $CaCO_3$? (Ca = 40, C = 12, O = 16)

(c) 0.25 mole of oxygen atoms ? (O = 16)

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CHAPTER 3

STOICHIOMETRY

3.1 Stoichiometry

That part of Chemistry which deals with the quantities of substances taking part in chemical reactions is called stoichiometry. Stoichiometry is based on the laws and principles of chemistry, primarily on:

1. Conservation of mass
2. Relative masses of atoms
3. The concept of the mole

The law of conservation of mass as applied to chemical reactions states that the total mass of the products formed must be equal to the total mass of the reactants. The masses of the substances taking part in a chemical reaction can be expressed in terms of the masses of their constituent atoms. In the grade 9 course we have dealt with the idea of relative masses of atoms and hence the relative masses of the elements in a compound. Consequent to these ideas, we have learned that quantities can be expressed in terms of numbers of atoms and molecules and this has led to the concept of the Avogadro number and the mole. This concept is fundamental to all aspects of stoichiometry.

What does stoichiometry involve?

Stoichiometry involves

1. Prediction of the quantities of materials required to produce a given quantity of products or, vice versa, the determination of the quantity of product which may be obtained from given quantities of reactants.
2. Interpreting the results of a chemical analysis.
3. Choosing the most economical way of carrying out a chemical reaction on a commercial scale.
4. Preparing solutions containing the required concentrations of dissolved substances.

3.2 Formula Masses (Formula Weights)

A formula is used to express the composition of a substance and it denotes the relative numbers of atoms of the respective elements in a molecule or formula unit of the substance. The masses of the molecules or formula units relative to ^{12}C are expressed by their molecular masses or formula masses respectively. These are computed by simply adding the relative atomic masses of each and every atom in the molecule or formula unit.

3.3 Formulae and Percent Composition

If the formula of a compound is known, the percent composition of the element present in the compound may be calculated. For this calculation, knowledge of the relative atomic masses (or atomic weights) is essential.

Example: Calculate the percent composition of magnesium nitrate. (Relative atomic masses of Mg = 24.31, N = 14.01, O=16)

In magnesium nitrate, $Mg(NO_3)_2$ each formula unit contains one Mg atom, two N atoms, and six O atoms.

$$\text{Formula mass} = 24.31 \text{ amu} + (2 \times 14.01) \text{ amu} + (6 \times 16)\text{amu}$$
$$= 148.33 \text{ amu}$$

$$\therefore \text{Percent of Mg} = \frac{24.31}{148.33} \times 100$$
$$= 16.39\ \%\ \text{Mg}$$

$$\text{Percent of N} = \frac{2 \times 14.01}{148.33} \times 100$$
$$= 18.89\ \%\text{N}$$

$$\text{Percent of O} = \frac{6 \times 16}{148.33} \times 100$$
$$= 64.72\ \%\ \text{O}$$

3.4 The Mole and the Millimole

A chemical formula may be used to refer to one atom, one molecule, one formula unit or to a mole of atoms, molecules or formula units.

The quantity of a substance in terms of moles may easily be determined if the mass of the pure substance in grams is known.

1 mole of the substance = Relative molecular mass expressed in grams

$$\text{Quantity of substance in moles} = \frac{\text{mass of substance in grams}}{\text{relative molecular mass}}$$

Molar mass = mass in grams per mole of a substance

= relative molecular mass expressed in g mol^{-1}

Example: How many moles of hydrogen gas are there in 27.0 g of hydrogen?

$$\text{moles of hydrogen} = \frac{27}{2.016}$$
$$= 13.4 \text{ mol } H_2$$

For experimental work It is sometimes convenient to use the millimole (mmol) as unit. This corresponds to 0.001 mole.

$$\text{Quantity of substance in millimoles} = \frac{\text{mass of substance in milligrams}}{\text{relative molecular mass}}$$

Molar mass = mass in milligrams per millimole of a substance

= Relative molecular mass expressed in mg mmol^{-1}

It is evident that 1 mole is equivalent to 1000 millimoles.

3.5 Chemical Equations in Stoichiometry

In every chemical reaction between a given set of reactants under a given set of conditions the same products will always be formed. Using such equations it is possible to predict the quantities of products which will be formed from the quantities of reactants used. To be useful in this manner,

1. the chemical equation must be balanced
2. the physical state of each of the reactants and products must be indicated by use of proper abbreviations in parentheses after the formulae: (s) for solid, (l) for liquid, (g) for gas, (aq) for aqueous solution.

Example : 4 g of a mixture of calcium carbonate and sand is treated with an excess of dilute hydrochloric acid, and 0.880 g of carbon dioxide is produced. What is the percentage of calcium carbonate in the original mixture?

The balanced chemical equation is

$$CaCO_3(s) + 2HCl(aq) \rightarrow CO_2(g) + CaCl_2(aq) \quad H_2O\,(l)$$

$CaCO_3(s)$	$CO_2(g)$
1mol	1mol
40 + 12 +(3 x 16)	12 +(2 x 16)
100 g	44 g

1 mol of CO_2 is expected from 1 mol of $CaCO_3$.

$\frac{0.88}{44}$ mol .... $\frac{0.88}{44}$ mol of $CaCO_3$

or $\frac{0.88}{44}$ x 100 g of $CaCO_3$

or 2.00 g of $CaCO_3$

$$\text{Percent } CaCO_3 \text{ in mixture} = \frac{2.00\text{ g of } CaCO_3}{4.00\text{ g of mixture}} \times 100$$

$$= 50.0\,\%$$

3.6 Limiting Quantities

When an experiment is actually conducted the relative quantities of the reactants present may differ from those required by the balanced chemical equation. If the reacting mixture contains one of the reactants in lesser quantity than is required by the equation, the reaction will simply stop when the reactant in lesser quantity is exhausted. The quantities of products formed will then be determined by the reactant present in lesser quantity.

Example: How many grams of sulphur would be precipitated on mixing 5 dm^3 of sulphur dioxide with 12 dm^3 of hydrogen sulphide if both gases were originally at 756 mm Hg pressure and 25 °C? (S=32)

$$\begin{array}{lllll} 2H_2S\,(g) & + \; SO_2\,(g) & \longrightarrow & 2H_2O\,(1) & + \; 3S(s) \\ 2\text{ mol} & \quad 1\text{ mol} & & & \quad 3\text{ mol} \\ 2\text{ vol} & \quad 1\text{ vol} & & & \end{array}$$

SO_2 gas is limiting quantity.

Initial state	**Final state(at STP)**
$V_1 = 5\ dm^3$	$V_2 = ?$
$P_1 = 756\ mmHg$	$P_2 = 760\ mmHg$
$T_1 = 25+273 = 298\ K$	$T_2 = 273\ K$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

$$V_2 = \frac{756\ mmHg \times 5\ dm^3 \times 273\ K}{760\ mmHg \times 298\ K} = 4.5564\ dm^3 \text{ at STP}$$

$\therefore$ Volume of SO_2 = 4.5564 dm^3 at STP

$$\therefore \text{ mol of } SO_2 = \frac{4.5564\ dm^3}{22.4\ dm^3\ mol^{-1}} = 0.2034\text{ mol}$$

1 mol of SO_2 on complete reaction with H_2S deposits 3 mol of S.

0.2034 mol .... 0.2034 x 3 = 0.6102 mol of sulphur

mass of sulphur in grams = amount (mol) x molar mass (g mol^{-1})

= 0.6102 mol x 32 g mol^{-1} = 19.53 g of sulphur

3.7 Stoichiometry in Solution: Volumetric Analysis

Molarity

The molarity (M) of a solution is the quantity in moles of the solute dissolved in one cubic decimetre (1 dm^3) of the solution.

A molar solution of a compound is one which contains one mole (the relative molecular mass in grams or the formula mass in grams for those compounds having giant structure) of the compound in one cubic decimetre (1 dm^3) of the solution. Note that it is one cubic decimetre of solution, not solvent, that is specified.

In common analytical use the formula usually accepted for a compound having giant structure is assumed to be molecular formula of that compound. Consequently the formula mass is used in place of relative molecular mass.

The formula mass or formula weight of a substance is the sum of the atomic masses or atomic weights of the elements in the formula, each taken the number of times the element occurs. Hence, a formula mass or formula weight gives the mass of one formula unit in atomic mass units.

We shall use the term molar solution for all formal solution in this text.

Thus, since sulphuric acid has a relative molecular mass of 98, molar sulphuric acid solution contains 98 g of pure sulphuric acid in one cubic decimetre of solution.

Similarly, molar sodium hydroxide solution contains 40 g of sodium hydroxide in one cubic decimetre of solution. A 0.5 molar solution of sodium hydroxide will obviously contain 20g of the solute in one cubic decimetre of solution.

In the case of sodium chloride which has a giant structure, the formula mass of the formula unit NaCl is used. Thus, a molar sodium chloride solution contains 58.5 g of sodium chloride in one cubic decimetre of solution.

1 mole of solute dissolved in 1 dm^3 of solution will give a solution of 1 M.

Since, 1 mole = 1000 millimoles

and $1\ dm^3 = 1000\ cm^3$

the above solution contains 1 millimole solute in 1 cm^3 of the solution.

Hence, molarity is also represents the quantity in millimoles solute per cm^3 of solution.

Example 1: Calculate the molarity of a solution prepared by dissolving 4.0 moles of solute in sufficient solvent to make 2.0 dm^3 of solution.

$$\text{molarity} = \frac{4\ \text{mol of solute}}{2\ dm^3\ \text{of solution}}$$

$$= 2\ M$$

Example 2: Calculate the molarity of a solution prepared by adding 100 g of pure sodium carbonate to sufficient water to make 1.5 dm^3 of solution.

$$\text{Relative molecular mass of } Na_2CO_3 = 2 \times 23 + 12 + 3 \times 16$$

$$= 106$$

$$\therefore 100\ g\ Na_2CO_3 = \frac{100}{106}\ \text{mol}$$

$$= 0.9654\ \text{mol}$$

$$\therefore \text{Molarity of solution} = \frac{0.9654}{1.5}\ \text{mol dm}^{-3}$$

$$= 0.6436\ M$$

Example 3 : What volume of 2.0 M sulphuric acid is required to react with 5.0 g of zinc?

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

1 mol 1 mol

$$5g\ \text{of}\ Zn = \frac{5}{65.4}\ \text{mol}$$

$$= 0.0765\ \text{mol of } Zn$$

$\therefore$ Amount of H_2SO_4 required= 0.0765 mol

2 mol of H_2SO_4 is present in 1 dm^3 or 1000 cm^3 of 2 M H_2SO_4.

$$\therefore 0.0765\ .... \frac{1000 \times 0.0765}{2}\ cm^3\ \text{of}\ 2\ M\ H_2SO_4$$

or 38.25 cm^3 of 2 M H_2SO_4

Dilution of a solution

When a given aqueous solution is diluted with water the quantity or mole of the solute does not change but the concentration or molarity does change. Such changes in concentration can be easily calculated from the definition of molarity.

Example: How many cubic centimetres of a 0.1 M solution must be diluted with water to make 2.0 dm^3 of 0.025 M solution?

2.0 dm^3 of 0.025 M solution must be made.

2.0 dm^3 of 0.025 M solution must contain 2 x 0.025 mole or 0.050 mole solute.

Now,

0.1 mol solute is contained in 1000 cm^3 of 0.1 M solution.

$\therefore$ 0.050 mol........................... $1000 \times \frac{0.050}{0.1}$ cm^3 of 0.1 M solution.

or 500 cm^3

Hence, 500 cm^3 of 0.1 M solution must be taken and diluted to 2 dm^3.

Alternative method

When a solution is diluted, the concentration decreases and the concentration of the resultant solution is inversely proportional to its final volume. Generally, for the same amount of solute,

$$\text{concentration} \propto \frac{1}{\text{volume}}$$

Provided we keep the units of concentration and volume unchanged.

$$\text{Concentration x volume} = \text{constant}$$

$$\therefore C_1V_1 = C_2V_2 = \text{constant}$$

If concentration is in terms of molarity and volume in cm^3

$$M_1V_1 = M_2V_2$$

$$0.1\,M \times V_1\,cm^3 = 0.025\,M \times 2000\,cm^3$$

$$\therefore V_1 \text{ in } cm^3 = \frac{0.025 \times 2000}{0.1}$$

$$= 500\,cm^3$$

Note: This formula $M_1V_1 = M_2V_2$ may be used for dilution of a solution where the total amount of solute does not change.

Example: If 20.0 cm^3 of 1.0 M sulphuric acid and 60.0 cm^3 of 0.2 M sulphuric acid are mixed what will be the molarity of the final solution?

We shall first find out the total quantity of sulphuric acid in millimoles (mmol) which will be present in the mixed solution. This will be the sum of millimoles sulphuric acid present in each solution.

Since molarity also expresses concentration in mmol cm^{-3},

1 cm^3 of 1.0 M H_2SO_4 contains 1 mmol H_2SO_4
20cm^3.......................... 20 x 1 mmol H_2SO_4
or 20 mmol H_2SO_4
60 cm^3 of 0.2 M H_2SO_4 contains 60 × 0.2 mmol H_2SO_4
or 12 mmol H_2SO_4
$\therefore$ Total mmol H_2SO_4 = 20 + 12
or 32 mmol H_2SO_4

This quantity is present in a total volume of (20 + 60) cm^3 or 80 cm^3

$$\therefore \text{ Concentration in mmol cm}^{-3} = \frac{32}{80} \text{ mmol cm}^{-3}$$

$$\therefore \text{ Molarity} = 0.40 \text{ M}$$

3.8 Terms and Units used in Volumetric Analysis

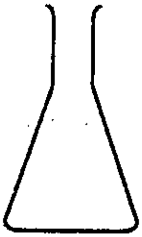
Titration

The term "titration" is used for the procedure in which a solution of a standard reagent (reactant)is added to a specific volume of a solution of unknown molarity. The volume of standard reagent solution which just reacts completely with the unknown solution is measured carefully. From this measurement the amount in moles of standard reagent required for the reaction can be calculated. Knowing the equation for the reaction we can determine the amount in moles of the other reactant. Titrations are possible if the following conditions are fulfilled.

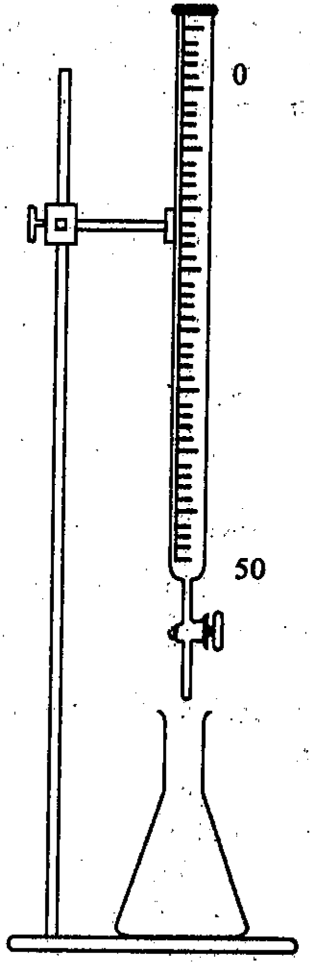
1. The standard reagent must react completely with the unknown solution.
2. The reaction must be reasonably fast.
3. The point at which the two reactants have just completely reacted, that is, the equivalence point must be easily detectable.
4. The equation for the chemical reaction must be exactly known for easy determination of the stoichiometric proportions in which the reactants react.

burette

pipette



conical flask



apparatus for titration

A weighed quantity of the unknown substance or a precisely known volume of the solution of the unknown, usually measured out by a pipette is placed in a conical flask or beaker.

A solution of known concentration is then added gradually from a burette. This addition is continued until the exact mole ratio required by the balanced chemical equation is reached. To detect this equivalence point suitable indicators (dyes), which change colour at this point are added to the solution. For example, the dye phenolphthalein is colourless in acid, and red in alkali solutions. Its colour changes from one to the other at the equivalence point. Methyl orange is red in acid and yellow in alkali.

The reaction between sulphuric acid and sodium hydroxide is represented by the following equation.

$$H_2SO_4(aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$$

This shows that one mole of sulphuric acid reacts with two moles of sodium hydroxide and so it follows that

1 dm^3 of M sulphuric acid reacts with 1 dm^3 of 2M sodium hydroxide

or

1 dm^3 of M sulphuric acid reacts with 4 dm^3 of 0.5 M sodium hydroxide.

Consider the general reaction in which compounds A and B react in the ratio of x moles of A to y moles of B. This reaction may be represented as

$$xA + yB \longrightarrow \text{products}$$

Suppose that in a titration V_A cm^3 of solution A which has molarity M_A reacts with V_B cm^3 of solution B whose molarity is M_B.

Since 1000 cm^3 of solution A contains M_A moles of A

V_A cm^3 of solution A contains $\frac{M_A \times V_A}{1000}$ moles of A

Similarly, since 1000 cm^3 of solution B contains M_B moles of B

V_B cm^3 of solution B contains $\frac{M_B \times V_B}{1000}$ moles of B

Therefore, the ratio of moles of A and B reacting is

$$\frac{x}{y} = \frac{\frac{M_A \times V_A}{1000}}{\frac{M_B \times V_B}{1000}}$$

which on rearranging

$$xM_BV_B = yM_AV_A$$

In any titration, only one of these variables is unknown and it may be calculated using this relationship.

Example: 1.0 dm^3 of sulphuric acid solution required 4.0 dm^3 of 0.1 M potassium hydroxide to neutralize it. Calculate the molarity of sulphuric acid.

$$\underset{1\text{mol}}{H_2SO_4\,(aq)} + \underset{2\text{ mol}}{2\,KOH\,(aq)} \longrightarrow K_2SO_4\,(aq) + 2H_2O\,(l)$$

For acid

$x = 1$ mol

$M_A = ?$

$V_A = 1.0\ \text{dm}^3$

For base

$y = 2$mol

$M_B = 0.1$ M

$V_B = 4.0\ \text{dm}^3$

$$x\,M_B\,V_B = y\,M_A\,V_A$$

$$M_A = \frac{xM_BV_B}{yV_A} = \frac{1\ \text{mol} \times 0.1\ \text{M} \times 4.0\ \text{dm}^3}{2\ \text{mol} \times 1.0\ \text{dm}^3} = 0.2\ \text{M}$$

Standard solution

The reagent of exactly known concentration that is used in a titration is called a standard solution.

The concentration of a standard solution is established either directly or indirectly.

1. by dissolving a carefully weighed quantity of the pure reagent and diluting to an exactly known volume,
2. by titrating a solution containing a weighed quantity of pure compound with the reagent solution.

In either method, a highly purified chemical compound called a primary standard is required as the reference material.

Primary standard

The accuracy of a volumetric analysis depends upon the primary standard. A primary standard is a highly pure and stable compound, used to establish the concentration of the standard solution. Important requirements for a substance to serve as a good primary standard include the following.

(1) Highest purity

(2) Stability

(3) Absence of hydrate water

(4) Ready availability at reasonable cost

(5) Reasonably high molecular mass

The requirements 1, 2 and 3 are important because the compound to be used as standard will conform to the composition prescribed by the molecular formula only if these requirements are met.

Standardization

The process by which the concentration of a standard solution is determined volumetrically by the use of a primary standard is called standardization.

Equivalence point and end point

In every titration the objective is to add the standard solution in an amount that is chemically equivalent to the substance with which it reacts. This condition is achieved at the equivalence point.

The equivalence point in a titration is a theoretical concept. In actual fact, its position can be estimated only by observing physical changes associated with the equivalence point. These changes occur at the end point of the titration.

A common method of end point detection in volumetric analysis involves the use of an indicator that exhibits a change in colour as a result of concentration changes near the equivalence points.

3.9 Standard Solutions in Acid-Base Titrations

For volumetric analysis a standard solution is required as a starting point. Actually few compounds are suitable for the direct preparation of standard solution. Some compounds, such as, sodium hydroxide, potassium hydroxide, and concentrated sulphuric acid absorb water from air. For this reason, these substances cannot be weighed out accurately.

Sodium hydroxide and potassium hydroxide also react with carbon dioxide from the air.

$$2NaOH(s) + CO_2(g) \longrightarrow Na_2CO_3(s) + H_2O(l)$$

$$2KOH(s) + CO_2(g) \longrightarrow K_2CO_3(s) + H_2O(l)$$

A compound which is commonly used for the direct preparation of a standard solution is anhydrous sodium carbonate. It is best prepared from sodium hydrogencarbonate of high purity. This is done by heating the sodium hydrogencarbonate to constant mass, which ensures completion of the decomposition.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$$

The anhydrous sodium carbonate so obtained is very pure and can be regarded as a primary standard if prepared just prior to its use. It can be used in ordinary weighings with no appreciable change in composition.

The preparation of a standard solution of sulphuric acid cannot be done directly because concentrated sulphuric acid absorbs water rapidly from the air and is never reliably pure. A solution is prepared which is a little above 0.1 M in concentration and it is then standardized against a primary standard and diluted with distilled water to exactly 0.1 M.

A molar solution of sulphuric acid contains 98 g of pure acid in 1 dm^3 of solution. So the 0.1 M acid contains 9.8 g of the acid in 1dm^3. The concentrated acid has a density of about 1.8 g cm^{-3}, so 10 g of it will occupy about 5.6 cm^3.

Thus, the preparation of a standard solution of sulphuric acid involves

(a) diluting a concentrated solution of sulphuric acid to an approximate molarity, and

(b) the standardization of the dilute acid solution using a previously standardized alkali solution.

3.10 Calculation

Example 1: Two drops of phenolphthalein solution was added to 10.00 cm^3 of hydrochloric acid solution , and this solution was titrated with 0.10 M sodium hydroxide. When 7.5 cm^3 of the sodium hydroxide solution had been added,part of the solution turned pink, but the colour disappeared upon mixing the solution. From this point onwards the sodium hydroxide solution was added dropwise with thorough mixing of the solution after each addition, until a lasting pink colour was developed.The equivalence point is now reached and the volume of 0.10 M sodium hydroxide added was 8.00 cm^3. What was the concentration of the hydrochloric acid solution?

$$\underset{1\ \text{mol}}{NaOH\,(aq)} + \underset{1\ \text{mol}}{HCl\,(aq)} \longrightarrow NaCl\,(aq) + H_2O\,(l)$$

The added NaOH in millimoles = 8.0 cm^3 x 0.1 mmol cm^{-3}

= 0.8 mmol

This base will neutralize an equivalent amount of HCl, i.e.,

0.8 mmol of HCl

Hence, 0.8 mmol of HCl must have been present in 10 cm^3 of the HCl solution.

$$\therefore \text{Molarity of HCl} = \frac{0.8\ \text{mmol HCl}}{10\ \text{cm}^3}$$

$$= 0.080\ \text{M}$$

Example 2: Vinegar contains an organic acid, acetic acid (ethanoic acid), $HC_2H_3O_2$. When 6 g of vinegar was titrated with 0.10 M sodium hydroxide, 40.00 cm^3 of this base had to be added to reach the equivalence point. What is the percentage by mass of acetic acid in this sample of vinegar? [H = 1, C = 12, O = 16]

$HC_2H_3O_2$ (aq) + NaOH(aq) $\longrightarrow$ $NaC_2H_3O_2$(aq) + H_2O(l)
1 mol 1mol

amount (mmol) of NaOH = molarity (mmol cm^{-3}) × volume (cm^3 of solution)
= 0.10×40.00
= 4 mmol

By equation, 1 mol of NaOH = 1 mol of $HC_2H_3O_2$
4 mmol of NaOH = 4 mmol of $HC_2H_3O_2$
= 4×10^{-3} mol
= 0.004 mol

molar mass of $HC_2H_3O_2$ = $(1 \times 4) + (12 \times 2) + (16 \times 2)$
= $4 + 24 + 32$
= 60 g mol^{-1}

mass of $HC_2H_3O_2$ = amount of $HC_2H_3O_2$ (mol) × molar mass (g mol^{-1})
= 0.004×60
= 0.24 g

6 g of vinegar contains 0.24 g of $H_3C_2H_3O_2$.

100 g of vinegar contains $= \dfrac{0.24 \times 100}{6}$ %
= 4 %

Example 3: 25 cm^3 of 0.1 M sodium carbonate solution required 24 cm^3 of sulphuric acid to neutralize it.

(i) Calculate the molar concentration of sulphuric acid.
(ii) What volume of water should be added to 24 cm^3 of sulphuric acid so that the concentration becomes exactly 0.1 M?

Na_2CO_3 (aq) + H_2SO_4 (aq) $\longrightarrow$ Na_2SO_4 (aq) + H_2O (l) + CO_2 (g)
1 mol 1 mol

Amount (mmol) of Na_2CO_3 = molarity (mmol cm^{-3})× volume (cm^3 of solution)
= 0.1×25
= 2.5 mmol

By equation, 1 mol of Na_2CO_3 = 1 mol of H_2SO_4.
$\therefore$ 2.5 mmol of Na_2CO_3 = 2.5 mmol of H_2SO_4.

Molarity of H_2SO_4 $= \dfrac{\text{amount of } H_2SO_4 \text{ (mmol)}}{\text{volume of } H_2SO_4 \text{ (cm}^3\text{)}}$
$= \dfrac{2.5 \text{ mmol}}{24 \text{ cm}^3}$
= 0.1042 M

(ii) Before dilution
M_1 = 0.1042 M
V_1 = 24 cm^3

After dilution
M_2 = 0.1 M
V_2 = ?

$$M_1 V_1 = M_2 V_2$$

$$V_2 = \frac{M_1 V_1}{M_2}$$

$$= \frac{0.1042 \text{ x } 24}{0.1}$$

$$= 25 \text{ cm}^3$$

Volume of water $= V_2 - V_1 = 25 - 24 = 1 \text{ cm}^3$

Example 4: 25 cm^3 of sodium carbonate solution required 23.5 cm^3 of 0.5 M hydrochloric acid solution to neutralize it. Calculate the molarity of sodium carbonate solution and convert the concentraction into g dm^{-3}. [C = 12, O = 16, Na =

$$Na_2CO_3\,(aq) + 2\,HCl\,(aq) \longrightarrow 2\,NaCl(aq) + H_2O\,(l) + CO_2\,(g)$$

1 mol 2 mol

Amount (mmol) of HCl $=$ molarity (mmol cm^{-3})× volume (cm^3 of solution)

$= 0.5 \times 23.5$

$= 11.75$ mmol of Na_2CO_3

By equation, 2 mol of HCl = 1 mol of Na_2CO_3

11.75 mmol of HCl $= \frac{11.75}{2} = 5.875$ mmol

$$\text{Molarity of } Na_2CO_3 = \frac{\text{amount of } Na_2CO_3 \text{ (mmol)}}{\text{volume of } Na_2CO_3 \text{ (cm}^3\text{)}}$$

$$= \frac{5.875 \text{ mmol}}{25 \text{ cm}^3}$$

$$= 0.2351 \text{ M of } Na_2CO_3$$

molar mass of $Na_2CO_3 = (2 \times 23) + 12 + (16 \times 3)$

$= 46 + 12 + 48$

$= 106 \text{ g mol}^{-1}$

Concentration of Na_2CO_3 in g dm^{-3} = molarity (mol dm^{-3}) × molar mass (g mol^{-1})

$= 0.2351 \text{ mol dm}^{-3} \times 106 \text{ g mol}^{-1}$

$= 24.91 \text{ g dm}^{-3}$

Example 5: 3 g of a mixture of sodium carbonate and sodium chloride were made up to 250 cm^3 of solution. 25 cm^3 of this solution required 21 cm^3 of 0.1050 M hydrochloric acid for neutralization. Calculate the percentage by mass of sodium chloride in the mixture. [C = 12, O = 16, Na = 23]

Only Na_2CO_3 in mixture neutralizes with HCl.

$$Na_2CO_3(aq) + 2HCl\,(aq) \longrightarrow 2\,NaCl(aq) + H_2O(1) + CO_2\,(g)$$

1 mol 2 mol

Amount (mmol) of HCl = molarity (mmol cm^{-3}) × volume (cm^3 of solution)

$= 0.1050 \times 21$

$= 2.205$ mmol

By equation, 2 mol of HCl = 1 mol of Na_2CO_3

2.205 mmol of HCl = $\frac{2.205}{2}$ = 1.1025 mmol of Na_2CO_3

25 cm^3 of mixture solution contains = 1.1025 mmol of Na_2CO_3

250 cm^3 of mixture solution contains = $1.1025 \times \frac{250}{25}$ = 11.025 mmol

= 11.025×10^{-3} mol

= 0.011025 mol

molar mass of Na_2CO_3 = $(23 \times 2) + 12 + (16 \times 3)$

= 46 + 12 + 48

= 106 g mol^{-1}

mass of Na_2CO_3 = amount of Na_2CO_3 (mol) × molar mass (g mol^{-1})

= 0.011025 mol × 106 g mol^{-1}

= 1.169 g

mass of NaCl = (3 – 1.169) g

= 1.831 g

Percentage of NaCl = $\frac{1.831}{3}$ x 100 %

= 61. 033 %

3.11 Calculations involving formulae and chemical equations

There are two kinds of formulae (i) the simplest or empirical formula and (ii) the molecular formula.

The simplest formula or the empirical formula gives us only the relative number of atoms of different elements in a compound. The molecular formula tells us show many atoms of various elements exist in an individual molecule. Usually the empirical formula is calculated first, since it is obtained directly from the chemical analysis of the compound. Other data are needed to determine the molecular formula.

When the empirical formula of a compound is known, the percentages by mass of each of the elements in a compound can be calculated. For example, let us calculate the percentages by mass of calcium, oxygen and carbon present in calcium carbonate.

The empirical formula of calcium carbonate is $CaCO_3$.

The formula mass of $CaCO_3$ is 40 + 12 + (3 x 16)= 100.

Out of 100 units of mass of $CaCO_3$, 40 units of mass are from calcium. That is, the fractional mass of calcium is $\frac{40}{100}$. Therefore the percentage by mass of Ca in $CaCO_3$ = $\frac{40}{100} \times 100 = 40$ %. Similarly the percentage by mass of C in

$CaCO_3 = \frac{20}{100} \times 100 = 12\,\%$. The percentage by mass of oxygen need not be calculated because-

$$\text{percentage of oxygen} = 100 - (\%\text{ of Ca} + \%\text{ of C})$$

$$= 100 - (40 + 12) = 48\,\%$$

We have seen that a chemical reaction can be represented by chemical equation. A balanced chemical equation can be used as summary of the mass changes that occur when reactants are converted to products.

Let us consider the chemical equation:

$$\begin{array}{ccccccccc} CaCO_3 & + & 2HCl & \longrightarrow & CaCl_2 & + & H_2O & + & CO_2 \\ 40+12+(3\times16) & + & 2(1+35.5) & \longrightarrow & 40+(2\times35.5) & + & (2\times1)+16 & + & 12+(2\times16 \\ 100 & & 73 & & 111 & & 18 & & 44 \end{array}$$

This equation tells us that one mole of calcium carbonate reacts with two moles of hydrochloric acid to form one mole of calcium chloride, one mole of water and one mole of carbon dioxide. When the appropriate formula masses are inserted as shown above, the equation also means 100 parts by mass of calcium carbonate reacts with 73 parts by mass of hydrochloric acid to form 111 parts by mass of calcium chloride, 18 parts by mass of water and 44 parts by mass of carbon dioxide.

Various problems can be solved by using balanced chemical equations.

Relative Atomic masses (nearest values) of elements for solving the problems are given in Table 3.1 .

Table 3.1 Relative atomic Masses (nearest values)

Aluminium	27	Hydrogen	1	Phosphorous	31
Barium	137	Iodine	127	Potassium	39
Bromine	80	Iron	56	Silver	108
Calcium	40	Lead	207	Sodium	23
Carbon	12	Magnesium	24	Sulphur	32
Chlorine	35.5	Mercury	201	Zinc	65
Chromium	52	Nitrogen	14		
Copper	64	Oxygen	16		

SUMMARY

In this chapter, the chemistry which deals with the quantities of substances taking part in chemical reactions is termed ‘ **Stoichiometry**’. Stoichiometry is based on the laws and principles of chemistry, such as conservation of mass, relative masses of atoms, and the concept of the mole. It involves formula masses (formula weights), formulae and per cent composition , mole , millimole of substances . It introduces the concept of limiting quantities in an experiment. In volumetric analysis (stoichiometry in solution), it explains the concepts of molarity, standard solution, primary standard, standardization, equivalence point, end point involve in acid-base titration. Various types of volumetric analysis have been presented with appropriate worked out examples followed by problems and questions.

Questions and Problems

1. What is the molarity of the following solutions?
   - (a) 3.2 g of sulphuric acid in 500 cm^3 of solution.
   - (b) 0.56 g of sodium carbonate in 100 cm^3 of solution.
   - (c) 1 g of caustic potash in 1 dm^3 of solution.
   - (d) 3.6 g of hydrogen chloride in 100 cm^3 of solution.
2. How many cubic centimetres of 1 M hydrochloric acid are needed to neutralize 0.40 g of caustic potash?
3. 5 g of a mixture of sodium chloride and anhydrous sodium carbonate were made up to 500 cm^3 of aqueous solution. 25 cm^3 of this solution required 18 cm^3 of 0.1 M sulphuric acid for neutralization. What was the mass of sodium chloride in this mixture?
4. 0.48 g of magnesium was dissolved in 50 cm^3 of 1 M hydrochloric acid. How many cubic centimetres of 0.1 M potassium hydroxide solution will be necessary to neutralize the excess acid?
5. 2.5 g of mixture of anhydrous sodium carbonate and sodium chloride were made up to 250 cm^3 with distilled water. 25 cm^3 of this solution required 20 cm^3 of 0.1 M hydrochloric acid. Calculate the percentage by mass of sodium chloride in the mixture.
6. 100 cm^3 of concentrated hydrochloric acid were dilute to 1 dm^3 with distilled water. 26.8 cm^3 of this diluted acid were needed to neutralize 25 cm^3 of 0.5 M sodium carbonate solution. What is the concentration in g dm^{-3} of the original acid?
7. Calculate the molecular mass or formula mass of each of the following compounds.
   - (a) Nitric acid
   - (b) Lead (II) chloride
   - (c) Calcium carbide
   - (d) Tetraphosphorus decaoxide (or) Phosphorus (V) oxide
   - (e) Dinitrogen tetroxide
   - (f) Barium carbonate
   - (g) Magnesium hydrogencarbonate
   - (h) Sodium dihydrogenphosphate
   - (i) Disodium hydrogenphosphate
   - (j) Potassium chlorate

8. Calculate the percentage by mass of the elements in each of the following compounds.

(a) Potassium chloride	(d) Nitrogen dioxide
(b) Iron (II) sulphate	(e) Trilead tetroxide
(c) Dinitrogen oxide	(f) Tetraphosphorus hexaoxide
	(g) Sodium thiosulphate

9. Find the percentage by mass of water present in copper (II) sulphate crystals.
10. How many grams of copper (II) sulphate crystals can you get from 50 g of malachite ore of formula $Cu(OH)_2 . CuCO_3$?
11. 1.905 g of silver is converted to silver nitrate. This silver nitrate is dissolved in distilled water and to this solution dilute hydrochloric acid is added in slight excess. The precipitate formed is filtered, washed and dried. The weight of this dried precipitate is 2.535 g. From this experimental result, formulate the equation for the precipitation reaction.
12. 5 g of a mixture of anhydrous sodium sulphate and sodium sulphate decahydrate on heating to constant mass produces 3.2 g of anhydrous salt. What percentages of anhydrous and hydrated salt are present in the mixture?
13. 0.02 g of hydrogen gas was evolved when 0.65 g of a divalent metal was treated with dilute sulphuric acid. Calculate the atómic mass of this divalent (combining capacity of 2) metal.
14. 100 cm^3 of iron (III) chloride solution is boiled and ammonium hydroxide is added in slight excess. The reddish brown precipitate is washed, dried and ignited. The weight of the residue obtained is 0.72 g. How many grams of iron (III) chloride is dissolved in 1 dm^3 of solution?
15. Write TRUE or FALSE for each of the following statements.
    (a) A standard solution is the reagent of exactly known concentration.
    (b) Sodium hydroxide may be used as primary standard.
    (c) Equivalence point and end point are identical in all types of titration.
    (d) A hygroscopic compound is preferrable to use as a primary standard.
16. Fill in the blanks with a suitable word or phrase or numerical value with unit as necessary.
    (a) One of the reactants in a reacting system that has the lesser quantities than is required by chemical equation is the .... substance.
    (b) A molar solution dissolves.......... of solute in 1 dm^3 of the solution.
    (c) The amount of........ does not change due to dilution.
    (d) One cubic centimetre of a molar solution contains.........of solute.
    (e) The process of determining the accurate volume of solution that is exactly reacted with other is called ....

17. Choose the correct term or terms given in the brackets.
   (a) The (amount of solute, amount solvent, molarity) does not change due to dilution.
   (b) A (pipette, burette, conical flask) is used to measure the amount of a solution.
   (c) Molarity means (mol dm^{-3}, mmol dm^{-3}, g dm^{-3}).
   (d) An indicator indicates the (equivalence point, end point, stoichiometric amount of reactants).
   (e) The compound with (hydrate water, low molecular mass, high purity) is preferable to use as a primary standard.

18. Match each of the items given in List A with the appropriate item in List B.

List A	**List B**
(a) pipette	(i) to indicate the end point
(b) indicator	(ii) formula mass
(c) molarity	(iii) finding the concentration of a solution
(d) standardization	(iv) mol dm^{-3}
(c) giant structure	(v) to withdraw a known volume

19. How will you assign the physical states of each of the reactants and products in a chemical equation ?

20. Define the term ' Molarity '.

21. Discuss the differences between molarity and a molar solution of a compound.

22. How many cm^3 of 0.1 mol dm^{-3} hydrochloric acid will be required to neutralize 25 cm^3 of 0.2 mol dm^{-3} sodium hydroxide solution?

23. If 25 cm^3 of potassium hydroxide is neutralized by 20 cm^3 of 2.5 mol dm^{-3} sulphuric acid what is the molarity of the alkali ?

****

CHAPTER 4

ELECTROLYSIS

4.1 Conductors and Electrolytes

A substance which conducts or allows the passage of electricity is called a **conductor.** Conductors are usually solids. One exception is mercury which is liquid at room temperature, but nevertheless conducts electricity and is therefore referred to as a conductor. All metals whether they are in the solid state or liquid state are conductors.

A solid substance which does not conduct electricity, is known as a **non-conductor** or **insulator.**

Those substances, other than metals, which in the molten state or as a solution in water, allow the passage of electricity are called **electrolytes.** The passage of electricity through electrolytes is usually accompanied by chemical decomposition. Electrolytes are ionic or electrovalent compounds.

A substance in a solution that does not conduct electric current is called a **non-electrolyte.**

Electrolysis

The decomposition of a compound, in solution or in the molten state, brought about by the passage of an electric current through it, is known as electrolysis.

4.2 Electrical Conductivity of Metals

In metals, the atoms are packed tightly together to form what is known as the metallic lattice. Such a lattice is shown in Fig. 4.1. The valence electrons from each atom in the lattice can move freely through the entire lattice. That is why metals are good conductors of electricity.

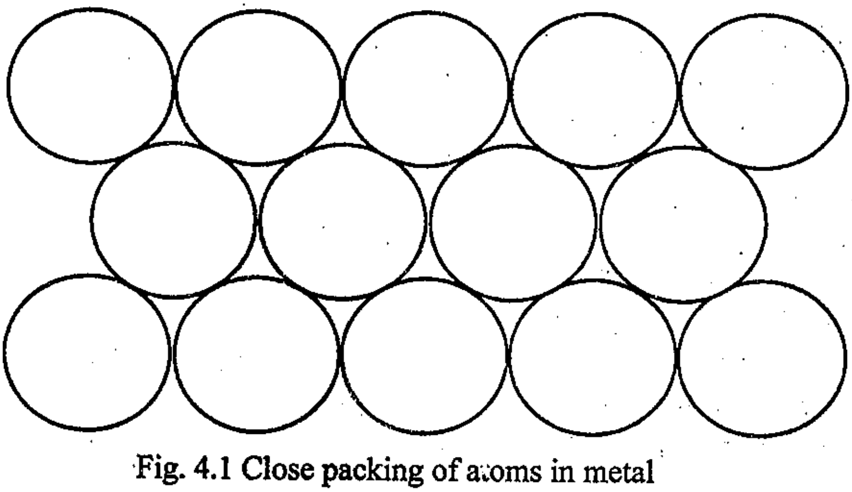


Fig. 4.1 Close packing of atoms in metal

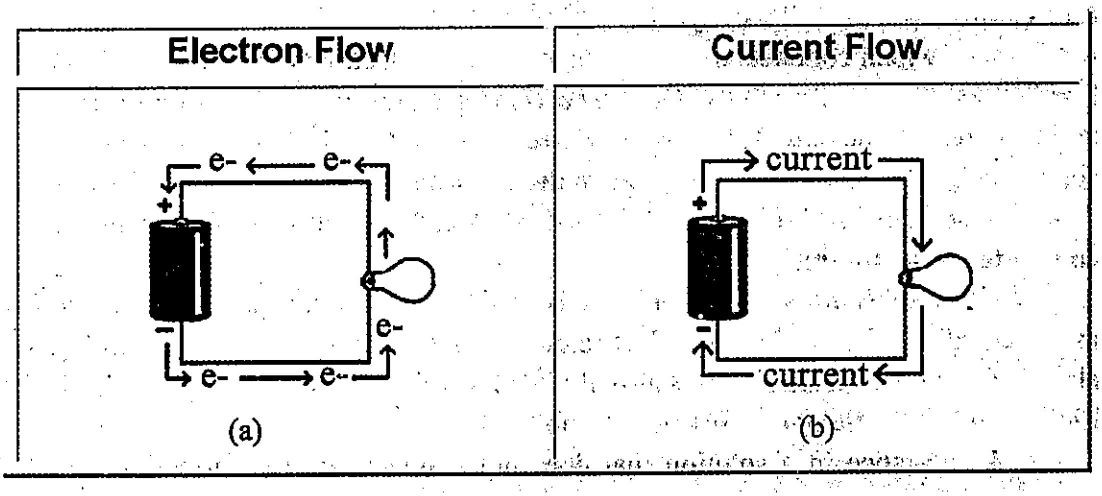


Fig. 4.2 Conduction in a metal wire

When the metal wire, like copper wire, is used to link up the terminals, as shown in Fig.4.2.(a) there is a flow of electrons towards the positive terminal, while fresh electrons are drawn into the wire from the negative terminal. Therefore, the electrons flow freely through the completed circuit. Current flow is the reverse of electron flow (Fig.4.2.b).

A metal like copper, conducts electricity both in its solid and liquid states. The electrical conductance of a metal is much greater than that of a solution of an electrolyte. One distinctive property of metallic conductance is that it decreases with increase in temperature. Silver, copper, gold and aluminium, in the order given, have the highest conductance among the metals.

4.3 The Ionic Theory

To explain the phenomenon of electrolysis; the Ionic Theory was put forward by Arrhenius about the year 1880.

This theory postulates that :

1. Electrolytes contain electrically charged particles called ions.
2. Electrolytes can conduct electricity due to the movement of these ions.
3. Non-electrolytes do not contain ions and so they cannot conduct electricity.

Ions are derived from atoms (or groups of atoms) but differ from them by having electrical charges. Generally, hydrogen ions and ions derived from metals are positive and the ions derived from non-metals are negative. The positive ions are called cations and the negative ions are called anions.

The number of electrical charges on an ion is equal to the valence of the corresponding atom or group.

Ions in some substances

For example ions contained in some substances are given in Table 4.1.

Table 4.1 Ions in some substances

Compound	Ions
Sodium chloride	Na^+Cl^-
Sodium hydroxide	Na^+OH^-
Copper (II) sulphate	$Cu^{2+}SO_4^{2-}$
Lead (II) nitrate	$Pb^{2+}2NO_3^-$

4.4 Electrolysis of Molten Salts

(a) Electrolysis of molten sodium chloride

At sufficiently high temperature sodium chloride may be melted. Molten or fused sodium chloride contains Na^+ and Cl^- ions. The flow of these ions is influenced by the direction of the electric current. Migration of ions during electrolysis is shown in Fig. 4.3.

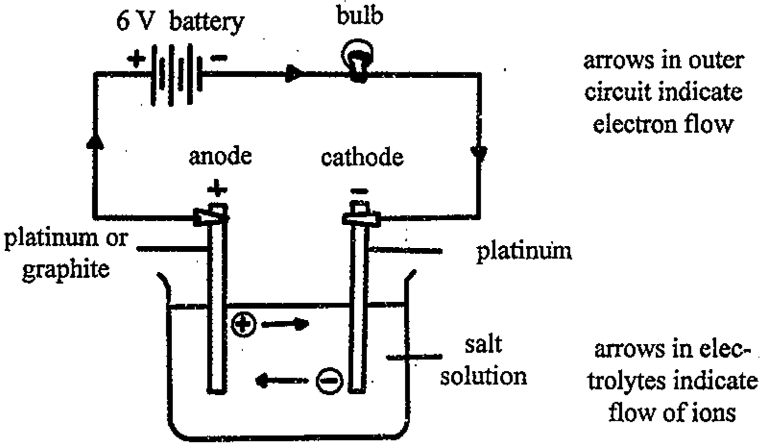


Fig. 4.3 Migration of ions during electrolysis

Sodium ions move to the cathode (a negative electrode in electrolysis) where they accept electrons and are discharged as sodium atoms. The chloride ions go to the anode (a positive electrode in electroylsis) where they give up their electrons and form chlorine gas which is given off at this electrode. The reactions at the electrodes may be represented as

reaction at cathode $Na^+ \; + \; \underset{\text{taken up from cathode}}{e^-} \; \rightarrow \; Na$

reaction at anode $Cl^- \; \rightarrow \; Cl \; + \; \underset{\text{given up at anode}}{e^-}$

$Cl \; + \; Cl \rightarrow Cl_2$

Positive ions(cations)migrate to the cathode, and negative ions(anions)move to the anode.

In this experiment the sodium atoms discharged at the cathode cannot attack the platinum electrode.

Note: Solid sodium chloride does not conduct electricity, because in the solid state the movement of Na^+ and Cl^- ions are restricted.

(b) Electrolysis of molten lead (II) bromide

The reactions at the platinum electrodes in the electrolysis of molten lead (II) bromide may be written as

reaction at cathode $Pb^{2+} + \underset{\text{taken up from cathode}}{2e^-} \rightarrow Pb$

reaction at anode $Br^- \rightarrow Br + \underset{\text{given up at anode}}{e^-}$

$Br \; + \; Br \rightarrow Br_2$

4.5 Conduction of Electricity by Aqueous Solutions

In the previous experiment, the sodium atoms discharged at the cathode cannot attack the platinum electrode. In general, ions discharged at the platinum electrode cannot attack the electrode.

By using the apparatus as shown in Fig. 4.3, we may test whether aqueous solutions of organic substances such as sugar and urea, and inorganic salts such as sodium chloride, calcium chloride, copper (II) sulphate etc., conduct electricity.

It is found that aqueous solutions of the above organic substances do not conduct electricity, whereas aqueous solutions of the inorganic salts conduct electricity.

Electrolysis of saturated aqueous sodium chloride solution (brine) using platinum electrodes

Aqueous sodium chloride solution contains Na^+ and Cl^- ions from the complete dissociation of sodium chloride and some H^+ and OH^- ions from slight dissociation of water. On electrolysis, the cations, i.e., Na^+ and H^+ ions, move to the cathode. However in the electrochemical series sodium is above hydrogen and so hydrogen ions accept electrons more readily than sodium ions. The electrochemical series is similar but not identical to the activity series. Generally, cations of element lower in the electrochemical series accept electron more readily than those above it.

Therefore, hydrogen gas is liberated at the cathode. This removal of hydrogen ions give rise to more water dissociating to replace the H^+ ions removed from the solution. The anions, i.e., OH^- and Cl^- ions move to the anode. If the amounts of OH^- and Cl^- ions are similar in the solution, OH^- ions will lose electrons more readily than Cl^- ions. However, in brine, i.e, saturated aqueous sodium chloride solution, the concentration of Cl^- ions is very high compared to that of OH^- ions. The OH^- ions are retained by the Na^+ ions and it is the Cl^- ions which lose electrons at the anode. Therefore chlorine gas is evolved at the anode. The reactions at the electrodes can be represented as

reaction at the cathode $H^+ + e^- \rightarrow H$
$H + H \rightarrow H_2$
reaction at the cathode $Cl^- \rightarrow Cl + e^-$
$Cl + Cl \rightarrow Cl_2$

Electrolysis of dilute aqueous copper (II) sulphate solution using platinum electrodes

Dilute aqueous copper (II) sulphate solution contains Cu^{2+} and SO_4^{2-} ions from the dissociation of copper (II) sulphate and H^+ and OH^- from slight dissociation of water. On electrolysis the positive ions, i.e., Cu^{2+} and H^+ ions move to the cathode. Since Cu is below H in the electrochemical series, Cu^{2+} ions accept electrons more readily than hydrogen ions and so copper is deposited on the cathode.

Both SO_4^{2-} and OH^- ions travel to the anode. The concentrations of SO_4^{2-} and OH^- ions are similar here, and the OH^- ions lose electrons more easily to the anode and are discharged. The reactions at the electrodes may be written as

reaction at the cathode $Cu^{2+} + 2e^- \rightarrow Cu$

reaction at the anode $OH^- \rightarrow OH + e^-$

$$OH + OH \rightarrow H_2O + O$$

$$O + O \rightarrow O_2$$

reaction at the anode $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$
may be summed up as

4.6 Electrolysis of Aqueous Solutions of Alkali and Acid using Platinum Electrodes

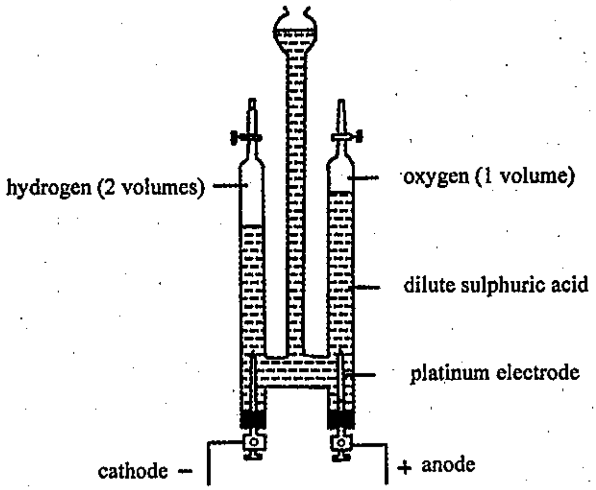


Fig. 4.4 Hofmann's voltameter for electrolysis of dilute sulphuric acid

Aqueous solutions of sodium hydroxide conduct electricity.

The sodium hydroxide solution contains Na^+, OH^- and H^+ ions. The Na^+ and H^+ ions both travel to the cathode. Since hydrogen is lower in the electrochemical series than sodium, hydrogen is liberated at the cathode.

The hydroxide ions are discharged at the anode.

Reactions at the electrodes are

reaction at the cathode $H^+ + e^- \rightarrow H$

$$H + H \rightarrow H_2$$

reaction at the anode $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

Note that an equal number of H^+ and OH^- ions are discharged at the electrodes and hence for every $4H^+$ discharged, two moles of hydrogen will be liberated while $4OH^-$ discharged will give rise to one mole of oxygen.

Dilute sulphuric acid conducts electricity (see Fig, 4.4). Sulphuric acid solution contains H^+, SO_4^{2-} and OH^- ions. On electrolysis, H^+ ions go to the cathode and accept electrons, eventually forming H_2 molecules.

SO_4^{2-} and OH^- ions both travel to the anode. Since the concentrations of these anions are similar, OH^- ions lose electrons more easily and are discharged at the anode where oxygen is eventually liberated.

Reactions at the electrodes are

reaction at the cathode $H^+ + e^- \rightarrow H$

$2H \rightarrow H_2$

reaction at the anode $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

Electrolysis of dilute sulphuric acid, in effect, result in the electrolysis of water.

4.7 Electrolysis of Aqueous Copper (II) Sulphate Solution using Copper Electrodes

The electrolysis of copper (II) sulphate solution using copper electrodes is carried out as shown in Fig. 4.5.

Aqueous copper (II) sulphate solution contains Cu^{2+}, SO_4^{2-}, H^+ and OH^- ions. As explained above Cu^{2+} ions are discharged at the cathode, where metallic copper is deposited. The SO_4^{2-} and OH^- ions go to the anode where three different reactions are possible:

(1) SO_4^{2-} ions can be discharged,

(2) OH^- ions can be discharged,

(3) Cu atoms from the anode can lose electrons forming Cu^{2+} ions which can dissolve into solution.

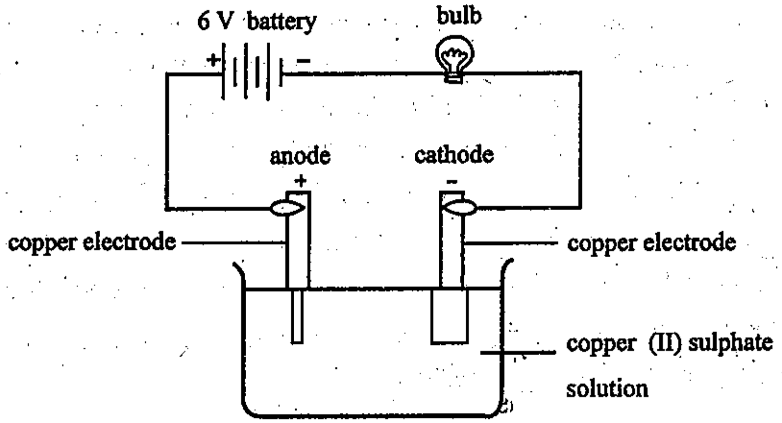


Fig. 4.5 Apparatus for electrolysis of aqueous copper (II) sulphate solution using copper electrodes

Actually the last process occurs.

Therefore, the reactions at the electrodes may be represented as

reaction at the cathode $Cu^{2+} + 2e^- \rightarrow Cu$

reaction at the anode $Cu \rightarrow Cu^{2+} + 2e^-$

The net result of the electrolysis of copper (II) sulphate using copper electrodes is the loss of copper from the anode and the deposition of copper at the cathode. This process is used for purification of crude copper, which is made the anode in the electrolytic process.

4.8 Summary of the Effects of Electrolysis

When an electric current is passed through an electrolyte, electrolysis takes place, the effects of which may be summarized as in the following Table 4.2.

Table 4.2 Summary of the effects of electrolysis

Electrolytes	*Cathode of*	*Anode of*	*At cathode*	*At anode*
Fused sodium chloride	platinum	platinum or graphite	sodium deposited	chlorine evolved
Saturated sodium chloride solution	platinum	platinum or graphite	hydrogen evolved	chlorine evolved
Sodium hydroxide solution	platinum	platinum	hydrogen evolved	oxygen evolved

Dilute sulphuric acid	platinum	platinum	hydrogen evolved	oxygen evolved
Copper (II) sulphate solution	platinum	platinum	copper deposited	oxygen evolved
Copper (II) sulphate solution	copper	copper	copper deposited	copper dissolved

4.9 Selective Discharge of Ions

In an aqueous solution of an electrolyte, there are usually more than one species of cations or anions e.g., in an aqueous solution of sodium hydroxide, there are Na^+, H^+ and OH^- ions. When electricity is passed through such a solution, the cations move towards the cathode and the anions move towards the anode but not all the positive ions or all the negative ions are discharged at the cathode or the anode at the same time. Usually one species of cations or anions is selectively discharged at the respective electrodes. The preferential discharge of these ions depends on the following three factors :

Position of the metal or group in the electrochemical series

Table 4.3 shows cations and anions arranged in the order of increasing readiness with which they are discharged from solution on passage of electricity. The arrangement of the cations corresponds to what is known as the electrochemical series.

Table 4.3 Arrangement of ions in the order of increasing readiness of discharge at electrodes (for dilute solutions)

	Ions	
increasingly easier to discharge ↓	K^+	→ to cathode
	Ca^{2+}	
	Na^+	
	Mg^{2+}	
	Al^{3+}	
	Zn^{2+}	
	Fe^{2+}	
	Sn^{2+}	
	Pb^{2+}	
	H^+	
	Cu^{2+}	
	Ag^+	
increasingly easier to discharge ↓	SO_4^{2-}	→ to anode
	NO_3^-	
	Cl^-	
	Br^-	
	I^-	
	OH^-	

If all other factors are equal, any ion lower in the series will be discharged from solution in preference to those above it, positive ions at the cathode and negative ions at the anode.

For example, in sodium hydroxide solution, containing positive ions of H^+ and Na^+, H^+ discharges in preference to Na^+; in copper (II) sulphate solution, containing OH^- and SO_4^{2-} as negative ions, OH^- is discharged in preference to SO_4^{2-}.

Concentration of electrolyte

As the concentration of an ion increases, the tendency of the ion to discharge from solution also increases, e.g., in concentrated hydrochloric acid containing OH^- and Cl^-, the concentration of Cl^- is very much greater than that of OH^-. In these circumstances, Cl^- is discharged first. But if the acid is very dilute, some discharge of OH^- will also occur.

The concentration effect can also be seen when brine is electrolysed. Here the order of discharge stated by the electrochemical series may be reversed by the concentration effect.

Nature of the electrode

The nature of the electrode is the deciding factor in some cases. The products of the electroysis of a saturated solution of sodium chloride with mercury cathode are quite different from those obtained by using the platinum cathode. With a platinum cathode, H^+ is discharged. This is in accordance with the positions of H^+ and Na^+ in the electrochemical series. H^+ is placed below Na^+ in the series. The cathode product is hydrogen gas.

If a mercury cathode is used, Na^+ is discharged to dissolve in the mercury. This requires less energy than the discharge of H^+ to hydrogen gas and so occurs in preference, and sodium amalgam is the product.

4.10 Chemical Energy into Electrical Energy

An electric current can be produced from a chemical reaction.

The apparatus is set up as shown in Fig. 4.6.

When the switch is pressed down to complete the circuit, reaction will take place quite rapidly and the bulb will light up, indicating the flow of electric current in the circuit.

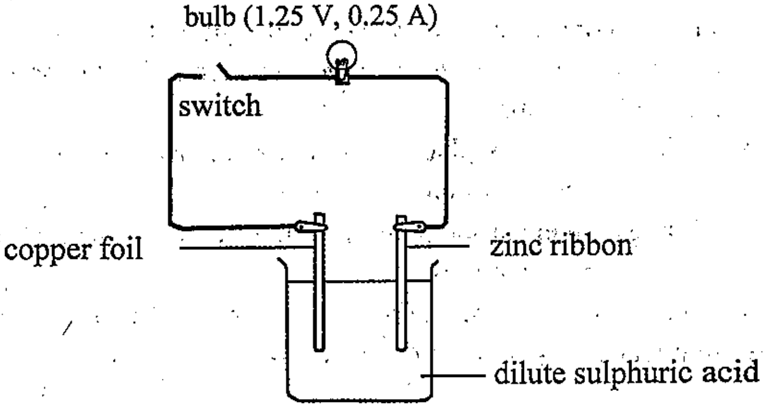


Fig. 4.6 A chemical cell

The reaction that takes place is as follows:

Zinc, the more electropositive of the two metals, ionizes by loss of electrons and these electrons pass from zinc to copper through the wire. This is equivalent to the flow of current in the opposite direction. At the copper surface, the electrons reduce hydrogen ions from the electrolyte which are eventually discharged as hydrogen gas. Reactions at the zinc and copper electrodes may be represented as

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

The copper then attracts the H^+ ions from the acid solution, and they are discharged.

$$H^+ + e^- \longrightarrow H \,;\, 2H \rightarrow H_2(g)$$

Current should continue to flow as long as materials last, but the bubbles of hydrogen adhere to the surface of the copper electrode, cutting off these surface areas of the electrode from contact with the electrolyte. This phenomenon slows down the reaction at the electrode. Under these circumstances the cell is said to be polarized. The whole process in the cell corresponds to the change.

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

The two metals, that are used to convert chemical energy into electrical energy, must be widely separated in the electrochemical series e.g., copper and magnesium, copper and zinc, etc. The greater the difference in reactivity between the two metals, the greater the voltage or electromotive force (emf) of the cell.

4.11 Electrochemical Series

One electrode may be adopted as a standard electrode and a series of cells constructed using a different second electrode in each cell. The voltage measured from each cell of such a series, may be used to arrange the metals in the order of increasing or decreasing electrode potential.

The series obtained by placing the metals in order of decreasing negative potential is known as the electrochemical series.

A high negative electrode potential shows that the metal has a strong tendency to go into solution as positive ions.

The electrochemical and activity series are similar but not identical. Part of the electrochemical series is given in Table 4.4.

Table 4.4 The electrochemical series

Element	*Standard electrode potential (volt)*
Potassium	- 2.92
Calcium	- 2.87
Sodium	- 2.71
Magnesium	- 2.39
Aluminium	- 1.66
Zinc	- 0.76
Iron	- 0.44
Tin	- 0.14
Lead	- 0.13
Hydrogen	0.0
Copper	+ 0.34
Silver	+ 0.80

4.12 Faraday's Laws of Electrolysis

These laws express the quantitative results of electrolysis.

Faraday's first law of electrolysis

The mass of a given element liberated during electrolysis is directly proportional: (1) to the magnitude of the steady current used and (2) to the time for which the current passes. That is, the mass of element liberated is directly proportional to the quantity of electricity passed through the solution during electrolysis.

To investigate the amount of substance liberated in electrolysis by different quantities of electricity

The apparatus is set up as shown in Fig. 4.7.

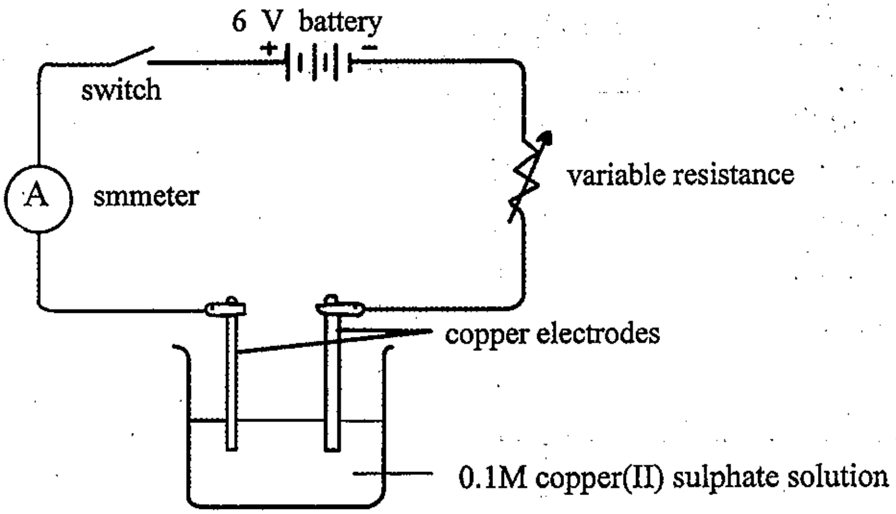


Fig. 4.7 The apparatus to investigate the amounts of copper liberated in electrolysis by different quantities of electricity

The beaker is filled two-thirds full with 0.1 M copper (II) sulphate solution. A piece of clean, dry copper foil, approximately 5 cm x 3 cm is weighed. This copper foil will be the cathode in the circuit and therefore attached to the negative pole of the battery.

Another piece of clean, dry copper foil will be the anode in the circuit and attached to the positive pole of the battery. Both the electrodes are dipped in the copper (II) sulphate solution.

Simultaneously, a stopclock is started and the current is switched on. Then the variable resistance is quickly adjusted to obtain a steady current of approximately 0.2 A. It may be necessary to alter the variable resistance from time to time to maintain the current at this steady value.

After about fifteen minutes, the current is switched off and the time on the stopclock noted. The copper cathode is removed, washed first with distilled water and then with a little ethanol and finally dried. When this cathode is completely dry, it is weighed and the increase in mass of the cathode is determined. This is the mass of copper deposited in the time for which the current flowed.

The cathode is replaced in the beaker, the stopclock is started and the current switched on. After another fifteen minutes, the current is switched off and the increase in mass of the copper cathode is determined as before.

This procedure is repeated twice. The results of one such experiment is shown in Table 4.5 .

Table 4.5 The amounts of copper deposited by different quantities of electricity

Current (amperes)	*Time (seconds)*	*Quantity of electricity (coulombs)*	*Mass of copper deposited (grams)*
0.21	15 x 60 = 900	900 x 0.21 = 189	0.063
0.21	30 x 60 = 1800	1800 x 0.21 = 378	0.129
0.21	45 x 60 = 2700	2700x 0.21= 576	0.187
0.21	60 x 60 = 3600	3600 x 0.21 = 756	0.250

Figure 4.8 is the graph obtained by plotting the masses of copper deposited against the quantities of electricity used.

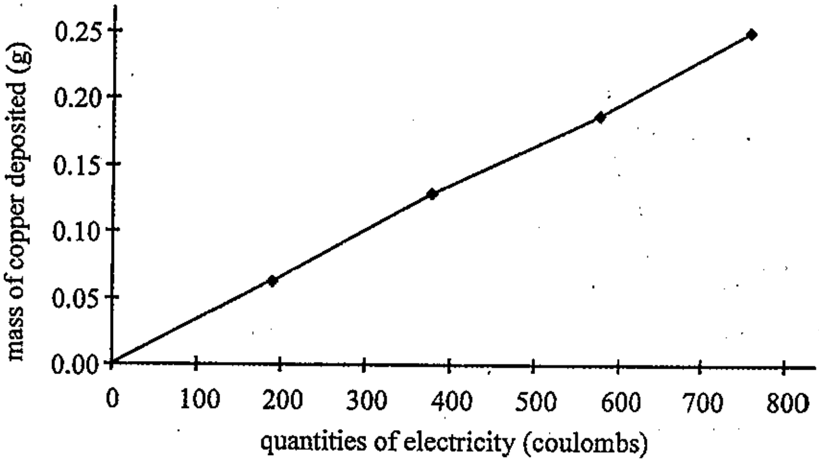


Fig. 4.8 Graph of masses of copper deposited against quantities of electricity used

The shape of the graph is a straight line passing through the origin, which shows that the mass of copper deposited is directly proportional to the quantity of electricity used. This experiment confirms the validity of Faraday's First Law of electrolysis.

Faraday's second law of electrolysis

When the same quantity of electricity is passed through solutions of different electrolytes the relative number of moles of the elements deposited are inversely proportional to the charges on the ions of each of the elements respectively.

To determine the amounts of different substances liberated by the same quantity of electricity

The apparatus is set up as shown in Fig. 4.9.

The copper electrodes and silver electrodes are cleaned, dried and weighed separately.

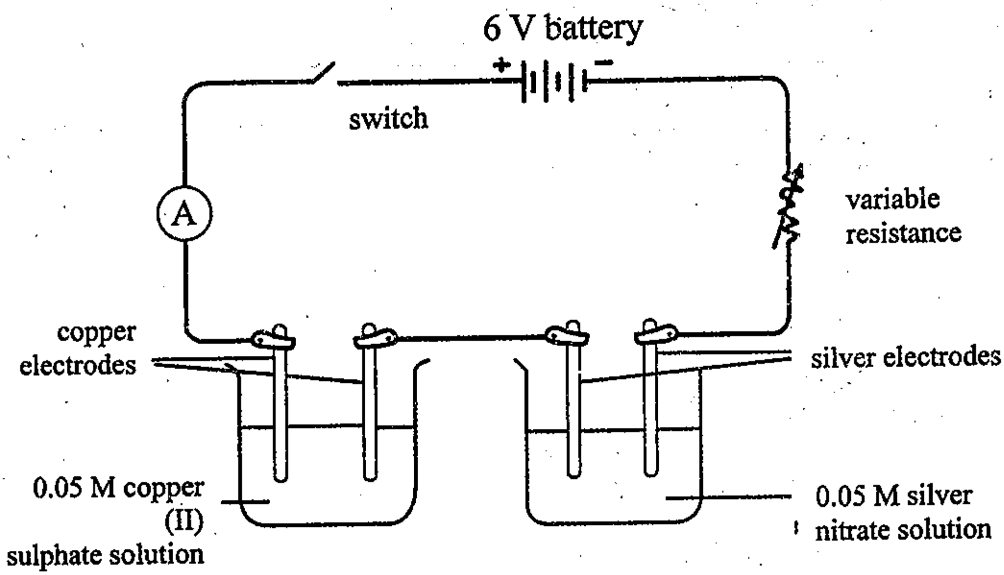


Fig. 4.9 The apparatus to determine the amounts of copper and silver deposited by the same quantity of electricity

The copper electrodes are immersed in 0.05 M copper (II) sulphate solution and the silver electrodes are immersed in 0.05 M silver nitrate solution. A current of about 0.5 A is passed for twenty to thirty minutes, after which the cathodes are removed, cleaned, dried and reweighed.

Data obtained from one such actual experiment are shown in Table 4.6.

Table 4.6 Amounts of copper and silver deposited by the same quantity of electricity

Current	=	0.45 A
Time	=	25 minutes
Mass of copper deposited	=	0.221 g
Mass of silver deposited	=	0.755 g

It can be seen that the masses of copper and silver deposited in the experiment are different. To compare the amounts of copper and silver deposited, the moles of atoms of each element must be calculated.

Therefore, the amount of copper deposited $= \frac{0.221}{63.5}$ mol

$= 0.0035$ mol

the amount of silver deposited $= \frac{0.755}{107.8}$ mol

$= 0.0070$ mol

That is, twice as many atoms of silver are deposited as atoms of copper by the same quantity of electricity,

This can be explained as follows:

Since the process at the cathode is addition of electrons to the cations,

$$X^{n+}(aq) \quad + \quad ne^- \longrightarrow X(s)$$

the quantity of electricity required to liberate one mole of X will depend upon the charge, n^+, on the ion.

In the case of copper and silver the charge on the copper ion (Cu^{2+}) is twice that on the silver ion (Ag^+) and therefore twice the quantity of electricity will be required to liberate one mole of copper as for the liberation of one mole of silver. Consequently, for the same quantity of electricity only half as many moles of copper will be obtained as silver.

This experiment confirms Faraday's Second Law of electrolysis.

4.13 The Faraday as a Unit Quantity of Electricity

The quantity of electricity required to liberate one mole of a univalent element is 96500 coulombs. This quantity of electricity is given a special name which is **the Faraday**, in honour of the man who carried out a lot of work on the study of electrolysis.

Thus, one Faraday of electricity will liberate one mole of hydrogen ions, one mole of sodium ions and one mole of potassium ions. Generally this can be represented as;

$$M^+(aq) + e^- \longrightarrow M(s)$$

which is the cathode reaction for a univalent metal M.

Therefore, for one mole of unipositive ions to be discharged electrons carrying an equivalent amount of negative charge would be necessary. This is called one mole of electrons.

Hence, one Faraday may be considered as the equivalent of one mole of electrons.

4.14 Determination of Relative Atomic Masses

From the data obtained on Table 4.6, the relative atomic masses of copper and silver may be calculated.

Experimental data:

Current = 0.45 A
Time = 25 minutes
Mass of copper deposited = 0.221 g
Mass of silver deposited = 0.755 g

Calculation:

Quantity of electricity = 0.45 x 25 x 60 coulombs
= 675 coulombs

For silver, 675 coulombs liberate = 0.755 g silver

$$\therefore 96500 \text{ coulombs liberate} = \frac{0.755 \times 96500}{675} \text{ g silver}$$
$$= 108.0 \text{ g silver}$$

Since silver forms unipositive ions (Ag^+), one mole of electrons or one Faraday of electricity will liberate one mole or the relative atomic mass of atoms. Hence 108 is the relative atomic mass of silver.

For copper,

675 coulombs liberate = 0.221 g copper

$$\therefore 96500 \text{ coulombs liberate} = \frac{0.221 \times 96500}{675} \text{ g copper}$$
$$= 31.6 \text{ g copper}$$

Since copper forms dipositive ions (Cu^{2+}), one mole of electrons or one Faraday of electricity will liberate half mole or half the relative atomic mass of atoms. Hence, the relative atomic mass of copper is 2 x 31.6 = 63.2 .

4.15 Electroplating

Electroplating is the electrical precipitation of one metal on another. Usually the appearance and the resistance to corrosion of the electroplated object are greatly improved.

In silver plating, articles such as spoons or ornaments, made of base alloys, (e.g., cupronickel) are made the cathode in a plating bath of potassium argentocyanide, $K[Ag(CN)_2]$solution. This solution contains silver ions, Ag^+, from the ionization of $K[Ag(CN)_2]$.

$$K[Ag\,CN)_2](aq) \rightleftharpoons K^+(aq) + Ag^+(aq) + 2CN^-(aq)$$

The anode is pure silver. When a direct current passes through this solution, the following reactions take place :

reaction at the cathode $Ag^+(aq) + e^- \longrightarrow \underset{\text{silver deposits}}{Ag(s)}$

reaction at the anode $Ag(s) - e^- \longrightarrow \underset{\text{silver dissolves}}{Ag^+(aq)}$

Steel parts are usually chromium plated. In chromium plating a steel object is plated first with nickel or copper, because chromium does not stick well onto a steel surface. The object is made the cathode in a plating bath of chromium(III) sulphate in sulphuric acid and water. The anode is made of lead. When a direct current passes through this solution, chromium deposits on the object at the cathode as a bright coherent layer.

reaction at the cathode $Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$

reaction at the anode $4OH^-_{(aq)} \longrightarrow 2H_2O(l) + O_2(g) + 4e^-$

This chromium layer resists rusting and gives a bright "silvery" surface.

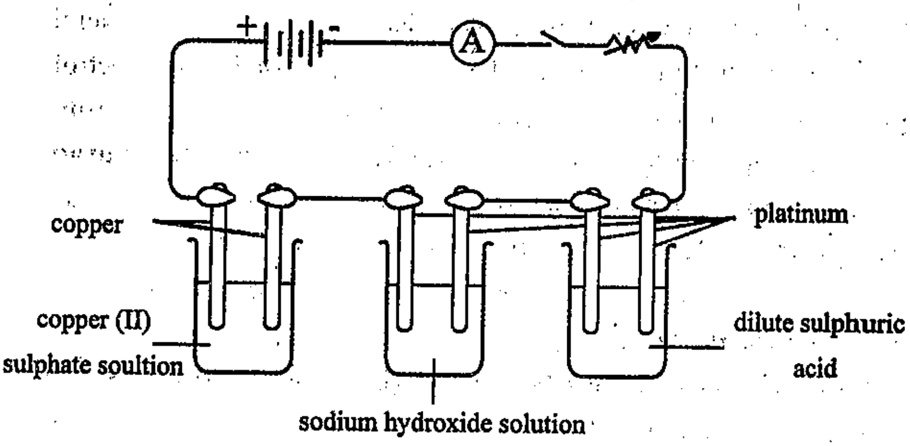
SUMMARY

This chapter is concerned with the application of electricity in electrolysis of solutions.It introduces the terms: such as; conductors, non-conductors (insulators), electrolytes, non-electrolytes, electrolysis, electroplating and electrical conductivity of metals. Electrolysis of saturated aqueous sodium chloride solution (brine) using platinum electrodes, electrolysis of dilute aqueous copper (II) sulphate solution using platinum electrodes, electrolysis of aqueous solutions of alkali and acid using platinum electrodes, have been illustrated. The concept of electrochemical series has been depicted with suitable examples. Faraday's laws of electrolysis such as Faraday's first law of electrolysis and Faraday's second law of electrolysis have been presented with appropriate examples. The term such as **one Faraday which is equivalent to 96500 coulombs,** and the application of the two laws in solving electrolysis problems have been elaborated.

Questions and Problems

1. A solution of copper (II) sulphate was divided into two portions. One portion was electrolysed using platinum electrodes. The other portion was electrolysed using copper electrodes. What changes in colour of the solution do you expect in each case?
2. Solid sodium chloride does not conduct an electric current. Fused sodium chloride conducts an electric current and sodium metal is formed at the cathode. Which of the following statements is an incorrect deduction concerning this experiment?
   (a) On electrolysis Na^+ ions move to the cathode and Cl^- ions move to the anode.
   (b) Since sodium chloride is neutral, there must be equal numbers of positive and negative charges present in the substance.
   (c) There are no ions in solid sodium chloride.
3. A large number of substances contain ions. Which of the following statements is false?
   (a) The atom of an element and the ion obtained from it have the same properties.
   (b) Those ions which travel towards the negative electrode are called cations; those which go to the positive electrodes are called anions.
   (c) The number of electrical charges on an ion is equal to the valency of the corresponding atom.

4. The apparatus is set up as shown in the following diagram.



A current of 0.5 A was switched on and allowed to flow for 15 minutes.

(a) Describe how the electricity is conducted in the copper (II) sulphate solution.

(b) Name the products formed during the electrolysis of sodium hydroxide solution at the electrodes.

(c) State, whether the masses of the copper cathode and the copper anode will increase, decrease or remain constant during the electrolysis.

(d) Write equations for the reactions taking place in dilute sulphuric acid at the cathode and anode.

(e) Calculate the volume of hydrogen which would be released from the dilute sulphuric acid (at STP) during the electrolysis.

(f) What would happen to the concentration of each solution during the passage of the current?

5. When an aqueous solution of silver nitrate is electrolysed with platinum electrodes, the products at the cathode and anode are two volumes of hydrogen and one volume of oxygen respectively. Also the cathode liquid becomes alkaline and the anode liquid acidic, Explain these results.

6. Two plates, one of zinc and one of copper, held apart and connected to a small light bulb, are dipped into dilute sulphuric acid. The bulb lights up but the light soon becomes dim.

(a) What would be observed at the copper plate? Write an equation for the reaction which occurs.

(b) What would happen at the zinc plate? Write an equation for this reaction.

(c) Explain why the light fades after a short time.

(d) If the zinc plate were replaced by an iron plate, would the lamp glow more or less brightly?

(e) If the zinc plate were retained but the copper plate were replaced by a silver plate, would the lamp glow more or less brightly?

7. Draw a fully labelled diagram of the apparatus you would use to electrolyse brine and measure the volumes of the gases produced at the electrodes.
   (a) Name these gases and state their relative volumes.
   (b) How can these gases be made to react with one another?
   (c) What is the product of the reaction of these two gases?
   (d) What will be the actual volume at STP of this product, if **96500 coulombs** were used in the electrolysis, assuming that complete **combination** of the **reacting gases** occurred?

8. Draw a **fully labelled** diagram of a voltameter suitable for the **electrolysis** of water acidified **with dilute** sulphuric acid, showing how the gaseous **products** are collected.
   (a) Give **the names and relative** proportions of the gases evolved.
   (b) Write down **the equations for the reactions** at the electrodes.
   (c) The same **result would be obtained** if the water was made alkaline **by** adding sodium hydroxide **instead of acidifying** with sulphuric acid.
   (d) State and explain the **effect** of electrolysing a dilute solution of sodium sulphate in the same **voltameter**.

9. What mass of (a) copper, (b) silver, (c) aluminium and what volume at STP of (d) oxygen and (e) chlorine will be liberated during electrolysis by a charge of one Faraday? (Cu = 63, Al = 27, O = 16, Cl = 35.5)

10. On passing a steady current of 0.75 A for 25 minutes through a copper (II) sulphate solution, 0.369 g of copper is deposited. Calculate the relative atomic mass of copper. (One Faraday = 96500 coulombs)

11. Calculate the mass of silver in grams deposited by passing a steady current of 0.1 A for one hour through an excess of silver nitrate solution, (Ag = 108, one Faraday= 96500 C)

12. An electric current is passed in turn through solutions of silver nitrate, copper (II) sulphate and dilute sulphuric acid in series. If 0.5 g of silver were deposited at the cathode of the first cell, calculate
   (a) the mass of copper deposited in the second cell and

(b) the volume of hydrogen liberated at 30 °C and 760 mmHg in the third cell.
(Ag = 108, Cu = 63, H= 1)

13. Write TRUE or FALSE for each of the following.
   (a) Anions are oxidized at the anode.
   (b) Metals are good insulators of electricity.
   (c) A conductor contains electrically charged ions.
   (d) In an electrolysis, the quantity of element discharged is directly proportional to the quantity of electricity used.
   (e) A chemical cell produces electricity due to the chemical reaction.

14. Fill in the blanks with a suitable words or phrase or numerical value with unit as necessary.
   (a) The decomposition of a molten salt brought about by the passage of electricity through it is known as the ....
   (b) Cation is reduced at the ....
   (c) The ions at the lower position of the .... are easier to discharge.
   (d) The electrical precipitation of one metal on another is known as ....
   (e) The metals more separate in the electrochemical series produce more ....when they are used as the electrodes.

15. Choose the correct term or terms given in the brackets.
   (a) (K^+, H^+, Cu^{2+}) ions are difficult to discharge.
   (b) Electrolytes can conduct due to the movement of (ions, electrons, molecules).
   (c) Polarization occurs in a chemical cell due to the (hydrogen bubbles, discharge of OH^- ions, disconnection of current)
   (d) More (separate, closed, adjacent) metals in the electrochemical series produce more e.m.f in a chemical cell.
   (e) Articles to be electroplated are connected to the (cathode, anode, electrode).

16. Match each of the items given in List A with the appropriate item in List B.

List A	**List B**
(a) 96500 C	(i) produce e.m.f.
(b) chemical cell	(ii) one Faraday
(c) electrolytic cell	(iii) chemical reaction by electric current
(d) inert electrode	(iv) tendency to flow the current
(e) conductance	(v) Pt

17. Describe the differences between
    (a) conductors and non-conductors
    (b) electrolytes and non-electrolytes
18. Answer the following questions.
    (a) What do we call a solid which does not conduct electricity ?
    (b) What do we call a liquid which does not conduct electricity ?
19. Describe the differences between
    (a) electrolysis of molten sodium chloride and
    (b) electrolysis of saturated aqueous sodium chloride (brine) using platinum electrodes.
20. Describe the differences between using platinum electrodes and copper electrodes in electrolysis of aqueous copper (II) sulphate solution.
21. What are the factors affecting the electrolysis products?
22. Distinguish between the following.
    (a) electrolysis and electrolyte
    (b) cathode and cation
    (c) anode and anion
    (d) conductor and insulator
23. Complete the following table and name the main anode and cathode products.

Electrodes	**Electrolytes**	**Anode product**	**Cathode product**
platinum	Fused sodium chloride		
platinum	Saturated sodium chloride solution		
platinum	Sodium hydroxide solution		
copper	Copper (II) sulphate solution		
platinum	Copper (II) sulphate solution		

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CHAPTER 5
OXIDATION AND REDUCTION

5.1 Concepts of Oxidation and Reduction

Originally, oxidation was defined as the addition of oxygen to a substance or the removal of hydrogen from a substance, e.g.,

$$2\,Cu\,(s) + O_2(g) \longrightarrow 2CuO\,(s)$$
$$H_2S\,(g) + Cl_2(g) \longrightarrow 2HCl\,(g) + S\,(s)$$

Conversely, reduction was defined as the addition of hydrogen to a substance or the removal of oxygen from a substance, e.g.,

$$Cl_2\,(g) + H_2\,(g) \longrightarrow 2HCl\,(g)$$
$$CuO\,(s) + H_2\,(g) \longrightarrow Cu\,(s) + H_2O\,(l)$$

We have studied that electronegative elements which tend to attract electrons are the non-metallic elements and electropositive elements which tend to donate electrons are the metallic elements. As you must have realized from your studies, chemical reactions are of great variety involving the participation of different substances as reactants. The definition of oxidation and reduction which is confined to the reactions with oxygen and hydrogen is too narrow to be satisfactory. There are numerous reactions in which these elements are not involved.

Oxygen belongs to that class of elements we have defined as electronegative. Similarly, hydrogen is an electropositive element. Based on this classification of elements as electronegative or electropositive, the concept of oxidation and reduction was extended one step further to include the electronegative and electropositive elements.

Thus, oxidation may now be defined as the addition of oxygen or an electronegative element to a substance or the removal of hydrogen or an electropositive element from a substance. Reduction is, therefore, the addition of hydrogen or an electropositive element to a substance or the removal of oxygen or an electronegative element from a substance, e.g.,

$$2Fe\,(s) + 3Cl_2\,(g) \longrightarrow 2FeCl_3\,(s)$$
$$Mg\,(s) + 2HCl(aq) \longrightarrow MgCl_2\,(aq) + H_2\,(g)$$

Oxidation and reduction in terms of change in oxidation number

Oxidation numbers (oxidation states) have been used as a device for assigning an electrical charge to an atom in a molecule.

Oxidation numbers are assigned according to the following rules :

1. The algebraic sum of the oxidation numbers of all atoms in a formula is equal to the net charge on the group of atoms represented by the formula. Thus the sum of the oxidation numbers in NaCl must be zero, and the sum of the oxidation numbers in MnO_4^- must be -1.
2. All elements in the free state (i.e., uncombined with any other elements) have an oxidation number of zero.
3. In a simple ion the oxidation number is the same as the charge on the ion. Thus, the ion Al^{3+} has an oxidation number of + 3 and the ion S^{2-} has an oxidation number of -2.
4. The alkali metals (Group IA metals) always exhibit an oxidation number of +1 in their compounds, and the alkaline earth metals (Group IIA metals) always exhibit an oxidation number of+2 in their compounds.
5. The oxidation number of oxygen in its compounds is taken to be -2 (except in O_2, O_3 and peroxides).
6. The oxidation number of hydrogen in its compounds is taken to be +1 (except in H_2, and ionic hydrides).

With these simple rules in mind the concepts of oxidation and reduction may now be further refined.

Oxidation-reduction reactions are characterized by changes in the oxidation numbers of some of the elements in the reactants. Any element which increases in oxidation number is said to be oxidized. Any element which decreases in oxidation number is reduced.

For example, in the reaction

$$2FeCl_2(s) \;+\; Cl_2(g) \longrightarrow 2FeCl_3(s)$$

the oxidation number of iron changes from + 2 in $FeCl_2$ to + 3 in $FeCl_3$, and therefore $FeCl_2$ has been oxidized to $FeCl_3$. Similarly, the oxidation number of the chlorine changes from 0 in the free element Cl_2 to -1 in $FeCl_3$, and the chlorine gas has therefore been reduced.

Thus, oxidation brings about an increase in oxidation number and reduction, a decrease in oxidation number.

Oxidation and reduction in terms of electron transfer

In the reaction

$$Zn. + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

it is obvious that the zinc is oxidized and the copper (II) ion is reduced. The formation of zinc ions is due to the loss of two electrons by each zinc atom. The change from copper (II) ions to copper metal is due to the gain of two electrons by each ion. Thus the loss of electrons by one species (electron donor) is accompanied by the gain of the electrons by another species (electron acceptor).

An oxidizing agent causes the oxidation of another species, and in the process it is reduced.

A reducing agent causes reduction of another species, and it in turn is oxidized.

From the electronic point of view the following are the definitions of oxidation and reduction.

Oxidation is the loss of electrons by an element, compound or ion.
Reduction is the gain of electrons by an element, compound or ion.
An oxidizing agent is an acceptor of electrons.
A reducing agent is a donor of electrons.

5.2 Oxidation-Reduction Reactions

Every oxidation must be accompanied by a corresponding reduction and vice versa, because if one substance loses electrons then another must gain them. Reactions in which simultaneous oxidation and reduction are occurring are often known as redox reactions.

The following example illustrates these reactions.

Example 1: Magnesium combines with oxygen to give magnesium oxide.

$$Mg\,(s) + \frac{1}{2}O_2\,(g) \longrightarrow MgO\,(s)$$

The electronic changes occurring are given by the two half-equations:

$$Mg - 2e^- \longrightarrow Mg^{2+} \text{ (Mg oxidized)}$$

$$\frac{1}{2}O_2 + 2e^- \longrightarrow O^{2-} \text{ (}O_2\text{ reduced)}$$

In these reactions the metal is oxidized by losing two electrons per atom. These electrons are accepted by oxygen atoms, which are reduced as a result. Magnesium (donating electrons) is reducing agent and oxygen (accepting electrons) is the oxidizing agent.

Example 2: Iron (II) chloride reacts with chlorine to give iron (III) chloride.

$$2FeCl_2(s) + Cl_2(g) \longrightarrow 2FeCl_3(s)$$

The two half-equations can be written as

$$Fe^{2+} \quad - \quad e^- \longrightarrow Fe^{3+} \ (Fe^{2+} \text{ oxidized})$$

$$Cl_2 \quad + \quad 2e^- \longrightarrow 2Cl^- \quad (Cl_2 \text{ reduced})$$

Addition of these two half-equations gives the full ionic equation.

$$2Fe^{2+} \quad + \quad Cl_2 \longrightarrow 2Fe^{3+} \quad + \quad 2Cl^-$$

The iron (II) ion, Fe^{2+}, is oxidized by losing one electron per ion and is the reducing agent. Chlorine acts as the oxidizing agent (electron acceptor) and is reduced.

Example 3: Passing hydrogen gas over hot copper (II) oxide gives the following reaction :

$$CuO(s) \quad + \quad H_2(g) \longrightarrow Cu(s) + H_2O(g)$$

The half-equations are

$$Cu^{2+} \quad + \quad 2e^- \longrightarrow Cu \quad (Cu^{2+} \text{ reduced})$$

$$H_2 \quad - \quad 2e^- \longrightarrow 2H^+ \quad (H_2 \text{ oxidized})$$

and hence the ionic equation is

$$Cu^{2+} \quad + \quad H_2 \longrightarrow Cu \quad + 2H^+$$

This ionic equation, however, does not give the complete picture. The oxide ion, O^{2-}, is strongly attracted by the H^+ ions and forms water which is almost completely covalent.

Example 4: Hydrogen sulphide reacts with chlorine to give hydrogen chloride and sulphur.

$$H_2S(g) \quad + \quad Cl_2(g) \longrightarrow S(s) + 2HCl(g)$$

The half-equations are

$$S^{2-} - 2e^- \longrightarrow S \quad (S^{2-}\ \text{oxidized})$$
$$Cl_2 + 2e^- \longrightarrow 2Cl^- \quad (Cl_2\ \text{reduced})$$

and the ionic equation is

$$S^{2-}(g) + Cl_2(g) \longrightarrow S(s) + 2Cl^-(g)$$

The hydrogen ion originally of the hydrogen sulphide is unchanged at the end of the reaction and it does not occur in the ionic equation.

Example 5: Electrolytic processes involve redox reactions. (See Chapter 4.) A cathode which is a source of electrons, is equivalent to a reducing agent, and the discharge of positive ions at a cathode is, chemically, a reduction.

For example, discharge of metallic ion (e.g., sodium ion) at a cathode is the reduction of that ion, Na^+, to the metal Na. The electron gained by the metallic ion is supplied by the cathode.

$$Na^+ + e^- \longrightarrow Na$$

By the same reasoning, an anode which is an electron acceptor, is equivalent to an oxidizing agent. Discharge of negative ions at an anode is an oxidation. For example, chloride ion, Cl^-, is oxidized to the atom, Cl, by electron loss, the electron being accepted by the anode, as

$$Cl^- - e^- \longrightarrow Cl$$

5.3 Oxidizing Agents

Oxidation is the loss of electrons from a substance. The loss of these electrons is brought about by the help of another substance which accepts the electrons. This other substance is the oxidizing agent. Hence, an oxidizing agent may be defined as an electron acceptor. Some important oxidizing agents and examples of their use are given below.

1. Oxygen $\frac{1}{2}O_2 + 2e^- \longrightarrow O^{2-}$

Oxygen oxidizes most metals and non-metals to their oxides.

$$2Cu(s) + O_2(g) \longrightarrow 2CuO(s)$$
$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

2. Chlorine $\frac{1}{2}Cl_2 + e^- \longrightarrow Cl^-$

Chlorine oxidizes heated iron to iron (III) chloride.

$$2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$$

3. Hydrogen peroxide $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$

The H^+ is supplied by water or dilute acid present in the reaction mixture.

Hydrogen peroxide oxidizes acidified solutions of potassium iodide, iodine being liberated. In this reaction the acid liberates hydrogen iodide from potassium iodide and it is the hydrogen iodide which is oxidized, i.e.,

$$2KI + 2HCl \longrightarrow 2KCl + 2HI$$
$$2HI + H_2O_2 \longrightarrow I_2 + 2H_2O$$

The full reaction is written as

$$2KI\ (aq) + 2HCl\ (aq) + H_2O_2(aq) \longrightarrow I_2(aq) + 2KCl(aq) + 2H_2O(1)$$

4. Nitric acid $\underset{(conc)}{4HNO_3} + 2e^- \longrightarrow 2NO_3^- + 2H_2O + 2NO_2$

$\underset{(dil)}{8HNO_3} + 6e^- \longrightarrow 6NO_3^- + 4H_2O + 2NO$

When copper reacts with concentrated nitric acid the products are copper (II) nitrate, water and nitrogen dioxide. But when copper reacts with a mixture of concentrated nitric acid and water in equal volumes the gaseous product is nitrogen oxide.

$$Cu(s) + 4HNO_3(conc) \longrightarrow Cu(NO_3)_2(aq) + 2H_2O(1) + 2NO_2(g)$$
$$3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2\ (aq) + 4H_2O(1) + 2NO(g)$$

5. Potassium permanganate $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

Acidified solutions of potassium permanganate oxidize sulphur dioxide. The purple solution turns colourless in the process.

$$5SO_2(g) + 2KMnO_4(aq) + 2H_2O(1) \longrightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 2H_2SO_4(aq)$$

6. Potassium dichromate $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

Acidified solutions of potassium dichromate oxidize iron (II) salts to iron (III) salts. The orange solution turns green.

$$K_2Cr_2O_7(aq) + 7H_2SO_4(aq) + 6FeSO_4(aq) \longrightarrow 3Fe_2(SO_4)_3(aq) + Cr_2(SO_4)_3(aq) + K_2SO_4(aq) + 7H_2O(1)$$

5.4 Reducing Agents

Reduction is the gain of electrons by a substance which accepts the electrons from another substance. Hence, reducing agents may be defined as electron donors. Some important reducing agents and examples of their use are given below.

1. Hydrogen (with heated metallic oxides) $H_2 + O^{2-} \longrightarrow H_2O + 2e^-$

   e.g., $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$

2. Carbon (with heated metallic oxides) $C + O^{2-} \longrightarrow CO + 2e^-$

   or $C + 2O^{2-} \longrightarrow CO_2 + 4e^-$

   e.g., $ZnO(s) + C(s) \longrightarrow Zn(s) + CO(g)$

3. Carbon monoxide (with heated metallic oxides)

   $CO + O^{2-} \longrightarrow CO_2 + 2e^-$

   e.g., $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

4. Hydrogen sulphide $S^{2-} \longrightarrow S + 2e^-$

   e.g., $2H_2S(g) + SO_2(g) \longrightarrow 3S(s) + 2H_2O(1)$

5. Sulphur dioxide (aqueous)

In aqueous solution, sulphur dioxide gives sulphurous acid which dissociates into hydrogen and sulphite ions.

$$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$$
$$H_2SO_3 \rightleftharpoons 2H^+ + SO_3^{2-}$$
$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

It turns acidified potassium dichromate solution from orange to green and acidified potassium permanganate solution from purple to colourless.

5.5 Balancing Oxidation-Reduction Equations

Two methods have been developed for balancing oxidation-reduction (redox) equations: The oxidation number method and ion-electron (half-reaction) method. To demonstrate these two methods the following equation will be used.

$K_2Cr_2O_7 + HI + HClO_4 \longrightarrow KClO_4 + Cr(ClO_4)_3 + I_2 + H_2O$

Oxidation number method

The oxidation number method makes use of the fact that the sum total of oxidation must equal the sum total of reduction in the overall chemical reaction. However, many examples of redox reactions are too complicated to balance by this method.

Step 1 Find which elements change oxidation number

$$Cr^{6+} \text{ (in } K_2Cr_2O_7) \longrightarrow Cr^{3+} [\text{in } Cr(ClO_4)_3] \text{ (change of - 3)}$$
$$I^- \text{ (in HI)} \longrightarrow I^0 (\text{in } I_2) \text{ (change of + 1)}$$

Step 2 To conserve oxidation number in the overall equation in a given example we must have three iodine atoms giving electrons for every chromium atom gaining electrons. Since the formula $K_2Cr_2O_7$ contains two chromium atoms, six HI molecules are required.

$$K_2Cr_2O_7 + 6HI + HClO_4 \longrightarrow KClO_4 + 2Cr(ClO_4)_3 + 3I_2 + H_2O$$

Step 3 Balance the metals that do not change oxidation number (K^+ in this case)

$$K_2Cr_2O_7 + 6HI + HClO_4 \longrightarrow 2KClO_4 + 2Cr(ClO_4)_3 + 3I_2 + H_2O$$

Step 4 Balance the anions that do not change (ClO_4^- in the case)

$$K_2Cr_2O_7 + 6HI + 8HClO_4 \longrightarrow 2KClO_4 + 2Cr(ClO_4)_3 + 3I_2 + H_2O$$

Step 5 Balance the hydrogen

$$K_2Cr_2O_7 + 6HI + 8HClO_4 \longrightarrow 2KClO_4 + 2Cr(ClO_4)_3 + 3I_2 + 7H_2O$$

Step 6 Balance the oxygen.

The oxygen atoms are already balanced: 39 on each side.

Ion-electron (half-reaction) method

The ion-electron method considers redox reactions as the sum of two half-reactions, one of which donates electrons and the other accepts those electrons. In all redox reactions the number of electrons donated by the reducing agent must be equal to the number of electrons accepted by the oxidizing agent.

Step 1 Omit ions which do not change in the reaction.

(K^+ and ClO_4^- in this case)

$$Cr_2O_7^{2-} + I^- + H^+ \longrightarrow Cr^{3+} + I_2 + H_2O$$

Step 2 Identify the elements oxidized and reduced, along with the oxidation and reduction products. Construct a half-equation for oxidation and reduction separately.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

$$2I^- \longrightarrow I_2$$

Step 3 Balance the atoms in the half-reactions by adding acid H^+ and H_2O, or base OH^- and H_2O (the number of oxygen and hydrogen atoms must be balanced).

Since H^+ is involved in the given reaction, H_2O and H^+ are used to balance the atoms.

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

$$2I^- \longrightarrow I_2$$

Step 4 Add electrons to balance the charge for each half-reaction. In step 3, the charge for the reactants of the first equation equals -2+14=+12 and for the products + 6. We must add six electrons to the reactants of that equation to achieve charge balance.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Similarly $2I^- \longrightarrow I_2 + 2e^-$

Step 5 If necessary, multiply one or both half-reactions by an integer to balance the number of electrons transferred in the two half reactions.

In this case, second half-reaction is multiplied by 3.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6I^- \longrightarrow 3I_2 + 6e^-$$

Step 6 Add the two half-reactions, cancelling species appearing on both sides of the resulting overall reaction. Electrons must cancel exactly.

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

The equation should now be balanced but a check should be made on the basis of charge balance. If the equation is really balanced, the net charges on each side will be equal.

$$\begin{array}{lllcl} -2 + & 14(+1) & +6(-1) & = & 2(+3)+3(0)+7(0) \\ -2 + & 14 & -6 & = & +6 \quad 0 \quad 0 \\ & & +6 & = & +6 \end{array}$$

$$K_2Cr_2O_7 + 6HI + 8HClO_4 \longrightarrow 2KClO_4 + 2Cr(ClO_4)_3 + 3I_2 + 7H_2O$$

Since all chemical reactions, excepting those occurring by double decomposition are redox reactions, the method of balancing equations described above may be applied generally. The following examples with further illustrate the method.

Example 1: $FeCl_2 + Cl_2 \longrightarrow FeCl_3$

Balance by ion-electron (half-reaction) method

1. Begin writing the half-reaction equations by showing reactants going to product.

$$Fe^{2+} \longrightarrow Fe^{3+}$$
$$Cl_2^0 \longrightarrow 2Cl^-$$

2. Balancing atoms - Atoms in the above two half-reaction equations are already balanced.
3. Adding electrons as needed to balance the charge.

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$
$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$

4. Multiplying first half-reaction by 2 to make the number of electrons in each half-reaction the same.

$$2Fe^{2+} \longrightarrow 2Fe^{3+} + 2e^-$$
$$Cl_2^0 + 2e^- \longrightarrow 2Cl^-$$

5. Adding the two half-reactions.

$$2Fe^{2+} \longrightarrow 2Fe^{3+} + 2e^-$$
$$Cl_2^0 + 2e^- \longrightarrow 2Cl^-$$
$$\overline{2Fe^{2+} + Cl_2 \longrightarrow 2Fe^{3+} + 2Cl^-}$$

Final check on charge balance

$$2(+2) + 0 = 2(+3) + 2(-1)$$
$$+4 \quad 0 = +6 \quad -2$$
$$+4 = +4$$
$$2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$$

Example 2: $MnO_4^- + S^{2-} \longrightarrow S + Mn^{2+}$

Balance by ion-electron (half-reaction) method

1. Writing the half-reaction equations.

$$MnO_4^- \longrightarrow Mn^{2+}$$
$$S^{2-} \longrightarrow S^0$$

2. Balancing atoms - Add H_2O and H^+ to balance the number of atoms.

$$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$
$$S^{2-} \longrightarrow S^0$$

3. Adding electrons as needed to balance the charge.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$S^{2-} \longrightarrow S^0 + 2e^-$$

4. Multiplying by coefficients (2 and 5, respectively) to make the number of electrons in each half-reaction the same.

$$2MnO_4^- + 16H^+ + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O$$
$$5S^{2-} \longrightarrow 5S^0 + 10e^-$$

5. Adding the two half-reactions.

$$2MnO_4^- + 16H^+ + 5S^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 5S$$

Final check on charge balance

$$2(-1) + 16(+1) + 5(-2) = 2(+2) + 8(0) + 5(0)$$
$$-2 + 16 - 10 = +4$$
$$+4 = +4$$

SUMMARY

This chapter is concerned with the concept of oxidation and reduction. The terms such as oxidizing agents and reducing agents are clearly defined with appropriate examples. Methods of balancing oxidation and reduction equations are presented with worked out examples. Problems and exercises are given at the end of this chapter for practice.

Questions and Problems

1. Define oxidation and reduction in terms of (a) oxygen, (b) hydrogen, (c) electrons.
2. What is a reducing agent? Give three examples of common reducing agents.
3. What is the oxidation number for the underlined element in each of the following substances?

   (a) $\underline{P}Cl_3$ (b) $\underline{Cr}_2O_7^{2-}$ (c) $H\underline{N}O_3$ (d) $K\underline{Cl}O_3$ (e) $\underline{P}_4$

   (f) $\underline{Mn}O_4^-$ (g) $\underline{N}_2O$ (h) $\underline{N}H_3$ (i) $\underline{S}_2O_6^{2-}$ (j) $NaH\underline{C}O_3$
4. Which of the following equations represent oxidation-reduction reactions? Identify each oxidizing and reducing agent.

(a) $H_2S + Cl_2 \longrightarrow S + 2HCl$

(b) $2H_2O + 2Cl_2 \longrightarrow 4HCl + O_2$

(c) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

(d) $CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$

(e) $PbO + C \longrightarrow Pb + CO$

(f) $Fe^{3+} + Al \longrightarrow Fe + Al^{3+}$

5. Select (a) an oxidizing agent and (b) a reducing agent from the following list: carbon, potassium permanganate, sodium sulphite, chlorine, copper (II) oxide.
6. State which reactant is oxidized in each of the following reactions. Give reason for your answers.

(a) $2Na + 2H_2O \longrightarrow 2NaOH + H_2$

(b) $Cu + CuCl_2 \longrightarrow 2CuCl$

(c) $SO_2 + H_2O + NaClO \longrightarrow NaCl + H_2SO_4$

7. Write balanced equations for the following reactions.

(a) $H^+ + NO_3^- + Fe^{2+} \longrightarrow Fe^{3+} + NO_2 + H_2O$

(b) $Cu^{2+} + I^- \longrightarrow CuI + I_2$

(c) $H_2O_2 + Cr_2O_7^{2-} + H^+ \longrightarrow Cr^{3+} + O_2 + H_2O$

(d) $H_2SO_4 + HI \longrightarrow I_2 + H_2S + H_2O$

(e) $MnO_4^- + NO_2^- + H_2O \longrightarrow NO_3^- + MnO_2 + OH^-$

8. Write TRUE or FALSE for each of the following statements.

(a) Oxidation number of hydrogen in hydrogen peroxide is +1.

(b) Electropositive elements may be reducing agents.

(c) Electrons are transferred from an oxidizing agent to a reducing agent.

(d) Electrolytic process involves redox reaction.

(e) Oxidation reaction takes place at the anode in an electrochemical reaction.

9. Fill in the blanks with a suitable word or phrase or numerical value with unit as necessary.

(a) An oxidizing agent is an ....

(b) Oxidation number of Cr in $Cr_2O_7^{2-}$ is ....

(c) When the oxidation number of an element is decreased, it is said to be ....

(d) A common laboratory oxidizing agent is ....

(e) Oxidation number of element in pure form is ....

10. Choose the correct term or terms given in the brackets.

(a) A cathode is a (an) (source of electron, electron acceptor, electron donor).

(b) An electrochemical reaction is a (an)(redox, catalytic, electron transferring) reaction.

(c) Oxidation is the (gain, loss, acceptor) of electrons.

(d) In the reaction:

$$Fe(s) + Cl_2(g) \longrightarrow FeCl_2(s)$$

Fe is a (an) (oxidizing, reducing, neither oxidizing nor reducing) agent.

(e) In the reaction:

$$S^{2-}(g) + Cl_2(g) \longrightarrow S(s) + 2Cl^-(g)$$

S^{2-} is (oxidized, reduced, neither oxidized nor reduced) to S.

11. Match each of the items given in List A with the appropriate item in List B.

List A	List B
(a) electropositive element	(i) oxidation number of sulphur is +6.
(b) electronegative element	(ii) oxidation number of sulphur is +4.
(c) SO_3	(iii) oxidizing agent
(d) SO_3^{2-}	(iv) electron donor
(e) element	(v) oxidation number is zero.

12 Answer the following questions.

(a) What is a loss of electrons called ?

(b) What is a gain in electrons called ?

(c) Are oxidizing agents good or bad at accepting electrons ?

(d) Are reducing agents good or bad at accepting electrons ?

(e) In the equation

$$2\,Br^-(aq) + Cl_2(g) \longrightarrow 2\,Cl^-(aq) + Br_2(l)$$

(i) What is being oxidized ?

(ii) What is being reduced ?

(iii) Which is the oxidizing agent ?

(iv) Which is the reducing agent ?

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CHAPTER 6

RATES OF REACTIONS AND EQUILIBRIA

The study of rates of reactions (chemical kinetics) and chemical equilibrium is central to the understanding of chemical reactions.

Questions are usually asked, such as

(1) why do chemical reactions occur?
(2) what factors determine the rates of the chemical reactions?
(3) even when a chemical reaction has occurred, the question is "whether the reaction is going to be complete or not".

These questions can only be answered, after one has studied the principles of rates of reactions and the concepts of chemical equilibria.

6.1 Rates of Reactions

An iron nail reacts slowly in air as it rusts. White phosphorus bursts into flame when exposed to air. Candle wax burns only after the wick of the candle is lighted. These reactions with the oxygen in air take place at different rates. The above examples show that reactions can proceed at different rates.

To understand the expression "the rate of a reaction", the following example may be used.

It is known that magnesium readily reacts with hydrochloric acid to form hydrogen and magnesium chloride. The equation for the reaction is

$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

Suppose we have a small clean strip of magnesium ribbon of known mass. When the magnesium strip is placed in dilute hydrochloric acid, reaction takes place. The magnesium ribbon is observed to disappear after some definite interval of time depending on its mass and the concentration of the acid. There is also an evolution of hydrogen gas during the course of the reaction.

The rate of disappearance of magnesium ribbon is the quotient obtained by dividing the mass of magnesium which has reacted completely by the time required for completion of reaction.

The rate of reaction (in terms of the reactant) is

$$\text{rate} = \frac{\text{mass of Mg reacted}}{\text{time of reaction}}$$

$$= \text{quantity of Mg reacted per unit time}$$

Similarly, the rate of reaction (in terms of the product) can be expressed as

$$\text{rate} = \frac{\text{volume of } H_2 \text{ collected under standard condition}}{\text{time of reaction}}$$

$$= \text{quantity of } H_2 \text{ produced per unit time}$$

Generally, in chemical reactions the rate of a reaction is measured in terms of change in concentration of reactant or product divided by time unit.

Hence, for an elementary chemical reaction of the type

$$A + B \longrightarrow C + D$$

the rate may be written as the decrease in concentration of reactant A with time, as expressed by the derivative $-\frac{d[A]}{dt}$, or the decrease in concentration of reactant B with time, $-\frac{d[B]}{dt}$. It may also be written as the increase in concentration of either C or D with time, i.e., $+\frac{d[C]}{dt}$ or $+\frac{d[D]}{dt}$

Thus in accordance with the stoichiometry of the reaction, the algebraic rate relation is

$$\text{rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

when the concentration of a particular reactant, which is decreasing in concentration with the progress of the reaction, is considered.

Alternatively, the rate may be derived by concentration of a particular product which has been formed in this case.

$$\text{rate} = +\frac{d[C]}{dt} = +\frac{d[D]}{dt}$$

Since the concentration of the product keeps on increasing with the progress of the reaction towards equilibrium.

The units of concentration can be in partial pressure units (for gases) or in moles, or in volumes (for solutions). The unit is usually expressed in moles per dm^3. Time is usually measured in terms of seconds, minutes, hours, days or months.The unit of rate of reaction is mol dm^{-3} s^{-1} or mol dm^{-3} min^{-1} or mol dm^{-3} hr^{-1}.

6.2 Factors influencing Reaction Rates

Effect of concentration of reactants

A chemical reaction will occur only if the molecules of the reacting substances come into contact with each other. Therefore, we postulate that chemical reactions depend upon collisions between the reacting particles-atoms, molecules or ions. This model of reaction rate behavior is called the collision theory. It states that the more frequent the contact between reacting species, the greater can be the rate of reaction. Thus, for a given set of reactants, an increase in the concentrations of those reactants will increase the number of reacting species per unit volume of the reaction system. Hence the chance for contact will be increased and therefore the rate of reaction will also increase accordingly. The rate of reaction is inversely proportional to the time taken (a fast reaction takes a short time, but a slow reaction takes a long time). Thus, it may be concluded that as the concentration of reactants is increased, the reaction time decreases, i.e., the rate of reaction increases.

Effect of pressure

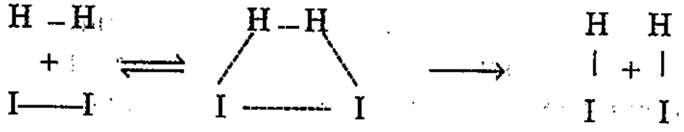
The effect of changing the pressure on reactions just involving liquids, solutions or solids is negligible since they are almost incompressible. However, the volumes of gases are greatly affected by pressure. The concentration of a gas is proportional to its (partial) pressure. At a given temperature the greater the quantities of gas in terms of moles in a given volume, the greater will be the pressure of that gas. Therefore, one can generally increase the rate of a reaction involving a gas by increasing its partial pressure. For example, iron filings burn slowly when heated in air, which contains only 20% oxygen; but when the hot iron filings are thrust into pure oxygen, combustion proceeds vigorously with a shower of sparks.

Effect of temperature

The observation that reactions proceed faster at higher temperatures than at lower ones is common experience. For example, the reason that foods are refrigerated for storage is to retard the reactions which would lead to spoilage at room temperature.

Chemical reactions occur when collisions occur but only when the collision involves more than a certain amount of energy. This can be explained by postulating that two molecules must collide with enough energy to form an activated complex which then can disintegrate into reaction products.

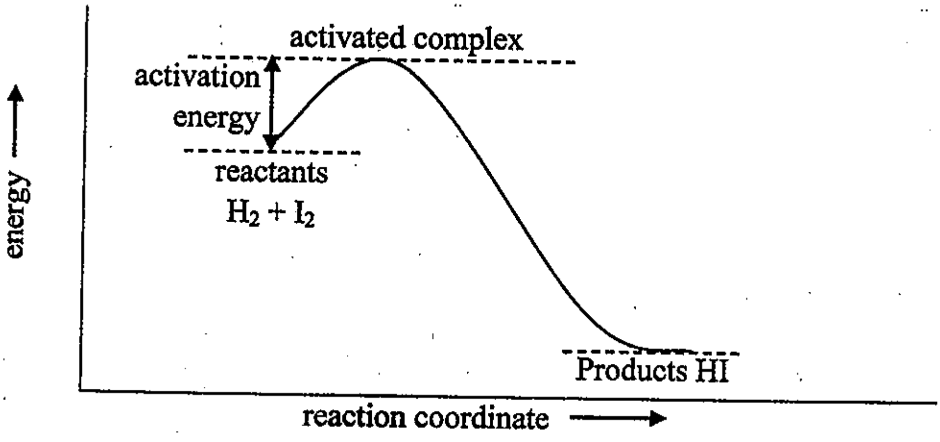
Many collisions are ineffective because molecules are not in proper orientation at the actual time of collision. Consider the reaction $H_2 + I_2 \rightarrow 2HI$. During collision, H_2 and I_2 molecules would come near each other, and prior to the formation of HI, the bonds between atoms in hydrogen and iodine molecules would be loosened due to molecular interactions and an intermediate complex, which is known as activated complex, will be formed as shown in Fig. 6.1.



activated complex

Fig. 6.1 Formation of HI

This **Intermediate state (also known as transition state)** being a species of high energy would be highly unstable and the activated complex can break into two HI or H_2 and I_2 molecules depending on a chance happening. The minimum energy required to form this activated complex is called **activation energy**. The progress of the reaction according to this concept is summarized in the energy diagram shown in Fig. 6.2



Reactants ⟶ Activated complex ⟶ Products

Fig. 6.2 Energy diagram for the reaction $H_2 + I_2 \longrightarrow 2HI$

Unless the colliding molecules have energy greater than the activation energy, the product molecules cannot be obtained. Of the many collisions which occur, only a small fraction of collisions have energy greater than the required activation energy. Hence, only a fraction of collisions lead to reaction products. As the temperature is raised, the number of collisions energetic enough to overcome the transition state increases and the reaction goes faster. Roughly, the rate of reaction becomes double when the temperature is increased by ten degrees.

Effect of catalysts

> A catalyst is a substance which alters the rate of a chemical reaction, but remains chemically unchanged at the end of the reaction.

Since catalysts are not consumed by the chemical reactions which they promote, a small quantity is sufficient to catalyze the reaction of a large quantity of reactants.

A catalyst that usually increases the rate of reaction is called **a positive catalyst. A negative catalyst** or an inhibitor decreases the rate of reaction, and this is occasionally used to suppress an unwanted reaction.

Catalysts are widely used in the chemical industry and in chemical research. Examples are: iron in the Haber Process for manufacturing ammonia ; vanadium (V) oxide or platinized asbestos in the Contact Process for manufacturing sulphur trioxide and manganese (IV) oxide in the preparation of oxygen from potassium chlorate.

$$N_2(g) \quad + \quad 3H_2(g) \quad \xrightleftharpoons{\text{Fe catalyst}} \quad 2NH_3(g)$$

$$2SO_2(g) \quad + \quad O_2(g) \quad \xrightleftharpoons[\text{catalyst}]{V_2O_5 \text{ or } Pt} \quad 2SO_3(s)$$

$$2KClO_3(s) \quad \xrightarrow[\text{catalyst}]{MnO_2} \quad 2KCl(s) \quad + \quad 3O_2\,(g)$$

A very large number of catalysts, called **enzymes**, are found in living tissues. Among the best known examples of these are the digestive enzymes such as the ptyalin in saliva and the pepsin in gastric juice. A common function of these two enzymes is to hasten the breakdown of large molecules, such as starch and protein, into simpler molecules that can be utilized by body cells.

Effect of radiation

Light is a source of energy and can influence the rate of some chemical reactions. For examples, the reaction between hydrogen and chlorine is extremely slow in the dark, but it becomes explosive when the reaction mixture is exposed to bright sunlight. Chlorine molecules absorb energy from light waves and, hence, become activated enough to decompose into chlorine atoms (also known as "free radicals") which are very reactive. These chlorine atoms combine with hydrogen molecules, forming hydrogen chloride molecules and hydrogen atoms. The hydrogen atom in turn reacts with a chlorine molecule producing another HCl molecule and a chlorine atom. In this way a reaction chain is set up and the reaction rate becomes very fast.

$$Cl_2 \xrightarrow[\text{(light)}]{h\nu} \dot{Cl} + \dot{Cl}$$

$$\dot{Cl} + H_2 \rightarrow HCl + \dot{H}$$

$$\dot{H} + Cl_2 \rightarrow HCl + \dot{Cl}$$

The above reaction is not the light catalyzed reaction. It is a photochemical reaction. A photochemical reaction is a reaction which takes place only when the reactant molecules absorb the light radiation ($h\nu$) when it is exposed.

Effect of surface area of reactants

The particle size may influence the rate of reaction in the chemical reactions involving solids. For example, aluminium foil reacts moderately with sodium hydroxide solution only when warmed but powdered aluminium reacts rapidly in the cold.

$$2Al(s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2NaAl(OH)_4\,(aq) + 3H_2(g)$$

These observations are due to the fact that reaction occurs at the surface of the solid. The larger the surface area, the greater the contact between the reactants and faster the reaction. For the same mass of substance, the smaller particles have a larger total surface area than larger particles. This explain why powdered aluminium reacts much more readily than aluminium foil.

6.3 Chemical Equilibria

Many reactions are reversible. That is, they can proceed in the forward as well as in the reverse directions under the appropriate conditions. Reversible reactions are indicated by using the $\rightleftharpoons$ sign in place of the usual single arrow sign. For example,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The reaction proceeding to the right is called the forward reaction; that occurring in the opposite direction is called the reverse reaction.

When hydrogen and iodine are mixed in a reaction vessel, only the forward reaction occurs as there is no hydrogen iodide. However, as the reaction proceeds, hydrogen iodide is formed and when its concentration is sufficiently high, the reverse reaction starts. As time passes, the concentrations of hydrogen and iodine decrease and so the forward reaction is slowed down. However, the reverse reaction speeds up since the concentration of hydrogen iodide increases. When the rates of the forward and reverse reactions become equal, there is no further change in the net concentration although the reactions in both directions may continue to take place. Equilibrium is said to be established at this stage. Equilibrium is a dynamic state, since both reactions are still proceeding; but since the two opposing reactions are proceeding at equal rates, no net change is observed.

6.4 Factors influencing Equilibrium - Le Chatelier's Principle

Once equilibrium is established in a system, no further change is apparent as long as the external conditions remain unchanged. If the external conditions are altered, the system will shift to a new state of equilibrium. The conditions affecting chemical equilibrium can be considered by the application of a principle known as Le Chatelier's principle, which is stated as follows:

> When anyone of the factors affecting the equilibrium of a chemical system such as temperature, pressure or concentration is changed, the system reacts in such a way as to nullify the effect of the change.

Effect of temperature

The effect of temperature on the position of equilibrium is illustrated by the following example.

In the Haber process, nitrogen and hydrogen take part in a reversible reaction to give ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The forward reaction (formation of ammonia) is accompanied by the evolution of heat while the reverse reaction (decomposition of ammonia into nitrogen and hydrogen) absorbs heat. If the temperature is raised, then according to Le Chatelier's principle, the system should counteract this by shifting the equilibrium to the left. In this way, the temperature will be lowered because the reverse reaction absorbs heat and decomposition of ammonia will be favoured. Conversely, lowering the temperature shifts the equilibrium in favour of the forward direction in which heat is evolved. That is, formation of ammonia will be favoured.

Effect of pressure

The effect of pressure change is much more noticeable in reactions occurring in the gaseous state than those occurring between solids and liquids, since the volumes of solids and liquids are very little affected by change in pressure.

A change in pressure causes a change in the volume of reacting gases. Consider the following reaction:

$$\underset{1\ \text{vol}}{N_2(g)} + \underset{3\text{vol}}{3H_2(g)} \rightleftharpoons \underset{2\ \text{vol}}{2NH_3(g)}$$

While going from left to right in the above reaction, there is a decrease in the total moles of gas or a decrease in volume. Increasing pressure would favour a decrease in volume. Since the gaseous system can counteract the effect of increased pressure only by a contraction of volume. Hence, a shift towards the right will take place. Thus, more ammonia is formed with increase in pressure. On the other hand, decreasing the pressure (increasing volume) results in the formation of more nitrogen and hydrogen.

The change in total pressure has no effect on those reactions in which there is no difference in the total moles of gas on either side of the equilibrium. That is, there is no change in the total moles as a result of the equilibrium reaction. For example, in the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

changing the total pressure will not shift the equilibrium since 2 moles of gaseous reactants produce 2 moles of gaseous product. The effect of pressure on gaseous systems may be summarized as follows :

> The pressure of a system is inversely proportional to its volume. Thus, high pressures favour reactions which take place with decrease in volume and low pressures favour reactions which take place with increase in volume.

Effect of concentration

Increasing the concentration of one of the substances in an equilibrium mixture causes the reaction to proceed in the direction which consumes the substance added.

Similarly, decreasing the concentration of a substance favours the reaction leading to the formation of the substance. The following reaction shows the effect of concentration on a system at equilibrium :

$Fe^{3+}(aq)$	$+ SCN^-(aq)$	$\rightleftharpoons$	$FeSCN^{2+}(aq)$
pale yellow	colourless (thiocyanate)		red coloured complex

Addition of more SCN^- ions to an equilibrium solution containing both Fe^{3+} and SCN^- ions brings about an increase in the concentration of the complex ion $FeSCN^{2+}$ and hence a corresponding increase in the intensity of colour. That is, the equilibrium shifts towards the right to form more $FeSCN^{2+}$ ion. Similarly, addition of more Fe^{3+} ions also shifts the equilibrium in the direction in which $FeSCN^{2+}$ is formed. On the other hand, if Fe^{3+} or SCN^- is removed from the equilibrium mixture the concentration of $FeSCN^{2+}$ will be relatively higher and the reaction will shift to the left, the solution will become paler. This is due to the conversion of some $FeSCN^{2+}$ into Fe^{3+} and SCN^-.

SUMMARY

The rate of reaction is measured interms of change in concentration of reactants or product divided by unit time (mol $dm^{-3}s^{-1}$or min^{-1} or hr^{-1})The substance used in a chemical reaction are called reactant and the substances produced in the reaction are called the products.Fast reaction takes a short time and slow reaction takes a long time.Concentration, pressure, temperature, catalyst, radiation and surface area of reactants are the six factors which influence the rate of reaction.A catalyst is a substance which alters the rate of a chemical reaction but remains chemically unchanged at the end of reaction.

Enzymes are biological catalysts.Inhibitors are catalysts which decreases the rate of reaction.Many reactions which can proceed in the forward as well as in the reverse directions under the appropriate conditions are called as reversible reactions.

$$(\text{Reactants} \rightleftharpoons \text{Products})$$

Equilibrium is used to be established, when the rates of the forward and reverse reactions become equal; there is no further change in the net concentration although the reactions in both directions may continue to take place, equilibrium is a **dynamic** state.According to Le Chatelier's principle, **increasing pressure** would favour **decrease in volume;** an **increase in temperature** would favour **endothermic reaction** (heat absorbing); and **increasing the concentration of one of the substances** in an equilibrium mixture causes the reaction to proceed **in the direction which consumes the substance added.**

Questions and Problems

1. Two gases X and Y are filled in a container. What effect will the following changes have on the rate of the reaction between these gases?
   (a) The pressure is doubled.
   (b) The number of molecules of gas X is doubled.
   (c) The temperature is decreased at constant volume.
2. Explain the following terms;
   (a) activation energy
   (b) transition state
   (c) reversible reaction
3. Write an equation for a reaction which can be catalyzed by manganese (IV) oxide. What would be the effect on the rate of this reaction if
   (a) more manganese (IV) oxide is added?
   (b) the same weight of catalyst is used but the particle size is increased?
4. Explain why rise in temperature increases the rate of reaction.
5. Why is chemical equilibrium referred to as a "dynamic equilibrium"?
6. Choose the correct statement from the following:
   (a) The addition of a catalyst changes the position of equilibrium.
   (b) A catalyst speeds up the forward reaction and slows down the reverse reaction.
   (c) The composition of equilibrium mixture is not changed by the catalyst.
   (d) Pressure change does not change the equilibrium concentration.
7. What is the effect of reducing the pressure on the following equilibrium?
   $$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
8. What is the effect of reducing the volume on the following equilibrium?
   $$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$$
9. What is the effect of increased pressure on the following equilibra?
   (a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   (b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
   (c) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
10. Using Le Chatelier's principle, predict the effects of
    (a) decreasing the temperature
    (b) increasing the temperature
    on each of the following equilibrium systems.
    (i) $N_2(g) + O_2(g) + \text{heat} \rightleftharpoons 2NO(g)$
    (ii) $H_2O(g) + \text{heat} \rightleftharpoons H_2(g) + {}^1\!/_2O_2(g)$
    (iii) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) + \text{heat}$
    (iv) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) + \text{heat}$

11. The dissociation of calcium carbonate is accompanied by the absorption of heat.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

What will be the effect of

(a) increasing the temperature?

(b) increasing the pressure on the equilibrium?

12. Sulphuric acid is manufactured by making use of the equilibrium reaction.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(a) Heat is given out in the formation of SO_3. State what effect there would be on the equilibrium concentration of SO_3 if

(i) the pressure were increased.

(ii) the temperature were raised.

(b) The actual conditions used in the process are

(i) an excess of air.

(ii) a temperature of about 450 °C.

(iii) a pressure slightly in excess of one atmosphere.

(iv) a catalyst.

Explain why each of the conditions is necessary.

13. State TRUE or FALSE for each of the following statements.

(a) A large particle has the larger surface area than the smaller particles of the same mass.

(b) The reaction is completely stopped at the equilibrium.

(c) At the equilibrium the reactions are still proceeding with equal rate on both sides.

(d) There is no pressure effect on the equilibrium of

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(e) More amount of product would be obtained by using a proper catalyst.

14. Fill in the blanks with a suitable word or phrase or numerical value with unit as necessary.

(a) The rate of reaction is inversely proportional to the ....

(b) A catalyst alters the ....

(c) A catalyst found in the living cell is known as ....

(d) An activated complex has the .... energy.

(e) A substance to slow down the rate of reaction is known as ....

15. Choose the correct term or terms given in the brackets.

(a) A catalyst changes (the rate of reaction, concentration of product, frequents of collisions).

(b) The rate of decomposition of A is denoted by $(-\frac{d[A]}{dt}, \frac{d[A]}{dt}, \frac{A}{t})$

(c) (Every collision, Collision with enough energy, Collision with low energy) leads to the chemical reaction.

(d) An activated complex is (stable, unstable, highly energetic) intermediate.

(e) Enzyme is a (an) (biocatalyst, inhibitor, intermediate).

16. Match each of the items given in List A with the appropriate item in List B.

List A	**List B**
(a) intermediate state	(i) amount of product formed per unit time
(b) activation energy	(ii) reaction by light
(c) inhibitor	(iii) transition state
(d) photochemical reaction	(iv) minimum energy for a chemical reaction
(e) rate of reaction	(v) slow down the rate of reaction.

17. Which change will not affect the ammonia in the following reactions ?

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2\,NH_3\,(g) + \text{heat}$$

(a) Increasing the temperature of the reaction vessel ?

(b) Adding a suitable catalyst.

(c) Increasing the pressure of the reaction.

(d) Increasing the concentration of hydrogen.

18. (a) What do you understand by the term ' reversible reaction ' ?

(b) In the following reversible reactions, name all the reactants and products and explain how you would move to the right hand side (products) of the equations.

(i) $CuSO_4 \cdot 5H_2O\,(s) \rightleftharpoons CuSO_4\,(s) + 5\,H_2O\,(g)$

(ii) $Fe_2O_3\,(s) + 3\,H_2\,(g) \rightleftharpoons 2\,Fe(s) + 3\,H_2O(l)$

(iii) $NH_4Cl\,(s) \rightleftharpoons NH_3\,(g) + HCl\,(g)$

(iv) $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$

(v) $2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$

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CHAPTER 7

ENERGY CHANGES IN CHEMICAL REACTIONS

Matter possesses energy of various kinds, which may be classified as :

(1) Kinetic energy - energy due to the moving of a body
(2) Potential energy - energy due to the position of a body, e.g., mass in a gravity field, a charged particle in an electric field
(3) Thermal energy - energy due to the effect of temperature
(4) Chemical energy - energy due to the structure of a substance and
(5) Other forms of energy such as electrical energy produced from a generator; mechanical energy produced from a motor.

Of the various forms of energy, that form of energy which most interests us is chemical energy. Chemicals such as dynamite or petrol (gasoline) have the capacity to undergo change. This capacity for change, called chemical energy is a kind of potential energy. The study of energy changes in chemical reactions is a subject in itself and is usually called "Chemical Energetics ". This subject deals with the change in energy, which is either released or absorbed when chemical reactions take place. Examples are; the burning of a match in air; the explosively violent reaction between hydrogen and oxygen initiated by a burning match; and the heat evolved when sulphuric acid reacts with sodium hydroxide.

7.1 Exothermic and Endothermic Reactions

Whenever a chemical reaction takes place between reactants to form products, there is always a marked heat change. In some reactions energy is absorbed whereas in some reactions energy is evolved as you have learnt in Grade Ten Chemistry.

For instance, when sulphuric acid is slowly poured into water, the beaker (or flask) becomes hot. This is a case of heat being released to the surroundings by the reacting system. This kind of change (reaction) is known as an exothermic change (reaction).

$$H_2SO_4(l) + H_2O(l) \longrightarrow H_2SO_4(aq) + \text{heat}$$

There is another kind of heat change when ammonium chloride is dissolved in water, the beaker becomes quite cold to the touch. This is a case of heat being absorbed from the surroundings by the reacting system. This kind of change (reaction) is known as an endothermic change (reaction).

$$NH_4Cl(s) + H_2O(l) + \text{heat} \longrightarrow NH_4Cl(aq)$$

An exothermic reaction is one which releases heat to the surroundings.
An endothermic reaction is one which absorbs heat from the surroundings.

7.2 Units of Heat Change

The unit of heat change is the joule (symbol J). The joule is expressed as follows:

1 J (joule) = 1 V (volt) x 1 C(coulomb)

Another common unit of heat change is the calorie (symbol cal). A calorie is the heat required to raise the temperature of 1 gram of water by 1°C. The kilocalorie (kcal) is used to represent 1000 calories.

The relation between calorie and joule is

1 cal (calorie) = 4.18 J (joule)

7.3 The Enthalpy Change of Chemical Reactions and Standard Conditions

The "heat change" of a chemical reaction is usually expressed by the terms "change in heat content" or "change in enthalpy" of the chemical reaction. **The heat absorbed or released in a process occurring at constant pressure is called the enthalpy change.** The change in enthalpy of a chemical reaction is represented by ΔH.

Most of the chemical reactions may occur at ambient room temperature and atmospheric pressure. Hence, the "heat change" of a chemical reaction is also expressed by the terms "Standard Enthalpy Change", symbolized as ΔH^{θ}. **The heat absorbed or released in a process occurring at standard conditions of temperature and pressure is called the standard enthalpy change.**

The standard conditions chosen for energy changes are as follows:

standard temperature = 298 K (25 °C)
standard pressure = 1 atm (760 mmHg)

For an exothermic reaction where energy is released, ΔH or ΔH^{θ} is negative i.e., negative sign.

For an endothermic reaction where energy is absorbed, ΔH or ΔH^{θ} is positive i.e., positive sign.

Examples of exothermic reactions are the following:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(1) \qquad \Delta H^{\theta} = -286\ \text{kJ mol}^{-1}$$

$$C\ (\text{graphite}) + O_2\ (g) \longrightarrow CO_2\ (g) \qquad \Delta H^{\theta} = -386\ \text{kJ mol}^{-1}$$

Examples of endothermic reactions are represented as follows;

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g) \qquad \Delta H^\theta = +90.3 \text{ kJ mol}^{-1}$$

$$C(\text{graphite}) + 2S(\text{rhombic}) \longrightarrow CS_2(1) \qquad \Delta H^\theta = +117 \text{ kJ mol}^{-1}$$

These equations (exothermic as well as endothermic), which include information regarding heat changes as well as physical states are called "thermochemical equations".

7.4 Types of Heat Change

Heat changes result from different kinds of chemical reactions. The usual chemical reactions are

(1) heat of combustion
(2) heat of formation of a compound
(3) heat of neutralization.

Heat of combustion

Many substances burn in air (or oxygen). This process is called combustion. The heat change involved in combustion is called heat of combustion. Heat of combustion of a substance is always negative i.e., heat is evolved when a substance is burned in oxygen.

> The heat of combustion of a substance is defined as the heat change which takes place when one mole of the substance is completely burned in oxygen.

For example, heats of combustion of the burning of one mole of hydrogen gas in oxygen, the burning of one mole of solid carbon in oxygen and the burning of one mole of methane gas in oxygen are – 286 kJ, –394 kJ and – 890 kJ, respectively. The reactions are written as follows :

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(1) \qquad \Delta H^\theta = -286.0 \text{ kJ mol}^{-1}$$

$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\theta = -396.0 \text{ kJ mol}^{-1}$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(1) \qquad \Delta H^\theta = -890.0 \text{ kJ mol}^{-1}$$

The heat of combustion is measured by using an equipment called a **bomb calorimeter.**

Heat of formation of a compound

Heat change in a chemical reaction is also expressed in terms of heat of formation of a compound, ΔH_f^θ

> The heat of formation is defined as the heat change when one mole of a compound is

formed from its elements in their standard states. The standard state of each element and each compound is defined as its most stable physical form at 1 atm pressure and 298 K.

By convention, the enthalpy of each element in the uncombined state is assumed to be zero when it is in its standard state.

For example, the heat of formation of one mole of liquid water is expressed as

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_f^\theta = -286\ kJ\ mol^{-1}$$

In this example $\Delta H_f^\theta = -286\ kJ\ mol^{-1}$ is not only "the heat of formation for the formation of one mole of H_2O (l) "; but it may be expressed depending on the choice of heat change that one wishes to express. In this case it is also " the heat of combustion of one mole of H_2 (g)"

However, the heat involved for the formation of one mole of carbon dioxide gas, CO_2 (g), from carbon monoxide and oxygen is not the "heat of formation", but rather the "heat of combustion of one mole of carbon monoxide gas" or simply the "heat of reaction". Note that the term "heat of formation", is used only when elemental reactants combine to form a compound.

Further examples of "heat of formation" reactions are:

$$S\ (rhombic) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H_f^\theta = -296.8\ kJ\ mol^{-1}$$

$$2Al(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(s) \qquad \Delta H_f^\theta = -1667.8\ kJ\ mol^{-1}$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g) \qquad \Delta H_f^\theta = -92.2\ kJ\ mol^{-1}$$

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g) \qquad \Delta H_f^\theta = -45.4\ kJ\ mol^{-1}$$

$$\frac{1}{2}N_2\ (g) + \frac{1}{2}O_2\ (g) \longrightarrow NO\ (g) \qquad \Delta H_f^\theta = +90.3\ kJ\ mol^{-1}$$

The way the reactions are written, giving special attention to the formation of one mole of product, should be noted. ΔH_f^θ may also be exothermic or endothermic.

Heat of neutralization

Whenever acids and bases react together in a neutralization reaction, to form a salt and water heat energy is always evolved.

$$\text{acid} + \text{base} \longrightarrow \text{salt} + \text{water}$$

In the neutralization reaction between any acid and a base the heat change that is involved, is only due to the formation of one mole of H_2O (1) from one mole of hydrogen ions from the acid and one mole of hydroxide ions from the base. It is not due to the reaction between one mole of acid and one mole of base.

The heat of neutralization is expressed as follows:

> The heat of neutralization is the heat change when one mole of hydrogen ions from an acid reacts with one mole of hydroxide ions from a base.

Thus, it may be written as

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \quad \Delta H^\theta = -57\ kJ\ mol^{-1}$$

This value of the heat of neutralization is the same for the neutralization between any pair of strong acid and strong base. All heats of neutralization are found to be exothermic.

The heat of neutralization of the reaction between HCl and NaOH is – 57 kJ mol^{-1}

$$Na^+OH^-(aq) + H^+Cl^-(aq) \longrightarrow Na^+Cl^-(aq) + H_2O(l) \quad \Delta H^\theta = -57\ kJ\ mol^{-1}$$

The heat given out by the neutralization of KOH and HNO_3 is also $\Delta H^\theta = -57$ kJ. But it is not the same when a complete reaction takes place between NaOH and H_2SO_4 or NaOH and H_3PO_4, since these two acids are not monobasic. That is, one mole of H_2SO_4 if completely ionized, contributes two moles of H^+ ions. It is dibasic.

7.5 Hess's Law of Constant Heat Summation

At a particular temperature, the enthalpy change of a chemical reaction depends only on the nature of reactants and products. It does not depend on whether the reaction is carried out by different methods. For example, consider the burning of carbon (graphite) to produce one mole of CO_2. The reaction is written as.

$$C\ (graphite) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H^\theta = -393\ kJ\ mol^{-1}$$

It is also possible to carry out this reaction by two steps. First, carbon is converted to carbon monoxide, and then followed by the oxidation of CO to CO_2. The relevant **thermochemical equations** may be written as:

$$\begin{array}{lcll} C\ (graphite) + \frac{1}{2}O_2(g) & \longrightarrow & CO(g) & \Delta H^\theta = -110\ kJ\ mol^{-1} \\ CO\ (g) + \frac{1}{2}O_2(g) & \longrightarrow & CO_2(g) & \Delta H^\theta = -283 kJ\ mol^{-1} \\ \hline C\ (graphite) + O_2(g) & \longrightarrow & CO_2(g) & \Delta H^\theta = -393\ kJ\ mol^{-1} \end{array}$$

The sum of the enthalpy changes in these two reactions gives the value of $\Delta H^\theta = -393\ kJ\ mol^{-1}$ which is the same as the enthalpy change for the burning of carbon to produce one mole of $CO_2(g)$.

$$\begin{tikzcd}
C_{(graphite)} \arrow[rr, "\Delta H_I^\theta"] \arrow[dr, "\Delta H_{II}^\theta"'] & & CO_2\,(g) \\
& CO\,(g) \arrow[ur, "\Delta H_{III}^\theta"'] &
\end{tikzcd}$$

$$\Delta H_I^\theta = \Delta H_{II}^\theta + \Delta H_{III}^\theta.$$

* A thermochemical equation summarizes the chemical reaction inclusive of the heat changes taking place in the reaction. Heat changes or enthalpy changes are expressed by using the symbol ΔH. Negative values of ΔH^θ indicate heat loss by the system, i.e., heat is evolved. Positive values of ΔH^θ indicate heat gain by the system, i.e., heat is absorbed.

When chemical equations are added or subtracted one must also add or subtract the corresponding enthalpy changes.

This conclusion is expressed by " **Hess's Law of constant heat summation**".

The net enthalpy change of a given chemical reaction remains the same, no matter by what methods the change is carried out.

Hess's law is found to be useful for thermochemical calculations. By using this law it is possible to calculate the enthalpy changes of reactions which cannot be determined directly by experiment. For example, the heat change for the formation of methane, represented by the equation,

$$C\,(graphite) + 2H_2(g) \longrightarrow CH_4(g)$$

cannot be carried out directly in a calorimeter. However, ΔH_f^θ for methane can be obtained by measuring the heats of combustion of methane and its constituent elements, carbon and hydrogen, represented by the following reactions.

(a) $C\,(graphite) + O_2\,(g) \longrightarrow CO_2(g) \qquad \Delta H^\theta = -393\ kJ\,mol^{-1}$

(b) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(1) \qquad \Delta H^\theta = -286\ kJ\,mol^{-}$

(c) $CH_4(g) + 2O_2\,(g) \longrightarrow CO_2(g) + 2H_2O(1) \quad \Delta H^\theta = -890\ kJ\,mol^{-1}$

(a) $\Rightarrow C(graphite) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\theta = -393\ kJ\,mol^{-}$

(b) x 2 $\Rightarrow 2H_2(g) + O_2(g) \longrightarrow 2H_2O(1) \qquad \Delta H^\theta = -572\ kJ$

$C(graphite) + 2H_2(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)\ \Delta H^\theta = -965\ kJ$

(c) $\Rightarrow \quad CH_4(g) + 2O_2\,(g) \longrightarrow CO_2(g) + 2H_2O(1) \ \ \Delta H^\theta = -890\ kJ\,mol^{-1}$

$C\,(graphite) + 2H_2(g) \longrightarrow CH_4(g)\ \Delta H^\theta = -75\ kJ\,mol^{-1}.$

Net operation $\Rightarrow$[(a) + 2(b)] - (c)

Another way of obtaining the thermochemical equation for the formation of methane as follows;

(a) $\Rightarrow C(graphite) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\theta_f = -393\ kJ\ mol^{-1}$

(b) x 2 $\Rightarrow 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H^\theta = -572\ kJ$

(c) reverse $\Rightarrow CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g) \qquad \Delta H^\theta = +890\ kJ$

$C\ (graphite) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H^\theta = -75\ kJ\ mol^{-1}$

Adding equations (a) and (b) and subtracting equation (c) from the sum gives the equation for the formation of CH_4. The reaction for the formation of methane is

Net operation ⇒[(a) + 2(b) + reverse of (c)]

SUMMARY

This chapter introduces some of the basic concepts of energy changes in chemical reactions. Various types of energy are presented in it. Every change either physical or chemical of a substance, is accompanied by a change of energy. In chemistry we are more concerned with heat and chemical energy. Chemical energy is a form of potential energy which exists in a substance. Every process occurring in daily life is associated with the change of energy. The study of energy changes in chemical reactions, chemical energetic, deals with the energy change which is either absorbed (endothermic) or released(exothermic) when chemical reactions are taking place. The target concept of this chapter is enthalpy (enthalpy change) denoted as ΔH which is measured under constant pressure. Most of the chemical reactions are allowed to occur at ambient temperature and pressure. We need to specify the standard conditions for chemical reactions. Hence, standard enthalpy change symbolized as ΔH^θ is introduced. It is measured at the temperature of 298 K(25 °C) and under the pressure of 1 atm(760 mmHg). Students can understand what the difference between standard conditions for both gaseous state and chemical reactions would be. Three types of heat change, namely heat of combustion, heat of formation of a compound and heat of neutralization are discussed in this chapter. Students should practice in writing the thermochemical equations concerning with such kinds of heat change. They should take care of units of enthalpy change or standard enthalpy change while writing thermochemical equations. In last portions of this chapter Hess's law of constant heat summation is described. This law is very useful tool in order to find out the enthalpy change of a chemical reaction that is impossible to take place directly by experiment. Students should study how to determine the enthalpy changes of chemical reactions by utilizing Hess's law. Since many methods can be applied to solve the Hess's law problems, teachers should encourage their students to understand the concepts which may be easy way of solving such kind of problems.

Questions and Problems

1. Explain the terms
   (a) an exothermic reaction
   (b) an endothermic reaction
   (c) enthalpy change
2. Which of the following are endothermic reactions?
   (a) $H_2SO_4(l) + H_2O(l) \longrightarrow H_2SO_4(aq) \quad \Delta H^\theta = -71\ kJ\ mol^{-1}$
   (b) $NH_3(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \quad \Delta H^\theta = +46\ kJ\ mol^{-1}$
   (c) $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g) \quad \Delta H^\theta = +90.3\ kJ\ mol^{-1}$
   (d) $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \quad \Delta H^\theta = -48\ kJ\ mol^{-1}$
3. Write the thermochemical equations indicating the sign of the enthalpy change for the following processes:
   (a) NH_4Cl is dissolved in water.
   (b) H_2SO_4 is added to water to form 2.0 M solution.
   (c) 1 mole of carbon (graphite) is heated with 2 moles of hydrogen.
   (d) 0.1 M hydrochloric acid is neutralized with 0.1 M potassium hydroxide solution.
4. Will the temperature of the surrounding air increase or decrease, if
   (a) an exothermic reaction is allowed to occur in air?
   (b) an endothermic reaction is allowed to occur in air?
5. The formation of methanol from hydrogen and carbon monoxide can be represented by

   $$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(1) \quad \Delta H^\theta = +91\ kJ\ mol^{-1}$$

   (a) What mass of hydrogen would react to cause this heat change?
   (b) What would be the effect on the equilibrium concentration of methanol in this endothermic reaction if
      (i) the temperature was increased?
      (ii) the pressure was increased?
      (iii)the hydrogen concentration was increased?
6. The heat evolved in the combustion of methane is given by the following equation:

   $$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(1) \quad \Delta H^\theta = -890\ kJ\ mol^{-1}$$

   (a) How many grams of methane would be required to produce when 445.15 kJ of heat is evolved?

(b) How many grams of carbon dioxide would be formed when 445.15 kJ of heat is evolved?

7. The heat change for the following exothermic reaction.

$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$ is $\Delta H^\theta = -57.3\ kJ\ mol^{-1}$

State the heat changes for the following reactions in dilute aqueous solutions and give reasons for your answers:

(a) $KOH\ (aq) + HNO_3\ (aq) \longrightarrow KNO_3\ (aq) + H_2O\ (1)$

(b) $2NaOH\ (aq) + H_2SO_4\ (aq) \longrightarrow Na_2SO_4\ (aq) + 2H_2O(1)$

8. Explain Hess's law of constant heat summation.

9. Calculate the heat of combustion of methane if its heat of formation is $-76\ kJ\ mol^{-1}$. The heats of formation of CO_2 (g) and H_2O (l) are $-393\ kJ\ mol^{-1}$ and $-286\ kJ\ mol^{-1}$, respectively.

10. Calculate the heat of formation of C_2H_5OH (1) if its heat of combustion is $-1368\ kJ\ mol^{-1}$. The heats of formation of CO_2 (g) and H_2O (l) are $-393\ kJ\ mol^{-1}$ and $-286\ kJ\ mol^{-1}$, respectively.

11. Calculate the heat of formation of CH_3COOH (1).

Given: ΔH^θ (combustion of carbon (graphite)) = $-393\ kJ\ mol^{-1}$.

ΔH^θ (combustion of hydrogen) = $-286\ kJ\ mol^{-1}$

ΔH^θ (combustion of CH_3COOH (l)) = $-872\ kJ\ mol^{-1}$

12. Calculate the heat of combustion of butane gas if its heat for formation is $-124\ kJ\ mol^{-1}$ The heats of formation of $CO_2(g)$ and $H_2O(l)$ are $-393\ kJ\ mol^{-1}$ and $-286\ kJ\ mol^{-1}$, respectively.

13. Calculate the heat of combustion of oxalic acid, $C_2H_2O_{4(s)}$ if its heat of formation is $-251\ kJ\ mol^{-1}$. The heats of combustion of carbon graphite and hydrogen are $-393\ kJ\ mol^{-1}$ and $-286\ kJ\ mol^{-1}$, respectively.

14. Write TRUE or FALSE for each of the following statements.

(a) The heat liberated by the combustion of one mole of graphite is greater than that of one mole of carbon monoxide.

(b) An endothermic process may be used as a cooling system.

(c) Mention of physical states of the substances is essential in writing thermochemical equation.

(d) The surrounding temperature is increased by an exothermic process.

(e) Combustion of fuels is exothermic.

15. Fill in the blanks with a suitable word or phrase or numerical value with unit as necessary.

(a) An exothermic reaction .... heat to the surroundings.

(b) Standard enthalpy change is denoted by the symbol............... and it is measured at ....

(c) The heat change by the combustion of one mole of substance in oxygen is known as ....

(d) Heat liberated by a chemical reaction is assigned by .... sign.

(e) When glucose is dissolved in water, the solution is cold to touch. So the process is ....

16. Choose the correct term or terms given in the brackets.

(a) (ΔH^{θ}, ΔH, H) is the symbol of standard enthalpy change.

(b) Melting of ice is a (an) (exothermic, endothermic, heat absorbing) process.

(c) Heat change by the combustion of one mole of hydrogen is (heat of formation of hydrogen, heat of formation of water, heat of combustion of hydrogen).

(d) Standard enthalpy change is measured at (0 °C, 273 K, 25 °C) and 760 mmHg.

(e) The temperature of surroundings (increases, decreases, remains unchanged) by the endothermic reaction.

17. Match each of the items given in List A with the appropriate item in List B.

List A	**List B**
(a) Endothermic process	(i) depends upon structures
(b) Heat of formation	(ii) ΔH_f^{θ}
(c) 1 cal	(iii) $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
(d) Heat of neutralization	(iv) heat absorbs
(e) Chemical energy	(v) to increase 1 g of water by 1 °C.

18. Give two examples of exothermic reactions.

19. Give two examples of endothermic reactions.

20. When hydrogen burns in oxygen, energy is released and water is formed.

(a) Give a balanced chemical equation for the reaction.

(b) Is the reaction exothermic or endothermic?

21 Give three possible forms of the energy released.

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CHAPTER 8

SOME IMPORTANT METALS AND THEIR COMPOUNDS

Metals are very important for the national economy of any country. They are widely used in our everyday life. Thus, the study of metals and their compounds is one of the important areas of chemistry.

In Table 8.1, the metals are arranged in order of the activity series. This arrangement more or less represents the inverse order of the ease with which the elements may be extracted.

Table 8.1 Metals arranged in decreasing order of reactivity and inverse of ease of extraction

reactivity decreases; extraction becomes easier ↓

K Na Ca Mg Al	Very reactive. Never found as free element. Extracted by electrolysis.
Zn Fe Pb	Moderately reactive. Found as oxides, carbonates or sulphides. Extracted by the reduction reaction.
Cu Hg Ag Au	Not very reactive. May be found in nature as the free element.

This chapter deals with the "Alkali Metals" Group I metals, such as sodium, potassium; the "Alkaline Earth Metals " Group II metals, such as magnesium, calcium; Group III metal, aluminium and Group IV metal, lead.

8.1 Group I Metals : Sodium and Potassium

The alkali metals are the members of Group IA in the periodic table. (See Table 8.1)

Table 8.1 Group IA The alkali metals

Symbol	*Name of the element*	*Atomic number*
Li	Lithium	3
Na	Sodium	11
K	Potassium	19
Rb	Rubidium	37
Cs	Caesium	55
Fr	Francium	87

In all these metals, the only one electron in the outermost shell occupies the s-orbital; hence these elements are sometimes called the s-block elements.

Oxidation number of the alkali metals

Table 8.2 shows the various physical properties of the alkali metals.

Table 8.2 Physical properties of the alkali metals

Element	*Li*	*Na*	*K*	*Rb*	*Cs*
Electronic structure	(He)$2s^1$	(Ne)$3s^1$	(Ar)$4s^1$	(Kr)$5s^1$	(Xe)$6s^1$
1st ionization energy (kJ mol^{-1})	520	495	418	403	374
2nd ionization energy (kJ mol^{-1})	7300	4600	3100	2700	2400
Atomic radius i.e., metallic radius (nm)	0.123	0.157	0.203	0.216	0.235
Melting point (°C)	180	98	64	39	29
Boiling point (°C)	1330	892	760	688	690
Density (g cm^{-3})	0.53	0.97	0.86	1.53	1.90

From Table 8.2 you can see that the first ionization potential for each of the element is much lower than that of the second. In the case of Na, it is nine times easier to remove the first electron than the second. The first electron, in s-orbital can be removed from the atom easily, but the second electron must be removed from a noble gas core, and therefore requires much more energy. Thus, sodium readily forms

Na^+ ions, but never forms Na^{2+} ions. This means that sodium and the other elements in Group IA have the one oxidation state of + 1 only in their compounds.

Physical properties of the alkali metals

The atomic radii increase with increasing atomic number down the group since each succeeding element has electrons in the next larger shell than those in the previous element.

The outermost s-electrons in these metals are held very weakly by the nucleus. Thus, the outer electrons can drift further from the nucleus than in most other atoms, and the elements in Group I have larger atomic radii than those elements which follow them in their respective periods.

The large atomic size results in weaker forces between neighbouring atoms since there is a reduced attraction by the nucleus for the shared mobile outer electrons as these electrons get further away. Consequently the alkali metals have lower melting points and lower boiling points than we would normally associate with metals. All the Group IA metals melt below 200 °C in contrast to most transition metals that melt above 1000 °C.

The reduced interatomic forces in these metals make them relatively soft. All the Group IA metals can be cut with a knife and they are generally softer than transition metals.

The s-block elements have larger atomic radii than transition metals of approximately the same relative atomic mass. Thus, the s-block elements will be less dense and have larger molar volumes. The densities of the alkali metals vary from approximately 0.5 g cm^{-3} to 2 g cm^{-3}. Most transition metals have a density greater than 7 g cm^{-3}.

Chemical properties of the alkali metals

The positions of the alkali metals are high in the electrochemical series. Hence these metals are very good reducing agents. With the exception of lithium, all alkali metals react vigorously with water, reducing it to hydrogen.

$$M(s) \longrightarrow M^+(aq) + e$$

$$H_2O(l) + \quad e \quad \longrightarrow \frac{1}{2}\, H_2(g) + OH^-\ (aq)$$

Excepting lithium, which reacts slower than all the other alkali metals, the reactivity of the elements with water closely follows their positions in the electrochemical series. For example, sodium reacts vigorously, fizzing and skating about on the water surface.

Potassium reacts even more vigorously producing small cracks and pops as the hydrogen explodes and burns with a lilac flame.

The alkali metals are such good reducing agents that they can react with chlorine, bromine, sulphur, hydrogen and oxygen on heating.

The alkali metals tarnish rapidly in air, forming a layer of oxide. Lithium, sodium and potassium are so reactive that they are usually stored under kerosene.

Sodium and Potassium

Occurrence

Although far too reactive to be found free these metals occur in nature in immense quantities in comparatively few compounds. They occur chiefly as the chloride, sodium chloride (common salt) and as potassium chloride (carnallite). Other sources of the elements are soda feldspar, $Na_2O.Al_2O_3.6SiO_2$; sodium carbonate, Chile salt-petre (sodium nitrate), potassium carbonate and potassium nitrate.

Extraction of sodium and potassium

Both metals are extracted by electrolysis of their fused chlorides. Since both metals are extracted in a similar manner, that for sodium only will be described.

The more common process for the electrolysis of fused sodium chloride to give its component elements is known as "Downs Process".The cell employed in this process is shown in Fig. 8.1. The container of the cell B is made of steel, lined with firebrick. The anode A is made of graphite and the cathode C is in the form of an iron ring. As the melting point of sodium chloride is high (804 °C), a small amount of calcium chloride is added to lower the melting point which is reduced to 600 °C. The added calcium chloride does not interfere with the electrolysis of sodium chloride. The fused electrolyte D, is placed in the cell. On electrolysis, chlorine is liberated at the anode, it escapes through the hood G. The sodium, which is liberated at the ring cathode, rises upward through the electrolyte, is collected by the annular sodium collector H and then passes through pipe I to the collector J. The chemical reactions involved in this process are as follows :

reaction at the cathode $Na^+ + e \longrightarrow Na$

reaction at the anode $Cl^- \longrightarrow Cl + e$

$Cl + Cl \longrightarrow Cl_2$

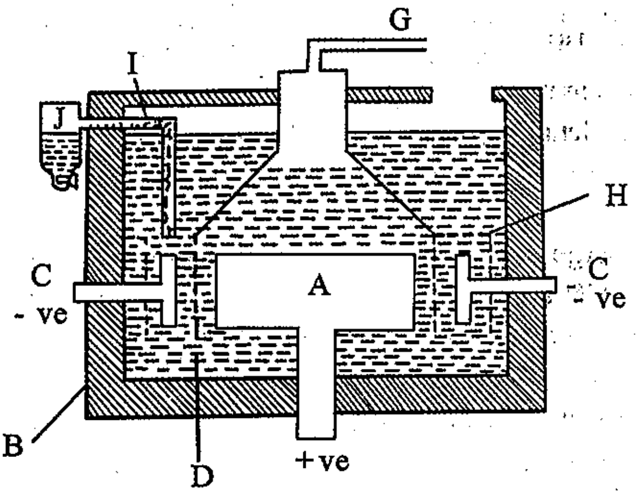

Fig. 8.1 Downs cell for the electrolytic manufacture of sodium

Properties of sodium

Physical properties

1. Sodium is a soft metal and may be cut easily with a knife.
2. It has a silvery lustre but it rapidly tarnishes in moist air.
3. It is a good conductor of heat and electricity.

Chemical properties

1. When heated in air, sodium burns readily with a bright yellow flame to form a mixture of oxide and peroxide.

$$4Na(s) + O_2(g) \longrightarrow \underset{\text{sodium monoxide}}{2Na_2O(s)}$$

$$2Na(s) + O_2(g) \longrightarrow \underset{\text{sodium peroxide}}{Na_2O_2(s)}$$

2. Sodium reacts vigorously with water giving hydrogen and sodium hydroxide.

$$2Na(s) + 2H_2O(l) \longrightarrow H_2(g) + 2NaOH(aq)$$

3. When heated, sodium combines directly with the halogens, phosphorus and sulphur to form the halides, phosphide and the various polysulphides respectively. When heated in hydrogen, sodium forms its hydride, NaH.

4. When heated at 300 - 400 °C in gaseous ammonia, sodium forms sodamide.

$$2Na(s) + 2NH_3(g) \longrightarrow 2NaNH_2(s) + H_2(g)$$

5. Sodium dissolves in mercury to form sodium amalgam.
6. Sodium reacts violently with acids. (Not to be tested)

Uses of sodium

Sodium is used in large quantities for the manufacture of sodium peroxide, Na_2O_2, sodium cyanide, NaCN and sodamide, $NaNH_2$. It is also used in the manufacture of tetraethyl lead, an anti-knock additive used in petrol.

Compounds of sodium

Oxides

Sodium peroxide Na_2O_2

Sodium burns in excess of air or oxygen giving sodium peroxide.

$$2Na(s) + O_2(g) \longrightarrow Na_2O_2(s)$$

Sodium peroxide reacts with cold water to form sodium hydroxide and hydrogen peroxide.

$$Na_2O_2(s) + 2H_2O(1) \longrightarrow 2NaOH(aq) + H_2O_2(aq)$$

If the water is not cold the following reaction occurs.

$$2Na_2O_2(s) + 2H_2O(1) \longrightarrow 4NaOH(aq) + O_2(g)$$

Sodium peroxide combines with carbon monoxide to give sodium carbonate.

$$Na_2O_2(s) + CO(g) \longrightarrow Na_2CO_3(s)$$

It also reacts with carbon dioxide in the following manner :

$$2Na_2O_2(s) + 2CO_2(g) \longrightarrow 2Na_2CO_3(s) + O_2(g)$$

Sodium peroxide may, therefore, be employed for removing carbon monoxide and carbon dioxide from the air in submarines. It is also used in portable breathing apparatus.

Sodium oxide (Disodium oxide) Na_2O

When sodium is heated in a limited amount of air or oxygen, sodium oxide is formed.

$$4Na(s) + O_2(g) \longrightarrow 2Na_2O(s)$$

Since it is difficult to obtain pure sodium oxide in this way, it is more satisfactory to heat gently sodium peroxide with the appropriate amount of sodium.

$$Na_2O_2(s) + 2Na(s) \longrightarrow 2Na_2O(s)$$

Sodium oxide reacts violently with water to give sodium hydroxide solution,

$$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$$

Sodium hydroxide (Caustic soda) NaOH

Sodium hydroxide is one of the most important industrial chemicals. On the commercial scale it is prepared by the electrolysis of a saturated solution of sodium chloride (brine). Chlorine resulting from the electrolysis is evolved at the graphite anode. At the mercury cathode the sodium ions are discharged where they react with the mercury to form sodium amalgam. Then the amalgam reacts with water in the receiving tank, to form sodium hydroxide solution and liberate hydrogen. The reactions involved in this process are as follows:

$$2NaCl + 2xHg \longrightarrow \underset{\substack{\text{sodium}\\ \text{amalgam}}}{2NaHg_x} + Cl_2$$

$$2NaHg_x + 2H_2O \longrightarrow 2NaOH + H_2 + 2xHg$$

Sodium hydroxide is a white deliquescent solid. It is readily soluble in water and much heat is evolved in this process.

It is a very strong alkali and attacks the skin. For this reason that it is termed "caustic" soda.

Sodium hydroxide is a strong base and reacts with all acids and acidic oxides. For example,

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

$$2NaOH(aq) + CO_2(g) \longrightarrow Na_2CO_3(aq) + H_2O(1)$$

It precipitates many metallic hydroxides from solutions of metallic salts. Thus,

$$CuSO_4(aq) + 2NaOH(aq) \longrightarrow Cu(OH)_2(s) + Na_2SO_4(aq)$$

$$FeCl_2(aq) + 2NaOH(aq) \longrightarrow Fe(OH)_2(s) + 2NaCl(aq)$$

Hot aqueous solutions of sodium hydroxide react with aluminium and with zinc forming the aluminate or zincate and liberating hydrogen.

$$2Al(s) + 2NaOH(aq) + 6H_2O(1) \longrightarrow 2NaAl(OH)_4(aq) + 3H_2(g)$$

$$Zn(s) + 2NaOH(aq) + 2H_2O(1) \longrightarrow Na_2Zn(OH)_4(aq) + H_2(g)$$

With elements from Group V to VII, sodium hydroxide reacts to give either the hydride or the sodium derivative of the element, but no hydrogen is evolved. The following examples illustrate this:

$$4P(s) + 3NaOH(aq) + 3H_2O(1) \longrightarrow PH_3(g) + 3NaH_2PO_2(aq)$$

phosphine sodium dihydrogen-hypophosphite

$$4S(s) + 6NaOH(aq) \longrightarrow 2Na_2S(aq) + Na_2S_2O_3(aq) + 3H_2O(1)$$

sodium thiosulphate

$$Cl_2(g) + 2NaOH(aq) \longrightarrow NaCl(aq) + NaOCl(aq) + H_2O(l)$$

In cold solution

sodium hypochlorite

$$3Cl_2(g) + 6NaOH(aq) \longrightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(1)$$

In hot solution

sodium chlorate

Sodium hydroxide is used in the manufacture of soap. It is also employed in the paper-making and dyeing industries. Other uses include its application for the refining of petroleum and in the rubber industry.

Sodium carbonate (Soda ash) Na_2CO_3

Sodium carbonate is manufactured by the Solvay process.

The principle of this process is that sodium hydrogencarbonate is precipitated from a mixed solution of brine (saturated NaCl solution) and ammonium hydrogencarbonate saturated with carbon dioxide. On subsequent heating of this sodium hydrogencarbonate, the normal salt is obtained.

The reactions involved may be shown as

$$NH_3(aq) + H_2O(l) + \underset{\text{excess}}{CO_2(g)} \longrightarrow NH_4HCO_3(aq)$$

ammonium hydrogencarbonate saturated with carbon dioxide

$$NH_4HCO_3(aq) + NaCl(aq) \longrightarrow NaHCO_3(s) + NH_4Cl(aq)$$

$$2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + H_2O(1) + CO_2(g)$$

Anhydrous sodium carbonate is a white powder. The salt dissolves in water and forms a series of hydrates containing one, seven or ten molecules of water of crystallization respectively. The decahydrate $Na_2CO_3.10H_2O$ is sold as washing soda.

In contrast to the carbonates of most metals, anhydrous sodium carbonate does not decompose on heating.

In aqueous solution it is alkaline since the salt reacts with water to form sodium hydroxide as follows :

$$Na_2CO_3(aq) + H_2O(l) \longrightarrow NaHCO_3(aq) + NaOH(aq)$$

When a salt reacts with water to form acid or alkali, the salt is said to be hydrolysed. The process is known as **hydrolysis.**

Sodium carbonate reacts with acid to liberate carbon dioxide. For example,

$$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

Sodium carbonate is used in large quantities for the softening of hard water. It is also employed in the manufacture of glass and water glass.

Sodium hydrogencarbonate $NaHCO_3$

Sodium hydrogencarbonate is obtained as an intermediate in the manufacture of sodium carbonate (Solvay process). It may be prepared in the laboratory by the following reactions :

$$NaOH(aq) + CO_2(g) \longrightarrow NaHCO_3(aq)$$
$$Na_2CO_3(aq) + H_2O(l) + CO_2(g) \longrightarrow 2NaHCO_3(aq)$$

If the aqueous solution of sodium hydrogencarbonate is heated decomposition occurs as follows ;

$$2NaHCO_3(aq) \longrightarrow Na_2CO_3(aq) + H_2O(1) + CO_2(g)$$

Addition of acids to sodium hydrogencarbonate results in liberation of carbon dioxide.

$$NaHCO_3(s) + HNO_3(aq) \longrightarrow NaNO_3(aq) + H_2O(l) + CO_2(g)$$

Sodium hydrogencarbonate is sold as baking soda. It also finds important application for medicinal purposes, such as the correction of stomach acidity.

Sodium chloride NaCl

Sodium chloride occurs in nature as rock salt and it is present in sea water. It is prepared in the laboratory by neutralizing hydrochloric acid with sodium hydroxide solution.

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(1)$$

It is a white crystalline solid. It is fairly soluble in water.

The most important use for sodium chloride is as an essential part of the human diet. It is also employed for the seasoning of foods.

Sodium nitrate $NaNO_3$

Sodium nitrate mostly occurs in Chile and is known as Chile salt-petre. It may be prepared in the laboratory by neutralization of sodium hydroxide with nitric acid.

$$NaOH(aq)+HNO_3(aq) \longrightarrow NaNO_3(aq) + H_2O(l)$$

It is a white, crystalline solid, which is very soluble in water.

It decomposes on strongly heating, forming sodium nitrite and oxygen.

$$2NaNO_3(s) \xrightarrow{\Delta} 2NaNO_2(s) + O_2(g)$$

Most other metal nitrates give the metal oxide.

Sodium nitrate is used as a fertilizer.

Sodium sulphate Na_2SO_4

Sodium sulphate may be prepared by strongly heating sodium chloride with concentrated sulphuric acid.

$$2NaCl(s) + H_2SO_4(conc) \longrightarrow Na_2SO_4(s) + 2HCl\ (g)$$

The salt crystallizes as the decahydrate, $Na_2SO_4.10\ H_2O$, which is known as "Glauber's salt". It is used as a purgative in medicine. The anhydrous salt is used in the manufacture of glass.

Sodium hydrogensulphate $NaHSO_4$

Sodium hydrogensulphate is made on a large scale by the Leblance process in which salt is heated with sulphuric acid.

$$NaCl(s) + H_2SO_4(aq) \longrightarrow NaHSO_4\ (aq) + HCl(aq)$$

On heating sodium hydrogensulphate it first decomposes with the formation of sodium pyrosulphate.

$$2NaHSO_4(s) \longrightarrow Na_2S_2O_7(s) + H_2O(g)$$

On further heating, at red heat, sodium sulphate and sulphur trioxide are formed.

$$Na_2S_2O_7(s) \longrightarrow Na_2SO_4(s) + SO_3\ (g)$$

Sodium hydrogensulphate still has acidic property since it contains a replaceable hydrogen atom.

Sodium thiosulphate $Na_2S_2O_3$

It is made on a large scale from calcium sulphide, CaS. When air is blown through a suspension of the sulphide in water, calcium thiosulphate is formed. This on reaction with either sodium carbonate or sodium sulphate, produces sodium thiosulphate.

$$CaS_2O_3\ (aq) + Na_2SO_4(aq) \longrightarrow CaSO_4(s) + Na_2S_2O_3(aq)$$
$$CaS_2O_3\ (aq) + Na_2CO_3(aq) \longrightarrow CaCO_3(s) + Na_2S_2O_3(aq)$$

Sodium thiosulphate reacts with many salts which are insoluble in water to form complex salts. For example,

$$Na_2S_2O_3\ (aq) + AgCl(s) \longrightarrow Na\ [AgS_2O_3]\ (aq) + NaCl\ (aq)$$

This particular reaction is employed in photography.

Sodium thiosulphate crystallizes as $Na_2S_2O_3.5H_2O$ and it is usually marketed in this form. The hydrated sodium thiosulphate is also known as photographic hypo.

8.2 Group II Metals: Magnesium and Calcium

Magnesium

Occurrence

Magnesium is so erective that that it is never fround free in nature.the oxide, carbonate, sulphate, chloride and silicate. It is also foung as the chloride or sulphate as a constituent of sea water and of deep well brines.

Extraction of magnesium

Large quantities of magnesium are extracted from sea water by converting the salt to the insoluble magnesium hydroxide and then heating this to give the oxide.

$$MgSO_4(aq) + 2NaOH(aq) \longrightarrow Mg(OH)_2(s) + Na_2SO_4(aq)$$
$$Mg(OH)_2(s) \xrightarrow{\Delta} MgO(s) + H_2O(l)$$

The magnesia (magnesium oxide) is heated with coke in a current of chlorine, to give magnesium chloride.

$$MgO(s) + C(s) + Cl_2(g) \longrightarrow MgCl_2(s) + CO(g)$$

Anhydrous magnesium chloride in the molten form is electrolysed. Magnesium is liberated at the cathode and chlorine is liberated at the anode.

Properties of magnesium

Physical properties

1. Magnesium is a silvery-white metal with a very low density.
2. It is stable in dry air, but in moist air becomes coated with an oxide film which prevents further attack by the moist air.

Chemical properties

1. When magnesium is heated in air, the oxide and a little of the nitride are formed.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$
$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

2. When magnesium is heated it combines directly with sulphur, chlorine, phosphorus, boron and carbon to form the sulphide, chloride, phosphide, boride and carbide respectively. However, it does not form a hydride.
3. Magnesium reacts with steam, forming the oxide and liberating hydrogen.

$$Mg(s) + H_2O(g) \longrightarrow MgO(s) + H_2(g)$$

4. Since magnesium is well up in the activity series, it reacts with dilute acids, with the formation of the corresponding magnesium salts and the evolution of hydrogen.

$$Mg(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2\,(g)$$

Hydrogen is evolved when magnesium reacts with very dilute nitric acid. With more concentrated nitric acid, oxides of nitrogen are produced instead of hydrogen. The other metals, with the exception of manganese, will not liberate hydrogen from nitric acid under any conditions.

5. Caustic alkalis have no action on magnesium.

Uses of magnesium

Magnesium based light alloys are the lightest known useful alloys for engineering construction. Magnesium ribbon and wire are used largely by the radio industry for de-gassing radio valves.

Compounds of magnesium

Magnesium oxide (Magnesia) MgO

Magnesium oxide may be prepared in the laboratory by the thermal decomposition of the hydroxide, carbonate or nitrate. It is also formed when the metal is heated in air, but in this case it is contaminated with the nitride, Mg_3N_2.

Magnesium oxide is a white powder and is only slightly soluble in water, giving a slightly alkaline solution. It is an extremely stable compound. Thus it may be heated to 2900 °C, without undergoing decomposition.

It reacts with acids giving the corresponding salts.

The most important use for magnesium oxide is in the manufacture of refractories (fire resistant materials). It is also used for medicinal purposes.

Magnesium hydroxide $Mg(OH)_2$

Magnesium hydroxide is formed as a white precipitate when alkali metal hydroxides are added to the solution of a soluble magnesium salt.

$$MgSO_4(aq) + 2NaOH(aq) \longrightarrow Mg(OH)_2(s) + Na_2SO_4(aq)$$

It is only slightly soluble in water. It is a strong base reacting with acids to form magnesium salts.

Magnesium carbonate $MgCO_3$

It occurs in nature as magnesite, $MgCO_3$ and as dolomite, $MgCO_3.CaCO_3$.

Magnesium carbonate may be prepared by the addition of a solution of sodium hydrogencarbonate to the solution of a soluble magnesium salt.

$$\begin{array}{lr} MgSO_4(aq) + 2NaHCO_3(aq) \longrightarrow & Na_2SO_4(aq) + Mg(HCO_3)_2(aq) \\ & \downarrow \text{warm} \quad \\ & MgCO_3(s) + H_2O(l) \\ & + CO_2(g) \end{array}$$

The addition of sodium carbonate solution, instead of the sodium hydrogencarbonate, results in the precipitation of white basic carbonates of the general formula, $xMgCO_3.yMg(OH)_2.H_2O$.

If carbon dioxide is passed through a suspension of magnesium carbonate in water a clear solution of magnesium hydrogencarbonate is produced.

$$MgCO_3(s) + H_2O(l) + CO_2(g) \longrightarrow Mg(HCO_3)_2(aq)$$

The basic carbonates of magnesium are used as "fillers" in tooth pastes, printing inks, paints and varnishes.

Magnesium sulphate $MgSO_4$

This salt occurs in nature as kieserite, $MgSO_4.H_2O$. In the laboratory, magnesium sulphate is prepared by the action of dilute sulphuric acid on the metal, oxide, hydroxide or carbonate.

For example,

$$MgCO_3(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2O(l) + CO_2(g)$$

It crystallizes as the heptahydrate, $MgSO_4.7H_2O$, which is known as Epsom salt. It is used as a purgative in medicine.

Calcium

Occurrence

Calcium is far too reactive it is not found free in nature but it is abundant as, the carbonate, sulphate, fluoride and silicate. The most important of these natural minerals is limestone, $CaCO_3$ (also known as chalk).

Extraction of calcium

Calcium is obtained by the electrolysis of the fused anhydrous calcium chloride. A little calcium fluoride is added to lower the melting point and hence the temperature of fusion. A steel cathode and a graphite anode are used. The metal, calcium, is deposited in the molten state at the steel cathode and chlorine is liberated at the graphite anode.

reaction at the cathode $Ca^{2+} + 2e \longrightarrow Ca$

reaction at the anode $2Cl^{-} \longrightarrow Cl_2 + 2e$

Properties of calcium

Physical properties

1. Pure calcium is a soft grey metal.
2. On exposure to air it becomes coated with a layer of oxide and hydroxide.

Chemical properties

1. When calcium is heated in air, calcium oxide together with a little calcium nitride, Ca_3N_2, is formed.

$$2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$$

$$3Ca(s) + N_2(g) \longrightarrow \underset{\text{calcium nitride}}{Ca_3N_2(s)}$$

2. It combines with hydrogen and carbon on heating to form calcium hydride, CaH_2, and calcium carbide, CaC_2, respectively.

3. Calcium reacts steadily with cold water and rapidly with hot water.

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

4. It reacts vigorously with acids to form calcium salts.

$$Ca(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2(g)$$

5. It does not react with alkalis.

Uses of calcium

Calcium is used in the manufacture of calcium hydride, CaH_2. It is also used as a drying agent in the laboratory.

Compounds of calcium

Calcium hydride CaH_2

It is prepared by the direct action of hydrogen on metallic calcium at 350 °C. Calcium hydride reacts with water, forming calcium hydroxide and liberating hydrogen.

$$CaH_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + 2H_2(g)$$

It is used as a means of producing hydrogen gas.

Calcium carbide CaC_2

Calcium carbide is prepared by heating a mixture of quicklime and carbon at about 2000 °C.

$$CaO(s) + 3C(s) \longrightarrow CaC_2(s) + CO(g)$$

It is a hard, brittle crystalline solid. It reacts with water to produce ethyne (acetylene).

$$CaC_2(s) + 2H_2O(l) \longrightarrow \underset{\text{acetylene}}{C_2H_2(g)} + Ca(OH)_2(s)$$

Calcium carbide when heated with nitrogen reacts to form calcium cyanamide, $CaCN_2$, which is an important fertilizer being known as "nitrolime".

$$CaC_2(s) + N_2(g) \longrightarrow \underset{\substack{\text{calcium}\\\text{cyanamide}}}{CaCN_2(s)} + C(s)$$

Nitrolime liberates ammonia on reaction with water.

$$CaCN_2(s) + 3H_2O(l) \longrightarrow CaCO_3(s) + 2NH_3(g)$$

Calcium oxide (lime or quicklime) CaO

Pure calcium oxide may be prepared in the laboratory by heating the hydroxide, carbonate or nitrate. It may also be obtained by burning calcium in oxygen.

It is made industrially by heating limestone at about 800 °C in a stream of air. The function of air is to remove the carbon dioxide.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Calcium oxide is a white powder. It is very stable and may be heated to a high temperature without undergoing any chemical decomposition.

It reacts with water to form calcium hydroxide, known as slaked lime. The process of preparing slaked lime is known as slaking of lime.

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$

Calcium oxide is a strongly basic oxide reacting vigorously with acids to form the corresponding calcium salts. For example,

$$CaO(s) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + H_2O(l)$$

It reacts with acidic oxides such as silica, on heating.

$$CaO(s) + SiO_2(s) \longrightarrow \underset{\text{calcium silicate}}{CaSiO_3(s)}$$

Calcium oxide is used in the manufacture of glass. It is also used as constituent of many types of cement and mortar.

Calcium hydroxide (slaked lime) $Ca(OH)_2$

It is made by slaking lime with water.

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$

Calcium hydroxide is a white powder. It is only slightly soluble in water an unlike most substances, its solubility decreases on increasing the temperature. The aqueous solution of calcium hydroxide is known as lime water and an aqueous suspension of calcium hydroxide is known as milk of lime.

If carbon dioxide is passed through lime water, a milky precipitate of calcium carbonate is formed.

$$Ca(OH)_2(aq) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l)$$

However, on continued passage of carbon dioxide, the insoluble carbonate is converted to the soluble hydrogencarbonate.

$$CaCO_3(s) + H_2O(l) + CO_2(g) \longrightarrow Ca(HCO_3)_2(aq)$$

The addition of calcium hydroxide to a solution of calcium hydrogencarbonate results in the precipitation of calcium carbonate.

$$Ca(HCO_3)_2(aq) + Ca(OH)_2(aq) \longrightarrow 2CaCO_3(s) + 2H_2O(l)$$

This reaction is important for the removal of hydrogencarbonates of calcium and magnesium present in hard water.

Mixtures of calcium hydroxide and ammonium salts yield ammonia on heating.

$$Ca(OH)_2(s) + 2NH_4Cl(s) \longrightarrow CaCl_2(s) + 2H_2O(l) + 2NH_3(g)$$

Passage of chlorine over slaked lime at atmospheric pressure yields bleaching powder.

$$Ca(OH)_2(s) + Cl_2(g) \longrightarrow \underset{\text{bleaching powder}}{CaOCl_2(s)} + H_2O(l)$$

Slaked lime is used in the manufacture of bleaching powder, in water softening and in the making of cements and mortar.

Calcium carbonate $CaCO_3$

It occurs in nature as limestone, marble and chalk.

It is insoluble in pure water, but in the presence of dissolved carbon dioxide, calcium carbonate readily dissolves owing to the formation of the soluble calcium hydrogencarbonate.

$$CaCO_3(s) + H_2O(l) + CO_2(g) \longrightarrow Ca(HCO_3)_2(aq)$$

Calcium hydrogencarbonate readily loses carbon dioxide to give calcium carbonate. The above reaction is therefore reversible. Formation of stalactites and stalagmites is due to this reversible reaction.

Calcium carbonate is employed in the manufacture of tooth pastes for medicinal purposes and for cosmetic preparations. In the laboratory it is often used as a source of carbon dioxide.

Calcium chloride $CaCl_2$

In industry, calcium chloride is produced as a by-product from the Solvay process for manufacturing sodium carbonate.

The hexahydrate $CaCl_2.6H_2O$ may be obtained in the laboratory by the action of hydrochloric acid on calcium carbonate.

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

Anhydrous calcium chloride absorbs water to form $CaCl_2.6H_2O$. Anhydrous calcium chloride is used as a drying agent in the laboratory. It cannot be used for drying ammonia since it forms an unstable complex with the gas.

Calcium sulphate $CaSO_4$

Calcium sulphate occurs in nature both as the anhydrous salt and as the dihydrate (gypsum). In the laboratory the dihydrate may be prepared by the addition of dilute sulphuric acid to an aqueous solution of calcium chloride.

$$CaCl_2(aq) + H_2SO_4(aq) + 2H_2O(1) \longrightarrow CaSO_4.2H_2O\ (s) + 2HCl\ (aq)$$

When heated just above 100 °C the dihydrate loses three quarters of its water of crystallization to give the hemihydrate, $CaSO_4.\ \frac{1}{2}\ H_2O$ or $2CaSO_4.H_2O$. This hemihydrate is the chief constituent of Plaster of Paris.

When Plaster of Paris is mixed with water it sets to form a hard mass which is a dihydrate.

Calcium sulphate is sparingly soluble in water. Gypsum is used to manufacture Plaster of Paris.

Calcium phosphate $Ca_3(PO_4)_2$

Calcium occurs in nature as a number of naturally occurring phosphates. One of the chief uses for these meterials is as fertilizers. An important fertilizer "superphosphate" is made by treating calcium phosphate with concentrated sulphuric acid.

$$Ca_3(PO_4)_2(s) + 2H_2SO_4(conc) \longrightarrow \underbrace{Ca(H_2PO_4)_2\ (s) + 2CaSO_4(s)}_{\text{superphosphate}}$$

8.3 Group III Metal: Aluminium

Occurrence

Aluminium occurs in nature as the silicate in rocks and clays. The main source is the naturally occurring oxide known as bauxite.

Extraction of aluminium

Aluminium is extracted by electrolysis of the fused oxide. Cryolite, Na_3AlF_6, is added to lower the temperature of fusion. Both electrodes are made of graphite. Aluminium is produced at the cathode and oxygen is liberated at the anode.

reaction at the cathode $2Al^{3+} + 6e \longrightarrow 2Al$

reaction at the anode $3O^{2-} \longrightarrow \frac{3}{2}O_2 + 6e$

Properties of aluminium

Physical properties

1. Aluminium is a silvery-white metal.
2. It has high ductility and high malleability.
3. It exhibits high electrical and thermal conductivities.
4. In moist air a film of oxide is formed on the metal surface which prevents further attack on the underlying metal.

Chemical properties

1. Aluminium, on heating, combines directly with the halogens, sulphur, nitrogen and carbon to form halides, sulphide, nitride and carbide respectively.
2. Aluminium is a strong reducing agent, thus, when metallic oxides are mixed with aliminium powder and then ignited, the metallic oxide is reduced to metal. This is the basis of the "Goldschmidt" or "Thermite" process for the extraction of high melting point metals from their oxides. The heat liberated in this reaction is so great as to produce molten metals.

As an example, this reaction is applied to the reduction of iron (III) oxide to produce molten iron. It is also used in welding of iron.

$$Fe_2O_3(s) + 2Al(s) \xrightarrow{\Delta} Al_2O_3(s) + 2Fe(l) + \text{heat}$$

3. Aluminium reacts slowly with dilute hydrochloric acid and vigorously with the hot acid.

$$2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g)$$

The reaction with dilute sulphuric acid is similar. With hot concentrated sulphuric acid aluminium gives aluminium sulphate, water and sulphur dioxide.

$$2Al(s) + 6H_2SO_4(conc) \xrightarrow{\Delta} Al_2(SO_4)_3(s) + 6H_2O(l) + 3SO_2(g)$$

Nitric acid, both dilute as well as concentrated, react very slowly with aluminium. The formation of the protective layer of oxide by the oxidizing acid prevents the acid from vigorously attacking the metal.

Aluminium reacts with alkalis as well as acids.

$$2Al(s) + 2NaOH(aq) + 6H_2O(l) \longrightarrow \underset{\text{sodium aluminate}}{2NaAl(OH)_4(aq)} + 3H_2(g)$$

Uses of aluminium

Aluminium is used in the chemical, food, dairy and pharmaceutical industries, in building and for architectural purposes, in the form of foil for packaging of foodstuffs, sweets, cigarettes, etc. Aluminium based light alloys are important in all branches of engineering construction.

Compounds of aluminium

Aluminium oxide (Alumina) Al_2O_3

Alumina occurs naturally in several forms. It also occurs in nature in the form of the gems such as the ruby and sapphire. In the laboratory, aluminium oxide may be prepared by heating aluminium hydroxide.

$$2Al(OH)_3(s) \xrightarrow{\Delta} Al_2O_3(s) + 3H_2O(g)$$

Alumina is very stable and has a very high melting point (2040 °C). It is an amphoteric oxide.

It is used as the source of aluminium and as an adsorbent in chromatography. It is also used as a refractory lining in furnaces.

Aluminium hydroxide $Al(OH)_3$

Aluminium hydroxide may be prepared as a white gelatinous precipitate when ammonium hydroxide is added to a solution of an aluminium salt.

$$Al_2(SO_4)_3(aq) + 6NH_4OH(aq) \longrightarrow 2Al(OH)_3(s) + 3(NH_4)_2SO_4(aq)$$

It is amphoteric, thus

$$Al(OH)_3(s) + 3HCl(aq) \longrightarrow AlCl_3(aq) + 3H_2O(1)$$

$$Al(OH)_3(s) + NaOH(aq) \longrightarrow NaAl(OH)_4(aq)$$

Aluminium hydroxide is used as a mordant or dye-fixing agent in the dyeing industry.

Aluminium chloride $AlCl_3$

Anhydrous aluminium chloride may be prepared either by heating chlorine with aluminium

$$2Al(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(s)$$

or by heating alumina with carbon and chlorine.

$$Al_2O_3(s) + 3C(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(s) + 3CO(g)$$

The reaction of hydrochloric acid with metallic aluminium gives a solution of aluminium chloride, which on evaporation gives crystals of the hexahydrate, $AlCl_3.6H_2O$.

Anhydrous aluminium chloride is a white crystalline substance which is extremely deliquescent. In moist air, fumes are produced because of the formation of hydrogen chloride.

$$AlCl_3\,(s) + 3H_2O(1) \longrightarrow Al(OH)_3(aq) + 3HCl(g)$$

On heating, aluminium chloride vaporizes readily at about 180 °C, without melting. At temperatures between 183 °C and 400 °C, the vapour consists of Al_2Cl_6 molecule, but at 400 °C dissociation to $AlCl_3$ commences and is complete at about 750 °C.

Anhydrous aluminium chloride is used as a catalyst in many organic chemical reactions, and in the petroleum industries.

Aluminium sulphate $Al_2(SO_4)_3$

It is prepared by the reaction of dilute sulphuric acid with aluminium hydroxide. On evaporation of the resulting solution, crystals of $Al_2(SO_4)_3.18H_2O$ are obtained.

$$2Al(OH)_3(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 6H_2O(1)$$

Aluminium sulphate is used as a mordant in the dyeing industry, as a filler in the manufacture of paper, in the tanning of leather, in fire extinguishers and in the purification of water.

Common alum $K_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O$

When a solution containing potassium sulphate and aluminium sulphate in the proper proportions is evaporated, colourless crystals of the double sulphate of potassium and aluminium are obtained, having the formula $K_2SO_4.Al_2(SO_4)_3.24H_2O$. This substance is known simply as alum or as potash alum. This compound is used as a mordant in the dye industy. It is also used for purifying of water.

Potash alum is a typical member of a group of compounds known as the alums which have the general formula $M_2SO_4.M'_2(SO_4)_3.24H_2O$, where M represents a univalent and M' represents a trivalent metal.

8.4 Group IV Metal: Lead

Occurrence

The main source of lead is the lead (II) sulphide which occurs in nature as, galena, PbS. Myanmar is one of the world's largest producers of lead ore.

Extraction of lead

Lead is extracted by heating the galena ore in air to give the oxide which is then reduced by heating with carbon. The process may be represented as

$$2PbS(s) + 3O_2(g) \xrightarrow{\Delta} 2PbO(s) + 2SO_2(g)$$

$$PbO(s) + C(s) \xrightarrow{\Delta} Pb(s) + CO(g)$$

Alternatively, reduction of galena to lead may take place as follows;

$$PbS(s) + 2PbO(s) \longrightarrow 3Pb(s) + SO_2(g)$$

$$PbS(s) + PbSO_4(s) \longrightarrow 2Pb(s) + 2SO_2(g)$$

Properties of lead

Physical properties

1. Lead is a bluish-grey metal.
2. It is the softest of the metals in common use, and can be pressed into any form.
3. It has a low melting point (328 °C).
4. It is a poor conductor of electricity and heat.
5. On exposure to air lead is tarnished owing to the formation of a layer of hydroxide and carbonate which prevents further attack.

Chemical properties

1. Lead does not react with water or steam.
2. It reacts slowly with hydrochloric acid, whether dilute or concentrated:

$$Pb(s) + 2HCl(aq) \longrightarrow PbCl_2(aq) + H_2(g)$$

Lead (II) chloride is sparingly soluble in cold water, but is soluble in hot water.

Dilute sulphuric acid has no appreciable action upon lead, but hot concentrated sulphuric acid reacts with lead to form lead (II) sulphate and liberate sulphur dioxide.

$$Pb(s) + 2H_2SO_4(conc) \longrightarrow PbSO_4(s) + 2H_2O(1) + SO_2(g)$$

The metal also reacts with dilute nitric acid

$$3Pb(s) + 8HNO_3(aq) \longrightarrow 3Pb(NO_3)_2(aq) + 4H_2O(1) + 2NO(g)$$

and with concentrated nitric acid.

$$Pb(s) + 4HNO_3(conc) \longrightarrow Pb(NO_3)_2(aq) + 2H_2O(1) + 2NO_2(g)$$

Uses of lead

Lead is used as a shield against radioactive material and X-rays. It is also used in car batteries and accumulators. Lead is also an important constituent in many important alloys, for example soft solders (lead and tin), and type metal (lead, antimony and tin) for use in printing.

Compounds of lead

Lead (II) oxide PbO

It is formed as a yellow powder when lead is heated gently in air. Lead (II) oxide is also known as litharge.

$$2Pb(s) + O_2(g) \longrightarrow 2PbO(s)$$

Lead (II) oxide is amphoteric, reacting with acids as well as alkalis.

$$PbO(s) + 2HCl(aq) \longrightarrow PbCl_2(s) + H_2O(l)$$

$$PbO(s) + 2NaOH(aq) \longrightarrow \underset{\text{sodium plumbite}}{Na_2PbO_2(aq)} + H_2O(l)$$

It is used in the manufacture of glass.

Di lead (II) lead (IV) oxide (Red lead) Pb_3O_4

Red lead is made by heating lead (II) oxide at temperature not exceeding 450 °C.

$$6PbO(s) + O_2 \xrightarrow{450\,°C} 2Pb_3O_4(s)$$

At temperatures in excess of 450°C the reverse reaction occurs.

In this chemical reaction, di lead (II) lead (IV) oxide behaves as a mixture of lead (II) oxide and lead (IV) oxide, $2PbO+PbO_2$.

With hydrochloric acid, lead (II) chloride is formed and chlorine is liberated.

$$Pb_3O_4(s) + 8HCl(aq) \longrightarrow 3PbCl_2(s) + Cl_2(g) + 4H_2O(l)$$

Red lead is used in surface coating such as paints for preventing corrosion.

Lead (IV) oxide PbO_2

It is prepared by the action of nitric acid on red lead.

$$Pb_3O_4(s) + 4HNO_3(aq) \longrightarrow PbO_2(s) + 2Pb(NO_3)_2(aq) + 2H_2O(l)$$

Lead (IV) oxide is amphoteric and is a powerful oxidizing agent

With concentrated hydrochloric acid, chlorine is evolved and with concentrated sulphuric acid oxygen is evolved.

$$PbO_2(s) + 4HCl(conc) \longrightarrow PbCl_2(s) + 2H_2O(l) + Cl_2(g)$$
$$2PbO_2(s) + 2H_2SO_4(conc) \longrightarrow 2PbSO_4(s) + 2H_2O(l) + O_2(g)$$

Lead carbonate $PbCO_3$

It is prepared by the addition of a solution of sodium hydrogencarbonate to the aqueous solution of a lead salt.

$$Pb(NO_3)_2(aq) + 2NaHCO_3(aq) \longrightarrow PbCO_3(s) + 2NaNO_3(aq) + H_2O(l) + CO_2(g)$$

The addition of sodium carbonate solution gives rise to the formation of basic lead carbonate, $Pb(OH)_2.2PbCO_3$. Basic lead carbonate is used as a white pigment.

Lead chromate $PbCrO_4$

It is precipitated as a yellow solid when the aqueous solution of a soluble chromate is added to the solution of a lead salt.

It is employed as a chrome yellow pigment. If the chromate is boiled with alkali solution it is converted into a red basic lead chromate, $PbCrO_4.Pb(OH)_2$. Basic lead chromate is employed as chrome red pigment.

SUMMARY

This chapter is concerned with the extraction of alkali metals such as sodium and potassium, alkaline earth metals such as calcium and magnesium , group III metal, aluminium , group IV metal, lead and their physical and chemical properties, preparation of compounds including their respective uses. Problems and exercises are given at the end of this chapter for practice.

Questions and Problems

1. Describe the extraction of sodium metal from common salt.
2. How does sodium react with
   (a) water (b) oxygen (c) hydrogen (d) chlorine (e) ammonia?
3. Give an account of manufacture of sodium hydroxide from common salt by electrolysis. How, and in what conditions, does sodium hydroxide react with
   (a) carbondioxide
   (b) aluminium
   (c) chlorine?

4. Give an account of manufacture of sodium carbonate by the Solvay process.
5. Describe the following.
    (a) the behaviour of sodium hydrogencarbonate when heated,
    (b) the behaviour of sodium on mixing with mercury,
    (c) the action of heat on sodium nitrate.
6. Describe the extraction of magnesium from sea water. Starting from magnesium, how would you prepare normal magnesium carbonate?
7. Starting from marble, how would you prepare
    (a) quicklime
    (b) slaked lime
    (c) nitrolime?
8. Starting from aluminium foil, how would you prepare
    (a) anhydrous aluminium chloride
    (b) alumina
    (c) potash alum?
9. Di lead (II) lead (IV) oxide behaves as a mixture of lead (II) oxide and lead (IV) oxide. Explain this statement.
10. State which of the metals Na, Pb, Al, Mg, Ca will react
    (a) readily with cold water
    (b) very slowly with cold water, but vigorously with steam
    (c) with neither cold water nor steam
    Place these metals in descending order of activity.
11. State TRUE or FALSE for each of the following statements.
    (a) The reactive metals are found free in nature.
    (b) The solubility of calcium hydroxide decreases with the increase of temperature.
    (c) The electronic structure shown by (He) $2s^1$ is lithium.
    (d) Alkali metals are easily inflammable when they touch to kerosene.
    (e) The metals at the lowest place of activity series may be found free in nature.
12. Fill in the blanks with a suitable word or phrase or numerical value with unit as necessary.
    (a) A small amount of .... is used to lower the melting point of sodium chloride.
    (b) Sodium hydroxide is commercially produced from saturated solution of .... by using electrolysis.
    (c) Most of sodium chloride is naturally found in ....
    (d) Reactive metals are usually manufactured by ....

(e) The mixture of calcium dihydrogenphosphate and calcium phosphate is sold as ....

13. Choose the correct term or terms given in the brackets.
   (i) (K, Fe, Ag) is usually manufactured by electrolysis.
   (ii) (K, Fe, Ag) is manufactured by reduction reaction.
   (iii)(K, Fe, Ag) is found as free element.
   (iv)Aluminium can react with (acid, alkali, water).
   (v) (Al, Pb, Na) is used to protect the radiation.

14. Match each of the items given in List A with the appropriate item in List B.

List A	**List B**
(a) washing soda	(i) $K_2SO_4.Al_2(SO_4)_3.24H_2O$
(b)Alum	(ii) Pb_3O_4
(c) An ingredient of paint	(iii)NaCl
(d) rock salt	(iv)$Na_2CO_3.10H_2O$
(e) baking powder	(v) $NaHCO_3$

15. Complete the following reactions.
   (a) metal + cold water ⟶ ?
   (b) metal + steam ⟶ ?
   (c) metal + dilute acid ⟶ ?

16. Answer the following observations.
   (a) If the metal hydroxide is decomposed to heat, what are the two products ?
   (b) If the metal carbonate is decomposed to heat, what are the two products ?
   (c) Most nitrates on heating gives off brown fumes. What is this brown fumes?

17. Answer the following questions.
   (a) What is the displacement reaction ?
   (b) Can you name a metal carbonate that is stable to heat ?
   (c) Can you name a metal hydroxide that is stable to heat ?

18. The following is a list of metals in order of reactivity with three unknown metals X, Y, and Z include in the list. Which of these unknown metals

X, Ca, Mg, Y, Zn, Fe, Pb, Cu, Z

   (a) will react with cold water ?
   (b) will react with steam ?
   (c) will not react with dilute acids ?
   (d) will form a hydroxide which is stable to heat ?
   (e) will form a nitrate which decomposes on heating to form an oxide ? What other products are formed ?
   (f) will form a least stable oxide ?

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CHAPTER 9
METAL REACTIVITY

9.1 Metal Reaction with acid

When magnesium metal reacts with dilute hydrochloric acid, effervescence takes place which is caused by bubbles of hydrogen gas being formed as the reaction between the two substances proceeds. The other product of this reaction is the salt, magnesium chloride.

magnesium + hydrochloric acid ⟶ magnesium chloride + hydrogen

$$Mg\,(s) + 2HCl\,(aq) \longrightarrow MgCl_2\,(aq) + H_2\,(g)$$

If a metal reacts with dilute hydrochloric acid then hydrogen and the metal chloride are produced.

If similar reactions are carried out using other metals with acid, an order of reactivity can be produced. This is known as a **reactivity series.** An order of reactivity, giving the most reactive metal first, using results from experiments with dilute acid, is shown in Table 9.1. The table also shows how the metals react with air/oxygen and water/steam, and, in addition, the ease of extraction of the metal.

Table 9.1 Order of reactivity of metals

Reactivity series	Reaction with dilute acid	Reaction with air/oxygen	Reaction with water	Ease of extraction
Potassium (K)	Produce H_2 with decreasing vigour	Burn very brightly and vigorously	Produce H_2 with decreasing vigour with cold water	Difficult to extract
Sodium (Na)				
Calcium (Ca)			React with steam with decreasing vigour	Easier to extract
Magnesium (Mg)		Burn to form an oxide with decreasing vigour		
Aluminium (Al)				
Zinc (Zn)				
Iron (Fe)				
Lead (Pb)				
Hydrogen (H)		React slowly to form the oxide		
Copper (Cu)	Do not react with dilute acid	Do not react	Do not react with water or steam	
Silver (Ag)				Found as the element (native)
Gold (Au)				
Platinum (Pt)				

Increasing Reactivity

Because aluminium reacts so readily with the oxygen in the air, a protective oxide layer is formed on its surface. This often prevents any further reaction and disguises aluminium's true reactivity. This gives us the use of a light and strong metal.

With air/oxygen

Many metals react with oxygen to form oxides. For example, magnesium burns brightly in oxygen to form the powder magnesium oxide.

magnesium + oxygen ⟶ magnesium oxide
$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$

With water/steam

Reactive metals such as potassium, sodium and calcium react with cold water to produce the metal hydroxide and hydrogen gas. For example, the reaction of sodium with water produces sodium hydroxide and hydrogen.

sodium + water ⟶ sodium hydroxide + hydrogen
$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$

The moderately reactive metals, magnesium, zinc and iron, react slowly with water. They will, however, react more rapidly with steam. In their reaction with steam, the metal oxide and hydrogen are formed. For example, magnesium produces magnesium oxide and hydrogen gas.

magnesium + water ⟶ magnesium oxide + hydrogen
$Mg(s) + H_2O(g) \longrightarrow MgO(s) + H_2(g)$

Generally, it is unreactive metals that we find the most uses for; for example, the metals iron and copper can be found in many everyday objects. However, magnesium is one of the metals used in the construction of Concorde.

Both sodium and potassium are so reactive that they have to be stored under kerosene. However, because they have low melting points and are good conductors of heat, they are used as coolants for nuclear reactors.

9.2 Using the reactivity series

What predictions can be made using the reactivity series? It is useful in predicting how metals react.

Competition reactions in the solid state

If a more reactive metal is heated with the oxide of a less reactive metal, then it will remove the oxygen from it (as the oxide anion). You can see from the reactivity series that iron is less reactive than aluminium. If iron(III) oxide is mixed with aluminium and the mixture is heated using a magnesium fuse, a very violent reaction occurs as the competition between the aluminium and the iron for the oxygen takes place.

The aluminium, being the more reactive metal, takes the oxygen from the less reactive iron. It is a very exothermic reaction. When the reaction is over, a solid lump of iron is left along with a lot of white aluminium oxide powder.

iron(III) oxide + aluminium ⟶ aluminium oxide + iron

$$Fe_2O_3(s) + 2Al(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$$

This is a redox reaction.This particular reaction is known as the **Thermite reaction.** Since large amounts of heat are given out and the iron is formed in a molten state, this reaction is used to weld together damaged railway lines. It is also used in incendiary bombs.

Some metals, such as chromium and titanium, are prepared from their oxides using this type of competition reaction.

Competition reactions in aqueous solution

In another reaction, metals compete with each other for other anions. This type of reaction is known as a **displacement reaction**. As in the previous type of competitive reaction, the reactivity series can be used to predict which of the metals will "win".

In a displacement reaction, a more reactive metal will displace a less reactive metal from a solution of a salt. Zinc is above copper in the reactivity series. When a piece of zinc metal is left to stand in a solution of copper (II) nitrate the copper (II) nitrate slowly loses its blue colour as the zinc continues to displace the copper from the solution and eventually becomes colourless zinc nitrate.

zinc + copper(II) nitrate ⟶ zinc nitrate + copper

$$Zn(s) + Cu(NO_3)_2(aq) \longrightarrow Zn(NO_3)_2(aq) + Cu(s)$$

The ionic equation for this reaction is:

zinc + copper ions ⟶ zinc ions + copper

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

This is also a redox reaction involving the transfer of two electrons from the zinc metal to the copper ions. The zinc is oxidized to zinc ions in aqueous solution, while the copper ions are reduced. (See Chapter 5, for a discussion of oxidation and reduction in terms of electron transfer.)

It is possible to confirm the reactivity series for metals using competition reactions of the types discussed in this section.

For example,

iron(III) chloride + sodium hydroxide ⟶ iron(III) hydroxide + sodium chloride

$FeCl_3(aq) + 3NaOH(aq) \longrightarrow Fe(OH)_3(s) + 3NaCl(aq)$

The ionic equation for this reaction is:

iron(III) ions + hydroxide ions ⟶ iron(III) hydroxide

$Fe^{3+}(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s)$

9.3 Extraction on metals from their ores

The majority of metals are too reactive to exist on their own in the Earth's crust, and they occur naturally in rocks as compounds in ores. These ores are usually carbonates, oxides or sulphides of the metal, mixed with impurities.

Some metals, such as gold and silver, occur in a native form as the free metal. They are very unreactive and have withstood the action of water and the atmosphere for many thousands of years without reacting to become compounds.

Some of the common ores are shown in Table 9.2.

Table 9.2 Some common ores

Metal	Name of ore	Chemical name of compound in ore	Formula	Usual method of extraction
Aluminium	Bauxite	Aluminium oxide	$Al_2O_3.2H_2O$	Electrolysis of oxide dissolved in molten cryolite
Copper	Copper pyrites	Copper iron sulphide	$CuFeS_2$	The sulphide ore is roasted in air
Iron	Haematite	Iron(III) oxide	Fe_2O_3	Heat oxide with carbon
Sodium	Rock salt	Sodium chloride	NaCl	Electrolysis of molten sodium chloride
Zinc	Zinc blende	Zinc sulphide	ZnS	Sulphide is roasted in air and the oxide produced is heated with carbon

Large lumps of the ore are first crushed and ground up by very heavy machinery. Some ores are already fairly concentrated when mined. For example, in some parts of the world, haematite contains over 80 % Fe_2O_3. However, other ores, such as copper pyrite are often found to be less concentrated, with only 1% or less of the copper compound, and so they have to be concentrated before the metal can be extracted. The method used to extract the metal from its ore depends on the position of the metal in the reactivity series.

Extraction of reactive metals

Because reactive metals, such as sodium, hold on to the element(s) they have combined with, they are usually difficult to extract. For example, sodium chloride (as rock salt) is an ionic compound with the Na^+ and Cl^- ions strongly bonded to one another. Consequently, the separation of these ions and the subsequent isolation of the sodium metal is difficult.

Electrolysis of the molten, purified ore is the method used in these cases. During this process, the metal is produced at the cathode while a non-metal is produced at the anode. As you might expect, extraction of metal by electrolysis is expensive. In order to keep costs low, many metal smelters using electrolysis are situated in regions where there is hydroelectric power.

Extraction of fairly reactive metals

Metals towards the middle of the reactivity series, such as iron and zinc, may be extracted by reducing the metal oxide with the non-metal carbon.

Iron

Iron is extracted mainly from its oxides, haematite (Fe_2O_3), and magnetite (Fe_3O_4), in furnace. The blast furnace is steel tower approximately 30 m high lined with heat-resistant bricks. It is loaded with the "charge" of iron ore (usually haematite), coke (made by heating coal) and limestone (calcium carbonate). A blast of hot air is sent in near the bottom of the furnace through holes which makes the "charge" glow as the coke burns in the preheated air.

$$\text{carbon} + \text{oxygen} \longrightarrow \text{carbon dioxide}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

A number of chemical reactions follow:

- The limestone begins to decompose:

$$\text{calcium carbonate} \longrightarrow \text{calcium oxide} + \text{carbon dioxide}$$

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

- The carbon dioxide gas produced reacts with more hot coke higher up in the furnace, producing carbon monoxide.

$$\text{carbon dioxide} + \text{coke} \longrightarrow \text{carbon monoxide}$$

$$CO_2(g) + C(s) \longrightarrow 2CO(g)$$

- Carbon monoxide is a reducing agent. It rises up the furnace and reduces the iron(III) oxide ore. This takes place at a temperature of around 700 °C.

$$\text{iron(III) oxide} + \text{carbon monoxide} \longrightarrow \text{iron} + \text{carbon dioxide}$$

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(l) + 3CO_2(g)$$

The molten iron produced trickles to the bottom of the furnace.

- The calcium oxide formed from the limestone reacts with acidic impurities. For example silicon(IV) oxide (sand) (SiO_2), in the iron ore forms a liquid **slag**, which is mainly calcium silicate.

$$\text{calcium oxide} + \text{silicon(IV) oxide} \longrightarrow \text{calcium silicate}$$

$$CaO(s) + SiO_2(s) \longrightarrow CaSiO_3(l)$$

This material also trickles to the bottom of the furnace, but because it is less dense than the molten iron, it floats on top of it. The molten iron as well as the molten slag, may be **tapped off** (run off) at intervals.

The waste gases, mainly nitrogen and oxides of carbon, escape from the top of the furnace. They are used in a heat exchange process to heat incoming air and so help to reduce the energy costs of the process. Slag is the other waste material. It is used by builders and road makers for foundation.

The iron obtained by this process is known as "pig" or cast iron and contains about 4 % carbon (as well as some other impurities such as small amounts of manganese, phosphorous, silicon and sulphur).

Removal of impurities from pig iron gives wrought iron. To produce wrought iron, cast iron is heated in a current of air, using a furnace lined with haematite.The carbon of cast iron is used up in the reduction of iron(III) oxide.

$Fe_2O_3(s) + 3C(s) \longrightarrow 2Fe(s) + 3CO(g)$

Some impurities are converted into gaseous oxides, e.g.,

$4P(s) + 5O_2(g) \longrightarrow P_4O_{10}(g)$

Other impurities,e.g., manganese and silicon , are oxidized and form a slag. Wrought iron is the purest form of industrial iron. It is tough, malleable and ductile.It is used for making wire and for ornamental iron work and horse-shoes.

Gas cylinders are sometimes made of cast iron, since they are unlikely to get deformed during their use.

The majority of the iron produced in the blast furnace is converted into different steel alloys such as manganese and tungsten steels as well as stainless steel.

Zinc

The principal source of zinc is zinc sulphide or zinc blende. This ore occurs mainly in Australia, Canada and the US. The zinc ore is first concentrated by a process called **froth flotation.** The crushed ore is fed into tanks of water containing a chemical collector and frothing agent. The collector sticks to the surface of the zinc sulphide particles giving them a water-repellant coating. Air is blown through so that the whole mixture froths up. The zinc sulphide particles are forced up the tank by the air bubbles and are skimmed off and dried. This ore now contains 55-75 % of zinc sulphide. The zinc sulphide is then heated very strongly in a current of air in a furnace to convert it to the oxide:

zinc sulphide + oxygen ⟶ zinc oxide + sulphur dioxide

$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$

The sulphur dioxide is a useful co-product and is used in the manufacture of sulphuric acid. The zinc oxide is mixed with powdered coke in a furnace and heated very strongly to a temperature of approximately 1400 °C.The zinc oxide is reduced by the coke to zinc.

zinc oxide + coke (carbon) ⟶ zinc + carbon monoxide

$ZnO(s) + C(s) \longrightarrow Zn(g) + CO(g)$

The mixture of zinc vapour and carbon monoxide passes through an outlet near the top of the furnace and the zinc metal cools and condenses. The heating costs of the furnace are reduced by burning the carbon monoxide which is produced.

Zinc is used in alloys such as brass. It is also used to galvanise steel and for electrodes in batteries.

Extraction of unreactive metals

Copper

Copper is quite a long way down the reactivity series. Copper can be found as the free metal element or "native" in the US. It is principally extracted, however, from copper pyrites, $CuFeS_2$. The crushed ore is concentrated by froth flotation. A chemical known as a collector sticks to the surface of the copper pyrites particles, giving them a water-repellant coating. Detergent is added and air is blown into the mixture to make it froth. The copper pyrites particles are concentrated in the froth and can be removed easily. They are then roasted in a limited supply of air to ensure conversion of copper pyrites to copper(I) sulphide:

copper pyrites + oxygen ⟶ copper(I) sulphide + sulphur dioxide + iron(II) oxide

$$2CuFeS_2(s) + 4O_2(g) \longrightarrow Cu_2S(s) + 3SO_2(g) + 2FeO(s)$$

Silica (SiO_2) is then added and the mixture is heated in the absence of air. The iron(II) oxide is converted into iron(II)silicate ($FeSiO_3$), which is run off. The remaining copper(I) sulphide is then reduced to copper by heating in a controlled amount of air.

copper(I) sulphide + oxygen ⟶ copper + sulphur dioxide

$$Cu_2S(s) + O_2 \longrightarrow 2Cu(s) + SO_2(g)$$

Copper is then refined by electrolysis to give a product which is at least 99.92 % pure. The purified copper is easily drawn into wires (it is highly ductile), which makes it useful for electrical wiring. It is also used in alloys, such as bronze and brass. Copper is also used to make water and central heating pipes, as well as steam boilers (it is a good conductor of heat).

Extraction of silver from silver glance by the cyanide process.

The crushed or fine state of silver glance or argentite ore is digested in large vats in a sodium cyanide solution.

$$4\,Ag(s) + 8\,NaCN(aq) + 2\,H_2O(l) + O_2(g) \longrightarrow 4\,Na[Ag(CN)_2](aq) + 4\,NaOH(aq)$$

Silver sulphide and silver chloride also dissolve in cyanide solution.

$$AgCl(s) + 2\,NaCN(aq) \longrightarrow Na[Ag(CN)_2](aq) + NaCl(aq)$$

$$Ag_2S(s) + 4\,NaCN(aq) \longrightarrow 2\,Na[Ag(CN)_2](aq) + Na_2S(aq)$$

The silver bearing solution is treated with zinc shavings, silver is thrown out as a precipitate .

$$Zn(s) + 2\,Na[Ag(CN)_2](aq) \longrightarrow \underset{\text{silver}}{2\,Ag(s)} + 2\,NaCN(aq) + Zn(CN)_2(aq)$$

The silver is collected , washed and melted. It is purified electrolytically.

9.4 Recycling metals

Recycling "banks" have become commonplace in recent years. Why should we really want to recycle metals? Certainly, if we extract less metals from the Earth then the existing reserves will last that much longer. Also, recycling metals prevents the creation of a huge environmental problem. However, one of the main considerations is that it saves money.

The main metals which are recycled include aluminium and iron. Aluminium is saved by many households as drinks cans and milk bottle tops, to be melted down and recast. Iron is collected at local authority tips in the form of discarded household goods and it also forms a large part of the materials collected by scrap metal dealers. Iron is recycled to steel. Many steel-making furnaces run mainly on scarp iron.

9.5 Rusting of iron

After a period of time, objects made of iron or steel will become coated with rust. The rusting of iron is a serious problem and wastes enormous amounts of money in the UK each year. It is estimated that iron of £500 million a year is spent on replacing iron and steel structures.

Rust is an orange-red powder consisting mainly of hydrated iron(III) oxide ($Fe_2O_3.xH_2O$). Both water and oxygen are essential for iron to rust, and if one of these two substances is not present then rusting will not take place. The rusting of iron is encouraged by salt.

Rust prevention

To prevent iron rusting, it is necessary to stop oxygen (from the air) and water coming into contact with it. There are several ways of doing this.

Painting

Ships, lorries, cars, bridges and many other iron and steel structures are painted to prevent rusting. However, if the paint is scratched, the iron beneath it will start to rust and corrosion can then spread under the paintwork which is still sound. This is why it is essential that the paint is kept in good condition and checked regularly.

Oiling/greasing

The iron and steel in the moving parts of machinery are coated with oil to prevent them from coming into contact with air or moisture. This is the most common way of protecting moving parts of machinery,but the protective film must be renewed.

Coating with plastic

The exteriors of refrigerators, freezers and many other items are coated with plastic, such as PVC, to prevent the steel structure rusting.

Plating

Cans for food can be made from steel coated with tin. The tin is deposited onto the steel used to make food cans by dipping the steel into molten tin. Some car bumpers, as well as bicycle handlebars, are electroplated with chromium to prevent rusting. The chromium gives a decorative furnish as well as protecting the steel beneath.

Galvanising

Some steel girders, used in the construction of bridges and buildings, are **galvanized.** Coal bunkers and steel dustbins are also galvanized. This involves dipping the object into molten zinc. The thin layer of the more reactive zinc metal coating the steel object slowly corrodes and loses electrons to the iron, thereby protecting it. This process continues even when much of the layer of zinc has been scratched away, so the iron continues to be protected.

Sacrificial protection

Bars of zinc are attached to the hulls of ships and to oil rigs. Zinc is above iron in the reactivity series and will react in preference to it and so iron is protected. As long as some of the zinc bars remain in contact with the iron structure, the structure will be protected from rusting. When the zinc runs out, it must be renewed. Gas and water pipes made of iron and steel are connected by a wire to blocks of magnesium to obtain the same result. In both cases, as the more reactive metal corrodes it loses electrons to the iron and so protects it.

Corrosion

Rusting is the most common form of **corrosion.** Corrosion is the name given to the process which takes place when metals and alloys are chemically attacked by oxygen, water or any other substances found in their immediate environment. The metals in the reactivity series will corrode to a greater or lesser extent. Generally, the higher the metal is in the reactivity series, the more rapidly it will corrode. If sodium and potassium were not store under oil they would corrode very rapidly indeed. Magnesium, calcium and aluminium are usually covered by a thin coating of oxide after initial reaction with oxygen in the air. Freshly produced copper is pink in colour. However, it soon turns brown due to the formation of copper(II) oxide on the surface of the metal.

In more exposed environments, copper roofs and pipes quickly become covered in verdigris. Verdigris is green in colour and is composed of copper salts formed on copper. The composition of verdigris varies depending on the atmospheric conditions, but includes mixed copper(II) carbonate and copper(II) hydroxide($CuCO_3$. $Cu(OH)_2$.

Gold and platinum are unreactive and do not corrode, even after thousands of years.

9.6 Alloys

The majority of the metallic substances used today are **alloys.** Alloys are mixtures of two or more metals and are formed by mixing molten metals thoroughly. It is generally found that alloying produces a metallic substance that has more useful properties than the original pure metal it was made from. Steel, which is a mixture of the metal iron and the non-metal carbon, is also considered to be an alloy.

Of all the alloys we use, steel is perhaps the most important.Many steels have been produced; they contain not only iron but also carbon and other metals. For example, nickel and chromium are the added metals when stainless steel is produced. The chromium prevents the steel from rusting while the nickel makes it harder.

Production of steel

The 'pig iron' obtained from the blast furnace contains between 3% and 5% of carbon and other impurities, such as sulphur, silicon and phosphorous. These impurities make the iron hard and brittle. In order to improve the quality of the metal, most of the impurities must be removed and in doing this, steel is produced.

The impurities are removed by the **basic oxygen process.** In this process, molten pig iron from the blast furnace is poured into the basic oxygen furnace.

A water-cooled 'lance' is introduced into the furnace and oxygen at 5-15 atm pressure is blown onto the surface of the molten metal. Carbon is oxidized to carbon monoxide and carbon dioxide while sulphur is oxidized to sulphur dioxide. Silicon and phosphorous are silicon (IV) oxide and phosphorous (V) oxide, which are solid oxides. Some calcium oxide (lime) is added to remove these solid oxides as slag. The slag may be skimmed or poured off the surface. Samples are continuously taken and checked for carbon content. When the required amount of carbon has been reached, the blast of oxygen is turned off The basic oxygen furnace can convert up to 300 tons of pig iron to steel per hour.

There are various types of steel that differ only in their carbon content. The differing amounts of carbon present confer different properties on the steel and they are used for different purposes (Table 9.3). Steel with carbon content of 1.5 % makes the maximum tensile strengh of it.If other types of steel are required then up to 35 % scrap steel is added, along with other metals (such as tungsten), are added and the carbon is burned off.

Table 9.3 Different types of steel

Steel	Typical composition	Properties	Uses
Mild steel	99.5 %iron, 0.5 %carbon	Easily worked, lost most of brittleness	Car bodies, large structures
Hard steel	99 % iron, 1 %carbon	Tough and brittle	Cutting tools, chisels, razor blades
Manganese steel	87 % iron, 13 %manganese	Tough, springy	Drill bits, springs
Stainless steel	74 % iron, 18 %chromium, 8 %nickel	Tough , does not corrode	Cutlery, kitchen sinks, surgical instruments
Tungsten steel	95 % iron, 5 %tungsten	Tough, hard, even at high temperatures	Edges of high speed cutting tools

Uses of common alloys

Alloy	Composition	Uses
Brass	65 %copper, 35 %zinc	Jewellery, machine bearings, electrical connections, door furniture
Bronze	90 %copper, 10 %tin	Castings, machine parts
Cupro nickel	30 %copper, 70 %nickel	Turbine blades
	75 %copper, 25 %nickel	Coinage metal
Duralumin	95 %aluminium,4 %copper, 1%magnesium, manganese and iron	Aircraft construction, bicycle parts
Magnalium	70 %aluminium, 30 %magnesium	Aircraft construction
Pewter	30 %lead, 70 %tin, a small amount of antimony	Plates, ornaments and drinking mugs
Solder	70 %lead, 30 %tin	Connecting electrical wiring

SUMMARY

In this chapter, reaction of metals with acids, air/oxygen, water and steam have been presented followed by extraction of these metals from their ores using the reactivity series. Extraction of reactive metals such as sodium, extraction of fairly reactive metals such as iron and zinc, extraction of unreactive metals such as copper and silver have been elaborated.

The topic on recycling metals, rusting of iron, rust prevention methods, corrosion of metals have been presented . In the final section of this chapter, different types of alloys, such as steel, their productions in industry are also provided.

Questions and Problems

1. Pig iron is obtained by feeding a mixture of iron ore, coke and limestone into a blast furnace. Give an account of the reactions that take place in the furnace.
2. Use the following list of metals to answer the questions (a) to (i):
   Iron, calcium, potassium, gold, aluminium, magnesium, sodium, zinc, platinum

(a) Which of the metals is found native?

(b) Which of the metals is found native as the ore :

(i) haematite? (ii) bauxite?

(c) Which metal is a carbonate found in nature called marble?

(d) Which of the metals will not react with oxygen to form an oxide?

(e) Which of the metals will react violently with cold water?

(f) Choose one of the metals in your answer to (e) and write a balanced chemical equation for the reaction which takes place.

(g) Which of the metals has a protective coating on its surface?

(h) Which of the metals reacts very slowly with cold water but extremely vigorously with steam?

(i) Which of the metals is used to galvanise iron?

3. Explain the following.

(a) Recycling metals can save money.

(b) Metals such as gold and silver occur native in the earth's crust.

(c) The parts of shipwrecks made of iron rust more slowly in deep sea water .

(d) Zinc bars are attached to the hulls of ships to prevent the hulls from rusting.

(e) Copper roofs quickly become covered with a green coating when exposed to the atmosphere.

4. Answer the following questions about the manufacture of iron.

(a) Give the name and formula of one mineral from which iron is extracted.

(b) Explain how carbon monoxide is formed in the furnace.

(c) Explain why limestone is used in the blast furnace.

(d) Name three impurities likely to be present in pig iron.

(e) Explain how these impurities are removed during the conversion of pig iron to wrought iron.

5. Iron is extracted from its ores haematite and magnetite. Usually it is extracted from haematite (iron(III) oxide) .The ore is mixed with limestone and coke and reduced to the metal in the blast furnace. The following is a brief outline of the reactions involved.

$$\text{Coke} + \text{oxygen} \longrightarrow \text{gas X}$$
$$\text{Gas X} + \text{coke} \longrightarrow \text{gas Y}$$
$$\text{Iron (III) oxide} + \text{gas Y} \longrightarrow \text{iron} + \text{gas X}$$

(a) Name the gases X and Y.

(b) Write balanced chemical equations for the reactions shown above .

(c) The added limestone is involved in the following reactions:

$$\text{Limestone} \longrightarrow \text{calcium oxide} + \text{gas X}$$

Calcium oxide + silicon (IV) oxide $\longrightarrow$ slag

(i) Give the chemical names for limestone and slag.

(ii) Write balanced chemical equations for the reactions shown above.

(iii) Describe what happens to the liquid iron and slag when they reach the bottom of the furnace.

(d) Explain why blast furnaces are usually found near to or on coal fields.

6. The iron obtained from the blast furnace is known as pig or cast iron. Because of the presence of impurities, such as carbon, it has a hard and brittle nature. Most of this type of iron is therefore converted into steel in the basic oxygen process. During this process either all or some of the carbon is removed. Calculated quantities of other elements are then added to produce the required type of steel.

   (a) Explain the meaning of the term alloy as applied to steel.

   (b) Name two impurities, other than carbon, which are present in cast iron and which are removed completely during the steel manufacture.

   (c) Describe the method of steel manufacture used which removes the impurities referred to in (b).

   (d) Name two metallic elements which may be added to the basic oxygen furnace to produce different varieties of steel.

   (e) Give two uses of stainless steel.

   (f) Give two advantages of stainless steel compared to cast iron.

7. How and under what conditions do the metals iron, copper, silver and zinc react with

   (a) water (steam if necessary)

   (b) oxygen

   (c) dilute sulphuric acid?

8. Zinc is extracted by roasting zinc blende in a current of air. This converts the sulphide ore to the oxide. Zinc oxide is then mixed with powdered coke in a furnace and heated very strongly. The oxide is converted to the metal according to the following equation.

$$ZnO(s) + C(s) \longrightarrow Zn(s) + CO(g)$$

Approximately 500 tons of zinc are produced per day from this process.

   (a) (i) What is the name of the chemical process by which zinc oxide is converted to zinc ?

   (ii) At what temperature does this process take place ?

   (b) It is very expensive business to maintain the high temperature needed to efficiently convert zinc oxide to zinc. How are the heating costs offset ?

(c) Calculate the quantity of zinc oxide required to produce 500 tons of zinc.
(Zn = 65, O = 16, C = 12)

9. Give the name and formula of a common ore of zinc and describe the chemistry involved in extracting zinc from it.
10. State and explain the results of placing pieces of zinc in aqueous solution of copper (II) sulphate.
11. Explain what happens when
    (a) dilute sulphuric acid is added separately to copper and zinc.
    (b) aqueous sodium hydroxide is added separately to aqueous solutions of copper (II) sulphate and zinc sulphate respectively until it is present in excess.
12. Write balanced equations for the reactions between :
    (a) iron and dilute hydrochloric acid
    (b) calcium and oxygen
    (c) potassium and water
    (d) magnesium and steam
    (e) magnesium and oxygen
13. Discuss the extraction of silver from silver glance by the cyanide process.
14. What is 'Thermite reaction'? Explain with suitable example.
15. Write an account on the extraction of copper from copper pyrites.
16. What is meant by the term 'rusting of iron'?
17. What are the methods used to prevent iron rusting?
18. What do you understand by the term 'Sacrificial protection'?
19. Explain the following terms:
    (a) Galvanising (b) Corrosion (c) Plating (d) Alloys
20. Explain different types of steel with suitable examples.
21. Write an account on the uses of common alloys.
22. What is meant by the term 'Recycling metals'?
23. Write TRUE or FALSE for each of the following statements.
    (a) The silicate impurity from the iron ore may be removed as calcium silicate.
    (b) The properties of steel depend upon the composition.
    (c) Iron as impurity in copper ore may be removed as a form of iron (II) silicate.
    (d) Steel with carbon content of 1.5 % makes the minimum tensile strength of it.
    (e) Frothing agent is used in copper production to float the copper bearing particles in froth.

24. Fill in the blanks with a suitable word or phrase or numerical value with unit as necessary.
   - (a) Iron ore is roasted to convert the carbonate and sulphide into ....
   - (b) ....reaction is uesd to weld together damage railway line.
   - (c) In electrolytic refining crude copper is attached to ....
   - (d) The formula of blue copper (II) sulphate is ....
   - (e) The elements above........... in the electrochemical series can displace hydrogen from the acids.

25. Select the correct term or terms given in the brackets.
   - (a) (Wrought iron, Pig iron. Slag) is the purest form of industrial iron.
   - (b) Galvanization is the term for deposition of thin layer of (zinc on iron, iron on copper, iron on silver).
   - (c) The most important source of silver is (argentite, calamine, haematite).
   - (d) The iron ore is reduced by (carbon monoxide, hydrogen, chlorine).
   - (e) (Electrolytic, Reduction, Oxidation) technique gives the metals of the highest purity.

26. Match each of the items given in List A with the appropriate item given in List B.

List A	**List B**
(a) Haematite	(i) zinc sulphide
(b) Bauxite	(ii) copper iron sulphide
(c) Copper pyrites	(iii) iron (III) oxide
(d) Rock salt	(iv) aluminium oxide
(e) Zinc blende	(v) sodium chloride

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CHAPTER 10

NITROGEN AND ITS COMPOUNDS

10.1 Occurrence

Nitrogen forms the major constituent of the atmosphere, being present to the extent of about 79 percent by volume or 76 percent by weight of the air. In chemical combination with other elements it occurs in sodium nitrate (Chile saltpetre), in proteins, and many other animal and vegetable products.

10.2 Methods of Preparation of Nitrogen

Preparation of nitrogen from the atmosphere

The most important gases present in dry air are oxygen (about 21 % by volume), carbon dioxide (about 0.03 % by volume), and atmospheric nitrogen (about 79 % by volume).

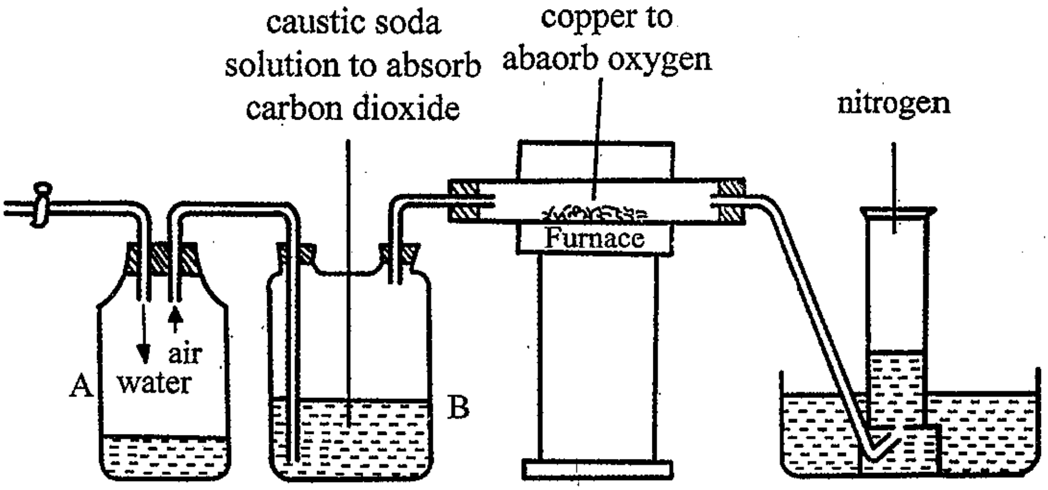


Fig. 10.1 Preparation of nitrogen from the atmosphere

copper + air ⟶ copper (II) oxide + nitrogen

$$2Cu + (N_2+O_2) \longrightarrow 2CuO + N_2$$

sodium hydroxide + carbon dioxide ⟶ sodium carbonate + water

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

The apparatus is set up as shown in Fig. 10.1. Water is allowed to flow into bottle A at a slow rate. Air from this bottle is displaced and made to pass through another bottle B containing caustic soda solution to remove carbon dioxide.

The carbon dioxide free air is then passed over heated copper which absorbs oxygen to form copper (II) oxide.

The nitrogen, so freed from oxygen, comes out from the combustion tube. Since the nitrogen is only slightly soluble in water, it is collected by the downward displacement of water.

If the nitrogen is required dry. it may be passed through a U-tube containing glass beads wetted with concentrated sulphuric acid and then collected in a syringe.

Note: The product of this experiment is almost pure nitrogen. It contains about 1 % by volume of the "noble gases", chiefly argon. The removal of these gases is not possible by chemical methods. The presence of these gases makes "atmospheric nitrogen" slightly denser than the pure gas.

Laboratory preparation of nitrogen

Nitrogen gas may be prepared by heating a solution of ammonium nitrite. However, ammonium nitrite decomposes slowly at ordinary temperatures, so that neither ammonium nitrite itself, nor its solution in water, should be kept in stock. The ammonium nitrite is obtained by a reaction between sodium nitrite and ammonium chloride solutions.

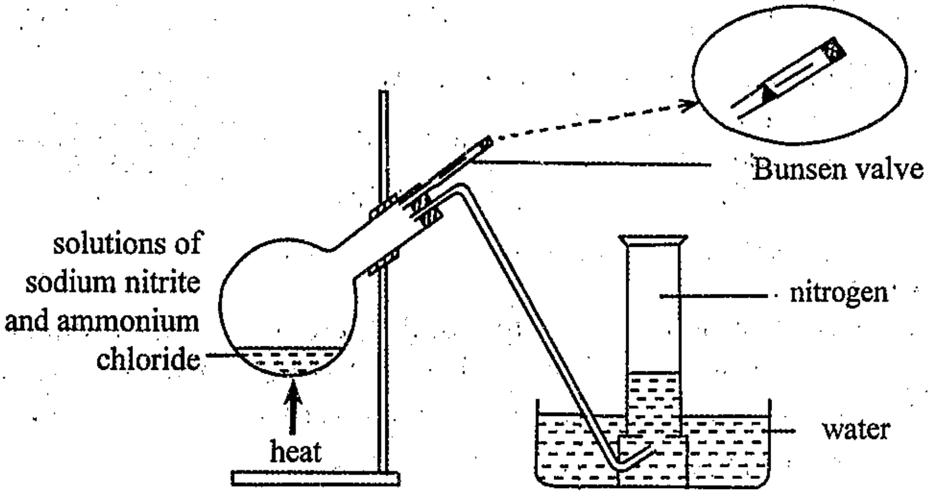


Fig. 10.2 Laboratory preparation of nitrogen

sodium nitrite + ammonium chloride $\xrightarrow{\Delta}$ sodium chloride + ammonium nitrite

$NaNO_2 + NH_4Cl \xrightarrow{\Delta} NaCl + NH_4NO_2$

ammonium nitrite $\longrightarrow$ nitrogen + water

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$

The apparatus is set up as shown in Fig. 10.2
Concentrated solutions of sodium nitrite and ammonium chloride are mixed in a round-bottomed flask. The flask is then heated gently.

Decomposition to nitrogen occurs as the solution becomes warm. Since nitrogen gas is slightly soluble in water, it may be collected over water. The nitrogen gas may be dried as described in the previous experiment.

Other chemical methods of preparation of nitrogen

1. The reaction of chlorine and excess ammonia

chlorine + ammonia $\longrightarrow$ nitrogen + ammonium chloride

$3Cl_2 + 8NH_3 \longrightarrow N_2 + 6NH_4Cl$

2. Passing ammonia gas over heated copper (II) oxide

ammonia + copper (II) oxide $\longrightarrow$ copper + nitrogen + water

$2NH_3 + 3CuO \longrightarrow 3Cu + N_2 + 3H_2O$

3. Reduction of oxides of nitrogen by heated copper

copper + nitrogen oxide $\longrightarrow$ copper (II) oxide + nitrogen

$2Cu + 2NO \longrightarrow 2CuO + N_2$

Manufacture of nitrogen

Nitrogen is obtained in industry by the fractional distillation of liquid air. This process is described in Chapter 10. When liquid air is distilled nitrogen boils off at -196 °C(77 K).Oxygen is left as liquid since its boiling point is higher than that of nitrogen. The separated nitrogen is then reliquefied.

10.3 Properties of Nitrogen

Physical properties

1. Nitrogen is colourless and odourless. It is slightly less dense than air and only slightly soluble in water. It condenses to a liquid (b.p. -196 °C), and freezes to a colourless solid (m.p. -210 °C).
2. Nitrogen gas is relatively inert and does not support combustion.

Chemical properties

1. Nitrogen combines with hydrogen and oxygen at higher temperatures.

$$\text{nitrogen} + \text{hydrogen} \xrightleftharpoons[\text{200 atm, 450°C}]{\text{finely divided powder Fe}} \text{ammonia}$$

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$\text{nitrogen} + \text{oxygen} \longrightarrow \text{nitrogen oxide}$$

$$N_2 + O_2 \longrightarrow 2NO$$

2. It combines with many metals, on heating to a dull red heat or higher temperatures, to form nitrides.

$$\text{magnesium} + \text{nitrogen} \longrightarrow \text{magnesium nitride}$$

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

Nitrides react with water to liberate the ammonia gas.

$$\text{magnesium nitride} + \text{water} \longrightarrow \text{ammonia} + \text{magnesium hydroxide}$$

$$Mg_3N_2 + 6H_2O \longrightarrow 2NH_3 + 3Mg(OH)_2$$

3. It combines directly with calcium carbide at about 1000 °C to form calcium cyanamide, $CaCN_2$, an important nitrogenous fertilizer.

$$\text{calcium carbide} + \text{nitrogen} \xrightarrow[\text{1000 °C}]{\Delta} \text{calcium cyanamide} + \text{carbon}$$

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

A mixture of calcium cyanamide and carbon is known as "nitrolime". Calcium cyanamide reacts with water to form ammonia.

$$\text{calcium cyanamide} + \text{water} \xrightarrow{\Delta} \text{calcium carbonate} + \text{ammonia}$$

$$CaCN_2 + 3H_2O \xrightarrow{\Delta} CaCO_3 + 2NH_3$$

10.4 Uses of Nitrogen

This principal use of nitrogen is in the manufacture of ammonia, from which nitrogenous fertilizers, nitric acid and urea are now mainly prepared.

10.5 Compounds of Nitrogen

Ammonia NH_3

This hydride of nitrogen, NH_3, can be formed by decomposition of nitrogenous materials. This decomposition is brought about by bacteria.

Preparation of ammonia

Laboratory preparation of ammonia

Ammonia may be prepared in the laboratory by heating any ammonium salt with an alkali. Usually, a mixture of ammonium chloride and calcium hydroxide (slaked lime) is used.

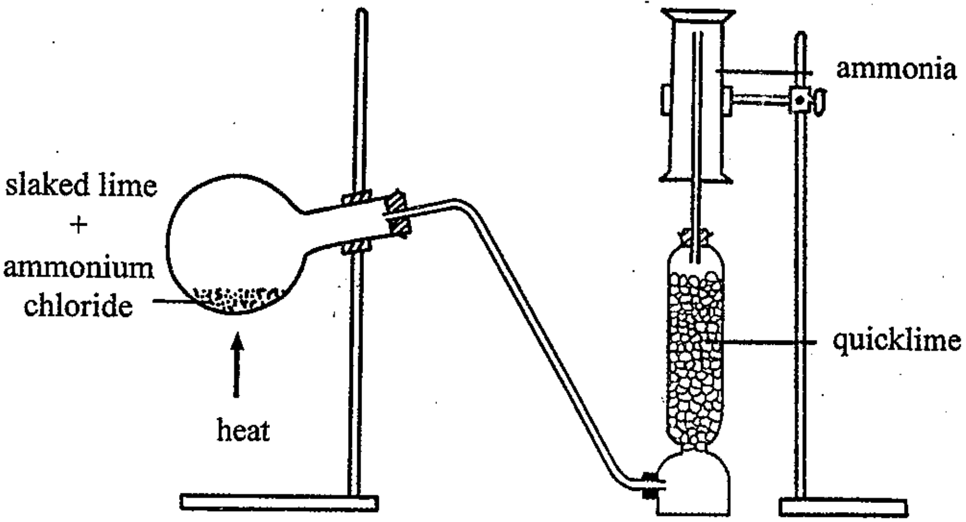


Fig. 10.3 Laboratory preparation of ammonia

$$\text{calcium hydroxide} + \text{ammonium chloride} \xrightarrow{\Delta} \text{calcium chloride} + \text{water} + \text{ammonia}$$

$$Ca(OH)_2 + 2NH_4Cl \xrightarrow{\Delta} CaCl_2 + 2H_2O \quad 2NH_3$$

An excess of the slaked lime and ammonium chloride are mixed. The mixture is ground by using a mortar and pestle, and placed in a round-bottomed flask. The apparatus is set up as shown in Fig. 10.3.When this mixture is heated ammonia gas is evolved.

It is dried by passage through a lime tower which contains the drying agent, quicklime, CaO.

Since ammonia is lighter than air and very soluble in water, it is collected by downward displacement of air. The gas jar is known to be filled with ammonia if a moist red litmus paper placed at the mouth of the gas jar turns blue.

Note: Ammonia gas should not be dried by usual drying agents, such as, calcium chloride, concentrated sulphuric acid and phosphorus (V) oxide. These compounds react with ammonia.

Manufacture of ammonia

Haber Process

Ammonia is obtained on an industrial scale by the Haber Process (Fig.10.4). This process is based on the direct combination of nitrogen and hydrogen.

$$\text{nitrogen} + \text{hydrogen} \rightleftharpoons \text{ammonia}$$

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

This is a reversible reaction.

For the process to be economically successful, the yield of the ammonia should be increased by driving the reaction towards the right.

This can be done

(a) by conducting the reaction at the lowest possible temperature,

(b) by increasing the pressure and

(c) by using a suitable catalyst to reduce the time required for the reaction.

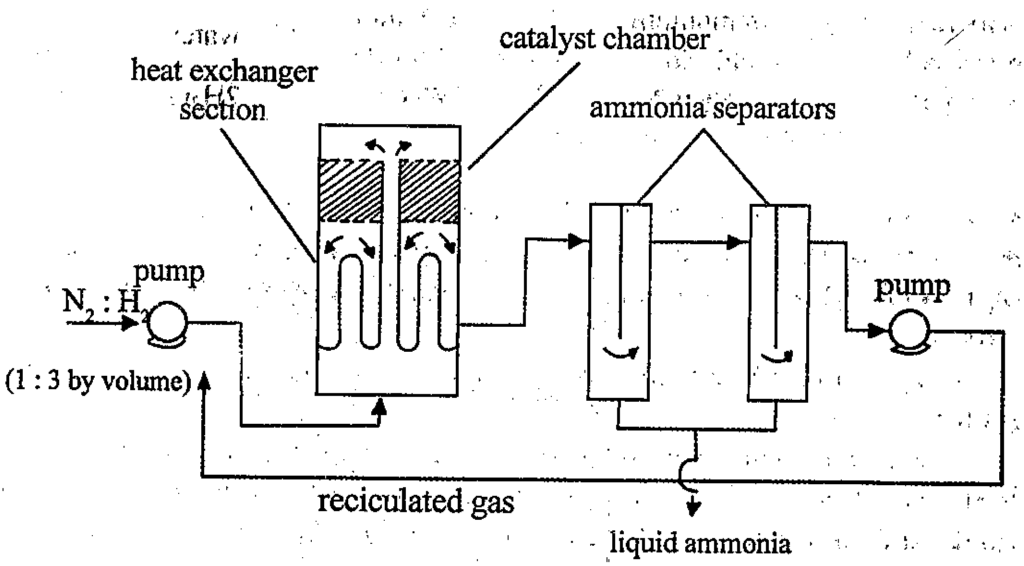


Fig. 10.4 Synthesis of ammonia

The mixture of nitrogen and hydrogen, in the ratio of one to three by volume, is compressed to 200 atmospheric pressure and passed over the catalyst heated at 450°C(723 K). The catalyst used is usually finely divided reduced iron impregnated with alumina, Al_2O_3. The hot gases leaving the catalyst chamber are passed through a heat exchanger in order to preheat the incoming hydrogen - nitrogen mixture. After, washing out the ammonia, or comperssing and removing it as the liquid, the residual gases are mixed with more hydrogen and nitrogen and again passed through the catalyst chamber. The recirculation is repeated as required.

The ammonia produced is liquefied and stored for further use.

Test for ammonia

Ammonia gas has a characteristic pungent smell. It turns moist red litmus paper blue. Dense white fumes are formed when the gas comes into contact with hydrogen chloride gas or concentrated hydrochloric acid.

Physical properties of ammonia

1. Ammonia is a colourless gas with a pungent odour. It is lighter than air.
2. It is extremely soluble in water. This considerable solubility is often demonstrated in the laboratory by the "fountain experiment" as illustrated in Fig. 10.5

The glass vessel is filled with dry ammonia gas and the apparatus arranged as shown. Some of the air inside the vessel is expelled by gently warming the bulb. On allowing the vessel to cool, a little water is drawn up the capillary tube and is discharged into the flask. This water immediately dissolves practically the whole of the ammonia gas in the flask to create a partial vacuum. Water rushes up the capillary the flask to fill the vacuum and a fountain like effect is produced.

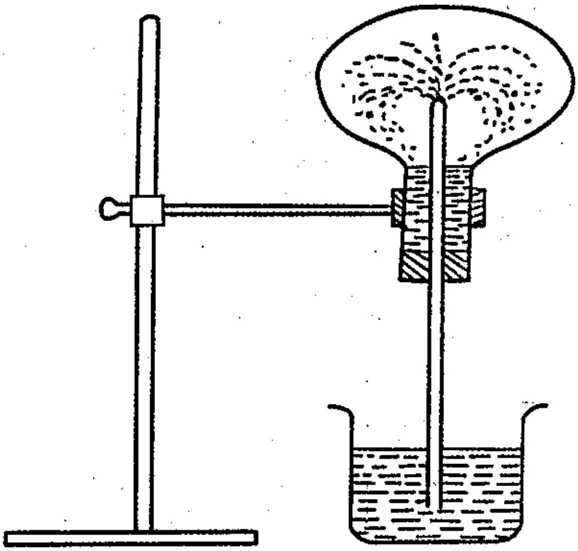


Fig. 10.5 Fountain experiment

The alkaline nature of ammonia can be shown in this experiment by adding a red litmus solution to the water in the trough. When the ammonia in the glass vessel dissolves in the litmus solution, it is turned blue.

Chemical properties of ammonia

1. Ammonia gas reacts with hydrogen chloride gas to form solid ammonium chloride.

ammonia	+	hydrogen chloride	$\longrightarrow$	ammonium chloride (dense fumes)
NH_3	+	HCl	$\longrightarrow$	NH_4Cl

2. Dry ammonia will burn in oxygen or in an atmosphere of air slightly enriched by oxygen but not in air alone.

ammonia	+	oxygen	$\longrightarrow$	nitrogen	+	water
$4NH_3$	+	$3O_2$	$\longrightarrow$	$2N_2$	+	$6H_2O$

3. When ammonia is passed over heated copper (II) oxide, it reduces the copper (II) oxide to copper.

copper (II) oxdide + ammonia ⟶ copper + water + nitrogen

$$3CuO + 2NH_3 \longrightarrow 3Cu + 3H_2O + N_2$$

4. Nitrogen is obtained when excess of ammonia reacts with chlorine,

ammonia + chlorine ⟶ nitrogen + ammonium chloride

$$8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$$

but if the chlorine is in excess, the explosive oily substance, nitrogen trichloride is formed.

ammonia + chlorine ⟶ nitrogen trichloride + hydrogen chloride

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

5. Ammonia combines directly with some metals on heating. Thus, dry ammonia passed over sodium metal heated to red heat forms sodamide. Magnesium however forms the nitride.

ammonia + sodium ⟶ sodamide + hydrogen

$$2NH_3 + 2Na \longrightarrow 2NaNH_2 + H_2$$

ammonia + magnesium ⟶ magnesium nitride + hydrogen

$$2NH_3 + 3Mg \longrightarrow Mg_3N_2 + 3H_2$$

Both sodamide and magnesium nitride are decomposed by water to regenerate ammonia gas.

sodamide + water ⟶ sodium hydroxide + ammonia

$$NaNH_2 + H_2O \longrightarrow NaOH + NH_3$$

magnesium nitride + water ⟶ magnesium hydroxide + ammonia

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

6. An ammonium hydroxide solution, obtained by dissolving ammonia gas in water is also known as ammonia solution.

ammonia + water ⟶ ammonium hydroxide

$$NH_3 + H_2O \longrightarrow NH_4OH$$

Uses of ammonia

The liquid of gas is used in refrigerators, and in the large-scale manufacture of:

(1) fertilizers, such as ammonium sulphate, ammonium nitrate and ammonium, phosphate,
(2) nitric acid and nitrates,
(3) urea and
(4) certain other organic compounds.

Oxides of nitrogen

There are three common oxides of nitrogen. They are dinitrogen oxide or nitrous oxide, N_2O; nitrogen oxide or nitric oxide, NO; and nitrogen dioxide, NO_2 or dinitrogen tetroxide, N_2O_4, depending on the conditions.

Dinitrogen oxide N_2O

Preparation of dinitrogen oxide

Dinitrogen oxide gas may be prepared by heating ammonium nitrate (or any mixture of salts which will yield ammonium nitrate on double decomposition).

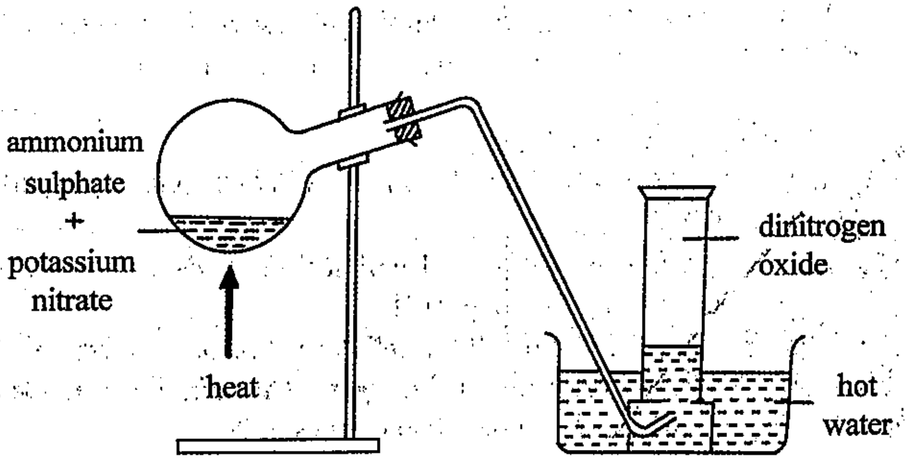


Fig. 10.6 Laboratory perparation of dinitrogen oxide

ammonium sulphate + potassium nitrate $\xrightarrow{\Delta}$ ammonium nitrate + potassium sulphate

$$(NH_4)_2SO_4 + 2KNO_3 \xrightarrow{\Delta} 2NH_4NO_3 + K_2SO_4$$

ammonium nitrate ⟶ dinitrogen oxide + water

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

A mixture of potassium nitrate and ammonium sulphate is placed in a flask. The apparatus is set up as shown in Fig. 10.6.

The flask is heated gently. On heating, the ammonium nitrate melts and effervesces (i.e., gives off bubbles of gas).

The gas liberated is collected over hot water. This gas is fairly soluble in cold water.

Note: Ammonium nitrate can give dinitrogen oxide on heating. It is, however, likely to explode on heating. But the reaction is quite safe if ammonium nitrate is generated in the flask by double decomposition during, the preparation as above.

Test for dinitrogen oxide

Dinitrogen oxide gas rekindles a brightly glowing splint.

Since the above test is similar to the test for oxygen, the two gases cannot be distinguished by this test. To distinguish them the following test may be carried out.

Invert a jar of the gas over cold water in a trough and shake it. If the gas is dinitrogen oxide the water level in the gas jar will rise above the level in the trough, showing the gas to be fairly soluble in water. Oxygen is almost insoluble in water and no rise in the water level would be observed.

Dinitrogen oxide does not give brown fumes with nitrogen oxide while oxygen with nitrogen oxide forms brown fumes of nitrogen dioxide.

Physical properties of dinitrogen oxide

1. Dinitrogen oxide is a colourless gas with a sweetish odour. It is fairly soluble in cold water. It is a neutral oxide.
2. It will relight a glowing splint, and will support combustion. However, if a splint is feebly glowing it will be extinguished.

To be rekindled, the glowing portion of the splint must be not enough to decompose some dinitrogen oxide into nitrogen and oxygen. The mixture will then be rich enough in oxygen to stimulate the combustion of the splint.

$$\text{dinitrogen oxide} \rightleftharpoons \text{nitrogen} + \text{oxygen}$$

$$2N_2O \rightleftharpoons 2N_2 + O_2$$

Chemical properties of dinitrogen oxide

1. Dinitrogen oxide is readily decomposed above 600 ° C.

$$\text{dinitrogen oxide} \xrightarrow[600\ ^\circ\text{C}]{\Delta} \text{nitrogen} + \text{oxygen}$$

$$2N_2O \longrightarrow 2N_2 + O_2$$

2. Dinitrogen oxide will support the combustion of those burning materials the flames of which are not enough to decompose it and so liberate free oxygen with which the material may combine.

$$\text{carbon} + \text{dinitrogen oxide} \longrightarrow \text{carbon dioxide} + \text{nitrogen}$$

$$C + 2N_2O \longrightarrow CO_2 + 2N_2$$

$$\text{phosphorus} + \text{dinitrogen oxide} \longrightarrow \text{phosphorus (v) oxide} + \text{nitrogen}$$

$$4P + 10N_2O \longrightarrow P_4O_{10} + 10N_2$$

$$\text{sodium} + \text{dinitrogen oxide} \longrightarrow \text{sodium oxide} + \text{nitrogen}$$

$$2Na + N_2O \longrightarrow Na_2O + N_2$$

$$\text{magnesium} + \text{dinitrogen oxide} \longrightarrow \text{magnesium oxide} + \text{nitrogen}$$

$$Mg + N_2O \longrightarrow MgO + N_2$$

Uses of dinitrogen oxide

It is used as an anaesthetic for minor surgical operations.
Hysteria sometimes follows recovery from the anaesthetic, and this gave rise to the name " Laughing gas".

Nitrogen oxide NO
Preparation of nitrogen oxide

Some copper turnings are placed in a flat-bottomed flask. The apparatus is set up as shown in Fig. 10.7.

Dilute nitric acid, made by adding an equal volume of concentrated nitric acid to water, is slowly added to the copper turnings. Vigorous effervescence occurs and the flask is filled with brown fumes. These brown fumes are nitrogen dioxide, produced partly by the action of the acid upon the copper and partly by the oxidation of the nitrogen oxide by the oxygen of the air in the flask.

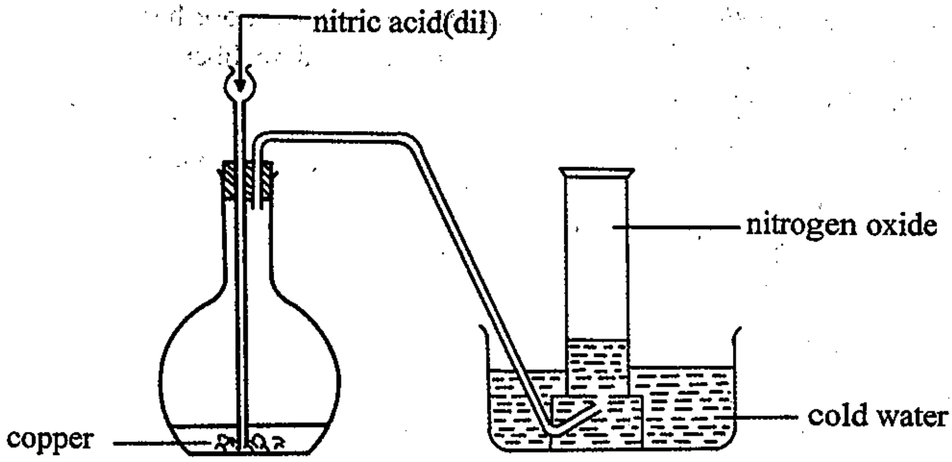


Fig. 10.7 Laboratory preparation of nitrogen oxide

copper + nitric acid (dil) ⟶ copper(II) nitrate + nitrogen oxide + water

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

nitrogen oxide + oxygen ⟶ nitrogen dioxide

$$2NO + O_2 \longrightarrow 2NO_2$$

The brown fumes dissolve in the water and the nitrogen oxide is collected as a colourless gas by the downward displacement of water.

Tests for nitrogen oxide

1. Remove the cover from a gas jar of nitrogen oxide. Reddish brown fumes are produced immediately when the nitrogen oxide comes into contact with oxygen of the air.

nitrogen oxide + oxygen ⟶ nitrogen dioxide

$$2NO + O_2 \longrightarrow 2NO_2$$

2. Pour a cold acidified solution of iron (II) sulphate into a gas jar of nitrogen oxide. A dark brown colouration caused by formation of a black compound, nitroso iron (II) sulphate, $FeSO_4.NO$, is obtained.

iron (II) sulphate + nitrogen oxide ⟶ nitroso iron (II) sulphate

$$FeSO_4 + NO \longrightarrow FeSO_4.NO$$

Physical properties of nitrogen oxide

1. It is a colourless gas.
2. It is insoluble in water.
3. It is neutral to litmus.

Chemical properties of nitrogen oxide

1. Nitrogen oxide combines directly with oxygen to form the brown gas, nitrogen dioxide.

nitrogen oxide + oxygen ⟶ nitrogen dioxide

$$2NO + O_2 \longrightarrow 2NO_2$$

2. Nitrogen oxide is soluble in solutions of iron (II) salts with which it forms brown nitroso complexes.

iron(II) sulphate + nitrogen oxide ⟶ nitroso iron (II) sulphate

$$FeSO_4 + NO \longrightarrow FeSO_4.NO$$

3. It combines directly with chlorine in the presence of charcoal to form nitrosyl chloride, NOCl.

nitrogen oxide + chlorine ⟶ nitorsyl chloride

$$2NO + Cl_2 \longrightarrow 2NOCl$$

4. Nitrogen oxide will support the combustion of those burning materials whose temperatures are high enough to decompose it and so liberate free oxygen with which the material may combine.

phosphorus + nitrogen oxide ⟶ phosphorus (V) oxide + nitrogen

$$4P + 10NO \longrightarrow P_4O_{10} + 5N_2$$

magnesium + nitrogen oxide ⟶ magnesium oxide + nitrogen

$$2Mg + 2NO \longrightarrow 2MgO + N_2$$

Nitrogen dioxide NO_2

Laboratory preparation of nitrogen dioxide

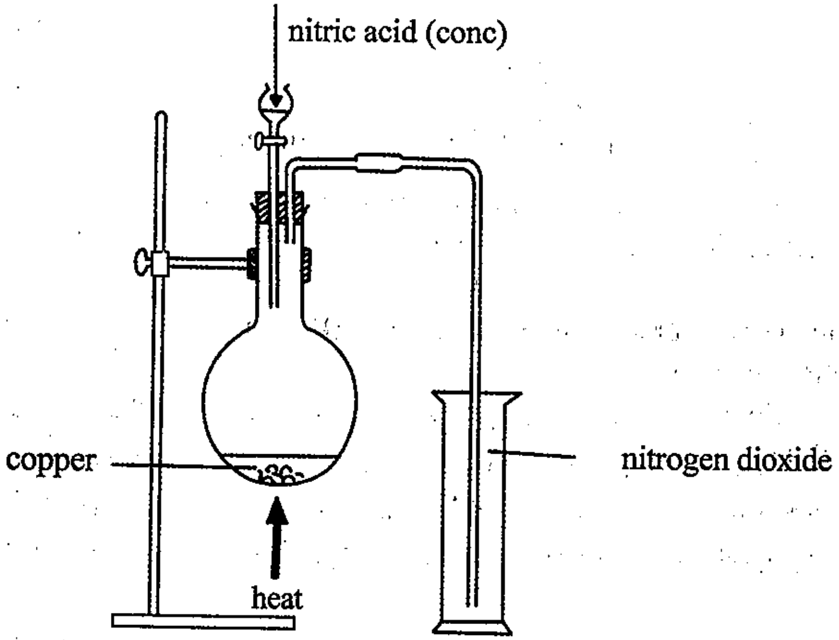


Fig. 10.8 Laboratory preparation of nitrogen dioxide

copper + nitric acid (conc) $\xrightarrow{\Delta}$ copper (II) nitrate + water + nitrogen dioxide

$$Cu + 4HNO_3 \xrightarrow{\Delta} Cu(NO_3)_2 + 2H_2O + 2NO_2$$

Some copper turnings are placed in a round-bottomed flask. The apparatus is set up as shown in Fig. 10.8.

Some concentrated nitric acid is cautiously added. The flask is heated gently.

Since nitrogen dioxide reacts with water and is heavier than air, the gas is collected by the upward displacement of air.

Since nitrogen dioxide is reddish brown, it is easily observed when the jar is full.

Physical properties of nitrogen dioxide

1. Nitrogen dioxide is usually seen as a reddish brown gas at room temperature. It may be liquefied at 22 °C under normal pressure and solidified at –10 °C under the same pressure. The solid is colourless when pure, and the liquid has a pale yellow colour. The depth of colour increases as the temperature is increased from the melting

point to about 150 °C. These colour changes result from the following dissociation reactions.

dinitrogen tetroxide	$\underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}}$	nitrogen dioxide
N_2O_4	$\rightleftharpoons$	$2NO_2$
(light yellow)		(dark brown)

This reversible reaction is an example of thermal dissociation.

2. It has a pungent, irritating smell.

Chemical properties of nitrogen dioxide

1. Thermal dissociation of N_2O_4

At –10 °C, nitrogen dioxide exists as a solid. The solid consists of the colourless "double" molecules N_2O_4, dinitrogen tetroxide. These molecules dissociate on heating to form the brown NO_2 molecules. At above 150 °C it begins to dissociate into the colourless nitrogen oxide and oxygen. The dissociation is complete at the temperature of 620 °C.

dinitrogen tetroxide	$\rightleftharpoons$	nitorgen dioxide	$\rightleftharpoons$	nitrogen oxide	+	oxygen
N_2O_4	$\rightleftharpoons$	$2NO_2$	$\rightleftharpoons$	$2NO$	+	O_2

Since all the above reactions or dissociations are reversible, reducing the temperature will cause the reverse reactions to occur.

2. It dissolves in water to form a mixture of nitric and nitrous acids, and may therefore be regarded as a mixed anhydride.

nitrogen dioxide	+	water	$\longrightarrow$	nitric acid	+	nitrous acid
$2NO_2$	+	H_2O	$\longrightarrow$	HNO_3	+	HNO_2

3. When nitrogen dioxide is absorbed in aqueous alkalis, the corresponding nitrates and nitrites are formed.

sodium hydroxide	+	nitrogen dioxide	$\longrightarrow$	sodium nitrate	+	sodium nitrite	+	water
$2NaOH$	+	$2NO_2$	$\longrightarrow$	$NaNO_3$	+	$NaNO_2$	+	H_2O

Manufacture of nitric acid

Nitric acid is manufactured by the Ammonia-Oxidation Process (Fig.10.9).

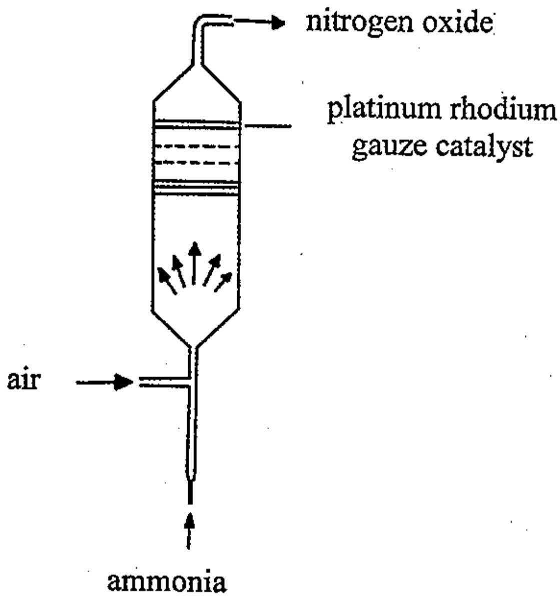


Fig. 10.9 Catalytic oxidation of ammonia in the manufacture of nitric acid

The oxidation of ammonia is carried out by passing ammonia gas and excess of air through a multilayered very fine gauze consisting of platinum (90%) rhodium (10%) catalyst. The reaction is initiated by heating the catalyst to red heat. Once the reaction is started the heat generated maintains the reaction temperature.

$$\text{ammonia} + \text{oxygen} \xrightarrow[\text{red heat}]{\text{Pt-Rh}} \text{nitrogen oxide} + \text{water}$$

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

The nitrogen oxide so formed is rapidly cooled and made to combine with oxygen from excess of air to form nitrogen dioxide.

$$\text{nitrogen oxide} + \text{oxygen} \longrightarrow \text{nitrogen dioxide}$$

$$2NO + O_2 \longrightarrow 2NO_2$$

The nitrogen dioxide in the presence of more air, is then absorbed in water to yield nitric acid.

$$\text{water} + \text{nitrogen dioxide} + \text{oxygen} \longrightarrow \text{nitric acid}$$

$$2H_2O + 4NO_2 + O_2 \longrightarrow 4HNO_3$$

Physical properties of nitric acid

Nitric acid is a colourless, fuming liquid.

Chemical properties of nitric acid

It is a very strong acid as well as a powerful oxidizing agent.

(a) Nitric acid acting as an acid

(i) It neutralizes bases, forming metallic nitrates.

potassium hydroxide	+	nitric acid (dil)	⟶	potassium nitrate	+	water
KOH	+	HNO_3	⟶	KNO_3	+	H_2O
copper (II) oxide	+	nitric acid(dil)	⟶	copper (II) nitrate	+	water
CuO	+	$2HNO_3$	⟶	$Cu(NO_3)_2$	+	H_2O

(ii) It liberates carbon dioxide in reaction with metallic carbonates and hydrogencarbonates.

calcium carbonate	+	nitric acid(dil)	⟶	calcium nitrate	+	carbon dioxide	+	water
$CaCO_3$	+	$2HNO_3$	⟶	$Ca(NO_3)_2$	+	CO_2	+	H_2O
sodium hydrogencarbonate	+	nitric acid(dil)	⟶	sodium nitrate	+	carbon dioxide	+	water
$NaHCO_3$	+	HNO_3	⟶	$NaNO_3$	+	CO_2	+	H_2O

(b) Nitric acid as an oxidizing agent

(i) It oxidizes metals to give nitrogen dioxide or nitrogen oxide.

copper	+	nitric acid (conc)	⟶	copper(II) nitrate	+	water	+	nitrogen dioxide
Cu	+	$4\ HNO_3$	⟶	$Cu(NO_3)_2$	+	$2\ H_2O$	+	$2\ NO_2$
copper	+	nitric acid (dil)	⟶	copper(II) nitrate	+	water	+	nitrogen oxide
3Cu	+	$8HNO_3$	⟶	$3Cu(NO_3)_2$	+	$4H_2O$	+	2NO

Other metals react similarly to give oxides of nitrogen, the nature of the gaseous product depending on the metal, the concentration of the acid and the temperature employed. (See the following section.)

(ii) Nitric acid can also oxidize, certain non-metallic elements and certain compounds.

iron (II) sulphate + sulphuric acid + nitric acid → iron(III) sulphate + water + nitrogen oxide

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

In the given example, the nitric acid has oxidized the green iron (II) sulphate to brown iron (III) sulphate.

Further examples, of the oxidizing actions of hot, concentrated nitric acid are the following.

carbon + nitric acid (conc) → water + nitrogen dioxide + carbon dioxide

$$C + 4HNO_3 \longrightarrow 2H_2O + 4NO_2 + CO_2$$

phosphorus + nitric acid(conc) → phosphoric acid + nitrogen dioxide + water

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

sulphur + nitric acid (conc) → sulphuric acid + nitrogen dioxide + water

$$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

iodine + nitric acid (conc) → iodic acid + nitrogen dioxide + water

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

Hydrogen sulphide + nitric acid (dil) → sulphur + nitrogen oxide + water

$$3H_2S + 2HNO_3 \longrightarrow 3S + 2NO + 4H_2O$$

Hydrogen iodide + nitric acid (dil) → iodine + nitrogen oxide + water

$$6HI + 2HNO_3 \longrightarrow 3I_2 + 2NO + 4H_2O$$

(c) Action of nitric acid on the metals

The action of nitric acid on the metals is particularly interesting in view of the number of different products that may be obtained. The only metals not attacked by the acid are the noble metals like gold and platinum, although certain other metals, such as iron and chromium become passive when treated with the strong acid. This passivity is thought to be due to the formation of an insoluble oxide film, which prevents further attack by the acid.

All the other metals react with nitric acid and the products of the reaction appear to be dependent on the reactivity of the metal, as determined by its position in the activity series and by the concentration of the nitric acid.

(i) With the very reactive magnesium metal and very dilute nitric acid, the rate of formation of nascent hydrogen is so very excessive that part of it is liberated as hydrogen gas.

magnesium + nitric acid (dil) ⟶ magnesium nitrate + Hydrogen

$$Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$$

With slightly more concentrated acid the balance is restored, and the main product is now ammonia, which is however neutralized by the excess acid to form ammonium nitrate.

magnesium + nitric acid (conc) ⟶ magnesium nitrate + ammonia + water

$$4Mg + 9HNO_3 \longrightarrow 4Mg(NO_3)_2 + NH_3 + 3H_2O$$

ammonia + nitric acid (conc) ⟶ ammonium nitrate

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

(ii) With a slight less reactive metal such as zinc or aluminium and hot dilute nitric acid, no free hydrogen escapes. The main product is ammonium nitrate, but this may decompose at the temperature of the reaction to liberate dinitrogen oxide gas.

zinc + nitric acid (dil) ⟶ zinc nitrate + ammonium nitrate + water

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

ammonium nitrate ⟶ dinitrogen oxide + water

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

(iii) With the metals, such as copper, silver and mercury which are below hydrogen in the electrochemical series, the reaction is an oxidation reaction. Copper with cold dilute nitric acid gives mainly nitrogen oxide,

copper + nitric acid(dil) ⟶ copper (II) nitrate + nitrogen oxide + water

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

but with the concentrated acid nitrogen dioxide is the main product.

copper + nitric acid (conc) ⟶ copper(II) nitrate + nitrogen dioxide + water

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(iv) In the case of tin with cold dilute nitric acid, the reaction is

tin + nitric acid (dil) ⟶ tin(II) nitrate + ammonium nitrate + water

$$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

with hot concentrated nitric acid, metastannic acid is produced.

tin + nitric acid (conc) ⟶ metastannic acid + nitrogen dioxide + water

$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$

(d) The ability of aqua-regia (3 volumes concentrated HCl +1 volume concentrated HNO_3) to dissolve the noble metal gold, is due to the oxidation of the hydrochloric acid by the nitric acid to liberate chlorine which converts the gold into gold (III) chloride. The latter dissolves in excess of hydrochloric acid to form the soluble chloroauric acid, $HAuCl_4$.

hydrochloric acid + nitric acid ⟶ chlorine + nitrosyl chloride + water

$$3HCl + HNO_3 \longrightarrow Cl_2 + NOCl + 2H_2O$$

gold + chlorine ⟶ gold (III) chloride

$$2Au + 3Cl_2 \longrightarrow 2AuCl_3$$

gold (III) chloride + hydrochloric acid ⟶ chloroauric acid

$$AuCl_3 + HCl \longrightarrow HAuCl_4$$

Uses of nitric acid

Nitric acid is used mainly of the manufacture of explosives and dyes. A valuable fertilizer can be obtained by neutralizing the acid with lime. The calcium nitrate obtained, mixed with excess lime forms a non-deliquescent basic salt which is applied to the soil.

Nitrates

The properties of the nitrates vary according to the position of the metal in the activity series.

K Na	Nitrates of these metals are decomposed by heat to the nitrite and oxygen. e.g., $2KNO_3 \longrightarrow 2KNO_2 + O_2$	All nitrates are soluble in water.
Ca Mg Al Zn Fe Pb Cu	Nitrates of these metals are-decomposed on heating to the oxide of the metal, nitrogen dioxide and oxygen. e.g., $2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$	
Hg Ag	Nitrates of these metals are decomposed on heating to the metal, nitrogen dioxide and oxygen. e.g., $Hg(NO_3)_2 \longrightarrow Hg + 2NO_2 + O_2$	

Note: Ammonium nitrate is decomposed into dinitrogen oxide and steam on heating.

ammonium nitrate	$\longrightarrow$	dinitrogen oxide	+	water
NH_4NO_3	$\longrightarrow$	N_2O	+	$2H_2O$

Test for nitrate radical

Add a little dilute sulphuric acid and two or three crystals of iron (II) sulphate into a solution of nitrate salt. Shake to dissolve them. Hold the test tube in a slanting position and pour a slow continuous stream of concentrated sulphuric acid down the side. It will form a separate layer underneath the aqueous layer and, at the junction of the two, a brown ring will be seen.

The formation of this brown ring is the characteristic test for a soluble nitrate and is known as the Brown Ring Test.

Explanation: The concentrated sulphuric acid and the nitrate react to yield nitric acid.

potassium nitrate	+	sulphuric acid (conc)	$\longrightarrow$	potassium hydrogensulphate	+	nitric acid
KNO_3	+	H_2SO_4	$\longrightarrow$	$KHSO_4$	+	HNO_3

The nitric acid is then reduced by some of the iron (II) sulphate to nitrogen oxide.

iron(II) sulphate	+	nitric acid	+	sulphuric acid	$\longrightarrow$	iron(III) sulphate	+	water	+	nitrogen oxide

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

The nitrogen oxide reacts with iron (II) sulphate to give the brown compound $FeSO_4.NO$, which appears as the brown ring.

iron (II) sulphate + nitrogen oxide ⟶ nitroso iron (II) sulphate

$$FeSO_4 + NO \longrightarrow FeSO_4.NO$$

SUMMARY

Nitrogen is colorless and odourless. It is slightly less dense than air and only slightly soluble in water. It condenses to a liquid (b.p. -196 °C), and freezes to a colourless solid (m.p.-210 °C).

Nitrogen forms the major constituent of the atmosphere, being present to the extent of about 79 percent by volume or 76 percent by weight of the air. In chemical combination with other elements it occurs in sodium nitrate (Chile saltpetre), in proteins, and many other animal and vegetable products.

Nitrogen can be prepared from the atmosphere (air) and also from the ammonium nitrite in the Laboratory. Nitrogen is obtained in industry by the fractional distillation of liquid air. This principal use of nitrogen is in the manufacture of ammonia (industrial scale by Haber process), from which nitrogenous fertilizers, nitric acid and urea are now mainly prepared.

There are three common oxides of nitrogen. They are dinitrogen oxide or nitrous oxide, N_2O; nitrogen oxide or nitric oxide, NO; and nitrogen dioxide, NO_2 or dinitrogen tetroxide, N_2O_4, depending on the conditions.

Nitric acid is manufactured by the Ammonia-Oxidation Process. Nitric acid is a colourless, fuming liquid. Nitric acid is used mainly of the manufacture of explosives and dyes. A valuable fertilizer can be obtained by neutralizing the acid with lime.

Questions and problems

1. How would you prepare nitrogen from

   (a) the air (b) an ammonium salt?

   What difference, if any, would there be, between the two samples so prepared?

2. Draw a fully labelled diagram and give an equation to show how you would prepare a dry sample of ammonia in the laboratory starting from a named ammonium salt and a named alkali.
3. Describe the Haber Process for the manufacture of ammonia.
4. Write equations for the following reactions. When ammonia is passed
   (i) into dilute sulphuric acid (ii) over heated copper (II) oxide.
5. In the laboratory, a steady stream of ammonia can be prepared by the reaction between ammonium sulphate and an alkali.
   (a) Name the alkali you would use.
   (b) State whether it is necessary to heat the mixture.
   (c) Write the equation for the reaction.
   (d) Name the reagent you would use to dry the gas and explain your choice.
   (e) State how you would collect a sample of dry ammonia.
6. Ammonia is manufactured by the Haber Process.
   (a) Name the sources from which the starting materials are obtained.
   (b) In what ratio by volume, should the nitrogen and hydrogen be mixed? Explain why this ratio is used.
   (c) What is the purpose of the catalyst?
   (d) Is there complete conversion of all the nitrogen and hydrogen to ammonia?
   (e) How can the ammonia be separated from the uncombined nitrogen and hydrogen?
   (f) How are the uncombined nitrogen and hydrogen left after removal of the ammonia treated?
7. Give the name, formula and colour of three gaseous oxides of nitrogen. Which of these gases is very soluble in water? Outline briefly the preparation of this oxide?
8. Which of the oxides of nitrogen could be confused with oxygen? Why? By what test can you distinguish between a jar of this gas and a jar of oxygen?
9. If you are provided with concentrated nitric acid, copper, and water but no other chemical substances, describe briefly the reactions you would use to prepare nitrogen oxide and nitrogen dioxide.

10. (a) Describe the manufacturing process of nitric acid from ammonia.
    (b) Describe two reactions each in which nitric acid acts
    (i) as an acid and (ii) as an oxidizing agent.
11. Outline the chemical reactions involved in the synthesis of nitric acid starting from nitrogen.

12. Describe and explain the action of nitric acid of varying concentrations on magnesium.
13. Write equations to illustrate the action of heat on ammonium nitrate, calcium nitrate, sodium nitrate and mercury (II) nitrate.
14. Give a chemical test which would enable you to decide if a given colourless solution contained the nitrate ion.
15. A concentrated acid. A, is added to copper turnings and water in a flask and a brown gas, B, is seen to fill the flask. In a second experiment the air is removed by filling the flask with nitrogen before the acid is added. It is found that a colourless gas, C, is formed. A fresh portion of acid. A, is diluted and neutralized with potassium hydroxide solution. The solution is carefully evaporated to dryness to give a white solid, D. On heating D a new solid, E, and a gas, F, are formed. F is found to ignite a glowing splint.Identify A, B, C, D, E, F and give equations for the reactions.
16. Write TRUE or FALSE for each of the following statements.
    (a) Nitrogen is present to the extent of about 79 percent by volume of the air.
    (b) Nitrogen gas is relatively active and support combustion.
    (c) The principal use of nitrogen is in the manufacture of ammonia.
    (d) Nitrogen can be manufactured by the Haber process.
    (e) Ammonia gas turns moist red litmus paper blue.
17. Fill in the blanks with a suitable word or unit or phrase.
    (a) Ammonia gas has a characteristic .... smell.
    (b) A mixture of calcium cyanamide and carbon is known as ....
    (c)The considerable solubility of ammonia is often demonstrated in the laboratory by the .... experiment.
    (d) Dinitrogen oxide is used as anaesthetic for minor operation and is given the name .... gas.
    (e) Nitric acid can be prepared by heating potassium nitrate crystals with concentrated ....
18. Select the correct word, or words given in the brackets.
    (a) Ammonia is prepared in the laboratory by heating ammonium chloride with (sodium oxide, calcium hydroxide, slaked lime).
    (b) Nitrogen is obtained in industry by (destructive, fractional, vacuum)distillation of liquid air.
    (c) Nitrogen combines with many metals on heating to a dull red heat or higher temperatures to form (oxides, nitrates, nitrides).

(d) The principal use of nitrogen is in the manufacture of (ammonia, urea, nitric acid).

(e) When nitric oxide comes in contact with oxygen of the air (white, brown, red) fumes are formed.

19. Match each of the items given in List A with the appropriate item in List B.

List A	List B
(a) Nitric acid neutralizes bases	(i) Haber process
(b) Dinitrogen oxide is also known as	(ii) Forming metallic nitrates
(c) The manufacturing method of ammonia	(iii) Nitrogen monoxide
(d) The solubility of ammonia can be tested	(iv) Laughing gas
(e) Reddish brown fumes are formed when a gas comes in contact with oxygen of the air	(v) Fountain experiment

20. What would be a suitable drying agent for ammonia gas?

(A) Calcium chloride (B) Concentrated sulphuric acid
(C) Phosphorus (V) oxide (D) Calcium oxide

21. A gas was neutral, colorless and did not support combustion. Which gas might it be?

(A) Ammonia (B) Oxygen (C) Nitrogen dioxide (D) Nitrogen

22. Ammonia gas is collected by the 'upward delivery' when prepared in the laboratory. The reason for this is because

(A) it is an extremely soluble gas (B) it is alkaline
(C) it is lighter than air (D) it is poisonous

23. Which of the following when heated would not give off ammonia?

(A) Ammonium nitrate and sodium hydroxide
(B)Sodium nitrate and potassium hydroxide
(C) Ammonium sulphate and calcium hydroxide
(D) Sodium hydroxide and ammonium sulphate

24. When a gas X is mixed with hydrogen chloride gas, a dense white smoke forms. Gas X is therefore: (A) carbon dioxide (B) ammonia (C) oxygen
(D) nitrogen

25. You are given the following gases and answer the following questions given below. nitrogen, ammonia, nitrogen oxide, dinitrogen oxide, nitrogen dioxide

(a) Which of the gas(es) is (are) neutral oxide?

(b) Which of the gas(es) is (are) very soluble in water? Name the experiment to confirm its solubility.

(c) Which of the gas(es) is (are) used in minor surgical operations?

(d) Which of the gas(es) solidify at –10 °C and under normal pressure?

(e) Which of the above gas(es) will give a brown ring when reacted with iron(II) sulphate? Give the formula of the brown ring compound.

****

CHAPTER 11

SULPHUR AND ITS COMPOUNDS

11.1 Occurrence

Sulphur is found in the free state in deposits below the surface of the earth. Free sulphur occurs in Sicily and USA. It is a yellow, strong smelling solid element.

Besides its occurrence in the free state, sulphur also occurs as natural compounds, chiefly combined with metals in the earth's crust. These compounds are iron pyrites, FeS_2; gypsum, $CaSO_4 . 2H_2O$; epsom salt, $MgSO_4 . 7H_2O$ and others.
Sulphur is a very abundant element, constituting about one percent of the earth's crust by weight and is a very important raw material for industries.

11.2 Extraction of Sulphur from Underground Deposits

Different processes are used in mining sulphur according to the nature of the deposits. Sulphur is found in shallow or deep deposits below the earth's surface. Sulphur, which is deposited at about 700 feet below the earth's surface, is mined or extracted by the Frasch Process.

The process description for extracting sulphur by the Frasch Process may be summarized as follows :

Three concentric pipes as shown in Fig. 11.1 are driven down to the deposit of sulphur.

Superheated steam at about 160 °C is forced down under pressure through the outermost pipe.

When superheated steam reaches the deposit, it melts the sulphur, forming a pool of molten sulphur.

Hot air under high pressure is forced down through the innermost pipe.

The pressure of hot air forces up the molten sulphur through the central pipe, between the inner and outer pipes.

The molten sulphur is collected in wooden containers and allowed to solidify. Sulphur obtained by this process is 99.5 per cent pure.

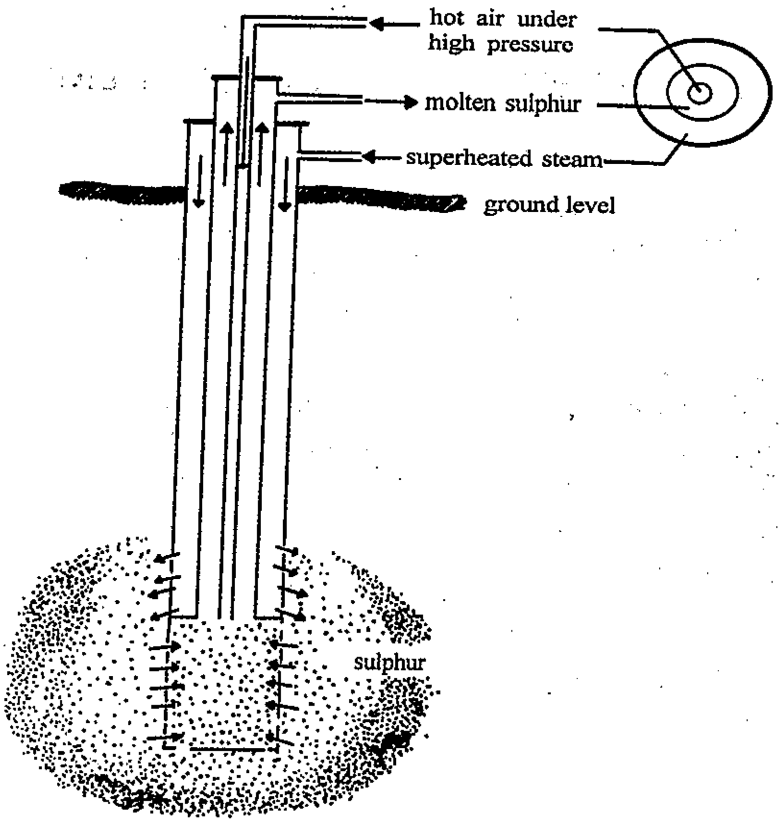
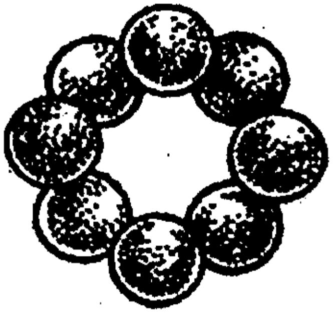


Fig. 11.1 The Frasch Process of mining sulphur

11.3 Structure of Sulphur

Sulphur is a molecular element. A molecule of sulphur consists of eight atoms joined together to form a ring as shown in Fig. 11.2. Therefore the formula S_8 should be written to represent the sulphur molecule, when it takes part in chemical reactions as the free element.



But to simplify the balancing of equations the empirical formula S is usually used instead of S_8 since the formula of most sulphur compounds contain only an atom of the element.

Fig. 11.2 A molecule of sulphur

11.4 Forms of Sulphur

Sulphur can exist in different allotropic forms like carbon and oxygen.We shall discuss three allotropes of sulphur, two of which are crystalline forms and the other non-crystalline.

Crystalline forms of sulphur

Solid sulphur can exist in two crystalline forms. They are, rhombic sulphur and monoclinic sulphur.

Rhombic sulphur

When a solution of sulphur in carbon disulphide is allowed to evaporate slowly at room temperature, the crystals of rhombic sulphur are deposited from the solution (Fig.11.3).

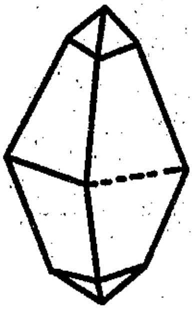


Fig. 11.3 A crystal of rhombic sulphur

Rhombic sulphur occurs as yellow, solid crystals. It has a specific gravity of 2.06. On rapid heating it melts at 112.8 C. On gradual heating it undergoes slow transformation into the monoclinic form of sulphur at 94.5 ° C.

Each crystal is composed of the S_8 ring molecules in orderly arrangement to form the characteristic shape of the crystals of rhombic sulphur. Rhombic sulphur is the most stable form of sulphur.

Monoclinic sulphur

Molten sulphur is poured into a wet filter paper in a funnel. When the sulphur has nearly set to solidify, the filter paper is carefully unfolded. Long, dark yellow, needle-like crystals of monoclinic sulphur will be seen (Fig.11.4). Monoclinic (or prismatic) sulphur slowly changes into the rhombic form at temperatures below 94.5 °C which is the transition temperature. It has a specific gravity of 1.96. The melting point is 119 °C.

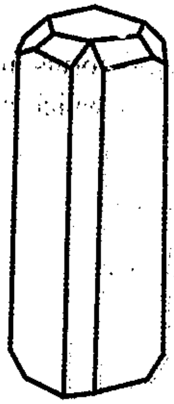


Fig. 11.4 A crystal of monoclinic sulphur

Monoclinic sulphur is also composed of S_8 ring molecules, but their arrangement is different from that of rhombic crystals. If monoclinic sulphur is left at room temperature for a sufficiently long time it changes into rhombic sulphur.

Plastic sulphur

When any form of sulphur is heated almost to its boiling point and then poured into cold water, plastic sulphur is formed.

Plastic sulphur is a soft, sticky, rubber-like substance with a transparent, brown colour.

In plastic sulphur the S_8 ring molecules are ruptured and the sulphur atoms join together to from long chains with a zing-zag arrangement as shown below (Fig.11.5). The elasticity of plastic sulphur is due to the stretching and recoling of these chains of atoms.

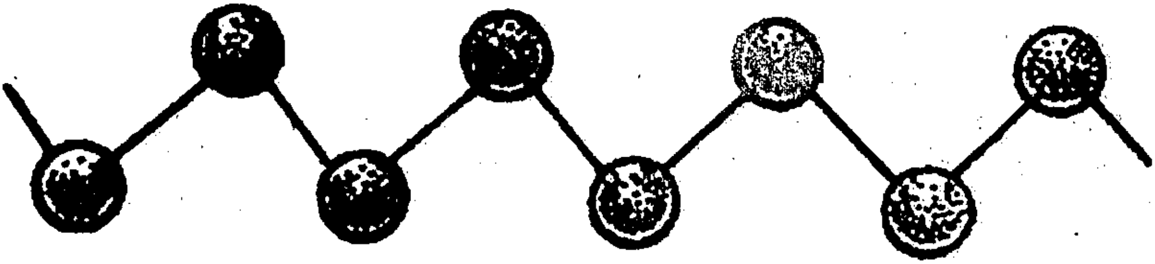


Fig. 11.5 Arrangement of sulphur atoms in plastic sulphur

11.5 Structure and Properties

Some elements such as carbon, oxygen; sulphur, exhibit allotropy, i.e., the same element may occur in different forms. The same element in different forms may have different physical properties, because though they are made up of the same atoms in each form, the arrangement of atoms is different in the different forms.

Therefore it is clear that the properties of the substances depend on

(1) the kind of atoms present in the substance,

(2) the arrangement of atoms in the substance.

Physical properties

The different allotropic forms of sulphur show different physical properties. You have studied the physical properties of these forms under the general heading of each allotropic form.

Chemical properties

We will discuss the chemical properties of sulphur with respect to its reactions with metals, non-metals, water and acids.

1. Reaction with metals

Sulphur can react with almost metals except gold and platinum. Sulphur reacts with metals forming sulphides. The oxidation number of sulphur in these compounds is -2.

$$\text{calcium} + \text{sulphur} \xrightarrow{\Delta} \text{calcium sulphide}$$

$$Ca + S \xrightarrow{\Delta} CaS$$

$$\text{iron} + \text{sulphur} \xrightarrow{\Delta} \text{iron (II) sulphide}$$

$$Fe + S \xrightarrow{\Delta} FeS$$

$$\text{silver} + \text{sulphur} \xrightarrow{\Delta} \text{silver sulphide}$$

$$2Ag + S \xrightarrow{\Delta} Ag_2S$$

2. Reaction with non-metals

Sulphur can react with some non-metals such as oxygen, hydrogen and others.

(a) When sulphur reacts with non-metallic elements which have negative oxidation numbers, the oxidation number of sulphur in the compound is either +4 or +6.

action with oxygen under ordinary conditions	$\text{sulphur} + \text{oxygen} \xrightarrow{\text{burns}} \text{sulphur dioxide}$ $S + O_2 \xrightarrow{\Delta} SO_2$
in the presence of catalyst and excess oxygen	$\text{sulphur} + \text{oxygen} \xrightarrow{\text{catalyst}} \text{sulphur trioxide}$ $2S + 3O_2 \xrightarrow{\Delta} 2SO_3$

(b) When sulphur combines with non-metallic elements which have positive oxidation numbers, the oxidation number of sulphur in the compound is -2.

$$\text{hydrogen} + \text{sulphur} \xrightarrow{\Delta} \text{hydrogen sulphide}$$
$$H_2 + S \xrightarrow{\Delta} H_2S$$

3. **Reaction with water**

Sulphur in the solid state does not react with cold water. But when steam is passed through the boiling sulphur, reaction occurs to form hydrogen sulphide and sulphur dioxide.

$$\text{sulphur} + \text{steam} \longrightarrow \text{hydrogen sulphide} + \text{sulphur dioxide}$$
$$3S + 2H_2O \longrightarrow 2H_2S + SO_2$$

4. **Reaction with acids**

Sulphur does not react with non-oxidizing acids such as dilute sulphuric acid and hydrochloric acid. But it can react with oxidizing acids such as hot concentrated sulphuric acid and nitric acid.

(a) With hot concentrated sulphuric acid

Hot concentrated sulphuric acid oxidizes sulphur into sulphur dioxide, and is itself reduced to sulphur dioxide.

$$\text{sulphur} + \text{sulphuric acid(conc)} \longrightarrow \text{water} + \text{sulphur dioxide}$$
$$S + 2H_2SO_4 \longrightarrow 2H_2O + 3SO_2$$

(b) With hot concentrated nitric acid

Hot concentrated nitric acid oxidizes sulphur into sulphur trioxide. The sulphur trioxide then dissolves in water to form sulphuric acid.

stages of reaction	S	+	$2HNO_3$	$\longrightarrow$	SO_3	+	H_2O	+	$2NO$
	SO_3	+	H_2O	$\longrightarrow$	H_2SO_4				

11.6 Hydrogen Sulphide H_2S

Hydrogen sulphide is the hydride of sulphur.

Laboratory preparation

In the laboratory, hydrogen sulphide is prepared by the action of non-oxidizing acids such as dilute sulphuric acid and dilute hydrochloric acid on metal sulphides. Iron(II) sulphide is the metal sulphide usually used in the preparation of hydrogen sulphide.

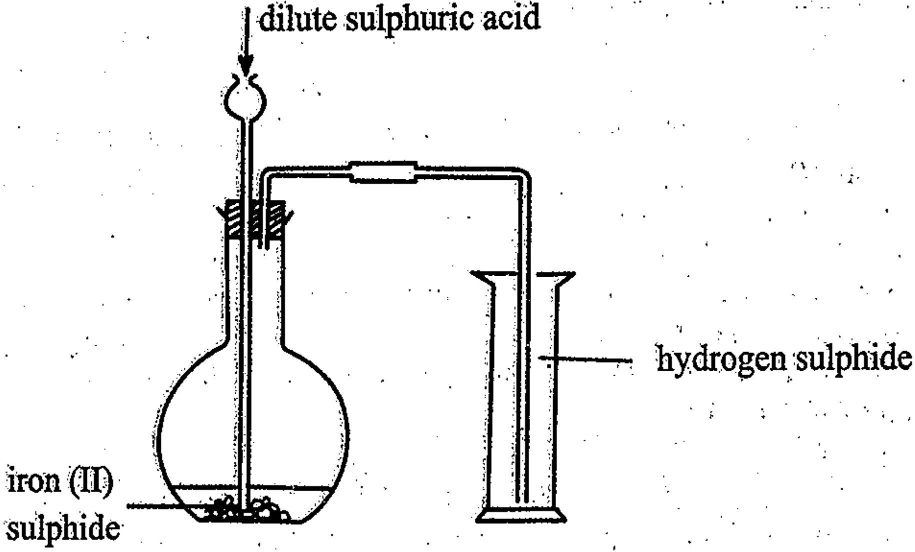


Fig. 11.6 Laboratory preparation of hydrogen sulphide

iron (II) sulphide	+	sulphuric acid(dil)	$\longrightarrow$	iron (II) sulphate	+	hydrogen sulphide
FeS	+	H_2SO_4	$\longrightarrow$	$FeSO_4$	+	H_2S

A few pieces of iron (II) sulphide are put into a flat-bottomed flask. The apparatus is set up as shown in Fig. 11.6. Dilute sulphuric acid is poured into the flask through the thistle funnel. Effervescence takes place and hydrogen sulphide gas is evolved.

The gas is soluble in cold water and heavier than air, so it is collected by upward displacement of air.

A piece of blotting paper is soaked with lead (II) nitrate solution and placed in the mouth of the gas jar.

The gas jar is full with hydrogen sulphide, if the lead (II) nitrate paper is turned black.

If the gas is required dry, it may be passed over anhydrous calcium chloride and collected by the upward displacement of air.

Why nitric acid cannot be used in the reaction

Nitric acid dilute or concentrated, is an oxidizing acid. If nitric acid is used in the reaction the acid will oxidize hydrogen sulphide into water and sulphur or oxide of sulphur.

Test for hydrogen sulphide

The gas turns lead(II) nitrate paper black. Lead (II) nitrate solution is turned black due to precipitation of lead (II) sulphide.

hydrogen sulphide + lead(II) nitrate ⟶ lead(II) sulphide + nitric aci

$$H_2S + Pb(NO_3)_2 \longrightarrow PbS + 2HNO_3$$

Physical properties

1. Hydrogen sulphide is a colourless gas.
2. It has the smell of rotten eggs. (The gas is very poisonous.)
3. It is an acidic gas, soluble in water. The solution is acidic.
4. It is heavier than air.

   You can calculate the relative density from its formula and compare with that of air which is 14.5.

Chemical properties

Test the gas with burning splint. Dry hydrogen sulphide burns in air.

Test the gas with blue litmus paper. The blue litmus turns pinks.

Now we have observed three chemical properties of hydrogen sulphide, they are :

Hydrogen sulphide burns in air.

Hydrogen sulphide turns blue litmus slightly pink.

Hydrogen sulphide turns lead (II) nitrate paper black.

These three very simple properties of hydrogen sulphide represent the three sets of important properties of hydrogen sulphide. Let us study these properties in detail.

1. Burning of hydrogen sulphide in air

The burning of hydrogen sulphide in air gives the information that the gas can combine with oxygen from air and therefore pure oxygen as well.

The reaction with oxygen forms different products in different conditions.

Reaction with oxygen under different conditions

(a) In a limited supply of oxygen, hydrogen sulphide burns producing water and sulphur.

hydrogen sulphide + oxygen ⟶ water + sulphur

$$2H_2S + O_2 \longrightarrow 2H_2O + 2S$$

(b) In excess of oxygen, hydrogen sulphide burns producing water and sulphur dioxide.

hydrogen sulphide + oxygen ⟶ water + sulphur dioxide

$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2$$

(c) When a solution of hydrogen sulphide in water is exposed to air for some time, sulphur precipitates out from the solution.

hydrogen sulphide + oxygen ⟶ water + sulphur

$$2H_2S + O_2 \longrightarrow 2H_2O + 2S$$

2. Reaction with litmus

The reaction with litmus gives the information that the gas has weak acidic properties. But being a weak acid it does not show all the general properties of acid.

Reaction as a weak acid

As an acid, hydrogen sulphide reacts with metals and alkali solutions. It is a weaker acid than carbonic and sulphurous acids. Hence it cannot react with solid salts of the stronger acids such as carbonate and sulphite.

Reaction with metals

Hydrogen sulphide reacts with all metals in the activity series except gold and platinum. When the metals is heated in a stream of hydrogen sulphide reaction occurs as follows:

zinc + hydrogen sulphide ⟶ zinc sulphide + hydrogen

$$Zn + H_2S \longrightarrow ZnS + H_2$$

silver + hydrogen sulphide ⟶ silver sulphide + hydrogen

$$2Ag + H_2S \longrightarrow Ag_2S + H_2$$

Reaction with alkali

Since the molecule of hydrogen sulphide consists of two replaceable hydrogen atoms, it can produce two acid radicals, the hydrogen sulphide radical, HS^- and the sulphide radical, S^{2-}. Therefore, when it reacts with alkalis such as potassium hydroxide, sodium hydroxide and calcium hydroxide, it can produce sulphide salts and hydrogensulphide salts according to the condition of the reaction. If hydrogen sulphide is in limited amount metallic sulphides are produced and if hydrogen sulphide is in excess, metallic hydrogensulphides are produced. These hydrogensulphides exist only in solution.

limited amount of hydrogen sulphide	hydrogen sulphide	+	sodium hydroxide	⟶	sodium sulphide	+	water
	H_2S	+	$2NaOH$	⟶	Na_2S	+	$2H_2O$
in excess of hydrogen sulphide	hydrogen sulphide	+	sodium hydroxide	⟶	sodium hydrogensulphide	+	water
	H_2S	+	$NaOH$	⟶	$NaHS$	+	H_2O

3. Precipitation of metallic sulphides from suitable salt solutions. Metallic salts may be classified into soluble and insoluble salts. Soluble salts generally include:

(a) all nitrates,
(b) all ethanoates except calcium ethanoate,
(c) all chlorides except lead, mercury, silver and gold chlorides,
(d) all sulphates except lead, barium, calcium and silver sulphates.

When hydrogen sulphide is passed into the solution of one of these salts, the metallic sulphides are formed according to the general reaction given below.

solution of metal salt + hydrogen sulphide ⟶ metallic sulphide + acid of salt

The solubility of metallic sulphides may be summarized as shown below.

K^+ Na^+ Ca^{2+} Ba^{2+} Mg^{2+}	sulphides are soluble in water, acid and alkali
Al^{3+}	sulphide is hydrolysed in aqueous solution. Precipitate of $Al(OH)_3$ results
Zn^{2+} Fe^{2+} Sn^{2+}	sulphides are soluble in acid; insoluble in alkali
Pb^{2+} Cu^{2+} Hg^{2+} Ag^+	insoluble in acid and alkali

colour of precipitate

ZnS	white
FeS	black
SnS	brown
PbS	black
CuS	black
HgS	black
Ag_2S	dark brown

When hydrogen sulphide is passed into solutions of soluble salts of Sn^{2+}, Pb^{2+}, Cu^{2+}, Hg^{2+} and Ag^+ the sulphides formed, being insoluble, are precipitated out.

$$\text{copper(II) sulphate} + \text{hydrogen sulphide} \longrightarrow \text{copper(II) sulphide} + \text{sulphuric acid}$$

$$CuSO_4 + H_2S \longrightarrow CuS\downarrow + H_2SO_4$$

$$\text{silver nitrate} + \text{hydrogen sulphide} \longrightarrow \text{silver sulphide} + \text{nitric acid}$$

$$2AgNO_3 + H_2S \longrightarrow Ag_2S\downarrow + 2HNO_3$$

When hydrogen sulphide is passed into the soluble salt solution of zinc and iron (II) salts the sulphide formed does not precipitate out as it is soluble in the acid produced by the reaction. When an alkali solution is added to neutralize the acid the sulphide is precipitated out.

ZnS does not precipitate out acid is neutralized	$ZnCl_2 + H_2S \longrightarrow ZnS + 2HCl$ $2HCl + 2NH_4OH \longrightarrow 2NH_4Cl + 2H_2O$
ZnS is precipitated out	$ZnCl_2 + H_2S + 2NH_4OH \longrightarrow ZnS + 2NH_4Cl + 2H_2O$

$$\text{zinc chloride} + \text{hydrogen sulphide} + \text{ammonium hydroxide} \longrightarrow \text{zinc sulphide} + \text{ammonium chloride} + \text{water}$$

4. Reducing properties of hydrogen sulphide

(a) Reduction by addition of hydrogen

Hydrogen sulphide reduces halogens to hydrogen halides.

hydrogen sulphide	+	chlorine	⟶	hydrochloric acid	+	sulphur
H_2S	+	Cl_2	⟶	$2HCl$	+	S

hydrogen sulphide	+	bromine	⟶	hydrobromic acid	+	sulphur
H_2S	+	Br_2	⟶	$2HBr$	+	S

hydrogen sulphide	+	iodine	⟶	hydroiodic acid	+	sulphur
H_2S	+	I_2	⟶	$2HI$	+	S

In these reactions sulphur is precipitated from the solution.

(b) Reduction by removal of oxygen

Hydrogen sulphide reduces concentrated nitric acid, concentrated sulphuric acid, acidified potassium permanganate and potassium dichromate in solution by removing oxygen from these compounds.

with concentrated nitric acid	hydrogen sulphide	+	nitric acid (conc)	⟶	water	+	nitrogen dioxide
	H_2S	+	$2HNO_3$	⟶	$2H_2O$	+	$2NO_2$
						+	sulphur
						+	S

Because of the reaction nitric acid cannot be used in the preparation of hydrogen sulphide from metal sulphides.

with concentrated sulphuric acid	hydrogen sulphide	+	sulphuric acid (conc)	⟶	water	+	sulphur dioxide
	H_2S	+	H_2SO_4	⟶	$2H_2O$	+	SO_2
						+	sulphur
						+	S

Because of this reaction concentrated sulphuric acid cannot be used in the preparation of hydrogen sulphide from metallic sulphide and a drying agent for hydrogen sulphide.Hydrogen sulphide reduces violet coloured acidified potassium permanganate solution to a colourless solution.

hydrogen sulphide + potassium permanganate + sulphuric acid ⟶ manganese (II) sulphate + potassium sulphate + water + sulphur

$$5H_2S + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5S$$

Hydrogen sulphide reduces orange coloured acidified potassium dichromate solution to a green solution.

hydrogen sulphide + potassium dichromate + sulphuric acid ⟶ chromium (III) sulphate + potassium sulphate + water + sulphur

$$3H_2S + K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + K_2SO_4 + 7\,H_2O + 3S$$

11.7 Oxides of Sulphur

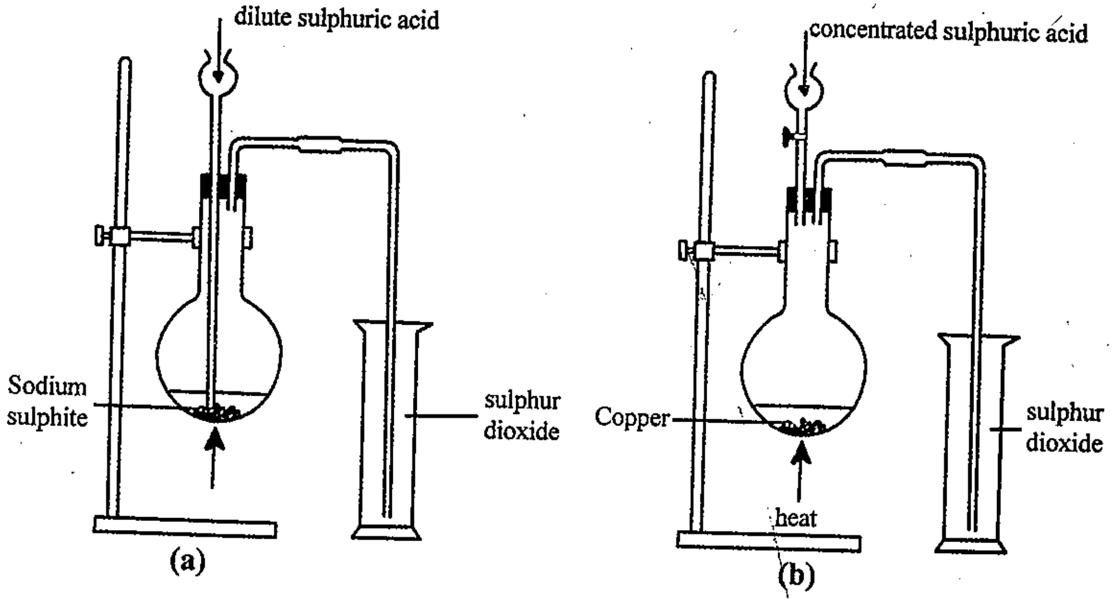
Sulphur in combination with oxygen has oxidation numbers of+4, +6 and oxygen has an oxidation number of - 2. The oxygen compounds of sulphur with oxidation number of + 4 is SO_2 and with sulphur of oxidation number + 6 is SO_3.

Oxides and acids of sulphur

Element	Oxide (acid anhydride)	Acid	Acid radicals in salts
S	SO_2	H_2SO_3(weak)	HSO_3^- and SO_3^{2-}
S	SO_3	H_2SO_4 (strong)	HSO_4^- and SO_4^{2-}

Laboratory preparations of sulphur dioxide, SO_2

1. By the action of dilute sulphuric acid on sodium sulphite



(a) (b)

Fig 11.7 Preparation of sulphur dioxide

$$\text{sodium sulphite} + \text{sulphuric acid(dil)} \xrightarrow{\Delta} \text{sodium sulphate} + \text{water} + \text{sulphur dioxide}$$

$$Na_2SO_3 + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 \quad H_2O + SO_2$$

Some sodium sulphite is put in a flask.The apparatus is set up as shown in Fig. 11.7. (a) Dilute sulphuric acid is added to the sodium sulphite in the flask.The flask is gently heated.Since sulphur dioxide gas is very soluble in water and is denser than air, it is collected by upward displacement of air.

To test whether the gas jar is full with sulphur dioxide, a piece of blotting paper soaked in potassium dichromate solution is placed in the opening of the gas jar. When potassium dichromate paper is turned green the gas jar is full with sulphur dioxide.

2. By the action of concentrated sulphuric acid on copper.

$$\text{copper} + \text{sulphuric acid (conc)} \xrightarrow{\Delta} \text{copper (II) sulphate} + \text{water} + \text{sulphur dioxide}$$

$$Cu + 2H_2SO_4 \xrightarrow{\Delta} CuSO_4 \quad 2H_2O \quad SO_2$$

A few pieces of copper foil are put in a flask. The apparatus is set up as shown in Fig.11.7(a) Concentrated sulphuric acid is added to the copper foil. The flask is gently heated.Since sulphur dioxide gas is very soluble in water and is denser than air, it is collected by upward displacement of air.

To test whether the gas jar is full with sulphur dioxide a piece of blotting paper soaked in potassium dichromate solution is placed in the opening of the gas jar.When potassium dichromate paper is turned green the gas jar is full with sulphur dioxide.

Physical properties

1. Sulphur dioxide is a colourless gas.
2. It has a pungent smell of burning sulphur.
3. It is denser than air.
4. It is very soluble in water.

Chemical properties

1. It turns blue litmus red.

This shows that sulphur dioxide is an acidic oxide.

2. It does not burn in air.

This shows that sulphur dioxide does not react with oxygen of the air under ordinary conditions.

3. Addition reactions of sulphur dioxide.

Sulphur dioxide does not react with oxygen under ordinary conditions. However, it combines with oxygen in the presence of catalyst at the appropriate temperature.

$$\text{sulphur dioxide} + \text{oxygen} \xrightarrow[450\text{-}500\ ^\circ C]{\text{Pt catalyst}} \text{sulphur trioxide}$$

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

It also directly combines with chlorine and lead (IV) oxide.

with chloride

$$\text{sulphur dioxide} + \text{chlorine} \xrightarrow{\text{sunlight}} \text{sulphuryl chloride}$$

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

The reaction is also catalysed by camphor.

$$\text{sulphur dioxide} + \text{lead (IV) oxide} \xrightarrow{\Delta} \text{lead(II) sulphate}$$

$$SO_2 + PbO_2 \xrightarrow{\Delta} PbSO_4$$

4. It is an acidic oxide.

Sulphur dioxide dissolves in water to form sulphurous acid.

sulphur dioxide + water ⟶ sulphurous acid

$SO_2 + H_2O \longrightarrow H_2SO_3$

It reacts with basic oxides such as potassium oxide, sodium oxide and calcium oxide to form sulphites.

sulphur dioxide + potassium oxide ⟶ potassium sulphite

$SO_2 + K_2O \longrightarrow K_2SO_3$

sulphur dioxide + sodium oxide ⟶ sodium sulphite

$SO_2 + Na_2O \longrightarrow Na_2SO_3$

sulphur dioxide + calcium oxide ⟶ calcium sulphite

$SO_2 + CaO \longrightarrow CaSO_3$

It also reacts with alkali solution forming sulphite or hydrogensulphite according to the amount of the reacting gas.

With potassium hydroxide

in limited amount of sulphur dioxide	sulphur dioxide + potassium hydroxide ⟶ potassium sulphite + water $SO_2 + 2KOH \longrightarrow K_2SO_3 + H_2O$
in excess amount of sulphur dioxide	sulphur dioxide + potassium hydroxide ⟶ potassium hydrogensulphite $SO_2 + KOH \longrightarrow KHSO_3$

When limited amount of sulphur dioxide is passed through the lime water, it turns milky.

sulphur dioxide + calcium hydroxide ⟶ calcium sulphite + water

$SO_2 + Ca(OH)_2 \longrightarrow CaSO_3 + H_2O$

In excess amount of sulphur dioxide, milky lime water is cleared up again.

sulphur dioxide + calcium sulphite + water ⟶ calcium hydrogensulphite

$SO_2 + CaSO_3 + H_2O \longrightarrow Ca(HSO_3)_2$

5. Reducing properties of sulphur dioxide

(a) Sulphur dioxide reduces halogens to hydrogen halides.

with chlorine solution	sulphur dioxide	+	water	+	chlorine	⟶	sulphuric acid	+	hydrochloric acid
	SO_2	+	$2H_2O$	+	Cl_2	⟶	H_2SO_4	+	$2HCl$
with bromine solution	sulphur dioxide	+	water	+	bromine	⟶	sulphuric acid	+	hydrobromic acid
	SO_2	+	$2H_2O$	+	Br_2	⟶	H_2SO_4	+	$2HBr$
					(yellowish brown)				(colourless)
with iodine solution	sulphur dioxide	+	water	+	iodine	⟶	sulphuric acid	+	hydroiodic acid
	SO_2	+	$2H_2O$	+	I_2	⟶	H_2SO_4	+	$2HI$
					(brown)				(colourless)

(b) Sulphur dioxide reacts with nitric acid to produce nitrogen dioxide.

sulphur dioxide	+	nitric acid	⟶	sulphuric acid	+	nitrogen dioxide
SO_2	+	$2HNO_3$	⟶	H_2SO_4	+	$2NO_2$

In this reaction sulphur dioxide reduces nitric acid to nitrogen dioxide.

(c) Sulphur dioxide can also reduce violet coloured acidified potassium permanganate solution to a colourless solution.

sulphur dioxide	+	water	+	potassium permanganate	⟶	potassium sulphate	+	manganese (II) sulphate
$5SO_2$	+	$2H_2O$	+	$2KMnO_4$	⟶	K_2SO_4	+	$2MnSO_4$
				(violet)		(colourless)		(colourless)
							+	sulphuric acid
							+	$2H_2SO_4$
								(colourless)

Sulphur dioxide can also reduce orange coloured acidified potassium dichromate solution to a green solution.

sulphur dioxide	+	sulphuric acid	+	potassium dichromate	⟶	potassium sulphate	+	chromium (III) sulphate
$3SO_2$	+	H_2SO_4	+	$K_2Cr_2O_7$	⟶	K_2SO_4	+	$Cr_2(SO_4)_3$
				(orange)				(green)
							+	water
							+	H_2O

(d) Sulphur dioxide bleaches colouring matter by reduction.

Sulphur dioxide gas does not contain hydrogen atoms, the gas alone cannot reduce other substances. But when water is present in the reaction, SO_2 reacts with water molecule to produce 2H as shown in the equation below.

$$\begin{array}{ccccccccc} \text{sulphur dioxide} & + & \text{water} & \longrightarrow & \text{sulphuric acid} & + & \text{nascent hydrogen} & & \\ SO_2 & + & 2H_2O & \longrightarrow & H_2SO_4 & + & \boxed{2(H)} & \xrightarrow{\text{to the other substance in the reaction}} & \end{array}$$

Therefore, the bleaching action of sulphur dioxide is due to the reducing property of the nascent hydrogen, which may add H to the molecule of the colouring substance, or remove O from the molecule of the colouring substance.
In this way sulphur dioxide decolourizes the colouring substances sush as wet flowers, wet litmus papers.

6. Oxidizing properties of sulphur dioxide

Sulphur dioxide can oxidize magnesium, carbon monoxide and hydrogen sulphide.

$$\begin{array}{ccccccc} \text{magnesium} & + & \text{sulphur dioxide} & \longrightarrow & \text{magnesium oxide} & + & \text{sulphur} \\ 2Mg & + & SO_2 & \longrightarrow & 2MgO & + & S \\ \text{carbon monoxide} & + & \text{sulphur dioxide} & \longrightarrow & \text{carbon dioxide} & + & \text{sulphur} \\ 2CO & + & SO_2 & \longrightarrow & 2CO_2 & + & S \end{array}$$

$$\begin{array}{ccccccc} \text{hydrogen sulphide} & + & \text{sulphur dioxide} & \longrightarrow & \text{water} & + & \text{sulphur} \\ 2H_2S & + & SO_2 & \longrightarrow & 2H_2O & + & 3S \end{array}$$

Manufacture of sulphuric acid

Contact Process

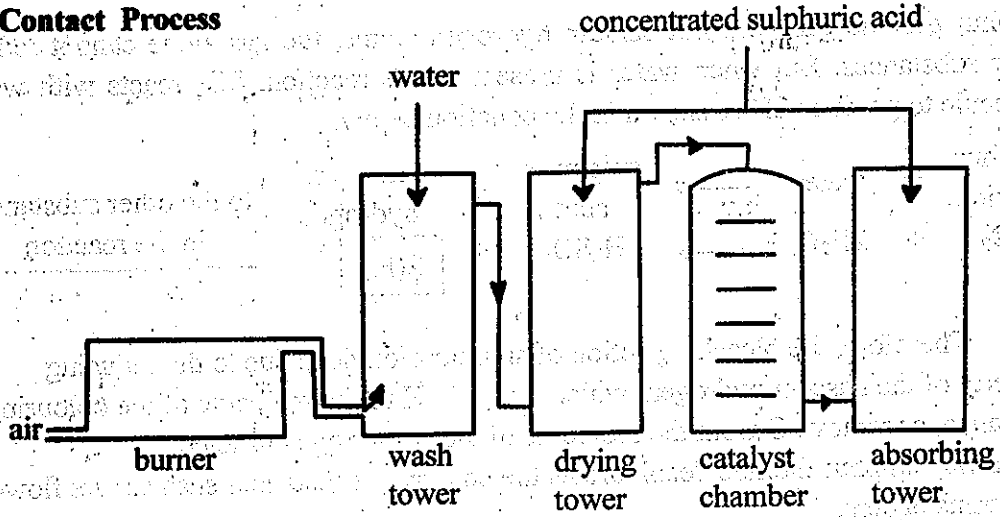


Fig. 11.8 Flow sheet of the Contact Process

Manufacture of sulphuric acid by the Contact Process (Fig.11.8) consists of the following main steps.

1. Preparation of sulphur dioxide.
2. Removing impurities.
3. Drying the gas.
4. Catalytic oxidation of sulphur dioxide to sulphur trioxide at the appropriate temperature.
5. Dissolution of sulphur trioxide.

1. Preparation of sulphur dioxide

Sulphur or iron pyrites is burnt in excess of air in the burner to produce sulphur dioxide.

burning sulphur	sulphur	+	oxygen	⟶	sulphur dioxide		
	S	+	O_2	⟶	SO_2		
burning iron pyrites	iron pyrites	+	oxygen	⟶	iron (III) oxide	+	sulphur dioxide
	$4FeS_2$	+	$11O_2$	⟶	$2Fe_2O_3$	+	$8SO_2$

2. Removing impurities

The gas mixture contains impurities (especially arsenious oxide) which might poison the catalyst. To remove these impurities the gas mixture is passed into a wash tower.

3. Drying the gas

The mixture of sulphur dioxide and excess air, free from impurities, is passed into the drying tower and dried by spraying with concentrated sulphuric acid.

4. Oxidation of sulphur dioxide to sulphur trioxide

The sulphur dioxide mixed with excess air is passed into the catalyst chamber where it is brought into contact with platinized asbestos or vanadium (V) oxide, V_2O_5 at the temperature of 450 °C-500 °C. In the presence of catalyst at 450 °C-500 °C the sulphur dioxide reacts with oxygen producing sulphur trioxide.

$$\text{sulphur dioxide} + \text{oxygen} \xrightarrow[450\text{-}500\ ^\circ\text{C}]{\text{catalyst}} \text{sulphur trioxide}$$

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

5. Dissolution of sulphur trioxide

Sulphur trioxide is easily dissolved in 98 % concentrated sulphuric acid. Therefore, sulphur trioxide produced in the catalyst chamber is absorbed in 98 % sulphuric acid to form oleum.

$$\text{sulphur trioxide} + \text{sulphuric acid} \longrightarrow \text{oleum}$$

$$SO_3 + H_2SO_4 \longrightarrow H_2SO_4.SO_3 \text{ or } H_2S_2O_7$$

The oleum so formed is mixed with water to obtain the acid of any desired concentration.

$$\text{oleum} + \text{water} \longrightarrow \text{sulphuric acid}$$

$$H_2SO_4.SO_3 + H_2O \longrightarrow 2H_2SO_4$$

Physical properties

1. Pure sulphuric acid is a colourless, oily, heavy liquid.
2. Its density is 1.84 g cm^{-3}.
3. It boils about 338 °C.

Chemical properties

Sulphuric acid can act as an acid, an oxidizing agent and as a dehydrating agent. It can displace more volatile acids from their salts.

1. Action as an acid

Dilute sulphuric acid has the general properties of an acid. It turns blue litmus to red.

Reaction with metals

Dilute sulphuric acid reacts with iron and the metals above it in the activity series producing sulphates and hydrogen.

iron + sulphuric acid ⟶ iron (II) sulphate + hydrogen

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

Similar reactions occur with zinc and magnesium.

Reaction with metallic oxides

Dilute sulphuric acid reacts with metallic oxides to produce sulphates and water.

sodium oxide + sulphuric acid ⟶ sodium sulphate + water

$$Na_2O + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O$$

copper (II) oxide + sulphuric acid ⟶ copper (II) sulphate + water

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

Similar reactions occur with potassium oxide, magnesium oxide, zinc oxide and iron (II) oxide.

Neutralization with hydroxides

It reacts with hydroxides producing sulphate and water.

sodium hydroxide + sulphuric acid ⟶ sodium sulphate + water

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

calcium hydroxide + sulphuric acid ⟶ calcium sulphate + water

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$$

aluminium hydroxide + sulphuric acid ⟶ aluminium sulphate + water

$$2Al(OH)_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 6H_2O$$

Similar reactions occur with potassium hydroxide, magnesium hydroxide, zinc hydroxide and other metal hydroxides.

Reaction with salts of weak acids

It reacts with salts of weak acids displacing the weak acid and producing the gases corresponding to the weak acids.

It reacts with carbonates producing sulphate, water and carbon dioxide.

sodium carbonate + sulphuric acid ⟶ sodium sulphate + water + carbon dioxide

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$

It reacts with hydrogencarbonates producing sulphate, water and carbon dioxide.

sodium hydrogencarbonate + sulphuric acid ⟶ sodium sulphate + water + carbon dioxide

$$2NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O + 2CO_2$$

It reacts with sulphites producing sulphate, water and sulphur dioxide.

sodium sulphite + sulphuric acid ⟶ sodium sulphate + water + sulphur dioxide

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2$$

It reacts with sulphides producing sulphate and hydrogen sulphide.

copper (II) sulphide + sulphuric acid ⟶ copper (II) sulphate + hydrogen sulphide

$$CuS + H_2SO_4 \longrightarrow CuSO_4 + H_2S$$

2. Displacement of more volatile acid from its salt

Concentrated sulphuric acid is less volatile than nitric acid and hydrochloric acid. When the salts of these acids react with hot concentrated sulphuric acid the acids of these salts are displaced.

with nitrate at low temperature	potassium nitrate	+	sulphuric acid	$\longrightarrow$	potassium hydrogensulphate	+	nitric acid
	KNO_3	+	H_2SO_4	$\longrightarrow$	$KHSO_4$	+	HNO_3
with nitrate at high temperature	potassium nitrate	+	sulphuric acid	$\longrightarrow$	potassium hydrogensulphate	+	nitric acid
	$2KNO_3$	+	H_2SO_4	$\longrightarrow$	$KHSO_4$	+	HNO_3
with chloride at low temperature	sodium chloride	+	sulphuric acid	$\longrightarrow$	sodium hydrogensulphate	+	hydrogen chloride
	$NaCl$	+	H_2SO_4	$\longrightarrow$	$NaHSO_4$	+	HCl
with chloride at high temperature	sodium chloride	+	sulphuric acid	$\longrightarrow$	sodium sulphate	+	hydrogen chloride
	$2NaCl$	+	H_2SO_4	$\longrightarrow$	Na_2SO_4	+	$2HCl$

With bromides and iodides, sulphuric acid first displaces the acids from the salts and then oxidizes the acids so formed to produce bromine and iodine.

(i) it displaces the acid first	sodium bromide	+	sulphuric acid	$\xrightarrow{\Delta}$	sodium hydrogensulphate	+	hydrogen bromide
	$NaBr$	+	H_2SO_4	$\xrightarrow{\Delta}$	$NaHSO_4$	+	HBr
(ii) Then it oxidizes the HBr formed in the first reaction	hydrogen bromide	+	sulphuric acid	$\xrightarrow{\Delta}$	water	+	sulphur dioxide
	$2HBr$	+	H_2SO_4	$\xrightarrow{\Delta}$	$2H_2O$	+	SO_2
						+	bromine Br_2

Iodides react in the same manner with hot concentrated sulphuric acid.

3. Action as an oxidizing acid

Hot concentrated sulphuric acid can oxidize non-metals and metals.

Oxidation of non-metals

Hot concentrated sulphuric acid oxidizes carbon and sulphur to the corresponding oxides.

$$\text{carbon} + \text{sulphuric acid} \longrightarrow \text{water} + \text{sulphur dioxide} + \text{carbon dioxide}$$

$$C + 2H_2SO_4 \longrightarrow 2H_2O + 2SO_2 + CO_2$$

$$\text{sulphur} + \text{sulphuric acid} \longrightarrow \text{water} + \text{sulphur dioxide}$$

$$S + 2H_2SO_4 \longrightarrow 2H_2O + 3SO_2$$

Hot concentrated sulphuric acid reacts with red phosphorus. At first phosphorus is oxidized to phosphorus (V) oxide.

$$\text{phosphorus} + \text{sulphuric acid} \longrightarrow \text{water} + \text{sulphur dioxide} + \text{phosphorus (V) oxide}$$

$$P_4 + 10H_2SO_4 \longrightarrow 10H_2O + 10SO_2 + P_4O_{10}$$

Then phosphorus (V) oxide reacts with water to form phosphoric acid.

$$\text{phosphorus (V) oxide} + \text{water} \longrightarrow \text{phosphoric acid}$$

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

Oxidation of mwtals

The reaction of hot concentrated sulphuric acid with metals involves two successive processes, i.e., oxidation and salt formation. It oxidizes the metal to metallic oxide. The metallic oxide so formed reacts with the excess sulphuric acid to form metal sulphate and water.

$$\begin{array}{l|l}
\text{(i)} & Cu + H_2SO_4 \longrightarrow CuO + H_2O + SO_2 \\
\text{(ii)} & CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O \\
\hline
\text{overall reaction} & Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2
\end{array}$$

$$\text{copper} + \text{sulphuric acid} \longrightarrow \text{copper (II) sulphate} + \text{water} + \text{sulphur dioxide}$$

4. Action as a dehydrating agent

Concentrated sulphuric acid is a very powerful dehydrating agent. It can absorb not only free water, such as moisture, but also the combined water or the elements water in some compounds.

Blue copper (II) sulphate becomes white when it is mixed with concentrated sulphuric acid.

$$\text{copper (II) sulphate crystal} \xrightarrow[-5H_2O]{H_2SO_4\text{ (conc)}} \text{copper (II) sulphate}$$

$$\underset{\text{(blue)}}{CuSO_4.5H_2O} \longrightarrow \underset{\text{(white)}}{CuSO_4}$$

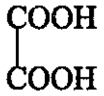
Methanoic (or formic) acid reacts with concentrated sulphuric acid decomposing it into carbon monoxide due to the loss of the elements of water.

$$\text{methanoic acid} \xrightarrow{H_2SO_4\text{ (conc)}} \text{water} + \text{carbon monoxide}$$

$$HCOOH \longrightarrow H_2O + CO$$

Ethanedioic acid reacts with concentrated sulphuric acid and is decomposed to carbon monoxide and carbon dioxide due to the loss of the elements of water.

$$\text{ethanedioic acid} \xrightarrow{H_2SO_4\text{ (conc)}} \text{water} + \text{carbon monoxide} + \text{carbon dioxide}$$



$$\begin{array}{l}COOH\\ |\\ COOH\end{array} \longrightarrow H_2O + CO + CO_2$$

Sugar, starch and other carbohydrates are dehydrated by concentrated sulphuric acid. Carbon is formed as the final product. Hence, when concentrated sulphuric acid is added to these compounds, they turn black.

$$\text{sugar} \xrightarrow{H_2SO_4\text{ (conc)}} \text{carbon} + \text{water}$$

$$C_{12}H_{22}O_{11} \longrightarrow \underset{\text{(black)}}{12C} + 11H_2O$$

$$\text{starch} \xrightarrow{H_2SO_4\text{ (conc)}} \text{carbon} + \text{water}$$

$$(C_6H_{10}O_5)_n \longrightarrow \underset{\text{(black)}}{6nC} + 5nH_2O$$

Salts of sulphuric acid

Sulphates

Sulphates which are normal salts of sulphuric acid are all solids.

Solubilities of sulphates

Barium, silver, lead (II) sulphates are insoluble in water. Other sulphates are soluble or slightly soluble in water.

Test for sulphates

1. Sulphates do not react with dilute and concentrated sulphuric acid.
2. (a) When barium chloride solution is added to a solution of sulphate, a white precipitate of barium sulphate is formed.

iron (II) sulphate + barium chloride ⟶ iron (II) chloride + barium sulphate

$$FeSO_4 + BaCl_2 \longrightarrow FeCl_2 + BaSO_4$$

(b) Carbonates and sulphites also form white precipitates of barium carbonate or sulphite with barium chloride solution. To distinguish the barium sulphate from the carbonate and sulphite, dilute hydrochloric acid must be added to the precipitate. Barium sulphate does not dissolve in dilute hydrochloric acid whereas carbonates and sulphites of barium are soluble in the acid.

SUMMARY

Sulphur is a molecular element containing eight atoms with the formula S_8. Sulphur exists in different allotropic forms. Rhombic sulphur and monoclinic sulphur are crystalline forms and plastic sulphur is a non-crystalline form. Sulphur can react with metals, non-metals and oxidizing acids such as hot concentrated H_2SO_4 and HNO_3.

HNO_3 cannot be used in the preparation of H_2S as it can oxidize $H_2S(g)$ to sulphur or oxide of sulphur. Manufacture of sulphuric acid by the Contact Process consists of five main steps. Sulphides possess the reducing properties.

SO_2 has both oxidizing and reducing properties. Concentrated H_2SO_4 is a very powerful dehydrating agent.

Questions and Problems

1. (a) Name two crystalline allotropic forms of solid sulphur.
   (b) Briefly describe the preparation of each.
   (c) How would you show that these two allotropic forms represent the same element sulphur?
2. (a) Starting from sulphur how would you obtain the following substances? Mention the conditions required for the reactions to take place. Give equation for each of the reactions.
      (i) sulphur dioxide
      (ii) sulphuric acid
      (iii) hydrogen sulphide
   (b) What mass and volume at STP of sulphur dioxide could be obtained from 16 g of sulphur?
3. (a) You are provided with iron filings, powdered sulphur, dilute sulphuric acid and the required laboratory apparatus including a burner but no other chemicals.
   With the aid of a diagram show how you would prepare and collect hydrogen sulphide.
   (b) Explain why nitric acid cannot be used for the preparation of hydrogen sulphide in the laboratory.
   (c) Explain why concentrated sulphuric acid cannot be used as a drying agent for hydrogen sulphide.
4. (a) What happens when dry hydrogen sulphide burns in air?
   Give two equations for the reaction under different conditions of burning.
   (b) What property of hydrogen sulphide is represented by its action on litmus?
   Give two different representative reactions to illustrate this property.
5. Write equations for the reduction of the following substances by sulphur dioxide.
   (a) chlorine (b) bromine
6. Write the equations for the reduction of the following substances by sulphur dioxide.
   (a) nitric acid (b) iodine

7. Write equations for the reduction of the following substances by hydrogen sulphide and sulphur dioxide.

   (a) $KMnO_4$ (b) $K_2Cr_2O_7$

Mention the conditions required for the reactions to take place.

8. If you are provided with a solution containing zinc and copper (II) sulphates, how would you separate copper and zinc as :

(a) copper (II) sulphide (b) zinc sulphide?

9. Sulphur dioxide has two reactions with the following substances. State the condition for each reaction and give equations.

   (a) chlorine (b) sodium hydroxide

10. Give representative reactions for each set of properties which show that sulphur dioxide is an acidic oxide as well as a reducing agent.

11. (a) With the aid of equations briefly describe the steps to prepare sulphuric acid from sulphur.

    (b) Write equations representative of the reaction of dilute sulphuric acid with metals, metallic oxides and hydroxides.

12. Write equations for the oxidizing reactions of hot concentrated sulphuric acid with the following substances :

    (a) carbon (b) sulphur (c) phosphorous (d) copper

13. (a) Give the reactions of hot concentrated sulphuric acid with two non metals and one metal.

    (b) What property does sulphuric acid show in the reaction with non metals?

    (c) What properties does sulphuric acid show in the reaction with metals?

14. (a) What are the actions of concentrated sulphuric acid on

    (i) methanoic acid (ii) ethanedioic acid (iii) blue copper (II) sulphate ?

    (b) What property does sulphuric acid show in the following reaction?

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2H_2O + 2SO_2$$

19.6 g of pure sulphuric acid are involved in the above reaction, how many moles of sulphuric acid are involved in the reaction? How many moles of carbon are involved in the reaction? What is the mass of carbon dioxide in the reaction? (C = 12 ; H = 1; S = 32 ; O = 16)

15. (a) Describe the industrial process for the production of pure sulphuric acid.
(b) 18 kg of water is added to every 178 kg of oleum produced by the above process. What is the percentage purity of sulphuric acid by weight after adding this amount of water? (H = 1 ; S = 32 ; O = 16)

16. (a) Write the equation for the reaction of sulphur trioxide with concentrated sulphuric acid.
(b) What is the molecular mass of 100 % pure sulphuric acid? (H = 1; S = 32; O = 16)
(c) How many kilograms of water is needed to convert 98 kg of oleum to 98 % pure sulphuric acid?

17. Write TRUE or FALSE for each of the following statements.
(a) Sulphur is a yellow, strong, smelling solid element.
(b) Sulphur cannot exist in different allotropic forms like carbon and oxygen.
(c) Solid sulphur can exist in two crystalline forms.
(d) Sulphur can react with non-oxidizing acids such as dilute sulphuric acid and hydrochloric acid.
(e) Hydrogen sulphide turns blue litmus slightly pink.

18. Fill in the blanks with a suitable word (s) or unit (s) or phrase (s).
(a) Two crystalline forms of sulphur are .... sulphur and ....sulphur.
(b) Hydrogen sulphide turns .... paper black.
(c) Sulphur dioxide can be prepared by the action of dilute sulphuric acid on ....
(d) Sulphur dioxide .... colouring matter by reduction.

19. Select the correct word or words given in the brackets.
(a) Sulphur dioxide can turn potassium dichromate paper (red, green, orange).
(b) Hydrogen sulphide gas can turn lead (II) nitrate paper (white, blue, black).
(c) Hydrogen sulphide (oxidizes, reduces, displaces) halogens.
(d) Sulphur dioxide (bleaches, oxidizes, reduces) colouring matter.

20. Match each of the items given in List A with the appropriate item in List B.

List A	**List B**
(a) Sulphur can exist in different allotropic forms	(i) plastic sulphur is formed.
(b) When any form of sulphur is heated almost to its boiling point and pour into cold water	(ii) like carbon and oxygen
(c) Dilute sulphuric acid is reacted with iron (II) sulphide	(iii) contact process
(d) Sulphur dioxide gas is treated with potassium dichromate paper	(iv) hydrogen sulphide is produced
(e) The manufacture of sulphuric acid	(v) the paper turns green

21.(a) A gas "G" is obtained by heating copper turnings with concentrated sulphuric acid.

What is gas "G"? Write down the equation.

(b) The gas "G" is collected by the upward displacement of air. Why?

(c) What is the odour of gas "G"?

(d) What would happen if gas "G" is passed into iodine solution?

22. Sulphuric acid is manufactured by the following processes. The reactions involved are as follows.

(a) sulphur + oxygen $\longrightarrow$ gas A
(b) gas A + oxygen $\xrightarrow{\text{catalyst B}}$ sulphur trioxide
(c) sulphur trioxide + liquid C $\longrightarrow$ oleum
(d) oleum + liquid D $\longrightarrow$ sulphuric acid

Give the names of gas A, catalyst B, liquid C, liquid D and write down the chemical equations in symbols for the processes (a), (b), (c) and (d).

****

CHAPTER 12

THE HALOGENS

The four elements, fluorine, chlorine, bromine and iodine are known as the halogens. "Halogen" is a term derived from Greek, meaning "salt formers", because they combine readily with metals to form salts.

Halogens resemble each other very closely in general chemical behaviour, but the first member of the group, fluorine, shows some differences from the rest. The chemical behaviour of the individual elements such as chlorine, bromine and iodine will be examined first, and then a comparison of their chemistry will be discussed.

12.1 Chlorine

Laboratory preparations of chlorine

1. **Preparation of chlorine from concentrated hydrochloric acid and manganese (IV) oxide**

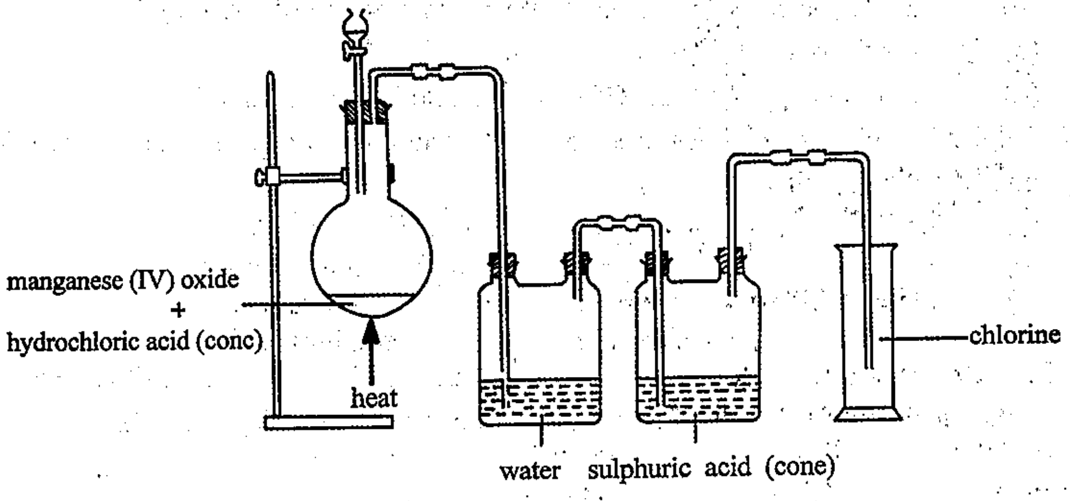


Fig. 12.1 Preparation of chlorine from concentrated hydrochloric acid and manganese (IV) oxide

$$\text{manganese(IV) oxide} + \text{hydrochloric acid (conc)} \xrightarrow{\Delta} \text{manganese(II) chloride} + \text{water} + \text{chlorine}$$

$$MnO_2(s) + 4HCl(aq) \xrightarrow{\Delta} MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$$

Concentrated hydrochloric acid is oxidized to chlorine by manganese (IV) oxide.

The apparatus is set up as shown in Fig. 12.1. Some manganese (IV) oxide is placed in the round-bottomed flask and concentrated hydrochloric acid poured down the dropping funnel. The mixture in the flask is heated and effervescence will take place. A greenish yellow gas with misty fumes is evolved. (The misty fumes are hydrogen chloride gas).

The gas mixture is passed into the first bottle which contains water. This removes the hydrochloric acid gas which is very soluble in water. The gas is then passed into a second bottle which contains concentrated sulphuric acid. This dries the gas which is collected by upward displacement of air since the gas is denser than air. Because of the greenish yellow colour of the gas, it can be seen quite clearly when the gas jar is full of chlorine.

2. Preparation of chlorine from concentrated hydrochloric acid and potassium permanganate

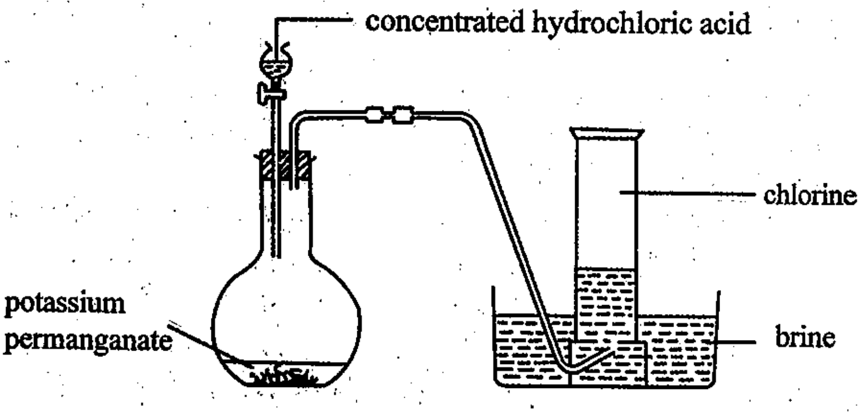


Fig. 12.2 Preparation of chlorine from concentrated hydrochloric acid and potassium permanganate

Note: If the chlorine is required pure and dry, insert wash-bottles containing (a) water and (b) conentrated sulphuric acid as in Fig. 12.1.

$$\begin{array}{c}\text{potassium}\\\text{permanganate}\end{array} + \begin{array}{c}\text{hydrochloric}\\\text{acid (conc)}\end{array} \longrightarrow \begin{array}{c}\text{potassium}\\\text{chloride}\end{array} + \begin{array}{c}\text{manganese(II)}\\\text{chloride}\end{array} + \text{water} + \text{chlorine}$$

$$2KMnO_4(s) + 16HCl(aq) \longrightarrow 2KCl(aq) + 2MnCl_2(aq) + 8H_2O(l) + 5Cl_2(g)$$

Concentrated hydrochloric acid is oxidized to chlorine by potassium permanganate.

The apparatus is set up as shown in Fig. 12.2. Solid potassium permanganate is put in the flat-bottomed flask and concentrated hydrochloric acid is dropped onto it from the dropping funnel. Heat is not required.

As each drop of acid reaches the permanganate, there is evolved at once the corresponding quantity of chlorine. Collect the gas by downward displacement of brine (concentrated aqueous sodium chloride).

3. Preparation of chlorine from sodium chloride

sodium chloride + manganese(IV) oxide + sulphuric acid(conc) ⟶ sodium hydrogensulphate + manganese(II) sulphate + water + chlorine

$$2NaCl(s) + MnO_2(s) + 3H_2SO_4(conc) \longrightarrow 2NaHSO_4(aq) + MnSO_4(aq) + 2H_2O(1) + Cl_2(g)$$

Concentrated sulphuric acid acts upon the sodium chloride to form hydrogen chloride, which is then oxidized to chlorine by manganese (IV) oxide.

The apparatus is set up as shown in Fig. 12.1. An intimate mixture of sodium chloride and manganese (IV) oxide is placed in the round-bottomed flask. Concentrated sulphuric acid is added into the flask and the flask is heated.

The gas evolved is washed with water, dried with concentrated sulphuric acid and collected by upward displacement of air.

4. Preparation of chlorine from bleaching powder

(i) $CaOCl_2(s) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + H_2O(1) + Cl_2(g)$
bleaching powder ... chlorine

(ii) $CaOCl_2(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + Cl_2(g)$
Bleaching powder ... chlorine

The apparatus is set up as shown in Fig. 12.2. Some bleaching powder is placed in the flat-bottomed flask and a dilute acid, e.g., nitric acid, is dropped onto the powder. Effervescence occurs with the evolution of a greenish yellow gas which may be collected by either of the methods mentioned previously. Heat is not required.

Manufacture of chlorine

Figure 12.3 shows the apparatus for the industrial preparation of chlorine.

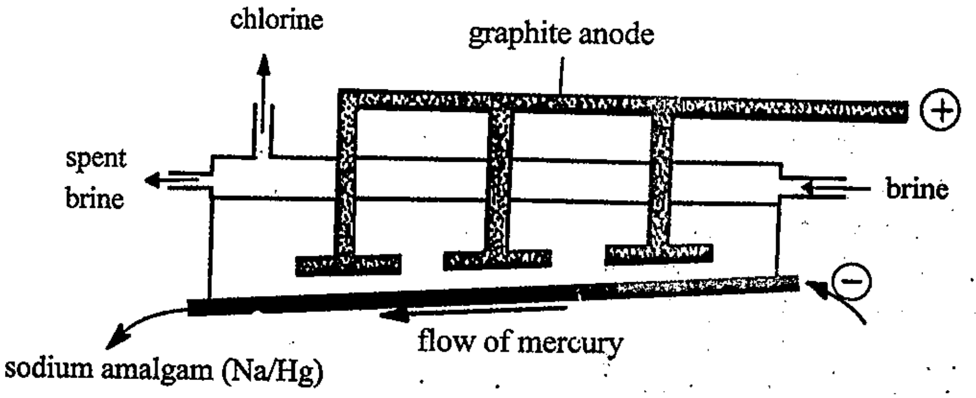


Fig 12.3 Manufacture of chlorine by electrolysis of saturated sodium chloride solution

The reactions at the electrodes may be represented as

reaction at the cathode $Na^+ + e \longrightarrow Na$

reaction at the anode $Cl^- \longrightarrow Cl + \bar{e}$

$$Cl + Cl \longrightarrow Cl_2$$

In the electrolytic process, chlorine is liberated at the graphite anodes whilst sodium is liberated at the mercury cathode. Sodium dissolves in the mercury forming as sodium amalgam which then flows into another cell where it reacts with water to form hydrogen and a solution of sodium hydroxide.

$$\underset{\text{sodium amalgam}}{Na/Hg(l)} + H_2O(l) \longrightarrow Na^+(aq) + OH^-(aq) + \frac{1}{2} H_2(g) + Hg(1)$$

Physical properties of chlorine

Chlorine is a greenish yellow gas with a choking, unpleasant smell. Chlorine is very poisonous if inhaled even in small quantities. One part of chlorine in 50,000 parts of air may be harmful. Chlorine is about $2\frac{1}{2}$ times as dense as air.

Chemical properties of chlorine

1. **Affinity for hydrogen**

   Chlorine reacts with most compounds containing hydrogen.

(a) Action on hydrogen

When a tube containing equal volumes of chlorine and hydrogen is exposed to sunlight, it explodes.

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

(b) Action on warm turpentine

Chlorine reacts with warm turpentine to form carbon and hydrochloric acid.

$$\underset{\text{turpentine}}{C_{10}H_{16}(l)} + 8Cl_2(g) \longrightarrow 10C(s) + 16HCl(g)$$

(c) Action on hydrogen sulphide

Chlorine reacts with hydrogen sulphide to form sulphur and hydrogen chloride.

$$H_2S(g) + Cl_2(g) \longrightarrow 2HCl(g) + S(s)$$

Note: In this reaction chlorine is the oxidizing agent and hydrogen sulphide is the reducing agent.

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$S^{2-} \longrightarrow S + 2e \quad \text{oxidation}$$

$$Cl_2 + 2e \longrightarrow 2Cl^- \quad \text{reduction}$$

2. **Action on metals**

(a) Action on copper

When a very thin sheet of an alloy of copper and zinc, mainly copper, is dropped into a chlorine jar, it burns brightly with a green flame.

$$Cu(s) + Cl_2(g) \longrightarrow CuCl_2(s)$$

$$Zn(s) + Cl_2(g) \longrightarrow ZnCl_2(s)$$

(b) Action on iron

Hot iron wire burns in chlorine.

$$2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$$

3. **Action on non-metal**

Action on phosphorus

Phosphorus burns spontaneously in chlorine.

$$P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(g)$$

$$P_4(s) + 10Cl_2(g) \longrightarrow 4PCl_5(g)$$

4. **Oxidizing properties**

(a) Bleaching action of chlorine

The chlorine reacts with water, forming hypochlorous acid, HOCl and hydrochloric acid.

$$Cl_2(g) + H_2O(l) \longrightarrow HOCl(aq) + HCl(aq)$$

This hypochlorous acid is a very reactive compound and readily gives up its oxygen to the dye, to form a colourless compound.

$$\underset{\text{coloured}}{\text{dye}} + HOCl \longrightarrow HCl + \underset{\text{colourless}}{(\text{dye} + O)}$$

(b) Action on iron (II) chloride solution

Chlorine reacts with iron (II) chloride solution to form iron (III) chloride.

$$2FeCl_2(aq) + Cl_2(g) \longrightarrow 2FeCl_3(aq)$$

(c) Action on sulphurous acid

Chlorine oxidizes sulphurous acid into sulphuric acid.

$$H_2SO_3(aq) + Cl_2(g) + H_2O(l) \longrightarrow H_2SO_4(aq) + 2HCl(aq)$$

(d) Action on caustic alkalis

(i) On the cold dilute aqueous solution

When chlorine is passed into a cold (⩽ 15 °C) solution of dilute sodium hydroxide solution, a soluble hypochlorite and chloride of the metal are formed. The colour of this solution is yellow.

$$Cl_2(g) + \underset{\text{dilute solution}}{2NaOH(aq)} \xrightarrow{\text{cold}} NaOCl(aq) + NaCl(aq) + H_2O(l)$$

$$Cl_2(g) + \underset{\text{dilute solution}}{2KOH(aq)} \xrightarrow{\text{cold}} KOCl(aq) + KCl(aq) + H_2O(l)$$

(ii) On the hot concentrated aqueous solution

When chlorine is passed into a hot (⩾ 70 °C) concentrated sodium hydroxide solution, a mixture of sodium chloride and sodium chlorate is formed.

$$\underset{\text{concentrated}}{6NaOH(aq)} + 3Cl_2(g) \longrightarrow \underset{\text{sodium chloride}}{5NaCl(aq)} + \underset{\text{sodium chlorate}}{NaClO_3(aq)} + 3H_2O(l)$$

sodium hydroxide solution

A similar reaction occurs when chlorine is passed into concentrated potassium hydroxide solution.

(iii) On slaked lime

When chlorine is passed over solid calcium hydroxide, bleaching powder is formed.

$$Ca(OH)_2(s) + Cl_2(g) \longrightarrow CaOCl_2.H_2O(s)$$ bleaching powder

5. Displacement of bromine and iodine from bromide and iodide

When chlorine is passed into a solution of sodium bromide or sodium iodide, the respective halogen is released by the substitution action of chlorine.

$$Cl_2(g) + 2NaBr(aq) \longrightarrow 2NaCl(aq) + Br_2(aq)$$
$$Cl_2(g) + 2NaI(aq) \longrightarrow 2NaCl(aq) + I_2(aq)$$

Uses of chlorine

Chlorine is used to sterilize water for domestic and industrial use, and as a bleaching agent. With the help of chlorine, many organic substances are prepared.

Tests for chlorides

The tests for chlorides are based on some of the reactions you have already studied. Details of these tests are given in the experimental chemistry book for the grade 10 students.

12.2 Bromine

Laboratory preparation of bromine

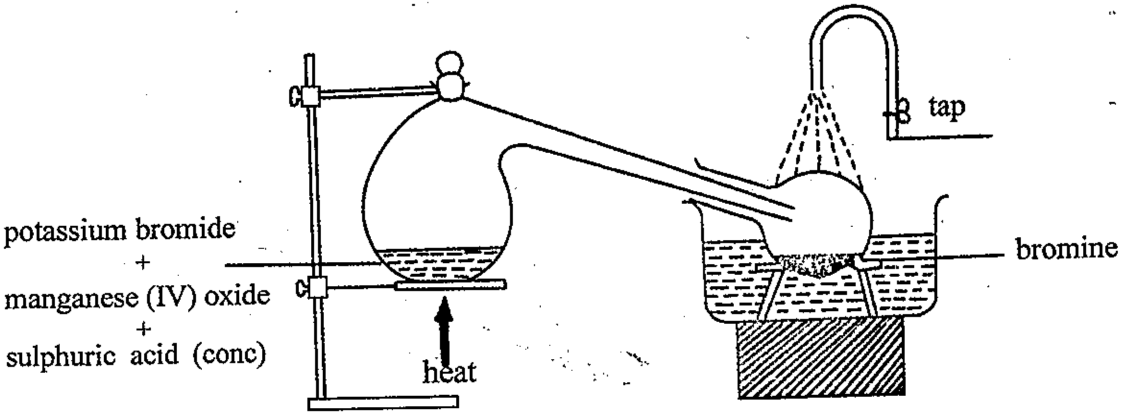


Fig. 12.4 Preparation of bromine

$$\text{Potassium bromide} + \text{manganese(IV) oxide} + \text{sulphuric acid(conc)} \xrightarrow{\Delta} \text{potassium hydrogensulphate} + \text{manganese(II) sulphate} + \text{water} + \text{bromine}$$

$$2KBr(s) + MnO_2(s) + 3H_2SO_4(conc) \xrightarrow{\Delta} 2KHSO_4(aq) + MnSO_4(aq) + 2H_2O(l) + Br_2(g)$$

Bromine is prepared in much the same way as chlorine.

A mixture of potassium bromide and manganese (IV) oxide is placed in the retort as shown in Fig. 12.4. Concentrated sulphuric acid is added to this mixture and the mixture warmed. A reddish brown gas of bromine is given off, together with some misty fumes of hydrogen bromide which condense to a red liquid in the cooled receiver.

Physical properties of bromine

Bromine is a heavy, red, volatile liquid. It has a choking, irritating smell. (Bromine means "a stench".) Liquid bromine causes burns on the flesh, which heal with difficulty. Bromine is slightly soluble in water, forming a yellowish red solution containing about 3 percent of bromine at ordinary temperatures.

Chemical properties of bromine

1. **Affinity for hydrogen**

Action on hydrogen

Bromine combines with hydrogen, but not as readily as chlorine does. A mixture of chlorine and hydrogen will explode when merely exposed to sunlight, but a mixture of bromine and hydrogen needs the application of heat to make them combine. Also, the hydrogen bromide formed is not as stable as hydrogen chloride.

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

2. **Reaction between bromine and other elements**

Bromine combines readily with most metals and non-metals to form bromides. For example, copper, iron, sodium and sulphur give the corresponding bromides.

Bromine explodes when mixed with yellow phosphorus. Phosphorus tribromide is made by gradually adding a solution of bromine in carbon tetrachloride to red phosphorus. (The solution is used to moderate the action.)

3. **Oxidizing property of bromine**

Bromine is an oxidizing agent, but it is not as strong an oxidizing agent as chlorine. Bromine will also give majority of oxidation reactions given by chlorine.

(a) Bleaching action of bromine

Bromine is a bleaching agent but it is not so effective as chlorine. Bromine bleaches moist litmus papers.

(b) Action on iron (II) sulphate solution

On shaking an acidified solution of iron (II) sulphate with a few drops of bromine in a test tube, the colour of bromine soon fades and the iron (II) sulphate becomes converted into iron (III) sulphate.

$$2Fe^{2+}(aq) + Br_2(l) \longrightarrow 2Fe^{3+}(aq) + 2Br^-(aq).$$

(c) **Action on the alkalis**

Bromine reacts on solutions of alkalis in the same way as chlorine.

e.g., $2\,KOH(aq) + Br_2(l) \xrightarrow{\text{cold}} KBr(aq) + KOBr(aq) + H_2O(l)$
dilute solution

$6KOH(aq) + 3Br_2(aq) \xrightarrow{\text{hot}} 5KBr(aq) + KBrO_3(aq) + 3H_2O(l)$
concentrated solution

In all these reactions bromine shows a great similarity to chlorine, but differs from it by its lower reactivity.

4. **Displacement of iodine from iodides**

Action on iodide

When bromine is passed into a solution of sodium iodide, iodine is liberated.

$$2NaI(aq) + Br_2(g) \longrightarrow 2NaBr(aq) + I_2(aq)$$

Test for bromides

The tests for bromides are based on some of the reactions you have already studied. Details of these tests are given in your experimental chemistry book for grade 10 students.

12.3 Iodine

Laboratory preparation of iodine

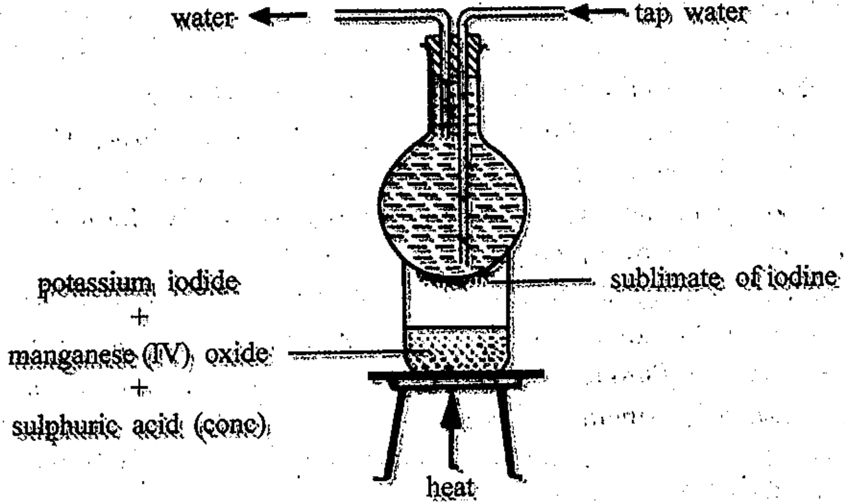


Fig. 12.5 Preparation of iodine

$$\begin{array}{ccccccccc} \text{Potassium} & + & \text{manganese(IV)} & + & \text{sulphuric} & \xrightarrow{\Delta} & \text{potassium} & + & \text{manganese(II)} \\ \text{iodide} & & \text{oxide} & & \text{acid(conc)} & & \text{hydrogensulphate} & & \text{sulphate} \end{array}$$

$$\begin{array}{ccccccccc} 2KI(s) & + & MnO_2(s) & + & 3H_2SO_4(conc) & \xrightarrow{\Delta} & 2KHSO_4(aq) & + & MnSO_4(aq) \\ & & & & & & + \text{water} & + & \text{iodine} \\ & & & & & & + 2H_2O(l) & + & I_2(g) \end{array}$$

Some potassium iodide and manganese (IV) oxide are mixed and ground in a mortar and the mixture placed in a beaker.

Concentrated sulphuric acid is added to the mixture in the beaker and a round-bottomed flask with arrangements to circulate flowing water from the tap is placed on the beaker as shown in Fig. 12.5.

The mixture is carefully warmed when violet vapours of iodine evolve and are condensed on the outside of the bottom of the cooled flask, as black shiny plates.

Note: Preparation of iodine is similar to that of chlorine from common salt. However, HI is easier to oxidize than even HBr.

Physical properties of iodine

Iodine is a black shiny solid. It sublimes when heated rapidly, forming a violet vapour from which the black solid can again be obtained by cooling.

Iodine is almost insoluble in water but readily dissolves in aqueous potassium iodide. This is due to the formation of a compound of potassium iodide and iodine, KI_3, which is very soluble. This solution is brown. Iodine also dissolves in ethanol and ether, forming brown solutions, and in carbon disulphide and carbon tetrachloride, forming violet solutions.

Chemical properties of iodine

1. Iodine does not bleach, and has little affinity for hydrogen. When HI is heated it decomposes.

2. Iodine is fairly active and will combine with many metals to form iodides, but it does so, much less readily than either chlorine or bromine.

3. Oxidizing properties

(a) Iodine is a mild oxidizing agent, but it will not perform many of the ordinary oxidizing actions attributed to chlorine and bromine. However, iodine oxidizes H_2S to form hydrogen iodide and liberate sulphur.

$$H_2S(g) + I_2(g) \longrightarrow 2HI(g) + S(s)$$

(b) Action on alkalis

The action of iodine on alkalis is similar to those of chlorine and bromine.

4. **Action on starch**

To a freshly prepared solution of starch add the smallest possible quantity of a solution of iodine. A blue colour forms immediately. [This test is sensitive to and is capable of detecting iodine if this element is present even in ppm (parts per million) amounts. Warm the mixture and this blue colour will disappear. It will return on cooling.

Note: This test is given only by free iodine and is not given by a solution of KI in water.

Uses of iodine

The antiseptic properties of iodine, due to its oxidizing nature, have been used in the treatment of small cuts and wounds. "Tincture of iodine", a dilute solution of iodine in alcohol is a household medicinal. Iodine is used as free iodine and as iodide in medicine to treat cases of goitre, a disease which is sometimes due to a deficiency of iodine intake into the body.

Tests for iodides Tests for iodides are based on some of the reactions you have already studied. Details of these tests are given in your experimental chemistry book for grade 10 students.

SUMMARY

Fluorine, chlorine, bromine and iodine are known as halogens. They have oxidizing properties. Chlorine and bromine have bleaching power but iodine cannot bleach. With the exception of fluorine, all other halogens form compound in which they have positive oxidation numbers up to +7.The preparation, physical and chemical properties and their uses are also presented in this chapter. Questions and problems are given at the end of the chapter so that students can understand and practice about various aspects of halogens.

Questions and Problems

1. What does the term "halogen" mean?
2. What are the halogens?
3. Why are all the halogens in Group VII B of the periodic table?
4. Write the name of three members of the halogens other than chlorine. State whether each of these halogens would react with hydrogen more vigorously or less vigorously, than would chlorine.
5. How would you prepare pure, dry chlorine? Describe what you would observe and say what is formed when

(a) a lighted candle is placed in a jar of chlorine? (Candle is made of a hydrocarbon $C_n H_{2n+2}$.)

(b) chlorine is passed into a potassium iodide solution?

6. Describe a method of manufacturing chlorine by an electrolytic process. Name the electrolyte and give the name, sign and material of each electrode. Name also the products for the reaction occuring at the etectrodes.

7. When dry hydrogen burns at a jet in a gas jar of dry chlorine the following changes are observed;

(a) the colour of the chlorine disappears

(b) a gas is formed with fumes in moist air and turns moist blue litmus red. Explain these observations.

8. Chlorine can be prepared by the oxidation of concentrated hydrochloric acid. Name three oxidizing agents which will bring about this oxidation.

9. Give equations for the three reactions which show the oxidizing property of chlorine.

10. Write equations in words and symbols for the following reactions.

(a) $Fe(s) + 3Cl_2(g) \longrightarrow ?$

(b) $Ca(OH)_2(s) + Cl_2(g) \longrightarrow ?$

(c) $Cl_2(g) + NaOH\ (aq)\ (dilute) \xrightarrow{cold} ?$

(d) $KBr(s) + MnO_2(s) + H_2SO_4(aq) \longrightarrow ?$

(e) $NaI(aq) + Br_2(g) \longrightarrow ?$

(f) $H_2S(g) + I_2(g) \longrightarrow ?$

(g) $Cl_2(g) + H_2O(l) \longrightarrow ?$

11. How many grams of potassium chlorate will be formed when chlorine is passed into a concentrated solution of potassium hydroxide containing 8 g of the alkali? (K = 39, O = 16, H = 1, Cl = 35.5)

12. You are shown two colourless salts which are supposed to be an alkali chloride and an alkali iodide. How will you distinguish the two by chemical means?

13. Sea water contains about 2.5 % by mass of sodium chloride and traces of potassium bromide. Suggest practical methods for obtaining from sea water.

(a) water, free from sodium ions and potassium ions.

(b) reasonably pure sodium chloride
(c) a sample of chlorine

14. Fluorine reacts with sodium to form fluoride. What properties would you expect this fluoride to have?

15. Which of the naturally occurring halogens provide examples of
(a) the largest atom
(b) the smallest ionization energy and
(c) the weakest acid HX?

16. State TRUE or FALSE for each of the following statements.
(a) All halogens always take positive oxidation number.
(b) All halogens have similar properties but not identical.
(c) Halogens are usually found as metal halides.
(d) Chlorine is stronger than bromine to bleach the colour.
(e) Bromine can displace the chlorine from chloride.

17. Fill in the blanks with a suitable word or phrase or numerical value with unit as necessary.
(a) Chlorine gas can be dried by passing through ....
(b) Chlorine can be collected by downward displacement of ....
(c) A disease, goitre, is caused due to deficiency of ....
(d) In halogens ....exists as solid at room temperature.
(e) Bromine explodes when mixed with yellow..............

18. Select the correct term or terms given in the brackets.
(a) The most reactive halogen is (fluorine, chlorine, bromine).
(b) (Chlorine, Bromine, Fluorine) never shows the positive oxidation number.
(c) (Cl_2, Br_2, I_2) is a liquid at room temperature.
(d) (Cl_2, Br_2,I_2) cannot bleach.
(e) Iodine readily dissolves in aqueous potassium iodide forming (brown, violet, reddish brown) solution.

19. Match each of the items given in List A with the appropriate item in List B.

List A	List B
(a) Amalgam	(i) Br_2
(b) Solvent for Iodine	(ii) Cl_2
(e) Sterilizing agent	(iii) potassium iodide solution
(d) Halogen in solid form	(iv) Na/Hg
(e) Reddish brown liquid	(v) I_2

20. Answer the following questions.

(a) Which compound is formed when chlorine is passed over heated iron? Write equation in **symbols** only.

(b) Which of the following statements about chlorine is **NOT TRUE**?
(A) In industry it is produced by the electrolysis of lime .
(B) It is used for purifying water.
(C) It is one of the most reactive of halogens.
(D) It combines directly with metals and non-metals.

(c) Which of the following pairs would react together most violently?
(A) sodium and iodine (C) magnesium and bromine
(B) potassium and chlorine

(d) Which of the following statements is the correct use of chlorine?
(A) Chlorine gas is used to sterilize drinking water.
(B) Chlorine is used to make the polymer Teflon.
(C) Chlorine is used in the manufacture of fertilizers.

21. Complete the following table on halogen family.

Name	Symbol	State	Colour
Fluorine			pale yellow
			pale green
Bromine	Br		
		solid	

****

CHAPTER 13

ACIDS, BASES AND THEIR NEUTRALIZATION

13.1 Development of the Theory of Acids and Bases

Lavoisier (1777) and Davy (1816)

One of the first generalizations about acids came from the French Scientist A.L. Lavoisier (1777). Many acids can be produced by reacting non-metallic oxides with water e.g., H_2SO_4, H_2SO_3, HPO_3, H_3PO_4, H_3AsO_3 which contain oxygen. Lavoisier made use of this fact to propose that all acids contained oxygen.

This generalization was proved to be incorrect when H. Davy (1816) demonstrated that hydrochloric acid contained only hydrogen and chlorine. Davy therefore proposed that all acids contained hydrogen.

M.P.E. Berthollet had also recognized that the acids HCN and H_2S did not contain oxygen.

Arrhenius (1887)

S.A. Arrhenius defined an acid as a compound which could produce hydrogen ions in water solution. An alkali, according to him is a compound which could produce hydroxide ions in water. A strong acid produces an abundance of hydrogen ions and a weak acid produces relatively fewer hydrogen ions. According to the Arrhenius theory, hydrochloric acid (a strong acid) is essentially completely ionized in water.

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

but ethanoic acid (a weak acid) is only partially ionized.

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

Strong bases such as sodium hydroxide are completely ionized in aqueous solution,

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

but weak bases such as aqueous ammonia are only partially ionized.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The process of neutralization occurs by the reaction of hydrogen and hydroxide ions.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(1)$$

Arrhenius theory has some weak points, one of which is that its application is limited to aqueous solutions.

Bronsted and Lowry (1922)

J.N.Bronsted defined an acid as a proton donor and a base as a proton acceptor. This definition applies to all solvents, not only to aqueous solutions. As far as aqueous solutions of acids are concerned, there are similarities between the Bronsted theory and the Arrhenius theory. But, the Bronsted theory does not consider an acid or a base separately. Every acid can function as such only in the presence of a base giving rise to an equilibrium. In this equilibrium, the original acid is related to the base in the reverse reaction, which is called the conjugate base. Similarly the original base is related to the acid in the reverse reaction which is called the conjugate acid.

For example when hydrogen chloride dissolves in water a reaction takes place and an equilibrium is established.

$$\underset{\text{acid 1}}{HCl(aq)} + \underset{\text{base 2}}{H_2O(l)} \rightleftharpoons \underset{\text{acid 2}}{H_3O^+(aq)} + \underset{\text{base 1}}{Cl^-\ (aq)}$$

According to the Bronsted theory, HC1 is an acid for the forward reaction, but the **hydroxonium** (hydronium) ion, H_3O^+, is an acid in the reverse reaction. It is the conjugate acid (acid 2) of water (base 2). Similarly, the chloride ion (base 1) accepts protons in the reverse reaction to form its conjugate acid (acid 1). In this theory acids are not confined to neutral species or positive ions. The hydrogensulphate ion can behave as an acid.

$$HSO_4^-\ (aq) + H_2O\ (1) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}\ (aq)$$

The hydrogen ion is extremely small consisting of a proton only. Its diameter is about 10^{-13} cm as compared with other ions which have diameters of the order of 10^{-8} cm. The charge density of the proton is very high and therefore it may not possibly be able to exist on its own in water or any other solvent. There is evidence to suggest that the proton attaches itself to water molecules by sharing the lone pairs of electrons on the oxygen atom.

$$H^+ + H_2\ddot{O} \longrightarrow H_3O^+$$

It is very difficult or impossible to indicate the exact number of water molecules which surround the ion. The species is written as H_3O^+ (aq) and called hydroxonium ion. Sometimes it is written as H^+ (aq) to simplify an equation.

Note that the presence of a "lone pair" of electrons is characteristic of a base.

Lewis(1939)

G.N.Lewis defined bases as species which can donate an electron pair, and acids as species which can accept an electron pair. Under this definition the hydrogen ion or proton is not the only acid. There are many other species which can function similarly For instance, the reaction of ammonia with boron trifluoride is an acid-base reaction.

$$\ddot{N}H_3(g) + BF_3(s) \rightleftharpoons H_3N^+ - {}^-BF_3$$

base acid salt

The ammonia molecule possesses a lone pair of electrons (on nitrogen atom) which is shared by the electron deficient BF_3 molecule. For this reaction, the NH_3 molecule donates an electron pair. Therefore it is a base. The BF_3 molecule, accepting an electron pair from NH_3, behaves as an acid.

13.2 Acidity, Alkalinity and Neutralization

An acid which is capable of losing a proton readily is called a strong acid; an acid which loses a proton with difficulty is called a weak acid. A strong acid has a weak conjugate base and a strong base has a weak conjugate acid.

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

For this reaction HCl(aq), which loses a proton with ease, is a strong acid and Cl^- (aq) is a weak base.

Nitric acid HNO_3, in aqueous solution, behaves as a strong acid and its conjugate base NO_3^- is a weak base.

$$HNO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_3^-(aq)$$

Ethanoic acid CH_3COOH, losing a proton with difficulty, is a weak acid, but its conjugate base ethanoate ion CH_3COO^- is a strong base.

$$CH_3COOH(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

When used with reference to acids and bases, the terms "strong" and "concentrated" denote quite distinct meanings.

A strong acid is one which is highly ionized in specified conditions. For example, in dilute solution, hydrochloric acid and sulphuric acid are strong. Under this condition, both dissociate completely (almost 100 %) into their ions.

A concentrated acid is one which contains the pure acid or a predominantly large proportion of the acid.

A weak acid is one which loses a proton with difficulty and is only slightly ionized.

A dilute acid is one which contains a relatively small amount of the acid in the form of a solution in water or some other solvent.An example of concentrated, weak acid is ethanoic acid (or glacial acetic acid). The percentage of water in it is very small and the acid loses its proton with difficulty. These terms can also be applied to bases.

The ionic dissociation of water

An acidic solution contains hydrogen ions, H^+ (actually hydroxonium ions, H_3O^+). A basic solution contains hydroxide ions, OH^- . The question is : "Are these ions present in pure neutral water? The answer is that they are present, in equal but very small concentration.

The means by which it has been found that pure water contains hydroxonium ions and hydroxide ions as the measurement of electrical conductivity of water. If pure water contained no ions, its electrical conductivity would be zero.

Water is purified by distilling it over and over again. The progress of the purification can be followed by measurement of the electrical conductance of the water. The electrical conductance will be found to fall gradually to a very low value, which cannot be further reduced. This constant electrical conductance is considered to be that of water itself. This is also considered to be the result of an ionization which is represented as

$$H_2O(1) \rightleftharpoons H^+(aq) + OH^-(aq)$$

or

$$2H_2O(1) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

A molecule, such as the water molecule, which can have both proton-accepting (protophilic) and proton-donating (protogenic) properties, is called an amphiprotic molecule. To write an equilibrium expression for the above reaction the upper simpler equation is generally used, except for special cases when the latter is written.

By the application of the equilibrium law,

$$K=\frac{[H^+][OH^-]}{[H_2O]}$$ the square brackets denote the concentrations in mol dm^{-3}

Since water ionizes to a very slight extent, the equilibrium concentration of undissociated water does not differ appreciably from the original concentration. In which case $[H_2O]$ may be considered constant and is incorporated in the equilibrium constant. The equation can now be written as

$$K[H_2O] = [H^+][OH^-]$$

or

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

The very small electrical conductance of pure water corresponds to the very small concentrations of hydrogen ion H^+, and hydroxide ion OH^-. Both ions have equal concentrations, each being 1×10^{-7} mol dm^{-3} at the temperature 298 K.

$$[H^+] = [OH^-] = 1 \times 10^{-7} \text{mol dm}^{-3} \text{ at } 298K$$

From these figures, the product of the concentration of hydrogen and hydroxide ions is given by

$$\begin{aligned} K_w &= [H^+][OH^-] \qquad \text{at } 298\text{ K} \\ &= \{(1 \times 10^{-7})\text{ mol dm}^{-3}\}\{(1 \times 10^{-7})\text{ mol dm}^{-3}\} \\ &= 1 \times 10^{-14}\text{ mol}^2\text{ dm}^{-6} \end{aligned}$$

This quantity, K_w is called the ionic product of water. This constant is always maintained unchanged in an aqueous solution at 298 K.

In pure water at 298 K, the concentrations of H^+ and OH^- ions are equal, both being 1×10^{-7} mol dm^{-3}.

A neutral aqueous solution is one in which the concentrations of hydrogen ion H^+ and hydroxide ion OH^- are equal at the value of 1×10^{-7} mol dm^{-3} at 298K.

At any other temperature, K_w will have a different value.

However, at 298 K the value of K_w is maintained at 1×10^{-14}. Any variation in the concentration of one of the ions must be balanced by a change in the concentration of the other ion.

For example, suppose hydrochloric acid is added to pure water until, the concentration of HCl is 10^{-3} mol dm^{-3}. At this concentration hydrochloric acid is considered to be completely dissociated. Therefore the concentration of hydrogen ion contributed by the hydrochloric acid is 10^{-3}mol dm^{-3} ($[H^+] = 10^{-3}$ M).Compared to this, the hydrogen ion concentration contributed by the dissociation of water is negligible. The hydrogen ions H^+ participate in the equilibrium of water.

$$[H^+][OH^-] = K_w = 1 \times 10^{-14}\text{mol}^2\text{dm}^{-6}$$

Consequently $[OH^-]$ falls to 10^{-14} mol dm^{-3}. The ionic product of water K_w is still maintained, but by an unequal concentration of H^+ and OH^- ions.

Similarly, suppose sodium hydroxide is added to pure water until the concentration of NaOH is 10^{-3} mol dm^{-3}. At this concentration sodium hydroxide is considered to be completely dissociated. Therefore the concentration of hydroxide ion is 10^{-3}mol dm^{-3}. ($[OH^-] = 10^{-3}$ M).(The $[OH^-]$ ions contributed by the dissociation of water is neglected.)

$K_w = 1 \times 10^{-14}$ is still maintained by a fall of H^+ concentration to 10^{-11} mol dm^{-3}.

From the above examples, it is important to note that

(1) whatever the concentration of H^+ may be, there is enough OH^- concentration to satisfy the requirement

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}.$$

(2) whatever the concentration of OH^- may be, there is enough H^+ concentration to satisfy this requirement

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}.$$

The hydroxide ion OH^- is a very strong base. The equilibrium position of its proton-accepting reaction

$$OH^- + H^+ \rightleftharpoons H_2O$$

or $OH^- + H_3O^+ \rightleftharpoons 2H_2O$ lies far to the right.

For practical purposes this reaction is considered to be irreversible. This reaction is the very familiar phenomenon of acid-alkali neutralization.

The hydrogen ion exponent (pH)

Instead of saying that the concentration of hydrogen ion in pure water is 1×10^{-7} mol dm^{-3}, it is customary to say that the pH of pure water is 7. This symbol, pH is defined as the negative logarithm to base 10 of the molar concentration hydrogen ions.

$$pH = -\log [H_3O^+ (aq)]$$

or simply $pH = -\log [H^+]$

Another useful way of remembering the relation is

$$[H^+] = 10^{-pH} = \text{antilog}(-pH)$$

Example 1 What is the pH of a solution with $[H^+] = 0.02$ mol dm^{-3}?

$$[H^+] = 0.02 \text{ mol dm}^{-3}$$

$$-\log [H^+] = -(\bar{2}.301)$$

$$= 2 - 0.301$$

$$\therefore pH = 1.699$$

Example 2 What is the hydrogen ion concentration of a solution with pH 4.30?

$$\begin{aligned}
\text{pH} &= 4.30 \\
-\log[\text{H}^+] &= 4.30 \\
\log[\text{H}^+] &= -4.30 \\
&= -4-0.30 \\
&= -4-1+1-0.30 \\
&= \bar{5}.70 \\
\therefore\ [\text{H}^+] &= \text{antilog}\ \bar{5}.70 \\
&= 5 \times 10^{-5}\ \text{mol dm}^{-3}
\end{aligned}$$

Water neutrality: The term water neutrality refers to the situation in pure water at 298 K.The pH of pure water is 7 i.e., a neutral aqueous solution at 298 K has a pH of 7.

Acid solutions: Consider a solution containing 0.001 M in HCl. At this concentration, HCl is considered to be completely dissociated and may be expressed as

$$\text{HCl} \longrightarrow \text{H}^+ + \text{Cl}^-$$

or $$\text{HCl} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$$

Therefore, the concentration of hydrogen ion is represented as $[\text{H}^+] = 10^{-3}$ mol dm^{-3}.

From this the pH of the solution is 3.

Similarly it can be shown that all other acidic solutions have pH less than 7.

Alkaline solutions: Although alkalinity is associated with hydroxide ion OH^- aqueous solution always shows the relation.

$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$$

In aqueous solutions at 298 K,

$$\begin{aligned}
[\text{H}^+][\text{OH}^-] &= 1 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6} \\
\log[\text{H}^+] + \log[\text{OH}^-] &= \log 1 \times 10^{-14} \\
\text{or} \quad -\log[\text{H}^+] + \{-\log[\text{OH}^-]\} &= -\log 10^{-14} \\
\text{pH} + \text{pOH} &= -\overline{14}.00 \\
&= 14
\end{aligned}$$

From this, it follows that pH + pOH=14. Therefore pOH is always related to pH in the same solution by the relation pH + pOH=14. For this reason, it is quite convenient to state both acidity and alkalinity in terms of pH.

Consider a solution containing 0.001 M in NaOH. If the NaOH is completely dissociated, the concentration of hydroxide ion $[OH^-] = 10^{-3}$ mol dm^{-3}. From this the pOH is 3 and the pH $= 14 - 3 = 11$ for this solution. It can also be shown that all other alkaline solutions have pH greater than 7.

Basicity: The basicity of an acid may be defined as the number of H^+ ions that one molecule of an acid can produce. The basicity of an acid consequently may be measured by the amount in moles of NaOH which will react with 1 mole of acid.

For example hydrochloric acid is said to be a monobasic acid or its basicity is one, because each molecule can give only one H^+ ion and neutralize one molecule of NaOH.

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

Sulphuric acid is dibasic or its basicity is two, since each molecule can provide two H^+ ions.

$$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

Acidity: The acidity of a base may be defined as being equivalent to the number of molecules of a monobasic acid, like HCl which will neutralize one molecule of the base, e.g., one molecule of NaOH neutralizes one molecule of HCl and therefore has an acidity of one. Na_2CO_3 neutralizes two molecules of HCl and therefore has an acidity of two.

13.3 Strength of Acids

It has been mentioned that a strong acid is one which readily loses a proton and is completely ionized in dilute aqueous solutions. A weak acid is one which loses a proton with more difficulty and is only slightly ionized.

The most common strong acids are the three mineral acids, hydrochloric, sulphuric and nitric acids. Hydrobromic acid and perchloric acid are also strong acids.

Ethanoic, ethanedioic, tartaric, citric and other organic acids are weak acids.

The division between strong and weak is not definite. Certain acids (like sulphurous acid H_2SO_3) which are moderately dissociated in aqueous solution, cannot be classified definitely as either a strong or a weak acid.

Method for comparing strength of acids

The formulation of acid-base theory in terms of an equilibrium suggests a way of measuring the strength of an acid.

In aqueous solution of acid **HA**, the equilibrium is written as:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

The equilibrium constant for this reaction is the dissociation constant for the acid, K_a, where

$$K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

The water is not included in the equilibrium expression as it is in such great excess that the concentration of water does not change significantly with changes in the concentrations of other species.

The dissociation constant of a weak electrolyte is sometimes expressed on a logarithmic scale, which for an acid is denoted by the relation $pK_a = -\log K_a$, and for a base, by $pK_b = -\log K_b$. The advantage of this scale is that the rather clumsy numbers are converted to relatively simple ones.

For example, for ethanoic acid $K_a = 1.99 \times 10^{-5}$ mol dm $^{-3}$

$$\begin{aligned} \log K_a &= \bar{5}.2989 \\ &= -5 + 0.2989 \\ &= -4.7011 \\ pK_a &= -\log K_a = 4.7011 \approx 4.7 \end{aligned}$$

Some typical dissociation constants for acids are given in Table 13.1.

Table 13.1 Some dissociation constants of acids at 298 K

Acids	K_a(mol dm^{-3})	pK_a
Hydrogensulphate ion	1.2×10^{-2}	1.9
Chloroethanoic acid	1.4×10^{-3}	2.9
Methanoic acid	1.8×10^{-4}	3.8
Ethanoic acid	1.8×10^{-5}	4.7
Hydrogen cyanide	4.8×10^{-10}	9.3

Small K_a values (corresponding to large pK_a values) indicate weak acids. Similar terms for bases, K_b and pK_b may be used to give an indication of their comparative strengths.

13.4 Salt Hydrolysis

Hydrolysis (which means cleavage by water) is traditionally treated as a separate, distinct phenomenon, but it is an aspect of acid-base equilibrium.

The following discussion will show that salt hydrolysis is appreciable except when the salt is derived from a strong acid and a strong base. There are four possible cases.

Salts are strong electrolytes and can be considered completely dissociated in aqueous solution.

Salt of a strong acid and a strong base

Consider the solution of salt, sodium chloride which is derived from strong acid, hydrochloric acid and the strong base, sodium hydroxide. It dissociates completely into sodium ion (Na^+) and chloride ion (Cl^-) which may be represented as

$$NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$$

and for water $$H_2O(l) \rightleftharpoons OH^-(aq) + H^+(aq)$$

Aqueous solution of NaCl contains four ions, Na^+, Cl^-, H^+ and OH^-. The cation of the salt, Na^+, is such a weak acid that it does not react appreciably with water. The anion of the salt, Cl^-, is such a weak base that it does not react appreciably with water. Sodium chloride solution is neutral because neither ion of such a salt reacts to disturb the equilibrium of water.

Salt of a weak acid and a strong base

The salt, sodium ethanoate is taken as an example. This salt is obtained from ethanoic acid (a weak acid) and sodium hydroxide (a strong base). In sodium ethanoate solution, the equilibria are represented as

$$CH_3COONa\ (aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The aqueous ethanoate (CH_3COO^- (aq)) ion reacts with H_2O to form ethanoic acid and hydroxide ion (OH^-) as follows:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

Since sodium hydroxide is a strong base, it can be considered to be completely dissociated into sodium and hydroxide ions. The NaOH molecule does not exist as such in aqueous solution. Ethanoic acid, being a weak acid, it can exist as undissociated molecules in aqueous solution as shown above. The H^+ ions from water are used up by CH_3COO^- ions to form undissociated CH_3COOH. This disturbs the equilibrium of water ($[H^+][OH^-]$)=K_w= $1\times10^{-14}mol^2dm^{-6}$ at 298K). More water ionizes to maintain K_w constant. This produces more $[OH^-]$ which causes the solution to be alkaline. A solution of a salt derived from a weak acid and a strong base always contains undissociated molecules of the weak acid and the resulting solution is alkaline.

Salts of a strong acid and a weak base

A salt, like ammonium chloride, is derived from the strong acid, hydrochloric acid and the weak base, ammonium hydroxide. The equilibria in ammonium chloride solution are represented as

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

$$H_2O(l) \rightleftharpoons OH^-(aq) + H^+(aq)$$

$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H^+_{(aq)}$$

Ammonium chloride (NH_4Cl), like, all other strong electrolytes, can be considered as completely dissociated. As explained above, hydrochloric acid is a strong acid, and in aqueous solution does not exist as HCl molecules. Ammonium hydroxide is a weak base so that the NH_4OH molecules are formed by using OH^- ions from water. This disturbs the ionic equilibrium of water.($[H^+][OH^-]$= K_w=1×10^{-14} $mol^2 dm^{-6}$ at 298 K.) To restore K_w, water ionizes further. This produces more H^+ which causes the solution to be acidic. A solution of salt from a strong acid and a weak base always contains undissociated molecules of the base and the resulting solution is acidic.

Salt of a weak acid and a weak base

Ammonium ethanoate is obtained from a weak base, ammonium hydroxide and the weak acid, ethanoic acid. The equilibria in this type of solution are represented as

$$CH_3COONH_4(aq) \longrightarrow CH_3COO^-(aq) + NH_4^+(aq)$$

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H^+_{(aq)}$$

Since the acid and base are both weak, undissociated molecules of both must be formed by using H^+ and OH^- ions derived from water. This disturbs the ionic equilibrium of water ($[H^+][OH^-]$=K_w=$1\times10^{-14}mol^2 dm^{-6}$at 298 K). In this particular case both acid and base are equally weak ($K_a \approx K_b \approx 2 \times 10^{-5}$). So the H^+ and OH^-

concentrations are maintained at about equal concentrations in the solution in spite of the hydrolysis. Ammonium ethanoate is strongly hydrolysed in solution, but the solution remains almost neutral.

In general, if the acid from which the salt is obtained is stronger than the base, the solution tends to be acidic or vice versa.

13.5 Buffer Solution

A buffer solution is defined as a solution that **resists changes in pH as a result of** (1) dilution (2) small addition of acids or bases.

The most effective buffer solution contains fairly large and approximately equal concentrations of a weak acid and its conjugate base.

A typical buffer solution for acidic values of pH, (e.g, pH 4 – 7) contains a weak acid and its sodium salt. A mixture of ethanoic acid and sodium ethanoate is commonly used.

The salt, sodium ethanoate, provides a large reserve of ethanoate ion. The weak acid, ethanoic acid, provides a large potential reserve of hydrogen ion, which can be obtained by ionizing as required.

Sodium ethanoate, being a salt, dissociates into Na^+ (aq) and CH_3COO^- (aq).

$$CH_3COONa(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$

and ethanoic acid gives rise to the equilibrium.

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

If a small amount of strong acid is added to this buffer solution, the hydrogen ions react with the base CH_3COO^- to form undissociated ethanoic acid. This prevents a change in pH of the solution.

$$CH_3COO^-_{(aq)} + H^+_{(aq)} \rightleftharpoons CH_3COOH_{(aq)}$$

If a small amount of strong base like NaOH is added, the hydroxide ions react with the undissociated weak acid, to form the conjugate base CH_3COO^- and undissociated water. Change of pH is therefore resisted.

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$$

A buffer solution of pH 7-11 can be prepared with a weak base and its conjugate acid. A mixture of ammonium hydroxide and ammonium chloride is usually used. The salt provides a large source of NH_4^+ ion, and a base potential source of OH^- ion.

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

If a small amount of strong base is added to the above solution, the OH^- ion will be used up by the formation of molecules of the weak base.

$$OH^-(aq) + NH_4^+(aq) \rightleftharpoons NH_4OH(aq)$$

If a small amount of strong acid is added to the above solution, the H^+ ion will be used up by the OH^- ion from the base, which then ionizes to restore the original situation almost exactly.

$$H^+_{(aq)} + NH_4OH_{(aq)} \longrightarrow NH^+_{4(aq)} + H_2O_{(l)}$$

Example Calculate the pH of a buffer solution containing 0.01 mol of ethanoic acid ($K_a = 1.8 \times 10^{-5}$) and 0.1 mol of sodium ethanoate per dm^3.

$$[CH_3COOH] = \frac{0.01mol}{1dm^3} = 0.01M$$

$$[CH_3COONa] = \frac{0.1mol}{1dm^3} = 0.1M$$

Sodium ethanoate is completely dissociated.

CH_3COONa (aq) $\longrightarrow$	CH_3COO^- (aq)	+	Na^+ (aq)
1 mol	1 mol		1 mol
0.1 M	0.1 M		0.1 M

$$[CH_3COO^-] = 0.1\ M$$

$$CH_3COOH\ (aq) \rightleftharpoons CH_3COO^-\ (aq) + H^+\ (aq)$$

$$Ka = \frac{[CH_3COO^-_{aq}][H^+_{aq}]}{[CH_3COOH(aq)]}$$

$$[H^+] = Ka \times \frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$= 1.8 \times 10^{-5} \times \frac{0.01}{0.1}$$

$$[H^+] = 1.8 \times 10^{-6}\ M$$

$$pH = -\log [H^+]$$

$$= -\log (1.8 \times 10^{-6})$$

$$= -\log 1.8 - \log 10^{-6}$$

$$= -0.2553 + 6$$

$$= 5.7447$$

Other buffer solutions may be prepared by using, citric acid and its sodium salt, sodium carbonate and sodium hydrogencarbonate, the two sodium phosphates Na_2HPO_4 and NaH_2PO_4.

SUMMARY

This chapter deals with acids, bases, and their neutralization. It covers the understanding of the development of acid-base theory, acidity, alkalinity, neutralization, pH , pOH, strength of acids and bases , hydrolysis of salts and buffer solution. Exercises are given to solve the problems on pH and buffer solutions.

Questions and Problems

1. When hydrogen chloride gas is dissolved in water, an equilibrium is represented by

$$\underset{\text{I}}{HCl(g)} + \underset{\text{II}}{H_2O(l)} \rightleftharpoons \underset{\text{III}}{H_3O^+(aq)} + \underset{\text{IV}}{Cl^-(aq)}$$

Using the Roman numerals shown below each formula, which of these combinations represents to two bases? (a) I and III (b) I and IV (c) II and III (d) II and IV (e) III and IV

2. Which of the following facts is true?
   A weak acid is best described as
   (a) a dilute acid
   (b) an acid that is harmless
   (c) an acid that does not easily donate protons
   (d) an acid that reacts with very few other substances
   (e) an acid that easily donates protons
3. What is meant by
   (a) a neutral aqueous solution?
   (b) pH of an aqueous solution?
   (c) neutralization in aqueous solution?
4. Calculate the pH of the following solutions.
   (a) 0.01 M HCl (b) 0.001 M KOH
   (c) an aqueous solution containing 7.3 g of HCl per dm^3
   (d) an aqueous solution containing 4g of NaOH per dm^3
5. Calculate the hydrogen ion concentration of the solutions having pH values of
   (a) 5.5 (b) 7 and (c) 8.7
6. (a) Explain the terms "strong" and "weak" as applied to acids.
   (b) What are the characteristic properties of an acid?
7. Describe one method by which the strength of two acids can be compared.

8. (a) What do you understand by the term hydrolysis?

(b) What are the properties of the solutions obtained by dissolving the following salts in water?

(i) Sodium ethanoate (iii) Ammonium nitrate
(ii) Potassium chloride (iv) Ammonium methanoate

9. Some ammonium chloride was dissolved in water and the solution had a pH of 5. Explain this result clearly.

10. Would the pH of a solution of sodium ethanoate be greater or less than 7? Give an explanation for this.

11. (a) What is meant by a buffer solution?

(b) Mention appropriate buffer solutions for

(i) moderately acidic conditions (ii) moderately alkaline conditions.

12. Calculate the pH of a buffer solution containing 0.01 mol of methanoic acid ($pK_a = 3.8$) and 0.1 mol of sodium methanoate per dm^3.

13. Write TRUE or FALSE for each of the following.

(a) A weak acid is formed by the addition of a large amount of water into a strong acid.

(b) Strength of acid can be measured in term of pK_a.

(c) Acid defined by Arrhenius is more common than that of Bronsted and Lowry.

(d) All salts are neutral.

14. Fill in the blanks with a suitable word or phrase or numerical value with unit as necessary.

(a) The hydrogensulphate ion is still acidic because it has a replaceable ....

(b) According to lewis an acid is an acceptor of ....

(c) A buffer solution resists the change of.................

(d) Strength of an acid may be indicated by the value of.............

15. Select the correct term or terms given in the brackets.

(a)

Acids	pKa
HSO_4^-	1.9
HCOOH	3.8
HCN	9.3

(HSO_4^-, HCOOH, HCN) has the highest strength.

(b) A base is an acceptor of (lone pair of electrons, protons, H^+ ions.)

(c) The presence of lone pair electrons is the characteristic of (an acid, a base, a salt).

(d) The purity of water may be indicated by (conductivity, K_a, K_b).

(e) Water is (protophilic, protogenic, amphiprotic).

16. Match each of the items given in List A with the appropriate item in List B.

List A	List B
(a) Acid by Arrhenius	(i) Neutral solution
(b) Acid-Base by Bronsted and lowry	(ii) An acid
(c) Acid - Base by lewis	(iii) proton transfer
(d) $pH < 7$	(iv) transfer of lone pair electrons
(e) $pH = 7$	(v) H^+ ion

17. Alongside the names of various chemicals are shown their respective pH values in aqueous solutions.

Potassium hydroxide	pH 13
Hydrogen bromide	pH 2
Calcium hydroxide	pH 11
Sodium chloride	pH 7
Hydrogen chloride	pH 2
Magnesium hydroxide	pH 10
Ethanoic acid	pH 4

Which of these substances is/are :

(a) a strong acid?

(b) a weak acid?

(c) a strong alkali?

(d) a weak alkali?

(e) a neutral substance?

In each case write a chemical equation to show the molecule/ions present in solution.

18. Write a chemical equation to represent the neutralisation of sulphuric acid by sodium hydroxide. Reduce this to the ionic equation. Account for any difference you see between the ionic equation you have written and that shown above for the reaction between hydrochloric acid and sodium hydroxide.

19. Complete the word equations, and write balanced chemical equations for the following soluble salt preparations :

(a) calcium carbonate + hydrochloric acid $\longrightarrow$?

(b) zinc oxide + hydrochloric acid $\longrightarrow$?

(c) potassium hydroxide + nitric acid $\longrightarrow$?

Also write ionic equations for each of the reactions.

****

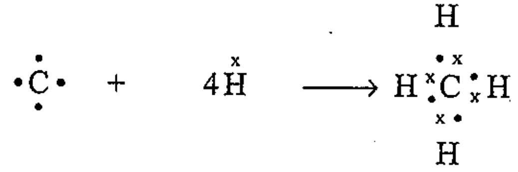
CHAPTER 14
ORGANIC CHEMISTRY

Organic chemistry, at one time, was defined as the chemistry of carbon compounds derived from living things, both animal and vegetable. In modern terms, however organic chemistry is the chemistry of carbon compounds in which there is at least one carbon to carbon bond or carbon to hydrogen bond. The elements carbon and hydrogen combine to form an unlimited number of different compounds. Furthermore, the elements oxygen, nitrogen, sulphur and the halogens form strong covalent bonds to carbon, making the number and variety of possible organic compounds almost limitless. Some idea of the work being done in the area of this subject may be obtained from the fact that every year some 100,000 new organic compounds are being discovered or prepared.

The elements which are commonly part of organic compounds are all located in the upper right corner of the periodic table. They are all non-metals and the bonds between atoms of this part of the periodic table are essentially covalent.

The carbon atom has four valence electrons represented as $\bullet\overset{\bullet}{\underset{\bullet}{C}}\bullet$.

In order to complete its octet, this carbon atom must share a total of four electron pairs. The bonding between carbon and hydrogen in the simplest organic compound, methane, may be given as an example.



$$\bullet\overset{\bullet}{\underset{\bullet}{C}}\bullet \quad + \quad 4\overset{\times}{H} \quad \longrightarrow \quad \begin{array}{c} H \\ H\,{}^{\times}_{\bullet}\overset{\bullet\times}{\underset{\times\bullet}{C}}{}^{\bullet}_{\times}\,H \\ H \end{array}$$

In the case of carbon, the driving force for the union with hydrogen is the tendency to complete its octet and so acquire the stable electronic structure of neon. With hydrogen, the tendency is to acquire one more electron and so obtain the stable electronic structure of helium.

In organic compounds, each carbon atom forms a total of four bonds with other atoms. The total bond order of carbon is, therefore, four. The bond order of hydrogen is one.

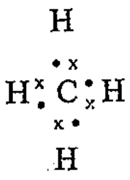
Table 14.1 Bond orders in organic compounds

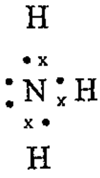
Element	*Symbol with valence electrons*	*Number of electrons required to complete octet (or stable electronic structure)*	*Total bond order (or valence)*
Carbon	$\overset{\bullet}{\underset{\bullet}{\bullet C \bullet}}$	4	4
Hydrogen	$H^{\bullet}$	1	1
Oxygen	$\overset{\bullet\bullet}{\underset{\bullet\bullet}{\bullet O \bullet}}$	2	2
Nitrogen	$\overset{\bullet}{\underset{\bullet}{:N \bullet}}$	3	3
Sulphur	$\overset{\bullet\bullet}{\underset{\bullet\bullet}{\bullet S \bullet}}$	2	2
Halogen	$\overset{\bullet\bullet}{\underset{\bullet\bullet}{:X \bullet}}$	1	1
Phosphorus	$\overset{\bullet}{\underset{\bullet}{:P \bullet}}$	3	3

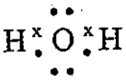
Example Write an electron dot structure for each of the following:

(a) CH_4 (b) NH_3 (c) H_2O

The sharing of electrons in each of the molecules may be written as :

(a) 

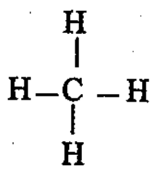
(b) 

(c) 

14.1 Graphic or Structural Formulae

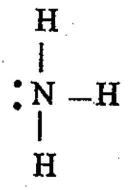
We have learned in the above discussion that each pair of electron shared between two atoms is equivalent to a bond order of one. Hence, in writing the **graphic** or **structural formula** for a compound each shared electron pair is represented by a line between the symbols of the elements.

The structural formulae for the compounds discussed in the preceding example may then be written as follows:



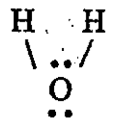
$H-\overset{H}{\underset{H}{C}}-H$

methane

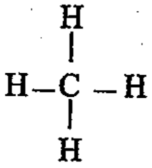


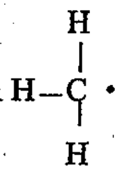
$:\overset{H}{\underset{H}{N}}-H$

ammonia



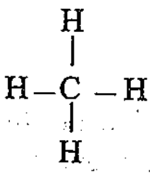
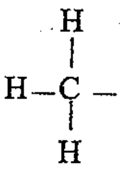
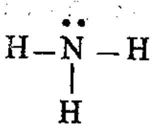
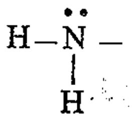
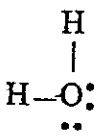
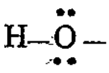
water

The structure for methane is  $H-\overset{H}{\underset{H}{C}}-H$

Each bond (represented by a line) linking the carbon to a hydrogen atom consists of a pair of electrons. If we remove one hydrogen atom together with one of the bonding electrons from the methane molecule we would be left with  $H-\overset{H}{\underset{H}{C}}\cdot$ or $CH_3\cdot$ which is called a methyl radical.

The group of atoms comprising the methyl radical is referred to simply as a methyl group (CH_3—). It is obvious that the methyl group has a bond order or valence of one. The methyl group is derived from methane.

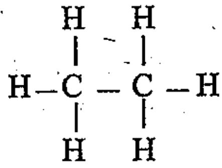
Other examples of derived groups are the following :

Molecule	*Structure*	*Derived group*	*Name of derived group*
Methane	 $H-\overset{H}{\underset{H}{C}}-H$ or CH_4	 $H-\overset{H}{\underset{H}{C}}-$ or CH_3—	methyl
Ammonia	 $H-\ddot{N}-H$ with H below, or $\ddot{N}H_3$	 $H-\underset{H}{\ddot{N}}-$ or NH_2—	amino
water	 $H-\overset{H}{\underset{\cdot\cdot}{O}}:$ or $H_2\ddot{O}$	 $H-\ddot{O}-$or HO—	hydroxyl

It is sometimes convenient to consider organic molecules as being built up of such derived groups.

Example: Write graphic formulae for the following : (a) Ethane C_2H_6 (b) Propane C_3H_8 (c) Ethanol C_2H_6O (The ethanol molecule contains a hydroxyl group) (d) Methanal or formaldehyde CH_2O (e) Methanoic acid or formic acid CH_2O_2.
In writing graphic formulae for organic compounds we must always remember that carbon has a bond order or valence of four.

(a)



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

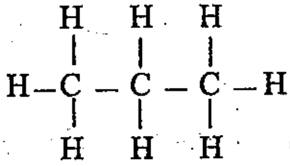
or CH_3-CH_3

or C_2H_6

ethane

Ethane may be considered as consisting of two methyl groups linked together. Removal of one hydrogen atom from ethane would give CH_3CH_2— or C_2H_5— which is an ethyl group.

(b)



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

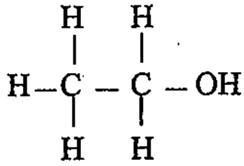
or CH_3-CH_2—CH_3

or C_3H_8

propane

The linkage of an ethyl group with a methyl group would give propane.

(c)



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & OH \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

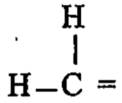
or CH_3 CH_2—OH

or C_2H_6O

ethanol

Ethanol consists of a hydroxyl group which is linked to an ethyl group.

(d)



$$\begin{array}{cccc} & & H & \\ & & | & \\ H & - & C & = \end{array}$$

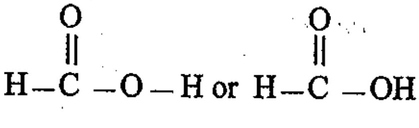
or HCHO

or CH_2O

methanal or formaldehyde

Note that the valences of carbon, oxygen and hydrogen which are respectively 4, 2 and 1 are all satisfied.

(e)



$H-\overset{\overset{O}{\|}}{C}-O-H$ or $H-\overset{\overset{O}{\|}}{C}-OH$

or CH_2O_2

methanoic acid or formic acid

This graphic structure of methanoic acid satisfies the valences of carbon, oxygen and hydrogen.

14.2 Alkanes

This class of compounds is sometimes referred to as the "saturated hydrocarbons". They are represented by the general formula C_nH_{2n+2}. The simplest member is methane CH_4, followed by ethane $CH_3\,CH_3$ (or C_2H_6) and propane $CH_3.CH_2.CH_3$ (or C_3H_8), to mention three of the lowest members. We may consider ethane as being derived from methane. If one hydrogen atom from methane is removed and a methyl group substituted in its place, the result is ethane.

$$CH_4 \xrightarrow{-H} CH_3- \xrightarrow{\overset{|}{+(CH_3)}} CH_3\text{-}CH_3$$

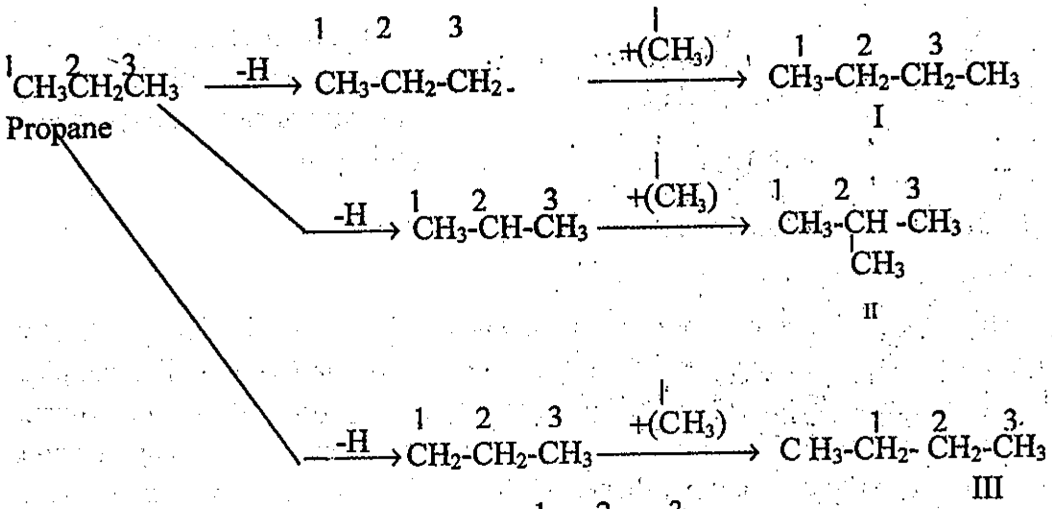
We may substitute any hydrogen atom in methane, CH_4, with a methyl group and still get ethane $CH_3.CH_3$.

Propane may similarly be considered as derived frpm ethane by substituting a hydrogen atom in it with a methyl group.

$$CH_3\text{-}CH_3 \xrightarrow{-H} CH_3CH_2- \xrightarrow{+(CH_3)} CH_3CH_2\,CH_3$$

The replacement of any hydrogen atom in ethane by a methyl group would result in the same compound propane, $CH_3CH_2CH_3$.

Let us continue this process of substitution with propane and examine the results we get. For convenience, we shall label the carbon atoms in propane with the superscripts 1, 2 and 3.



Note that there is no difference between $\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_2-CH_3$ (I) and $CH_3-\overset{1}{CH_2}-\overset{2}{CH_2}-\overset{3}{CH_3}$ (III). They represent one and the same compound. This compound, $CH_3CH_2CH_2CH_3$ is called normal butane (n-butane) and the compound $\overset{1}{CH_3}-\underset{CH_3}{\overset{2}{C}H}-\overset{3}{CH_3}$ (II) is different form n-butane, and is called iso-butane.

Normal butane and iso-butane both have the same molecular formula C_4H_{10}, but they have different structural formulae and hence different properties.

Compounds having the same molecular formula but different structural formulae have different physical and chemical properties and are said to be **structural isomers.** The phenomenon is known as **structural isomerism.**

Alkyl radicals or groups

The radicals derived from alkanes are called alkyl radicals. For instance, methyl CH_3-, ethyl CH_3CH_2-, propyl $CH_3CH_2CH_2$- and butyl $CH_3CH_2CH_2CH_2$- radicals or groups are derived from the corresponding alkanes by removal of an H atom and are called alkyl radicals or groups.

Alkyl groups are represented generally as R—, where $R = C_nH_{2n+1}$. All alkyl groups have a bond order or valence of one as indicated by the single horizontal line following R.

Nomenclature of alkane

Three different naming systems are currently in use.

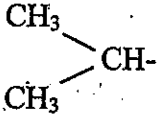
The Trivial System : In the Trivial system, the alkanes are simply called by the names which have become established through common usage. For instance, methane, ethane, propane and butane are the trivial names for alkanes with 1,2,3 and 4 carbon atoms respectively.

Alkanes as derivatives of methane: This system uses the trivial system partly and considers the alkanes as alkyl substituted methane.

It is interesting to make a comparison of the two naming systems so far discussed.

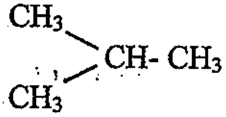
The Trivial System

According to the Trivial System, this compound is called iso-butane. The prefix **iso**-is used whenever the group



$(CH_3)_2CH-$ or $(CH_3)_2$ CH- is present

There are four carbon atoms in the molecule, hence, the name iso-butane.



$(CH_3)_2CH-CH_3$

$(CH_3)_2$ CH CH_3

or

$(CH_3)_3CH$

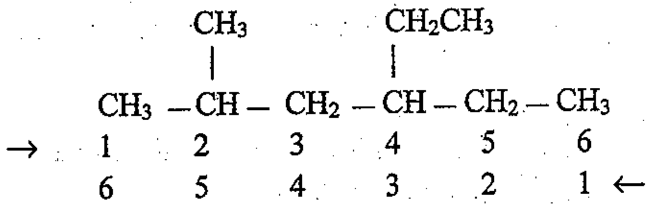
Naming as derivative of methane

According to the system of naming alkanes as derivatives of methane, this compound is called trimethyl methane. The name is obvious if we note that three hydrogen atoms in CH_4 are replaced by **three** methyl groups to give this compound.

Both these systems have only limited applicability and use. They break down when alkanes with complicated structures have to be named.

IUPAC (International Union of Pure and Applied Chemistry) System or Geneva System: In this system, the structure of the alkane to be named must first, be examined to determine the longest carbon chain.

1. The number of carbon atoms in the longest chain determines the name of the parent alkane.



$$\begin{array}{ccccccc} & & \text{CH}_3 & & \text{CH}_2\text{CH}_3 & & & \\ & & | & & | & & & \\ & \text{CH}_3 - & \text{CH} - & \text{CH}_2 - & \text{CH} - & \text{CH}_2 - & \text{CH}_3 & \\ \rightarrow & 1 & 2 & 3 & 4 & 5 & 6 & \\ & 6 & 5 & 4 & 3 & 2 & 1 & \leftarrow \end{array}$$

The alkane shown above has six carbon atoms in the longest chain. The parent hydrocarbon is, therefore, hexane.

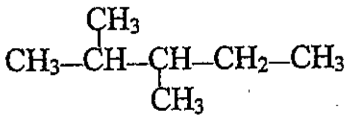
2. In the next step, each carbon atom in the selected long chain must be numbered with consecutive numbers starting with 1; The end of the chain to be numbered 1 must be that end nearer to those carbon atoms which have substituted groups or substitutents.

In the given example, if we number the longest chain from left to right, the methyl substituents fall on carbons numbered 2 and 4. If the chain is numbered from right to left, the same methyl substituents fall on carbons numbered 3 and 5. We must therefore number this particular carbon chain from left to right since 2 and 4 are smaller numbers than 3 and 5.

3. The alkane can now be named by writing for each substituent: the number of the carbon atom carrying the substituent, the name of the substituent and finally the name of the parent hydrocarbon.

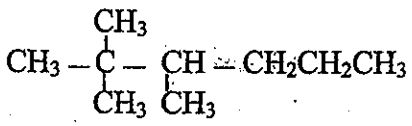
The compound given as an example then takes the name 2-methyl-4-ethyl hexane.

The compounds given below are named according to the IUPAC or Geneva System. Examine the structures and the names to familiarize yourself with this system.

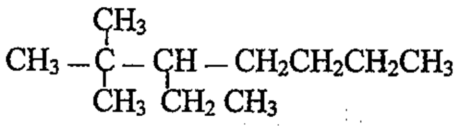


$$\begin{array}{ccccc} & \text{CH}_3 & & & \\ & | & & & \\ \text{CH}_3- & \text{CH}- & \text{CH}- & \text{CH}_2- & \text{CH}_3 \\ & & | & & \\ & & \text{CH}_3 & & \end{array}$$

2,3-dimethyl pentane
(The longest carbon chain has five atoms. We do not say 2-methyl-3-methyl pentane. Instead of repeating methyl twice, we mention their positions, 2 and 3, and write di-to indicate the presence of two methyl groups as substituents.)



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_3}{CH}-CH_2CH_2CH_3$ 2,2,3-trimethyl hexane.



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_2\,CH_3}{CH}-CH_2CH_2CH_2CH_3$ 2,2-dimethyl-3-ethyl heptane.

Preparation of alkanes

Laboratory method of preparation

In the laboratory, alkanes are prepared by heating the sodium salt of a carboxylic acid with soda-lime. Soda-lime is a mixture of calcium oxide (lime) and sodium hydroxide.

$$\underset{\text{sodium ethanoate}}{CH_3COONa} + \underset{\text{soda-lime}}{NaOH} \longrightarrow \underset{\text{methane}}{CH_4} + Na_2CO_3$$

The reaction is generally applicable for the preparation of other alkanes.

$$\underset{\text{sodium propanoate}}{CH_3CH_2COONa} + NaOH \longrightarrow \underset{\text{ethane}}{CH_3CH_3} + Na_2CO_3$$

$$R\text{-}COONa + NaOH \longrightarrow R\text{-}H + Na_2CO_3$$

or

$$(C_nH_{2n+1})COONa + NaOH \longrightarrow C_nH_{2n+2} + Na_2CO_3$$

Other methods of preparation

Of the many other reactions which may be used for the preparation of alkanes, only two methods will be mentioned.

1. Reduction of alkyl halides

(a)

$$\underset{\text{ethyl iodide}}{CH_3CH_2I} + \underset{\text{hydrogen iodide}}{HI} \longrightarrow \underset{\text{ethane}}{CH_3CH_3} + I_2$$

$$\underset{\text{alkyl iodide}}{RI} + HI \longrightarrow \underset{\text{alkane}}{R\text{-}H} + I_2$$

(b)

$$\underset{\text{methyl iodide}}{CH_3I} + H_2 \xrightarrow{Pd} \underset{\text{methane}}{CH_4} + HI$$

$$\underset{\text{alkyl halide}}{R\text{-}X} + H_2 \xrightarrow{Pd} \underset{\text{alkane}}{R\text{-}H} + HX$$

The reduction of alkyl halides with molecular hydrogen takes place in the presence of catalysts like platinum, Pt; and palladium, Pd.

2. Reduction of alkenes

$$\underset{\text{ethene or ethylene}}{CH_2{=}CH_2} + H_2 \xrightarrow{\text{Ni, }300\,^\circ C} \underset{\text{ethane}}{CH_3.CH_3}$$

$$\underset{\text{propene or propylene}}{CH_3CH = CH_2} + H_2 \xrightarrow{\text{Ni, }300\,^\circ C} \underset{\text{propane}}{CH_3CH_2CH_3}$$

Properties of alkanes

Under ordinary conditions, the alkanes are unreactive towards acid, alkalis, oxidizing reagents and reducing reagents.

The normal alkanes from C_1 to C_4 (i.e., from methane to butane) are colourless gases, C_5 to C_{17} are colourless liquids and from C_{18} onwards they are solids. The boiling points rise fairly regularly with increasing number of carbon atoms. Other physical properties such as melting point, viscosity, refractive index also increase in the same way.

Chemical properties

As mentioned above, the alkanes are relatively inert towards other chemical reagents.

The most important chemical reactions of these saturated hydrocarbons, as the alkanes are called, is their reaction by substitution. When methane is mixed with chlorine in diffused sunlight the following stepwise reactions occur, where one chlorine atom replaces one hydrogen atom in each step.

$$\underset{\text{methane}}{CH_4} + Cl_2 \xrightarrow[\text{sunlight}]{\text{diffused}} \underset{\text{methyl chloride}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow[\text{sunlight}]{\text{diffused}} \underset{\text{methylene chloride}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow[\text{sunlight}]{\text{diffused}} \underset{\text{chloroform}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow[\text{sunlight}]{\text{diffused}} \underset{\text{carbon tetrachloride}}{CCl_4} + HCl$$

These reactions are known as chlorination reactions.Other alkanes also undergo chlorination with chlorine Chlorination may be brought about by light, heat or catalysts.

Homologous series

A series of compounds like the alkanes in which each member differs from the preceding or succeeding one by a CH_2 group is known as a homologous series. Each member of the series is known as a homologue. The members of a homologous series behave in a particular way and many properties are common to all members. Hence generalizations may be made regarding the properties of the members of a homologous series. The homologues may also be prepared by methods common to all. They are also represented by a general formula.

Name	Molecular formula	Melting point °C	Boiling point °C	Density g cm^{-3}
Methane	CH_4	-183	-182	gas
Ethane	C_2H_6	-172	-89	gas
Propane	C_3H_8	-188	-42	gas
Butane	C_4H_{10}	-135	- 1	gas
Pentane	C_5H_{12}	-130	36	0.626
Hexane	C_6H_{14}	-95	69	0.659
Heptane	C_7H_{16}	-91	98	0.684
Octane	C_8H_{18}	-57	126	0.703
Nonane	C_9H_{20}	-54	151	0.718
Decane	$C_{10}H_{22}$	-30	174	0.730

14.3 Alkenes

The alkenes of olefins, as they are often called, are another series of homologous hydro-carbons having the general formula C_nH_{2n}, where n is a number equal to or greater than 2.

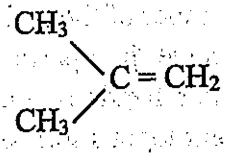
Alkene molecules contain a double bond each, commonly called ethylenic bonds.

Nomenclature of alkenes

Three different methods may be used for naming the alkenes.

The Trivial System: In this naming system, the name of the alkene is derived from the corresponding alkane by changing the suffix **-ane** of the alkane to **-ylene.** The first member of this series $CH_2{=}CH_2$ which corresponds to ethane become ethylene.

Following this naming system, C_3H_6 or $CH_3CH = CH_2$ is named propylene. C_4H_8 corresponding to the alkane, butane should then be named butylene. There are, however, three structurally isomeric butylenes.

$CH_3CH_2\overset{\beta}{C}H = \overset{\alpha}{C}H_2$; $CH_3CH = \overset{\beta}{C}H\ \overset{\alpha}{C}H_3$ and 

The positions of the double bond in the first two butylenes are indicated by using the Greek letters α, β, etc., or by using the numbers 1, 2 etc.

$CH_3CH_2CH = CH_2$ then becomes α butylene or 1-butylene

$CH_3CH{=}CH.CH_3$ then becomes β butylene or 2-butylene

The other butylene is named iso-butylene.

Naming as derivative of ethylene: There are four hydrogen atoms in ethylene. Other alkenes may be considered as alkyl substituted ethylenes.

$CH_3CH = CH_2$	methyl ethylene
$CH_3CH = CHCH_3$	symmetrical or s-dimethyl ethylene

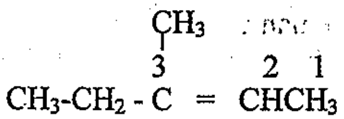
The IUPAC or Geneva System: In this system, alkanes are named after the alkanes with the same number of carbon atoms, the suffix **-ane** of the alkane being replaced by **-ene.** The first member of the series $CH_2{=}CH_2$ which corresponds to ethane is named ethene.

$CH_3CH = CH_2$	is named propene
$CH_3CH_2CH = CH_2$	1-butene
$CH_3CH = CHCH_3$	2-butene

For naming structurally more complicated molecules, the following IUPAC rules must be observed.

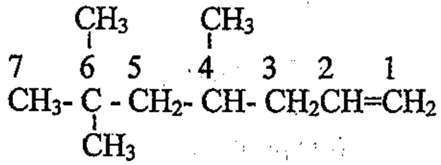
1. The longest chain in the molecule containing the double bond is selected as representing the parent compound and the alkene is named as a derivative of this compound.
2. The carbon atoms in the long chain are given consecutive numbers starting from the end nearest to the double bond. The position of the double bond is then defined using the smaller of the two numbers which represent the two double bonded carbon atoms.
3. Side chains and substituents are included in the name after properly indicating the number of the carbon atoms to which they are linked.

Example



$$\overset{\overset{CH_3}{|}}{\underset{3}{}}\;CH_3\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{\underset{}{C}}}_{3} = \overset{2\ \ 1}{CHCH_3}$$

3-methyl -2-pentene



$$\overset{7}{CH_3}\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}_{6}\text{-}\overset{5}{CH_2}\text{-}\overset{\overset{CH_3}{|}}{CH}_{4}\text{-}\overset{3}{CH_2}\overset{2}{CH}=\overset{1}{CH_2}$$

4,6,6-trimethyl 1-heptene

Preparation of alkenes

1. Dehydration of alcohols

Ethene may be prepared by the dehydration of ethanol. Two methods may be used for this dehydration.

(a) Heating with concentrated sulphuric acid at 160 °C

When ethanol is heated with concentrated sulphuric acid at 160 °C ethene is formed. The reaction which results in the loss of the elements of water occurs by two stages.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + H_2SO_4 \xrightarrow{100\ °C} \underset{\text{ethyl hydrogensulphate}}{CH_3CH_2SO_4H} + H_2O$$

$$\underset{\text{ethyl hydrogensulphate}}{CH_3CH_2SO_4H} \xrightarrow{160\,°C} \underset{\text{ethene}}{CH_2=CH_2} + H_2SO_4$$

Sulphuric acid is regenerated at the end of the dehydration reaction.
The net reaction may be summarized as follows:

$$\underset{\text{ethanol}}{CH_3CH_2OH} \xrightarrow[160\ °C]{H_2SO_4(conc)} \underset{\text{ethene}}{CH_2=CH_2} + H_2O$$

According to this understanding of the reaction, since the sulphuric acid is regenerated in the reaction mixture, we should be able to use the sulphuric acid over and over again and obtain ethene indefinitely so long as we go on adding ethanol. However, the hygroscopic sulphuric acid traps the water produced in the reaction and is diluted by it. At the same time, sulphuric acid, being an oxidizing acid, is reduced to sulphur dioxide by part of the alcohol. In this way, a stage is reached when the sulphuric acid is no longer strong enough to generate ethene.

Syrupy phosphoric acid (metaphosphoric acid, HPO_3) may be used instead of sulphuric acid. Since this acid is not hygroscopic and is not an oxidizing agent, it may be used over and over again for dehydrating ethanol.

Other alcohols are also similarly dehydrated.

$$\underset{n\text{-propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow{H_2SO_4,\ 160\ ^\circ C} \underset{\substack{\text{propene}\\ \text{(or) propylene}}}{CH_3CH=CH_2} + H_2O$$

or

$$\underset{\text{alcohol}}{RCH_2CH_2OH} \xrightarrow{H_2SO_4,160\ ^\circ C} \underset{\text{alkene}}{RCH=CH_2} + H_2O$$

(b) Passing the vapours of the alcohol over alumina, Al_2O_3, heated at 350°C.

$$\underset{\text{ethanol}}{CH_3CH_2OH} \xrightarrow{Al_2O_3,350\ ^\circ C} \underset{\substack{\text{ethene}\\ \text{(or) ethylene}}}{CH_2=CH_2} + H_2O$$

$$\underset{\text{alcohol}}{RCH_2CH_2OH} \xrightarrow{Al_2O_3,350\ ^\circ C} \underset{\text{alkene}}{RCH=CH_2} + H_2O$$

2. Dehydrohalogenation of alkyl halides

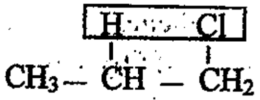
The term dehydrohalogenation is used when a halogen atom and a hydrogen atom on an adjacent carbon of the same molecule are simultaneously removed as hydrogen halide.

When ethyl chloride is heated with an alcoholic solution of potassium hydroxide on a water bath, ethene is formed.

$$\underset{\text{ethyl chloride}}{CH_3CH_2Cl} + KOH \xrightarrow[\Delta]{\text{ethanol}} \underset{\text{ethene}}{CH_2=CH_2} + KCl + H_2O$$

Similarly, the dehydrohalogenation of *n*-propyl chloride or *iso*-propyl chloride results in the formation of propene.

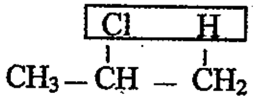
$$\underset{n\text{-propyl chloride}}{CH_3CH_2CH_2Cl} + KOH \xrightarrow[\Delta]{\text{ethanol}} \underset{\text{propene}}{CH_3CH=CH_2} + KCl + H_2O$$



$$CH_3-\overset{\boxed{H}}{\overset{|}{C}}H-\overset{\boxed{Cl}}{\overset{|}{C}}H_2$$

n-propyl chloride

$$\underset{\textit{iso}\text{-propyl chloride}}{CH_3CHCl\,CH_3} + KOH \xrightarrow[\Delta]{\text{ethanol}} \underset{\text{propene}}{CH_3CH=CH_2} + KCl + H_2O$$



$$CH_3-\overset{\boxed{Cl}}{\overset{|}{C}}H-\overset{\boxed{H}}{\overset{|}{C}}H_2$$

iso -propyl chloride

Generally,

$$\underset{n\text{-alkyl chloride}}{RCH_2CH_2X} + KOH \xrightarrow[\Delta]{\text{ethanol}} \underset{\text{alkene}}{RCH=CH_2} + KX + H_2O$$

$$\underset{\substack{\text{sec-alkyl chloride}\\ \text{(secondary alkyl chloride)}}}{RCHX\,CH_3} + KOH \xrightarrow[\Delta]{\text{ethanol}} \underset{\text{alkene}}{RCH=CH_2} + KX + H_2O$$

Properties of alkenes

Physical properties

The members containing two to four carbon atoms are gases; those containing five to fifteen are liquids; alkenes containing more than sixteen carbon atoms are solids at room temperature. They are all lighter than water in which they are insoluble. They burn in air with a luminous, smoky flame.

Chemical properties

Ethene, $CH_2 = CH_2$, under proper reaction conditions can add on one molecule (or two atoms) of hydrogen to form ethane. This reaction shows the unsaturated character of ethene which accomodates the addition of two atoms of hydrogen to become saturated as ethane. This unsaturated nature of ethene and other alkenes is shown in the reactions of alkenes.

Addition reactions

1. Addition of hydrogen (Hydrogenation)

$$\underset{\text{ethene}}{CH_2=CH_2} + H_2 \xrightarrow[\text{divided form room temp}]{\text{Pt or Pd catalyst in finely}} \underset{\text{ethane}}{CH_3CH_3}$$

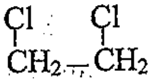
Although platinum and palladium metals in finely divided form catalyse the addition of hydrogen to ethane and other alkenes at room temperature, higher temperatures are required when nickel is used as the hydrogenating catalyst.

$$\underset{\text{alkene}}{RCH = CH_2} + H_2 \xrightarrow[\text{divided form Room temp}]{\text{Pt or Pd catalyst in finely}} \underset{\text{alkane}}{RCH_2CH_3}$$

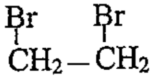
$$\underset{\text{alkene}}{RCH = CH_2} + H_2 \xrightarrow[200 - 300\ ^\circ C]{\text{Ni catalyst}} \underset{\text{alkane}}{RCH_2CH_3}$$

2. Addition of chlorine and bromine

The addition of halogen to alkenes can take place in the dark, but is accelerated by light.This reaction also takes place readily in the liquid phase, or in a solvent such as petrol or ethanol and is catalysed in solution by halide ions.



$$\underset{\text{ethene}}{CH_2 = CH_2} + Cl_2 \longrightarrow \underset{\text{ethylene chloride}}{\overset{Cl\quad\ Cl}{CH_2 - CH_2}} \text{ or } \underset{\text{ethene dichloride}}{CH_2Cl.CH_2Cl}$$



$$\underset{\text{ethene}}{CH_2 = CH_2} + \underset{\text{reddish brown}}{Br_2} \longrightarrow \overset{Br\quad\ Br}{CH_2 - CH_2} \text{ or } CH_2Br.CH_2Br$$

ethylene bromide
(or) ethene dibromide
colourless

$$\underset{\text{alkene}}{RCH = CH_2} + \underset{(X = Cl,Br)}{X_2} \longrightarrow \underset{\text{alkene dihalide}}{RCHX.CH_2X}$$

3. Addition of hydrogen halides or halogen acids

The conditions for the addition are similar to those for halogens.

$$\underset{\text{(symmetrical)}}{CH_2 \overset{\vdots}{\underset{\vdots}{=}} CH_2} + \underset{\substack{\text{(unsymmetrical)}\\(X = Cl,Br,I)}}{H \vdots X} \longrightarrow \underset{\substack{\text{ethyl halide}\\\text{(only one product formed)}}}{CH_3CH_2X}$$

$$\underset{\text{(unsymmetrical)}}{CH_3\, CH \overset{\vdots}{\underset{\vdots}{=}} CH_2} + \underset{\text{(unsymmetrical)}}{H \vdots X} \longrightarrow \underset{\substack{\text{I}\\\textit{iso}\text{-propyl halide}\\\text{major product}}}{CH_3CHX.CH_3} + \underset{\substack{\text{II}\\\textit{n}\text{-propyl halide}}}{CH_3CH_2CH_2X}$$

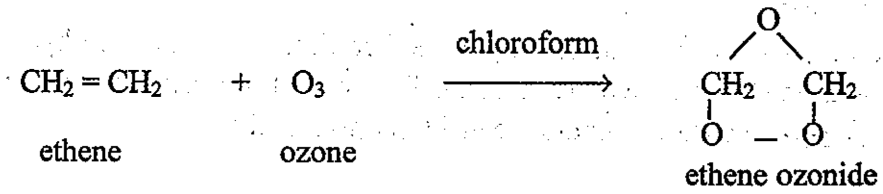
Note that the halogen atom X is more negative than H.

Although both products I and II are formed, I is usually produced in larger proportion than II. This reaction and similar ones, provide the basis for **Markownikoff's rule** which may be stated as follows :

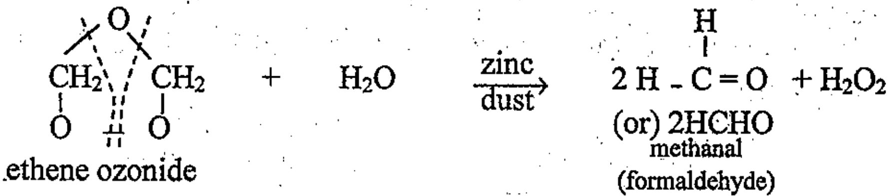
> **When an unsymmetrical addendum (HX) adds on to an unsymmetrical alkene, two products are possible; but that product where the negative part of the addendum adds on to the carbon with the least number of hydrogen atoms is the major product.**

4. Formation of ozonide and ozonolysis

When a stream of ozonized oxygen is passed into a solution of alkene in glacial ethanoic acid (acetic acid) or chloroform, addition of ozone to alkene takes place with formation of alkene ozonide.



This ozonide is readily decomposed by water.

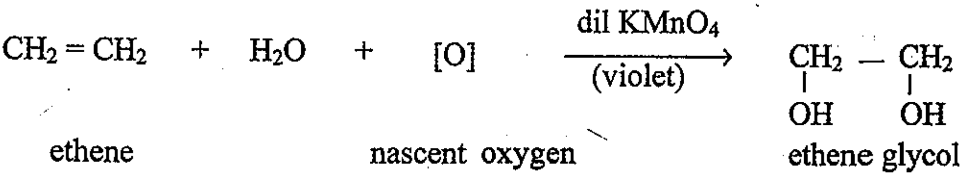


The complete process of preparing the ozonide and decomposing it is called **ozonolysis.**

In practice, the ozonide is treated with water and zinc dust in the presence of traces of silver and hydroquinone. The function of zinc dust and hydroquinone is to destroy the hydrogen peroxide and prevent further oxidation of the aldehyde, methanal.

5. Hydroxylation of alkenes

When ethene is passed into cold dilute potassium permanganate solution, ethene glycol is formed.



$$\underset{\text{ethene}}{CH_2=CH_2} + H_2O + \underset{\text{nascent oxygen}}{[O]} \xrightarrow[\text{(violet)}]{\text{dil }KMnO_4} \underset{\substack{\text{ethene glycol}\\ \text{(colourless)}}}{\underset{OH\quad\;\; OH}{CH_2-CH_2}}$$

In the process the colour of dilute (1%) $KMnO_4$ is discharged.

The useful reactions for qualitative identification of alkenes are the following.

(a) **Decolourization of bromine solution:** If an alkene is shaken with or passed into a 1% solution of Br_2 in carbon tetrachloride, CCl_4, the bromine colour is discharged.

(b) **Decolourization of 1% $KMnO_4$ solution:** The violet colour of aqueous 1% $KMnO_4$ solution is discharged by passing the vapours of an alkene into it.

Uses of ethene and alkenes

Ethene is used for ripening fruit. Unripe fruit on exposure to ethene gas for a few days ripens just like the natural ripened fruit. Ethene is used industrially in the manufacture of chemical solvents and intermediates and also in the manufacture of plastics.

14.4 Alkynes

The alkynes, or acetylenes, are yet another class of unsaturated hydrocarbons. They contain one triple or acetylenic bond. The general formula for this homologous series is C_nH_{2n-2}, where n is a number equal to or greater than 2.

Nomenclature of alkynes

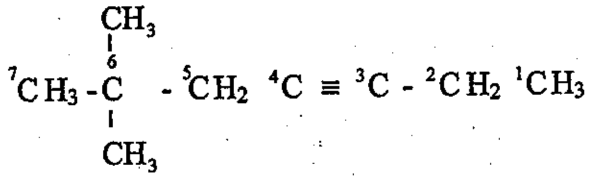
The first member of the series is known as acetylene or ethyne.

The Trivial System: In this naming system, the higher homologues are named as derivatives of acetylene.

$CH_3C \equiv CH$	methyl acetylene
$CH_3C \equiv CCH_3$	dimethyl acetylene
$CH_3C \equiv CCH_2CH_3$	methyl ethyl acetylene

The IUPAC or Geneva System : The alkynes are named after the alkane having the same number of carbon atoms. The suffix **-ane** of the alkane is replaced by **-yne.** The rules for numbering are the same as for the alkenes.

$CH \equiv CH$	ethyne
$CH_3C \equiv C.CH_3$	2-butyne



$$^{7}CH_3-\overset{CH_3}{\underset{CH_3}{\overset{6}{C}}}-{}^{5}CH_2\ {}^{4}C\equiv{}^{3}C-{}^{2}CH_2\ {}^{1}CH_3$$

6,6-dimethyl 3- heptyne

Preparation of alkynes:

1. Calcium carbide is treated with water to liberate ethyne.

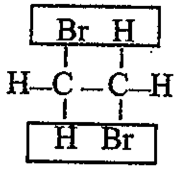
$$\underset{\substack{\text{calcium}\\\text{carbide}}}{CaC_2} + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\substack{\text{ethyne or}\\\text{acetylene}}}{CH\equiv CH}$$

The calcium carbide required for this reaction is industrially prepared by heating calcium oxide with coke in an electric furnace.

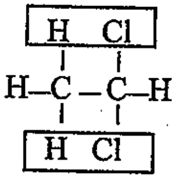
$$\underset{\substack{\text{calcium}\\\text{oxide}}}{CaO} + \underset{\text{coke}}{3C} \xrightarrow[\text{furnace}]{\text{electric}} \underset{\substack{\text{calcium}\\\text{carbide}}}{CaC_2} + \underset{\substack{\text{carbon}\\\text{monoxide}}}{CO}$$

2. By the dehydrohalogenation of ethene dibromide or ethylidene chloride

$$\underset{\text{ethene dibromide}}{CH_2BrCH_2Br} + 2KOH \xrightarrow[\Delta]{\text{ethanol}} \underset{\substack{\text{ethyne (or)}\\\text{acetylene}}}{CH\equiv CH} + 2KBr + 2H_2O$$



$$\underset{\text{ethylidene chloride}}{CH_3CHCl_2} + 2KOH \xrightarrow[\Delta]{\text{ethanol}} \underset{\substack{\text{ethyne (or)}\\\text{acetylene}}}{CH\equiv CH} + 2KCl + 2H_2O$$



Properties of alkynes

Owing to the presence of the triple bond, the alkynes are also unsaturated. In fact they are more unsaturated than the alkenes, as will be evident from the addition reactions we shall study.

Addition reactions

1. Addition of hydrogn

$$\underset{\text{ethyne}}{CH \equiv CH} + H_2 \xrightarrow{\text{Pt or Pd}} \underset{\text{ethene}}{CH_2 = CH_2}$$

$$\underset{\text{ethene}}{CH_2 = CH_2} + H_2 \xrightarrow{\text{Pt or Pd}} \underset{\text{ethane}}{CH_3CH_3}$$

The reaction proceeds in two distinct stages. It is possible to control the reaction and stop it after the first stage of " hydrogenation" as the addition reaction of hydrogen is known. Generally, it can be shown as follows.

$$\underset{\text{alkyne}}{RCH_2C \equiv CH} \xrightarrow[\text{Pt or Pd}]{H_2} \underset{\text{alkene}}{RCH_2CH{=}CH_2} \xrightarrow[\text{Pt or Pd}]{H_2} \underset{\text{alkane}}{RCH_2CH_2CH_3}$$

2. Addition of halogens

Ethyne adds on chlorine and bromine in the dark to form acetylene di- and tetrahalides. The direct combination between ethyne and chlorine can be explosive. This is prevented by the presence of a catalyst.

The addition is catalysed by light and the metallic halides.

$$\underset{\text{ethyne}}{CH \equiv CH} + Cl_2 \longrightarrow \underset{\text{ethyne dichloride}}{CHCl{=}CHCl}$$

$$CHCl = CHCl + Cl_2 \longrightarrow \underset{\text{ethyne tetrachloride}}{CHCl_2.CHCl_2}$$

With aqueous bromine,

$$\underset{\text{ethyne}}{CH \equiv CH} + Br_2(aq) \longrightarrow \underset{\text{ethyne dibromide}}{CHBr{=}CHBr}$$

With liquid bromine, in the absence of solvent.

$$\underset{\text{ethyne}}{CH \equiv CH} \xrightarrow{Br_2(l)} \underset{\text{ethyne dibromide}}{CHBr = CHBr} \xrightarrow{Br_2(l)} \underset{\text{ethyne tetrabromide}}{CHBr_2CHBr_2}$$

Iodine adds on with difficulty

$$\underset{\text{ethyne}}{CH \equiv CH} + I_2 \xrightarrow{\text{ethanol}} \underset{\text{ethyne diiodide}}{CHI = CHI}$$

3. Addition of the hydrogen halide or halogen acids, HX

The order of the readiness with which these hydrogen halides add on is HI>HBr>HCl>HF.

The addition takes place in the dark but is catalysed by light and metallic halides.

$$\underset{\text{ethyne}}{CH \equiv CH + HBr} \longrightarrow \underset{\text{vinyl bromide}}{CH_2 = CHBr}$$

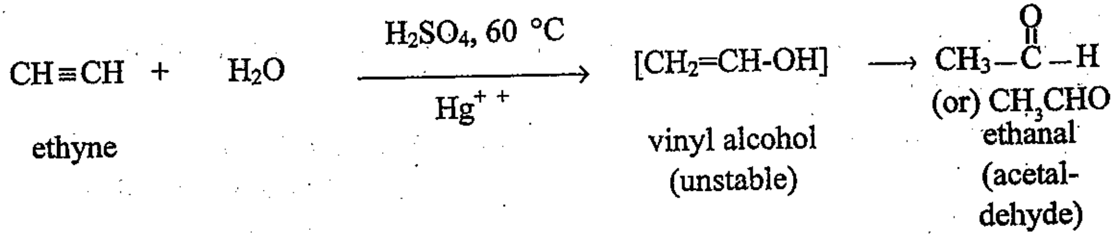
Vinyl bromide, being still unsaturated adds on another molecule of HBr.

$$\underset{\text{unsymmetrical}}{CH_2 = CHBr} + \underset{\text{unsymmetrical}}{HBr} \longrightarrow \underset{\text{ethylidene bromide}}{CH_3.CHBr_2}$$

Note that the addition is in accordance with Markownikoff's rule.

4. Addition of the elements of water

When acetylene is passed into dilute sulphuric acid containing mercury (II) sulphate, at 60 °C, the following reaction occurs.



$$\underset{\text{ethyne}}{CH\equiv CH} + H_2O \xrightarrow[Hg^{++}]{H_2SO_4,\ 60\ °C} \underset{\substack{\text{vinyl alcohol}\\ \text{(unstable)}}}{[CH_2{=}CH\text{-}OH]} \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

(or) CH_3CHO
ethanal
(acetaldehyde)

5. Substitution reactions

Formation of metallic acetylides

When acetylene is passed over heated sodium, one or both hydrogen atoms may be replaced or substituted by sodium to form mono- and di- sodium acetylides.

$$\underset{\substack{\text{Acetylene or}\\ \text{ethyne}}}{CH \equiv CH} + Na \longrightarrow \underset{\substack{\text{monosodium}\\ \text{acetylide}}}{CH \equiv C\text{ - }Na} + \frac{1}{2}H_2$$

$$CH \equiv CNa + Na \longrightarrow \underset{\substack{\text{disodium}\\ \text{acetylide}}}{NaC \equiv CNa} + \frac{1}{2}H_2$$

The H atoms in ethyne which are replaced by metals are, therefore, acidic. Similar replacements with Cu or Ag give the acetylides of these metals.

When ethyne is passed into an ammoniacal solution of copper (I) chloride or silver oxide, the corresponding metallic acetylides are precipitated.

$$2HC \equiv C\text{-}H + Cu_2Cl_2 + 2NH_3 \longrightarrow 2HC \equiv C\text{-}Cu\downarrow + 2NH_4Cl$$

acetylene — mono copper(I) acetylide (red ppt.)

$$2HC \equiv C\text{-}Cu + Cu_2Cl_2 + 2NH_3 \longrightarrow 2CuC \equiv C\ Cu\downarrow + 2NH_4Cl$$

monocopper(I) acetylide — dicopper(I) acetylide (red ppt.)

$$2HC \equiv CH + Ag_2O + NH_3 \longrightarrow 2HC \equiv CAg\downarrow + NH_4OH$$

acetylene — monosilver acetylide (white ppt)

$$HC \equiv CAg + Ag_2O + NH_3 \longrightarrow AgC \equiv CAg\downarrow + NH_4OH$$

monosilver acetylide — disilver acetylide (white ppt)

$CH_3C \equiv CH$ still contains a hydrogen atom on the triple bonded carbon and will form metallic acetylides.

$$2CH_3C \equiv CH + Cu_2Cl_2 + 2NH_3 \longrightarrow 2CH_3C \equiv CCu\downarrow + 2NH_4Cl$$

methyl acetylene — copper(I)methyl acetylide (red ppt.)

$$2CH_3C \equiv CH + Ag_2O + NH_3 \longrightarrow 2CH_3C \equiv CAg\downarrow + NH_4OH$$

methyl acetylene — silver methyl acetylide (white ppt.)

$CH_3C \equiv CCH_3$ contains no hydrogen on the triple bonded carbon and will not form metallic acetylides.

Uses of ethyne

The most important use of ethyne is as one of the gases in the oxy-acetylene flame. Ethyne is also an important starting material in the manufacture of plastics.

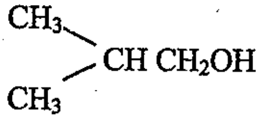
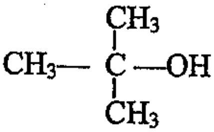
14.5 The alcohols

The alcohols may be considered as derivatives of alkanes. The replacement of one hydrogen atom in an alkane by a hydroxyl (-OH) group gives the corresponding alcohol. They form a homologous series having the general formula $C_nH_{2n+2}O$, where n is a number equal to, or greater than 1.

Nomenclature

The first member of the series is methanol, CH_3OH, called variously as methyl alcohol of wood spirit. The next member, corresponding to ethane is called ethanol, ethyl alcohol or simply alcohol.Since you are by now familiar with the naming systems for the hydrocarbons, you should have no difficulty in understanding the way the alcohols in Table 14.2 are named. Note that the suffix **-ane** in alkane is simply replaced by **-ol** in the IUPAC system.

Table 14.2 Naming of alcohols

Formula	*Structure*	*Common name*	*Name according to IUPAC system*
CH_4O	$CH_3\ OH$	wood spirit, methyl alcohol	methanol
C_2H_6O	$CH_3CH_2\ OH$	rectified spirit, ethyl alcohol or simply alcohol	ethanol
C_3H_8O	$CH_3CH_2\ CH_2OH$	*n*-propyl alcohol	propan-1-ol or 1-propanol
	$CH_3CHOHCH_3$	*iso*-propyl alcohol	propan - 2 - ol or 2-propanol
$C_4H_{10}O$	$CH_3CH_2CH_2CH_2OH$	*n*-butyl alcohol	butan -1 -ol or 1-butanol
	$CH_3CH_2CHOHCH_3$	secondary butyl alcohol or (*sec*-butyl alcohol)	butan-2-ol or 2-butanol
	 $\begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!>CH\ CH_2OH$	*iso*-butyl alcohol	2-methyl propan-1 -ol
	 $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH$	tertiary butyl alcohol or (*ter*-butyl alcohol)	2-methyl propan-2 -ol

Ethanol or ethyl alcohol is one of the most important alcohols.

Preparation of alcohols

By the hydrolysis of alkyl halides

$$\underset{\text{ethyl chloride}}{CH_3CH_2Cl + NaOH} \longrightarrow \underset{\text{ethanol}}{CH_3CH_2OH} + NaCl$$

The ethyl chloride is heated under reflux with an aqueous solution of sodium or potassium hydroxide. Similarly,

$$\underset{\text{alkyl halide}}{RCH_2X + NaOH} \longrightarrow \underset{\text{alcohol}}{RCH_2OH} \quad + NaX$$

This reaction may be extended and alkyl hydrogensulphate used instead of alkyl halides. Here simple reflux with water is sufficient to effect hydrolysis.

$$\underset{\text{ethyl hydrogensulphate}}{CH_3CH_2SO_4H} \quad + \quad H_2O \longrightarrow \underset{\text{ethanol}}{CH_3CH_2OH} \quad + \quad H_2SO_4$$

Ethene may be used as the starting point for the preparation of ethanol.

Manufacture of ethanol from petroleum refinery products

Hydrocarbons of very high molecular weight are heated to 520 °C under 12 atm pressure when they break down to give alkanes in the range of C_5H_{12} to C_9H_{20} which may be used as petrol. At the same time, ethene is produced as a gaseous by-product. This gas is passed into sulphuric acid when ethyl hydrogensulphate and diethyl sulphate are formed.

$$\underset{\text{ethene}}{CH_2 = CH_2} + H_2SO_4 \longrightarrow \underset{\text{ethyl hydrogensulphate}}{CH_3CH_2SO_4H}$$

$$\underset{\text{ethene}}{CH_2 = CH_2} + \underset{\text{ethyl hydrogensulphate}}{CH_3CH_2SO_4H} \longrightarrow \underset{\text{diethyl sulphate}}{(CH_3CH_2)_2SO_4}$$

If these products are diluted with water, hydrolysis takes place to give ethanol.

$$\underset{\text{ethyl hydrogensulphate}}{CH_3CH_2SO_4H} + H_2O \longrightarrow \underset{\text{ethanol}}{CH_3CH_2OH} + H_2SO_4$$

$$\underset{\text{diethyl sulphate}}{(CH_3CH_2)_2SO_4} + 2H_2O \longrightarrow \underset{\text{ethanol}}{2CH_3CH_2OH} + H_2SO_4$$

The ethanol formed is fractionally distilled. Ethanol is commonly known as ethyl alcohol.

Manufacture of ethanol by fermentation

Starch is used as the raw material for the preparation of ethanol industrially. Potatoes, maize, rice and other starchy cereals may be used in the process.

The major steps in this manufacturing process may be summarized as follows:

(a) Starch is pressure-cooked to release the starch granules. The cooked starch is cooled and then treated with freshly germinated barley which is called malt for 1 hour at 60 °C. Malt contains the enzyme diastase. Starch so treated breaks down into a sugar called maltose.

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + \frac{n}{2}H_2O \xrightarrow{\text{diastase}} \underset{\text{maltose}}{\frac{n}{2}C_{12}H_{22}O_{11}}$$

(b) Yeast is added to the maltose at room temperature when an enzyme, maltase present in it, catalyses its breakdown into glucose.

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{(maltase)}]{\text{yeast}} \underset{\text{glucose}}{2\,C_6H_{12}O_6}$$

In the next step, another enzyme, zymase, present in yeast catalyses the decomposition of glucose to ethanol.

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow[\text{(zymase)}]{\text{yeast}} \underset{\text{ethanol}}{2\,CH_3CH_2OH} + 2CO_2\uparrow$$

The product contains about 11 % ethanol. It is fractionally distilled to yield the rectified spirit of commerce which contains about 95 % ethanol.

Cane sugar and fruit juices contain the sugar, sucrose, $C_{12}H_{22}O_{11}$ and glucose, $C_6H_{12}O_6$ respectively. They may be used to manufacture ethanol. To do so, the manufacturing process follows the outline in paragraph (b) above.

Properties of alcohols

Physical properties

Alcohols from methanol, CH_3OH, to butanol, $CH_3CH_2CH_2CH_2OH$, are mobile liquids : those from $C_5H_{11}OH$ to $C_{11}H_{23}OH$ are oily liquids; above $C_{12}H_{25}OH$ they are usually solids. The first two members methanol and ethanol are miscible with water in any proportion. The most toxic member is methanol.

Chemical properties

1. **Reactions of the hydroxyl group**

Since the hydroxyl group (-OH) is common to all alcohols, most of the common reactions of all alcohols are due to the reactions of this group.

(a) **Reaction with metallic sodium**

When a piece of sodium is added to ethanol reaction occurs at room temperature, liberating hydrogen.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + Na \longrightarrow \underset{\text{sodium ethoxide}}{CH_3CH_2ONa} + \tfrac{1}{2}H_2$$

Methanol and most of the liquid alcohols also behave similarly.

(b) **Reaction with PCl_5**

PCl_5 reacts with ethanol at room temperature liberating HCl gas, and CH_3CH_2Cl gas.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + PCl_5 \longrightarrow \underset{\text{ethyl chloride}}{CH_3CH_2Cl\uparrow} + POCl_3 + HCl\uparrow$$

Methanol and the other liquid mobile alcohols also behave similarly.

(c) **Reaction with sulphuric acid**

When ethanol is heated with an excess of concentrated sulphuric acid at 160 °C, ethene is the product (see alkenes).

With a smaller proportion of concentrated sulphuric acid, di-ethyl ether is formed when the reaction temperature is kept at 140 °C.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + H_2SO_4 \xrightarrow{100\,^{\circ}C} \underset{\text{ethyl hydrogensulphate}}{CH_3CH_2SO_4H} + H_2O$$

$$\underset{\text{ethyl hydrogensulphate}}{CH_3CH_2\boxed{SO_4H}} + CH_3CH_2O\boxed{H} \xrightarrow{140\,^{\circ}C} \underset{\text{diethyl ether}}{CH_3CH_2OCH_2CH_3} + H_2SO_4$$

(d) **Formation of esters**

Sulphuric acid and the halogen acids (HI, HBr and HCl) are inorganic acids. They react with alcohol to form alkyl hydrogensulphate and the alkyl halides. These derivatives are called inorganic esters.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + \underset{\substack{\text{(concentrated}\\ \text{acid or gas)}}}{HI} \longrightarrow \underset{\substack{\text{ethyl iodide}\\ \text{(inorganic ester)}}}{CH_3CH_2I} + H_2O$$

HBr reacts similarly. HCl reacts only in the presence of anhydrous zinc chloride.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + HCl \xrightarrow{ZnCl_2} \underset{\text{ethyl chloride}}{CH_3CH_2Cl} + H_2O$$

Ethanoic acid (acetic acid) also reacts with ethanol when a small amount of concentrated sulphuric acid is added as catalyst.

$$\underset{\text{ethanoic acid}}{CH_3CO\boxed{OH}} + \underset{\text{ethanol}}{CH_3CH_2\,O\boxed{H}} \xrightarrow[H^+]{H_2SO_4} \underset{\substack{\text{ethyl ethanoate}\\ \text{(ethyl acetate)}}}{CH_3COOCH_2CH_3} + H_2O$$

Ethyl ethanoate is an ester. It has a pleasant fruity odour characteristics of most esters.

(e) **Oxidation**

(i) Dehydrogenation

When ethanol is passed over freshly reduced copper heated at 300 °C, removal of hydrogen occurs with formation of ethanal or acetaldehyde.

$$\underset{\substack{\text{ethanol}\\ \text{(vapour)}}}{CH_3CH_2OH} \xrightarrow{Cu,\ 300\,^{\circ}C} \underset{\text{ethanal}}{CH_3CHO} + H_2$$

(ii) Oxidation by oxidizing mixtures

When heated with a mixture of potassium dichromate and dilute sulphuric acid, oxidation takes place in two stages to finally give ethanoic acid.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + [O] \xrightarrow[\text{dil } H_2SO_4]{K_2Cr_2O_7 +} \underset{\text{ethanal}}{CH_3CHO} + H_2O$$

$$\underset{\text{ethanal}}{CH_3CHO} + [O] \xrightarrow[\text{dil } H_2SO_4]{K_2Cr_2O_7 +} \underset{\text{ethanoic acid}}{CH_3COOH}$$

14.6 Petroleum Industry and Petrochemicals

Crude Oil and other Fossil Fuels

This section covers the following ideas:

(i) fossil fuels
(ii) the formation and fractional distillation of crude oil
(iii) catalytic cracking
(iv) alternative transport fuels
(v) coal
(vi) biogas.

There are three major fossil fuels:

(i) coal,
(ii) crude oil,
(iii) natural gas.

Fossil fuels were formed in the Earth's crust from material that was once living. Coal comes from fossil plant material. Crude oil and natural gas are formed from the bodies of marine microorganisms. The formation of these fuels took place over geological periods of time (many millions of years). These fuels are therefore non-renewable and finite resources.

14.7 Crude Oil

The Formation of Crude Oil

Crude oil is one of the Earth's major natural resources. The oil is the result of a process that began up to 400 million years ago. Prehistoric marine creatures died and sank to the sea-bed and were covered and surrounded by mud. The change into crude oil and natural gas was brought about by high pressure, high temperature and bacterial acting over millions of years. The original organic material broke down into hydrocarbons.

Compression of the mud above the hydrocarbon mixture transformed it into shale. Then geological movements and pressure changed this shale into harder rocks, squeezing out the oil and gas. The oil and gas moved upwards through the porous rocks, moving from high-pressure to low-pressure conditions. Sometimes they reached the surface, but often they became trapped by a layer of non-porous rock. Reservoirs of oil and gas were created. These occur where the rock layers form an anticline or at the junction of a fault. These reservoirs are not lakes of oil or pockets of gas. Instead, the oil or gas is spread throughout the pores in coarse rocks such as sandstone or limestone, rather as water is held in a sponge.

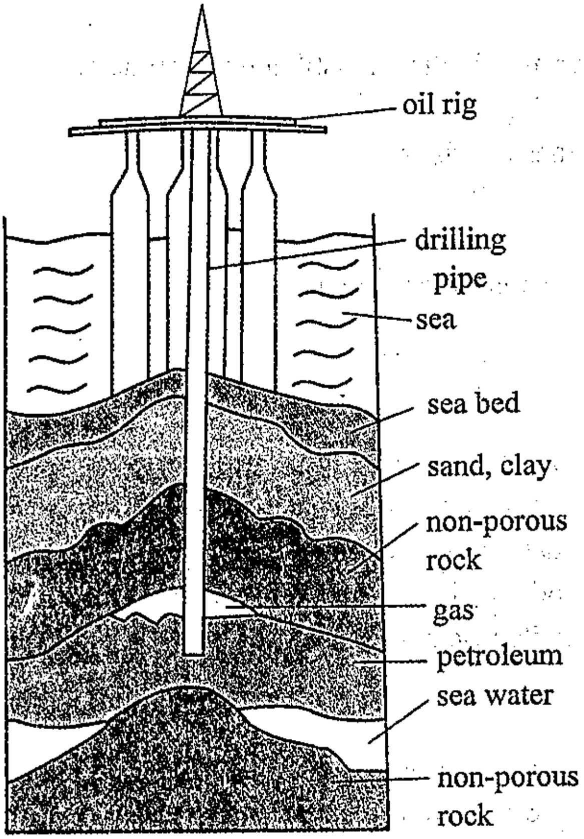


Fig. 14.1 The extraction of petroleum from an undersea deposit

Oil-fields and gas-fields are detected by a series of geological searches. Surveys from aeroplanes and satellites can provide detailed pictures of surface features. These give clues about the underlying rocks. Variation in gravity and magnetic field can also give clues. Finally, a **seismic** survey is carried out. These can be carried out both at sea and on land. Shock waves in the ground are produced by setting off small explosions. At sea, compressed air guns are used. Detailed information on the rock formations in an area can be found by tracking and timing the shock waves. Promising areas are then drilled. These drilling can simply be to gain more geological information. But if oil or gas is found, they can be used to see how extensive the oil-field or gas-field is. Once a field is established, then production oil-rigs can be set up.

Fractional Distillation

Fractional distillation is the separation of a liquid mixture into fractions differing in boiling point by means of distillation using a fractionating column.

Crude oil is a mixture of many different **hydrocarbon** molecules. Most of the crude oil that is extracted from the ground is used to make fuel, but around 10 % is used as a **feedstock,** or raw material, in the chemical industry. Before it can be used, the various hydrocarbon molecules are separated by **refining.**

At a refinery, crude oil is separated into different **fractions** – groups of hydrocarbons that have different boiling points. These different boiling points are roughly related to the number of carbon atoms in the hydrocarbon (Table 14.3).

Table 14.3 Various Crude Oil* Fractions

Fraction	**Approximate number of carbon atoms in hydrocarbons**		**Approximate boiling range (°C)**	
Refinery gas	1-4	(C_1-C_4)	Below 25	↓ b.p. and viscosity increasing
Petrol*	4-12	(C_4-C_{12})	40-100	
Naphtha	7-14	(C_7-C_{14})	90-150	
Paraffin*	9-16	(C_9-C_{16})	150-240	
Diesel oil	15-25	(C_{15}-C_{25})	220-250	
Lubricating oil	20-70	(C_{20}-C_{70})	255-350	
Bitumen residue	over 70	($> C_{70}$)	above 350	

* Different terms are used in the UK and the USA. Note that 'crude oil' (UK) is the same as 'petroleum' (USA); 'petrol' (UK) is the same as 'gasoline' (USA); and 'paraffin' (UK) is the same as 'kerosene' (USA).

Separation of the hydrocarbons takes place in a **fractional distillation column**, or fractionating tower. At the start of the refining process, crude oil is preheated to a temperature of 350-400 °C and pumped in at the base of the tower. As it boils, the vapour passes up the tower. It passes through a series of bubble caps and cools as it rises further up the column. The different fractions cool and condense at different temperatures, and therefore at different heights in the column. The fractions condensing at the different levels are collected on trays. Fractions from the top of the tower are called 'light' and those from the bottom 'heavy'. Each fraction contains a number of different hydrocarbons. The individual single hydrocarbons can then be obtained by further **distillation.** Figure 14.2 shows the separation into different fractions and some of their uses.

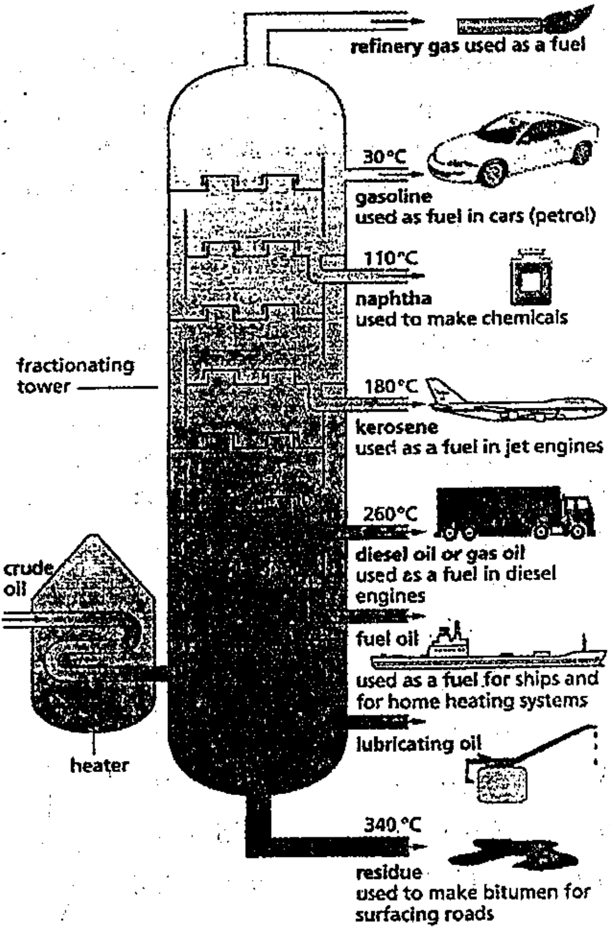


Figure 14.2 Fractional distillation of crude oil in a refinery

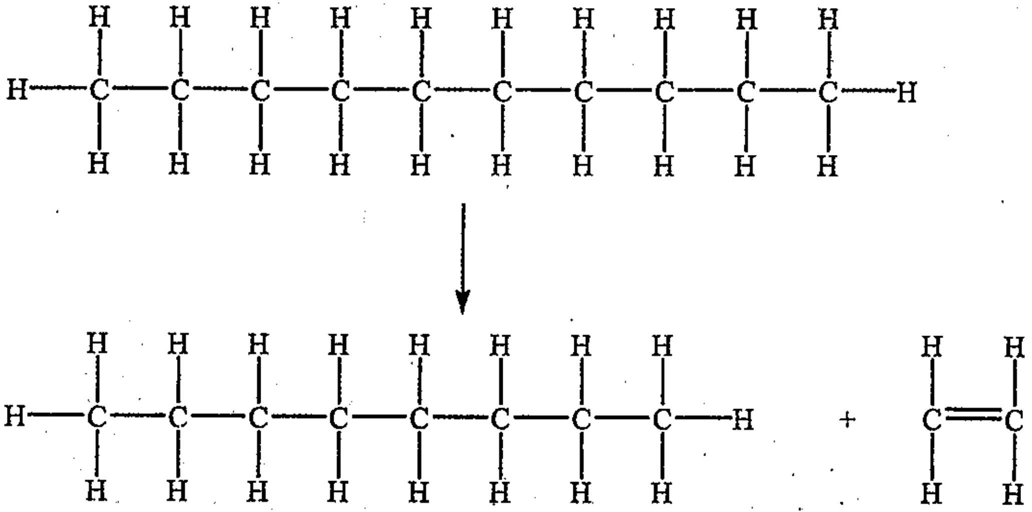
Catalytic Cracking

The demand for the various fractions from the refinery does not necessarily match with their supply from the oil. For lighter fractions such as gasoline (petrol), the demand is greater than the supply. The opposite is true for heavier fractions such as kerosene (paraffin) and diesel. Larger molecules from these heavier fractions can be broken into smaller, more valuable, molecules. This process is called **catalytic cracking** ('cat cracking'). Cracking takes place in huge reactor. In this reactor, particles of catalyst (made of powdered minerals such as silica, alumina and zeolites) are mixed with the hydrocarbon fraction at a temperature around 500 °C. The cracked vapours containing smaller molecules are separated by distillation.

The shortened hydrocarbon molecules are produced by the following type of reaction:

$$\text{decane} \xrightarrow[\text{catalyst}]{\text{heat}} \text{octane} + \text{ethene}$$

$$C_{10}H_{22} \rightarrow C_8H_{18} + C_2H_4$$



This is just one possible reaction when decane is cracked. The molecules may not all break in the same place. The alkene fragment is not always ethene; propene and but-1-ene may also be produced. All **cracking reactions** give two types of products:

(i) an **alkane** with a shorter chain than the original, and

(ii) a short-chain **alkene** molecule.

Both these products are useful. The shortened alkanes can be blended with the gasoline fraction to enrich the petrol. The alkenes are useful as raw materials for making several important products. Figure 14.3 shows the various uses for the ethene produced. Propene polymerises to poly(propene) (trade-name 'polypropylene'), while butene polymerises to produce synthetic rubber.

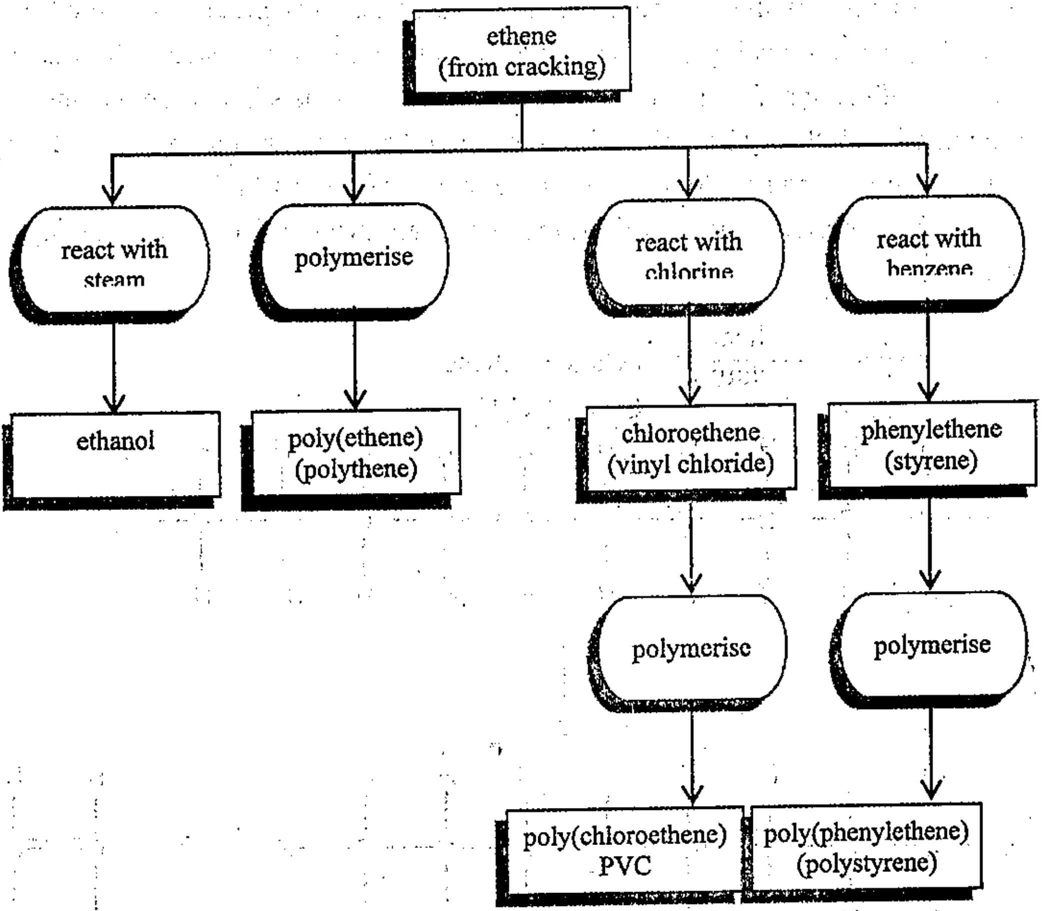


Fig. 14.3 Important products can be made from the ethene produced by catalytic cracking

Blending Gasoline

Some of the products from cracking are added to the gasoline fraction to improve the quality of the petrol. As many as 12 different compounds (containing over 300 different hydrocarbons and additives) may be used in a blend of petrol for the motorist. An important consideration is how easily the fuel vapour **ignites.** If the fuel ignites too easily, then the engine will not run smoothly – 'knocking' will occur. However, if the fuel is too difficult to ignite, then the engine will be difficult to start, especially on cold mornings. High-quality petrol contains many branched-chain hydrocarbons, make in a process known as **reforming**, so that the fuel does not ignite too soon.

'Lead' (actually tetraethyl-lead) was added to gasoline to prevent 'knocking'. But this caused high levels of lead in the air, particularly in large cities. This led to concern over the link with brain damage in young children. Unleaded fuel is now widely available and has to be used in modern cars fitted with catalytic converters (the lead would poison the catalyst and so prevent it working).

The removal of sulphur from gasoline fractions is now very efficient. Car exhaust emissions contain very little sulphur dioxide. The carbon monoxide (CO), unburnt hydrocarbons (HC) and oxides of nitrogen (NO_x) in exhaust fumes do continue to cause concern. The levels of emission of these compounds are reduced by fitting a catalytic converter to the exhaust.

Gasoline vapour also escapes into the air at petrol stations. Modern pumps now have hoods on the nozzles to cut down the escape of fumes. When handling liquid fuels generally, you need to consider the flash-point and ignition temperature of the fuel. These are not the same. The **flash-point** is the temperature at which the vapour will ignite in air in the presence of a flame. This temperature is usually low for a fuel(Table 14.4). The **ignition temperature** is the temperature at which a fuel: air mixture ignites without a flame-for petrol it is 550 °C.

Table 14.4 Flash-points of Some Common Flammable Liquids

Liquid	**Flash-point (°C)**
Methanol	+11
Ethanol	+13
Hexane	–21
Octane	+13

14.8 Alternative Transport Fuels

Gasoline from methanol

New Zealand has large reserves of natural gas (mainly methane) but very little crude oil. The problem of producing petrol has been transformed by a catalyst known as zeolite ZSM-5 (A zeolite is one of a large group of alumino-silicates of sodium, potassium, calcium and barium). Methane is first converted into methanol. The methanol produced is then turned into hydrocarbons using the ZSM-5 catalyst:

$$\text{methanol} \xrightarrow{\text{ZSM-5}} \text{hydrocarbons} + \text{water}$$

$$n\,CH_3OH \longrightarrow (CH_2)_n + n\,H_2O$$

ZSM-5 is an artificial zeolite composed of aluminium, silicon and oxygen. It was first made by two chemists working for the US Mobil Oil Company.

Diesel

High-speed diesel engines in cars, buses and trucks use fuel (DERV – Diesel Engine Road Vehicle) containing hydrocarbon molecules consisting of between 9 and 20 carbon atoms per molecule. Slower-speed diesel engines for ships, etc., use a slightly heavier fuel. Diesel engines are compression ignition engines (the fuel ignites spontaneously without a spark). Diesel engines are more efficient than petrol engines and produce much less carbon monoxide. However, because their working temperature is higher, they produced more oxides of nitrogen. The major problems are smoke and odour.

Biodiesel

In organic chemistry, transesterification is the process of exchanging the alkoxy group of an ester compound by another alcohol.

Plants and animals oil may serve as the source of biodiesel.

The plant or animal oil has to be converted to biodiesel by the chemical process known as **"Transesterification".** The conversion involves four stages. First stage is the preparation of nearly 100% pure methanol or ethanol. Second stage is the addition of potassium hydroxide or sodium hydroxide basic catalyst to the prepared pure methanol or ethanol . Third stage is the treatment of the seed oil with the prepared basic catalytic solution and the solution heated to 60°C which is the **transesterification** process producing methyl or ethyl ester as **the product (biodiesel)** of the reaction . Fourth stage is the removal of glycerine and sodium or potassium salt of fatty acids (soap) from the reaction mixture by washing with water and pure biodiesel is separated out by using the **biodiesel processor.** At present in Myanmar, biodiesel is used to power tractor engines, petro-diesel engines .and electricity generating engines. It is the potential substitute for petro-diesel since the source of the biodiesel is very much cost effective.

LPG and CNG

Liquid petroleum gas (LPG) is composed of propane and butane. Compressed natural gas (CNG) is 90 % methane. These products already have a significant market in some countries. For example, all the taxis in Japan use LPG. Their use requires pressurized tanks for on-board storage. In Myanmar, most of the taxis , buses and vehicles use CNG since we have abundant supply of natural gas from Yetagun and Yadana Offshore Natural Gas Oil Enterprises. LPG has been utilized in most Myanmar households, restaurants, hotels and motels for cooking and frying and for other heating systems.

Rapeseed oil

The potential for adding plant oils to diesel fuel is being investigated world-wide. Such fuel is widely used in China. The future use of these fuels will depend on economic factors. Some countries grow oil-producing crops , such as rapeseed plant , sunflower plant, palm oil plant etc. but do not have their own reserves of crude oil.

14.9 Coal and Biogas

Coal

Coal is our most abundant fossil fuel. Many of the organic chemicals we now make from oil can also be made from coal. It may well be that coal will again become an important source of chemical raw materials.

Coal is not a single substance. It is a complex mixture of compounds that occur naturally in varying grades. It has the approximate composition formula $C_{135}H_{96}O_9NS$. There are several different types of coal depending on the geological processing of the deposit (Table 14.5). Peat is the first step in the coal-forming process, but it is not itself a coal. With heat and pressure over a long timescale, it first forms ‘lignite’ (or ‘brown coal’), and then the harder types of coal. Anthracite is the hardest coal, with the highest carbon content.

The future use of coal will need to be cleaner. It must be visibly cleaner (less dust and soot), and must also produce lower amounts of acidic gases (SO_2 and NO_x).

These **chemicals** can be obtained from coal:

(i) **ammonia** (often turned into ammonium sulphate) – for fertilizers,
(ii) **coal gas** (mainly hydrogen and carbon monoxide) – for industrial heating,
(iii) **coal tar** (separated into various fractions like crude oil) – for paint, dyes, creosote and pitch,
(iv) **coke** – for iron- and steel-making and for home and industrial heating.

Table 14.5 The Different Types of Coal

Type		Description		Heat content	Sulphur content
Peat (not a coal)		partially decay plant matter in bogs and swamps		low	-
heat ↓ pressure					
Lignite (brown coal)	↑ increasing moisture content	limited supplies in most areas	↓ increasing heat and carbon content	low	low
heat ↓ pressure					
Bituminous coal (soft coal)		heavily used because of high heat content and wide availability		high	high
heat ↓ pressure					
Anthracite (hard coal)		very desirable because of high heat content and low sulphur content, but limited supplies in most areas		high	low

Biogas

Methane gas is formed naturally under a number of different circumstances. Anaerobic bacteria helped decompose organic matter under geological conditions to produce natural gas. Methane accumulates in coal-mines, where it can cause explosions. Marsh gas, which bubbles up through the stagnant water of marshes, swamps and rice paddy-field, is also methane. Methane produced in this way contributes to the 'greenhouse effect'.

Methane is produced from organic waste (**biomass**) when it decays in the absence of air. This can be exploited as a source of energy. In developing countries such as India and China, biomass digesters are important sources of fuel for villages. The methane is useful for heating and cooking, and the solid residue is used as a fertilizer.

Industrialised countries produce large amounts of waste, which is deposited in landfill sites. Biogas forms as the rubbish decays. This gas can be used as a fuel for local industry. In some parts of Myanmar, biogas has been generated from cow dung . The generated biogas has been utilized to power the electricity generating engines . Many villages in Myanmar such as villages in kyaukse township have electricity supply from generating engines powered by biogas.

Summary of core material

You should know that:

(i) there are three major fossil fuels – coal, crude oil and natural gas,

(ii) these fuels were created by the action of heat and pressure on buried organic material acting over geological periods of time,

(iii) these resources are a source of energy and also of a wide variety of chemicals,

(iv) the fractional distillation of crude oil produces a series of different hydrocarbon fractions, each with its own uses,

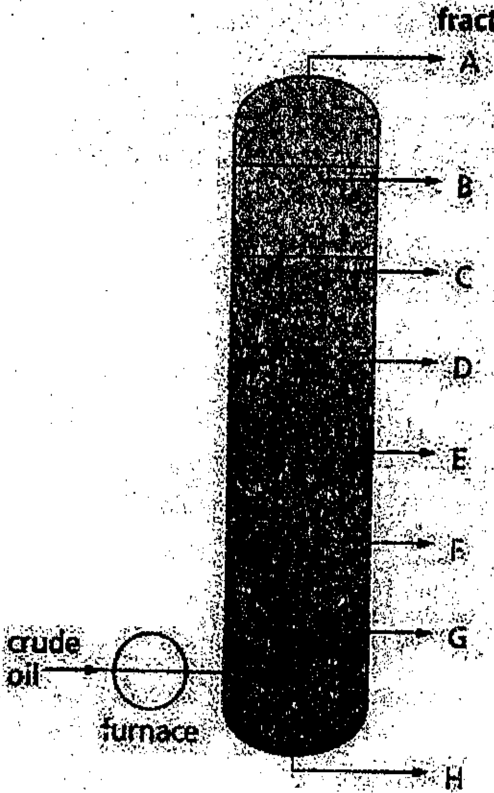
(v) these hydrocarbons can be further changed by processes such as catalytic cracking – producing shorter-chain alkane molecules and alkenes from the original longer chains.

SUMMARY

After studying this chapter, the students could understand the meaning of organic chemistry. It deals with the studies of writing graphic or structural formulae of organic compounds, nomenclature of organic compounds especially by IUPAC system, laboratory and manufacturing methods and also properties of organic compounds such as alkanes, alkenes, alkynes, and alcohols, including their uses. In addition, in the final section, students would be able to study about petrol chemicals, and polymers, which covers the topics such as fossil fuels, the formation and fractional distillation of crude oil(producing petrol (gasoline), paraffin (kerosene)(aviation turbine fuel), diesel oil, and other lubricating oil,) catalytic cracking, alternative transport fuels, such as biodiesel or plant oil , coal and biogas.

Problems on Petroleum Industry

1. Petroleum (crude oil) is a mixture of several compounds which are separated in a refinery by means of an apparatus as shown below.



(a) What is the name of the apparatus?

(b) What is the name of the process which is used in separating crude oil?

(c) On what physical property of the compounds in the mixture does the separation depend?

(d) Use the letters **A** to **G** to describe where the following could be found.

  (i) The fraction that represent gases.

  (ii) The fraction with the largest molecules.

  (iii) The fraction that represents liquids with the lowest boiling point.

2. Deposits of crude oil are found trapped in some rock structures. Crude oil is a mixture of many different hydrocarbons.

   (a) Describe how petrol is obtained from crude oil.

   (b) Petrol (octane) can be made into ethene:

   $$\underset{\text{octane}}{C_8H_{18}} \longrightarrow \underset{\text{ethene}}{4\,C_2H_4} + \underset{\text{hydrogen}}{H_2}$$

      (i) State what happens to the octane in this reaction.

      (ii) Give two conditions needed for this reaction.

   (c) (i) Give a balanced symbolic equation for the complete combustion of petrol (octane) (C_8H_{18}).

      (ii) What is the mass of one mole of octane (C_8H_{18})?

      (iii) The combustion of one mole of octane produces 5500 kJ. The density of octane is 0.7 g cm^3. Calculate the energy produced by one litre (1000 cm^3) of octane. Show clearly how you obtain your answer.

3. Fill in the blanks with the correct word(s), notation(s), term(s), unit(s), etc., as necessary.

   (a) Petroleum is a complex mixture of ………… .

   (b) Petroleum is composed of compounds of ………… and ………… .

   (c) Petroleum is a fossil fuel and was formed millions of years ago from dead ……. and animals.

   (d) ……… is produced from organic waste (biomass) when it decays in the absence of air.

   (e) Methane is useful for heating and cooking , and the solid residue is used as a ……… .

4. What is meant by 'cracking'?

5. What is a fuel?

6. What are the three major fossil fuels?

7. What is the long form of (i) LPG and (ii) CNG ?

8. What are the uses of LPG and CNG in Myanmar?

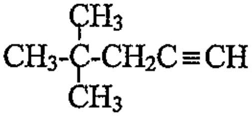
9. Name the chemicals which can be obtained from coal and mention their uses.

10. What is meant by the term 'biodiesel'? Explain the uses of biodiesel in Myanmar.

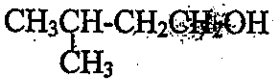
11. What is 'Biogas'? Explain the uses of biogas in Myanmar.

Questions and problems

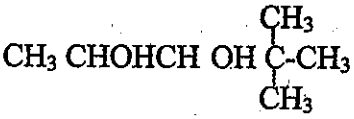
1. (a) Give the graphic representation of the structural formulae of
   (i) ethane (ii) ethene (iii) ethyne.
   (b) How does ethene react with
   (i) hydrogen (ii) hydrogen chloride (iii) sulphuric acid?
   In each case mention the reaction conditions.
2. (a) What products would you expect when
   (i) CH_3COONa is heated with soda-lime?
   (ii) RCH_2COONa is heated with soda-lime?
   (b) Discuss a substitution reaction of alkanes.
3. (a) Under what conditions does ethyne react with an excess of
   (i) hydrogen (ii) hydrogen bromide (iii) bromine?
   (b) How would you obtain ethanal from ethyne?
4. (a) Briefly explain, in terms of the electronic theory the bonding between atoms in
   (i) methane (ii) ethane.
   (b) Discuss the Markownikoff's rule for the addition reaction between an unsymmetrical alkene and an unsymmetrical addendum.
5. Outline an example each to illustrate the following reactions.
   (i) Chlorination (iv) Dehydrogenation
   (ii) Dehydrohalogenation (v) Esterification
   (iii) Dehydration (vi) Polymerization
6. (a) How would you obtain ethanol from rice starch?
   (b) Discuss the reactions of ethanol with
   (i) ethanoic acid (iii) H_2SO_4 at 140 °C
   (ii) PCl_5 (iv) freshly heated copper at 300 °C.
7. (a) Describe how you would obtain ethanol from ethene.
   (b) How would you differentiate between two isomeric compounds having the formula C_4H_6? Discuss, giving the relevant equations.
8. (a) Name the following compounds.
   (i) $CH_3CH_2CH = CHCH_3$
   (ii)



$$CH_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{-}CH_2C\equiv CH$$

(iii) 

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{-}CH_2CH_2OH$

(iv) 

$CH_3\,CHOHCH\,OH\,\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}\text{-}CH_3$

(b) Give the graphic structural formulae of the following.
   - (i) 3 methyl 4 ethyl 1-heptene
   - (ii) 3,4,4 - trimethyl hexan-1-ol

9. (a) Write full structural formulae for the two isomers of butane. Butene has 3 isomers. Write their structural formulae and name them.
   (b) How do you think iso-butene would react with
      (i) HBr and
      (ii) H_2SO_4?

10. State TRUE or FALSE for each of the following.
   (a) Carbon atom has a bond order of four.
   (b) Alkanes may undergo substitution reaction.
   (c) Colour of bromine solution may be discharged by passing it through alkene.
   (d) First four members of alkanes are gases.
   (e) Structural isomers may have different properties.

11. Fill in the blanks with a suitable word or phrase or numerical value with unit as necessary.
   (a) IUPAC name of isobutylene is ....
   (b) .... alkenes give two products by the reaction with HBr.
   (c) Hydration of ethene gives ....
   (d) Glucose is converted to ethanol by the enzyme, ...
   (e) Hydrogen from the .... bonded carbon may be displaced by metals.

12. Choose the correct term or terms given in the brackets.
   (a) (Alkanes, Alkenes. Alkynes) are saturated hydrocarbons.
   (b) (Alkanes, Alkenes, Alkynes) may undergo both substitution and addition reactions.
   (c) (Alkyl chloride, Alkyl bromide, Alkyl iodide) is usually used to prepare an alkane by the reduction with hydrogen.
   (d) Starch is hydrolysed by (diastase, maltase, zymase).
   (e) Hydration of (acetylene, ethene. ethane) gives acetaldehyde.

13. Match each of the items given in List A with the appropriate item in List B.

List A	**List B**
(a) acetaldehyde	(i) Hydrogenation
(b) ethanol	(ii) 1,2-dichloroethane
(c) isomer of 1,1-dichloroethane	(iii) chlorination
(d) photochemical reaction	(iv) ethanal
(e) reduction	(v) ethyl alcohol

14. What happens when

(a) ethene is passed into a bromine solution?

(b) ethene is passed into 1 % $KMnO_4$ solution?

(c) ethyne is passed into an ammoniacal solution of copper (I) chloride?

15. How would you distinguish between the following pairs? (Give the relevant equations.)

(a) ethane and ethene

(b) ethene and ethyne

16. Complete the following equations and name the organic compounds.

(a) $CH_3\text{-}COONa + NaOH \xrightarrow{\Delta} ?$

(b) $CH_4 + O_2 \xrightarrow{\Delta} ?$

(c) $CH_2Br\text{-}CH_2Br + KOH \xrightarrow[\Delta]{\text{ethanol}} ?$

(d) $n(CH_2{=}CH_2) \xrightarrow[\Delta]{>1000\text{ atm}} ?$

(e) $CH_3\text{-}C{\equiv}CH \xrightarrow[NH_3]{Ag_2O} ?$

17. (a) A gas "X" is obtained by heating a mixture of sodium ethanoate and soda-lime . What is gas "X" ? Write down the equation.

(b) Gas "X" can also be obtained by hydrogenation of an alkyl halide using a palladium catalyst. Name the alkyl halide. Write down the equation.

(c) Is the gas "X" saturated or unsaturated hydrocarbon ?

18. (a) By heating a mixture of sodium propionate and soda-lime, a gas "A" is evolved. What is gas "A"? Write down the equation.

(b) Gas "A" can also be formed by hydrogenation of an alkene using a nickel catalyst at 300 °C. Name the alkene. Write down the equation.

(c) Is the gas "A" saturated or unsaturated hydrocarbon? Write down the general formula .

19. (a) A gas "G" is obtained by passing the vapour of ethanol over alumina at 350 °C. What is gas "G"? Write down the chemical equation.

(b) Gas "G" can also be produced by heating an alkyl halide with alcoholic potassium hydroxide. Name the alkyl halide. Write down the equation.

(c) Is the gas "G" saturated or unsaturated hydrocarbon? Give a chemical equation to support your answer.

20. A gas "B" is obtained by treating calcium carbide with water.

(a) What is gas "B"? Write down the chemical equation.

(b) A gas "B" can also be obtained by heating alkene dibromide with alcoholic potassium hydroxide. Name the alkene dibromide. Write down the equation.

(c) Is the gas "B" saturated or unsaturated hydrocarbon?

(d) What type of reaction can gas "B" undergo (addition or substitution)? Give a chemical equation to support your answer.

21. (a) A gas "Y" is obtained by heating a mixture of ethanol and concentrated sulphuric acid at 160 °C. What is gas "Y"? Write down the chemical equation.

(b) Gas "Y" can also be obtained by heating an alkyl halide with alcoholic solution of potassium hydroxide on water bath. Name the alkyl halide. Write down the equation.

(c) Is the gas "Y" saturated or unsaturated hydrocarbon? Give the general formula of gas "Y".

22. (a) When ethyl chloride is refluxed with an aqueous solution of sodium hydroxide, compound "Z" is formed. What is compound "Z"? Write down the equation.

(b) Compound "Z" can also be formed by the fermentation of glucose with enzyme (yeast). Name an enzyme and write down the equation.

(c) What will happen when compound "Z" is heated with ethanoic acid in the presence of small amount of concentrated sulphuric acid? Write down the equation.

(d) Give the general formula of organic compounds to which compound "Z" belongs.

****

CHAPTER 15

CHEMISTRY IN SOCIETY

15.1 Chemistry in Modern Agriculture

The world population is increasing day by day and year by year. There is an urgent need for increasing food production to feed the increasing population. Chemistry helps to increase food production in agriculture.

Elements required by plants

All plants require at least 22 elements for their growth. The ten elements which are required in significant quantities are carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, sulphur, magnesium and iron. The other elements are required in very small traces.

Sources of plant nutrients

Plants get their nutrient elements from three sources; air, water and soil.Plants get carbon and oxygen from air, hydrogen and oxygen from water and other elements from the soil.

How plants obtain carbon, hydrogen and oxygen from air and water

Air is a gaseous mixture of nitrogen, oxygen and carbon dioxide. Plants get carbon dioxide from the air and water from the soil. In the presence of sunlight the green parts of the plant can bring about a chemical reaction that combines carbon dioxide and water to form sugar which is further converted to other food forms and is stored in the plant. This chemical reaction is known as photosynthesis, the process of which is very complex. But the overall reaction of photosynthesis may be expressed by the following equation.

$$6CO_2(g) + 6H_2O(l) \xrightarrow[\text{green parts}]{\text{sunlight in}} C_6H_{12}O_6(s) + 6O_2(g)$$

Sugar is a compound of carbon, hydrogen and oxygen. This sugar is used by the plant to build new compounds and also to furnish energy, both of which are essential in all vital processes, for sustaining the plants' life. With the exception of carbon, hydrogen and oxygen, all other elements are obtained from the soil.

Soil

The soil is the source of plant nutrients. It supplies water and other elements to the plants. Plants absorb their mineral nutrients from the soil in the form of dissolved salts. Rain water washes away the available soluble salts. Thus the amount of plant nutrients in the soil is continually depleted. Therefore it is necessary to supplement these plant nutrients to produce better crops. This is achieved through the use of fertilizers.

Fertilizers

Fertilizers are substances that supply nutrients to plants. They may be classified as (a) natural and (b) chemical fertilizers.

Natural fertilizers

There are two types of natural fertilizers; manure and humus. Manure is obtained by the decomposition of animal dung and urine. Humus comes from plant residues.

Although natural fertilizers are excellent nutrients for plants, these are not enough for adequate yields. Therefore chemically synthesized fertilizers are used to supplement this need.

Chemical fertilizers

Chemical fertilizers are salts and other chemical compounds containing elements necessary for plant growth. Roots of plants absorb the food from the soil in the form of soluble salts.

Nitrogen, phosphorus and potassium (NPK)

The most important elements that are required by plants from the soil are nitrogen, phosphorus and potassium (NPK) because these three elements are essential for the growth of plants. Therefore the basic composition of chemical fertilizers may constitute any one, two or all three of these elements (NPK).

Effects of nitrogen, phosphorus and potassium (NPK) on plants

Nitrogen is an essential and important constituent of the plant's body. Likewise, phosphorus is another important constituent. Potassium is not a constituent element, of the plant body. It, however, occurs in the plant as soluble salts. Its role is catalytic.

Leaf crops like cabbage, require abundant nitrogen, a fair amount of phosphorus but not much potassium. Root crops require a good amount of potassium, fair amount of phosphorus but very little nitrogen. Seed bearing plants such as peas, beans and tomatoes require a good amount of phosphorus and potassium, but little nitrogen. Flowering needs a fair amount of phosphorus and potassium, but little nitrogen. Fruiting and seed formation require higher potassium but very little nitrogen.

Classification of chemical fertilizers

According to the elements contained in them the chemical fertilizers are divided into the following groups

(1) nitrogen fertilizers,
(2) phosphorus fertilizers,
(3) potassium fertilizers.

Nitrogen fertilizers

The important nitrogen fertilizers are: urea, ammonium sulphate, ammonium nitrate, sodium nitrate and calcium nitrate.

Urea

The composition of urea according to its formula is $CO(NH_2)_2$. The percentage of nitrogen in this compound is 46 %. It has an acid reaction and the application of urea to the soil increases the acidity of the soil.

Production of urea

Urea is manufactured on a very large scale by heating ammonia and carbon dioxide under pressure with a suitable catalyst.

$$CO_2(g) + 2NH_3(g) \xrightarrow[\text{catalyst}]{\Delta\ \text{pressure}} CO(NH_2)_2(s) + H_2O(g)$$

Ammonia may be obtained by the Haber process and carbon dioxide from the combustion of petroleum products like natural gas.

Urea is being produced from natural gas in some fertilizer plants in Upper Myanmar. The urea fertilizer is produced as white pellets.

Reaction in the soil

In the soil urea reacts with water to form ammonia and carbon dioxide.

$$CO(NH_2)_2(s) + H_2O(l) \longrightarrow 2NH_3(g) + CO_2(g)$$

The bacteria in the soil converts ammonia to nitrites and then to nitrates.

$$\text{ammonia} \xrightarrow{\text{bacteria}} \text{nitrites} \xrightarrow{\text{bacteria}} \text{nitrates}$$

The plants absorb soluble nitrogen in the form of NH_4^+ and NO_3^- ions which are dissolved in the soil.

Ammonium sulphate

The composition according to its formula is $(NH_4)_2SO_4$. It contains 21% nitrogen. It has an acid reaction and so it increases the acidity of the soil.

Ammonium nitrate

The composition according to its formula is NH_4NO_3. It contains 34.35 % nitrogen.

Calcium nitrate

The composition according to its formula is $Ca(NO_3)_2$. Commercial calcium nitrate fertilizers contain 13 to 16 per cent of nitrogen.

Phosphate fertilizers

Superphosphate

The important phosphate fertilizer is superphosphate. Superphosphate is marketed in two grades containing 18 and 45 percent phosphoric acid respectively. The composition of superphosphate may be represented as $Ca(H_2PO_4)_2 . 2CaSO_4$. 18 percent superphosphate contains 18 % P_4O_{10} solution in water. 45 percent superphosphate contains 45 %P_4O_{10} soluble in water. Superphosphate is a white or grey powder or granule.

Bone meal

Bone meal is not a chemical fertilizer. It is prepared by crushing defatted bones. It contains about 3 percent of nitrogen and 22 percent phosphoric acid. Therefore it is used as a phosphate fertilizer.

Potassium fertilizers

The important potassium fertilizers are potassium chloride and potassium sulphate.

Soil reaction

You have learned that some chemical fertilizers such as urea and ammonium sulphate increase the acidity of the soil. Acidity and alkalinity of the soil is one of the important factors because the plants do not grow well on the soil of high acidity or high alkalinity.

Test for soil reaction

Soil reaction is easily tested by litmus papers. The given samples of soil are taken in separate test tubes. Some water is added in each test tube and stirred well. The contents are filtered and the filtrate tested separately with blue and red litmus papers.

Neutralization of soil acids

Lime is added to the soil to neutralize the soil acids. Lime is usually supplied to the soil as limestone, $CaCO_3$, quicklime, CaO and slaked lime, $Ca(OH)_2$. Quicklime should not be applied direct to growing plants. Lime not only neutralizes the soil acids but also supplies calcium to the soil. Calcium is one of the elements necessary for the growth of air crops.

Neutralization of soil alkali

Gypsum, $CaSO_4 . 2H_2O$ is added to the soil to neutralize soil alkali.

Insecticides

Insecticides are chemicals that kill insects. BHC or benzene hexachloride $C_6H_6Cl_6$, also known a Gammexane is used for spraying or dusting of plants, especially cotton. The insecticide Endrin is toxic to mammals and should be used with caution. Endrin is an excellent all purpose plant spray.

Aldrin and Dieldrin are other well-known insecticides which can be obtained as emulsion or powder, and are used as soil fumigant.

Growth substances

Indoleacetic acid(IAA) is the principal chemical substance which in the normal plant is responsible for many different growth regulatory activities.

Depending upon its concentration IAA can variously activate the growth of leaves, stems, roots, flowers, fruits and seeds.

The artificial application of IAA to a plant brings about characteristic growth responses.

IAA and its structurally related chemical compounds, for example, naphthalene acetic acid(NAA) could be readily synthesized. The latter substance, showing similar activities to IAA, could be manufactured more cheaply. Thus it is more economical for utilization.

These growth substances can be used in many ways in agriculture. They are used to induce flower initiation, fruit development, to delay leaf fall and fruit drop, and to produce seedless fruits. Some of them are used even as herbicides.

For example, naphthalene acetic acid could, bring about flower initiation and is successfully used for promoting simultaneous fruiting in pineapple plantations.

15.2 Cement Production

Cement

Cement is used in the construction of buildings. It is mixed with sand and water and sometimes with quicklime, CaO. Cement finds use as binder in construction works.

Cement is a grey powder. It is composed of lime, alumina, silica and iron (III) oxide (haematite) as tetracalcium alumino-ferrate, $4CaO. Al_2O_3, Fe_2O_3$, dicalcium silicate, $2CaO. SiO_2$, tricalcium silicate, $3CaO. SiO_2$, and tricalcium aluminate, $3CaO. Al_2O_3$.

Raw materials for making cement

Raw materials used for cement production are haematite, Fe_2O_3, limestone, $CaCO_3$ and clay which is composed of silicon dioxide, SiO_2 and aluminium oxide, Al_2O_3. These raw materials are ground and heated in a special furnace called Rotary Kiln.

Rotary Kiln

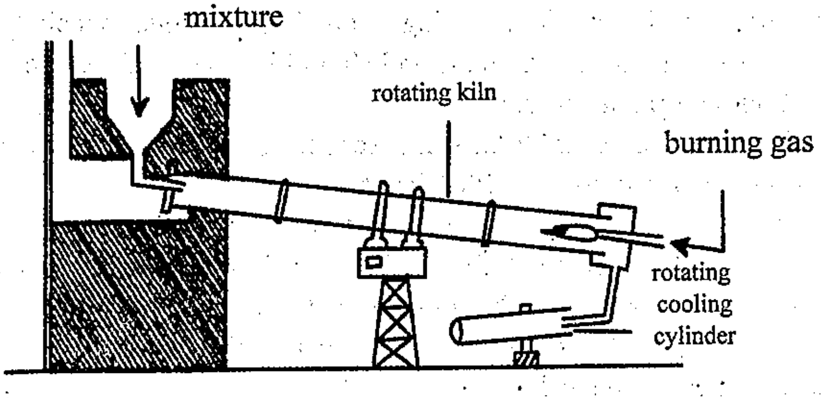


Fig. 15.1 The Rotary Kiln

The rotary kiln is essentially a wide long steel tube lined inside with fire clay bricks(Fig.15.1). The kiln rests on rollers and is held in a slightly inclined position. The kiln can be rotated slowly by a motor and so it is called a rotary kiln. The mixture in the kiln is heated by burning gas at the lower end of it.

Manufacturing process

The four main stages in the manufacturing process of cement are, mixing, heating, cooling and grinding.

1. Mixing

Limestone, haematite and clay are finely ground and mixed in the right proportions.

2. Heating

The rotary kiln is rotated by the motor. The mixture of ground limestone, haematite and clay is fed continuously from the top end of the rotary kiln and heated by the burning gas at the lower end of the kiln. As the mixture moves slowly down the inclined kiln it meets an increasingly higher temperature. The roasted product which is called clinker, comes out from the lower end of the kiln.

3. Cooling

The roasted clinker is allowed to cool in a rotating cylinder by cool air.

4. Grinding

After cooling, the clinker is mixed with the right percentage of gypsum, $CaSO_4.2H_2O$ and ground in a grinding mill. The resultant powder is cement. The gypsum regulates the setting time of cement.

Cement production in Myanmar

There are a number of cement factories in Myanmar, the oldest of which is situated near Thayetmyo.

15.3 Plaster of Paris (POP)

Plaster of Paris is a fine white powder which is used for making casts of various objects. Plaster of Paris is hydrated calcium sulphate, $2CaSO_4.\ H_2O$. This hydrate, $2CaSO_4.H_2O$ is obtained by heating gypsum, $CaSO_4.\ 2H_2O$ to about 125 °C.

When Plaster of Paris is mixed with water, the hydrate, $2CaSO_4.\ H_2O$ forms a paste, which hardens quickly, expanding slightly in the process, as a result of crystallization. Due to this property, Plaster of Paris is used for making casts and for cementing glass to metals.

15.4 Salt Production

Dissolved and undissolved substances in sea water

Sea water consists of some undissolved substances and dissolved substances. About 3.5 % by weight of salts are dissolved in sea water out of which 2.7 % is commonsalt, NaCl.

The undissolved and dissolved substances in sea water are as follows:

undissolved substances	1. Suspensions	
	2. Al_2O_3	
	3. $CaCO_3$	
	4. $CaSO_4$	
dissolved substances	5. NaCl	↓ increasing solubilities
	6. KCl	
	7. $MgSO_4$	
	8. $MgCl_2$	
	9. $MgBr_2$	

Salt production areas

The principal areas for production of salt from sea water are coastal regions.

Traditional method of production

Production sites are usually chosen where the underlying ground is almost impermeable to water since it is not economical to line the salt ponds (salterns) with concrete in small scale production. The sea water is channelled into ponds or is allowed to flow into the ponds at high tides and sealed off.

In some sites engines are used for pumping sea water. In these ponds suspensions are settled down from the sea water and clear sea water is obtained. Then the clear sea water is pumped or channelled in stages through a series of ponds during which the sun evaporates the water and the sea water is concentrated. This concentrated sea water is evaporated in iron pans by wood fires until only a small amount of water remains. The common salt crystallizes out.

Common salt obtained by the traditional method or production is not pure, since dissolved substances such as $MgSO_4$ and $MgCl_2$ together with small amounts of $CaSO_4$ remain mixed with common salt.

Pure sodium chloride is not a deliquescent substance. But it is common experience that common salt become damp when it is exposed to air for some time.

The dampness is due to the presence of magnesium chloride as one of the impurities. Magnesium chloride is hygroscopic and can absorb moisture from the atmosphere.

Disadvantages of the traditional method of production

1. The percentages of the different impurities are high in the common salt produced by the traditional method, and therefore, it is not very suitable for industrial use.
2. In the traditional method of production wood fires are used for evaporation and considerable areas of forest are destroyed yearly because of the felling of trees for firewood. It is estimated that 15000 acres of forest are depleted every year due to the use of firewood in the traditional method of salt production.

Prevention of unnecessary wastage of forests may be achieved to some extent, by using solar evaporation for production of salt.

Salt production by solar evaporation

The production of salt by solar evaporation may be carried out only during the dry, hot season. Therefore December to middle of May is the suitable time for the production of salt by solar evaporation. The production process is as follows:

A series of solar ponds, usually five in number, is made on the selected ground which should be almost impermeable. In large scale production sites, the ponds are lined with concrete. The sea water is pumped or channelled or allowed to flow into the first pond during high tides. The undissolved suspensions settle down in the first pond. This sea water is pumped or channelled into the second solar pond in which Al_2O_3 settles down. The sea water is next allowed to flow into the third pond where $CaCO_3$ settles down.

In this way undissolved particles from the sea water are removed in the first three of the series of ponds. Evaporation also takes place in these ponds and the sea water, to some extent, is concentrated.

Then the almost clear water, free from undissolved substances is allowed to flow into the fourth solar pond. In the fourth pond crystallization of dissolved substances starts to take place. During the day evaporation takes place and crystallization occurs mainly at night when the temperature drops.

Salt production by solar evaporation takes place at the fifth pond located in the field.

In this pond $CaSO_4$ which is less soluble than NaCl, KCl and $MgSO_4$ starts to crystallize out. The concentrated sea water is next channelled into the fifth solar pond and NaCl crystallizes in this pond. After the crystallization of NaCl is complete, the water in which KC1, $MgSO_4$, $MgCl_2$ and $MgBr_2$ are still dissolved is allowed to flow out from the pond. The crystals of NaCl remain in this pond. The crystals of NaCl are then scooped out, washed with concentrated salt solution to clean them and dried in the sun.

In this way 99.5 % pure solar evaporated sodium chloride is obtained.

Bittern

The water that flows out from the fifth solar pond consists of dissolved $MgSO_4$, $MgCl_2$ and $MgBr_2$. This water is called bittern. Bittern is the source from which $MgSO_4$, $MgCl_2$ and $MgBr_2$ can be extracted.

15.5 Plastics and Polymers

Polymerization

This section covers the following ideas:

(i) addition polymerization
(ii) condensation polymerization
(iii) thermoplastic and thermosetting polymers
(iv) the disposal and recycling of plastic waste.

All living things contain **polymers**. Proteins, carbohydrates, wood and natural rubber are all polymers. What nature first invented, chemists have learnt to copy, alter and use successfully. **Synthetic polymers**, often called plastics, are to be found everywhere in modern technological societies, made into bulky objects, films and fibres. They have properties to suit particular needs, ranging from car and aircraft components, to packaging and clothing.

Polymers are large organic **macromolecules**. They are made up of small repeating units known as **monomers**. These units are repeated any number of times from about a hundred to more than a million. Some are **homopolymers**, containing just one monomer. Poly(ethene), poly(propene) and poly(chloroethene) are three examples of homopolymers. Other macromolecules are **copolymers** made of two or more different types of monomers. For example, nylon is made from two monomers, and biological proteins are made from 20 different monomers, the amino acids.

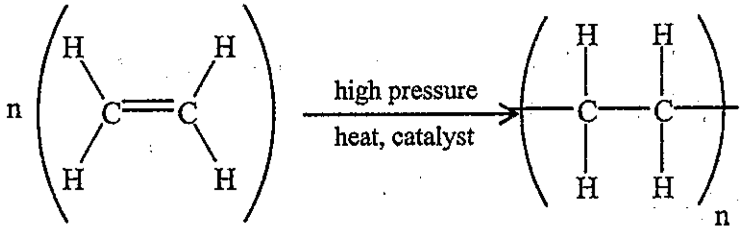
The alkene fragments from the catalytic cracking of crude oil fractions produced the starting monomers for the first plastics.

15.5.1 Addition Polymerisation

Alkenes such as ethene contain a C=C double bond. These molecules can take part in **addition reaction** where the double bond is broken and other atoms attach to the carbons. The double bond in ethene enables many molecules of ethene to join to each other to form a large molecule, poly(ethene) (Figure 15.2). This is an **addition polymer**. When first made by **Imperial Chemical Industries (ICI),** it was a revolutionary new material called 'Alkathene'. It is now commonly called by the trade-name 'polythene'.

Various conditions can be used to produce different types of poly(ethene). Generally a high pressure, a temperature at or above room temperature and a catalyst are needed. The reaction can be summarized by the equation:

$$\text{ethene} \xrightarrow[\text{heat, catalyst}]{\text{high pressure}} \text{poly(ethene)}$$



where n is a very large number.

Poly(ethene) was found to be a chemically resistant material that was very tough and durable, and a very good electrical instructor.

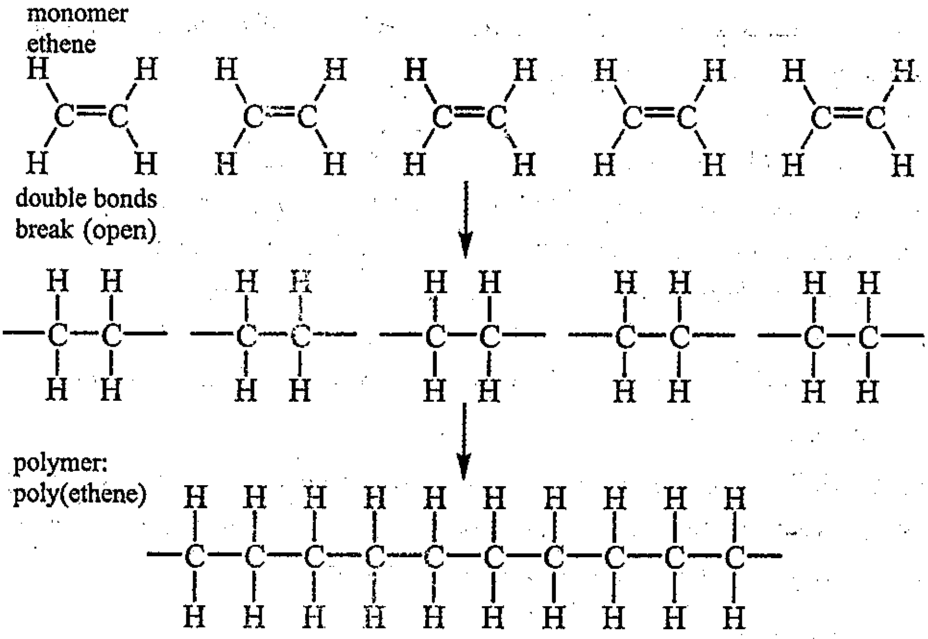
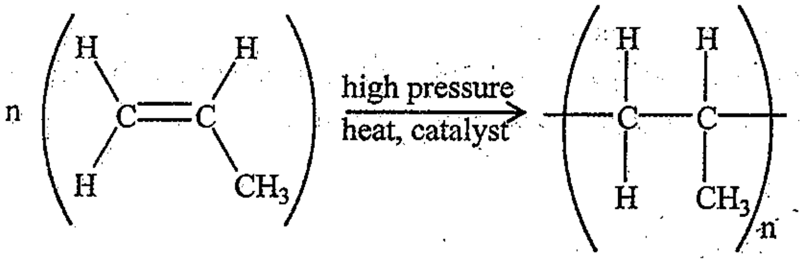


Fig. 15.2 The polymerization of ethene produces poly(ethene), whose structure is shown.

Other alkene molecules can also produce addition polymers. Propene will polymerise to produce poly(propene):

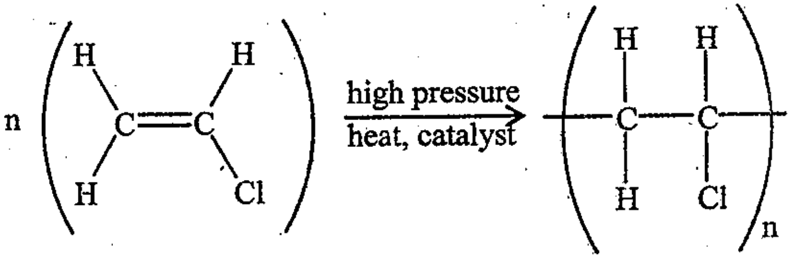
propene ——→ poly(propene)



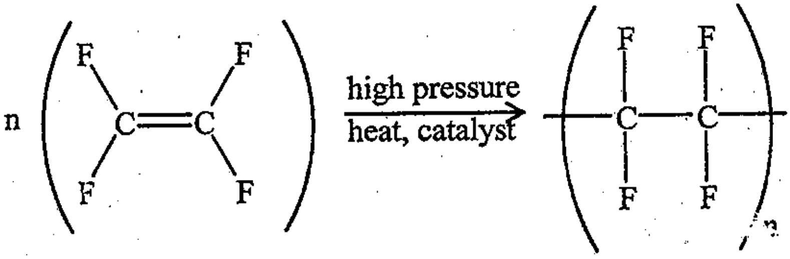
This long-chain molecule is similar in structure to poly(ethene) but with a methyl (—CH_3) group attached to every other carbon atom in the chain. It is commonly referred to by its trade-name 'polypropylene'.

Chemists also experimented with other substituted alkenes to produce plastics with particular properties in mind. Poly(chloroethene) (known as the trade-name of polyvinyl chloride or PVC) and poly(tetrafluoroethene) (known as the trade-name of polytetrafluoroethylene, 'teflon' or PTFE) are two such polymers:

chloroethene ⟶ poly(chloroethene)
(vinyl chloride) (PVC)



tetrafluoroethene ⟶ poly(tetrafluoroethene)
(PTFE)



Poly(chloroethene) (PVC) was found to be stronger and harder than poly(ethene) and therefore good for making pipes for plumbing. PTFE proved to have some unusual properties. It was very stable at high temperatures and formed a very slippery surface. The properties of some addition polymers are given in Table 15.1. Such synthetic polymers have proved to be very versatile. Many, for example poly(propene), are easy to shape by melting and moulding. Thus poly(propene) is used to make sturdy plastic objects such as crates. However, it can also be drawn out into long fibres for making ropes.

Some of the properties of addition polymers.

(i) All polymers are long-chain molecules made by joining together a large number of monomer molecules.
(ii) Addition polymerization involves monomer molecules that contain a C=C double bond.
(iii) Addition polymers are homopolymers, made from a single monomer.
(iv) During addition, the double bonds open up and the molecules join to themselves to make a molecule with a very long chain.

Table 15.1 Examples of some widely used addition polymers

Polymer (and trade-name(s))	Monomer	Properties	Examples of use
Poly(ethene) (polyethelene, polythene, PE)	Ethene $CH_2=CH_2$	tough, durable	plastic bags, bowls, bottles, packaging
Poly(propene) (polypropylene, PP)	propene $CH_3CH=CH_2$	tough, durable	crates and boxes, plastic rope
Poly(chloroethene) (polyvinyl chloride, PVC)	chloroethene $CH_2=CHCl$	strong, hard (not as flexible as polythene)	insulation, pipes and guttering
Poly(tetrafluoroethene (polytetrafluoroethylene, teflon, PTFE)	Tetrafluoro-ethene ($CF_2=CF_2$)	non-stick surface, withstands high temperatures	non-stick frying pans, non-stick taps and joints
Poly(phenylethene) (polystyrene, PS)	phenylethene (styrene) $C_6H_5CH=CH_2$	light, poor conductor of heat	insulation, packaging (foam)

Summary of core material: You should know that:

(i) alkene molecules (containing a C=C double bond) can be polymerized into very useful products

(ii) other unsaturated molecules can be polymerized to extend the range of useful addition polymers.

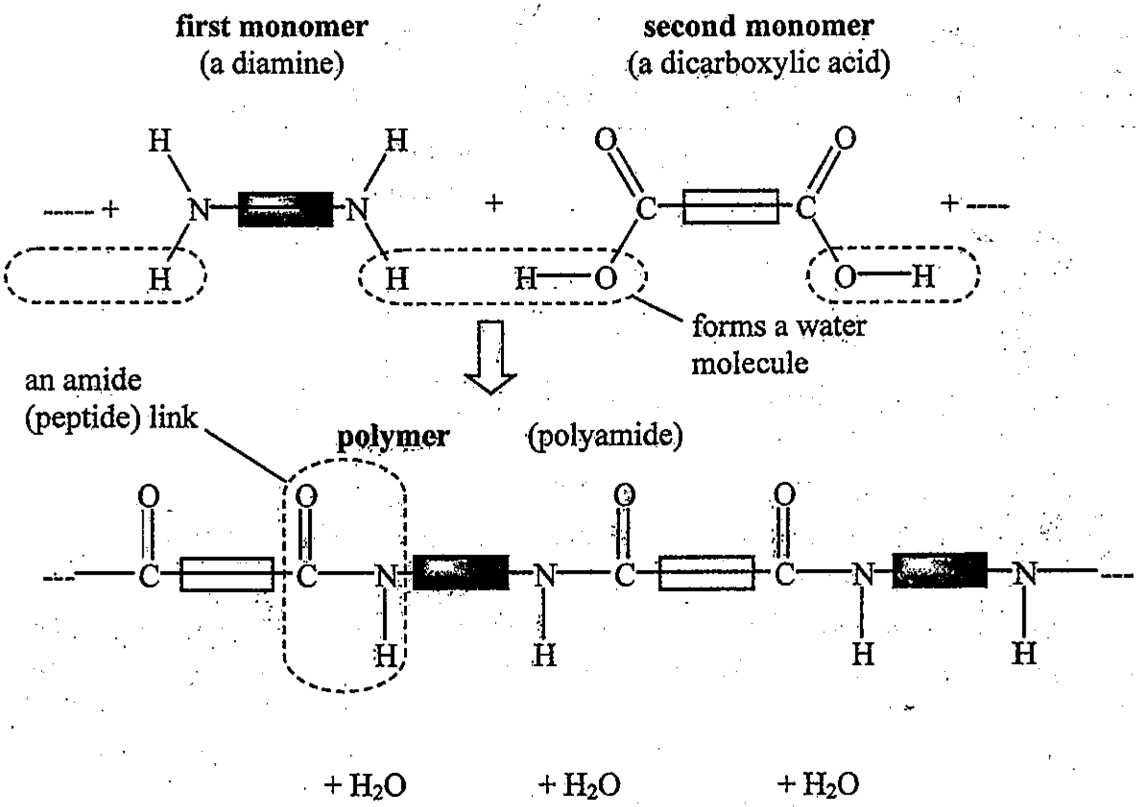
15.5.2 Condensation Polymerization

Nylon

In the early 1930s, Dupont were interested in research into artificial fibres. Knowledge of silk and wool gave clues as to how protein molecules are built. Carothers imitated the linkage in proteins and produced the first **synthetic** fibre, 'nylon'.

Nylon is a solid when first formed, but it can then be melted and forced through small holes. The long filaments cool, and the fibres produced are stretched to align the polymer molecules and dried. The fibres can be woven into fabric to make shirts, ties, sheet, etc., or turned into ropes or racquet strings. However, nylon is not just made into fibres. It has proved to be a very versatile material, and can be moulded into strong plastic items such as gear-wheels.

Nylon is a copolymer of two different monomers, a diamine and a dicarboxylic acid. Each monomer consists of a chain of carbon atoms (which are shown in the following diagrams simplified as boxes). At both ends of the monomers are **functional groups**. An amine group (—NH_2) on the first monomer reacts with a carboxylic acid group (—COOH) on the second monomer to make a link between the two molecules. Each time a link is made, a water molecule is lost:



As a result, this type of polymer is known as a **condensation polymer.** Because an **amide link** (or peptide link) is formed during polymerization, nylon is known as a **polyamide.** A version of nylon polymerization can be carried out in the laboratory (Figure 15.3).

15.5.3 Polyester

Condensation polymerization can also be used to make other polymers with properties different from those of nylon. **Polyesters** are condensation copolymers made from two monomers. One monomer has an alcohol group (—OH) at each end. The other monomer has a carboxylic acid group (—COOH) at each end. When the monomers react, an **ester link** is formed, with water being lost each time:

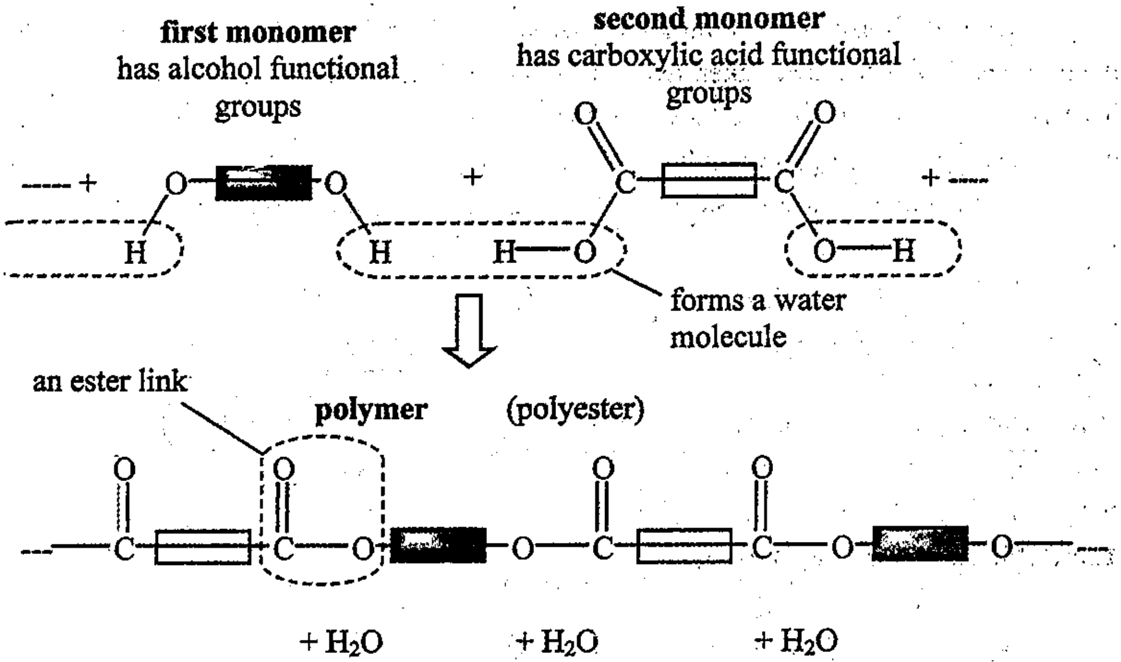


Fig. 15.3 Nylon is a polyamide and can be made in the laboratory.

One such polyester has the trade-name 'terylene'. Like nylon, terylene can be turned into fibres and woven into clothing. Terylene clothing is generally softer than that made from nylon.

15.5.4 Thermoplastic and thermosetting polymers

Most of the plastics that we use, like poly(ethene) ['polythene'], poly(chloroethene) ['PVC'] and poly(phenylethene) ['polystyrene'], can be softened on heating and melted. They set again when cooled. Such plastics are useful because they can be re-moulded. These polymers are known as **thermoplastic polymers** (or thermoplastics or thermosoftening polymers).

Another, more restricted, group of polymers can be heated and moulded only once, for example melamine. Such polymers are known as **thermosetting polymers** (or thermosets). The chains in these polymers are cross-linked to each other.

These cross-links in the plastic are permanent chemical bonds. They make the structures rigid when moulded, and no softening takes place on heating.

15.6 The Re-use, Recycling and Disposal of Plastic Waste

Plastic rubbish is a common but unwelcome sight around the world. Over the past 30 years, plastics have taken over as replacement materials in many applications. This is not surprising because they are light, cheap and corrosion-resistant, and they can be easily moulded and dyed bright colours. The problem arises from the fact that most plastics are not **biodegradable** – there are no natural microorganisms that can break them down.

Incineration (**pyrolysis**) can be used to burn plastic waste, though care must be taken not to release toxic fumes into the air. Most of the products from pyrolysis can be used as fuels or separated by fractional distillation. They can then be made into monomers for making more plastics. Research is also being carried out to produce plastics that are **biodegradable** or **photodegradable**. One poly(ethenol) plastic has been developed that is soluble in hot water.

15.6.1 Methods for recycling plastic waste:

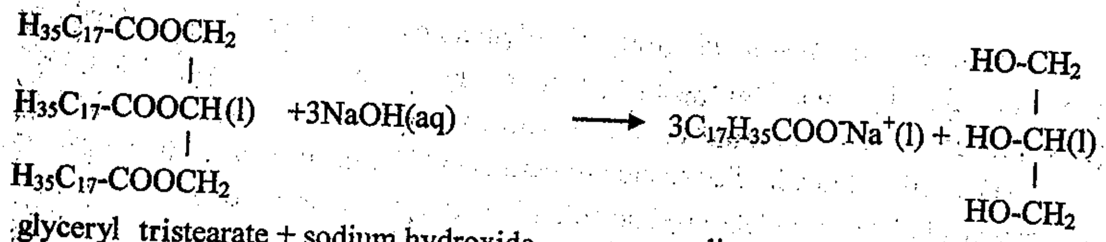
(a) **thermoplastic polymers** – (i) heat at low temperatures;(ii) obtain molten or softened polymer; (iii) re-mould into new thermoplastic products),

(b) **thermosetting polymers** – (i) heat at high temperatures (700 °C) in the absence of air; (ii) obtain new monomers and other chemicals; (iii) re-polymerise into new product(s).

15.7 Soaps and detergents

Millions of tons of soaps and soapless detergents are manufactured worldwide every year. Soap is manufactured by heating natural fats and oils of either plants or animals with a strong alkali. The fats and oils, called triglycerides, are complicated ester molecules.

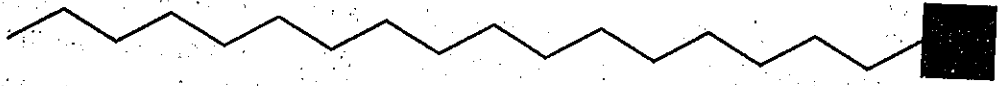
Fat is boiled with aqueous sodium hydroxide to form soap. The esters are broken down in the presence of water- hydrolysed. This type of reaction is called **saponification.** The equation given below is that for the saponification of glyceryl stearate (a fat) with sodium hydroxide.



$$\begin{array}{lcll} H_{35}C_{17}\text{-}COOCH_2 & & & HO\text{-}CH_2 \\ \quad\quad\quad | & & & \quad | \\ H_{35}C_{17}\text{-}COOCH(l) & +3NaOH(aq) \longrightarrow & 3C_{17}H_{35}COO^-Na^+(l) + & HO\text{-}CH(l) \\ \quad\quad\quad | & & & \quad | \\ H_{35}C_{17}\text{-}COOCH_2 & & & HO\text{-}CH_2 \end{array}$$

glyceryl tristearate + sodium hydroxide ⟶ sodium stearate (soap) + glycerol

The cleaning properties of the soap or detergent depend on its structure and bonding. Sodium stearate consists of a long hydrocarbon chain which is hydrophobic (water hating) attached to an ionic head which is hydrophilic (water loving).



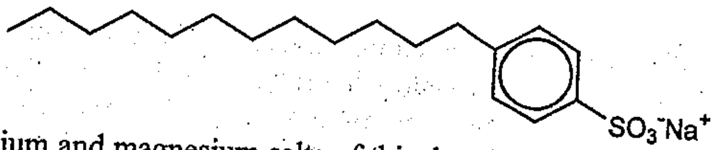
Covalent compounds are generally insoluble in water but they are more soluble in organic solvents. Ionic compounds are generally water soluble but tend to be insoluble in organic solvents. When a soap is put into water which has greasy dish (or a greasy cloth) in it, the hydrophobic hydrocarbon chain on each soap molecule becomes attached to the grease and becomes embedded in it.

On the other hand, the hydrophilic ionic head group is not attached to the grease but is strongly attached to the water molecules. When the water is stirred, the grease is slowly released and is completely surrounded by the soap molecules. The grease is, therefore, 'solubilised' and removed from the dish. The soap is able to remove the grease because of the combination of the covalent and ionic bonds present.

15.7.1 Soapless detergents

We discussed the way in which, in hard water areas, an insoluble scum forms when soap is used. This problem has been overcome by the development of synthetic **soapless detergents.** These new substances do not form scum with hard water since they do not react with Ca^{2+} and Mg^{2+} present in such water. Futhermore, these new soapless detergent molecules have been designed so that they are biodegradable. Bacteria readily break down these new molecules so that they do not persist in the environment.

Sodium alkyl benzene sulphonates were developed in the early 1970s. The structure of sodium 4-dodecyl benzene sulphonate, $C_{18}H_{29}SO_3Na$, is given below.



The calcium and magnesium salts of this detergent molecule are water soluble, so the problem of scum is solved. Very many of our washing powders (and liquids) contain this type of substance.

SUMMARY

This chapter deals with the various roles of chemistry in human society. In this chapter , the students would be able to learn that chemistry plays an important role in food production in agriculture sector such as chemical fertilizers production, cement production for building construction, plaster of paris production , and solar salt and its by-products production from sea water for household use and industrial application. The final section of this chapter is concerned with production of plastics and polymers involving recycling of thermoplastic polymers and thermosetting plastic polymers, soaps and detergents that are essential commodities for every household.

Questions and Problems

1. Calculate the percentage of nitrogen in the following nitrogen fertilizers.
   (a)Urea, $CO(NH_2)_2$ (b) Ammonium nitrate, NH_4NO_3
   (C=12; N=14; H=1, O=16)
2. A field of rice needs 15 kg nitrogen per acre. How many kilograms of ammonium nitrate are required for 10 acres?
3. The price of 100kg of ammonium sulphate is 15000 kyats and the price of 100 kg of urea is 40000 kyats.
   (a) What is the price of 1 kg of nitrogen in ammonium sulphate?
   (b) What is the price of 1kg of nitrogen in urea?
4. The price of 100kg of sodium nitrate is 80000 kyats. The price of 100kg of urea is 40000 kyats, Which fertilizer will you buy for nitrogen? Give reasons.
5. If 20 kg of nitrogen is taken by crops and 3 kg of nitrogen is carried away by running water from one acre of soil, how much of urea should be added to the soil to recover its original nitrogen content?
6. Ammonium sulphate increases the soil acidity. To prevent the increment of acidity, a farmer wants to mix the ammonium sulphate with lime, $Ca(OH)_2$ before adding these substances to the soil. Do you agree with him? Give reasons with necessary chemical equations.
7. Ammonium fertilizers should never be stored together with lime, $Ca(OH)_2$ nor should they be put in empty lime containers. With the help of the relevant equation explain why.
8. Which element N or P or K is most suitable for growing cabbage? Give reasons.
9. (a) Write an equation for the preparation of ammonium sulphate.

(b) Write an equation for the preparation of ammonium nitrate.
(c) Write an equation for the preparation of sodium nitrate.
(d) Write an equation for the formation of calcium dihydrogenphosphate, $Ca(H_2PO_4)_2$.
(e) Write an equation for the preparation of potassium chloride.
(f) Write an equation for the preparation of potassium sulphate.

10. You are provided with sodium hydroxide, barium chloride solution, dilute hydrochloric acid, and some test tubes. How would you identify a given ammonium sulphate fertilizer?

11. You are provided with calcium hydroxide, concentrated sulphuric acid, the crystals of iron (II) sulphate, distilled water and some test tubes. How would you identify the given ammonium nitrate fertilizer?

12. (a) Draw and label a diagram of a Rotary Kiln.
(b) What are the raw materials used in the production of cement?
(c) Why is gypsum mixed with clinker and ground in the final stage of cement production?

13. (a) What are the chief compounds present in cement?
(b) Describe the four important stages in the manufacture of cement.
(c) Describe how Plaster of Paris is obtained from gypsum.

14. When common salt is exposed to the air it becomes damp.
(a) Is sodium chloride a deliquescent substance?
(b) Why does common salt become damp when it is exposed to the air?

15. (a) Arrange the substances that dissolve in sea water according to their increasing solubilities.
(b) Describe the substances that separate out from sea water before the crystallization of sodium chloride.
(c) Describe the substances that remain in solution after the crystallization of sodium chloride.

16. (a) Describe why common salt produced solar evaporation is relatively more pure than that produced by wood fire evaporation.
(b) Write a paragraph to describe why salt production by solar evaporation can help forest conservation.

17. Write TRUE or FALSE for each of the following statements.
(a) Plants absorb oxygen and release carbon dioxide.
(b) Natural fertilizers are more preferrable than chemical fertilizers.
(c) Sodium chloride is a deliquescent substance.
(d) The growth of the plants is activated by IAA (indoleacetic acid).

(e) The plants grow on the soil of high acidity.

18. Fill in the blanks with a suitable word or phrase or numerical value with unit as necessary.
   (a) Plants produce the food by the process of.............
   (b) Sugar is utilized by the plants to produce new compounds and...........
   (c) NPK means..............
   (d) An important nitrogen fertilizer is ....
   (e) The function of soil bateria is to convert ammonia to ....

19. Select the correct term or terms given in the brackets.
   (a) Plants get(carbon, hydrogen, oxygen) from air.
   (b) (Flowering plants, Seed bearing plants, Root crops) require good amount of phosphorous.
   (c) Over use of (humus, manure, chemical) fertilizer changes the acidity of soil.
   (d) (Gypsum, Lime, Urea) is used to neutralize the soil acid.
   (e) Gypsum used in cement is to (improve the binding capacity, increase the bulk volume, regulate the setting time).

20. Match each of the items given in List A with the appropriate item in List B

List A	**List B**
(a) POP	(i) activate the growth of plants.
(b) Gypsum	(ii) Plaster of Paris.
(c) IAA	(iii) phosphate fertilizer
(d) Bone meal	(iv) $CaSO_4.2H_2O$
(e) Endrin	(v) an insecticide.

21. Answer the following questions.
   (a) What is meant by a polymer?
   (b) What are the properties of addition polymers?
   (c) Draw the structural formula of the following compounds:
      (i) Chloroethene(Vinyl chloride)
      (ii) Tetrafluoroethene and suggest the name of the polymer formed from each compound. Write down the equations.

22. What type of polymerization would the following compounds can undergo? Write down the equations.
   (a) $CH_3\text{-}CH = CH_2$ (b) $CF_2 = CF_2$.

23. Draw the polymer formed between the following compounds.
   (a) $HOOC-\boxed{}-COOH$ and $H_2N-\boxed{}-NH_2$
   (b) $HO-\boxed{}-OH$ and $HOOC-\boxed{}-COOH$

24. Fill in the blanks with a suitable word or phrase or numerical value with unit as necessary.

  (a) Propene will polymerize to produce ....
  (b) The trade name for polyester is ....
  (c) The trade name for polyamide is ....
  (d) Ethene will polymerise to form ....
  (e) Chloroethene will polymerise to produce ....
  (f) Tetrafluoroethene will polymerise to form ....

25. What is the long form of each of the following substances? Mention their uses.

  (a) PVC (b) PTFE (c) PP (d) PS (e) PE

26. Select the correct term or terms given in the brackets.

  (a) ($CH_3\text{-}CH = CH_2$, $CH_3\text{-}CH_2\text{-}Cl$, CH_3COOH) will undergo addition polymerization.
  (b) ($HO\text{-}CH_2\text{-}CH_2\text{-}OH$, $CH_3\text{-}CH_2\text{-}COOH$, $HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH$) will not undergo condensation polymerization.

  (c) ($CH_3\text{-}CH = CH_2$, $CH_3\text{-}CH_2\text{-}COOH$, $HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH$) will undergo condensation polymerization.
  (d) ($CH_3\text{-}CH = CH_2$, $CH_3\text{-}CH_2\text{-}Cl$, $CH_2 = CH_2$) will not undergo addition polymerization.

27. Explain the following terms:

  (a) thermoplastic polymers
  (b) thermosetting polymers
  (c) nylon
  (d) polyester

28. How can the plastic wastes be recycled?

29. What is soap ? Explain with suitable example.

30. What is meant by the following terms?

  (a) detergent (or) soapless detergent (b) saponification

31. Explain the cleaning action of soap.

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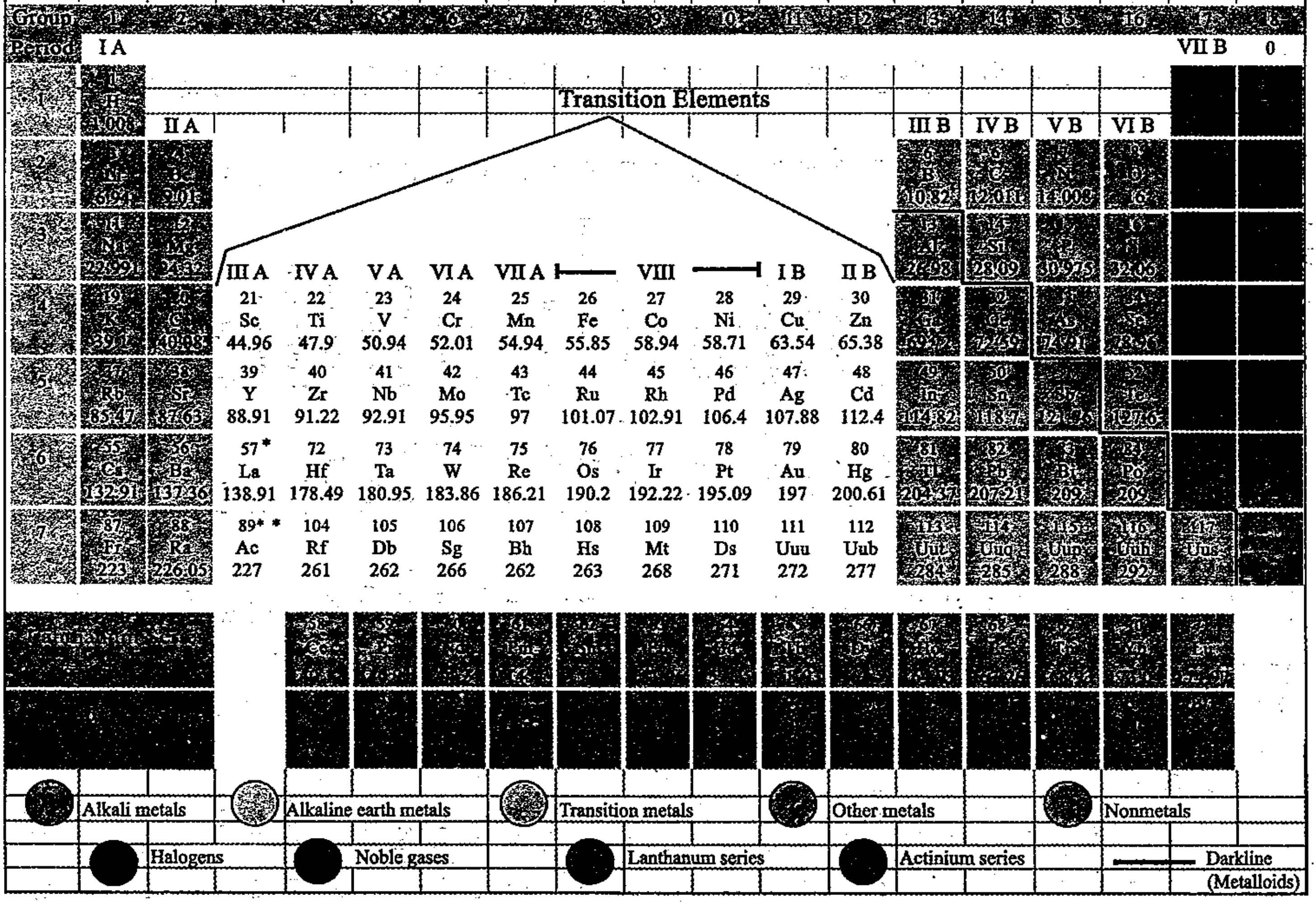
Appendix 1

PERIODIC TABLE OF THE ELEMENTS



Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period	I A																VII B	0
			Transition Elements															
1	1 H 1.008	II A											III B	IV B	V B	VI B	[illegible]	[illegible]
2	3 Li 6.941	4 Be 9.01											5 B 10.82	6 C 12.011	7 N 14.008	8 O 16	[illegible]	[illegible]
3	11 Na 22.991	12 Mg 24.32	III A	IV A	V A	VI A	VII A	VIII	VIII	VIII	I B	II B	13 Al 26.98	14 Si 28.09	15 P 30.975	16 S 32.06	[illegible]	[illegible]
4	19 K 39.1	20 Ca 40.08	21 Sc 44.96	22 Ti 47.9	23 V 50.94	24 Cr 52.01	25 Mn 54.94	26 Fe 55.85	27 Co 58.94	28 Ni 58.71	29 Cu 63.54	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.91	34 Se 78.96	[illegible]	[illegible]
5	37 Rb 85.47	38 Sr 87.63	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc 97	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.88	48 Cd 112.4	49 In 114.82	50 Sn 118.7	51 Sb 121.75	52 Te 127.6	[illegible]	[illegible]
6	55 Cs 132.91	56 Ba 137.36	57* La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.86	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.09	79 Au 197	80 Hg 200.61	81 Tl 204.37	82 Pb 207.21	83 Bi 209	84 Po 209	[illegible]	[illegible]
7	87 Fr 223	88 Ra 226.05	89** Ac 227	104 Rf 261	105 Db 262	106 Sg 266	107 Bh 262	108 Hs 263	109 Mt 268	110 Ds 271	111 Uuu 272	112 Uub 277	113 Uut 284	114 Uuq 285	115 Uup 288	116 Uuh 292	117 Uus [illegible]	[illegible]

[illegible]		58 Ce [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

● Alkali metals ● Alkaline earth metals ● Transition metals ● Other metals ● Nonmetals

● Halogens ● Noble gases ● Lanthanum series ● Actinium series —— Darkline (Metalloids)

Appendix 2 start

Table of relative atomic numbers and atomic masses of the elements

Element	Atomic Number	Symbol	Atomic mass	Element	Atomic Number	Symbol	Atomic mass
Actinium	89	Ac	227	Mercury	80	Hg	200.61
Aluminium	13	Al	26.98	Molybdenium	42	Mo	95.95
Americium	95	Am	243	Neodymium	60	Nd	144.24
Antimony	51	Sb	121.76	Neon	10	Ne	20.183
Argon	18	Ar	39.944	Neptunium	93	Np	237.05
Arsenic	33	As	74.91	Nickel	28	Ni	58.71
Astatine	85	At	210	Niobium	41	Nb	92.91
Barium	56	Ba	137.36	Nitrogen	7	N	14.008
Berkelium	97	Bk	247	Nobelium	102	No	255
Beryllium	4	Be	9.01	Osmium	76	Os	190.2
Bismuth	83	Bi	209.00	Oxygen	8	O	16
Boron	5	B	10.82	palladium	46	Pd	106.4
Bromine	35	Br	79.916	Phosphorus	15	P	30.975
Cadmium	48	Cd	112.40	Platinum	78	Pt	195.09
Calcium	20	Ca	40.08	Plutonium	94	Pu	244
Californium	98	Cf	251	Polonium	84	Po	209
Carbon	6	C	12.011	Potassium	19	K	39.100
Cerium	58	Ce	140.12	Praseodymium	59	Pr	140.91
Caesium	55	Cs	132.91	Promethium	61	Pm	145
Chlorine	17	Cl	35.457	Protactinium	91	Pa	231.04
Chromium	24	Cr	52.01	Radium	88	Ra	226.05
Cobalt	27	Co	58.94	Radon	86	Rn	222
Copper	29	Cu	63.54	Rhenium	75	Re	186.21
Curium	96	Cm	247	Rhodium	45	Rh	102.91
Dysprosium	66	Dy	162.5	Rubidium	37	Rb	85.47
Einsteinium	99	Es	254	Ruthenium	44	Ru	101.07
Erbium	68	Er	167.26	Samarium	62	Sm	150.4
Europium	63	Eu	151.96	Scandium	21	Sc	44.96
Fermium	100	Fm	257	Selenium	34	Se	78.96
Fluorine	9	F	19.00	Silicon	14	Si	28.09
Francium	87	Fr	223	Silver	47	Ag	107.880
Gadolinium	64	Gd	157.25	Sodium	11	Na	22.991
Gallium	31	Ga	69.72	Strontium	38	Sr	87.63

Element	Atomic Number	Symbol	Atomic mass	Element	Atomic Number	Symbol	Atomic mass
Germanium	32	Ge	72.59	Sulphur	16	S	32.066
Gold	79	Au	197.0	Tantalum	73	Ta	180.95
Hafnium	72	Hf	178.49	Technetium	43	Tc	97
Helium	2	He	4.003	Tellurium	52	Te	127.60
Holmium	67	Ho	164.93	Terbium	65	Tb	158.93
Hydrogen	1	H	1.008	Thallium	81	Tl	204.37
Indium	49	In	114.82	Thorium	90	Th	232.04
Iodine	53	I	126.91	Thulium	69	Tm	168.93
Iridium	77	Ir	192.22	Tin	50	Sn	118.70
Iron	26	Fe	55.85	Titanium	22	Ti	47.90
Krypton	36	Kr	83.80	Tungsten (Wolfram)	74	W	183.86
Lanthanum	57	La	138.91	Uranium	92	U	238.07
Lawrencium	103	Lr	260	Vanadium	23	V	50.94
Lead	82	Pb	207.21	Xenon	54	Xe	131.30
Lithium	3	Li	6.940	Ytterbium	70	Yb	173.04
Lutetium	71	Lu	174.97	Yttrium	39	Y	88.91
Magnesium	12	Mg	24.32	Zinc	30	Zn	65.38
Manganese	25	Mn	54.94	Zirconium	40	Zr	91.22
Mendelevium	101	Md	258				

Sr	Atomic No.	Symbol	Name	Atomic Wt	Electronic Structure	Metal	Discovered Year
1	104	Rf	Rutherfordium	261	2.8.18.32.32.10.2	Transition	1969
2	105	Db	Dubnium	262	2.8.18.32.32.11.2	Transition	1970
3	106	Sg	Seaborgium	266	2.8.18.32.32.12.2	Transition	1974
4	107	Bh	Bohnium	264	2.8.18.32.32.13.2	Transition	1976
5	108	Hs	Hassium	263	2.8.18.32.32.14.2	Transition	1984
6	109	Mt	Meitnerium	268	2.8.18.32.32.15.2	Transition	1982
7	110	Ds	Darnstadtium	271	2.8.18.32.32.17.2	Transition	1994
8	111	Uuu	Unununium	272	2.8.18.32.32.18.1	Transition	1994
9	112	Uub	Ununbium	277	2.8.18.32.32.18.2	Transition	1996
10	113	Uut	Ununtrium	284	2.8.18.32.32.18.3	Other elements	2003
11	114	Uuq	Ununquadium	285	2.8.18.32.32.18.4	Other elements	1998
12	115	Uup	Ununpentium	288	2.8.18.32.32.18.5	Other elements	2003
13	116	Uuh	Ununhexium	292	2.8.18.32.32.18.6	Other elements	2000
14	117	Uus	Ununseptium	-	-	Other elements	-
15	118	Uuo	Ununoctium	-	-	Other elements	-

Vapour Pressure of Water

Temperature °*C*	*Pressure* *mm Hg*	*Temperature* °*C*	*Pressure* *mm Hg*
0	4.6	23	21.2
1	4.9	24	22.4
2	5.3	25	23.8
3	5.7	26	25.2
4	6.1	27	26.7
5	6.5	28	28.3
6	7.0	29	30.0
7	7.5	30	31.8
8	8.0	35	42.2
9	8.6	40	55.3
10	9.2	45	71.9
11	9.8	50	92.5
12	10.5	55	118.0
13	11.2	60	149.4
14	12.0	65	187.5
15	12.8	70	233.7
16	13.6	75	289.1
17	14.5	80	355.1
18	15.5	85	433.6
19	16.5	90	525.8
20	17.5	95	633.9
21	18.7	100	760.0
22	19.8	105	906.1

Table of Activity Series

The Activity Series

Appendix 4

Element	Electro-positivity	Action of water	Action of acids	Action of air	Action of H_2 on heated oxide	Action of C on heated oxide	Nature of hydroxide	Action heat on nitrate	Occours naturally as
K	Steadily decreases	Violent at room, temperture	Explosive, Gives off H_2	Tarnishes very rapidly KOH K_2CO_3	No reaction	Give the carbide at high temparatures	Strong bases stable to heat	Give the nitrite and oxygen	Chloride
Na		Vigorous at room, temperture	Violent, Give off H_2	Tarnishes very rapidly NaOH Na_2CO_3					Chloride
Ca		Steady reaction with cold water	Vigorous reaction giving H_2	Tarnishes very rapidly CaO $Ca(OH)_2$,$CaCO_3$			Strong base, gives oxide on heating	Give oxide, nitrogen dioxide and oxygen	Chloride and carbonate
Mg		Reacts with steam	Gives off H_2	Become coated with a protective layer of oxide			Weak base, gives oxide on heating		Chloride and carbonate
Al		Red hot metal reacts with steam					Amphoteric, Give oxide on heating		Oxide
Zn						Reduction to the metal			Oxide and sulphate
Fe		Reversible		Rusts slowly	Reversible reduction		Weak base, gives oxide on heating		Oxide and sulphate
Pb		No reduction		Oxideze readily on treating	Rapid reduction		Amphoteric, Give oxide on heating		sulphide
H							Neutral		Oxide
Cu			Do not liberate H_2		Rapid reduction		Weak base, gives oxide on heating		Sulphide
Ag			Attacked only by oxiditions acids	Attacked only by traces of sulphur compounds	Oxide decomposes on heating without the need for H_2	Decomposes by heat alone	Unstable at room temperature	Give the metal nitrogen dioxide and xoygen	Sulphide and as free metal