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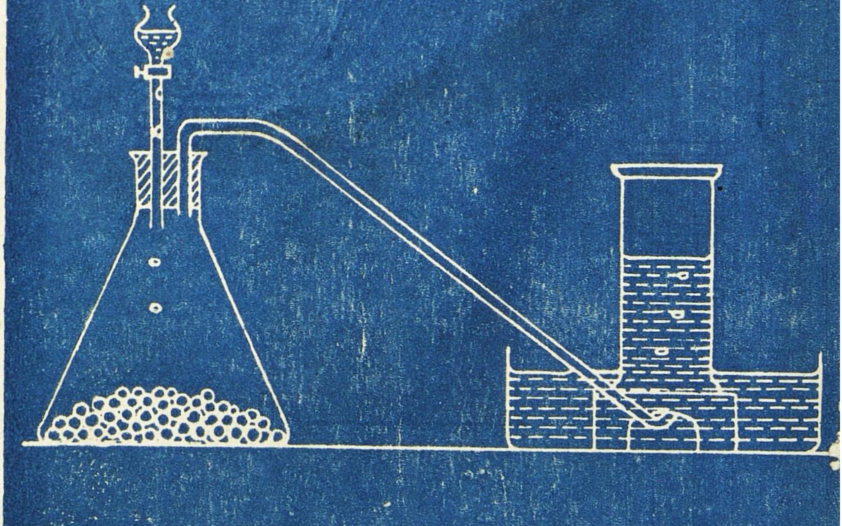

TAMILNADU TEXTBOOK SOCIETY

CHEMISTRY

HIGHER SECONDARY — FIRST YEAR

Untouchability is a Sin
Untouchability is a Crime
Untouchability is Inhuman

TAMIL NADU TEXT BOOK SOCIETY
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Section A—PHYSICAL CHEMISTRY

THE INTERNATIONAL SYSTEM OF UNITS (SI)

Physical and chemical calculations are concerned with measurements of various quantities like length, volume, mass, density, velocity, pressure, energy etc. Each quantity is expressed by a number and a unit. The choice of a coherent and comprehensive system of units will greatly simplify physico-chemical calculations. The system that is widely followed is the 'Systeme Internationale d'Unites' (a French name meaning 'International System of Units' abbreviated as SI). Basically it is an extension of the MKS system. The SI system of units is replacing the other systems in Science and Technology.

The SI system of units is based on seven basic physical quantities each with its own unit. The physical quantities and their respective units are given in Table 1.

TABLE 1

SI PHYSICAL QUANTITIES AND UNITS

Physical Quantity	Symbol for Quantity	SI Unit	Unit Symbol
length	l	metre	m
mass	m	kilogram	kg
time	t	second	s
electric current	I	ampere	A
thermodynamic temperature	T	kelvin	K
luminous intensity	I_v	candela	cd
amount of substance	n	mole	mol

SI UNITS FOR OTHER PHYSICAL QUANTITIES

From the set of basic units are derived the units for other physical quantities by multiplication or division without the introduction of a factor. For example, the basic unit of length is metre. Since volume is length cubed (l^3) the derived unit of volume will be cubic metre (m^3). The SI derived units for other common physical quantities are given in Table 2.

TABLE 2

SI DERIVED UNITS FOR OTHER PHYSICAL QUANTITIES

Physical Quantity	Symbol for Quantity	SI Unit	Unit Symbol
Area	A	square metre	m^2
Volume	V	cubic metre	m^3
Density	ρ	kilogramme per cubic metre	$kg\ m^{-3}$
Velocity	v	metre per second	ms^{-1}
Acceleration	a	metre per second per second	ms^{-2}
Force	F	Newton	N ($N = kg\ ms^{-2}$)
Pressure	P	Pascal (Newton per square metre)	Nm^{-2}
Energy	J	Joule	J ($kg\ m^2s^{-2}$)
Molar mass	M	kilogramme per mole	$kg\ mol^{-1}$
Electrical unit of charge	Q	Coulombs	C ($C = As$)

All measured quantities of heat, energy and work are expressed in joules.

PREFIXES FOR SI UNITS

A system of prefixes to indicate multiples and submultiples of the basic SI units or derived SI units is used. This method is particularly adopted when the physical quantity measured is many times larger or smaller than the basic SI unit. The prefixes commonly used are listed in Table 3.

TABLE 3

RECOGNIZED PREFIXES FOR SI UNITS

Multiple	Prefix	Symbol
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{2}	hecto	h
10	deka	da
Submultiple	**Prefix**	**Symbol**
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p

The prefixes are usually added to the basic SI unit. For example :

1 kilometre (km) = 10^{3}m = 1000 m
1 decimetre (dm) = 10^{-1}m = 0·1m

$\mu = 1 \times 10^{-6}$m. It is known as micron and not micrometre.

The exception is the kilogramme. This is already a multiple of the gramme. In this case it is customary to add the prefix to the gramme rather than to the SI unit kilogramme. For example :

1 kilogramme = 10^3 gram

1 milligramme = 10^{-3} gram

POINTS TO BE REMEMBERED REGARDING THE USE OF SI UNITS

1. The magnitude of the physical quantity measured and the unit should be written together

2. The symbol (°) and the word degree should not be used with the kelvin.

3. The multiples and submultiples of the SI units are used only when needed.

4. Compound prefixes should not be used. For example : 10^{-9}m = 1nm, not 1mμ m.

   No space should be left between the prefix and the unit.

5. Very large and very small numbers are expressed as shown in the following illustrations with a single digit before the decimal point :

   101300 is written as 1·013 × 10^5.

   0·0007501 is written as 7·501 × 10^{-4}.

6. If a quantity begins with a decimal point, a zero is placed before the decimal point. For Example, it is correct to write 0.6023.

7. When the number of units is greater than 1, for example : 10 metre, it is still written as 10 m and not 10 ms. The unit 10 ms actually means 10 × metre × second.

8. The unit for mass is retained as gram in some cases for the sake of convenience.

Some Useful Constants

Constant	Value in SI Unit
Dulong and Petit's constant	$2{\cdot}68 \times 10^{4}$ JK^{-1} kg^{-3}
Avogadro Number	$6{\cdot}023 \times 10^{23}$ mol^{-1}
Molar gas constant	$8{\cdot}3143$ JK^{-1} mol^{-1}
Molar volume	$2{\cdot}24 \times 10^{-2}$ m^{3}
Standard Temperature	273 K
Standard Pressure	$1{\cdot}013 \times 10^{5}$ Nm^{-2}
Charge of Electron	$1{\cdot}602 \times 10^{-19}$ C
Mass of Electron	$9{\cdot}109 \times 10^{-31}$ kg
Mass of Proton	$1{\cdot}6726 \times 10^{-27}$ kg
Mass of Neutron	$1{\cdot}6749 \times 10^{-27}$ kg
Velocity of Light	$2{\cdot}9979 \times 10^{8}$ ms^{-1}

CHAPTER 1

ATOMIC AND MOLECULAR WEIGHTS

Atomic Weights

Introduction : An atom is the smallest particle of matter which can take part in chemical change. The weights of individual atoms are very small. The lightest atom namely hydrogen atom has a weight of $1{\cdot}673 \times 10^{-24}$g. Even the heaviest atom has a weight less than 5×10^{-22}g. The absolute weights of atoms cannot be determined. For the sake of convenience a relative scale of atomic weights has been set up in which the weight of an atom of an element is expressed as a number relative to the weight of one carbon atom. The weight of carbon atom is taken as 12 units.

Definition : The atomic weight of an element is defined as the ratio of the weight of an atom of the element to $^{1}/_{12}$ part of the weight of a carbon atom (C-12).

$$\left.\begin{array}{l}\text{Atomic weight}\\ \text{of an element}\end{array}\right\} = \frac{\text{Weight of an atom of an element}}{\frac{1}{12}\text{ part of the weight of a carbon atom (C - 12)}}$$

A number of elements exist in several isotopic forms. These isotopes differ in their mass number. The elements occur in nature as mixtures of a constant proportion of isotopes. For example natural chlorine is an isotopic mixture of Cl^{35} and Cl^{37} in the percentage ratio of 77 : 23. The average relative atomic weight of chlorine worked out from these figures will be 35·46.

$$\frac{35 \times 77 + 37 \times 23}{100} = 35{\cdot}46$$

The atomic weight of an element is a number. If the atomic weight is expressed in gram, it is known as the **gram atomic weight.** Thus the gram atomic weight of carbon is 12g.

Molecular Weights

Definition : The molecular weight of an element or compound is defined as the ratio of the weight of one molecule of it to $\frac{1}{12}$ part of the weight of a carbon atom.

Based on carbon standard,

$$\left.\begin{array}{l}\text{Molecular weight of an}\\ \text{element or compound}\end{array}\right\} = \frac{\text{Weight of one molecule of an element or compound}}{\frac{1}{12}\text{ part of the weight of a carbon atom (C - 12)}}$$

Molecular weight is a number. If the molecular weight is expressed in gram, it is known as **gram molecular weight.**

Molecular Formula

A formula that expresses the number of atoms of each element in one molecule of compound is called the **molecular formula** of that compound. The molecular weight of a compound can be determined from a knowledge of its molecular formula and the atomic weights of its constituent elements.

Atomic weight and equivalent weight

The atomic weight of an element is related to its equivalent weight by a simple expression.

Derivation : Let one atom of an element A combine with n atoms of hydrogen to form a compound of formula AH_n. Let the atomic weight of the element be x. The atomic weight of hydrogen is 1·008.

$n \times 1{\cdot}008$ parts by weight of hydrogen is in combination with x parts by weight of the element.

$\therefore$ 1·008 parts by weight of hydrogen will combine with $\frac{x}{n}$ parts by weight of the element.

By definition the equivalent weight of the element is the number of parts by weight of the element which combines with or displaces 1·008 parts by weight of hydrogen. Therefore, the value $\frac{x}{n}$ represents the equivalent weight 'E' of the element.

$$E = \frac{x}{n}$$

'n' represents the number of atoms of hydrogen that has combined with one atom of the element. Therefore 'n' represents the valency of the element. Hence

$$\text{Equivalent weight} = \frac{\text{Atomic weight}}{\text{Valency}}$$

Determination of Atomic Weights

Dulong and Petit's Law : This law is made use of in the determination of the atomic weights of a number of solid elements. P. L. Dulong and A. T. Petit determined the specific heats of a number of elements in the solid state. In the SI system the specific heat of a substance represents the amount of heat in joules required to raise the temperature of 1 kg. of a substance through a temperature of 1 K. Its unit is $J\ kg^{-1}\ K^{-1}$.

$$1\ cal\ g^{-1}K^{-1} = 4{\cdot}184\ Jg^{-1}K^{-1} \simeq 4{\cdot}184 \times 10^{3}\ Jkg^{-1}K^{-1}$$

Dulong and Petit found that the product of the atomic weight and the specific heat of the solid element is a constant. This constant is referred to as the **atomic heat**. The experimental results were stated in 1819 in the form of a law known as Dulong and Petit's law.

The product of the atomic weight of an element and its specific heat in the solid state is a constant and is approximately equal to $2{\cdot}68 \times 10^{4}\ Jkg^{-1}K^{-1}$

$$\text{Atomic weight} \times \text{specific heat} \simeq 2{\cdot}68 \times 10^{4}$$

This law is strictly obeyed by solid elements, generally metals whose atomic weight exceed 20. This constancy is not noted in elements such as carbon, silicon, boron, etc.

Determination of atomic weight using Dulong and Petit's law

$$\text{Atomic weight} = \text{Equivalent weight} \times \text{Valency}$$

From the above relationship it is clear that the atomic weight of any element can be determined from a knowledge of its accurate equivalent weight and correct valency. The correct valency of the element can be arrived at using Dulong and Petit's law.

(i) **Calculation of approximate atomic weight** according to Dulong and Petit's law :

$$\text{Atomic weight} \times \text{specific heat} = 2{\cdot}68 \times 10^4$$

The specific heat of the element is determined.

$$\therefore \text{Atomic weight} = \frac{2{\cdot}68 \times 10^4}{\text{specific heat}}$$

The atomic weight thus calculated is only approximate since the value $2{\cdot}68 \times 10^4$ is only approximate.

(ii) **Calculation of approximate valency** :

$$\text{Atomic weight} = \text{Equivalent weight} \times \text{valency}$$

$$\therefore \text{Valency} = \frac{\text{Atomic weight}}{\text{Equivalent weight}}$$

The equivalent weight of the element is determined accurately by any suitable method. The valency thus calculated is the approximate valency since we have substituted approximate atomic weight in the equation.

(iii) **Calculation of correct atomic weight** :

Valency being a whole number, the approximate valency is corrected to the nearest whole number. The accurate atomic weight is then calculated by multiplying the exact equivalent weight by the correct valency.

Problem (1) : An oxide of a metal was found to contain 79·9% of the metal. The specific heat of the metal is $3{\cdot}92 \times 10^2$ Jkg^{-1}K^{-1}. Calculate the accurate atomic weight of the metal.

$$\text{Atomic weight} \times \text{specific heat} = 2{\cdot}68 \times 10^4$$

$$\text{Specific heat of the metal} = 3{\cdot}92 \times 10^2\ \text{Jkg}^{-1}\text{K}^{-1}$$

$$\text{Approximate atomic weight} = \frac{2{\cdot}68 \times 10^4}{3{\cdot}92 \times 10^2} = 68{\cdot}36$$

(i) Calculation of the equivalent weight of the metal :

Weight of metallic oxide = 100

Weight of metal = 79·9

Weight of oxygen = 20·1

20·1 parts by weight of oxygen has combined with 79·9 parts by weight of the metal.

8 parts by weight of oxygen will combine with $\frac{79{\cdot}9}{20{\cdot}1} \times 8$ = 31·79 parts by weight of the metal

∴ Equivalent weight of the metal = 31·79

(ii) Calculation of approximate Valency :

$$\text{Atomic weight} = \text{Equivalent weight} \times \text{Valency}$$

$$\text{Approximate valency} = \frac{\text{Approximate atomic weight}}{\text{Equivalent weight}}$$

$$\text{Approximate valency} = \frac{68{\cdot}36}{31{\cdot}79} = 2{\cdot}151$$

(iii) Calculation of correct atomic weight :

Corrected Valency = 2

(2·151 is corrected to the nearest whole number)

Correct atomic weight = 2 × 31·79 = 63·58

Problem (2) : 1 gram of a metal gives 1·328 g. of its chloride. The specific heat of the metal is $2{\cdot}339 \times 10^2$ $\text{Jkg}^{-1}\ \text{K}^{-1}$. Calculate the exact atomic weight of the metal.

Weight of metallic chloride = 1·328 g

Weight of metal = 1·000 g

Weight of chlorine = 0·328 g

0·328 parts by weight of chlorine has combined with 1 part of the metal.

35·46 parts by weight of chlorine will combine with $\frac{1}{0\cdot328} \times 35\cdot46 = 108\cdot1$ parts by weight of the metal.

$$\text{Equivalent weight of the metal} = 108\cdot1$$

$$\text{Atomic weight} \times \text{specific heat} = 2\cdot68 \times 10^4$$

$$\text{Approximate atomic weight} = \frac{2\cdot68 \times 10^4}{2\cdot339 \times 10^2} = 114\cdot6$$

$$\text{Valency} = \frac{\text{Atomic weight}}{\text{Equivalent weight}}$$

$$\text{Approximate valency} = \frac{114\cdot6}{108\cdot2} = 1\cdot059$$

$$\text{Corrected valency} = 1$$

$$\text{Accurate atomic weight} = 108\cdot1 \times 1 = 108\cdot1$$

Problem (3) : 0·702g. of cadmium when dissolved in dilute hydrochloric acid evolved $1\cdot4 \times 10^{-4}$ m^3 of hydrogen at S.T.P. If the specific heat of the metal is $2\cdot10 \times 10^2$ Jkg^{-1}K^{-1}. Calculate the equivalent weight and accurate atomic weight of the metal.

At S.T.P. $1\cdot4 \times 10^{-4}$ m^3 hydrogen is evolved by 0·702 g. of metal.

At S.T.P. $1\cdot12 \times 10^{-2}$ m^3 hydrogen will be evolved by $\frac{1\cdot12 \times 10^{-2}}{1\cdot4 \times 10^{-4}} \times 0\cdot702$ g. of the metal $= 56\cdot15$

$$\text{Equivalent weight of the metal} = 56\cdot15$$

$$\text{Atomic weight} \times \text{specific heat} = 2\cdot68 \times 10^4$$

$$\text{Approximate atomic weight} = \frac{2\cdot68 \times 10^4}{2\cdot10 \times 10^2} = 127\cdot7$$

$$\text{Valency} = \frac{\text{Atomic weight}}{\text{Equivalent weight}}.$$

Approximate valency $= \frac{127 \cdot 7}{56 \cdot 15} = 2 \cdot 274$

Corrected valency $= 2$

Accurate atomic weight = Equivalent weight × Correct valency

$= 56 \cdot 15 \times 2 = 112 \cdot 30$

Accurate atomic weight of the metal = 112·30

Equivalent weight of the metal = 56·15

Atoms and molecules: Avogadro pointed out that there are two kinds of ultimate particles—the atom and the molecule. The atom is the ultimate particle of matter which cannot exist freely and which can take part in a chemical change. The molecule is the ultimate particle which can exist freely and which is made up of atoms of the constituent elements. A molecule of an element may have one or more atoms of the same element present in it, while a molecule of a compound must always contain two or more atoms of different elements. In 1811 Avogadro stated his hypothesis.

Avogadro's Hypothesis: 'Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules'. Applying this hypothesis to the example cited above,

1 volume of hydrogen + 1 volume of chlorine → 2 volumes of hydrogen chloride

Let the number of molecules present in one volume be n

n molecules of hydrogen + n molecules of chlorine → 2 n molecules of hydrogen chloride

1 molecule of hydrogen + 1 molecule of chlorine → 2 molecules of hydrogen chloride

Hence each molecule of hydrogen chloride contains half molecule of hydrogen and half molecule of chlorine which is quite understandable as a molecule can have two or more atoms.

Applications of Avogadro's Hypothesis

This hypothesis clearly explains Gay Lussac's Law of Gaseous Volumes. *Further it helps us to calculate* the following:

1. **Deduction of Atomicity of Elements**: Atomicity represents the number of atoms present in one molecule of an element. *In the reaction* between hydrogen and chlorine it is shown that

1 molecule of hydrogen + 1 molecule of chlorine →
2 molecules of hydrogen chloride.

A molecule of hydrogen chloride should contain at least one atom of hydrogen and one atom of chlorine. Hence two molecules of hydrogen chloride must contain at least two atoms of hydrogen and two atoms of chlorine. These two hydrogen atoms must have come from one molecule of hydrogen. Similarly the cource of two chlorine atoms is one molecule of chlorine. Therefore a molecule of hydrogen must contain at least two atoms of hydrogen i.e. hydrogen molecule is diatomic. Similarly a molecule of chlorine contains two atoms of chlorine. It can be shown that all elementary gases like hydrogen, chlorine, nitrogen, oxygen etc. are diatomic. Gaseous elements like hydrogen, oxygen, chlorine etc, are diatomic. Metals like sodium, potassium, iron etc. are monoatomic. The *molecular weight of an element* can be calculated from the expression.

$$\left.\begin{array}{c}\text{Molecular weight}\\ \text{of an element}\end{array}\right\} = \text{Atomic weight} \times \text{Atomicity}$$

The molecular weight of a diatomic element is twice its atomic weight. For example molecular weight of hydrogen $= 1{\cdot}008 \times 2 = 2{\cdot}016$. In the case of monoatomic elements the atomic weight is the same as the molecular weight.

2. **Molecular Weight and Vapour Density**: Using Avogadro's hypothesis we can derive an expression relating vapour density and molecular weight of a gas. The density of a gas is defined in two ways.

(i) The normal density or absolute density of a gas is the weight in kg of one m^3 of the gas at standard temperature and pressure.

(ii) The relative density of a gas is a number which represents how many times a certain volume of the gas is heavier than an equal volume of a standard gas usually hydrogen under the same conditions of temperature and pressure. Absolute density is expressed in kg m^{-3} while relative density is a number. Many substances which are solids or liquids at ordinary temperatures can be vapourised at higher temperatures so that it is possible to find the relative densities of these substances also in the same way as for substances which are gases at ordinary temperatures. The relative density of a gas is then called **vapour density**.

$$\text{Vapour density} = \frac{\text{Weight of a certain volume of a gas under the same conditions of temperature and pressure}}{\text{Weight of an equal volume of hydrogen under the same conditions of temperature and pressure}}$$

Let there be 'n' molecules in a certain volume of the gas

$$\text{Vapour density} = \frac{\text{Weight of 'n' molecules of the gas}}{\text{Weight of 'n' molecules of hydrogen}}$$

$$\textbf{Vapour density} = \frac{\textbf{Weight of one molecule of the gas}}{\textbf{Weight of one molecule of hydrogen}}$$

$$\textbf{Vapour density} = \frac{\textbf{Molecular weight of the gas}}{\textbf{Molecular weight of hydrogen}}$$

Molecular weight of hydrogen = Atomic weight of hydrogen × atomicity

$$= 1{\cdot}008 \times 2 = 2{\cdot}016 \simeq 2$$

$$\textbf{Vapour density} = \frac{\textbf{Molecular weight of the gas}}{\textbf{2}}$$

Molecular weight = 2 × Vapour density.

3. Molar Volume : An important application of Avogadro's hypothesis is to arrive at the value of molar volume of all gases. It has-been found experimentally that the density of hydrogen is 0·08987 kg m^{-3} at standard temperature and pressure. The volume occupied by 0·08987 kg of hydrogen at S. T. P. is 1 m^3.

∴ The volume occupied by $2{\cdot}016 \times 10^{-3}$ kg of hydrogen at S. T. P. is $\frac{1}{0{\cdot}0899} \times 2{\cdot}016 \times 10^{-3} = 2{\cdot}243 \times 10^{-2}\ m^3$

In the above calculation $2{\cdot}016 \times 10^{-3}$ represents the molecular weight of hydrogen in kilogram.

$$\text{Vapour density} = \frac{\text{Weight of a certain volume of the gas}}{\text{Weight of an equal volume of hydrogen}}$$

Let the volume be taken as $2{\cdot}24 \times 10^{-2} m^3$ at S. T. P.

$$\left.\begin{matrix}\text{Vapour}\\ \text{density}\end{matrix}\right\} = \frac{\text{Weight of } 2{\cdot}24 \times 10^{-2} m^3 \text{ of the gas at S.T.P.}}{\text{Weight of } 2{\cdot}24 \times 10^{-2} m^3 \text{ of hydrogen at S.T.P.}}$$

The weight of $2{\cdot}24 \times 10^{-2} m^3$ of hydrogen at S.T.P. is equal to 2.

$$\therefore \left.\begin{matrix}\text{Vapour}\\ \text{density}\end{matrix}\right\} = \frac{\text{Weight of } 2{\cdot}24 \times 10^{-2} m^3 \text{ of the gas at S.T.P.}}{2}$$

∴ Weight of $2{\cdot}24 \times 10^{-2} m^3$ of the gas at S.T.P.
= 2 × Vapour density

Molecular weight = 2 × Vapour density

∴ Weight of $2{\cdot}24 \times 10^{-2} m^3$ of the gas at S.T.P.
= Molecular weight of the gas

Thus $2{\cdot}24 \times 10^{-2} m^3$ of any gas at standard temperature and pressure has a weight equal to its molecular weight. This constant volume ($2{\cdot}24 \times 10^{-2} m^3$ at S.T.P.) is known as gram molecular volume or molar volume. The **molar volume** of a gas is the volume occupied by one gram molecular weight or one mole of the gas at standard temperature and pressure.

4. **Calculation of Density of Gases:** Avogadro's hypothesis enables us to calculate the density of a gas. If the formula of a gas is known, its density can be calculated. **Illustration**: To calculate the density of oxygen at S.T.P.

$$\text{Density} = \frac{\text{Weight in kg}}{\text{Volume in m}^3}$$

The gram molecular weight of oxygen is 32 g. When expressed in kg the value is 32×10^{-3} kg. Thus the volume occupied by 32×10^{-3} kg of oxygen at S.T.P. is $2{\cdot}24 \times 10^{-2}\,\text{m}^3$.

$$\therefore \text{ Density of oxygen} = \frac{32 \times 10^{-3}}{2.24 \times 10^{-2}} = 1{\cdot}429 \text{ kg m}^{-3}$$

At S.T.P. the density **of oxygen is $1{\cdot}429$ kg m^{-3}.**

Problem (4): The density of methane at S.T.P. is $0{\cdot}717$ kg m^{-3}. Calculate the molecular weight of methane.

The weight of 1 m^3 of methane at S.T.P. in $0{\cdot}717$ kg.

The weight of $2{\cdot}24 \times 10^{-2}\,\text{m}^3$ of methane at S.T.P. is

$$0{\cdot}717 \times 2{\cdot}24 \times 10^{-2} \text{ kg}$$
$$= 1{\cdot}606 \times 10^{-2} \text{ kg.}$$

Gram molecular weight of methane $= 1{\cdot}606 \times 10^{-2} \times 1000$ g
$= 16{\cdot}06$ g.

Problem (5): Calculate the volume of oxygen evolved at S.T.P. when $2{\cdot}45$ kg of potassium chlorate is completely decomposed.

$$\underset{245}{2\,KClO_3} \longrightarrow 2KCl + \underset{96}{3O_2}\uparrow$$

245 g of potassium chlorate on decomposition gives 96 g of oxygen.

$2{\cdot}45 \times 10^3$g potassium chlorate will give on decomposition

$$\frac{2{\cdot}45 \times 10^3 \times 96}{245} = 960 \text{ g}$$

The volume occupied by 32 g of oxygen at S.T.P is

$$2{\cdot}24 \times 10^{-2}\,\text{m}^3$$

The volume occupied by 960 g of oxygen at S.T.P. is

$$\frac{2{\cdot}24 \times 10^{-2} \times 960}{32} = 6{\cdot}72 \times 10^{-1}\,\text{m}^3$$

AVOGADRO NUMBER

The gram molecular weight of any gas occupies the same volume of $2{\cdot}24 \times 10^{-2} m^3$ at standard temperature and pressure. This is the **molar volume.** Hence it follows that the molar volume of any gas ($2{\cdot}24 \times 10^{-2} m^3$ at S.T.P.) must contain the same number of molecules. Therefore the number of molecules present in one gram molecular weight of all gases must be constant. This constant number is known as the **Avogadro Number.**

Definition : The Avogadro Number is the number of molecules present in one gram molecular weight or one mole of any element or compound. It is also the number of atoms present in one gram atomic weight of an element. Avogadro number is denoted by the symbol N and it has the value of $6{\cdot}023 \times 10^{23}$. The gram molecular weight of a carbon dioxide is 44 g. 44 g of carbon dioxide contains $6{\cdot}023 \times 10^{23}$ molecules of carbon dioxide. Similarly 1·008 g of hydrogen contains $6{\cdot}023 \times 10^{23}$ atoms of hydrogen. $2{\cdot}24 \times 10^{-2} m^3$ of carbon dioxide at S.T.P. contains $6{\cdot}023 \times 10^{23}$ molecules.

Problem (6) : Calculate the number of atoms present in 1 kg of silver.

The gram atomic weight of silver = 107·9 g.

When expressed in kilogram its value is $107{\cdot}9 \times 10^{-3}$ kg.

Avogadro Number = $6{\cdot}023 \times 10^{23}$

$107{\cdot}9 \times 10^{-3}$ kg. silver contains $6{\cdot}023 \times 10^{23}$ atoms of silver.

1 kg. silver contains $\dfrac{6{\cdot}023 \times 10^{23}}{107{\cdot}9 \times 10^{-3}} \times 1 = 5{\cdot}584 \times 10^{24}$ atoms of silver.

Problem (7) : How many atoms are present in 1 g of gold?

Gram atomic weight of gold = 197 g.

197 g of gold contains $6{\cdot}023 \times 10^{23}$ atoms of gold.

1 g of gold will contain $\dfrac{6{\cdot}023 \times 10^{23}}{197} \times 1 = 0{\cdot}03057 \times 10^{23}$

$= 3{\cdot}057 \times 10^{21}$ atoms of gold.

Problem (8) : Calculate the number of molecules in 11 g. of carbon dioxide.

Gram molecular weight of carbondioxide = 44 g

$$\left.\begin{array}{l}\text{Number of molecules present in}\\ \text{44 g of carbon dioxide}\end{array}\right\} = 6.023 \times 10^{23}$$

$$\left.\begin{array}{l}\text{Number of molecules}\\ \text{present in 11 g of}\\ \text{carbondioxide}\end{array}\right\} = \frac{6{\cdot}023 \times 10^{23} \times 11}{44} = 1{\cdot}506 \times 10^{23}$$

Problem (9) : What is the weight of (a) 1 atom of silver (b) 1 molecule of hydrogen chloride ?

(a) Avogadro Number = $6{\cdot}023 \times 10^{23}$

The weight of $6{\cdot}023 \times 10^{23}$ atoms of silver is 107·9 g.

The weight of 1 atom of silver is $\frac{107{\cdot}9}{6{\cdot}023 \times 10^{23}} \times 1$

$$= \frac{107{\cdot}9}{6{\cdot}023} \times 10^{-23}$$

$$= 17{\cdot}92 \times 10^{-23}$$

$$= 1{\cdot}792 \times 10^{-22} \text{ g.}$$

(b) Gram molecular weight of hydrogen chloride = 36·47g.

$6{\cdot}023 \times 10^{23}$ molecules of hydrogen chloride weighs 36·47 g.

One molecule of hydrogen chloride will weigh

$$\frac{36{\cdot}47}{6{\cdot}023 \times 10^{23}} \times 1$$

$$= \frac{36{\cdot}47}{6{\cdot}023} \times 10^{-23}$$

$$= 6{\cdot}053 \times 10^{-23} \text{ g.}$$

1 molecule of hydrogen chloride will have the weight $6{\cdot}053 \times 10^{-23}$ g.

Problem (10) : How many molecules are present in $3{\cdot}6 \times 10^{-3} m^3$ of oxygen at standard temperature and pressure?

Gram molar volume = $2{\cdot}24 \times 10^{-2}$ m^3

Avogadro Number = $6{\cdot}023 \times 10^{23}$

$2{\cdot}24 \times 10^{-3}$ m^3 of oxygen at S.T.P. contains $6{\cdot}023 \times 10^{23}$ molecules

$5{\cdot}6 \times 10^{-3}$ m^3 of oxygen at S.T.P. will contain

$$\frac{6{\cdot}023 \times 10^{23}}{2{\cdot}24 \times 10^{-2}} \times 5{\cdot}6 \times 10^{-3}$$

$$= 1{\cdot}506 \times 19^{23} \text{ molecules.}$$

The mole concept

Chemical reactions take place between large number of particles such as atoms, molecules or ions. Each of these particles has its own relative weight. It is necessary to have a basic unit which relates the amount of each substance and the weight. The basic independent practical unit for amount of substance is the mole represented by the symbol 'n'. The abbreviation for mole is 'mol'.

Definition : The mole is the amount of substance which contains the same number of particles as there are atoms in 12 g of carbon (C^{12}). This number is known as the Avogadro Number and has the value $6{\cdot}023 \times 10^{23}$. The concept of mole may be applied to molecules, atoms, or ions and therefore it is essential to specify the particles concerned. For example ;

A mole of silver atoms has a weight of 107·9 g.

A mole of hydrogen molecules has a weight of 2·016 g.

A mole of hydrogen atoms has a weight of 1·008 g.

A mole of sulphate ions has a weight of 96·06 g.

The concept of mole is very often used in chemical calculations. For example consider the reaction

$$H_2 + Cl_2 \rightarrow 2HCl$$

1 mole of hydrogen and 1 mole of chlorine combine to give two moles of hydrogen chloride. Substituting the molecular weight of each substance, 2 g of hydrogen and 71 g of chlorine combine to give 73 g of hydrogen chloride. Using such balanced chemical equations, the weights of the products formed in the reaction can be calculated. The volume of the gaseous product can also be calculated from the weight of the product formed.

Problem (11) : How many moles are present in

(a) 4 g methane (b) 50 g calcium carbonate (c) 10 g water.

Molecular weight of methane (CH_4) $= 12 + 4 = 16$.

$$\text{Moles of methane} = \frac{\text{Weight of methane in gram}}{\text{Gram molecular weight of methane}} = \frac{4}{16}$$

$$= 0{\cdot}25 \text{ mole.}$$

(b) **Molecular weight** of calcium carbonate ($CaCO_3$)

$$= 40 + 12 + 48 = 100$$

$$\left.\begin{array}{c}\text{Moles of calcium}\\ \text{carbonate}\end{array}\right\} = \frac{\text{Weight of calcium carbonate in gram}}{\text{Gram molecular weight of calcium carbonate}}$$

$$= \frac{50}{100}$$

$$= 0{\cdot}5 \text{ mole.}$$

(c) **Molecular weight of water** $= 18$

$$\textbf{Moles of water} = \frac{\text{Weight of water in gram}}{\text{Gram molecular weight of water}}$$

$$= \frac{10}{18} = 0.55 \text{ mole.}$$

Problem (12) : Which of the following is the heaviest?

(a) 0·5 mole water (b) $1{\cdot}12 \times 10^{-2}\ m^3$ oxygen at standard temperature and pressure (c) $2{\cdot}24 \times 10^{-2} m^3$ ammonia at S.T.P. (d) 0·1 mole of silver (e) $5{\cdot}6 \times 10^{-3}\ m^3$ sulphur trioxide at S.T.P.

(a) Gram molecular weight of water $= 18$ g.
Weight of 0·5 mole of water $= 18 \times 0{\cdot}5 = 9$ g.

(b) The weight $2{\cdot}24 \times 10^{-2}\ m^3$ of oxygen at S.T.P. $= 32$g.
The weight of $1{\cdot}12 \times 10^{-2}\ m^3$ of oxygen at S.T.P.

$$= \frac{32}{2{\cdot}24 \times 10^{-2}} \times 1{\cdot}12 \times 10^{-2}$$

$$= \mathbf{16\ g}.$$

(c) Gram molecular weight of ammonia = 17 g.
$2{\cdot}24 \times 10^{-2}\ m^3$ ammonia at S.T.P. has a weight of 17 g.

(d) The weight of 1 mole of silver = 107·9 g.
The weight of 0·1 mole of silver = 10·79 g.

(e) Gram molecular weight of sulphur trioxide = 80 g.
$2{\cdot}24 \times 10^{-2}\ m^3$ sulphur trioxide at S.T.P. has a weight of 80 g.
$5{\cdot}6 \times 10^{-3}\ m^3$ sulphur trioxide at S.T.P. has a weight

of $\frac{80}{2{\cdot}24 \times 10^{-2}} \times 5{\cdot}6 \times 10^{-3} = 20$ g.

∴ $5{\cdot}6 \times 10^{-3} m^3$ sulphur trioxide at S.T.P. is the heaviest.

Problem (13) : Calculate the percentage composition of calcium carbonate. How many kg. of carbon dioxide can be obtained from 50 kg. limestone containing 90% pure calcium carbonate?

Molecular weight of calcium carbonate $= 40 + 12 + 48 = 100$.

100 g of calcium carbonate contains 40 g of calcium, 12 g of carbon and 48 g of oxygen.

% composition of Calcium Carbonate

$$\text{Calcium} = \frac{40}{100} = 40\%$$

$$\text{Carbon} = \frac{12}{100} = 12\%$$

$$\text{Oxygen} = \frac{48}{100} = 48\%$$

On heating, calcium carbonate decomposes to give calcium oxide and carbon dioxide.

$$\underset{(100)}{CaCO_3} \longrightarrow \underset{(56)}{CaO} + \underset{(44)}{CO_2} \uparrow$$

Substituting the molecular weights

100 g of calcium carbonate on heating gives 44 g of carbon dioxide.

100 kg of calcium carbonate on heating will give 44 kg of carbon dioxide.

50 kg of calcium carbonate will give $\frac{44}{100} \times 50$

$= 22$ kg of carbon dioxide.

If the sample contains 100% pure calcium carbonate the weight of carbon dioxide formed is 22 kg.

If the sample contains 90% pure calcium carbonate the weight of carbon dioxide formed is $\frac{22}{100} \times 90 = 19{\cdot}8$ kg.

Problem (14): A sample of impure cinnabar ore contain 43·10% mercury. Find the percentage purity of mercury (II) sulphide in the sample.

Molecular weight of mercury (II)sulphide $= 200{\cdot}60 + 32{\cdot}06$
$= 232{\cdot}66$

232.66 g mercury (II) sulphide contains 200·6 g mercury.

100 g mercury (II) sulphide will contain $\frac{200{\cdot}6}{232{\cdot}66} \times 100$
$= 86{\cdot}20$ g mercury.

Percentage of mercury present in cinnabar if the sample contains 100% pure mercury (II) sulphide is 86·20.

If the percentage of mercury is 43·10 then the sample contains $\frac{43{\cdot}10}{86{\cdot}20} \times 100 = 50\%$ pure mercury (II) sulphide

Percentage purity of mercury (II) sulphide = 50%

Problem (15) : How many moles of barium and chlorine are contained in 48·84 g barium chloride dihydrate ($BaCl_2 . 2H_2O$)? Calculate the number of molecules of water of hydration present in this same amount.

Molecular weight of crystalline barium chloride
($BaCl_2 . 2\,H_2O$)
$= 137{\cdot}3 + 35{\cdot}46 + 35{\cdot}46 + 36$
$= 244{\cdot}2$

244·2 g of crystalline barium chloride contains 1 mole of barium.

48·84 g of crystalline barium chloride contains $\frac{48 \cdot 84}{244 \cdot 2} \times 1$

$= 0 \cdot 2$ mole of barium.

Number of moles of chlorine $= \frac{48 \cdot 84}{244 \cdot 2} \times 1 = 0 \cdot 2$ mole.

Number of moles of water of crystallisation $= \frac{48 \cdot 84}{244 \cdot 2} \times 2 = 0 \cdot 4$ mole.

The number of molecules of water present in 1 mole of water $= 6 \cdot 023 \times 10^{23}$

Number of molecules in 0·4 mole of water

$$= \frac{6 \cdot 023 \times 10^{23}}{1} \times 0 \cdot 4$$

$$= 2 \cdot 4092 \times 10^{23}$$

Number of moles of barium $= 0 \cdot 2$ mole

Number of moles of chlorine $= 0 \cdot 4$ mole

Number of molecules of water of hydration $= 2 \cdot 409 \times 10^{23}$

DETERMINATION OF MOLECULAR WEIGHT

Victor-Meyer's Method : This method is used to determine the molecular weights of volatile compounds.

Principle : In this method a known weight of a volatile liquid or solid is converted into its vapour by heating in a Victor-Meyer's tube. The vapour displaces its own volume of air. The volume of air displaced by the vapour is measured at the experimental temperature and pressure. The volume of the vapour at S.T.P. is then calculated. From this the weight of $2 \cdot 24 \times 10^{-2}$ m^3 of the vapour at S.T.P. is calculated. This value represents the molecular weight of the substance.

Description of the Apparatus : The apparatus used known as the Victor-Meyer apparatus is shown in **Fig. 1.** It consists of an inner Victor-Meyer tube, the lower end of which is in the form of a bulb. The upper end of the tube has a side tube which leads to a trough of water. The Victor-Meyer tube is surrounded by an outer jacket. In the outer jacket is placed a liquid which boils at a temperature at least 30 K higher than the boiling point of the volatile substance under study. A small quantity of glass wool or asbestos fibre covers the bottom of the Victor-Meyer tube to prevent breakage when the bottle containing the substance is dropped in

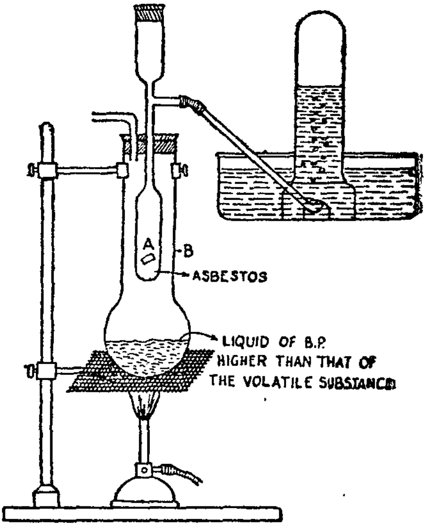


Fig. 1
Victor - Meyer Apparatus

Procedure

To begin with, the liquid in the outer jacket is allowed to boil and when no more air escapes from the side tube, a graduated tube filled with water is inverted over the side tube dipping in a trough full of water. A small quantity of the substance is accurately weighed in a small stoppered bottle and quickly dropped in the heated Victor-Meyer tube and the cork immediately replaced. The bottle falls on the asbestos pad and its contents suddenly change into vapour, blow out the stopper and displace an equal volume of air which collects in the graduated tube. The volume of air in the graduated tube is measured by taking it out by closing its mouth with the thumb and dipping it in a jar full of water. When the water levels outside and inside the tube are the same, the volume of air displaced is noted. The atmospheric pressure and laboratory temperature are noted.

Calculations

Weight of the volatile substance = W g.

Volume of air displaced = Volume of vapour = V_1 m^3

Laboratory temperature $= T_1$ K

Pressure of dry vapour $=$ Atmospheric pressure — aqueous tension at T_1 K.

If p Nm^{-2} is the aqueous tension at that temperature

Pressure of dry vapour $= P_1 = (P-p)\ Nm^{-2}$

Standard Temperature $= 273$ K

Standard Pressure $= 1{\cdot}013 \times 10^5\ Nm^{-2}$

Let the volume of the vapour at standard temperature and pressure be $V_0\ m^3$.

From gas equation it follows

$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

$$V_0 = \frac{P_1 V_1}{T_1} \times \frac{T_0}{P_0}$$

The weight of $V_0\ m^3$ of vapour at S.T.P. is W g.

$\therefore$ The weight of $2{\cdot}24 \times 10^{-2}\ m^3$ of the vapour at S.T.P. is $\frac{W}{V_0} \times 2{\cdot}24 \times 10^{-2}$.

The value thus calculated represents the molecular weight.

Molecular weight $= 2 \times$ Vapour density.

From the above expression the vapour density of the substance is calculated.

Problem (16) : In the determination of molecular weight by Victor-Meyer method $0{\cdot}125$ g of a volatile liquid displaced $3{\cdot}85 \times 10^{-5}\ m^3$ of moist air at 290 K and $1{\cdot}009 \times 10^5\ Nm^{-2}$ pressure. Calculate the molecular weight and vapour density of the compound. Aqueous tension at 290 K is $1{\cdot}932 \times 10^3$

Weight of the substance $= 0{\cdot}125$ g.

Volume of air displaced $=$ Volume of vapour

$V_1 = 3{\cdot}85 \times 10^{-5}\ m^3$

P_1 = Atomospheric pressure—aqueous tension at 290 K.

$P_1 = 1{\cdot}009 \times 10^5 - 1{\cdot}932 \times 10^3$

$P_1 = 1{\cdot}009\times10^5 - 0{\cdot}01932\times10^5$

$P_1 = 0{\cdot}9897\times10^5$

$T_1 = 290\ K$

$T_o = 273\ K$

$P_o = 1{\cdot}013\times10^5\ Nm^{-2}$

$$\frac{P_oV_o}{T_o} = \frac{P_1V_1}{T_1}$$

∴ Volume of vapour at S.T.P.

$$= V_o = \frac{0{\cdot}9897\times10^5\times3{\cdot}85\times10^{-5}\times273}{290\times1{\cdot}013\times10^5}$$

$$= 3{\cdot}542\times10^{-5}\ m^3$$

At S.T.P. $3{\cdot}542\times10^{-5}\ m^3$ of vapour weighs 0·125 g.

∴ At S.T.P. $2{\cdot}24\times10^{-2}\ m^3$ of vapour will weigh

$$\frac{0{\cdot}125}{3{\cdot}542\times10^{-5}}\times2{\cdot}24\times10^{-2}$$

$$= 79{\cdot}05\ g.$$

Molecular weight of the substance = 79·05

Molecular weight = 2 × vapour density

∴ Vapour density $= \frac{79{\cdot}05}{2} = 39{\cdot}5$

Vapour density = 39·5.

EXERCISE

1. Calculate the number of molecules present in each of the following substances :
   (a) 5·845 g sodium chloride
   (b) 88 g carbon dioxide
   (c) 1 m^3 ammonia at standard temperature and pressure
   (d) $1{\cdot}12\times10^{-2}\ m^3$ oxygen at S.T.P.
   (e) 1 kg water

[Ans: (a) $6{\cdot}023\times10^{22}$ (b) $1{\cdot}205\times10^{24}$
(c) $2{\cdot}689\times10^{25}$ (d) $3{\cdot}011\times10^{20}$
(e) $3{\cdot}346\times10^{25}$]

2. What is the average weight of

(a) one hydrogen atom **(b) one carbon atom**
(c) one magnesium atom **(d) one copper atom**
(e) one water molecule.

[Ans : (a) $1{\cdot}673 \times 10^{-24}$ (b) $1{\cdot}993 \times 10^{-23}$
(c) $4{\cdot}036 \times 10^{-23}$ (d) $1{\cdot}055 \times 10^{-22}$
(e) $2{\cdot}99 \times 10^{-23}$]

3. **Calculate the percentage of water of hydration of magnesium sulphate heptahydrate ($MgSO_4 . 7H_2O$)**

[Ans : 51·17%]

4. How many moles of copper and oxygen are contained in 24·95 g of copper sulphate pentahydrate ($CuSO_4 . 5H_2O$)? How many molecules of water of hydration are in this same amount?

[Ans : 0·1, 0·4, $3{\cdot}011 \times 10^{23}$]

5. How many moles are represented by

(a) 20 g of sodium hydroxide (b) 85 g ammonia
(c) 11 g of carbon dioxide (d) 12·25 g sulphuric acid (e) 5·85 g sodium chloride.

[Ans : (a) 0·5 (b) 5 (c) 0·25
(d) 0·125 (e) 0·1]

6. (a) How many grams of calcium chloride are contained in 0·4 mole of calcium chloride?

(b) Hou many grams of calcium and chlorine are contained in 0·4 mole of calcium chloride?

(c) How many molecules of calcium chloride are contained in 0·4 mole of calcium chloride?

(d) How many atoms of calcium and chlorine are present in 0·4 mole calcium chloride?

[Ans : (a) 44·4 g (b) 16·03, 28·36 g
(c) $2{\cdot}41 \times 10^{23}$ (d) $2{\cdot}41 \times 10^{23}$,
$4{\cdot}82 \times 10^{23}$]

7. Calculate the percentage composition of crystalline ferrous ammonium sulphate (Mohr's salt).

[Ans : iron = 14·24%, oxygen = 57·14%
hydrogen = 5·10%, sulphur = 16·33%
nitrogen = 7·16%]

8. Calculate the percentage composition of potassium chlorate ($KClO_3$).

How many kilograms of oxygen can be obtained by heating 36·75 kg potassium chlorate that is 90% pure?

[potassium = 31·1%, chlorine = 28·96%.
oxygen = 39·14; 12·96 kg]

9. Calculate the weight of silver in kilogram present in 85 kg of a crude sample of silver nitrate whose percentage purity is 60.

[Ans : 32·4 kg]

10. Calculate the percentage of sulphur in each of the following compounds :

(a) hydrogen sulphide (b) sulphur dioxide
(c) sulphur trioxide (d) sulphuric acid.

[Ans : (a) 94% (b) 50% (c) 40% (d) 32·65%]

11. Which of the following is the heaviest?

(a) one mole of nitrogen.
(b) $2{\cdot}24 \times 10^{-2}$ m^3 hydrogen chloride at standard temperature.
(c) 2 moles of ammonia.
(d) 10 moles of hydrogen.
(e) $1{\cdot}12 \times 10^{-2}$ m^3 carbondioxide at S.T.P.

[Ans : $2{\cdot}24 \times 10^{-2}$ m^3 hydrogen chloride)

12. The density of ammonia at S.T.P. is 0·771 kg m^{-3}. Calculate the molecular weight of ammonia.

[Ans : 17·27]

13. Calculate the percentage of nitrogen in (a) ammonium nitrate ($NH_4 NO_3$) and (b) urea (NH_2-CO-NH_2).

[Ans : (a) 35% (b) 46·67%]

14. A 100 g sample of zinc which is 95% pure is treated with hydrochloric acid. What volume of hydrogen is evolved at standard temperature and pressure?

[Ans : $3{\cdot}25 \times 10^{-2}$ m^3]

15. 0·1525 g of a volatile substance displaced $6{\cdot}5 \times 10^{-5}$m^3 of moist air at 298 K and $9{\cdot}995 \times 10^{-4}$ pressure. Calculate the vapour density and molecular weight of the substance. Aqueous tension at 298 K is $3{\cdot}166 \times 10^3$ Nm^{-2}.

[Ans : 30, 60·01]

16. 0·485 g of a volatile compound displaced $1{\cdot}051 \times 10^{-4}$m^3 of air measured over water at 300 K and $9{\cdot}995 \times 10^{-4}$ Nm^{-2} pressure. Calculate the molecular weight of the substance. Aqueous tension at 300 K is $4{\cdot}24 \times 10^3$.

[Ans : 120·1]

17. Give the correct answer for the following questions :

(i) Calculate the number of moles of oxygen required to oxidise 0·5 mole of sulphur dioxide.

(ii) How many moles are represented by 50 g calcium carbonate?

(iii) What is the weight in kg of one mole of oxygen?

(iv) Calculate the weight in gram of $1{\cdot}12 \times 10^{-2}$ m^3 carbon dioxide at S.T.P.

(v) Calculate the volume at S.T.P. occupied by 8 g of methane.

(vi) What is the weight in kg of 2·24 m^3 sulphur dioxide at S.T.P.?

[Ans : (i) 0·25 (ii) 0·5 (iii) $3{\cdot}2 \times 10^{-2}$ kg
(iv) 22 g (v) $1{\cdot}12 \times 10^{-2}$ m^3 (vi) 6·4 kg]

18. Complete the following :

(i) Molecular weight = Vapour density × ———

(ii) Molecular weight of an element = Atomic weight of the element × ———

(iii) Gram molar volume = ———

(iv) Number of atoms present in gram atom of an element } = ———

(v) The number of moles of carbon dioxide formed by the complete decomposition of 0·25 mole copper carbonate is ———

[Ans : (i) 2 (ii) Atomicity (iii) $2{\cdot}24 \times 10^{-2} m^3$ (iv) $6{\cdot}023 \times 10^{23}$ (v) 0·25]

Problems based on Dulong and Petit's Law :

19. The chloride of a metal is found to contain 34·43% of the metal. The specific heat of the metal is $4{\cdot}769 \times 10^2$ Jkg^{-1} K^{-1}. What is the accurate atomic weight of the metal?

[Ans : 55·86]

20. On analysis 1·674 g of an oxide of a metal is found to contain 0·12 g of oxygen. The specific heat of the metal is found to be $1{\cdot}268 \times 10^2$ Jkg^{-1} K^{-1}. Calculate the approximate and correct atomic weight of the metal.

[Ans : 211·3, 207·2]

21. 0·1634 g of a metal when dissolved in hydrochloric acid liberated $5{\cdot}6 \times 10^{-5}$ m^3 of hydrogen measured at S.T.P. The specific heat of the metal is $3{\cdot}932 \times 10^2$ Jkg^{-1} K^{-1}. Calculate the approximate and correct atomic weight of the metal.

[Ans : 68·16, 65·36]

22. A metallic chloride contains 25·5% chlorine. The specific heat of the metal is found to be $1{\cdot}297 \times 10^2$

Jkg^{-1} K^{-1} What is the correct atomic weight of the metal? Write the formula of the metallic chloride.

[Ans : 207·2, MCl_2]

23. On analysis 1 g of a metallic oxide is found to contain 0·6842 g of metal. The specific heat of the metal is found to be $4{\cdot}75\times10^{2}$ Jg^{-1} K^{-1}. Calculate the equivalent weight and correct atomic weight of the metal.

[Ans : 17·34, 52·02]

24. When 0·673 g of a metal is dissolved in dilute sulphuric acid, 0·0755 g of hydrogen is evolved. The specific heat of the metal is found to be $9{\cdot}627 \times 10^{2}$ Jkg^{-1} K^{-1}. Calculate (i) the equivalent weight and (ii) the accurate atomic weight of the metal.

[Ans : (i) 8·982 (ii) 26·95]

CHAPTER II

EQUIVALENT WEIGHTS

Introduction : The concept of equivalent weight in Chemistry is very old. From the law of definite proportions it is clear that whenever elements combine they do so in fixed proportion by weight.

$$H_2 + Cl_2 \rightarrow 2HCl$$

Thus 1·008 parts by weight of hydrogen combine with 35·46 parts by weight of chlorine to form hydrogen chloride. Again 23 g of sodium combine with 35·46 g of chlorine to form sodium chloride. 23 g of sodium combine with 1·008 g of hydrogen to form sodium hydride.

$$2Na + H_2 \rightarrow 2NaH$$

Water contains 2·016 parts by weight of hydrogen combined with 16 parts by weight of oxygen.

$$2H_2 + O_2 \rightarrow 2H_2O$$

In water 1·008 parts by weight of hydrogen is in combination with 8 parts by weight of oxygen. Thus 23 g of sodium, 35·46 g of chlorine, 8 g of oxygen are the weights which separately combine with 1·008 g of hydrogen to form sodium hydride, hydrogen chloride and water respectively. These relative weights of elements are called their combining weights or equivalent weights or chemical equivalents.

Definition : The equivalent weight of an element is the number of parts by weight of the element which combines with or displaces 1·008 parts by weight of hydrogen or 8 parts by weight of oxygen or 35·46 parts by weight of chlorine.

Equivalent weight is simply expressed as a number. If the equivalent weight is expressed in gram it is called the gram equivalent weight. Thus it is clear that one equivalent of any substance will react with one equivalent of any other substance. The gram equivalent weight of zinc is 32·68 g. and of copper 31·7 g. Thus 32·68 g. of zinc will completely displace 31·7 g. of copper from copper sulphate solution. The equivalent weight of hydrogen is 1·008. Thus 32·68 parts by weight of zinc will displace 1·008 parts by weight of hydrogen from dilute hydrochloric acid.

Modern Concept : The equivalent weight of an element is now defined as the fraction of its atomic weight associated with the loss or gain of 1 electron. For example, in the reaction

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

the number of parts by weight of iron associated with the loss of one electron will be one half of its atomic weight.

$$\therefore \left.\begin{array}{l}\text{Equivalent}\\ \text{weight of iron}\end{array}\right\} = \frac{\text{Atomic weight of iron}}{2} = \frac{55{\cdot}85}{2} = 27{\cdot}92$$

Similarly in the reaction

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

$$\left.\begin{array}{l}\text{Equivalent}\\ \text{weight of copper}\end{array}\right\} = \frac{\text{Atomic weight of copper}}{2} = \frac{63{\cdot}54}{2} = 31{\cdot}77$$

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

The equivalent weight of sodium is the same as its atomic weight.

$$Cl^- \longrightarrow Cl + e^-$$

The equivalent weight of chlorine is the same as the atomic weight of chlorine.

Variable Equivalent Weights : According to the law of multiple proportions, two elements combine in different ratios to form more than one compound. For example, copper combines with oxygen to form two oxides namely copper (I) oxide and copper (II) oxide. In the formation of copper (II) oxide, 31·7 parts by weight of copper combines with 8 parts by weight of oxygen. In copper (I) oxide 63·54 parts by weight of copper combines with 8 parts by weight of oxygen. Thus copper has two different equivalent weights. In copper (II) oxide, the equivalent weight of copper is 31·77 and in copper (I) oxide 63·54. We already studied that

Atomic weight = Equivalent weight × Valency.

In copper (I) oxide, the valency of copper is 1 and so its equivalent weight is the same as its atomic weight. In copper (II) oxide the valency of copper is 2. Similarly iron exhibits variable equivalent weights. In iron (II) chloride, the equivalent weight of iron is 27·92 and in iron (III) chloride, 18·62 since valency of iron is 2 in iron (II) chloride and 3 in iron (III) chloride. Therefore elements exhibiting variable valency also exhibit variable equivalent weights.

DETERMINATION OF EQUIVALENT WEIGHTS OF ELEMENTS

1. Hydrogen Displacement Method

Principle of the method : This method is used to determine the equivalent weight of those metals which react completely with dilute acids and readily displace hydrogen ; for example, metals such as zinc, magnesium, aluminium etc.

$$Mg + 2\,HCl \longrightarrow MgCl_2 + H_2 \uparrow$$

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \uparrow$$

From the weight of the metal and the volume of hydrogen displaced the equivalent weight of the metal can be calculated.

Procedure : An air tight apparatus of the type shown in Fig. 2 is used. An accurately weighed quantity of the metal is placed in a conical flask along with a little water. A test tube containing dilute hydrochloric acid is lowered in it taking care that no acid flows out from the tube till the apparatus has been completely fitted. A graduated tube filled with water is then placed in position as shown in the diagram. The flask is now tilted. The acid reacts with the metal completely and the liberated hydrogen collects in the graduated tube by displacing the water in it. The volume of hydrogen liberated is measured after careful levelling i.e. by lowering the graduated tube in a jar of water till the levels of water inside and outside are the same. This is done to bring gas to atmospheric pressure. The atmospheric pressure and temperature are also recorded.

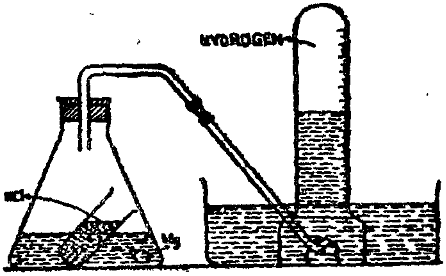


Fig. 2
Hydrogen displacement method

Calculations

Weight of the metal $= W$ g

Volume of hydrogen displaced $= V_1$ m^3

Laboratory temperature $= T_1$ K

(The room temperature in centigrade unit is converted to the Kelvin scale by adding 273 to it)

Atmospheric pressure $= P$ Nm^{-2}

P Nm^{-2} is the pressure due to wet hydrogen since hydrogen is collected over water.

Pressure due to dry hydrogen $= P$ — Pressure due to water-vapour.

Aqueous tension at T K $= p$ Nm^{-2}

$\therefore$ Pressure of dry hydrogen $= P_1 = (P - p)$ Nm^{-2}

Standard temperature $= T_0 = 273$ K

Standard pressure $= P_0 = 1{\cdot}013 \times 10^3$ Nm^{-2}

Let the volume of hydrogen at S.T.P. be V_0 m^3

According to gas equation $\frac{P_0V_0}{T_0} = \frac{P_1V_1}{T_1}$

$$\therefore \quad V_0 = \frac{P_1V_1}{T_1} \times \frac{T_0}{P_0}$$

One gram equivalent of the metal will displace one gram equivalent of hydrogen i.e. 1·008 g of hydrogen from the acid. According to Avogadro's hypothesis 1·008 g of hydrogen occupies a volume equal to $1{\cdot}12 \times 10^{-2}$ m^3 at S.T.P.

At S.T.P. V_0 m^3 of hydrogen is displaced by 'W' g of the metal.

At S.T.P, $1{\cdot}12 \times 10^{-2}$ m^3 of hydrogen will be displaced by $\frac{W}{V_0} \times 1{\cdot}12 \times 10^{-2}$ g of the metal.

The value thus calculated, represents the equivalent, weight of the metal.

Problem (1) : In an experiment 0·218 g of a metal evolved $2{\cdot}181 \times 10^{-4}$ m^3 of hydrogen collected over water at a temperature of 300 K and a pressure of $1{\cdot}041 \times 10^5$ Nm^{-2}. Calculate the equivalent weight of the metal. Aqueous tension at 300 K is $3{\cdot}561 \times 10^3$ Nm^{-2}.

Weight of the metal taken $= 0{\cdot}218$ g.

Volume of hydrogen collected $= V_1 = 2{\cdot}181 \times 10^{-4}$ m^3

Laboratory temperature $= T_1 = 300$ K

Pressure due to dry hydrogen $= P_1 = 1{\cdot}041 \times 10^5 - 3{\cdot}561 \times 10^3$ Nm^{-2}

$= 1{\cdot}041 \times 10^5 - 0{\cdot}0356 \times 10^5$ Nm^{-2}

$= 1{\cdot}0054 \times 10^5$ Nm^{-2}

Normal pressure $= P_0 = 1{\cdot}013 \times 10^5$ Nm^{-2}

Normal temperature $= T_0 = 273$ K

From gas equation, $\frac{P_0\,V_0}{T_0} = \frac{P_1\,V_1}{T_1}$

$$\therefore \quad V_0 = \frac{1{\cdot}0054 \times 10^5 \times 2{\cdot}181 \times 10^{-4}}{300} \times \frac{273}{1{\cdot}013 \times 10^3}$$

$$\therefore \quad V_0 = 1{\cdot}970 \times 10^{-4}\ m^3$$

At S.T.P. $1{\cdot}970 \times 10^{-4}$ m^3 of hydrgen is displaced by 0·218 g of the metal.

At S.T.P. $1{\cdot}12 \times 10^{-4}$ m^3 of hydrogen will be displaced by

$$\frac{0{\cdot}218}{1{\cdot}970 \times 10^{-4}} \times 1{\cdot}12 \times 10^{-4} \text{ of the metal}$$

$$= 12{\cdot}34.$$

Equivalent weight of the metal = 12·34

Problem (2) : 1·623 g of a metal was dissolved in dilute acid and 0·0291 g of hydrogen was evolved. Calculate the equivalent weight of the metal.

0·0291 g of hydrogen is displaced by 1·623 g of the metal.

$\therefore$ 1·008 g of hydrogen is displaced by $\frac{1{\cdot}623}{0{\cdot}0291} \times 1{\cdot}008$ of metal

$$= 56{\cdot}19.$$

Equivalent weight of the metal = 56·19.

2. Oxide Method

Principle of the method : This method is used to determine the equivalent weights of those elements which readily form their oxides e.g. magnesium, copper, carbon, sulphur etc. An element may be converted into its oxide either directly or indirectly. Magnesium forms magnesium oxide directly on heating.

$$2\,Mg + O_2 \longrightarrow 2\,MgO.$$

In the case of copper, the oxide is obtained indirectly. A known weight of copper is dissolved in concentrated nitric acid and the copper (II) nitrate formed is strongly heated to give copper (II) oxide.

$$Cu + 4\,HNO_3 \longrightarrow Cu\,(NO_3)_2 + 2\,H_2O + 2\,NO_2\uparrow$$

$$2\,Cu(NO_3)_2 \xrightarrow{\Delta} 2\,CuO + 4\,NO_2\uparrow + O_2\uparrow$$

Procedure : A known weight of the element is converted into its oxide either directly or indirectly. The weight of the oxide formed is determined. Let the weight of the element be W_1g and the weight of oxide W_2g. From these two weights the equivalent weight of the element is calculated.

Calculations

Weight of the oxide of the element $= W_2$g

Weight of the element taken $= W_1$g

Weight of oxygen $= (W_2 - W_1)$g

$(W_2 - W_1)$ g of oxygen has combined with W_1g of the element.

$\therefore$ 8 g of oxygen will combine with $\frac{W_1}{(W_2 - W_1)} \times 8$ of the element.

This value represents the equivalent weight of the element.

Problem (3) : 0·608 g of a metal gave on oxidation 1·008 g of its oxide. Calculate the equivalent weight of the metal.

Weight of metallic oxide $= 1{\cdot}008$ g.

Weight of metal $= 0{\cdot}608$ g.

Weight of oxygen $= 0{\cdot}400$ g.

0·4 g of oxygen has combined with 0·608 g of the metal

$\therefore$ 8 of oxygen will combine with $\frac{0{\cdot}608}{0{\cdot}4} \times 8$ of the metal

$= 12{\cdot}16$

Equivalent weight of the metal $= 12{\cdot}16$

3. Chloride Method

Principle of the method : This method is used to determine the equivalent weights of those metals which readily form their chlorides, for example tin, silver, lead, iron etc. A known weight of pure silver is dissolved completely in dilute nitric acid. The resulting silver nitrate solution is treated with pure hydrochloric acid when silver chloride is precipitated. It is then filtered, dried and weighed.

Procedure : A known weight of the metal is converted into its chloride. The weight of the chloride formed is determined. Let the weight of the metal be W_1g and the weight of the chloride W_2g. From these two weights the equivalent weight of the metal is calculated.

Calculations

Weight of metallic chloride = W_2 g

Weight of metal taken = W_1 g

Weight of chlorine that has combined with the metal = (W_2-W_1) g

(W_2-W_1) g of chlorine has combined with W_1 g of the metal

35·46 g of chlorine will combine with $\frac{W_1}{(W_2-W_1)} \times 35{\cdot}46$ of the metal.

This value represents the equivalent weight of the metal.

Problem (4) : The chloride of a metal contains 75·25% of the metal. Calculate the equivalent weight of the metal.

Weight of metallic chloride = 100 g

Weight of metal = 75·25 g

∴ Weight of chlorine combined = 24·75 g

24·75 parts by weight of chlorine has combined with 75·25 parts by weight of the metal

∴ 35·46 parts by weight of chlorine will combine with

$\frac{75{\cdot}25}{24{\cdot}75} \times 35{\cdot}46 = 107{\cdot}7$ parts by weight of the metal.

Equivalent weight of the metal = **107·7**

QUESTIONS

1. Explain the modern concept of equivalent weight.
2. Describe the principle involved in the determination of the equivalent weight of an element by the hydrogen displacement method.

3. How would you determine experimentally the equivalent weight of copper?

4. How is the equivalent weight of an element determined by the chloride method?

5. Given that the equivalent weight of silver is 107·9. Calculate the equivalent weight of magnesium if 0·1818 g of magnesium displaces 1·6125 g of silver from silvernitrate.

[Ans : 12·16]

6. In an experiment 1·62 g of zinc gives 2·02 g of zinc oxide. Calculate the equivalent weight of zinc.

[Ans : 32·4]

7. On heating 0·8567 g of copper (II) oxide in a current of hydrogen, the resulting copper weighed 0·6842 g. What is the equivalent weight of copper?

[Ans : 31·73]

8. 1·620 g of metallic oxide on analysis was found to contain 1·133 g of a metal. Calculate the equivalent weight of the metal.

[Ans : 18·61]

9. Two oxides of a metal contain (a) 88·12% and (b) 78·77% of the metal respectively. Calculate the equivalent weight of the metal in the two oxides.

[Ans : (a) 59·35 (b) 29·68]

10. The chloride of a metal was found to contain 44·5% of the metal. Calculate the equivalent weight of the metal.

[Ans : 28·43]

11. 0·2047 g of a metal when dissolved in hydrochloric acid liberated $3{\cdot}87 \times 10^{-5}$ m^3 of hydrogen measured at S.T.P. Calculate the equivalent weight of the metal.

[Ans : 59·24]

12. $1{\cdot}683 \times 10^{-4}$ kg of iron displaced $1{\cdot}890 \times 10^{-4}$ kg of another metal from its salt solution. If the equivalent weight of iron is 27·9, calculate the equivalent weight of the metal.

[Ans : 31·33]

13. In a determination of the equivalent weight of silver by the chloride method 0·55 g of silver gave 0·73 g of silver chloride. Determine the equivalent weight of silver.

[Ans : 108.3]

14. 0·290 g of a metal when dissolved in dilute hydrochloric acid evolved $2{\cdot}95 \times 10^{-4} m^3$ of hydrogen when collected over water at 290 K and $9{\cdot}86 \times 10^4$ Nm^{-2} pressure. Calculate the equivalent weight of the metal. Aqueous tension at 290 K is given to be $1{\cdot}92 \times 10^3$ Nm^{-2}.

[Ans : 12·25]

15. In a determination of the equivalent weight of a metal by the hydrogen displacement method, 0·1063 g of a metal evolved $3{\cdot}7 \times 10^{-5}$ m^3 of dry hydrogen at a temperature of 285 K and a pressure of $1{\cdot}04 \times 10^5$ Nm^{-2}. Calculate the equivalent weight of the metal.

[Ans : 32·71]

CHAPTER III

ATOMIC STRUCTURE

John Dalton and his contemporaries viewed in 1803, the atom as an indivisible object. This concept helped to stimulate and to guide the experimental work of chemists for almost one hundred years. However, a series of astounding discoveries, X-rays in 1895, radioactivity in 1896, the electron in 1897 and radium in 1898 brought out sufficient data to indicate that the atom has a substructure of smaller particles. Only three of these subatomic particles are of interest : electron, proton and neutron.

An electron has a negative charge, a proton has a positive charge and a neutron is uncharged. The charges on the electron and proton are equal in magnitude. Atoms have no net electrical charge. Hence there are equal numbers of negatively charged electrons and positively charged protons in an atom. The protons and neutrons of an atom reside together in a relatively tiny volume within the atom. This tiny volume is known as nucleus of the atom. Most of the rest of the atom is an empty space. The electrons are moving only in this empty space. The proton and neutron have approximately equal masses. But the electron has only about 1/1835 as much as proton. The masses of these particles in kilo grams are presented in Table 1. Thus the tiny nucleus carries most of the mass of the atom.

The electrons are held in the atom by the attraction that exists between the positive nucleus and the negative electrons which are particles of unlike electrical charge. This attraction is known as **coulombic** or **electrostatic attraction.** Because electrons are at the periphery of the atom, they play an important role in chemical reactions.

TABLE 1

COMPARISON OF THE ELECTRON, PROTON AND NEUTRON

Particle	Charge	Mass
Electron	Negative (—1)	$9{\cdot}11 \times 10^{-31}$ kg
Proton	Positive (+1)	$1{\cdot}67 \times 10^{-27}$ kg
Neutron	None	$1{\cdot}67 \times 10^{-27}$ kg

The present theory which overturned Dalton's atomic theory views the atom as a divisible particle consisting of a massive but relatively tiny positive nucleus with one or more negatively charged electrons associated with it. Let us consider some of the discoveries which led to the present theory.

Cathode rays

Under ordinary circumstances, gases are electrical insulators. Even if a high potential difference (1000 volts) is established between two electrodes in a gas filled tube, no current flows between the electrodes. However gases can be made to conduct electric currents when their pressures are reduced.

Let us take a glass tube fitted with two electrodes and apply a potential difference of about 1000 volts (Fig. 3). No current flows between the electrodes. Let us evacuate the tube by means of a vacuum pump and thus reduce the pressure of the air inside the tube to about $1{\cdot}0 \times 10^{-1}$ Nm^{-2}. Now current

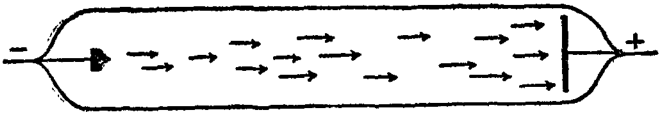


Fig 3
A cathode ray tube

flows from one electrode to the other with a greenish glow or luminescence. This radiation became known as cathode rays because it emanated from the cathode (i.e. negative electrode).

Properties of cathode rays

Cathode rays have shown the following properties. Simple tests serve to demonstrate these properties :

1. They travel in straight lines away from the cathode (Fig. 3).

2. They are negatively charged. This is evident from the fact that they are deflected by magnetic and electric fields in a manner expected for negatively charged particles (Fig. 4).

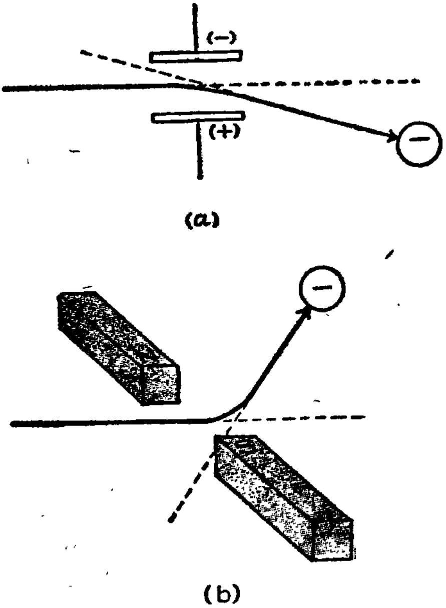


Fig. 4
The behaviour of a negatively charged particle moving through (a) an electric field and (b) a magnatic field

3. They are composed of material particles. This is evident from the fact that they cause rotation of a light paddle wheel placed on their path.

These and a number of additional facts suggest that the radiation consists of a stream of negatively charged particles. These particles are called electrons. The nature of the cathode rays (electrons) is found to be the same irrespective of the following :

(1) The material with which the cathode is made.

(2) The type of the residual gas present in the tube.

(3) The kind of metal wires used to conduct the current to the cathode.

(4) The materials used to produce the current.

All these evidences indicate that electrons are fundamental particles present in all matter.

Charge on the electron

R. A. Millikan determined the actual charge on the electron in 1909, by the famous oil drop experiment- It was performed in the type of apparatus illustrated in Fig. 5.

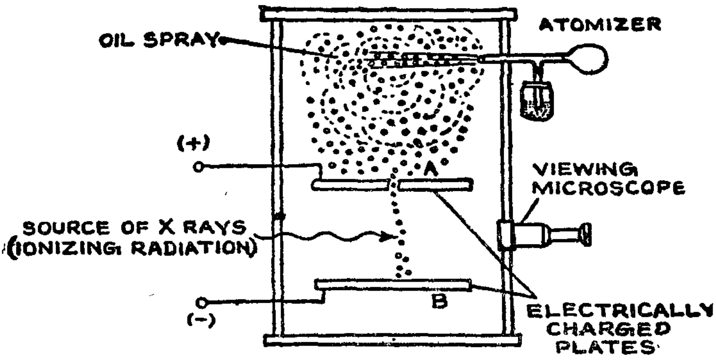


Fig. 5
The Millikan Oil drop experiment

This apparatus consists of two metal plates, A and B, supported in a closed chamber containing air at low pressure. As shown, the plates can be charged by a high voltage source. An atomizer is used to introduce a fine spray of oil. A droplet of oil is admitted between the two uncharged metal plates and the rate of fall of the droplet under the influence of gravity is measured with the aid of a microscope. A beam of X-rays is then admitted which causes some electrons to be detached from the gas molecules present. The oil droplet will then absorb one or more electrons and thus become negatively charged.

If the upper plate is now charged positively and the lower one negatively, the oil droplet will be attracted to the upper plate. If one electron is absorbed by the droplet, it will fall more slowly than it did under the influence of gravity alone. If a sufficient number of electrons are absorbed, the droplet may even rise. The charge on the droplet at various times can be calculated from data on the changes in velocity of the oil drop as it absorbs one or more electrons. It is found that the charge on the droplet is either a certain minimum charge or an integral multiple thereof. This minimum charge is the charge on one electron. This is $1{\cdot}60 \times 10^{-19}$ C.

Mass of the electron

Knowing the charge of an electron and charge-to-mass ratio from Thomson's experiment, it is possible to calculate the mass of an electron :

$$\text{Mass} = m = \frac{e}{e/m}$$

$$= \frac{1{\cdot}60 \times 10^{-19}\text{C}}{1{\cdot}76 \times 10^{11}\text{C}}\ \text{kg}^{-1}$$

$$= 9{\cdot}11 \times 10^{-31}\ \text{kg}.$$

This is 1 / 1838 of the mass a hydrogen atom.

The proton

Atom, as a whole is a neutral particle. But the electron an essential constituent of atom is negatively charged particle. Hence it follows that positively charged particles must also be present in atom.

Indeed, in 1886 **E. Goldstein** used a perforated cathode in a discharge tube with space behind cathode. When the tube was operating, he noted streaming luminous rays on the side of the cathode away from the anode (Fig. 6). He called these rays as **canal rays**, because they seemed to come through the holes on the cathode.

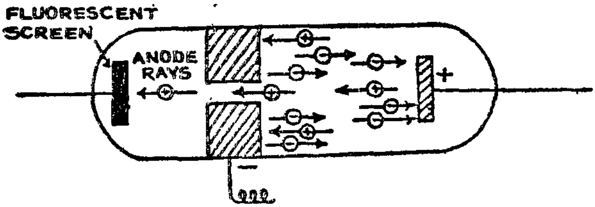


Fig. 6
The production of canal rays

Canal rays or anode rays or positive rays were quickly shown to be positively charged particles. Experiments performed to give e/m ratio for a variety of these particles in the canal rays gave results much lower than the e/m ratio for the electron. Thus, all these positive particles must have a much greater mass than the electron. In fact, the lightest particle found in this manner came from hydrogen. It has a mass of 1837/1838 that of a hydrogen atom and a charge of plus one. This particle, the proton, is the nucleus of the hydrogen atom.

The neutron

Some researchers in Germany were bombarding beryllium, boron and lithium with alpha rays from the naturally radio active element polonium. They obtained a highly penetrating radiation from the bombarded samples. In addition, this radiation was unaffected by electric and magnetic fields. The behaviour of this new form of radiation was confusing.

James Chadwick, in 1932, hit upon the answer to this. He pointed out that all of the observed properties of the new radiation were readily explainable if it was assumed that the radiation consisted of neutral particles with no charge and mass almost equal to that of the proton.. The newly identified particle was named as the neutron.

The nucleus of the atom

We have described the charge and mass of the positive, the negative and the neutral particles obtainable from an atom. Let us now examine information bearing on the spatial distribution of these particles in the atom.

J. J. Thomson developed a model of the atom. This model pictured the atom as a cloud of positive charge in which negatively charged electrons were embedded like seeds in a water melon. In 1910, Rutherford and his associates performed an experiment. This led to the downfall of Thomson's model. This experiment consisted of bombarding alpha particles at thin metellic foils and observing how the particles were deflected by the foil. Let us describe this experiment and summarise the ideas inferred from the observations.

Alpha particles are the nuclei of helium atoms. They contain two neutrons and two protons. They are emitted by certain radioactive elements like radium.

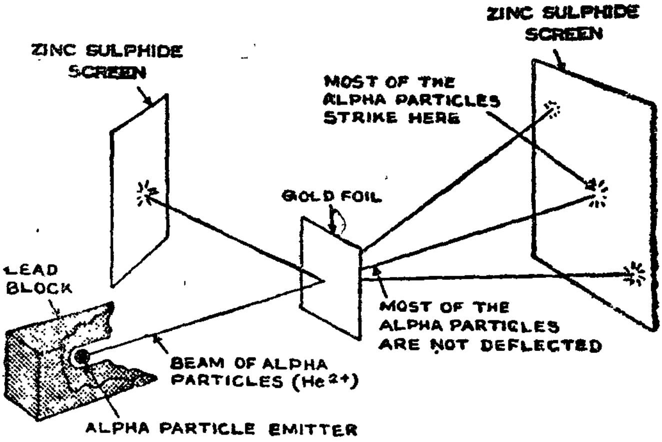


Fig. 7

Rutherford's scattering experiment

If a thin gold foil is bombarded by a stream of alpha particles (Fig. 7) most of the alpha particles pass through unaffected. This proves that an atom is mostly empty space. However, a few alpha particles undergo a deflection of 90° or more. These deflections indicate that the gold atoms must possess small positive nuclei. The nucleus must be positive because it repels the positively charged alpha particles. The nucleus must be small because so few alpha particles are deflected. These inferences are rationalised in Fig. 8.

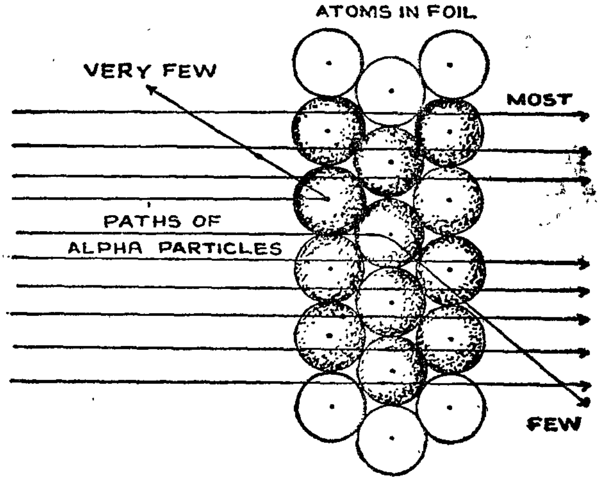


Fig. 8
Rutherford's model explaining his experiment with alpha particles

On the basis of his experiments, Rutherford put forth the hypothesis that the atom consists of a massive but relatively tiny positive nucleus at its centre, surrounded by electrons at relatively large distances from the nucleus.

Atomic number

Rutherford could not calculate the exact charge on the nucleus by his experiments. But, one of his co-workers, H.G.J. Moseley did it by a highly ingenious method. Let us describe it.

If a metallic target is placed in a cathode-ray tube and bombarded with electrons, X-rays are produced (Fig. 9). These are electromagnetic waves of short wave length. Each metal (indeed each element) emits X-rays of its own characteristic wave length.

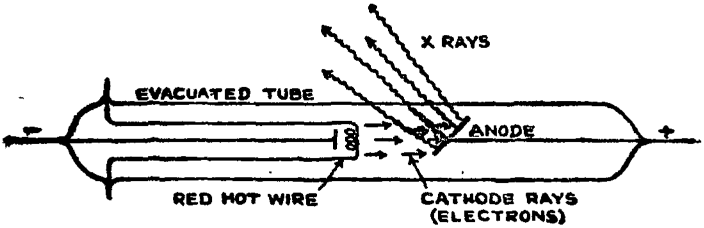


Fig. 9
An X-ray tube

The X-rays emitted by different elements can be diffracted by a crystalline substance towards photographic plates and recorded there. The positions of the lines in the spectra thus obtained can be directly related to the wave lengths of the X-rays. If these spectra are compared, a regular decrease in the wave lengths of the emitted X-rays with an increase in the atomic weights of the elements can be observed (Fig. 10)

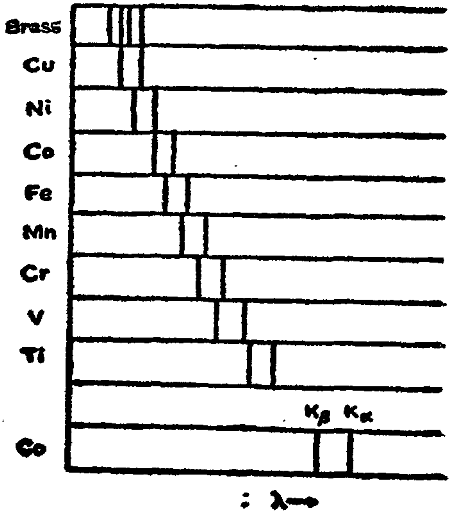


Fig. 10
X-ray spectra

Moseley showed that the wavelength of the X-rays emitted by an element is a function of the positive charge on the nucleus and developed equation 3 which relates the frequency (ν) and hence wave length of the emitted X-rays and positive charges on the nucleus.

$$\sqrt{\nu} = \sqrt{\frac{c}{v}} = a\ (Z - b) \qquad \text{.........}(3)$$

where Z is the number of positive charges, a and b are parameters obtainable from observations on elements of known positive charges.

This equation enables us to calculate the positive charge in the nucleus from the observed wave length. This positive charge on the nucleus is called the **atomic number.** This is equal to the number of protons in the nucleus.

The mass of the electron is negligible compared to the mass of the proton and neutron. So it is clear that practically all the mass of the atom is concentrated in the nucleus which contains neutrons and protons. If Z represents the atomic number and A represents the mass number, it follows that :

the number of neutrons in the nucleus = A — Z
the number of protons in the nucleus = Z
the number of electrons in the atom = Z

Planck's Quantum Theory

In his studies of radiations from black bodies or perfect radiators, **Max Planck** was led to the hypothesis that radiant energy, such as light and heat, is emitted or absorbed by a body not continuously but discontinuously in packets called **quanta**. This theory was generalized by **Albert Einstein,** who suggested that all radiation is composed of quanta. The energy of a quantum is given by :

$$\epsilon = h\nu$$

where ϵ is the energy of a quantum, h is the Planck's constant ($= 6{\cdot}624 \times 10^{-27}$ erg. sec.) and ν is the frequency of radiation in units of sec.$^{-1}$. This equation has been substantiated by experimental observations. Thus the essence of Planck's quantum theory is that a body can emit or absorb either one quantum of energy (i.e. $h\nu$) or any whole number multiples of this unit (i.e. $2h\nu$, $3h\nu$......$nh\nu$) quanta of energy.

Line Spectra

When a solid is heated to incandescence and the radiation passed through a spectrograph, a continuous spectrum is obtained. When a gas is heated to incandescence, a series of lines called **line spectra** obtained or bands called **band spectra** is obtained. Line spectra are emitted by atoms. Band spectra are emitted by molecules.

The simplest line spectrum is emitted by atomic hydrogen. This consists of a number of lines. These lines can be classified into several series. They are :

(i) Lyman series
(ii) Balmer series
(iil) Paschen series
(iv) Bracket series
(v) Pfund series

Of these only the **Balmer series** is present in the visible region of radiation. When one views the lines in this series of a hydrogen atom using a spectroscope, these lines appear to the viewer as shown in Fig. 11.

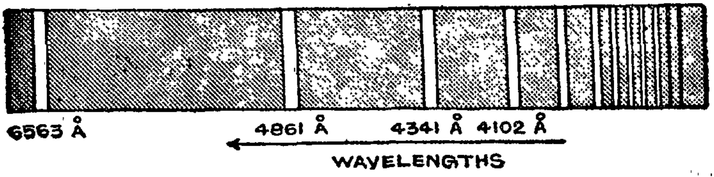


Fig. 11
Balmer series of hydrogen spectrum

The wave length of various lines in a given series can be related by a general and empirical relationship. This is known as **Ritz combination principle.** This relationship is the following :

$$\frac{1}{\lambda} = \bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \qquad \ldots (4)$$

where λ is the wave length in centimeter of a line in the series, $\bar{\nu}$ is the wave number which is the number of waves that can be accommodated in one centimeter and is equal to the reciprocal of the wave length, R_H is the **Rydberg constant,** the value of which is 109,677·76 cm^{-1}, n_1 is an integer which is a constant for a given series and n_2 is the one in a series of integers the smallest of which is one greater than n_1. The various possible values of n_1 and n_2 corresponding to various series are summarised in Table 2.

TABLE 2

Series	n_1	n_2
Lyman	1	2, 3, 4 etc.
Balmer	2	3, 4, 5 etc.
Paschen	3	4, 5, 6 etc.
Bracket	4	5, 6, 7 etc.
Pfund	5	6, 7, 8 etc.

Failure of early atom models

We have already discussed the two models of atomic structure namely the Thomson's model and the Rutherford's model. Let us look into their competence to account for the stability of the atoms.

Thomson suggested that atoms are positively charged spheres, inside of which electrons are uniformly distributed to make the sphere neutral (Fig. 12).. This model proved unsatisfactory for two reasons :

(1) Too many electrons are required to account for atomic mass.

(2) Rutherford's findings about nuclear structure in no way fit the model.

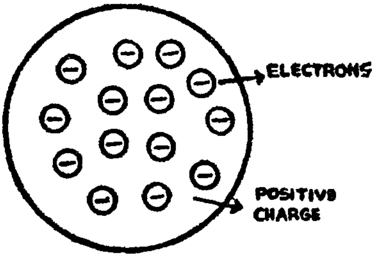


Fig. 12
Thomson's atom model

Rutherford pictured the positive charge of the atom as being concentrated in the massive but relatively tiny central nucleus. The negative charge, consisting of electrons, is then uniformly distributed around the nucleus in space. This led to the planetary atom model ·according to which the electrons revolve around the nucleus in well-defined orbits (Fig. 13).

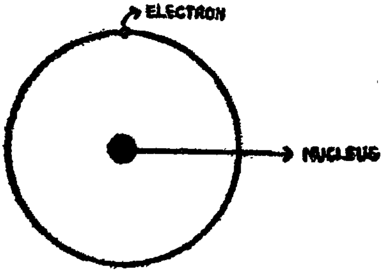


Fig. 13
Rutherford's atom model

According to a well-defined principle in electro-dynamics, the revolving electron should continually radiate energy and because of this energy loss it should spiral round the nucleus and fall into it within a period of about 10^{-8} seconds (Fig. 14).

Contrary to this the atoms are stable. Thus the Rutherford's atom model fails to hold up.

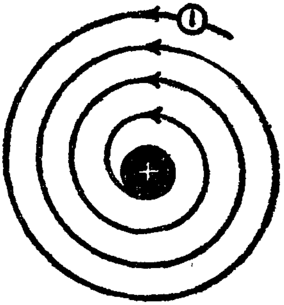


Fig. 14
Spiraling of an electron into nucleus

Bohr's theory of the hydrogen atom :

In order to provide a theory of the atom capable of explaining the significance of Ritz combination principle and the stability of the atoms, Niels Bohr made the following postulates :

(1) The Rutherford model is assumed to be correct. The atom consists of a heavy positively charged nucleus around which orbits a light negatively charged electron.

(2) These orbits are assumed to be stable and while the electron occupies one of them it cannot radiate energy.

(3) Emission of radiation occurs whenever the electron moves from an orbit of higher energy to one of the lower energy. The frequency of this radiation is given by

$$\nu = \frac{\Delta E}{h} \qquad \dots (5)$$

where ΔE is the difference in energy between the orbits

The various emission series resulting from inward electron transitions are illustrated in Fig. 15. This theory thus rationalises the Ritz combination principle which is empirical in nature and accounts for the stability of atoms.

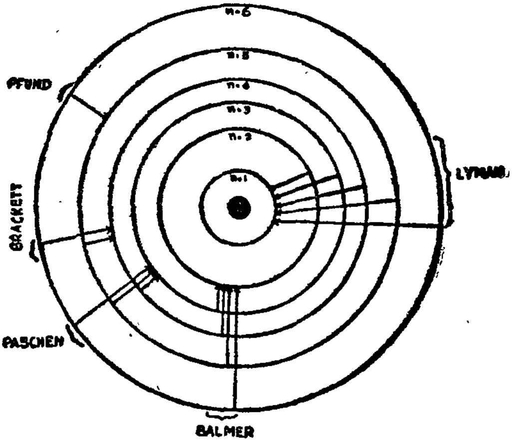


Fig. 15
The origin of hydrogen spectrum

Defects of the Bohr atom model

Bohr's theory is quite successful as far as the hydrogen atom is concerned. But it fails when extended even to helium atom. It is deficient because it does not take adequate account of the repulsions between electrons. We know that charged particles of the same sign repel one another. Thus in any atom containing two or more electrons, the electrons repel one another. But there is no provision in Bohr's theory to take these into consideration.

Lines in atomic spectra are often found to have a fine structure under single resolution. In other words the lines are composed of two or more lines. Further these lines are found to be affected by magnetic fields. In Bohr's theory there is no satisfactory explanation for this effect.

Modification of the Bohr's model of the atom

Certain modifications to the Bohr's theory have been made.

(1) It is suggested that the electron does not actually revolve around the nucleus, but rather about the centre of gravity of the entire atom.

(2) Elliptical orbits are introduced (Fig 16).

(3) It is suggested that the axes of the elliptical orbits also rotate about the centre of gravity of the atom.

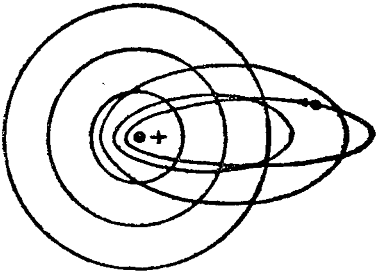


Fig. 16
Some of the circular and elliptical orbits for a single electron in hydrogen atom

Quantum Numbers

The revolutionary suggestion of Niels Bohr, mentioned earlier, mark the beginnings of quantum mechanics. This is the study of the laws governing the motions of very small particles. The quantum numbers, which describe the energy of an electron in terms of small numbers, grew out of the development of Bohr's approach.

From Bohr's work, it is clear that only specific energy levels are available for electrons in an atom. These energy levels are numbered, n = 1, 2, 3, 4, etc. The number n, is called the **principal quantum number.**

The energy levels correspond to these values of n=1,2,3,4, etc. are known as K,L,M,N etc. orbits respectively. These energy levels can accommodate a maximum of $2n^2$ electrons.

Thus the first energy level (K orbit) can accommodate two electrons, the second (L orbit) eight electrons, the third (M orbit) eighteen electrons and so on.

As we have mentioned earlier, the so-called single spectral lines are really groups of very fine lines. This led to further speculation about the possible energy states of the electron within the atom. As a result, a second quantum number *l*, is introduced. This number, *l*, is called the **azimuthal quantum number.** This quantum number is related to the shape of the orbit. In addition, it specifies energy sub-levels. The values of this quantum number corresponding to a principal quantum number run from zero upto n — 1. The various sublevels with $l = 0, 2, 3, 4$ are designated as s, p, d and f orbitals respectively.

Two additional quantum numbers have been added later. On the assumption that electron orbits will change if the atom is placed in a strong magnetic field, the **magnetic quantum number**, m, is proposed. This number designates the orientation of the orbital in space. This number corresponding to a value of *l* may have values of $0, +1, -1, +2, -2$ etc., up to $+ l$ and $- l$.

Finally, it has been suggested that electrons experience spin about their own axes. Hence, the **spin quantum number**, s, is introduced. This indicates the direction of the spin of the electron. The spin quantum number has values of $+\frac{1}{2}$ and $-\frac{1}{2}$.

Thus any electron in an atom can be defined by four quantum numbers, viz.

(i) **The principal quantum number (n)**: This may have any positive integral value except zero i.e $n=1,2,3,4$ etc.

(ii) **The azimuthal quantum number (*l*).** This may have values 0, 1, 2, 3 etc. up to (n—1).

(iii) **The magnetic quantum number** (m). This is also an integer. This may have any positive or negative value from + *l* to − *l* including zero.

(iv) **The spin quantum number** (s). This has only two values viz. + ½ and — ½.

The Pauli Exclusion Principle

One important law enables us to make use of these quantum numbers. This is the **Pauli exclusion principle.** This states that no two electrons in a given atom may have the same set of four quantum numbers.

This principle tells us that there are limits on the quantum numbers that the electrons may have. Let us consider for example the first energy level i.e K orbit. This corresponds to $n = 1$ and $l = 0$. Hence it is known as 1 s orbital, i.e. the 1 s orbital corresponds to values $n = 1$, $l = 0$ and $m = 0$. The electron that occupies this orbital can have a spin quantum number (s) of + ½ or — ½. If one electron has quantum number $n = 1$, $l = 0$, $m = 0$ and $s = +\frac{1}{2}$, then a second electron can have $n = 1$, $l = 0$, $m = 0$ and $s = -\frac{1}{2}$. Thus, the exclusive principle requires that there can be atmost two electrons in the 1s orbital. On this basis, it follows that a 2p level corresponding to $n = 2$, $l = 1$ and $m = -1, 0, +1$ can have 3 orbitals and hence it may contain upto 6 electrons. A 3 rd level corresponding to $n = 3$, $l = 2$, $m = -2, -1, 0, +1, +2$ can have 5 orbitals and may accommodate totally 10 electrons.

Total energy of an electron

The four quantum numbers together completely specify an electron's energy state within an atom. Let us see just how this is accomplished. All electrons having the same value of n form one major energy level. The energy of these electrons is then subdivided by the value of *l*. The different values of *l* for the same value of n indicate energy differences that are smaller than those between the major energy levels. These are the energy sub-levels. The magnetic quantum number (m) separates the energy sub-levels into what we call **orbitals.** In general, the electrons in a given set of orbitals have the same energy state.

Energy Level Diagram

The electrons in an atom in its normal or ground state are arranged so that the energy content of the atom is a minimum. That is, they assume the most stable arrangement available in terms of the rules, set above. Fig. 17 shows this normal state.

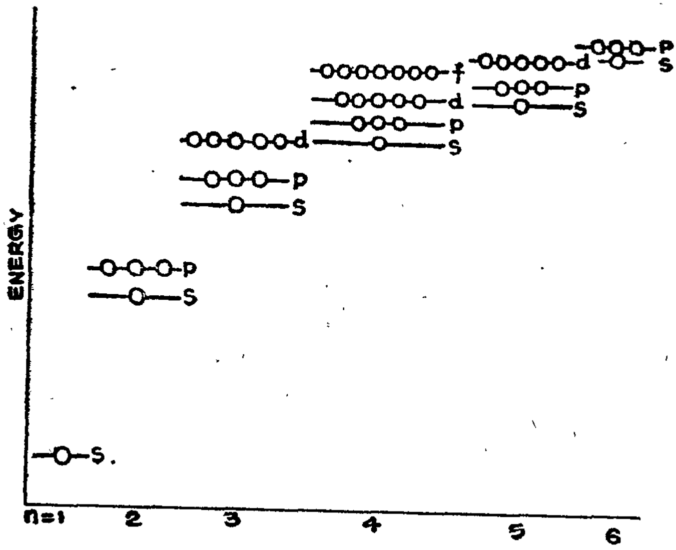


Fig. 17
Energy levels of atomic electrons

As the diagram indicates the electrons in the first energy level (n = 1) possess the lowest possible energy. The other sets of lines drawn in (n = 2, n = 3, n = 4 etc.) represent higher energy levels. Note that the electrons with quantum number n = 3, l = 2 and various m and s values i.e. 3rd electrons are of higher energy than those with n = 4, l = 0, m = 0 i.e. 4 s electrons. Similar types of inversions occur with n = 4 and higher levels.

Further note that the difference between the first two energy levels corresponding to n = 1 and n = 2 is greater than that between the energy levels with n = 2 and n = 3. This trend continues and this is partly responsible for the inversions in energy levels mentioned above.

Filling-up of the orbitals

The filling up of the orbitals in the ground state by electrons is governed by the following set of rules :

1. The maximum number of electrons in any orbit is $2n^2$ where n is principal quantum number of the orbit.

2. The maximum number of electrons in a sub-level (s,p, etc.) is given by $2(2l+1)$ where l is the azimuthal number.

3. Orbitals are filled in the order of increasing energy. This is known **aufbau principle.** The order of filling up orbitals can be determined with the help of energy level diagram (Fig. 17). The order is shown in the diagram (Fig. 18).

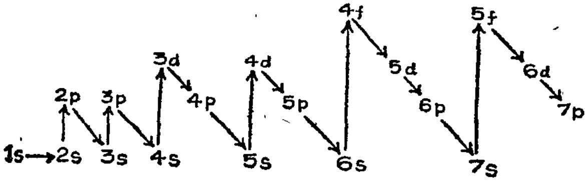


Fig. 18
The order of filling up of orbitals

4. Electrons never pair in any s, p, d or f orbitals until no available empty orbitals are left to them. This is known as **Hund's rule.**

5. An orbital cannot contain more than two electrons. This is known as **Pauli's exclusion principle.**

6. Energy levels tend to become either completely full or exactly half full of electrons.

Employing these rules let us make an attempt to fill up the orbitals with electrons and thus to construct the electronic configuration of a few elements. To start with, hydrogen has an atomic number of 1 and therefore it has one electron in the 1s– orbital. Hence the structure of the hydrogen atom is

$_{1}H \quad 1s^1$

But, since each orbital may include two electrons, the structure of a helium atom is

$_{2}He \quad 1s^2$

The lithium atom has the two electrons given above, plus a third one in the 2s orbital :

$_{3}Li \quad 1s^2\ 2s^1$

The structure of beryllium is then

$_{4}Be \quad 1s^2\ 2s^2$

Boron is an element with atomic number five and has all of the electrons above, plus one in the 2 p orbital.

$_{5}Be \quad 1s^2\ 2s^2\ 2p^1$

The 2p sub-level, however, can have upto six electrons. Hence, the structures of the elements with atomic numbers 6, 7, 8, 9 and 10 are :

$_{6}C \quad 1s^2\ 2s^2\ 2p^2$
$_{7}N \quad 1s^2\ 2s^2\ 2p^3$
$_{8}O \quad 1s^2\ 2s^2\ 2p^4$
$_{9}F \quad 1s^2\ 2s^2\ 2p^5$
$_{10}Ne \quad 1s^2\ 2s^2\ 2p^6$

There is a special significance to the completed 2s and 2p sub-levels in neon atom. This structure is called **an octet of electrons.** This is more stable than other outer-electron configurations. All of the relatively inert rare gases (eg. Ne, Ar, Kr, Xe, Rn) have this unique structure.

The next element sodium has atomic number 11 and thus contains 11 electrons. Its structure is

$_{11}Na\ 1s^2\ 2s^2\ 2p^6\ 3s^1$

Now following the sequence indicated in Fig. 19 we find the structures of the atoms with atomic numbers 12, 13, 14, 15, 16, 17 and 18 in the following.

$_{12}\mathrm{Mg}$ $1s^2\ 2s^2\ 2p^6\ 3s^2$
$_{13}\mathrm{Al}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
$_{14}\mathrm{Si}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$
$_{15}\mathrm{P}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
$_{16}\mathrm{S}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
$_{17}\mathrm{Cl}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
$_{18}\mathrm{Ar}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Potassium is the next element. Its atoms have the inner electronic structure of argon, plus a 4s electron. Similarly calcium atom has two 4s electrons in addition to the argon inner structure.

$_{19}\mathrm{K}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
or
$_{19}\mathrm{K}$ (Ar) $4s^1$
$_{20}\mathrm{Ca}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$
or
$_{20}\mathrm{Ca}$ (Ar) $4s^2$

In these the 3d orbitals are skipped. This is because 4s electrons are lower in energy content than 3d electrons. This is evident from the energy level diagram.

QUESTIONS

1. How can you show experimentally that cathode rays are electrically charged particles ?
2. How can the e/m ratio of an electron be determined ?
3. Write a short note showing how the electronic charge is calculated.
4. State the physical properties of the electron.

5. Explain the experimental proof that protons are more massive than electrons.

6. What are the physical properties of the proton ?

7. Compare the properties of the neutron with those of the proton.

8. How does Rutherford's experiment indicate that matter is largely empty space ?

9. Explain the essential features of the planetary atom model ?

10. State the suggestions of Niels Bohr which solved the problem of dynamic unstability of the Rutherford's atom model.

11. How is the origin of the various spectral series in the atomic spectrum of hydrogen accounted for ?

12. State the significance of the principal, azimuthal magnetic and spin quantum numbers.

13. What is the Pauli exclusion principle, and how is it applied to the atom's electronic structure ?

14. State Hund's rule.

15. Write out the electronic structures for ${}_{19}K$, ${}_{16}S$, ${}_{20}Ca$, and ${}_{10}Ne$.

CHAPTER IV

CHEMICAL BONDS

In the chapter on atomic structure we learned about the Bohr theory of atomic structure and how it accounts for the arrangements of electrons within the atom. Only after the acceptance of this theory, a satisfactory explanation of chemical bonding was offered. Kossel and Lewis independently put forward in 1916 the electronic theory of valency. This theory was subsequently elaborated by Langmuir, Sidgwick and others. In this theory chemical combination was brilliantly accounted for in terms of the sharing or transfer of electrons between the atoms.

Valency and Electronic Configuration

According to the electronic theory of valency, the bonds which hold the atoms in a molecule together are related electronic configuration of the atoms. We know the relatively inert gases namely Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), Xenon (Xe) etc have the electronic configuration indicated below.

	K	L	M	N	O	P
He	2					
Ne	2	8				
Ar	2	8	8			
Kr	2	8	18	8		
Xe	2	8	18	18	8	
Rn	2	8	18	32	18	8

These gases are highly stable and practically inert. Therefore it follows that an outer group of two electrons in cases where only the first energy level is involved or eight electrons (octet) constitutes an exceptionally stable arrangement. The stability inherent in these systems also manifests itself in the combination of atoms to form compounds. Mostly, atoms combine in such a manner as to attain an electronic configuration like that of an inert gas i.e., with two or eight electrons in their outer energy level. Hence the valency of an element is either equal to the number of outermost electrons or is equal to the eight minus this number. For example, the valencies of certain elements are tabulated along with their electronic configurations in Table 1.

TABLE 1

VALENCY AND ELECTRONIC CONFIGURATION

Element	Li	Be	B	C	N	O	F	Ne
Electronic configuration	2, 1	2, 2	2, 3	2, 4	2, 5	2, 6	2, 7	2, 8
Valency	1	2	3	4	3	2	1	0

Types of Bonding

According to the electronic theory, there are several different ways in which atoms can combine. They are the loss, the gain, or the sharing of one or more electrons. Formally, these processes give rise to different types of bonding viz., the electrovalent bond, the covalent bond and the co-ordinate bond.

If the combination of atoms to form the compound occurs by the **transfer of an electron** or electrons from one atom (or groups of atoms) to another atom (or groups of atoms), then the resulting compound is an ionic compound and the type of bonding is **electrovalent**. Conversely, if the combination occurs by the **sharing of electrons** between the combining atoms, the resulting compound is a covalent compound and the type of bonding is **covalent**. If the electrons, subjected to sharing, came from only one of the two combining atoms, the resulting compound and bond are termed **co-ordination compound** and co-ordinate bond respectively.

(i) The Electrovalent Bond

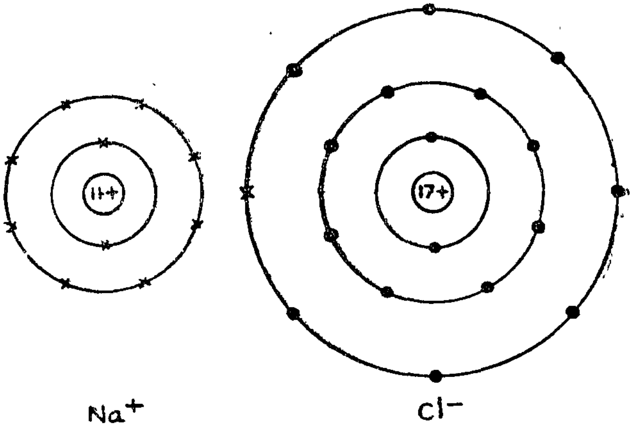
In this type, as we mentioned in the preceding para. an atom (or group of atoms) gives up one or more of its electrons to an atom (or groups of atoms) with which it combines. Let us consider the atom (or groups of atoms) which loses electron (s) in this process. This becomes positively charged. This is because it now contains fewer electrons than protons. On the other hand, the atom (or group of atoms) which gains electron (s) becomes negatively charged. This is because it now has an excess of electrons over protons. The two ions are held together by electrostatic attraction between the ions. These facts can be exemplified by the formation of sodium chloride from sodium and chlorine through the following processes :

$$\underset{(2,\,8,\,1)}{Na} \longrightarrow \underset{(2,\,8)\ \text{Ne — like}}{Na^+ + e^-}$$

and

$$\underset{(2,\,8,\,7)}{Cl + e^-} \longrightarrow \underset{(2,\,8,\,8)\ \text{Ar — like}}{Cl^-}$$

These changes are shown diagrammatically in Figure 19. In this the electrons in the sodium atom are shown as crosses and those in the chlorine atom as dots.



Na^+
(2, 8)

Cl^-
(2, 8, 8)

Fig. 19

The electronic configuration in sodium chloride.

When magnesium combines with oxygen to form magnesium oxide, each magnesium atom gives up two electrons to an oxygen atom as follows

$$\underset{(2,\ 8,\ 2)}{\mathrm{Mg}} \longrightarrow \underset{(2,\ 8)}{\mathrm{Mg}^{2+}} + 2e^-$$

and

$$\underset{(2,\ 6)}{\mathrm{O}} + 2e \longrightarrow \underset{(2,\ 8)}{\mathrm{O}^{2-}}$$

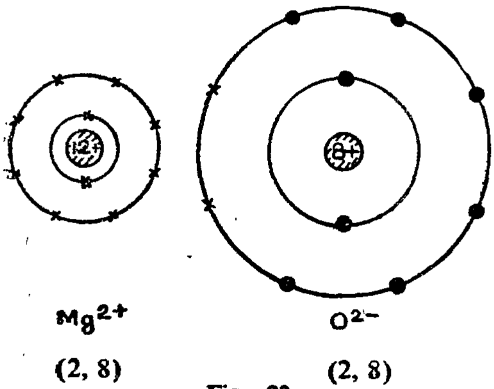


Fig. 20
The electronic configuration in magnesium oxide

In these examples the ions of opposite charges are held together by electrostatic attraction. This is called the **ionic bond or electrovalent bond.** The ions formed in these cases possess the stable electronic configurations of the noble gases. Hence, once these configurations have been achieved, there is no tendency on the part of the ions to lose or gain any further electrons. Thus the valency number of any atom forming electro-valent bonds is that number of electrons it must lose or gain to achieve the nearest inert gas configuration.

Factors Favouring Formation of Electrovalent Bonds

The formation of an electrovalent bond is obviously related to the case of formation of the positively charged ions (cations) and negatively charged ions (anions) from the neutral atoms. This depends mainly on two factors namely ionization potential and electron affinity.

(i) **Ionization potential** : The energy required to remove an electron completely from a gaseous atom is defined as the **ionization potential** This can be measured by spectroscopic methods. This is usually expressed in electron volts (eV). The ionization potential values for some elements (alkali metals) are tabulated in Table 2.

TABLE 2
IONIZATION POTENTIAL OF SOME ELEMENTS

Elements	Ionization potential (eV)
Li	5·4
Na	5·1
K	4·3
Rb	4·2
Cs	3·9

The energy required to remove an electron from an atom, the one we have discussed now, is the first ionization potential. The energy required to remove an electron from a univalent unipositive ion to form a divalent cation is called the second ionization potential and so on. The ionization potential value increases in the order 1st<2nd <3rd. For example, the various ionization potentials of magnesium illustrates this, (Table 3).

TABLE 3
IONIZATION POTENTIALS OF MAGNESIUM

Ionization potential	Value in eV
First	7·60
Second	15·0
Third	80·1

The formation of an electrovalent bond is through the formation of a cation and anion. Since the formation of cation is by the removal of electron(s) from an atom, the lower the value of ionization potential, the greater will be the case of formation of the cation and thus the electrovalent bond will be formed.

(ii) **Electron affinity** : The energy released when an electron is added to a neutral gaseous atom to form an anion is termed the **electron affinity**. The value of this like ionization potential, is usually expressed for one mole of ions. Some typical values for univalent anions are shown in Table 4. A large positive value for the electron affinity of any ion indicates that such an ion is formed from the atom with a considerable release of energy and hence that it readily forms an anion. The highest electron affinities are observed in the case of halogens.

TABLE 4

ELECTRON AFFINITIES OF SOME ELEMENTS

Element	Electron affinity m K. cal. mol^{-1}
F	83·5
Cl	87·3
Br	82·0
I	75·7

Properties of Electrovalent Compounds

In general, electrovalent compounds have high melting and boiling points, conduct an electric current when melted or dissolved in water. These are soluble in polar liquids such as water, alcohol etc. but insoluble in non-polar liquids such as benzene, carbon tetrachloride etc.

The ions constituting the electrovalent compound are held together by strong electrostatic force in the solid state. Hence considerable energy is needed to overcome these forces and break down the solid. The high melting and boiling points of such compounds is a direct consequence of this fact. When an electrovalent compound is melted or dissolved in water, the binding forces in the crystal disappear, the component ions become mobile and thus conduct electricity.

When an electrovalent solid is placed in polar solvents like water, the molecules of the solvent interact strongly with ions of the crystal. The **solvation energy** resulting out of this interaction, is sufficient to overcome the electrostatic forces which hold the ions together This is the reason for the solubility of electrovalent compounds in solvents like water But the non-polar solvents like benzene do not salvate the ions. Hence electrovalent compounds are insoluble in such solvents.

(2) The Covalent Bond

In this type, electrons contributed equally by the two combining atoms are shared between the two atoms. By sharing in this way, the number of electrons in the outermost orbit of each atom increases to attain the stable configuration of one of the inert gases.

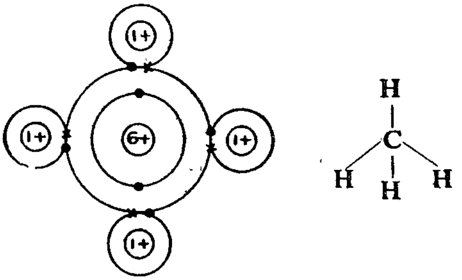


Fig. 21
The electronic configuration in methane

A good example of a covalent bond is provided by methane In this, each hydrogen atom is bonded to the carbon atom by a pair of shared electrons as shown in Fig. 21 In this electrons originated from hydrogen atoms are represented by crosses and those from carbon by dots.

In this, each hydrogen atom gains an electron and assumes the stable configuration of an inert gas helium. The carbon atom also gains four electrons and thus attains a stable configuration of neon. In the diagram, the four covalent bonds are arranged at right angles to each other in one plane. This is done only for convenience. In fact, the bonds are directed to the four corners of a regular tetrahedron owing to their strong mutual repulsion.

Ammonia molecule provides another example of covalent bonding. Since the nitrogen in ammonia has already five electrons in its outermost orbit, it takes up only three electrons by sharing with three hydrogen atoms to attain the stable inert gas configuration. This is shown in Fig. 22. The two electrons in the outermost orbit which are not involved in forming a covalent bond remain as a **lone pair**

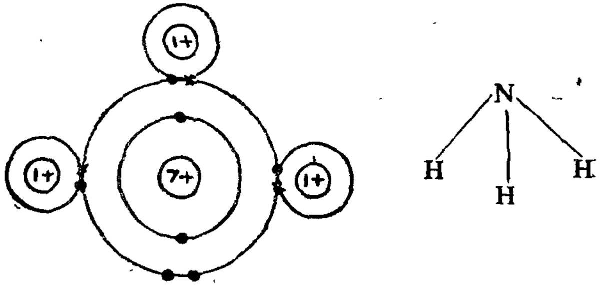


Fig. 22
The electronic configuration of ammonia molecule

The molecules of the most non-metallic elements contain covalent bonds. For example, the molecules of hydrogen and chlorine contain covalent bonds (Fig 23).

One, two or even three covalent bonds may be formed between two atoms by the simultaneous sharing of one, two or three pairs of electrons in between them. This is well exemplified by ethane, ethylene and acetylene molecules respectively and illustrated in Fig. 24.

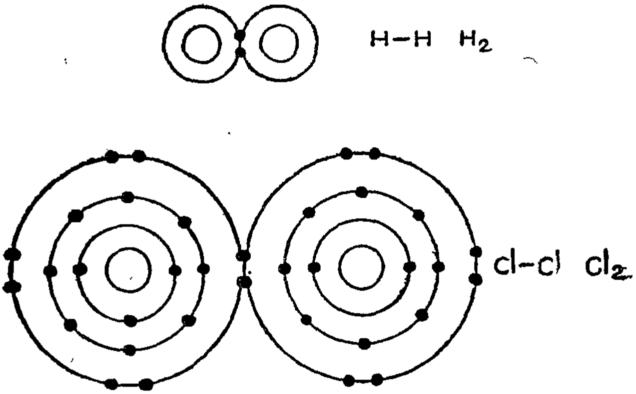


Fig. 23
The electronic configuration of hydrogen and chlorine molecules.

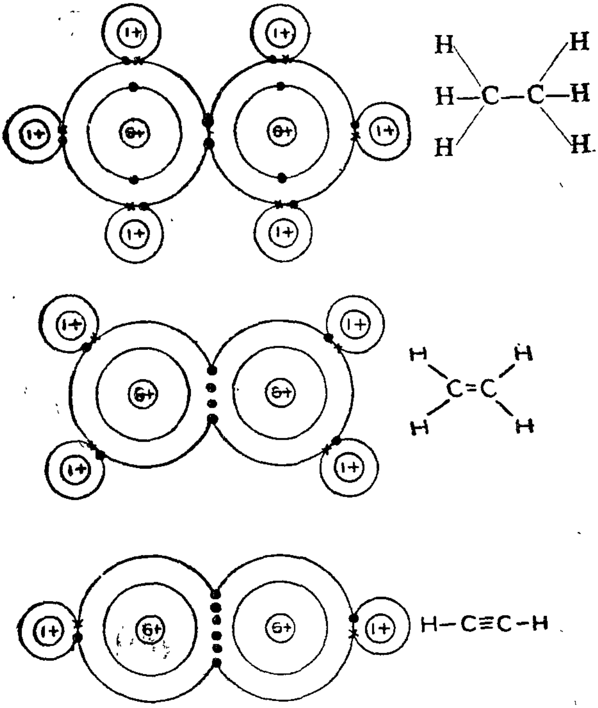


Fig. 24
The electronic configurations of ethane, ethylene and acetylene:

Properties of covalent compounds

Covalent compounds ordinarily exist as single molecules which are held together by very weak forces. Hence these are generally gases or low boiling liquids. But if their molecular weights are high, these exist as solids. In general, these have low melting and boiling points. This is also because of the weak forces which hold the separate molecules together. When such compounds are heated these weak forces break readily, causing the compounds to melt and vapourise. These compounds in general will not conduct an electric current in the molten state nor when in solution. This is because of the absence of any ions or free electrons in these compounds. These are insoluble in polar solvents but soluble in non-polar solvents The latter can be ascribed to the similar covalent nature of the molecules of solute and solvent (i.e. like dissolves like).

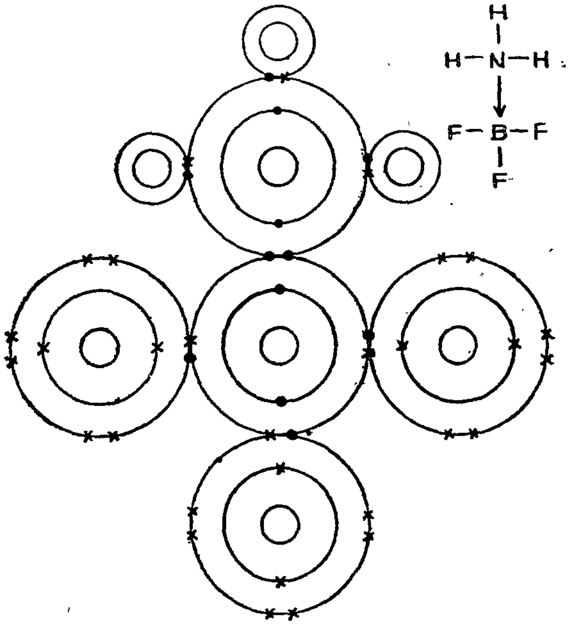


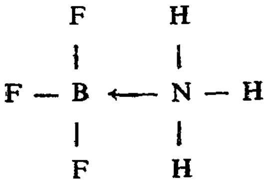
Fig. 25
A typical co-ordinate bond

The Co-ordinate Bond

In the covalent bonds considered in the previous section, each atom taking part in the formation of the covalent bond contributes one electron to the electron pair If both electrons are supplied by one atom, a co-ordinate bond is formed.

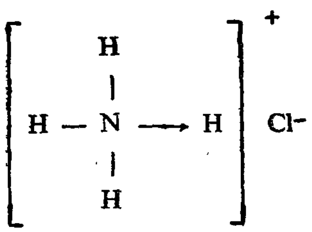
A good example of this type of bond is provided by the compound formed by the reaction of boron trifluoride with ammonia. i.e. BF_3NH_3. In this, the bond between the boron and nitrogen atoms is a co-ordinate bond. This is formed by the nitrogen atom which uses its lone pair of electrons for this purpose as shown in Fig. 25.

The co-ordinate bond resembles the covalent bond. Hence to distinguish this from covalent bonds and also to indicate the one-sided origin of the electrons, this type of bond is represented in structural formula by an arrow pointing from the **donor atom** (i.e. the atom which donates the pair of electrons) to the **acceptor atom**. Then the above cited compound may be represented as follows :



$$\begin{array}{ccccc} & F & & H & \\ & | & & | & \\ F - & B & \longleftarrow & N & - H \\ & | & & | & \\ & F & & H & \end{array}$$

Another compound containing the co-ordinate bond is ammonium chloride which has the formula.



$$\left[\begin{array}{ccc} & H & \\ & | & \\ H - & N & \longrightarrow H \\ & | & \\ & H & \end{array}\right]^{+} Cl^{-}$$

Here each of three hydrogen atoms is linked to the nitrogen atom by single covalent bond as in ammonia i.e. by a pair of shared electrons, one originating from the hydrogen and the other from nitrogen. On the other hand, the bond between nitrogen and the fourth hydrogen (originated from HCl) is a co-ordinate bond since both electrons making up the bond have come from the nitrogen atom. The chloride ion is held to the resulting complex ion (NH_4^+) by an electrovalent bond.

SHAPES OF THE MOLECULES

(1) Electron-pair repulsion theory

An atom is bonded to another atom in covalent molecules by electron pairs. These electron pairs are attracted to the central nucleus by the electron-nucleus attractive force. At the same time they are repelled by the other electron pairs about the central atom. As a result, the electron pairs remain as far apart from one another as possible, while maintaining their distance from the central nucleus.

In covalent compounds, as observed in the previous sections, the most commonly observed electronic arrangement is an octet i.e. four pairs of electrons. These can be arranged about a central atom in two fashions namely tetrahedron and square planar arrangements (Fig. 26). Of these the tetrahedral arrangement has the electron pairs as far apart as possible for a given distance from the central nucleus and thus has a minimum electron-pair repulsions. Hence the octet of electrons prefers the tetrahedral arrangement. Thus each of the four pairs of electrons constituting the octet occupies a region of space directed towards the vertex of a tetrahedron. If each of these four electron pairs bonds the central atom to

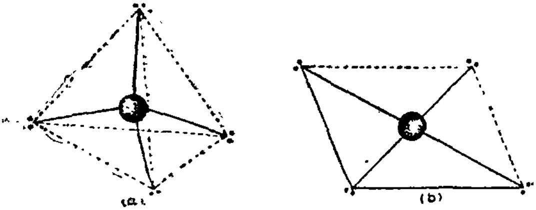


Fig. 26
Tetrahedral and square planar arrangements

another atom, then the resulting arrangement of bonded atoms about the central atom is tetrahedral. Methane provides an example for this situation.

This model for molecular geometries is known as **valence-shell electron - pair repulsion theory** (VSEPRT) or shortly as electron-pair repulsion model This can be extended to other molecules which differ in numbers of electron pairs. Fig. 27 shows some common examples

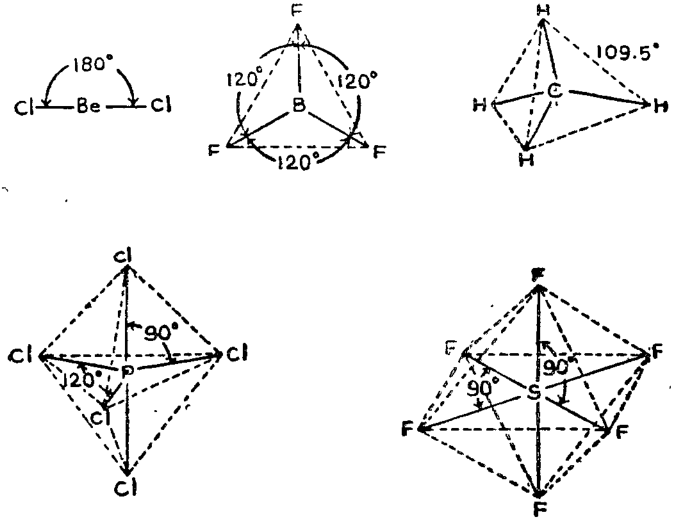


Fig. 27
Some examples of different molecular shapes

Beryllium chloride, $BeCl_2$, contains two covalent bonds (two electron pairs). Because of the repulsion which the two covalent bonds exert upon each other, the molecule is linear Similarly in boron trifluoride, BF_3, there are three bonds. These all lie in the same plane at an angle of 120° to each other owing to their mutual repulsion. In methane, there are four covalent bonds. These are directed tetrahedrally for the same reason. In phosphorus pentachloride, PCl_5, the five bonds are arranged in a trigonal bipyramid fashion. In sulphur hexafluoride, SF_6, the six bonds are distributed in an octahedral fashion.

The shape of many other simple molecules can be explained in terms of this mutual electron-pair repulsion of covalent bonds. For example, in ammonia the four pairs of electrons (octet) are arranged tetrahedrally about the nitrogen atom as they are around carbon atom in methane. In ammonia, however, one of the pairs remains as a lone pair as we have witnessed earlier. This lone pair, appears to occupy more volume than ordinary shared pairs i.e., covalent bonds. Thus it causes a reduction of the interbond angle between two hydrogen atoms to 107° (Fig. 28). The same effect is observed in the water molecule where two lone pairs of electrons on the oxygen atom reduces the bond angle to 104·5° from the expected angle of 109·5° for an exactly tetrahedral molecule (Fig 28). Thus ammonia molecule assumes a **pyramidal** shape and water molecule a **bent** shape.

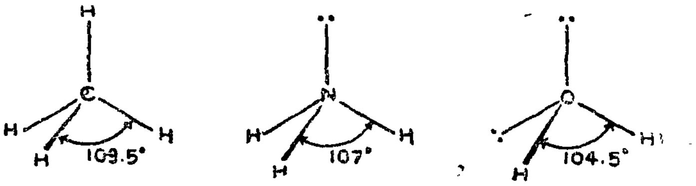


Fig. 28
Shape of CH_4, NH_3 and H_2O molecules

This model can also be extended to predict the geometry of molecules containing double or triple bonds. For example let us consider carbon dioxide. This contain two double bonds. Each double bond behaves as a single electron pair. This means there are two electron pairs as in $BeCl_2$. The molecule should therefore be linear. The CO_2 molecule is in fact observed to be **linear**.

(2) Valence-bond model

The electron-pair repulsion theory provides a simple model for predicting the shapes of molecules. However, it does not explain why bonds exist between atoms. The valence bond theory answers this and accounts for the shapes.

of molecules from another direction. Covalent bonding, as we have discussed earlier, occurs when atoms share electrons. But sharing of electrons can occur only if an atomic orbital of one atom overlaps with an atomic orbital of another. This idea is illustrated in Fig. 29, which shows the overlap of the 1s orbital on one H atoms with that on the other in the formation of H_2 molecule.

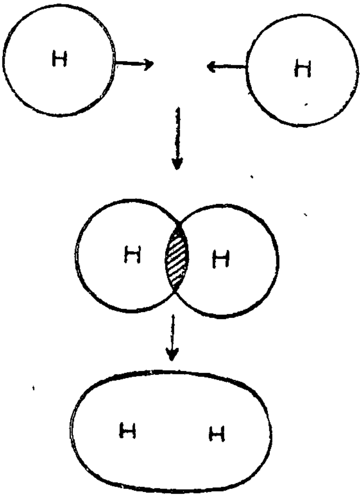


Fig. 29
Overlap of atomic orbitals

The bond formed in the formation of H_2 molecule by this type of overlap of atomic orbitals is called a **σ bond.** A corresponding formation of a σ bond in the HCl molecule is illustrated in Fig. 30. The electronic structure of an unbound chlorine is $1s^2\ 2s^2\ 2p^4\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$.

	1s	2s	$2p_x$	$2p_y$	$2p_z$	3s	$3p_x$	p_y	p_z
Chlorine	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑

In the formation of HCl, the half-filled p_z orbital on the chlorine atom overlaps with the 1s orbital of the hydrogen atom to give linear structure.

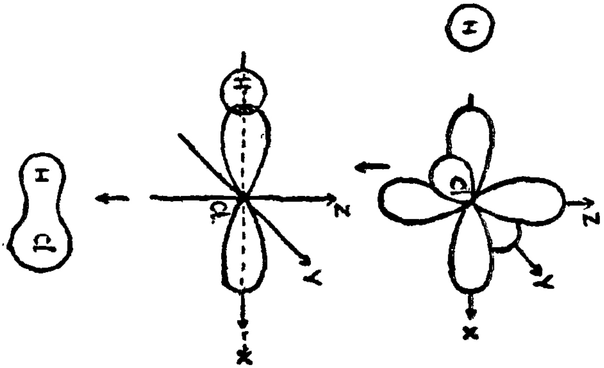


Fig. 30
Formation of HCl by Overlapping of atomic orbitals

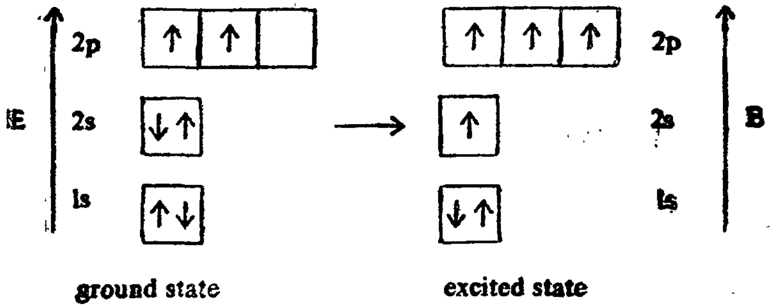
Let us consider the bonding in molecules with more than two atoms. Methane (CH_4) serves as an example. Any theory of bonding must be consistent with the following facts :

(i) The four C—H bonds are equal in strengh.

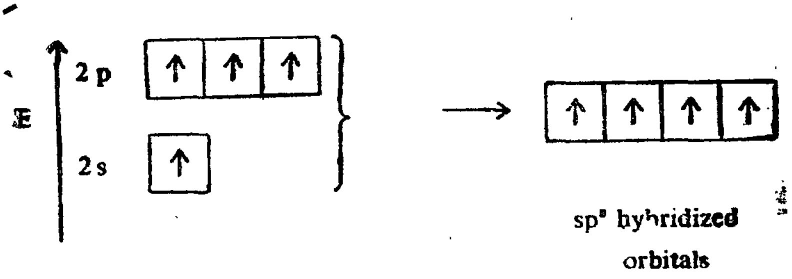
(ii) The four H—C—H bond angles are the same ; they are 109°28'

The carbon has $1s^2$ $2s^2$ $2p^2$ configuration. This has only two unpaired electrons. But it must provide four equivalent atomic orbitals for bonding in methane. This cannot occur when the electrons are in s and p orbitals, because the energies of these subshells are different. The actual equivalence of all four bonds is explained by assuming that four equivalent orbitals are produced by mixing of the 2s and the three 2p orbitals. This mixing is called **hybridization**. This process actually consists of two steps :

(i) **Promotion** : Absorption of sufficient energy in reaction uncouples one of the 2s electrons and excites it to the 2p level. This process is called **promotion**.



(ii) **Hybridization** : The 2s and 2p orbitals with unpaired electrons differ only slightly in energy. These orbitals therefore, mix with each other and produce a new set of four equivalent orbitals. This process is called hybridization. Since the new set of orbitals are derived from one s and 3p orbitals they are called sp^3 hybridized orbitals.



Formation of sp^3 hybridized orbitals set is shown in Fig. 31. These orbitals are directed symmetrically in space i.e. tetrahedrally. Each sp^3 hybridized orbital overlaps with the 1s orbital of hydrogen atom. Such interactions to form methane are shown in Fig. 32. The resulting bond angle of 109° is a excellent agreement with the observe angle 109°.

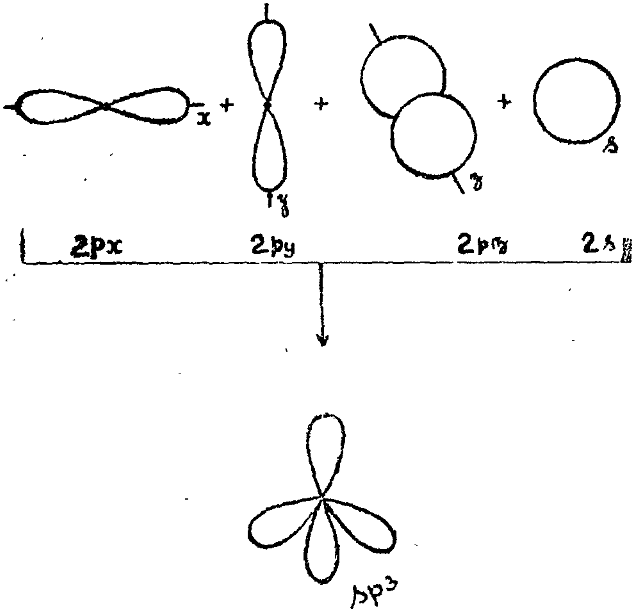


Fig. 31
sp hybridization

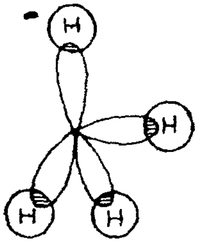


Fig. 32
Overlap of sp³ hybrid orbitals with 1s orbitals of hydrogen

The concept of hybridization is also used to account for the shape of the molecules such as ammonia and water. In these the central atom has about it four electron parts. The orbitals used by the central atom can be thought of sp^3 hybridized orbitals. In ammonia one of the sp^3 hybridized orbitals contains the unshared pair of electrons, the other three are employed in the bonds to hydrogen (Fig. 33). Hence, the molecule assumes a trigonal pyramid shape. In water molecule two of the orbitals contain unshared pairs, two are employed in bonds to hydrogen (Fig. 33). In these molecules, the bond angles about the central atom are not exactly the 109°, tetrahedral angle. They are 107° and 105° respectively. So in these cases the hybridised orbitals are not pure sp^3 hybrids. This is due to greater contribution from s in one hybrid orbital than a little smaller in another.

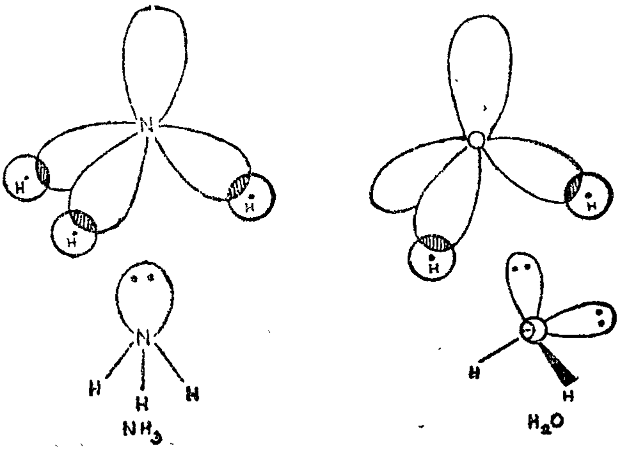
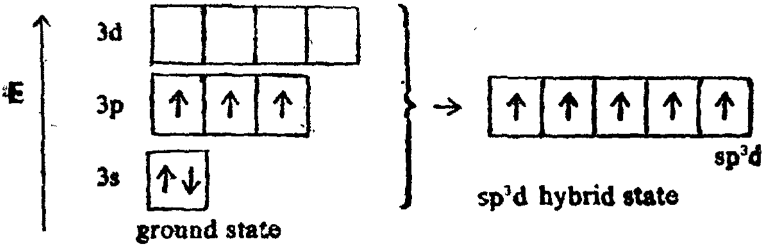


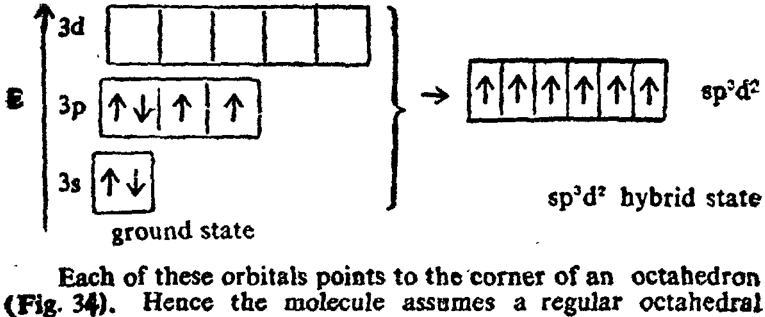
Fig. 33
Shapes of ammonia and water molecules

Elements of third and higher periods have d orbitals available for bonding. Consequently they may have more than four pairs of valence electrons. For example, in the molecules PCl_5 and SF_6 the central atoms, phosphorus and sulphur respectively have five and six pairs respectively. In PCl_5, five orbitals are needed to accommodate the five pairs of electrons. It is suggested that one **d** orbital hybridises with the one **s** and three **p** orbitals of the same level to give five sp^3d hybrid orbitals. Thus the phosphorus atom in gaseous

PCl_5, uses the 3s, three 3p and one 3d orbitals to form the five sp^3d hybrid orbitals. Both the ground state and the sp^3d hybrid state are the following :



The PCl_5 molecule has a shape of trigonal bipyramid (Fig. 34). Three chlorine atoms lie at the corners of an equilateral triangle with a Cl-P-Cl bond angle of 120° while the fourth and fifth lie above and below the centre of the triangle with Cl-P-Cl angle of 90°. In SF_6, six orbitals are needed to accommodate six pairs of electrons. In this case, it is suggested that two **d** orbitals hybridise with one s and three **p** orbitals. In this way, six equivalent sp^3d^2 hybrid orbitals are formed.



Each of these orbitals points to the corner of an octahedron (Fig. 34). Hence the molecule assumes a regular octahedral shape.

Similar to the formation of sp^3 hybrid orbitals, formation of other type of hybrid orbitals from s and **p** orbitals, namely, sp^2 and **sp**, are possible. As the name implies sp^2 hybrid orbitals, three in number, are the outcome of blending one **s** and 2p orbitals and sp hybrid orbitals, two in number, are the outcome of blending of one s and one p orbitals.

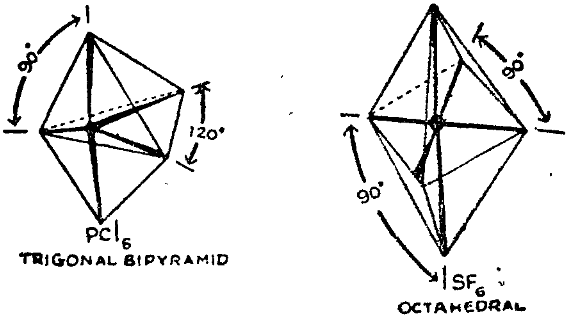


Fig. 34
Shape of PCl_5 and SF_6 molecules

Carbon dioxide is a linear molecule. In this both C = O bonds are equivalent. To account for the linear shape, it is suggested that the s orbital hybridises with the one p orbital of the same level of carbon atom to give two sp hybrid orbitals. These hybrid orbitals are employed in σ bonds to oxygen atoms (Fig. 34). The carbon atom also has two p orbitals each of which overlaps laterally with a p orbital of an adjacent oxygen atom to give two π bonds (Fig. 34).

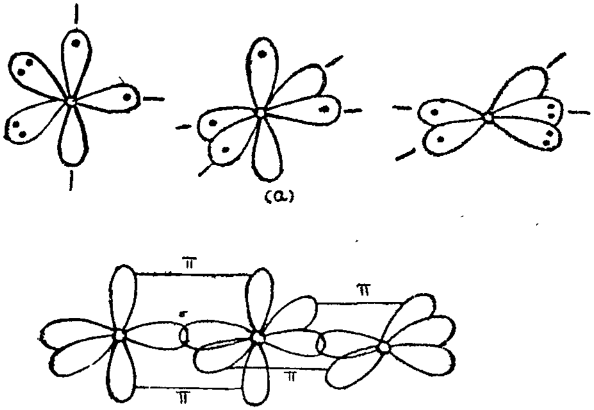


Fig. 35
Formation of a CO_2 molecule

Transition from covalent to ionic character and vice versa

Covalent bond is due to the sharing of electrons between the combining atoms. Equal sharing of the pair of electrons which constitute the covalent bond occurs in homo-atomic molecules like H_2 molecule. But if the two bonded atoms are dissimilar as in HCl, the sharing is unequal; one atom is likely to attract electrons more strongly than the other. The atom that attracts electrons more strongly develops some negative charge, the other atom develops some positive charge. These fractional charges are denoted as $\delta +$ and $\delta -$. For example, since a chlorine atom is more electron-attractive than a hydrogen atom hydrogen chloride is represented as

$$H^{\delta+} - Cl^{\delta-}$$

Electrovalent bond is due to the transfer of electron(s) from one atom to the other and thus due to the formation of ions, the separation of charge is not complete in all ionic compounds. For example in the ionic solid NaCl, the actual charges on Na and Cl atoms are about + 0·67 and — 0·67 respectively. This indicates that the electrovalent bond has some covalent character. The presence of covalent character in such ionic bonds is due to the following reason.

When two oppositely charged ions approach each other closely to form the ionic bond, the cation attracts the outermost electrons and repels nucleus of the anion, followed by some sharing of electrons between the two ions. Consequently the ionic bond acquires a certain degree of covalent character.

From the foregoing discussions it is clear that there is no sharp distinction between electrovalency and covalency Indeed the modern view is that a bond between atoms of two different elements is rarely entirely electrovalent or completely covalent but is usually intermediate between these two extreme types, with the characteristics of one of them predominating.

Fajans' rule

In 1924 Fajans' put forward some simple rules. These summarised the situations in which an ionic bond shows the greatest covalent character.

1. When the charge on both anion and cation is high
2. When the cation is small
3. When the anion is large

Formation of an electrovalent bond involves transfer of electrons from one atom to other. Therefore, any factor which makes more difficult the loss or gain of electrons will favour the adulteration of ionic bond with covalent character. With this in mind, let us proceed to justify briefly the above situations.

If the charge on the cation is large it will attract more strongly the electrons of the anion and will cause more polarisation. Hence this will lead to a sharing of a fraction of electrons between the anion and cation. Similarly if the charge on the anion is large it will respond easily to the influence exerted by the cation, and thus it will favour the introduction of covalent character to some extent. Thus the first situation cited above is justifiable. If the cation is very small, the elctrostatic force exerted by its nucleus will be greater and thus it can wield more influence on the electrons of the anion. Thus, this can offer a satisfactory explanation for the second situation. If the anion is large, it can hold its outermost electrons only less firmly and thus it will aid the call for the electrons from the cation and hence favour the admission of more covalent character into the electrovalent bond. Thus the third situation is also justifiable.

QUESTIONS

1. From the point of view of atomic structure, discuss the different ways in which atoms are linked in the formation of compounds. Illustrate your answer by some examples.

2. What is meant by (a) the electrovalent, (b) covalent bond ? Illustrate your answer with suitable examples.

3. What properties do you associate with the electrovalent and the covalent bond ?

4. Distinguish carefully between electrovalency and covalency, illustrating your answer by reference to HCl and methane.

5. The principal types of bonds occurring in compounds are according to the electronic theory of valence, described as electrovalence, covalence and co-ordinate valences. Explain (a) what is meant by these terms (b) the properties conferred by such linkages on the compounds in which the occur.

6. Give your reasons for believing that the bonds (a) in methane are covalent (b) in sodium chloride are ionic.

7. What is a σ bond ? Give examples of σ bond formed by overlap of s orbitals, s and p orbitals, two p orbitals.

8. What is meant by a hybridised orbital ? How has the concept of hybridised orbitals been applied to explain the tetravalency of carbon ?

9. What is meant by a π bond ? Describe the structure of carbon dioxide.

10. What shape would you expect for the following ? (a) NH_3 (b) PCl_5 (c) SF_6

11. What is meant by sp, sp^2 and sp^3 hybridisation ?

12. Discuss the shapes of CH_4, NH_3 and H_2O molecules. What is meant by bond angle ? The bond angles in CH_4, NH_3 and H_2O are, respectively, 109°, 107° and 105°. How would you account for this difference ?

13. Under what situations will the ionic bond contain more covalent character ?

14. The shape of a covalent molecule depends upon the number of electrons present in the outermost shell of a central atom. How would you justify this statement ?

15. If sp^3 hybrid orbitals are involved in CH_4, NH_3 and H_2O molecules, why are bond angles in the three cases different ?

CHAPTER V

ACIDS, BASES AND SALTS

Acids and Bases

The word acid is derived from the Latin term *acidus* meaning sour. According to Robert Boyle an acid is a substance which (i) has a sour taste, (ii) turns blue litmus into red, (iii) usually corrosive in nature, (iv) neutralises bases to give salts and water, (v) contains hydrogen atoms which can be replaced wholly or in part by metal atoms. Examples of acids are hydrochloric acid, sulphuric acid, and acetic acid.

A base is a substance which is (i) soapy to touch, (ii) turns red litmus in to blue, (iii) neutralises acids to give salts and water. Examples of bases are sodium hydroxide, pottassium hydroxide, calcium hydroxide etc.

Arrhenius theory of acids and bases : According to Arrhenius theory, an acid is a substance that dissociates to give hydrogen ions when dissolved in water. For example hydrogen chloride is an acid because it gives hydrogen ions when dissolved in water.

$$HCl \overset{\text{water}}{\rightleftharpoons} H^+ + Cl^-$$

According to Arrhenius Theory, a base is a substance which dissociates into hydroxyl ions when dissolved in water.

$$NaOH \overset{\text{water}}{\rightleftharpoons} Na^+ + OH^-$$

Strengths of acids and bases : The acids which have high degree of dissociation and produce a high concentration of hydrogen ions aqueous solution are called **strong acids.** Examples of strong acids are hydrochloric acid, sulphuric acid, nitric acid, etc. The acids which have low degree of dissociation and produce a low concentration of hydrogen ions in aqueous solution are called **weak acids**. Examples of weak acids are acetic acid, oxalic acid etc. The bases which have degree of dissociation and produce a high concentration of hydroxyl ions in aqueous solution are called **strong bases**. Examples of strong bases are sodium hydroxide, potasium hydroxide etc. Bases which have low degree of dissociation and produce a low concentration of hydroxyl ions in aqueous solution are called **weak bases**. Examples of weak bases are ammonium hydroxide, magnesium hydroxide etc.

Arrhenius theory of acids and bases is applicable only in aqueous solutions and therefore requires modification.

Lowry and Bronsted theory of acids and bases

In 1923 T. M. Lowry and J. N. Bronsted suggested a more general theory of acids and bases which is applicable to both aqueous and non-aqueous solutions. According to this theory an acid is a substance which has a tendency to donate a proton to any other substance and a base is a substance which has a tendency to accept a proton from any other substance. In water medium the proton is combined with at least one water molecule to give the **hydronium** ion (H_3O^+).

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

When an acid loses a proton the residual part of it will have a tendency to regain the proton. Therefore it will behave as a base. The relation between an acid and a base may therefore be represented by the general equation.

$$\text{Acid} \rightleftharpoons H^+ + \text{Base}$$

The acid and base which differ by a proton are known as **conjugate pair**.

Illustration : Consider the ionization of acetic acid in water

$$CH_3\,COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

Acetic acid donates a proton to water and thus behaves as an acid. Water accepts a proton and therefore acts as a base. In the reverse reaction hydronium ion donates a proton to acetate ion and thus acts as an acid. The acetate ion accepts a proton and thus acts as a base. Therefore acetic acid is the conjugate acid of the base acetate ion. Water is the conjugate base of the acid hydronium ion. In such reactions the solvent acts as a donor or acceptor of proton. The universal solvent water can act both as a donor and acceptor of proton. Therefore water is referred to as **amphiprotic solvent.**

Thus it is clear that

(i) A substance is able to show its acidic character only if another substance capable of accepting a proton (a base) is present.

(ii) In aqueous solution H^+ exists as H_3O^+ (hydronium ion.)

(iii) Apart from molecules even ions can act as acids and bases. Thus the anion of any acid acts as a base.

The ionisation of ammonia in water may be represented as

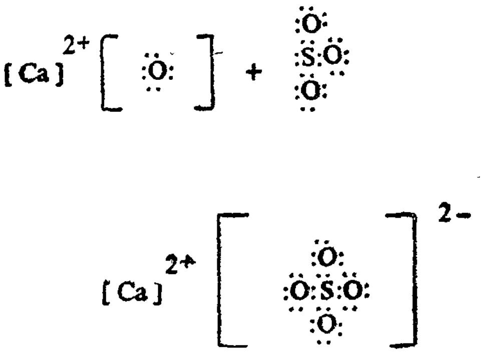
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Ammonium ion is the conjugate acid of the base ammonia and hydroxyl ion is the conjugate base of the acid water.

Although this theory is more comprehensive than the Arrhenius theory, this theory cannot explain some phenomena like the neutralisation of acidic oxides such as sulphur dioxide, carbon dioxide, sulphur trioxide etc. With basic oxides like calcium oxide, barium oxide etc, This neutralisation does not involve the transfer of protons. To explain these aspects G.N. Lewis put forward a more general theory of acids and bases based on the electronic theory of valency.

Lewis theory of acids and bases : According to G. N. Lewis an acid is a substance which can accept a pair of electrons to form a co-ordinate bond and a base is a substance which can furnish a pair of electrons to form a co-ordinate bond. Thus an acid is an **electron acceptor** while a base is an **electron donor.**

According to Lewis theory the neutralisation reaction between calcium oxide and sulphur trioxide may be represented as follows



Thus the lone pair of electrons from the oxygen of calcium oxide is donated to sulphur trioxide. Therefore calcium oxide acts as electron donor or base. Sulphur trioxide which accepts a pair of electrons acts as an acid.

Summary

Serial number	Name of the theory	Concept of acid	Concept of base
1	Arrhenius Theory	Dissociates to give hydrogen ions in aqueous solution	Dissociates to give hydroxyl ions in aqueous solution
2	Lowry—Bronsted Theory	Proton donor	Proton acceptor
3	Lewis Theory	Electron acceptor	Electron donor

Salts

An acid reacts with a base to give salt and water. This reaction is known as neutralisation. For example.

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

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$$

Types of Salts

Salts are classified as (i) Normal salts, (ii) Acid salts, (iii) Basic salts, (iv) Mixed salts, (v) Double salts, and (vi) Complex sals.

(i) Normal Salts : These are formed by the complete replacement of all the replaceable hydrogen atoms of an acid, Examples of normal salts are potassium chloride, sodium nitrate, sodium sulphate, sodium phosphate etc.

$$H_3PO_4 + 3\,NaOH \longrightarrow Na_3PO_4 + 3H_2O$$

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

(ii) Acid Salts : When only a part of the replaceable hydrogen atoms of an acid is replaced by a basic radical, the resulting salt is known as an acid salt. Such a salt can further react with a base.

Examples : Sodium bicarbonate, potassium hydrogen sulphate, sodium hydrogen phosphate (Na_2HPO_4) etc.

$$H_2SO_4 + KOH \longrightarrow KHSO_4 + H_2O$$

$$KHSO_4 + KOH \longrightarrow K_2SO_4 + H_2O$$

(iii) Basic Salts : A basic salt is formed by the incomplete neutralisation of a base by an acid.

Examples : Bismuth oxychloride ($BiOCl$), basic copper carbonate, $CuCO_3$. $Cu(OH)_2$ and $Mg\,(OH)Cl$.

The basic salt still contains one or more hydroxyl groups in it.

$$Mg(OH)_2 + HCl \longrightarrow Mg(OH)Cl + H_2O$$

(iv) **Mixed Salts** : Mixed salts contain more than one acid or basic radicals. Examples of mixed salts are sodium potassium sulphate $NaKSO_4$ calcium chloro hypochlorite CaClOCl and sodium potassium tartrate (Rochelle salt).

(v) **Double Salts** : Double salts are formed by the union of two simple salts. When equimolar quantities of iron (II) sulphate and ammonium sulphate are dissolved in water and the solution crystallised, then crystals of the double salt, namely, iron (II) ammonium sulphate separate out.

$$FeSO_4\,(NH_4)_2\,SO_4 \cdot 6H_2O$$

In solution this double salt answers the tests for iron (II) ion, ammonium ion and sulphate. Alums are familiar examples of double salts.

Potash alum $K_2SO_4Al_2\,(SO_4)_3 \cdot 24H_2O$

Ferric alum $(NH_4)_2\,SO_4 \cdot Fe_2\,(SO_4)_3 \cdot 24\,H_2O$

(vi) **Complex Salts** : A complex salt resembles a double salt in composition but in solution it behaves in a different way. When dissolved in water a complex salt gives one simple and one complex ion. Examples of complex salts are

Potassium ferrocyanide $K_4\,[Fe\,CN_6]$

Sodium argentocyanide $Na\,[Ag(CN)_2]$

When dissolved in water, potassium ferrocyanide gives potassium ions and ferrocyanide ions. But the solution does not answer the test for iron, since iron, is present as ferrocyanide which is a complex ion.

OXIDATION AND REDUCTION

Oxidation

Magnesium burns in oxygen to form magnesium oxide.

$$2Mg + O_2 \longrightarrow 2\,MgO$$

Similarly sulphur, hydrogen, carbon and copper combine with oxygen as represented by the chemical equations

$$S + O_2 \longrightarrow SO_2 \uparrow$$
$$2H_2 + O_2 \longrightarrow 2H_2O$$
$$C + O_2 \longrightarrow CO_2$$
$$2Cu + O_2 \longrightarrow 2\,CuO$$

We say that these elements have all undergone oxidation in a limited sense, oxidation means addition of oxygen to a substance either element or compound.

Oxygen belongs to a class of elements which are non-metallic or electro-negative. Therefore the term oxidation is extended not only to reactions involving oxygen alone but also to reactions involving other electro-negative elements like chlorine, bromine etc. For example

$$2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$$
$$SnCl_2 + Cl_2 \longrightarrow SnCl_4$$

Therefore addition of any electro-negative element to a substance is also oxidation.

When copper is heated with concentrated sulphuric acid the products are copper sulphate, sulphur dioxide and water. In this reaction copper is oxidised to copper sulphate by the addition of the electro-negative radical, sulphate radical.

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2 \uparrow$$

Similarly concentrated nitric acid oxidises iron (II) sulphate to iron (III) sulphate.

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO \uparrow$$

Therefore addition of any electro-negative radical is also oxidation.

In the laboratory chlorine is prepared by heating a mixture of manganese dioxide and concentrated hydrochloric acid. In this reaction manganese dioxide takes away hydrogen from hydrochloric acid and oxidises it to chlorine.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2 \uparrow$$

Another example for the removal of hydrogen is

$$H_2S + Cl_2 \longrightarrow 2HCl + S \downarrow$$

Removal of hydrogen from a compound is also considered as oxidation.

Hydrogen is an electro-positive element. Therefore removal of any other electro-positive element or radical from a compound is also oxidation. For example chlorine oxidises potassium iodide to iodine by the removal of the electro-positive element potassium.

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

In general, oxidation is a chemical change which involves the addition of oxygen or any other electro-negative element or radical to a substance or the removal of hydrogen or any other electro-positive element or radical from a substance.

Reduction

Reduction is the opposite of oxidation. Hydrogen and chlorine combine in the presence of sunlight to form hydrogen chloride. In this reaction hydrogen is added to chlorine. We say that chlorine is reduced to hydrogen chloride.

$$H_2 + Cl_2 \longrightarrow 2HCl$$

Similarly hydrogen sulphide reduces chlorine to hydrogen chloride. In a limited sense, reduction means the addition of hydrogen to an element or compound.

The reaction between sodium and chlorine may be written as

$$2Na + Cl_2 \longrightarrow 2NaCl$$

In this case the electro-positive element sodium is added to chlorine.

Therefore reduction involves the addition of any electro-positive element or radical to a substance.

When hydrogen is passed over heated copper (II) oxide, the oxide loses oxygen and is reduced to copper.

$$CuO + H_2 \longrightarrow H_2O + Cu$$

Reduction is a chemical change which involves the removal of oxygen from a compound.

Hydrogen sulphide reduces iron (III) chloride to iron (II) chloride. In this reaction the electro-negative element chlorine is removed from iron (III) chloride.

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S\downarrow$$

Similarly nascent hydrogen reduces iron (III) sulphate to iron (II) sulphate. This reaction involves the removal of the electro-negative radical, sulphate.

$$Fe_2(SO_4)_3 + 2[H] \longrightarrow 2FeSO_4 + H_2SO_4$$

Reduction also involves the removal of any electro-negative element or radical from a compound.

In general, reduction is a chemical change which involves the addition of hydrogen or any other electro-positive element or radical to a substance or the removal of oxygen or any other electro-negative element or radical from a substance.

The process of oxidation and reduction always go hand in hand. In the reaction.

$$H_2S + Cl_2 \longrightarrow 2HCl + S\downarrow$$

Chlorine is the oxidising agent and hydrogen sulphide is the reducing agent. Chlorine oxidises hydrogen sulphide to sulphur getting itself reduced to hydrogen chloride. The oxidising agent is reduced and the reducing agent is oxidised. Similarly in the reaction.

$$CuO + CO \longrightarrow Cu + CO_2 \uparrow$$

Copper (II) oxide oxidises carbon monoxide to carbon dioxide getting itself reduced to copper. The reducing agent carbonmonoxide gets oxidised to carbon dioxide. Examples of oxidising agents are potassium permanganate, potassium dichromate, chlorine, manganese dioxide etc. Examples of reducing agents are hydrogen sulphide, sulphur dioxide, hydrogen, iron (II) sulphate etc.

Electronic Theory of Oxidation and Reduction

When iron (II) ion is transformed into iron (III) ion, one electron is lost in the reaction.

$$Fe^{+2} \longrightarrow Fe^{+3} + e^-$$

Similarly the transformation of a neutral atom to a positive ion is accompanied by the loss of electrons. For example

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

The electrons are represented by the symbol e^- and the symbol e^- is written on the right hand side of the equation in all these cases. While writing the equation, the total charge on the two sides of the equation should be equal.

Therefore **oxidation is a chemical change in which electrons are lost by an atom or ion.**

When iron (III) ion is reduced to iron (II) ion, the reaction is accompanied by the gain of one electron.

$$Fe^{+3} + e^- \longrightarrow Fe^{+2}$$

Similarly the transformation of neutral element to an anion is accompanied by the gain of electrons and is classified as reduction. For example,

$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$

Reduction is a chemical change in which electrons are gained by an atom or ion.

Oxidation and reduction always occur simultaneously and the total number of electrons lost in the oxidation reaction must be equal to the total number of electrons gained in reduction.

For example, iron (II) chloride is oxidised by chlorine to iron (III) chloride.

$$2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$$

$$Fe^{+2} \longrightarrow Fe^{+3} + e^-$$

$$Cl + e^- \longrightarrow Cl^-$$

The oxidising agent chlorine accepts one electrons and gets reduced to chloride ion. The reducing agent Fe^{+2} loses one electron and is oxidised to iron (III) ion. In an oxidation reduction reaction, the oxidising agent accepts electrons and gets reduced while the reducing agent adds electrons to the oxidising agent and thereby gets oxidised.

OXIDATION NUMBER

It is not possible to find out whether a substance is undergoing oxidation or reduction from the ionic charge alone. For example, manganese dioxide reacts with hydrochloric acid as represented by the equation.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2 \uparrow$$

In this reaction the neutral substance MnO_2 is converted into Mn^{2+} that is manganese (II) ion. In spite of this reaction, we infer that MnO_2 is reduced to manganese (II) salt since chloride ion is oxidised to neutral chlorine. The concept of oxidation state or oxidation number enables us to find out quickly the state of oxidation or reduction of certain atoms in compounds such as manganese dioxide. Oxidation state or oxidation number of an atom in a compound is the arbitrary electrical charge assigned. to that atom according to a prescribed set of rules. The oxidation state is not the same as formal charge.

Determination of oxidation number

The determination of oxidation number of an element can be effected by bearing the following points in mind :

1. In ionic binary compounds, the oxidation number is equal to the charge on the ion. For example, in barium chloride, barium possesses a charge of + 2. Therefore its oxidation number is + 2. Each chloride ion possesses a charge of — 1 and an oxidation number of — 1.

2. (i) *In the case of covalent compounds, the following* method is adopted to find out the oxidation state of an element. When two atoms of the same element are involved in bond formation one bonding electron is assigned to each *of the two atoms. For example, in hydrogen molecule, each* hydrogen atom is assigned one electron. A hydrogen with one electron is the same as free hydrogen atom. Thus the oxidation state is zero. Thus the oxidation state of free *and uncombined element is zero.*

(ii) If the atoms involved in a bond formation are different, both the electrons are arbitrarily assigned to the atom having *greater electro-negativity. Therefore the* oxidation number of one atom will be positive and the oxidation number of the more electro-negative element will be negative. For example, in hydrogen chloride the oxidation number of hydrogen *is + 1 and that of chlorine is — 1.*

(iii) The oxidation number of hydrogen in its compounds is usually + 1, except in the case of metallic hydrides where it is — 1.

(iv) The oxidation number of oxygen in compounds is usually — 2 except in peroxides where it is — 1.

3. (i) The algebraic sum of the oxidation numbers of all atoms in a compound is equal to zero. For example, in KNO_3 the algebraic sum of the oxidation numbers of constituent elements will be $+ 1 + 5 - 6 = 0$.

(ii) The algebraic sum of the oxidation numbers of all atoms in an ion is equal to the charge of the ion. For example, the charge of sulphate ion is -2. i.e.,

SO_4^{2-}

$+6-8=-2.$

Calculation of the oxidation number of an element in a compound can be illustrated with the following examples.

1. Calculation of the oxidation number of sulphur in sulphuric acid (H_2SO_4)

Let the oxidation number of sulphur be x.

The oxidation number of hydrogen $= +1$

The oxidation number of oxygen $= -2$

$\therefore 2 \times (+1) + x + 4 \times (-2) = 0$

$2 + x - 8 = 0$

$x = 8 - 2 = 6$

Oxidation number of sulphur $= +6$.

2. Calculation of oxidation number of sulphur in sulphurous acid (H_2SO_3)

Let the oxidation number of sulphur be x

Then $+2 + x - 6 = 0$

$x = 6 - 2 = 4$

Oxidation number of sulphur $= +4$

3. Calculation of the oxidation number of phosphorus in phosphate ion (PO_4^{3-})

Let the oxidation number of phosphorus be x.

$+x + 4 \times (-2) = -3$

$+x - 8 = -3$

$x = -3 + 8 = +5$

Oxidation number of phosphorus in phosphate ion $= +5$.

4. Calculation of the oxidation number of Mn in (i) $KMnO_4$, (ii) K_2MnO_4 and (iii) MnO_2

(i) $KMnO_4$

Let the oxidation number of Mn be x.

Oxidation number of potassium $= +1$

Oxidation number of each oxygen atom $= -2$

Oxidation number of four oxygen atoms $= -8$

Since the algebraic sum of the oxidation numbers is zero

$$+1 + x - 8 = 0$$
$$x = +8 - 1$$
$$x = +7$$

Oxidation number of Mn in $KMnO_4$ is + 7.

(ii) K_2MnO_4

$$+2 + x - 8 = 0$$
$$x = 8 - 2 = 6$$

Oxidation number of Mn in K_2MnO_4 is + 6.

(iii) MnO_2

$$x - 4 = 0$$
$$x = 4$$

Oxidation number of Mn in MnO_2 is + 4

Variable oxidation Numbers

Many elements have only one oxidation state in addition to zero for the uncombined atom. Some elements have several oxidation numbers depending upon the compounds formed by them.

For example

The oxidation number of Mn in $KMnO_4$ is + 7

The oxidation number of Mn in K_2MnO_4 is + 6

The oxidation number of Mn in MnO_2 is + 4

The oxidation number of S in H_2SO_4 is +6

The oxidation number of S in H_2SO_3 is + 4

Problem

Determine the oxidation numbe. of chromium in (i) potassium dichromate (ii) potassium chromate.

(i) $K_2Cr_2O_7$

Oxidation number of potassium $= +1$

Oxidation number of each oxygen atom $= -2$

Oxidation number of 7 oxygen atoms $= -14$

Let the oxidation number of chromium be x

Oxidation number of two chromium atoms $= 2x$

Since the sum of the positive and negative oxidation numbers is zero

$$+2 + 2x - 14 = 0$$

$$2x = 14 - 2$$

$$x = \frac{12}{2}$$

$$x = 6$$

Oxidation number of Cr in $K_2Cr_2O_7$ is $+6$.

(ii) K_2CrO_4

Let the oxidation number of chromium be x.

Oxidation number of potassium $= +1$

Oxidation number of oxygen $= -2$

$$+2 + x - 8 = 0$$

$$x = 8 - 2$$

$$x = +6$$

Oxidation number of Cr in K_2CrO_4 is $+6$.

Definition of oxidation and reduction in the light of oxidation numbers : In the oxidation of potassium manganate (K_2MnO_4) to potassium permanganate ($KMnO_4$), the oxidation state of manganese is changed from $+6$ to $+7$ In the oxidation of chromium (III) chloride ($CrCl_3$) to potassium dichromate, the oxidation state of chromium is changed from $+3$ to $+6$. In the oxidation of zinc to zinc ion (Zn^{++}), the oxidation number of zinc changes from zero to + 2. Thus in the light of the theory of oxidation states we can say that the increase of oxidation number is oxidation.

In the reduction of manganese dioxide to manganese (II) ion (manganous salts) the oxidation state of manganese is changed from +4 to +2. In the reduction of iron (III) chloride to iron (II) chloride, the oxidation number of iron is decreased from +3 to +2. In the reduction of chlorine to chloride ion the oxidation number of chlorine changes from zero to—1. Therefore reduction involves the decrease of oxidation number.

IONIC EQUATIONS

The reaction between a solution of iron (III) chloride and in (II) chloride may be represented by the equation.

$$2FeCl_3 + SnCl_3 \longrightarrow 2FeCl_2 + SnCl_4$$

This equation is known as the "stoichiometric" or molecular equation. The same reaction may be represented by another equation taking into account the ionisation of these electrolytes.

$$2Fe^{+3} + 6Cl^- + Sn^{+2} + 2Cl^- \longrightarrow 2Fe^{+2} + 4Cl^- + Sn^{+4} + 4Cl^-$$

Cancelling the common terms.

$$2Fe^{+3} + Sn^{+2} \longrightarrow 2Fe^{+2} + Sn^{+4}$$

This is called an "ionic equation". This equation is simpler than the stoichiometric equation. The ions which are common on both sides of the equation such as 8 Cl^- are not really involved in the reaction and are therefore cancelled.

Similarly the neutralisation reaction between sodium hydroxide and hydrochloric acid is given by the stoichiometric equation

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

Taking into account the ionisation of these electrolytes, the equation may be written as

$$Na^+ + OH^- + H^+ + Cl^- \longrightarrow Na^+ + Cl^- + H_2O$$

Cancelling out the common terms

$$H^+ + OH^- \longrightarrow H_2O$$

This is the ionic equation for the neutralisation of sodium hydroxide by hydrochloric acid.

Ionic equation is an equation which indicates the actual particles taking part in a chemical reaction. All the ions which are not taking part in the reaction are excluded.

The undermentioned points are to be remembered in writing ionic notation for equations :

(1) The formulae of compounds or ions that have true chemical existence like MnO_2, H_2 etc., are written in the equations.

(2) Ionic substances are written in the ionic form only if the ions remain separated in the reaction medium. Insoluble substances are written in the molecular form.

(3) Partially ionised substances are written in the ionic form only if the extent of ionisation is appreciable. Water is written only in the molecular form.

Equivalent weights of acids, bases, salts, oxidising agents and reducing agents

Equivalent weight of an acid : We have already studied that all acids contain one or more replaceable hydrogen atoms. The number of replaceable hydrogen atoms present in a molecule of the acid is referred to as its basicity. Suppose the basicity of an acid is *n*. Then one gram mole of the acid will contain $n \times 1{\cdot}008$ grams by weight of replaceable hydrogen atoms.

Therefore the number of parts by weight of the acid which contains 1·008 gms. by weight of replaceable hydrogen atom will be

$$\frac{\text{Molecular weight of the acid}}{\text{Basicity of the acid}}$$

This value represents the equivalent weight of the acid. Thus equivalent weight of an acid is the number of parts by weight of the acid which contains 1·008 gms. by weight of replaceable hydrogen atoms.

e.g. Hydrochloric acid contains one replaceable hydrogen atom.

Hence its equivalent weight is the same as the molecular weight. The basicity of sulphuric acid is 2.

$$\therefore \text{Equivalent weight of sulphuric acid} = \frac{\text{Its molecular weight}}{2}$$

$$= \frac{98}{2} = 49$$

In the case of phosphoric acid (H_3PO_4) the equivalent weight is $\frac{1}{3}$ of its molecular weight, since the basicity of of phosphoric acid is 3. In general

$$\text{Equivalent weight of an acid} = \frac{\text{Molecular weight of the acid}}{\text{Basicity}}$$

Oxalic acid contains two replaceable hydrogen atoms.

$$\left.\begin{array}{r}\text{Equivalent weight of crystalline oxalic acid} \\ \text{i.e. } (COOH)_2 .\ 2H_2O\end{array}\right\} = \frac{126}{2} = 63.$$

Equivalent weight of a base : The equivalent weight of a base is the number of parts by weight of the base which contains one replaceable hydroxyl ion or which completely neutralises one gram equivalent of an acid. The number of hydroxyl groups present in one molecule of a base is known as the **acidity of the base.** Sodium hydroxide, potassium hydroxide, ammonium hydroxide are examples of monoacidic bases. Calcium hydroxide is a diacidic base.

$$\text{Equivalent weight of sodium hydroxide} = \frac{40}{1} = 40$$

In general equivalent weight of a base

$$= \frac{\text{Molecular weight of the base}}{\text{Acidity of the base}}$$

One gram-equivalent of hydrochloric acid completely neutralises 40 parts by weight of sodium hydroxide

∴ Equivalent weight of sodium hydroxide is 40.

The equivalent weight of sodium carbonate can be calculated as follows.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2\uparrow$$

2 equivalents of hydrochloric acid completely react with 106 parts by weight of sodium carbonate.

$$\therefore \text{Equivalent weight of sodium carbonate} = \frac{106}{2} = 53$$

Equivalent weight of a salt : In the case of a salt like sodium chloride, the salt is formed by the neutralisation of one equivalent of an acid by a base.

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

Therefore the equivalent weight of the salt is equal to its molecular weight. In the case of sodium sulphate the salt is formed according to the equation.

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

∴ Equivalent weight of sodium sulphate

$$= \frac{\text{Its molecular weight}}{2}$$

Equivalent weight of a salt is the number of parts by weight of the salt that is produced by the neutralisation of one equivalent of an acid by a base.

Equivalent weight of an oxidising agent : The equivalent weight of an oxidising agent is the number of parts by weight of it which can furnish 8 parts by weight of oxygen for oxidation either, directly or indirectly. For example, the equivalent weight of potassium permanganate may be calculated as follows.

In acid medium potassium permanganatereacts as follows :

$$\underset{316}{2KMnO_4} + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + \underset{80}{5[O]}$$

80 parts by weight of oxygen are made available by 316 parts by weight of potassium permanganate.

∴ 8 parts by weight of oxygen will be furnished by $\frac{316}{80} \times 8 = 31{\cdot}6$ parts by weight of potassium permanganate.

∴ Equivalent weight of potassium permanganate = 31·6

Similarly the equivalent weight of potassium dichromate is calculated from the equation

$$\underset{294}{K_2Cr_2O_7} + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + \underset{48}{3[O]}$$

48 parts by weight of oxygen are furnished for oxidation by 294 parts by weight of potassium dichromate.

8 parts by weight of oxygen will be furnished by $\frac{294}{48} \times 8 = 49$ parts by weight of potassium dichromate.

∴ Equivalent weight of potassium dichromate = 49

Equivalent weight of a reducing agent . The equivalent weight of a reducing agent is the number of parts by weight of the reducing agent which is completely oxidised by 8 parts by weight of oxygen or with one equivalent of any oxidising agent.

In acid medium, iron (II) sulphate is oxidised to iron (III) sulphate according to the equation.

$$\underset{2\times152}{2FeSO_4} + H_2SO_4 + \underset{16}{[O]} \longrightarrow Fe_2(SO_4)_3 + H_2O$$

2 × 152 parts by weight of iron (II) sulphate are oxidised by 16 parts by weight of oxygen.

∴ 8 parts by weight of oxygen will oxidise 152 parts by weight of iron (II) sulphate.

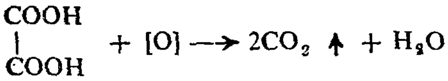
The equivalent weight of iron (II) sulphate (anhydrous) is equal to 152.

The equivalent weight of crystalline iron (II) sulphate $FeSO_4 \cdot 7H_2O$ is given by 152 + 126 = 278.

126 is the weight corresponding to 7 moles of water.

The equivalent weight of oxalic acid can be calculated as follows.

In acid medium oxalic acid is oxidised according to the equation.



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} + [O] \longrightarrow 2CO_2 \uparrow + H_2O$$

16 parts by weight of oxygen will oxidise 90 parts by weight of anhydrous oxalic acid.

∴ 8 parts by weight of oxygen will oxidise 45 parts by weight of anhydrous oxalic acid.

Equivalent weight of anhydrous oxalic acid is 45.

But equivalent weight of crystalline oxalic acid $= \frac{126}{2} = 63$.

126 is the molecular weight of $(COOH)_2 \cdot 2H_2O$

Electronic concept : Since oxidation involves **loss of** electrons and reduction **gain** of electrons, the equivalent weight of an oxidising or reducing agent is defined as the number of parts by weight of the oxidising or reducing agent associated with the gain or loss of one electron respectively, for that particular reaction.

For example mercury (II) chloride oxidises tin (II) chloride to tin (IV) chloride getting itself reduced to mercury.

$$HgCl_2 + SnCl_2 \longrightarrow SnCl_4 + Hg$$

Sn^{+2} is oxidised to Sn^{+4} by the loss of two electrons.

$$Sn^{+2} \longrightarrow Sn^{+4} + 2e^-$$

∴ Equivalent weight of tin (II) chloride

$$= \frac{\text{Its molecular weight}}{2}$$

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

Similarly equivalent weight of mercury (II) chloride

$$= \frac{\text{Its molecular weight}}{2};$$

Variable equivalent weight

A given oxidising or reducing agent can have more than one equivalent weight depending on the reaction studied. For example, permanganate ion is reduced to manganese (II) ion in acid solution. In this reaction one mole of permanganate loses five electrons.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$$

Equivalent weight of MnO_4

$$= \frac{\text{Weight of one mole of } MnO_4^-}{5}$$

In strongly alkaline solution it is reduced as follows

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$$

Equivalent weight of MnO_4^-

$$= \frac{\text{Weight of one mole of } MnO_4^- \text{ ions.}}{1}$$

VOLUMETRIC ANALYSIS

There are two major methods of analysis of substances. They are (i) qualitative analysis (ii) quantitative analysis. Qualitative analysis deals with the analysis of the quality or chemical nature of the substance determining the acid and basic radicals. Quantitative analysis enables us to find out the quantity or exact amount of a substance present in a given sample. Again quantitative analysis may be either gravimetric analysis or volumetric analysis. In gravimetric analysis, the quantity of the substance is determined by methods which make use of direct weighing.

Volumetric analysis, as the name implies, is concerned with the analysis of the volume of one of the reacting solutions in various types of reactions such as neutralisation or acid base reactions, oxidation reduction reactions, precipitation reactions etc. The amount of the substance present in the given volume of the solution is then calculated.

Standard solution: Consider a solution of sodium hydroxide containing 4 grams of sodium hydroxide dissolved in 1 litre of the solution. The strength of such a solution is specified. Therefore it is a standard solution. A solution of known strength is called a standard solution. The strength of a solution is usually expressed in terms of a factor known as normality.

Normality: The normality of a solution is the number of equivalents of a substance contained in one litre of a solution. Consider a solute for example, sodium hydroxide. The equivalent weight of sodium hydroxide is 40.

If 40 g of sodium hydroxide is dissolved in one litre of its solution, it is said to be a normal solution of sodium hydroxide and is denoted by the letter N. If 4 g of sodium hydroxide is present in one litre of its solution, the strength of the solution is $\frac{N}{10}$. It is referred to as a decinormal solution. Similarly a centinormal solution of sodium hydroxide contains 0·4 g of sodium hydroxide dissolved in one litre of the solution. The equivalent weight of hydrochloric acid is equal to its molecular weight and is equal to 36·5. The equivalent weight of sulphuric acid is 49. Thus 36·5 gm hydrochloric acid dissolved in one litre of the solution gives a normal solution of hydrochloric acid. If 49 grams of sulphuric acid are present in one litre of the solution, we get a normal solution of sulphuric acid.

Relationship between the normality of the solution and the weight of the solute present in 1 litre of the solution: We already studied that one litre of normal solution of sodium hydroxide contains 40 g of sodium hydroxide

$$40 \times 1 = 40$$

In the above equation, the equivalent weight of sodium hydroxide is expressed as 40. The normality of the solution is denoted as 1. 4 g of sodium hydroxide is contained in 1 litre of 0·1 or $\frac{N}{10}$ solution of sodium hydroxide.

$$\therefore 40 \times 0{\cdot}1 = 4$$

The equivalent weight of sodium hydroxide = 40

Normality of the solution = 0·1

Similarly 1 litre of 0·01N or $\frac{N}{100}$ solution of sodium hydroxide contains 0·4 g of sodium hydroxide.

$$40 \times 0{\cdot}01 = 0{\cdot}4$$

Here the normality of the solution is 0·01.

1 litre of $\frac{N}{2}$ or 0·5 N solution of sodium hydroxide contains 20 grams of sodium hydroxide.

$$40 \times 0{\cdot}5 = 20.$$

In this case, the normality of the solution is 0·5N.

In general, we can say that the weight per litre of a solution is the product of the equivalent weight and the normality. i.e.

Equivalent weight × Normality = Weight per litre.

PRINCIPLE INVOLVED IN VOLUMETRIC ANALYSIS

Consider the neutralisation reaction between hydrochloric acid and sodium hydroxide.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

Thus one equivalent of hydrochloric acid (36·5g) completely neutralises 1 equivalent (40g) of sodium hydroxide. 1g equivalent hydrochloric acid i.e. 36·5 g of hydrochloric acid is present in 1 litre of N solution of the acid. Similarly one equivalent of sodium hydroxide i.e. 40 gram of sodium hydroxide are present in 1 litre of N solution of sodium hydroxide. Therefore 1 litre of N solution of hydrochloric acid and 1 litre of N solution of sodium hydroxide will completely interact. If we start with 100 cm^3 of N solution of hydrochloric acid, this solution will require 100 cm^3 of N solution of sodium hydroxide for complete neutralisation. Similarly 20 cm^3 of 0·5N solution of sodium hydroxide will completely neutralise 20 cm^3 of 0·5N solution of hydrochloric acid. From the above examples, it is clear that **equal volumes of equinormal solutions interact.**

This statement is known as the **law of volumetric analysis.** If the normalities of the two solutions are different, the interacting volumes will also be different. If the normality of the acid is less than that of the base, the volume of the acid required for neutralisation will be more than the volume of the base. Consider the analogy of the strengths of milk and decoction in the preparation of coffee. If the milk is very dilute, then more milk is required for a certain volume of decoction to get the coffee colour. If the milk is concentrated then the volume of milk needed for the same volume of decoction for the appearance of coffee colour will be less.

If the volume of the acid is represented as V_1, the normality of the acid as N_1, volume of base as V_2, the normality of the base as N_2, then from the law of volumetric analysis it follows that

$$V_1 \times N_1 = V_2 \times N_2$$

Knowing any three quantities, the fourth one can readily be calculated using the above expression.

Titration

The experimental procedure made use of in volumetric analysis is known as **titration**. Indicators are often used to find out end point of a titration.

Indicators : An **indicator** is a substance which indicates the end point of a particular course of reaction by possessing two different colours in the two solutions, or coloured in one solution and colourless in the other. Depending upon the type of reaction studied, the indicators are classified as neutralisation indicators, redox indicators (oxidation reduction indicators) etc.

Two common indicators are made use of in neutralisation titrations. They are (i) phenolphthalein (ii) methyl orange. Phenolphthalein is used as an indicator in the titration of hydrochloric acid against sodium hydroxide, and also in the titration of oxalic acid against sodium hydroxide. In general phenolphthalein is used in the titration of a strong acid or weak acid against a strong base. Phenolphthalein is **pink** in alkaline solution and **colourless** in acid solution. Methyl orange is used as an indicator in the titration of a strong acid against a strong base or weak base. Methyl orange is used in the titration of hydrochloric acid against a solution of sodium carbonate. Methyl orange is **yellow** in basic solution and **pink** in acidic solution.

In oxidation-reduction titrations, for example, in the titration of acidified oxalic acid against potassium permanganate solution or acidified iron (II) sulphate solution against a solution of potassium permanganate, the permanganate itself acts as the indicator. Hot acidified oxalic acid decolourises potassium permanganate. When the entire quantity of oxalic acid has been completely reacted upon in this way the addition of the next drops of permanganate gives a permanent pale pink colour to the solution. This indicates the end point of the titration. Similarly potassium permanganate itself acts as the indicator in the titration of acidified iron (II) sulphate solution against a solution of potassium permanganate. The solution turns pale pink at the end point.

Titration : Experimental procedure

Suppose we want to estimate the weight of sulphuric acid present in 500 cm^3 of the given solution using a standard sodium hydroxide solution. The following experimental procedure may be made use of. The normality of the sulphuric acid solution is first determined.

A standard solution of sodium hydroxide is taken and 20 cm^3 of it is pipetted out into a previously well cleaned conical flask and a drop of phenolphthalein indicator is added to it. The solution turns pale pink in colour. A burette is washed with tap water, then with distilled water and rinsed with a small quantity of the sulphuric acid. The burette is then filled with the acid making sure that the nozzle portion of the burette is also filled with the acid and there are no air bubbles. The initial reading of the burette is noted. The reading corresponding to the lower meniscus must be taken in the case of all colourless solutions. In the case of all coloured solutions the reading corresponding to the upper meniscus is noted. The burette is then clamped vertically. The conical flask containing 20 cm^3 of the alkali and a drop of the indicator is placed over a white procelain tile kept underneath the burette. The acid is then added slowly into the conical flask. The contents of the conical flask are shaken thoroughly after each addition of acid. Care is taken to see the colour change in the conical flask, for when the pink colour just disappears the end point is reached. The burette reading is carefully noted when the solution in the conical flask just turns colourless. The experiment is repeated to concordant values and the titre values are carefully tabulated as follows :

Serial number	Volume of sodium hydroxide solution	Initial burette reading	Final burette reading	Volume of sulphuric acid
1.	20 cm^3			
2.	20 cm^3			
3.	20 cm^3			

Calculations : If V_1 is the volume of sodium hydroxide solution, V_2 the volume of sulphuric acid, N_1 the normality of sodium hydroxide solution and N_2 the normality of sulphuric acid, then from the law of volumetric analysis

$$V_1N_1 = V_2N_2$$

Knowing V_1, N_1 and V_2 the normality of sulphuric acid (N_2) may be calculated.

Weight per litre = Normality × Equivalent weight.

The equivalent weight of sulphuric acid = 49.

Weight per litre of sulphuric acid = normality of the acid × 49.

Weight of sulphuric acid in 500 cm^3 of the solution

$$= \frac{\text{Weight per litre}}{2}$$

Problem (1) : Calculate the equivalent weight of phosphoric acid assuming complete reaction with sodium hydroxide.

Phosphoric acid reacts with sodium hydroxide

$$H_3PO_4 + 3\,NaOH \rightarrow Na_3PO_4 + 3H_2O.$$

Thus phosphoric acid contains 3 replaceable hydrogen atoms per molecule. Its basicity is 3.

$$\text{Equivalent weight of an acid} = \frac{\text{Molecular weight of the acid}}{\text{Basicity}}$$

$$\therefore \text{Equivalent weight of phosphoric acid} = \frac{98}{3} = 32{\cdot}67.$$

Problem (2) : Calculate the equivalent weight of barium hydroxide. Barium hydroxide reacts with acids as shown by the equation

$$Ba(OH)_2 + 2HCl \longrightarrow BaCl_2 + 2H_2O$$

One mole of barium hydroxide requires two equivalents of hydrochloric acid for complete neutralisation. Hence one equivalent of hydrochloric acid will neutralise completely a quantity equal to

$$\frac{\text{Molecular weight of barium hydroxide}}{2}$$

∴ Equivalent weight of barium hydroxide

$$= \frac{\text{Its molecular weight}}{2}$$

$$= \frac{171{\cdot}36}{2}$$

$$= 85{\cdot}68.$$

Problem (3) : Calculate the equivalent weight of sodium bicarbonate.

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2 \uparrow$$

One equivalent of hydrochloric acid reacts with one mole of sodium bicarbonate. Hence equivalent weight of sodium bicarbonate is equal to its molecular weight.

∴ Equivalent weight of sodium bicarbonate = 84.

Problem (4) : Calculate the equivalent weight of the oxidising agent (manganese dioxide) in the following reaction :

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$$

$$\left.\begin{array}{r}\text{Equivalent weight of the}\\ \text{oxidising agent}\end{array}\right\} = \frac{\text{Its molecular weight}}{\text{Number of electrons gained}}$$

$$\therefore \left.\begin{array}{r}\text{Equivalent weight of}\\ \text{manganese dioxide}\end{array}\right\} = \frac{86{\cdot}94}{2} = 43{\cdot}47.$$

Problem (5) : Calculate the equivalent weight of the reducing agent hydrogen sulphide in the following reaction :

$$H_2S + Cl_2 \longrightarrow 2HCl + S\downarrow$$

Two equivalents of chlorine completely oxidise one mole of hydrogen sulphide. Hence the amount of hydrogen sulphide which is fully oxidised by one equivalent of chlorine

$$= \frac{\text{Molecular weight of hydrogen sulphide}}{2}$$

∴ Equivalent weight of hydrogen sulphide

$$= \frac{\text{Its molecular weight}}{2}$$

$$= \frac{34}{2} = 17.$$

Problem (6) : If 250 cm^3 of a solution of sulphuric acid contains 0·6125 g of the acid, calculate the normality of the acid.

Weight of sulphuric acid in 250 cm^3 = 0·6125 g.

Weight of sulphuric acid in 1 litre or $1000 cm^3$

$$= \frac{0 \cdot 6125 \times 1000}{250}$$

$$= 2 \cdot 45 \text{ g}$$

Weight per litre = Normality × Equivalent weight

Equivalent weight of sulphuric acid = 49.

$$\therefore \left.\begin{matrix}\text{Normality of}\\ \text{sulphuric acid}\end{matrix}\right\} = \frac{\text{Weight per litre}}{\text{Equivalent weight}} = \frac{2 \cdot 45}{49} = 0 \cdot 05.$$

Problem (7) : Calculate the weight of potassium dichromate required to prepare 250 cm^3 of 0·1N potassium dichromate solution

Weight per litre = Equivalent weight × Normality.

$$\text{Weight per litre of potassium dichromate} = 49 \times 0 \cdot 1$$
$$= 4 \cdot 9 \text{ g.}$$

Weight of potassium dichromate in 250 cm^3 of the solution

$$= \frac{4 \cdot 9}{1000} \times 250$$

$$= 1 \cdot 225 \text{ g.}$$

$$\left.\begin{matrix}\text{Weight of potassium dichromate needed}\\ \text{to prepare 250 cm}^3\text{ of 0·1 N solution}\end{matrix}\right\} = 1 \cdot 225 \text{ g.}$$

Problem (8) : What is the normality of

(i) a 1 molar solution of sulphuric acid ?

(ii) a 1 molar solution of phosphoric acid ?

$$\text{Normality} = \text{Molarity} \times \frac{\text{Molecular weight}}{\text{Equivalent weight}}$$

(i) Normality of sulphuric acid $= 1 \times \frac{98}{49} = 2.$

$\therefore$ 2N solution of sulphuric acid = 1 M solution of the acid

$\therefore$ $1\ M-H_2SO_4 \equiv 2N-H_2SO_4$

(ii) Normality of phosphoric acid $= 1 \times \frac{98}{32 \cdot 67} = 3$

(since molecular weight of phosphoric acid $= 98$
and equivalent weight of phosphoric acid $= 32 \cdot 67$)

∴ 3N solution of phosphoric acid = 1 M solution of the acid

∴ $1\ M - H_3PO_4 \equiv 3N - H_3PO_4$.

Problem (9) : Calculate the equivalent weight of an acid if 0·1110 g of the acid completely neutralises 18·5 cm^3 of 0·1 M sodium hydroxide solution.

0·1 M sodium hydroxide = 0·1 N sodium hydroxide

(since the equivalent weight of sodium hydroxide = its molecular weight)

From the law of volumetric analysis,

18·5 cm^3 of 0·1 N sodium hydroxide will neutralise 18·5 cm^3 of 0·1 N acid.

18·5 cm^3 of 0·1 N solution of the acid contains 0·111 g of the acid.

∴ 1000 cm^3 of 1 N solution of the acid will contain

$$\frac{0 \cdot 1110 \times 1000 \times 1}{18 \cdot 5 \times 0 \cdot 1} = 60$$

∴ Equivalent weight of the acid = 60.

Problem (10) : 25 cm^3 of a solution of potassium permanganate containing 3·16 g of potassium permangante per litre of the solution oxidises 20 cm^3 of a solution of iron (II) sulphate. Calculate the weight of crystalline iron (II) sulphate in 500 cm^3 of the solution.

$$\left.\begin{array}{r}\text{Weight of potassium permanganate}\\ \text{per litre of the solution}\end{array}\right\} = 3 \cdot 16 \text{ g.}$$

$$\text{Normality of the solution} = \frac{\text{Weight per litre}}{\text{Equivalent weight}}$$

$$= \frac{3 \cdot 16}{31 \cdot 6} = 0 \cdot 1$$

$$V_1N_1 = V_2N_2$$

Volume of potassium permanganate $= V_1 = 25 \text{ cm}^3$

Normality of potassium permanganate $= N_1 = 0{\cdot}1$

Volume of iron (II) sulphate $= V_2 = 20 \text{ cm}^3$

Normality of iron (II) sulphate $(N_2) = \frac{V_1 N_1}{V_2}$

$$= \frac{25 \times 0{\cdot}1}{20}$$

$$= 0{\cdot}125 \text{ N}$$

Weight per litre of crystalline iron (II) sulphate $= 0{\cdot}125 \times 278$

$= 34.74$ g.

(Equivalent weight of crystalline iron (II) sulphate = 278).

Weight of crystalline iron (II) sulphate in 500 cm^3 of the solution $= \frac{34{\cdot}74}{2} = 17{\cdot}37$ g.

QUESTIONS

1. Give an account of Lewis' Theory of Acids and Bases.
2. What are strong and weak acids? Give one example of each type.
3. Give a brief account of the electronic concept of oxidation and reduction.
4. What are the different types of salts? Give one example for each type.
5. Determine the oxidation state of the elements other than hydrogen and oxygen in the following compounds:

   (a) Fe_2O_3 (b) HNO_3 (c) $Ca(OH)_2$ (d) MnO_2
   (e) $Cr(OH)_3$ (f) $K_2Cr_2O_7$
6. Write balanced ionic equations to represent the following reactions :

   (a) $Cu + HNO_3$ (conc) →
   (b) $H_2C_2O_4 + KMnO_4 + H_2SO_4$ →

(c) $I_2 + HNO_3 \rightarrow$
(d) $MnO_2 + HCl \rightarrow$
(e) $H_2S + SO_2 \rightarrow$
(f) $CuSO_4 + Fe \rightarrow$
(g) $FeCl_3 + H_2S \rightarrow$
(h) $BaCl_2 + H_2SO_4 \rightarrow$

7. Calculate the weight of sodium carbonate required to prepare 500 cm^3 of 0·5 N solution.

(Ans : 13·25 g)

8. Calculate the volume of 0·05 N iron (II) sulphate solution which will be completely oxidised by 25 cm^3 of 0·02 N potassium permanganate solution.

(Ans : 10 cm^3)

9. Calculate the equivalent weight of an acid if 1·22 g of the acid requires exactly 0·4 g of sodium hydroxide for neutralisation.

(Ans : 122)

10. 2 g of a monobasic acid is made upto 250 cm^3 in a standard flask. 25 cm^3 of this solution neutralises completely 20 cm^3 of 0·1 N sodium hydroxide. Calculate the molecular weight of the acid.

(Ans : 100)

11. Calculate the equivalent weight of (a) HNO_3 (the oxidising agent) and (b) $FeSO_4$ (reducing agent) in the following reaction. [Unbalanced equation is given.]

$$FeSO_4 + HNO_3 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + NO + H_2O$$

[Ans : (a) 21 (b) 151·9]

12. **Complete the following :—**

(i) Oxidation involves ——— of electrons.

(ii) Reduction involves ——— of electrons.

(iii) During oxidation - reduction reaction the oxidising agent ——— electrons and the reducing agent ——— electrons.

(iv) The oxidation number of sulphur in sodium thio sulphate is ———.

(v) The indicator used commonly in the standardisation of hydrochloric acid against sodium carbonate is ———.

(vi) Atoms in elemental form possess an oxidation number of ———.

(vii) In oxygen compounds, the oxidation number of oxygen is usually ———.

(viii) The oxidation number of hydrogen in magnesium hydride is ———.

(ix) If the oxidation number of manganese is + 6 in manganate ion, the charge on the manganate ion is ———.

(x) An acid is a proton ———.

(xi) A base is an electron ———.

(xii) $\left.\begin{array}{r}\text{Molecular weight}\\ \text{of an acid}\end{array}\right\} = \left.\begin{array}{r}\text{Equivalent weight}\\ \text{of the acid}\end{array}\right\} \times$ —

(xiii) $\left.\begin{array}{l}\text{The sum of the positive and negative}\\ \text{oxidation numbers in a compound is}\end{array}\right\} =$ ——.

(xiv) An acid and a base react to give —— and ——.

(xv) Alums are examples of ——— salts.

CHAPTER VI

GASEOUS STATE

Characteristics of Gases

1. Gases possess neither a definite shape nor a definite volume of their own.

2. Gases possess the characteristic property of diffusion.

3. Gases possess a comparatively low density.

4. Gases exert a pressure on the surface in contact with them and this pressure is the same in all directions.

5. Gases expand when their temperature is raised at a constant pressure.

6. A gas has to be cooled below a certain temperature known as **critical temperature** before it can be liquefied by the application of pressure.

Gas Laws

At sufficiently low pressures and high temperatures, all gases have been found to obey three simple laws. These laws relate the volume of a gas to the pressure and temperature. A gas which obeys these laws is called an **ideal gas or perfect gas.** These laws are therefore called the **ideals gas laws.** These laws are applicable to gases which do not undergo change in chemical complexity when the temperature or pressure is varied.

(i) **Boyle's law:** When the temperature is kept constant, the volume of a given mass of gas varies inversely with the pressure to which the gas is subjected.

If the temperature T is constant.

$$p \propto \frac{1}{V}$$

or $$PV = \text{constant}$$

If V_1 is the volume of the gas at temperature T_1 and pressure P_1 and V_2 the volume of the gas at the same temperature T_2 and pressure P_2, then according to Boyle's law

$$P_1V_1 = P_2V_2$$

$$\therefore V_2 = \frac{P_1V_1}{P_2}$$

This equation is used to determine the change in volume produced as a result of alteration in pressure at constant temperature.

(ii) **Charle's Law I:** At constant pressure the volume of a given mass of gas varies directly with the absolute temperature.

When the pressure P is constant

$$V \propto T$$

or $$\frac{V}{T} = \text{constant} \qquad (1)$$

(iii) **Charles's Law II:** At constant volume, the pressure of a given mass of gas varies directly with the absolute temperature.

When V is constant

$$P \propto T$$

or $$\frac{P}{T} = \text{constant} \qquad (2)$$

Equations (1) and (2) represent the mathematical expressions of Charles's law.

The Absolute Scale of temperature (Kelvin Scale of Temperature)

This scale of temperature is based on another statement of Charles's law according to which 'at constant pressure the volume of a given mass of gas changes by $\frac{1}{273}$ of its volume at 0°C for every rise or fall in temperature by 1°C.'

If the volume of the gas at 0°C is V_0 and its volume at 1°C is V_1 then according to Charles's law

$$V = V_0 + \frac{V_0}{273}$$

$$V = V_0\left(1 + \frac{1}{273}\right)$$

If V_t is the volume at t°C, then

$$V_t = V_0 + \frac{V_0 t}{273}$$

$$= V_0\left(1 + \frac{t}{273}\right)$$

If t = –273°C, then the volume at –273°C is given by

$$V_{-273} = V_0\left(1 + \frac{-273}{273}\right)$$

$$= V_0\left(\frac{273-273}{273}\right)$$

$$= 0$$

The hypothetical temperature of –273°C at which a gas will have zero volume is known as '**Absolute Zero**'.

– 273°C = 0 Kelvin.

This temperature is not attainable. The scale of temperature built up with absolute zero as the zero of the scale is known as the **absolute scale of temperature or Kelvin scale of temperature**. The temperature on the centigrade scale may be converted into the Kelvin scale by adding 273 to it.

t°C = (273 + t) K.

Standard temperature and pressure

Standard temperature and pressure denote a temperature of 273 K and normal atmospheric pressure namely $1{\cdot}013 \times 10^5$ Nm^{-2}. Since both the volume and density of any gas are affected by changes of temperature and pressure, it is customary to reduce all gas volumes to standard conditions for purpose of comparison.

Gas Equation

From Boyle's law at constant temperature

$$P \propto \frac{1}{V}$$

From Charles's law, when the volume of a given mass of gas is constant

$$P \propto T$$

Hence when both volume and temperature vary

$$P \propto \frac{T}{V}$$

$$\text{or } PV \propto T$$

If R represents the constant of proportionality

$$PV = RT$$

This equation is known as the **gas equation**. The value of **R** calculated by considering one mole of an ideal gas under standard conditions is applicable to all gases. R is then known as the **universal gas contant**. Generally the gas equation is written as

$$PV = nRT$$

where R = Molar gas constant
n = Number of moles of the gas

The number of moles **n** can be replaced by m/M.

$$\text{i.e. } n = \frac{m}{M} = \frac{\text{The weight of the gas in kg}}{\text{Molecular weight of the gas in kg}}$$

$$\therefore PV = \frac{m}{M} RT \qquad \dots \quad (3)$$

Gas equation and absolute density of a gas

The density of a gas ρ at standard temperature and pressure is written as

$$\rho = \frac{m}{V} \text{ kg m}^{-3}$$

$$\therefore \quad m = \rho V$$

Substituting this value of m in equation (3)

$$PV = \frac{\rho V}{M} RT$$

$$\therefore \rho = \frac{PVM}{VRT} = \frac{PM}{RT}$$

From this relationship the density of a gas at standard temperature and pressure can be evaluated directly.

Value of gas constant in different units

The numerical value of ' R ', the gas constant, depends upon the unit in which the pressure and volume are expressed.

(1) Value of R in S.I. unit

When the standard temperature is expressed in Newtons per square metre, standard temperature in Kelvin, molar volume in cubic metres, the value of R in S.I. unit is 8·314 J $mole^{-1}K^{-1}$

$$P = 1{\cdot}013\times 10^{5}\ Nm^{-2}\ ;\ V = 2{\cdot}24\times 10^{-2}\ m^{3}\ ;\ T = 273\ K$$

$$R = \frac{PV}{nT} = \frac{1{\cdot}013 \times 10^{5}\ Nm^{-2} \times 2{\cdot}24 \times 10^{-2}\ m^{3}}{1\ mole \times 273\ K}$$

$$= 8{\cdot}314\ Nm\ mol^{-1}\ K^{-1}$$

$$= 8{\cdot}314\ J\ mol^{-1}\ K^{-1}$$

= **8·314 Joules per mole per Kelvin**

(2) Value of R in Calories

1 caloric $\doteq$ 4·184 Joules

So the value of R in calories is

$$R = \frac{8{\cdot}314}{4{\cdot}184}$$

= **1·987 calorie.**

(3) Value of R in litre-atmosphere

When the pressure is expressed in atmospheres (P=1 atm.) the volume is expressed in litres or dm^2 (V=22·4*l*) temperature in Kelvin (T=273K) and n in moles (n = 1 mole) then the value of gas constant R is given by

$$R = \frac{PV}{nT} = \frac{1\ atm. \times 22{\cdot}4\ l}{1\ mole \times 273K} = 0{\cdot}0821\ lit.atm\ mol^{-1}K^{-1}$$

$$= \mathbf{0{\cdot}0821\ dm^{3}\ atm.\ K^{-1}\ mol^{-1}}$$

Dalton's Law of partial pressures

Consider a gas, say hydrogen collected by the displacement of water. The observed pressure of a gas collected over water is equal to the sum of the pressure of the dry gas and the pressure of water vapour. Hence, the pressure of the dry gas is equal to the observed pressure of the moist gas minus the pressure of water vapour (aqueous tension) at the temperature of the experiment. Consider a mixture of three gases A, B and C enclosed in a given volume at a certain temperature, Let p_1, p_2 and p_3 be the individual pressures exerted by A, B and C respectively, in the given mixture at this temperature. Let P be the total pressure exerted by the mixture of gases. Then

$$p = p_1 + p_2 + p_3$$

p_1, p_2 and p_3 are refered to as the partial pressure of A, B and C respectively. The partial pressure of a gas is the pressure exerted by that gas if present alone in the given volume at the same temperature. The relationship between the total pressure of a mixture of gases and the partial pressures of the component gases was deduced by John Dalton in 1801 in the form of a law known as Dalton's law of partial pressures. This law may be stated as follows : ‘ At a constant temperature, the total pressure exerted by a mixture of non-reacting gases is equal to the sum of the partial pressure of each component gas of the mixture.’

Thus the total pressure P of a mixture of r gases may be represented mathematically as

$$P_t = \sum_{i=1}^{r} p_i$$

where p_i is the partial pressure of component i in the mixture. If P and the molar composition of the mixture are known, p_i can be calculated using the expression,

$$pi = xiP$$

where x_i is the mole fraction of component i and is given by

$$x_i = \frac{n_i}{n}$$

where n_i the number of moles of component i and n is the total number of moles present in the mixture.

Graham's Law of Diffusion

If a small amount of a gas A is added to one end of a closed cylinder containing another gas B, gas A will distribute itself uniformly or diffuse throughout the cylinder in a short time. Different gases have different rates of diffusion. Thus diffusion is the tendency of any gaseous substance to distribute itself uniformly through out the available space. The simplest experiment known is an effusion experiment in which the gas is allowed to escape through small holes into an evacuated space. The term effusion is used for the movement of a gas through a small hole. From a study of the rates of diffusion of several gases. **T. Graham** put forward the generalisation known as Graham's law of diffusion.

Statement : "The rates of diffusion (or effusion) of two different gases under similar conditions of temperature and pressure are inversely proportional to the square root of their densities"

If the rates of diffusion of two gases A and B are r_1 and r_2, and their absolute densities ρ_1 and ρ_2 then, according to Graham's law

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

Thus gases possessing low densities diffuse readily. Since the density of a gas is dependent on its molecular weight, it follows that the rates of diffusion should be inversely proportional to the square root of the molecular weights.

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Where M_1 and M_2 represent the molecular weights of the two gases. From this equation the molecular weight of a gas can be determined from a knowledge of the rate of diffusion.

Problem (1) : What will be the pressure required to reduce 600 m^3 of a dry gas at standard pressure to exactly half its volume at the same temperature ?

$$P_1 V_1 = P_2 V_2$$

$$P_1 = 1{\cdot}013 \times 10^5 \text{ Nm}^{-2}$$

$$V_1 = 600 \text{ m}^3$$

$$P_2 = ?$$

$$V_2 = 300 \text{ m}^3$$

$$\therefore P_2 = \frac{1.013 \times 10^5 \times 600}{300} = 2.026 \times 10^5 \text{ Nm}^{-2}$$

$$\text{Pressure} = 2.026 \times 10^5 \text{ Nm}^{-2}$$

Problem (2) : What volume will 10m^3 of nitrogen measured at 285 K occupy at 309 K assume constant pressure ?

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

Since pressure is constant,

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

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

$$= \frac{10 \times 309}{285} = 10{\cdot}8 \text{ m}^3$$

$$\text{Volume} = 10.8 \text{ m}^3$$

Problem (3) : The rates of diffusion of carbon dioxide and ozone were found to be 0·29 and 0·276 respectively. The relative density of carbon dioxide is 22. What is the relative density of ozone ?

According to Graham's law of diffusion

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

$$r_1 = 0{\cdot}29$$

$$r_2 = 0{\cdot}276$$

$$d_1 = 22$$

$$d_2 = ?$$

$$\frac{0{\cdot}29}{0{\cdot}276} = \sqrt{\frac{d_2}{22}}$$

$$\sqrt{d_2} = \frac{0{\cdot}29}{0{\cdot}276} \times \sqrt{22}$$

$$= 4{\cdot}928$$

$$\therefore \quad d_2 = 24{\cdot}29$$

The relative density of ozone = 24·29

KINETIC THEORY OF GASES

The kinetic theory of gases has been put forward to explain the general behaviour of gases. This theory has developed and from the ideas of **D. Bernouilli, J. J. Waterson, K. A. Kronig** and **R. Clausius.** The present mathematical form of this theory is due to **J.C. Maxwell** and **L. Boltzmann.** This theory is obeyed by ideal gases.

The kinetic theory of gases is based on the following postulates :—

Postulates of Kinetic Molecular Theory of gases

(1) A gas consists of particles called molecules. All the molecules of the same gas are identical. But the molecules of any two gases differ in mass, size etc.

(2) The actual volume of the molecules is small and negligible relative to the volume of the container.

(3) The molecules are in random motion and have no mutual attractions.

(4) The molecules move about freely in all directions. They travel in straight lines and collide with one another and with the walls of the container. These collisons are perfectly elastic which means conservation of energy and momentum.

(5) The pressure of a gas is due to the bombardment of the molecules on the walls of the container.

(6) The average kinetic energy of the molecules is proportional to the absolute temperature.

Kinetic equation for gases : Based on the above postulates, it is possible to derive a mathematical expression of the kinetic theory of gases. Consider a gas enclosed in a cubical vessel of length 1 metre. Let the number of molecules of the gas in the cube be 'n' and let the mass of each molecule be 'm' kg. The molecules are moving in all possible directions and at any moment the velocity of the molecules can be resolved into three components u, v and w in three directions x, y and z parallel to the three edges of the cube so that

$$c^2 = u^2 + v^2 + w^2$$

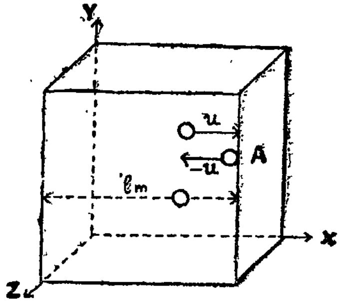


Fig. 36

Since no direction of motion is preferred, it is reasonable to assume that

$$u^2 = v^2 = w^2$$

$$\therefore \quad u^2 = \frac{1}{3}c^2$$

All the molecules are assumed to have the same velocity m s^{-1}. Consider a single molecule moving between the two opposite faces and striking the face A at intervals. The velocity of the molecule before it strikes the face is u ms^{-1} and since the molecule is perfectly elastic it will rebound with the same velocity − u.

Momentum of the molecules before it strikes the face

$= mu$ kg ms $^{-}$

Momentum of the molecule after impact $= -$ mu kg ms^{-1}

Change in momentum $= mu - (-mu)$ kg ms^{-1}

$$\left.\begin{array}{l}\text{Change in momentum for a}\\ \text{single impact per molecule}\end{array}\right\} = 2mu \text{ kg ms}^{-1}$$

$$\left.\begin{array}{l}\text{Change in momentum for a}\\ \text{single impact for n molecules}\end{array}\right\} = 2mnu$$

To hit the same face again the molecule should move to the other face i.e. a distance of $2l$ metre.

The velocity of the molecule $= u$ ms^{-1}

So the number of impacts per second $= \frac{u}{2l}$

$$\left.\begin{array}{l}\text{The total change of momentum for all}\\ \text{the impacts per second for n molecules}\end{array}\right\} = 2mnu \times \frac{u}{2l}$$

$$= \frac{mnu^2}{l} \text{ kg ms}^{-2}$$

But $u^2 = \frac{c^2}{3}$

$\therefore$ Change of momentum $= \frac{1}{3}\frac{mnc^2}{l}$

Since force is defined as rate of change of momentum, the average force acting on face A $= \frac{1}{3}\frac{mnc^2}{l}$ kg ms^{-2}

$$\text{Pressure} = \frac{\text{Force (in Newtons)}}{\text{Area (in sq. metre)}}$$

$$= \frac{1}{3}\frac{mnc^2}{l} \times \frac{1}{l^2}$$

$$= \frac{1}{3}\frac{mnc^2}{l^3} \text{ Nm}^{-2}$$

l^3 is the volume of the cube expressed in metre^3 and is equal to V.

$$\therefore P = \frac{1}{3}\frac{mnc^2}{V}$$

$$\therefore PV = \frac{1}{3} mnc^2$$

This is the fundamental equation of the kinetic theory of gases and is known as the **kinetic equation for gases.**

Kinetic Energy of an ideal gas

From the kinetic molecular theory, it follows that

$$PV = \frac{1}{3} mnc^2$$

If one mole of an ideal gas is considered, **mn** can be replaced by M the molecular weight of the gas.

$$\therefore PV = \frac{1}{3} Mc^2$$

The average kinetic energy for one mole of a gas is given by $\frac{1}{2} mnc^2$ Since $mn = M$

$$\text{kinetic energy} = \frac{1}{2} Mc^2$$

Substituting this value in the equation for PV

$$PV = \frac{2}{3} K.E.$$

(K.E. represents the kinetic energy)

Since $PV = RT$

$$\frac{2}{3} K.E. = RT$$

$$\therefore \text{kinetic energy} = \frac{3RT}{2}$$

Derivation of gas laws from kinetic equation

(1) **Derivation of Boyle's Law:** The kinetic equation of gases is $PV = \frac{1}{3} mnc^2$

According to kinetic theory of gases the average kinetic energy of the molecule is directly proportional to the absolute temperature.

$$\frac{1}{2} mnc^2 \propto T$$

$$\frac{1}{2} mnc^2 = kT$$

where k is the constant of proportionality.

$$PV = \frac{1}{3} mnc^2$$

$$PV = \frac{2}{3} \times \frac{1}{2} mnc^2$$

$$PV = \frac{2}{3} kT$$

(since $\frac{1}{2} mnc^2 = kT$)

Thus the product PV is a constant at constant temperature which is the statement of Boyle's law.

(2) Derivation of Charles's law :

It has been shown already that

$$PV = \tfrac{2}{3}\,kT$$

$$V = \left[\frac{2k}{3P}\right]T$$

Hence at constant pressure $V \propto T$

This is the expression for Charles's law I.

$$P = \left[\frac{2k}{3V}\right]T$$

Hence at constant volume $P \propto T$

This is the expression for Charles's law II.

(3) Derivation of Graham's law of diffusion

From kinetic equation of gases

$$PV = \tfrac{1}{3}\,mnc^2$$

If one mole of an ideal gas is considered, mn can be replaced by M the molecular weight of the gas.

$$PV = \tfrac{1}{3}\,Mc^2$$

$$c^2 = \frac{3PV}{M}$$

Since the density of a gas $\rho = \dfrac{M}{V}$ kg m^{-3}

$$c^2 = \frac{3P}{\rho}$$

$$c = \sqrt{\frac{3P}{\rho}}$$

The rate of diffusion of a gas depends on the velocity of the molecules.

$$r \propto \sqrt{\frac{3P}{\rho}}$$

$$r \propto \sqrt{\frac{1}{\rho}}$$ if P is maintained a constant.

Thus the rate of diffusion of a gas is inversely proportional to the square root of its density, if pressure remains constant. This is the statement of Graham's law of diffusion.

(4) Derivation of Avogadro's Hypothesis

If equal volumes of two gases are considered at the same pressure, then

$$PV = \frac{1}{3} m_1 n_1 c_1^2 \text{ for one gas}$$

For another gas

$$PV = \frac{1}{3} m_2 n_2 c_2^2$$

$$\therefore \frac{1}{3} m_1 n_1 c_1^2 = \frac{1}{3} m_2 n_2 c_2^2 \quad \dots \quad (4)$$

If the temperature of both the gases remains the same then the average kinetic energy per molecule will be same.

$$\therefore \frac{1}{2} m_1 c_1^2 = \frac{1}{2} m_2 c_2^2 \quad \dots \quad (5)$$

Dividing equation (4) by equation (5)

$$\frac{1 \times m_1 n_1 c_1^2 \times 2}{3 \times m_1 c_1^2} = \frac{1 \times m_2 n_2 c_2^2 \times 2}{3 \times m_2 c_2^2}$$

$$\frac{2}{3} n_1 = \frac{2}{3} n_2$$

$$n_1 = n_2$$

Thus equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. This is the statement of Avogadro's hypothesis.

(5) Derivation of Dalton's law of partial pressures

Suppose n_1 molecules of a gas A each of mass m_1 are contained in a vessel of volume V, then the pressure exerted by the gas is

$$P_A = \frac{1}{3} \frac{m_1 n_1 c_1^2}{V}$$

where c_1^2 represents the mean square velocity of gas A. Suppose n_2 molecules each of mass m_2 of another gas B which does not chemically react with A are enclosed in the same vessel at the same temperature, then the pressure exerted by gas B is

$$P_B = \frac{1}{3}\frac{m_2 n_2 c_2^2}{V}$$

c_2^2 indicates the mean square velocity of gas B.

Since both the gases are enclosed in the same vessel at the same temperature the total pressure exerted by the mixture of gases will be $P = \frac{1}{3}\frac{m_1 n_1 c_1^2}{V} + \frac{1}{3}\frac{m_2 n_2 c_2^2}{V}$

$$P = P_A + P_B$$

Similarly if more than two gases are present in the same vessel the total pressure of the mixture of gases will be

$$P = P_A + P_B + P_C + P_D + \ldots\ldots\ldots$$

This is the expression for **Dalton's law of partial pressures** of gases.

Problem

(i) Calculate the average kinetic energy for one mole of an ideal gas at 298 K.

(ii) Calculate the average kinetic energy of a molecule of an ideal gas at 298 K.

(i) Kinetic energy $= \frac{3RT}{2}$

$R = 8{\cdot}314 \text{ J mol}^{-1} \text{ K}^{-1}$

$T = 298 \text{ K}$

$$\text{Kinetic energy} = \frac{3 \times 8{\cdot}314 \times 298}{2}$$

$$= 3{\cdot}716 \times 10^3 \text{J mol}^{-1} \text{ K}^{-1}$$

(ii) Kinetic energy per mole of an ideal gas $= 3{\cdot}716 \times 10^3$J.

$$\left.\begin{matrix}\text{Kinetic energy of a single} \\ \textbf{molecule} \text{ of an ideal gas}\end{matrix}\right\} = \frac{3{\cdot}716 \times 10^3}{\text{Avogadro number}}$$

$$= \frac{3{\cdot}716 \times 10^3}{6{\cdot}023 \times 10^{23}}$$

$$= 6{\cdot}17 \times 10^{-21}\text{J}$$

Kinetic energy for a mole of an ideal gas
$= 3{\cdot}716 \times 10^{3}J$

Kinetic energy of a single molecule of an ideal gas
$= 6{\cdot}17 \times 10^{-21}J$

Distribution of Molecular Velocities

All the molecules in a gas do not have the same velocity, since the molecules are colloiding with one another frequently and hence their velocities keep on changing. The distribution of molecules between different possible velocities was worked out by Maxwell using probability considerations. This led to the formulation of **Maxwell's law** of distribution of molecular velocities. The general form of the distribution of molecular velocities is shown in Fig. 37. The figure indicates the fraction **of molecules having** various velocities.

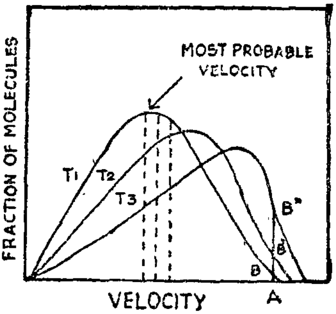


Fig. 37
Distribution of Molecular velocities

From these plots it is clear that the fraction of molecules having velocity equal to zero is very small. Again the fraction of molecules having velocities greater than zero goes on increasing with increase in velocities, reaches a certain maximum value and then begins to fall towards zero again for very high velocities. From the curves it is seen that the fraction of molecules with too low or too high velocities is very small. There is a certain velocity for which the fraction of molecules is maximum. This particular velocity is indicated by the peak of the curve. This velocity is known as the **most probable velocity.**

Effect of temperature on distribution of Molecular Velocities

On increasing the temperature the general shape of the distribution curve remains the same but the maximum of the curve becomes somewhat flat which occurs at a higher velocity. In other words, as the temperature is raised there is a wider distribution of molecular velocities and the fraction of molecules possessing high velocities increases. Let us consider a particular velocity shown by point A. At temperature T_1 the fraction of molecules having velocity A is given by BA in the diagram. At a slightly higher temperature T_2 the fraction of molecules possessing velocity A is given by B'A. At a still higher temperature T_3 the fraction of molecules possessing this velocity A is given by B''A. From the curve it is clear that B''A > B'A > BA. Thus the most probable velocity increases with **rise in temperature.**

Classification of Molecular Velocities: Molecular velocities are classified into

(1) Most probable velocity

(2) Average velocity

(3) Root mean square velocity

(4) Mean square velocity

(1) Most probable velocity: The most probable velocity of a gas is the velocity possessed by maximum number of molecules of the gas at a given temperature. It is represented by the symbol C. The value of most probable velocity is given by the expression.

$$C = \sqrt{\frac{2RT}{M}}$$

The most probable velocity depends upon the molecular weight and the temperature. It is directly proportional to the absolute temperature and inversely proportional to the molecular weight of the gas.

(2) **Average velocity:** The average velocity is the average of the velocities of all the molecules present in the given sample of the gas. In a gas if n_1, n_2, n_3 etc., molecules have velocities c_1, c_2, c_3 etc. respectively, then the average velocity 'v' is given by

$$V = \frac{n_1c_1 + n_2c_2 + n_3c_3 + \ldots\ldots}{n_1 + n_2 + n_3 + \ldots\ldots}$$

$$= \sqrt{\frac{8RT}{\pi M}}$$

(3) **Root mean square velocity (R.M.S. velocity):** The root mean square velocity 'U' is defined as the square root of the average of the squares of the velocities of all the molecules present in the given sample of the gas.

$$U = \sqrt{\frac{n\ c_1^2 + n_2c_2^2 + n_3c_3^2 + \ldots\ldots}{n_1 + n_2 + n_3 + \ldots\ldots}}$$

$$= \sqrt{\frac{3RT}{M}}$$

Derivation :

According to Kinetic theory of gases

$$PV = \tfrac{1}{3}\, mnU^2$$

$$U^2 = \frac{3PV}{mn} = \frac{3PV}{M}$$

where M = mn. (the mass of n molecules of the gas)

If the volume represents molar volume, then M is the molecular weight of the gas. Under these conditions PV = RT Substituting this value of RT

$$U^2 = \frac{3RT}{M}$$

$$U = \sqrt{\frac{3RT}{M}}$$

The root mean square velocity is directly proportional to the square root of the temperature and inversely proportional to the square root of the molecular weight of the gas.

(4) **Mean square velocity :** Mean square velocity is the average of the squares of the velocities of all the molecules present in the given sample of the gas.

$$U^2 = \frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \ldots\ldots\ldots}{n_1 + n_2 + n_3 + \ldots\ldots\ldots}$$

Illustration : Suppose five molecules of a hypothetical gas possess velocities of 1, 2, 2, 3 and 4 units. The most probable velocity is 2. This is the velocity possessed by largest number of molecules. Two molecules out of five possess this velocity.

Most Probable Velocity = 2

$$\text{The average velocity} = \frac{1 + 2 + 2 + 3 + 4}{5} = \frac{12}{5} = 2{\cdot}4$$

Average velocity = 2·4

$$\text{Mean square velocity} = \frac{1+4+4+9+16}{5} = \frac{34}{5} = 6{\cdot}8$$

Mean square velocity = 6·8

Root mean square velocity $= \sqrt{6{\cdot}8} = 2{\cdot}608$

Root mean square velocity = 2·608

Relation between most probable velocity, root mean square velocity and average velocity : From Kinetic theory considerations, the three types of velocities are inter-related. This relationship between the three types of velocities may be derived as follows :—

$$\textbf{Most probable velocity (C)} = \sqrt{\frac{2RT}{M}}$$

$$\textbf{Root mean square velocity (U)} = \sqrt{\frac{3RT}{M}}$$

$$\textbf{Average velocity (V)} = \sqrt{\frac{8RT}{\pi M}}$$

$$\begin{aligned}
C : U : V &= \sqrt{\frac{2RT}{M}} : \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} \\
&= \sqrt{2} : \sqrt{3} : \sqrt{\frac{8}{\pi}} \\
&= 1 : \sqrt{\frac{3}{2}} : \sqrt{\frac{8}{2\pi}} \\
&= 1 : \sqrt{1.5} : \sqrt{1.27} \\
&= 1 : 1.225 : 1.127
\end{aligned}$$

The expression relating root mean square velocity and average velocity is given by

$$U : V = 1{\cdot}225 : 1{\cdot}127$$

$$\text{or } U : V = 1 : 0{\cdot}92$$

Average velocity = Root mean square velocity × 0·92

Problem : Calculate the root mean square velocity and average velocity of hydrogen molecules at 298 K.

$$\text{Root mean square velocity} = \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{\frac{3 \times 8{\cdot}314 \times 298}{2{\cdot}016 \times 10^{-3}}}$$

since $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$M = 2{\cdot}016 \times 10^{-3}$ kg

$T = 298$ K

$\therefore$ Root mean square velocity $= 1{\cdot}92 \times 10^{3} \text{ms}^{-1}$

Average velocity $= 1{\cdot}92 \times 10^{3} \times 0{\cdot}92$

(since average velocity = Root mean square velocity × 0·92)

$\therefore$ **Average velocity = $1{\cdot}766 \times 10^{3} \text{ms}^{-1}$**

EXERCISE

1. Calculate the value of R in joules and $\text{dm}^3 \text{ atm}^{-1} \text{ K}^{-1}$.
2. Assuming an equimolar mixture of nitrogen and helium, how many times faster will helium initially leak through a pinhole in the container. [Ans : 2·646]
3. If a gas occupies $15{\cdot}7 \text{ m}^3$ at 290 K and $1{\cdot}014 \times 10^{5}$ Nm^{-2} pressure what volume would it occupy at 318 K and $1{\cdot}724 \times 10^{5}$ Nm^{-2}. [Ans : 10 m^3]
4. State the postulates of the molecular Kinetic theory.
5. Derive the Kinetic gas equation $PV = \frac{1}{3} mnc^2$.

6. Deduce from the kinetic gas equation the relation between the average kinetic energy of a gas and the absolute temperature.

7. Derive from the kinetic gas equation
   (a) Boyle's law (b) Charles's law
   (c) Avogadro's hypothesis (d) Graham's law of diffusion and (e) Dalton's law of partial pressures

8. From gas laws derive the gas equation.

9. Explain Graham's law of diffusion of gases.

10. Mention an important application of Dalton's law of partial pressures of gases.

11. What is the value of R in litre-atmosphere ?

12. Calculate the ratios of most probable velocity, root mean square velocity and average velocity for an ideal gas.

13. Calculate the (i) root mean square velocity and (ii) most probable velocity of oxygen molecule at 298 K.

[Ans : (i) $4{\cdot}82 \times 10^{2} ms^{-1}$
(ii) $3{\cdot}934 \times 10^{2} ms^{-1}$]

14. Calculate the (i) root mean square velocity and (ii) average velocity of nitrogen molecule at standard temperature and pressure.

[Ans : (i) $4{\cdot}932 \times 10^{2} ms^{-1}$
(ii) $4{\cdot}537 \times 10^{2} ms^{-1}$]

15. Calculate the ratio of the root mean square velocities of neon and argon at 298 K.

[Ans : 1.9811]

CHAPTER VII

DILUTE SOLUTIONS

A solution is regarded as a homogeneous mixture of two or more substances. In connection with solutions two terms are used. They are solute and solvent. The substance which is present in excess in solution is known as **solvent.** The substance which is dissolved by the solvent is known as **solute.**

If a solution is comprised of one solute in a solvent then solution consists of two components. It is known as a **binary solution.** If a solution contains two solutes, it is known as ternary solution and if it contains three solutes, it is known as quaternary solution and so on.

If a solution contains a maximum possible amount of solute at a given temperature it is known as saturated solution at that temperature. On the other hand if it contains less than the maximum, it is an unsaturated solution. If the amount of solute present in a solution is very little, then it is a dilute solution.

The concentration of a solution is the amount of solute present in a given quantity of solution. This can be expressed in several ways :

(1) **Molarity :** This is represented by c. This is the number of moles of solute dissolved in 1 litre of solution.

(2) **Molality :** This is represented by m. This is the number of moles of solute dissolved in 1 kg. of solvent.

(3) **Mole fraction :** This is represented by x. This is the fraction of the number of moles of a particular solute in the total number of moles of all components comprising the solution.

(4) **Normality :** This is the number of gram equivalent of the solute present in a litre of the solution.

Vapour pressure of a liquid

Consider a liquid in a closed container. When it evaporates the molecules which escape from the liquid gradually accumulate in the space above the liquid. These molecules frequently colloide with one another and with the walls of the container. Consequently these molecules exert a pressure which is known as the **vapour pressure** of the liquid.

After, suffering numerous collisions some of the molecules in the vapour phase return to the liquid phase i.e. condense into liquid. Eventually a dynamic equilibrium is established when the number of molecules escaping from the liquid in a given time is equal to the number returning (Fig. 38). At this stage the vapour pressure assumes a constant value known as the saturated vapour pressure.

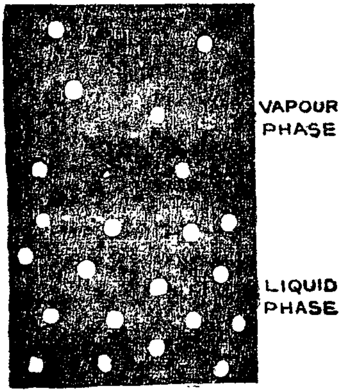


Fig. 38
Dynamic equilibrium between liquid and vapour phase

The saturated vapour pressure is often referred to merely as the vapour pressure of the liquid. This depends on the nature of the liquid and temperature. But this does not depend upon either the quantity or the surface area of the liquid or the volume of the vapour.

Vapour pressure of a solution

The presence of a non-volatile solute in a liquid lowers the vapour pressure of the solvent. This fact is known experimentally for a very long time. This is an important effect. This is explained in terms of the kinetic theory as follows. The molecules of the solute are distributed uniformly throughout the solution. Thus some of the volatile solvent molecules in the surface layer are replaced by non-volatile solute molecules. These solute molecules partially block the escape route of the fast-moving solvent molecules but not the return route of the vapour molecules (Fig. 39). As a result the rate of evaporation is lowered whilst the rate of condensation remains unaltered by the solute. Hence the equilibrium between the evaporation and condensation is altered and is achieved at lower vapour pressure.

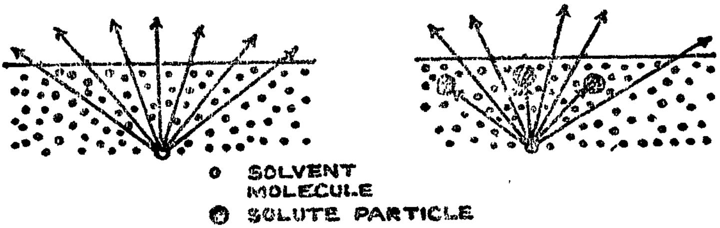


Fig. 39

The effect of solute upon vapour pressure

Vapour pressure lowering

The relationship between the concentration of the non-volatile solute and the lowering of vapour pressure produced by it was experimentally investigated and successfully quantified by **Raoult**. He embodied his results in the following generalization.

"The lowering of the vapour pressure of a solvent by a solute relative to the vapour pressure of the pure solvent is equal to the mole fraction of the solute."

If p_0 and p are the vapour pressures of pure solvent and the solution respectively and n_1 and n_2 are the respective numbers of moles of solvent and solute, the Raoult's law may be expressed in the form.

$$\frac{p_0-p}{p_0} = \frac{n_2}{n_1+n_2} = x_2 \qquad \text{.........(1)}$$

where x_2 is the mole fraction of the solute in solution. The quantity $(p_0-p)/p_0$ is known as the relative lowering of vapour pressure.

Vapour pressure lowering in dilute solutions

In a dilute solution the number of moles of the solute (n_2) is small compared with the number of moles of the solvent. Therefore the Raoult's law expressed by equation (1) can be simplified to

$$\frac{p_0 - p}{p_0} = \frac{n^2}{n_1}$$

If mass m_2 of solute of molecular weight M_2 is dissolved in mass m_2 of solvent of molecular weight M_1, then

$$n_2 = \frac{m_2}{M_2}$$

and

$$n_1 = \frac{m_1}{M_1}$$

Now equation (2) takes the form

$$\frac{p_0 - p}{p_0} = \frac{m_2}{M_2} \times \frac{M_1}{m_1} \qquad \text{.........(3)}$$

Hence if the vapour pressures of the pure solvent (p_0) and solution (p), the mass (m_1) and molecular weight (M_1) of the solvent and the mass of the solute (m_2) dissolved are known the molecular weight of the solute (M_2) can be calculated from equation (3) by rearranging it to

$$M_2 = \frac{m_2 M_1}{m_1} \times \frac{p_0}{(p_0-p)} \qquad \text{.........(4)}$$

Determination of vapour pressure lowering and molecular weight of the solute

The determination of vapour pressure lowering can be effected by a number of methods. Of which the simplest method is due to **Ostwald and Walker**. This method is particularly suitable for aqueous solutions. The apparatus generally used in this method, is shown in (Fig. 40). This consists of two sets of bulbs and one set of 'V' tubes. One set of bulbs is filled with the solution and the other with the pure solvent to half the level. The set of 'V' tubes is filled with calcium chloride (a dehydrating agent).

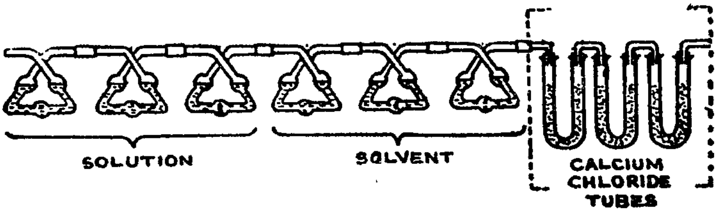


Fig. 40
Apparatus used in the Ostwald and Walker method

In a typical experiment, each one of the first two sets is weighed accurately. Then a stream of pure dry air is passed slowly through the solution and then successively through the solvent and the dehydrating agent for some time. The two sets of bulbs are weighed again. The loss of weight in each set is determined.

When air bubbles through the solution, it becomes saturated with solvent vapours to the vapour pressure (p) of of the solution. Thus the solution bulbs lose solvent. The weight thus lost (w_1) is proportional to the vapour pressure of the solution (p). When the air comes out of the solution bulbs and bubbles through the solvent it becomes further saturated with solvent vapours to the pressure p_o, the vapour pressure of the pure solvent. The weight of the solvent thus lost (w_2) is proportional to $p_o - p$ i.e.

$$w_1 \propto p$$
$$w_2 \propto p_0 - p$$

Hence equation (3) becomes

$$\frac{p_0-p}{p_0}=\frac{w_2}{(w_1+w_2)}=\frac{m_2}{M_2}\times\frac{M_1}{m_1} \quad \ldots\ldots (5)$$

and equation (4) becomes

$$M_2=\frac{m_2M_1}{m_1}\times\frac{(w_1+w_2)}{w_2} \quad \ldots\ldots (6)$$

Thus the determination of molecular weight (M_2) of the solute is possible.

Example 1 : 10 g of a non-volatile solute was dissolved in 100 g of water at 30°C. The vapour pressure was lowered from 17·535 to 17·235 mm. Calculate the molecular weight of the solute.

Solution

$$M_2 = \frac{m_2M_1}{m_1}\times\frac{p_0}{p_0-p}$$

where

M_1 = molecular weight of the solvent = 18
m_1 = mass of the solvent = 100g.
m_2 = mass of the solute = 10g.
p_0 = vapour pressure of the pure solvent = 17·535 mm.
p = vapour pressure of the solution = 17·235.

Hence, the molecular weight of the solute is

$$M_2=\frac{10\times 18}{100}\times\frac{17\cdot535}{17\cdot535-17\cdot235} = 105$$

Example 2 ; A current of dry air was bubbled through a set of bulbs containing 7·31 g of urea in 50 g of water and then through water and finally through a tube containing calcium chloride. The loss in weight of the water bulbs is 0·087 g and the gain in weight of the calcium chloride tube is 2·036 g calculate the molecular weight of urea.

Solution

Loss in weight of solution bulbs $\propto p$
Loss in weight of solvent bulbs = 0·087 g $\propto p_0$
Gain in weight of $CaCl_2$ bulb = 2·036 g $\propto p_0$

Hence,

$$\begin{aligned} M_2 &= \frac{m_2 M_1}{m_1} \times \frac{p_0}{p_0 - p} \\ &= \frac{7{\cdot}31 \times 18}{50} \times \frac{2{\cdot}036}{0{\cdot}087} \\ &= 58{\cdot}9 \end{aligned}$$

Boiling point elevation

The boiling point of a liquid is that temperature at which its vapour pressure is equal to the external pressure. Since the presence of a non-volatile solute lowers the vapour pressure of a solution it follows that the boiling point of a solution must be raised. This is evident from Fig. 41.

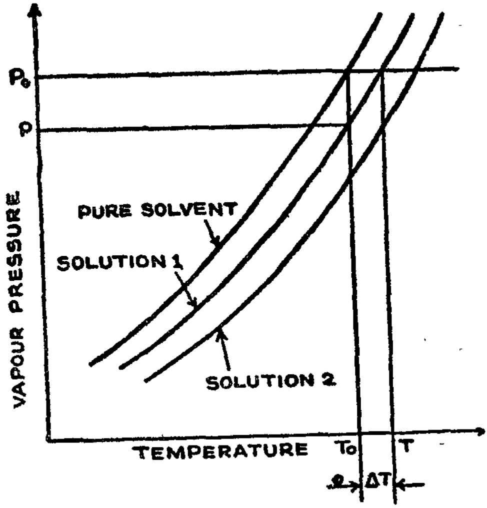


Fig. 41
Elevation of boiling point

The extent by which the boiling point is raised is known as the **elevation of boiling point.** In the case of dilute solutions the extent of the elevation of boiling point is proportional to the lowering of the vapour pressure. This can be seen from Fig. 41 by assuming that the various vapour pressure curves are approximately parallel to each other in the region of the boiling point. If T_0 and T are the boiling points and p_0 and p are vapour pressures of the solvent and solution respectively, then

$$T - T_0 \propto P_0 - p$$

i.e.

$$\Delta T \propto p_0 - p$$

or

$$\Delta T = k\,(p_0 - p) \qquad \text{........ (7)}$$

According to a form (equation 2) of Raoult's law applicable to a dilute solution.

$$\frac{p_0 - p}{p_0} = \frac{n_2}{n_1}$$

or

$$p_0 - p = p_0\left(\frac{n_2}{n_1}\right) \qquad \text{... .... (8)}$$

Substitution of equation (8) in (7) gives

$$\Delta T = k\,p_0\left(\frac{n_2}{n_1}\right)$$

$$= k'\left(\frac{n_2}{n_1}\right) \qquad \text{.........(9)}$$

where k and k' are constants, n_1 is the number of moles of solvent, and n_2 is the number of moles of the solute. If mass m_2 of solute of molecular weight M_2 is dissolved in mass m_1 of solvent of molecular weight M_1, then

$$n_1 = \frac{m_1}{M_1}$$

$$n_2 = \frac{m_2}{M_2}$$

and equation (9) becomes

$$\Delta T = k' \times \frac{m_2}{M_2} \times \frac{M_1}{m_1}$$

$$= k' \times \frac{M_1}{m_1} \times \frac{m_2}{M_2} \qquad \text{.........(10)}$$

For a given quantity of a given solvent M_1 and m_1 are constant. Then equation (10) becomes

$$\Delta T = k'' \frac{m_2}{M_2} \qquad \text{.........(11)}$$

where

$$k'' = k' \frac{M_1}{m_1}$$

If 1 kg of solvent is specified for m_1, then k'' becomes K_b, the molal elevation constant or the ebullioscopic constant and equation (11) becomes

$$\Delta T = K_b \frac{m_2}{M_2} \qquad \text{.........(12)}$$

Now m_2 is the mass of the solute in 1 kg of the solvent. Equation 12 enables us to calculate the molecular weight of the solute from the elevation of boiling point. Thus

$$M_2 = K_b \frac{m_2}{\Delta T} \qquad \text{.........(13)}$$

Example 1 : 2·0 g of a substance dissolved in 125 g of water causes a boiling point elevation of 0·139 K. Given that K_b for 1000 g of water is 0·52 K mol^{-1} kg^{-1} calculate the molecular weight of the substance.

Solution

$$M_2 = K_b \frac{m_2}{\Delta T}$$

where

ΔT = boiling point elevation = 0·139 K

K_b = ebullioscopic constant = 0·52. K mol^{-1} kg^{-1}

m_2 = mass of solute in 1 kg of solvent

= 2 × 8 = 16 g.

M_2 = molecular weight of solute.

$$\therefore M_2 = K_b \frac{m_2}{\Delta T}$$

$$= 0{\cdot}52 \times \frac{16}{0{\cdot}139}$$

$$= 59{\cdot}9$$

Example 2 : If 10 g of a certain non-volatile substance is dissolved in 100 g of benzene the boiling point is raised from 80·2°C to 83·3°C. Given that K_b for 1000 g of benzene is 2·57 K. mol^{-3} kg^{-1} calculate the molecular weight of the substance.

Solution :

Elevation of boiling point $= \Delta T = 83{\cdot}3 - 80{\cdot}2$
$= 3{\cdot}1°C$

Ebullioscopic constant $= 2{\cdot}57$ K. mol^{-1} kg^{-1}

$$\left.\begin{array}{l}\text{Mass of the solute in}\\ \text{1000 g of benzene}\end{array}\right\} = 10 \times \frac{1000}{100} = 100 \text{ g}$$

$$\text{Molecular weight of the solute} = M_2 = K_b \frac{m_2}{\Delta T}$$

$$= 2{\cdot}57 \times \frac{100}{3{\cdot}1}$$

$$= 82{\cdot}9$$

Determination of boiling point elevation

There are three principal experimental methods to determine the elevation of boiling point. They are.

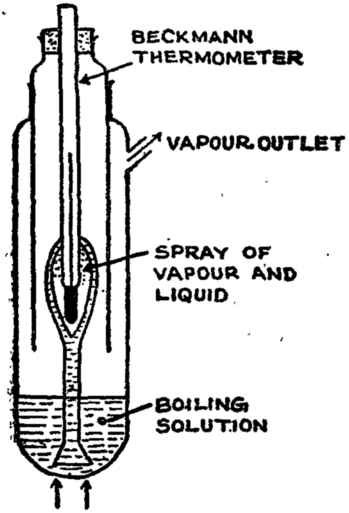


Fig. 42
Cottrell's apparatus

(1) Landsberger's method

(2) Cottrell's method

(3) Beckmann's method.

Of which the Cottrell's method is described here. The apparatus used in this method is shown in Fig 42. It consists of a boiling tube containing the liquid under examination and an inverted funnel tube. The latter arrangement helps to pump the liquid and vapour over the bulb of a **Beckmann's** thermometer.

In a typical experiment a known weight of the solvent (m_1) is placed in the boiling tube and its boiling point T_0 is determined. Then, after sufficient cooling, a weighed amount of the solute (m_2) is added and the boiling point of the solution (T) is determined. From these temperatures, the elevation in boiling point $T - T_0$ is computed.

The thermometer used in this method is Beckmann's thermometer. This was originally devised by Beckmann to record small temperature changes over any select 5 K range. This consists of a large bulb, very thin capillary tube and a reservoir of mercury at the top (Fig. 43). The scale is not calibrated to read the actual temperature but only the difference in the boiling points or freezing points of the pure solvent and solution.

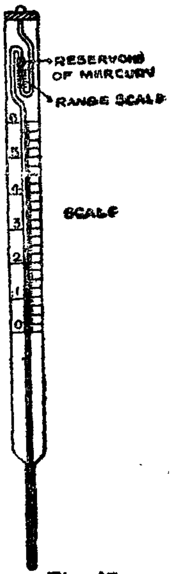


Fig. 43
Beckmann's thermometer

Freezing point depression

The freezing point of a liquid is that temperature at which its vapour pressure is equal

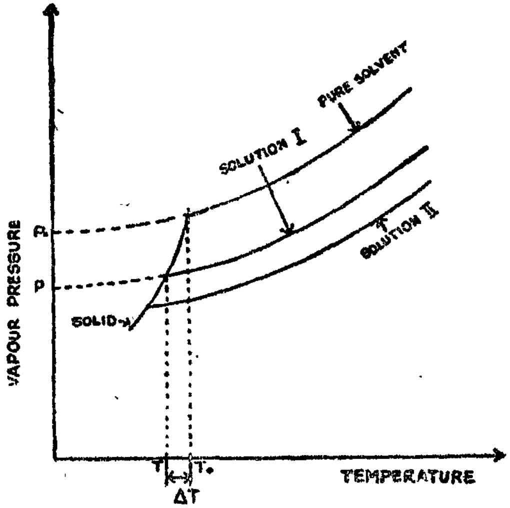


Fig. 44
Depression of the freezing point

to the vapour pressure of the pure solid. Thus, a solution containing a non-volatile solute which has a lower vapour pressure than the pure solvent, freezes at a lower temperature than the pure solvent. This is evident from Fig. 44.

According to the definition of the freezing point, T_0 and T are the freezing points of pure solvent and solution respectively. It is seen that T is less than T_0 and $T_0 - T = \Delta T$ is the depression in freezing point due to the presence of a non-volatile solute. In Fig. 44, P_0 and p mark the vapour pressures of pure solvent and solution respectively at their freezing points. Again, for dilute solutions the extent of the freezing point depression is proportional to the lowering the vapour pressure. This can be seen by assuming that the vapour pressure curves for the solvent and solutions are parallel straight lines in the vicinity of freezing point. Then it follows

$$To - T \propto p_0 - p$$

i.e.

$$\Delta T \propto p_0 - p$$

or

$$\Delta T = k(p_0 - p) \qquad \text{.........(14)}$$

According to equation (2), we know for dilute solutions

$$\frac{p_0 - p}{p_0} = \left(\frac{n_2}{n_1}\right)$$

$$\therefore p_0 - p = p_0 \left(\frac{n_2}{n_1}\right) \qquad \text{........ (15)}$$

Employing this in equation (14), we get

$$\Delta T = k . p_0 \frac{n_2}{n_1}$$

Since p_0 is constant for a given solvent at a given temperature

$$\Delta T = k' \frac{n_2}{n_1} \qquad \text{........ (16)}$$

where n_1 and n_2 are the number of moles of solvent and solute. If m_1 and m_2 are the masses of solvent and solute respectively in solution and if M_1 and M_2 are their respective molecular weights,

$$n_1 = \frac{m_1}{M_1}$$

and

$$n_2 = \frac{m_2}{M_2}$$

Then equation (16) takes the form,

$$\Delta T = k' \times \frac{m_2}{M_2} \times \frac{M_1}{m_1}$$

$$= k' \times \frac{M_1}{m_1} \times \frac{m_2}{M_2} \qquad \text{.........(17)}$$

For a given quantity of a given solvent, m_1 and M_1 are constant. Then equation (17) becomes

$$\Delta T = k'' \frac{m_2}{M_2} \qquad \text{.........(18)}$$

in which

$$k'' = k' \frac{M_1}{m_1}$$

If 1000 g of solvent is specified for m_1 then k'' becomes K_f, the molal depression constant or the cryoscopic constant and equation (18) becomes

$$\Delta T = K_f \frac{m_2}{M_2} \qquad \text{........ (19)}$$

Hence

$$M_2 = k_f \frac{m_2}{\Delta T} \qquad \text{.........(20)}$$

Equation (20) enables us to calculate the molecular weight of the solute from the magnitude of the depression in freezing point caused by it.

Example 1 : 10·0 g of a substance dissolved in 100 g of water lowered the freezing point of water by 1·0°C. Calculate the molecular weight of the substance. The molal depression constant of water is 1·86 K mol^{-1} kg^{-1}

Solution

$$M_2 = K_f \frac{m_2}{\Delta T}$$

where

M_2 = molecular weight of the solute

K = molal depression constant = 1·86 K. mol^{-1} kg^{-1}

m_2 = mass of solute in 1000 g of solvent

$$= \frac{10}{100} \times 1000 = 100 \text{ g}$$

ΔT = freezing point depression = 1·0°C

Therefore

$$M_2 = 1{\cdot}86 \times \frac{100}{1{\cdot}0}$$

$$= 186$$

Example 2 : On dissolving 2·0 g of an organic substance in 100 g of ether the freezing point of ether was lowered by 0·6°C The molal depression constant of ether is 5·12 K mol^{-1} kg^{-1} Calculate the molecular weight of the substance.

Solution

$$M_2 = K_f \frac{m_2}{\Delta T}$$

$$= \frac{5{\cdot}12 \times 20}{0{\cdot}6}$$

$$= 170{\cdot}67$$

Determination of freezing point depression.

Beckmann method described below is the most occurate and convenient method of determining the freezing point depression due to the solute and hence the molecular weight of the solute. The apparatus used in this method is shown in Fig. 45. It consists of a tube (A) fitted with a side arm (D), stirrer and Beckmann thermometer (E). It is surrounded by an air jacket (B) and immersed in a freezing mixture (C) or cooling bath.

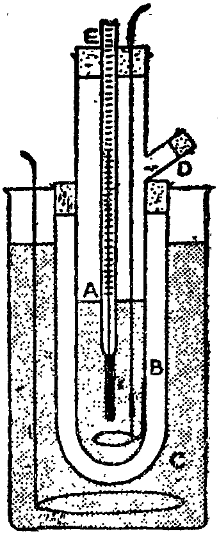


Fig. 45
Beckmann's apparatus

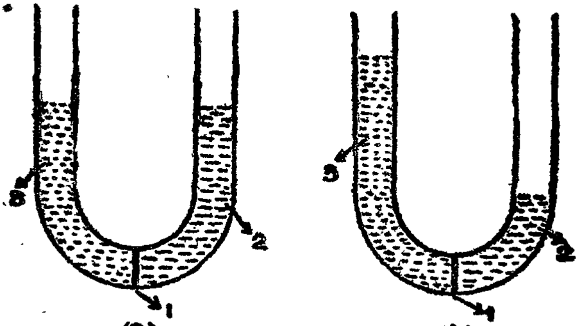
In a typical experiment, a known weight of pure solvent is placed in the tube A. It is cooled with gentle continous stirring. At first the temperature falls below the freezing point of the solvent. But as the solvent begins to freeze, the temperature rises rapidly and finally becomes steady. This temperature (T_0), which is the freezing point of the solvent is noted.

The tube A is then removed from the freezing mixture and warmed slightly to melt the crystals. A weighted amount of solute (preferably in pellet form) is then introduced through the side arm (D) and allowed to dissolve. The freezing point of the solution (T) is then determined in the same way. The difference between the two freezing points i.e. $T_0 - T$ gives the freezing point depression.

Osmosis

Certain materials, including many membranes in biological systems, are **semi-permeable**. These allow some particles to pass through but not others. When a solvent and a solution or two solutions of differing solute concentrations are separated by such semi-permeable membrane, a net flow of solvent from pure solvent to solution or from dilute to stronger solution through the membrane occurs. This phenomenon is known as **osmosis**.

This can be simply demonstrated as follows. Consider two solutions (2, 3) of differing concentrations separated by a semi-permeable membrane (1) as shown in Fig. 46. A net migration of solvent occurs from the right arm to the left arm of the apparatus as if the solutions were trying to equalise their concentrations. Pressure can be applied to the left arm, as shown in Fig. 47 to prevent the osmosis. The pressure required to stop osmosis from pure solvent into solution is known as the osmotic pressure (π) of the solution.



(a) (b)

Fig. 46
Demonstration of osmosis

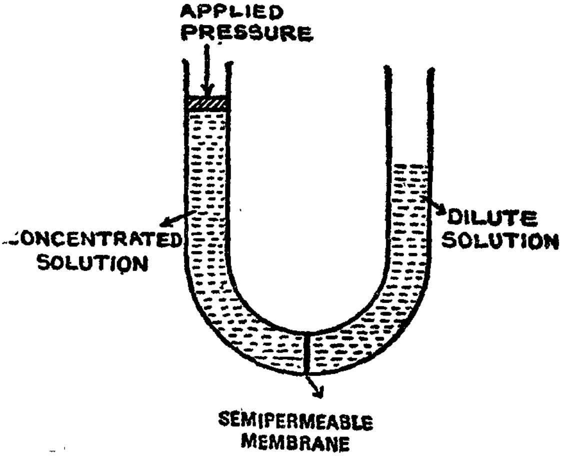


Fig. 47
Demonstration of osmotic pressure

The Laws of Osmosis

W. F. **Pfeffer** in 1877 measured the osmotic pressure (π) of a series of sucrose solutions at different concentrations and temperatures. **J. H. Van't Hoff** in 1886 summarized Pfeffer's results in the following laws :

1. At constant temperature, the osmotic pressure of a solution is proportional to the concentration of the solution i.e.

$$\pi \propto c$$

since the concentration is the reciprocal of the volume (V litres) containing one mole

$$\pi \propto \frac{1}{V}$$

2. For a given concentration the osmotic pressure is proportional to the absolute temperature. i.e

$$\pi \propto T$$

The proportionality between osmotic pressure and reciprocal of the volume resembles Boyle's law and that between osmotic pressure and absolute temperature resembles Charles's law for gases. Combining these two laws of osmasis we get

$$\pi V = k T \qquad \text{.........(21)}$$

where k is a constant. For n moles of solute

$$\pi V = n\,kT \qquad \text{.........(22)}$$

Van't Hoff showed that the term k has the same value for all solutes and is equel to the universal gas constant, R. Consequently, the equation (22) becomes

$$\pi V = n R T \qquad \text{.........(23)}$$

$$\therefore \pi = \frac{nRT}{V} \qquad \text{.........(24)}$$

Example . **10 g of urea (mol. wt. = 60) is dissolved in 1·0 litre of water. Calculate the osmotic pressure of the solution at 20°C.**

Solution

Osmotic pressure of a solution is

$$\pi = \frac{nRT}{V}$$

where

n = number of moles of solute = $\frac{10}{60}$

R = gas constant = 0·082 litre atm. deg^{-1} mole

T = temperature = 20°C = 293 K.

V = volume of the solution = 1·0 litre.

Hence

$$\pi = \frac{\frac{10}{60} \times 0{\cdot}082 \times 293}{1{\cdot}0}$$

$= 4{\cdot}0$ atm.

Determination of osmotic pressure

The osmotic pressure of a solution is determined by Berkeley and Hartley's method. The apparatus used in this method is sown in Fig. 48. This consists of a porous pot carrying a semi-permeable membrane (deposited copper ferrocyanide) surrounded by a steel pot, a piston for the application of pressure and a guage for the measurement of external pressure. The porous pot is fitted on either side with a solvent reservoir and a capillary indicator.

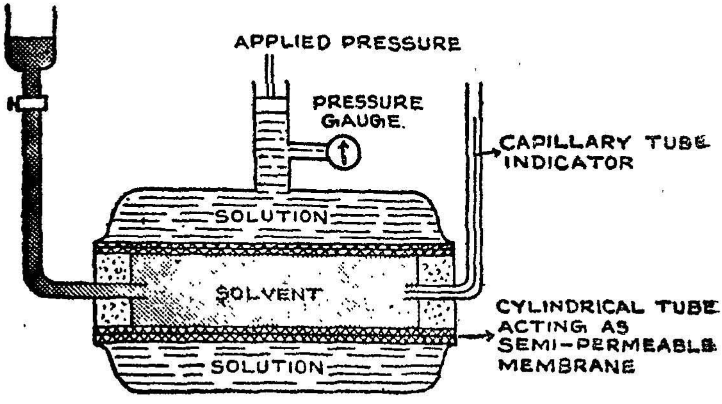


Fig. 48
Berkeley and Hartley's apparatus

In a typical experiment the porous pot is filled with pure solvent and the steel pot with the solution under study. The solvent tends to flow into the solution through the membrane with the result that the level in the indicator moves downwards. External pressure is now applied by moving the piston direct and the level in the indicator is restored. The external pressure is now equal to the osmotic pressure and is read off on the pressure gauge.

Osmotic pressure and molecular weight of solute

We know from equation 23,

$$\pi V = nRT$$

If m is the mass of the solute present in V litres of the solvent and M is the molecular weight of the solute, then

$$\pi V = \frac{m}{M} RT$$

$$\therefore M = \frac{mRT}{\pi V}$$

This enables us to calculate the molecular weight of the solute (M) from the value of the osmotic pressure (π).

Example: A solution of glucose containing 18 g per litre has an osmotic pressure of 2·46 atm. at 27°C Calculate the molecular weight of glucose.

Solution

The molecular weight,

$$M = \frac{mRT}{\pi V}$$

where

M = molecular weight of the solute

m = mass of the solute = 18 g.

R = gas constant = 0·082 litre atm. deg^{-1} mole^{-1}

T = absolute temperature = 300 K

π = osmotic pressure = 2·46 atm.

V = volume of the solution = 1·0 litre.

Therefore

$$M = \frac{18 \times 0{\cdot}082 \times 300}{2{\cdot}46 \times 1{\cdot}0}$$

$$= 180$$

Colligative properties :

In the preceeding sections we have seen that if a non-volatile substance is dissolved in a solvent the vapour pressure is lowered, the boiling point is elevated, the freezing point is depressed, and the phenomenon known as osmotic pressure manifests itself. These four properties are all inter-related. These properties depend in fact upon the number of particles of solute in a given volume of solution and not upon their nature Hence these are known as **colligative properties.**

QUESTIONS

1. What is vapour pressure? What are the factors which affect the vapour pressure ?
2. State Raoult's law for vapour pressure lowering? How is it derived from theoretical considerations ?
3. Describe a method for the determination of molecular weight by the relative lowering of vapour pressure of a pure solvent produced by a non-volatile solute.
4. What is meant by the saturated vapour pressure ?
5. Define the boiling point and freezing point of a liquid.
6. What is the kinetic molecular picture of dissolving of a solid solute in a liquid ?
7. What is a colligative property ? Give examples.
8. Show that Raoult's vapour pressure laws follow from the kinetic molecular theory.
9. Show qualitatively that the lowering of vapour pressure of a solvent due to the addition of a non-volatile solute is related to the elevation of the boiling point of the liquid.

10. Describe how the molecular weight of a dissolved substance may be determined by the ebullioscopic method.

11. Describe the cryoscopic method for the determination of the accurate molecular weight of a substance

12. What is meant by the, cryoscopic constant of a solvent ? How may the depression of the freezing point of a solvent due to the addition of a solute be determined accurately and how may the value be used to calculate the molecular weight ?

13. State the laws of osmotic pressure.

14. How is osmotic pressure measurement used to evaluate the molecular weight of a solute ?

15. What is meant by osmotic pressure of a solution? Explain clearly the analogy between gas pressure and osmotic pressure

16. Write a note on semi-permeable membrane

17. What is the osmotic pressure of a 10% solution of cane sugar at 25°C? Molecular weight of cane sugar is 342.

Section B

INORGANIC CHEMISTRY

CHAPTER 1

PERIODIC TABLE

The origin of the Periodic Table

With the discovery of more and more elements and their compounds, need was felt for having a rational system for classifying the elements. Many attempts were made by chemists to classify the elements into metals and non-metals and as electro-positive and electro-negative elements. But none was satisfactory. In all these systems, an element appeared in more than one group, or elements with only few common properties among them happened to be grouped together

Dobereiner's Triads

Probably the first attempt to correlate the chemical properties with atomic weight was made by Dobereiner in 1829. He showed that when elements with similar properties were arranged in groups of three, for example Li, Na, K and Cl, Br, I, the atomic weight of the middle element was the mean of other two. But, it has only limited application, since all elements could not be fitted into the triad system.

Newland's Law of Octaves

Newlands in 1864 related the properties of elements to the ordinal numbers (first, second, third and so on) of the elements. When they are arranged in the increasing order of the atomic weights, he found that in such a list, elements with similar properties occur at intervals of seven. He called the relationship **the law of octaves.**

1	2	3	4	5	6	7	8	9
Li	Be	B	C	N	O	F	Na	Mg
6·9	9·0	10·8	12·0	14·0	16·0	19·0	23·0	24·3

Mendeleeff's Periodic Table

In 1869, Mendeleeff arranged the then known elements in the increasing order of their atomic weights and formulated the periodic law : "The physical and chemical properties of the elements are periodic functions of their atomic weights."

Mendeleeff left gaps for the elements which had not been discovered by that time. A gap in the Periodic Table means a space for an undiscovered element. With the help of his periodic law, he predicted the properties of elements. He said that these elements existed and will be discovered sometime. He had such a clean picture of the periodicity of properties in his mind that he predicted the properties of the missing elements with great accuracy. Surprisingly when the elements were discovered, their properties remarkably agreed with the predicted ones. Such of these elements were scandium, gallium and germanium.

Name given by Mendeleeff	Name of the element discovered
1 Eka - Boron	Scandium
2. Eka - Aluminium	Gallium
3 Eka - Manganese	Technetium (Synthetic element
4. Dvi - Manganese	Rhenium

Predicted and observed properties of Germanium

Properties	Eka Silicon (predicted by Mendeleeff in 1871)	Germanium, Ge (discovered in 1886 by Winkler)
1. Colour	Dull grey	Greyish white
2 Atomic weight	72	72·3
3 Atomic volume	13	13·2

Properties	Eka Silicon (predicted by Mendeleeff in 1871)	Germanium, Ge (discovered in 1886)
Density	5·5	5·4699
Action of heat in air	White EsO_2	White $Ge\,O_2$
Nature of the oxide	Refractory	Refractory
Physical state of the chloride	Liquid	Liquid

However, Mendeleeff's Table is not without demerits. (1) Elements of higher atomic weights precede those of lower atomic weights (for example : Ar and K, Co and Ni, Te and (I) (2) Dissimilar elements are grouped together (Cu and Na) and chemically similar elements are far apart. So, it is clear that the atomic weight is not the only criterion in deciding the periodicity of the properties of the elements. **Moseley** showed that the atomic number and not the atomic weights is the fundamental property of an element. The periodic law, therefore, is stated as that "the properties of the elements are periodic functions of their atomic numbers." It is creditable that Mendeleeff's Periodic classification does not differ much from the periodic table based on atomic numbers. In the modern periodic table, attempt has been made to correlate the chemical properties with electronic configuration of the elements.

Long form of the Periodic Table

The most popular and simple periodic table is the long form of the periodic table, which is an extended form of Mendeleeff's table. Here the sub-groups of Mendeleeff's table are removed in order to overcome the defects of his table. In the long form of the periodic table, the elements are arranged in the order of increasing atomic number. All elements are placed in horizontal rows called **periods**. The vertical columns in the table are called **groups**. Within the group, chemical similarities are most striking.

← s block → ← d block → ← p block →

IA	IIA	III A	IV A	V A	VI A	VII B	VIII			I B	II B	III B	IV B	V B	VI B	VII B	0
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	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 – 71 * Lanthanides	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 – 103 ** Actinides	104 Ku														

* Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
** Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

Fig. 49
Long form of the Periodic Table

The main features of long table can be summarised as follows :—

1. In this table, there are 18 vertical columns called groups. These are numbered IA, IB, IIA, IIB ... VIIA, VIIB, VIII and O.

2. Some elements i.e. IA, IIA, IIIB, IVB, VB, VIB, VIIB have only their outermost shells incomplete. Each one of their inner shells is complete. These are called **normal elements.**

3. Some other elements i.e. IIIA, IVA, VA, VIA, VIIA, VIII have their outermost as well as the penultimate shell incomplete. These are termed **transition elements.**

4. Elements of group O have all their shells complete. They do not show any reactivity, and so are termed noble gases.

5. Horizontal rows are called periods. There are seven periods in the table .

Ist period : 2 elements (H—He)

2nd and 3rd periods 8 elements each Li — Ne, Na—Ar (Short period)

4th and 5th periods 18 elements each K — Kr and Rb—Xe (Long period)

6th period 32 elements Cs—Rn including rare earth elements (57—71), called **lanthanides**

7th period : 18 elements (incomplete) radioactive, elements with atomic Numbers 93-105 are synthetic elements discovered during atomic research includes actinides 89-103

6. The long periods have been extended to accommodate the transitional elements.

7. The noble gases have been grouped at the extreme right of the table.

8. The *lanthanides* and *the actinides* have been grouped separately and placed at the bottom.

9. VIII group elements shown in three columns have many properties in common.

10. Elements up to atomic number 105 have been discovered. Names of elements up to atomic number 103 are mentioned in the figure.

Element *with Atomic* No. *104 is* Kurchatovium
,, ,, 105 is Hahnium

Advantages of the long form of the periodic table

(1) It reflects the electronic arrangements in atoms. Electrons are successively added with the increase of atomic number. (2) Noble gases with their completely filled up shells are placed at the end of the table. (3) Elements have been placed in groups to which they clearly belong. B is now with Al. C is no more associated with Ti, Zr and Hf. (4) Metallic elements are placed on the left and non-metallic elements on the right side of the periodic table. (5) A diagonal line drawn from B, Si, As, Te roughly separates the metals from metalloids and non-metals. (6) It affords a satisfactory position to group VIII. Earlier, the elements of this group were placed between VII and zero group. In the long form, they occupy proper places with other transition elements.

The long form of the periodic table is also not free from *all defects found in the* Mendeleeffs *table.* (1) The position of hydrogen, lanthanides and actinides is not settled. (2) Elements *with similar chemical properties like* Ba and Pb are separated. (3) There is no place in the periodic table for the isotopes of the elements. (4) It does not reflect the sequence of the filling of electrons in the order of sub-energy levels s, p, d, f.

In spite of this, the long form of the periodic table is preferred to other tables because (1) it correlates the atomic structure of the elements with their position in the periodic table and (2) it reflects similarities, differences and trends in physical and chemical properties more systematically.

Electronic structure

The physical and chemical properties of an element are closely connected with its electronic configurations. The nucleus of an atom contains protons and neutrons. Surrounding the nucleus there are electrons. The electrons are moving round the nucleus in fixed orbits or shells which are named K, L, M, N, O, P in the order of increasing energy (it is also the order of increasing distance from nucleus). The K, L, M, N etc. energy levels are also numbered n = 1, 2, 3, 4 etc. where n is called the **principal quantum number.** The maximum number of electrons that can be present in any given shell is $2n^2$, where n represents the number of orbit or shell. Thus the K shell can have only 2 electrons, the L shell 8 electrons, the M shell 18 electrons, and the N shell 32 electrons.

Each of the energy shells (except the first) is again divided into sub-shells which are designated by the symbols **s, p, d, f.** An **s** sub-shell may contain up to 2 electrons, a **p** sub-shell up to 6 electrons, a **d** sub-shell up to 10 electrons and an **f** shell up to 14 electrons.

An electron in the **p** sub-shell of L is called 2 p electron, 2 being its principal quantum number. A 3 s electron belongs to the s-sub-shell of M. The number of electrons in a given sub-shell is shown by superscript. For example $1s^2$ means that two electrons are present in the s-sub-shell of K. The sub-shells are again divided into orbitals. The s-sub-shell is itself a single orbital. The p-sub-shell contains 3 orbitals, the **d** sub-shell 5 orbitals and the f-sub-shell 7 orbitals. There is an important condition that there cannot be more than 2 electrons in any orbital.

The electrons in an atom in its normal state occupy shells and sub-shells in such a way that the atom has the lowest possible energy.

The energy is seen to increase in the order :

$$
\begin{aligned}
&1s \rightarrow 2s \rightarrow 2p \rightarrow \\
&3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p \rightarrow \\
&5s \rightarrow 4d \rightarrow 5p \rightarrow 6s \rightarrow 4f \rightarrow \\
&5d \rightarrow 6p \rightarrow 7s \rightarrow 5f \rightarrow 6d
\end{aligned}
$$

As we pass from hydrogen to lawrencium the atomic number increases one by one (i.e.) the number of orbital electrons increases by one.

Table below shows the electron distribution in some elements.

Atomic Number	Element n =	K 1 s	L 2 s p	M 3 s p d	N 4 s p d f	O 5 s p d f	P 6 s p d f	Q 7 s
1	H	1						
2	He	2						
3	Li	2	1					
19	K	2	2, 6	2, 6	1			
21	Sc	2	2, 6	2, 6, 1	2			
30	Zn	2	2, 6	2, 6, 10	2			
57	La	2	2, 6	2, 6, 10	2, 6, 10	2, 6, 1	2	

There are four types of elements based on their complete and incomplete electron shells.

Type I. Elements with atoms in which the s-and p-subshells are complete. s level can accommodate not more than 2 electrons and p level not more than 6 electrons. When these levels are complete, the outer shell will have the configuration ns^2 np^6 (where n represents the number of the outermost energy level). Helium has 1s^2 configuration with a complete shell. Noble gases have the general electronic configuration, ns^2 np^6 Because they possess stable electronic configurations, they do not enter into ordinary chemical reactions. They constitute the group zero of the periodic table.

Type II: Elements with atoms in which all but the outer most shell is complete. The electronic configuration in the outermost shells of these atoms varies from ns^1 to ns^2 up^5 They are called normal elements or representative elements. They have been further classified as (a) s-block elements and (b) p block elements.

s block		p block				
IA	IIA	IIIB	IVB	VB	VIB	VIIB
ns^1	ns^2	$ns^2\,np^1$	$ns^2\,np^2$	$ns^2\,np^3$	$ns^2\,np^4$	$ns^2\,np^5$

(a) **s-Block elements** :—Elements of groups IA and IIA have electrons only in their outer s-sub-shell and are termed s-block elements. Each s-block element is a strongly electropositive metal. It gives colourless ions in solution. It exists in the same oxidation state in almost all its compounds.

(b) **p-Block elements** :—Elements of groups IIIB to VIIB come under this group. The last electrons in the atoms of these elements enter in p-orbital and hence they are called p-block elements. They have completed s-sub-shells but incomplete p sub-shell in their outermost shell. The electronic configuration of the outermost shell may vary from $\mathbf{ns^2\,np^1}$ to $\mathbf{ns^2\,np^5}$ Most p-block elements are non-metals. They form two series of compounds in which the metal exists in two different oxidation states. They undergo chemical reactions by losing, gaining or sharing of electrons in the outermost shell.

Type III . d-block Elements (Transition Elements)

Elements with atoms in which the two outermost shells are incomplete. Elements of IIIA-VIIA, VIII, IB and IIB groups of the periodic table belong to this class. Since they are situated between s-and p-block elements, they are termed **transition elements.** They serve as a bridge between highly electropositive s-block elements and the electronegative p-block elements. They are termed as d-block elements because their penultimate shell of electrons is being expanded from 8 to 18 by the addition of d-electrons. They make up three complete rows of 10 elements and an incomplete fourth row in the periodic table.

Series	(n $_1$) d^1ns^2	d^2s^2	d^3s^2	d^5s^1	d^5s^2	d^6s^2	d^7s^2	d^8s^2	$d^{10}s^1$	$d^{10}s^2$
3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4d	Y	Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag	Cd
5d	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

In these elements, the s-orbital of the outermost shell is completely filled (i. e. there are 2 electrons) or half filled (i.e. there is only 1 electron) but their penultimate (last but one shell) is not completely filled. The electronic structure of these elements is due to the preferential occupancy of (n—1) d-orbitals, which are progressively in atomic number. These elements have many physical and chemical properties in common.

Type IV : f-Block Elements (Inner-Transition Elements)

They are commonly known as inner transition elements or the f-block elements. They are called inner transition elements because they have not only an incomplete d-sub-shell but also sub-shell which is not completely filled. They are called f-block elements because their antepenultimate (third from the outermost) shell of electrons is being expanded from 18 to 32 by the addition of f-electrons. Rare earth elements or the lanthanides (atomic numbers 58 to 71) and the actinides (atomic numbers 90 to 103) belong to this class. Elements within each of these groups are very similar in their chemical properties. The number of electrons in the outermost shell is essentially the same for all the members. The differentiating electron goes to fill up the antepenultimate shell. For this reason, they are called Inner Transition Elements and are different from the regular transition elements (where the penultimate d-sub-shell fills up). It is because of the similarity of chemical behaviour that lanthanides and actinides cannot be accommodated in the conventional periodic table. They are placed as two separate groups outside the main periodic table.

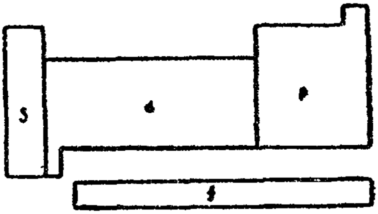


Fig. 50
Division of the long form of the periodic table in terms of blocks of s, p, d, f electrons.

Lanthanides and Actinides

The electronic configurations of lanthanides (58-71) and actinides (90-103) is the cause of their analogous chemical behaviour. In the lanthanide group, the additional electrons occupy 4f-sub level in preference to 5d or 6p (i.e.) previous to the penultimate shell, due to energy considerations. In the actinides the 5f-subshell is filled up preferentially over the 6d or 7 p.

Elements	At. No.	K	L	M	N				O				P				Q
					4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s
La	57	2	8	18	2	6	10		2	6	1		2				
Ce	58	2	8	18	2	6	10	2	2	6			2				
Pr	59	2	8	18	2	6	10	3	2	6			2				
Yb	70	2	8	18	2	6	10	14	2	6			2				
Lu	71	2	8	18	2	6	10	14	2	6	1		2				
Pa	91	2	8	18	2	6	10	14	2	6	10	2	2	6	1		2
U	92	2	8	18	2	6	10	14	2	6	10	3	2	6	1		2
Lr	103	2	8	18	2	6	10	14	2	6	10	14	2	6	1		2

It is because of these electrons going much inside the outermost shell that the elements of the series show very small in chemical properties. Their separation by chemical means is not very easy. The electrons occupy the inner shells. The charge on the nucleus increases with increase of atomic number. The pull on the negatively charged electrons becomes greater with the increase in atomic number. As a result, a decrease in the atomic volumes of the lanthanides is observed. This results in certain discrepancies in the group properties of elements following the lanthanides. The covalent radius of Hf should have been higher than that of Zr but actutally it is lower. This is due to the fact that 14 elements (lanthanides) interpose between La and Hf. The phenomenon is termed **lanthanide contraction**.

Periodicity of properties of elements from the point of their electronic configurations : Variation of atomic volume, atomic radius, ionic radius, ionisation energy and electronegativity, in various periods and groups is discussed below.

The physical and chemical properties of the elements vary periodically with atomic number. The periodic properties mainly depend upon the electrons in the outermost shell, since these are responsible for the forces between the atoms. Density, atomic volume, atomic and ionic radii, ionisation potential, electron affinity, electronegativity are the periodic properties. An examination of the electronic configurations of atoms shows that a particular configuration repeats regularly when the elements are arranged according to their atomic numbers. This repetition at regular intervals is called **periodicity**.

C	Si	Ge	Sn	Pb	ns^2	np^2
N	P	As	Sb	Bi	ns^2	np^3
F	Cl	Br	I	At	ns^2	np^5

Atomic volume : The atomic volume of an element is expressed as the volume occupied by one gram atom of it in solid form. Mathematically, it is the atomic weight divided by density in the solid state.

$$\text{Atomic volume} = \frac{\text{Atomic weight}}{\text{Density}}$$

The plot of atomic volume against atomic number (Fig. 51) gives a more regular curve than when it is plotted against the atomic weight. The figure below shows how the atomic volumes vary with atomic number. Thus the atomic volume is a periodic property.

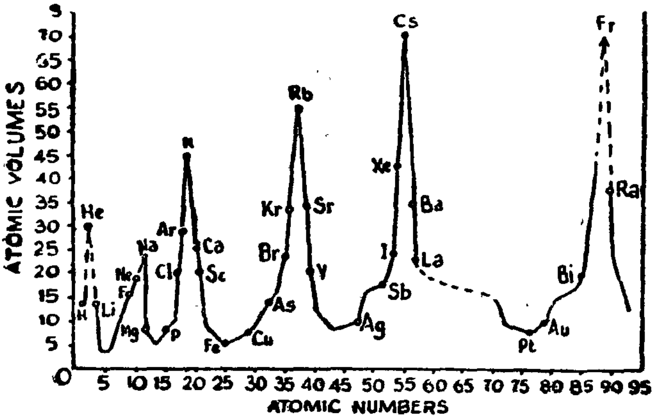


Fig. 51
Variation of Atomic Volume with Atomic Number

It is of interest to note that the ascending portions of the atomic volume contain electronegative elements and descending portions the electropositive elements. The most electropositive elements Na, K, Rb, Cs occupy the maximum positions.

Atomic Radii : Size of an atom may be described in terms of its radius. Radius of an atom is taken as the distance between the centre of the nucleus to the electrons in the outermost shell (valency electron). It is impossible to isolate an individual atom and measure its radius. However, we can deduce the radii of atoms from the internuclear distances (i.e.) the distances between the centres of adjacent atoms.

Atomic radii of normal elements

	s. Block elements		p Block elements				
Period	IA	II A	III B	IVB	V B	VIB	VII B
1	H						
	0·37						
2	Li	Be	B	C	N	O	F
	1.34	0·90	0·82	0·77	0·75	0·73	0·72
3	Na	Mg	Al	Si	P	S	Cl
	1.54	1.30	1·18	1·11	1·06	1·02	0·99
4	K	Ca	Ga	Ge	As	Se	Br
	1.96	1·74	1·26	1·22	1·19	1·16	1·14

From the data it is clear that atomic radius of an element is a periodic property.

In any given period, the atomic radii of the elements decrease steadily as the atomic number increases. In any period, the nuclear charge increases steadily but the electrons get added into the same energy level. The electrons in the various energy levels experience an increasing attraction towards the positively charged nucleus. This causes the displacement of the different energy levels towards the nucleus (i.e. contraction of the shells). In other words, the distance between nucleus and the outermost electrons steadily decreases, resulting in the decrease of the atomic radii.

In any group, the atomic radii of the elements increase from top to bottom. As we move down a group, the number of energy levels (shells) increases. The size of the atom increases. The nuclear charge increases. This causes the decrease in the atomic radii. But this effect is dominated by the addition of new shells.

Ionic Radii :—The radii of atoms are altered by the addition or loss of electrons. Since the charge on the nucleus remains the same during these alterations, the change in size (hence change in radii) is attributed either directly or indirectly to the change in the number of electrons.

Like atomic radii, the ionic radii can also be deduced from the internuclear distances (i.e.) the distances between the centres of adjacent ions.

When neutral atoms gain or lose electrons, ions are formed. A cation is formed by removing one or more electrons from an atom. The positive ion will be much smaller than the parent atom because (1) all the electrons present in the outermost shell are removed in ion formation. This causes reduction in size. (2) the nuclear charge acts on fewer electrons than normal and pull them all closer.

Atomic radius of Na = 1·57 Å

Ionic radius of Na^+ = 0·98 Å

Atomic radius of Fe = 1·17 Å

Ionic radius Fe^{2+} = 0·76 Å

Ionic radius Fe^{3+} = 0·64 Å

The radius of an ion decreases with an increase in the number of electrons lost.

An ion is formed by the gain of one or more electrons. Hence the effective nuclear charge is reduced, the electrons acquire a great freedom in getting away from the nucleus, and thus the electron cloud expands. Hence, the negative ion will be larger in size than the atom from which it was obtained.

Radius of Cl atom = 0·99 Å

Ionic radius of Cl^- ion = 1·81 Å

Like atomic radii, the ionic radii also decrease as we pass from left to right in a period, and increase as we pass from top to bottom in a group. The concept of atomic and ionic radii are of fundamental importance, because so many properties of the elements depend on the size of the atoms and ions.

Ionisation Potential : It is one of the fundamental properties of the elements which can be measured directly. It is defined as the energy required to pull off an electron from an isolated gaseous atom of an element.

$M \rightarrow M^+ + e^-$(first ionisation potential)

$M^+ \rightarrow M^{++} + e^-$(second ionisation potential)

Ionisation potential is expressed in **electron volts** (eV). When expressed as kilo calories per gram atom, it is known as **ionisation energy** (1eV = 23·06 kcal). IP values vary in the order : first IP < second IP < third IP and so on. The factors influencing ionisation potential of an element is governed by three factors.

(1) **Atomic radius :** The larger the size of the atom, the smaller would be its ionisation potential. This is so because the farther the most loosely bounded electron will be from the nucleus, the easier it would be to pull it away from the atom. The smaller the size of an atom, greater is the influence of the positive charge on the outermost electron and hence greater will be the ionisation potential.

(2) **Nuclear charge** : The ionisation potential increases with increase in the charge of the nucleus. The greater the nuclear charge, the more tightly are the electrons held. It would be difficult to pull off electrons, because of the enhanced attraction of the nucleus for them.

(3) **Number of inner electrons** : The electrons in the inner energy levels shield the outer electrons from the nucleus. Hence, increase in the number of inner electrons tend to reduce ionisation potential. These factors are usually interrelated.

In moving across any period from left to right, the ionisation potential in general, gradually increases. This is mainly due to the effect of increase in nuclear charge. In any group, the ionisation potential gradually decreases from top to bottom. This is mainly due to the effect of increase in atomic size.

Period	Group IA	Group IIA	Group IIIB	Group IVB	Group VB	Group VIB	Group VIIB	Group Zero
2	Li 5·4	Be 9·3	B 8·3	C 11·3	N 14·6	O 13·6	F 17·4	Ne 21·6
3	Na 5·14	Mg 7·6	Al 6·0	Si 8·15	P 11·0	S 10·4	Cl 13·0	Ar 15·8

Inert gases have very high ionisation potential value. This is attributed to the extremely high stability of a completed p-sub level. Fig. 52 gives the variation of ionisation potential with atomic number.

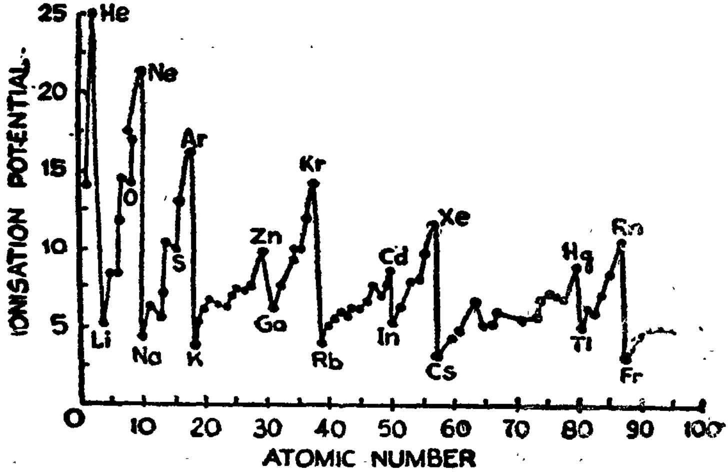


Fig. 52
A curve showing the relation between Ionisation Potential and Atomic Number

Electronegativity : The power of an atom to attract the shared electrons in a molecule towards itself was defined by Pauling as the electronegativity of the atom. Let us consider a covalent molecule A-B. If B has greater attraction for electron than A, the shared electrons will be shifted towards B. Thus B will acquire a negative charge ; as a result of it a positive charge will be developed on A. Non-metals which have a strong attraction for electrons have electro negativity values between 2 and 4. Metals which have weak attraction for electrons have relatively low electronegativity values between 0·7 and 2·2. Since noble gases do not form bonds, no electronegativity values are given to them. Electronegativity is influenced by the same factors which influence ionisation energies.

(1) **Atomic radius :** Small atoms have greater attraction for electrons than large ones. Therefore, they are electronegative. Electronegativity decreases with increasing size of the atom.

(2) **Nuclear charge :** Electronegativity increases with increasing nuclear charge.

(3) **Number of inner electrons :** Increase in the number of inner electrons tend to decrease the electronegativity.

Electronegativity of elements in periods 2 and 3

Period	Group IA	Group IIA	Group IIIB	Group IVB	Group VB	Group VIB	Group VII B
2	Li 1·0	Be 1·5	B 2·0	C 2·5	N 3·0	O 3·5	F 4·0
3	Na 0·9	Mg 1·2	Al 1·5	Si 1·8	P 2·1	S 2·5	Cl 2·8

In any given period, electronegativity increases from left to right. This is due to the decrease in size and increase in nuclear charge. In any group, the electronegativity decreases from top to bottom

Uses : (1) The electronegativities of the elements are useful in approximating the bond energies and in establishing qualitatively the thermal stabilities of the compounds. (2) It is easy to predict which of the elements will form ionic compounds. Ionic compounds will result between elements of the most widely divergent electronegativities :

Na	Cl
0·9	2·8

QUESTIONS

PART A

1. Which of the following is a periodic property? (a) atomic weight. (b) atomic volume. (c) atomic number. (d) mass number.

2. Which of the following properties display progressive increase down a group in the Periodic Table? (a) Size of the atom. (b) Electronegativity. (c) Electron affinity. (d) Ionisation potential.

3. Which of the following properties display progressive increase with the rise in atomic number across a period in the Periodic Table? (a) Size of the atom. (b) Electronegativity. (c) Electron affinity. (d) Ionisation potential.

4. Elements whose atoms have 3 outermost shells incomplete are called (1) Normal elements. (2) Transition elements. (3) Rare gases. (4) f-block elements.

5. With increasing metallic character (a) ionisation potential increases. (b) electronegativity increases. (c) ionisation potential decreases.

6. The atomic radius decreases as we go from left to right in a period because (1) the nuclear charge increases. (2) the nuclear charge decreases. (3) the ionisation potential increases. (4) the electron affinity increases.

7. The similarity between Li and Mg or Be and Al is due to (a) similar ionic radii (b) the high electropositivity (c) similarity in the charge of their ions. (d) their high reactivity.

8. According to the modern periodic law, the properties of elements are periodic functions of their.........

The size of a positive ion is ...... while that of a negative ion is......... than that of the parent atom.

10. On going down a group in the periodic table, basicity ....

11. Atomic volume is the volume occupied by .... atom of an element.

12. The shrinkage in size from La to Lu is known as ....

13. The measure of the tendency of an atom to lose electrons is called its ....

14. Arrange the following as required : Increasing atomic volume : Cs. Na, K, Li, Rb.

15. Decreasing electronegativity : Na, C, F, O, I

16. In the periodic table, atomic size decreases from left to right across a period. Why ?

PART B

17. What is ionisation potential ? Why does it increase across the periods and decrease down the groups in the Periodic Table ?

18. Does an atom with a high electron affinity likely to have a high or low ionisation potential? Why ?

19. How do the atomic radii of elements vary (a) down a group (b) across a period. How is this accounted for ?

20. The periodic law has been started as follows: The periodicity of the element is the function of the atomic number what does this mean ?

21 Distinguish between the following terms : Atomic number, mass number and atomic weight.

PART C

22. To what extent is the extended form of the Periodic Table an improvement over the Mendeleeff Table ?

23. How are the elements classified according to their electronic structure ? On this basis, classify the following elements : (1) U (2) Co (3) Te.

24. (a) What is lanthanide contraction ? (b) How is it accounted for ? (c) What are its effects ?

25. How do the properties (1) atomic radius. (2) electro negativity (3) electron affinity, vary (a) within a group (b) in a period ?

26. (a) What are short and long periods ? (b) Account for the number of elements in them.

27. The electronic configutation of an element is 2, 8, 18, 7 without classifying the element, give reasons to the following (a) What is the valency of the element towards hydrogen ? (b) Is the element an oxidising agent or reducing agent ? (c) Will it form a positively charged ion or negatively charged ion ? (d) Is the element likely to occur in the free state in nature or not ?

CHAPTER II

HYDROGEN

Symbol : H. **Molecular Formula** : H_2, **Valency** : 1

Atomic weight 1·008. **Atomic number** : 1

Occurrence : Hydrogen occurs in the free state in volcanic gases, and in the outer atmosphere of the sun. In combination, hydrogen occurs in water, acids and alkalis.

Methods of Preparation

1. **From water :** Alkali metals (Na, K) react violently with water at room temperature with liberation of hydrogen. Other metals which follow hydrogen in the electrochemical series displace hydrogen from water at higher temperatures (In the electrochemical series, metals are arranged in order of increasing ease of reduction, i.e., ability to lose electrons.)

$$2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$$

Hydrogen may also be produced by passing steam over hot iron in a heated tube, or over hot coke. Electrolysis of acidulated water also gives hydrogen.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2\uparrow$$
$$C + H_2O \rightarrow CO + H_2\uparrow$$
$$H_2O \rightleftharpoons H^+ + OH^-$$
$$H^+ + e^- \rightarrow H \text{ at cathode}$$
$$H + H \rightarrow H_2\uparrow$$

2. **From Acids:** Alkali metals react with violence with acid solutions even at room temperature. Other metals below hydrogen in the series can likewise rapidly react in acid solutions with liberation of hydrogen. On a laboratory scale, the usual method

of preparing hydrogen is based on the action of dilute sulphuric acid on metallic zinc.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \uparrow$$

3. **From Alkalis:** Hydrogen can be prepared by the action of sodium or potassium hydroxide on metals like aluminium, silicon or zinc.

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2 \uparrow$$
$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2 \uparrow$$

Industrial Preparation of Hydrogen

1. **Electrolysis of water:** Where a cheap source of electric power is available, hydrogen can be obtained in a pure state and quite economically by the electrolysis of water containing a little dilute sulphuric acid. The electrolysis is carried out in

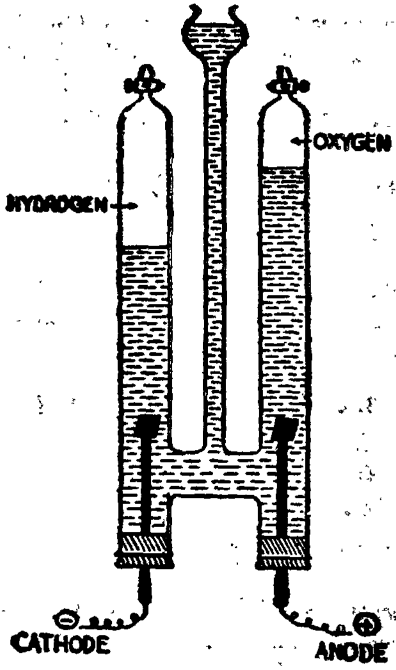


Fig. 53
Electrolysis of Water

a number of cells each provided with nickel electrodes. Water gets electrolysed giving hydrogen and oxygen.

The following reaction takes place

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4$$

At Cathode $H^+ + e^- \rightarrow H$

$H + H \rightarrow H_2$

At Anode : $SO_4^{2-} \rightarrow SO_4 + 2e^-$

$SO_4 + H_2O \rightarrow H_2SO_4 + O$

$O + O \rightarrow O_2$

About 18% of the world production of hydrogen is obtained by the electrochemical method.

2. **Lane's Process :** When steam is passed into vertical retorts packed with iron and heated to red heat (600—800°) in a furnace, it is decomposed into hydrogen and magentic oxide of iron.

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2 \uparrow$$

This is a reversible reaction. But as the steam supply is maintained, only hydrogen is produced. When all the iron is oxidised, the steam supply is cut off, and a current of water gas ($CO + H_2$) is passed over the iron oxide. At red heat, both the constituents of the water gas (H_2 and CO) reduce Fe_3O_4 to iron.

$$Fe_3O_4 + 4\,CO \rightarrow 3Fe + 4\,CO_2 \uparrow$$

$$Fe_3O_4 + 4\,H_2 \rightarrow 3Fe + 4\,H_2O$$

Thus, by alternately passing steam and water gas over the iron, hydrogen can be obtained in large amounts from a limited amount of iron.

3. **Bosch Process :** (From water gas) In this method, water gas which is a mixture of carbon monoxide and hydrogen is produced by passing steam over white hot coke.

$$C + H_2O \rightleftharpoons CO + H_2$$

Water gas so formed is mixed with an excess of steam and the mixture is led over a catalyst of iron or cobalt oxide with chromic oxide as a promoter at 400°C Carbon monoxide is oxidised to CO_2

$$CO + H_2O \rightarrow CO_2 + H_2$$

The reaction is carried out in a steel box containing a number of trays on which the catalyst is placed.

From this mixture, CO_2 is removed by absorption in water under 20 atmospheres pressure and traces of carbon monoxide by ammoniacal cuprous chloride solution. Hydrogen is left over.

Physical properties : Hydrogen is a colourless, tasteless and odourless gas. It is the lightest gas known. It can be liquefied and solidified under suitable conditions of temperature. It shows the highest diffusion velocity because of its low molecular weight and highest thermal conductivity of all gases. Many metals such as palladium can absorb or occlude hydrogen is considerable quantities. Hydrogen is an inflammable gas since it combines with oxygen of air with evolution of heat and giving a non-luminous flame.

Chemical properties : Hydrogen combines with many metals and non - metals giving characteristic compounds called hydrides. It acts as a reducing agent for many metal oxides. Hydrogen has a tendency to form bond a covalent electron-pair. Bonds with highly electropositive elements are mostly ionic. Those with highly electronegative elements exhibit partial ionic character.

Uses of hydrogen : (1) It is used as lifting agent in filling balloons. (2) In Haber process, ammonia is manufactured from nitrogen and hydrogen. (3) Methyl alcohol is manufactured by passing a mixture of water gas and half its volume of hydrogen over a heated catalyst like zinc oxide.

$$CO + H_2 + H_2 \rightarrow CH_3OH$$

Typical reactions of hydrogen are summarised below :—

Reaction	Examples and conditions
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	Exothermic
$H_2 + X_2 \rightarrow 2HX$	X = F, Cl, Br. I (catalyst required in the case of iodine)
$3H_2 + N_2 \rightarrow 2NH_3$	Yield of NH_3 favoured at low temperature and high pressure
$x\,H_2 + 2M \rightarrow 2MH_x$	M—Alkali and Alkaline earth metals
	With many other metals, metallic hydrides are formed
$Y\,H_2 + M_xO_y \rightarrow xM + y\,H_2O$	With oxides of metals less active than Fe

(4) It is used for the hydrogenation of coal to yield synthetic petrol. (5) Hydrogenation of fats and oils is done by passing hydrogen into oil in the presence of finely divided nickel at 180°C. Large quantities of artificial ghee and butter are made by this process. (6) It is used as a reducing agent for the preparation of certain metals like tungsten in a pure state. (7) Oxy-hydrogen flame which gives a temperature of about 2800°C is used for melting quartz, platinum and other substances.

Types of Hydrides : Binary compounds of hydrogen with other elements are known as **hydrides** :

Element + Hydrogen→Hydrides.

The type of hydrides which an element forms depends on its electronegativity. The types are.

(1) Salt like, saline or ionic hydride e.g. hydrides of groups I A and II A

(2) Covalent or molecular hydrides e.g. hydrides of groups IIIB—VIIB

(3) Metallic hydrides (e.g.) hydrides of groups IVA. VIIA, VIII and IB-II B (i.e., hydrides of transitional elements)

1. Salt like Hydrides or Ionic Hydrides

Elements with low electronegatives (e.g.) alkali and alkaline earth metals are reducing agents, which are strong enough to transfer electrons to the hydrogen atom giving salt hydrides. They are crystalline compounds which are generally obtained by direct reactions between the pure metals and hydrogen at 150-700°c.

Properties (1) Ionic hydrides are solids with high melting points. (2) In the fused state, they conduct electricity. (3) On electrolysing a fused metallic hydride (LiH), the metal is liberated at the cathode and hydrogen at the anode (4) They are hydrolysed by water with the formation of the hydroxide and liberation of hydrogen. This establishes that the lattices of salt like hydrides are ionic and contain negative hydride ion (H^-). (5) They are powerful reducing agents especially at high temperatures.

$$2CO + NaH \rightarrow HCOONa + C$$

2. Covalent or Molecular Hydrides

The most highly electronegative elements (i.e.) non-metals in groups IIIB-VIIB share electrons with hydrogen to form covalent hydrides. They are prepared by a number of methods: (1) direct combination of the element with hydrogen e.g. NH_3, H_2O (2) hydrolysis of metal boride, carbide (3) reduction of certain compounds with H_2 (4) reduction of suitable halide in ether solution with $LiAlH_4$ (e.g.) SiH_4. Elements forming covalent hydrides are given in the table.

Table of elements forming covalent hydrides.

Group :	IIIB	IVB	VB	VIB	VIIB
	B Al Ga In	C Si Ge Sn Pb	N P As Sb Bi	O S Se Te Po	F Cl Br I

Properties : They are soft, have low melting and boiling points. They are highly volatile and do not conduct electricity.

Group IIIB hydrides are electron-deficient and polymeric. e.g. B_2H_6 and $(Al\ H_3)n$ are polymeric. Except group VIIB, all the other elements form polynuclear hydrides in which two or more of the non-metal atoms are directly bonded to each other. The tendency is at a maximum with carbon, where an almost infinite number of compounds are formed.

Metallic Hydrides

Many metals absorb or occlude hydrogen directly at moderate or elevated temperatures. The d-block transition elements and Be and Mg (s-block) form metallic hydrides provided they react with H_2.

Properties : (1) The properties of metallic hydrides are not much different from those of the parent metals. (2) They are less dense than the parent metal. (3) Their composition is variable. (4) They are strong reducing agents. (5) They are often termed interstitial solid solutions since hydrogen enters the metal lattice occupying the interstices between metal atoms and ions.

Some examples are : ZnH 1·92 TaH 0·76

Special forms of Hydrogen

(1) Nascent Hydrogen

Nascent hydrogen is that hydrogen which is liberated at the time of birth. It is more active than ordinary hydrogen.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H \text{ (nascent hydrogen)}$$
$$H + H \rightarrow H_2 \text{ (ordinary hydrogen)}$$

If granulated zinc is added to iron (III) chloride solution acidified with dilute H_2SO_4, the fresh-formed nascent hydrogen reduces iron (III) Chloride solution to iron (II) chloride. But, if hydrogen gas is bubbled even for hours together, $FeCl_3$ is not reduced to $FeCl_2$. Evidently the freshly generated hydrogen is more reactive than the molecular hydrogen.

Initially, it was considered that hydrogen at the moment of its liberation is in the atomic state, and hence is much more reactive. But this idea failed, because nascent hydrogen obtained by different sources was not equally effective. It is difficult to say that nascent hydrogen truly represents the atomic state. The part of energy liberated as a result of reaction producing hydrogen becomes associated with the hydrogen evolved, so that nascent hydrogen is simply hydrogen molecules possessing extra energy. It has been suggested that the activity of nascent hydrogen is due to its being generated in very small bubbles under great pressure, for it has been observed that ordinary hydrogen under great pressure reduces some metallic salts in solution.

(2) Atomic hydrogen

The molecule of hydrogen can be split into two free hydrogen atoms.

$$H_2 \rightarrow H + H;\ \triangle H = +\ 98 \text{ to } 101 \text{ kcals.}$$

The reaction is endothermic, large quantities of energy being absorbed. Atomic hydrogen is produced by passing hydrogen through an electric arc maintained between tungsten electrodes. The atoms set free at once recombine in contact

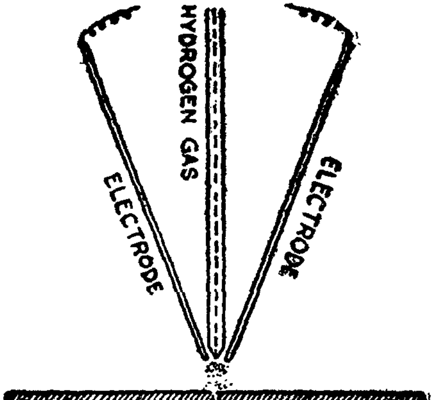


Fig. 54
Atomic hydrogen welding torch

with metallic surface producing a high temperature 4000-5000°C. This principle is utilised in making the atomic hydrogen welding torch (Fig. 54). No flux needed to keep the metallic surface (to be welded) free of the oxide film and this is an inherent advantage of atomic hydrogen welding over welding with oxy-hydrogen blow-pipe.

Properties : Atomic hydrogen is stable only for $\frac{1}{3}$ of a second, but its life-time can be extended under special circumstance to 10 seconds It is a powerful reducing agent. It gives the following reactions :

$AgNO_3 \rightarrow Ag^0$ (Metal),
$S \rightarrow H_2S$
$P \rightarrow PH_3$
$Ci_2 \rightarrow HCl$

Uses : (1) $H + H \rightarrow H_2 + 101$ kcals. The recombination produces enormous heat, which is utilised in the atomic hydrogen welding torch. (2) It is used for the preparation of hydrides. (3) It reduces unsaturated compounds to saturated ones.

(3) Ortho and Para-Hydrogen

The hydrogen molecule exists in two different forms known as ortho-and para-hydrogen. They slightly differ in their physical properties.

A hydrogen molecule consists of two hydrogen atoms, each atom having one proton in the nucleus with an electron moving around it. In a molecule of hydrogen, which is diatomic, there will be two protons and two electrons. In the hydrogen atom, the nucleus will be spinning like a top. In a molecule the electrons will always have an opposite spin but the protons may have their spins either in the same direction or in opposite directions. This gives rise to two forms of hydrogen. If the spins of the two nuclei are in the same direction, we get one form of hydrogen known as the ortho hydrogen; and if the spins are in the opposite directions, we get the second form of hydrogen known as the para hydrogen (Fig. 55).

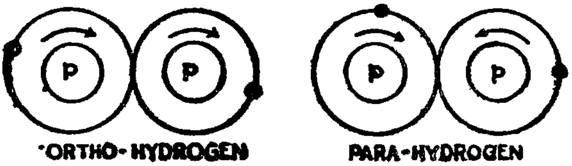


Fig. 55
Ortho and Para Hydrogen

Ordinary hydrogen at room temperature is a mixture of 75% of the ortho-form and 25% of the para-form. At low temperature there will be a greater proportion of para.

Preparation of para-hydrogen

Ordinary hydrogen is a mixture of 75% ortho and 25% para. It is absorbed by activated charcoal contained in a quartz vessel maintained at a temperature of 20° A (i.e., the temperature of liquid hydrogen). The charcoal absorbs practically pure para-hydrogen. When the gas is pumped off from it, the sample is found to contain about 98% of para-hydrogen.

Preparation of ortho-hydrogen

Ortho form is more stable than para-hydrogen, which always tends to revert to the ortho-hydrogen. The process is accelerated by mixing with atomic hydrogen or by passing electric discharge or by treating with a catalyst like Pt or Fe. However it has not been found possible to obtain the ortho form in a pure condition.

Isotopes of Hydrogen

If the atoms of the same element have different mass numbers, they are called **isotopes**. The difference in mass number arises because the nucleus contains a different number of neutrons. Three isotopes of hydrogen are known:

(1) Protium (2) Deuterium (3) Tritium, with mass numbers 1, 2 and 3 respectively.

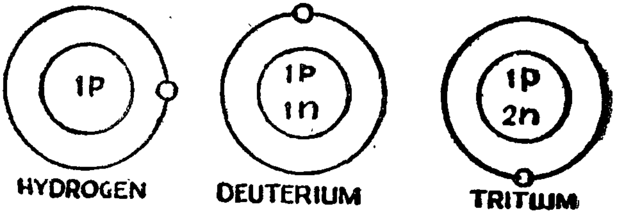


Fig. 56
Isotopes of Hydrogen

These three isotopes of hydrogen have the same electronic configuration (Fig. 56) and hence have the same chemical properties. Since the mass of these isotopes vary widely, they show greater differences in physical properties than are found between the isotopes of other elements. The only differences in chemical properties are in equilibrium constants and rates of reactions.

Heavy Hydrogen or Deuterium D_2

Heavy hydrogen is a heavier isotope of hydrogen having a mass number 2. The nucleus of heavy hydrogen contains only one proton and one neutron, while ordinary hydrogen nucleus contains only one proton. Heavy hydrogen is denoted by the symbol D_2 (deuterium).

This isotope is present to the extent of I part in about 6000 parts of ordinary water. The first evidence for deuterium or heavy hydrogen is due to Urey (1931). Urey and Washburn, by repeated electrolysis of ordinary water, obtained a sample of water having higher molecular weight, higher boiling point and higher density than ordinary water. This was called **heavy water** or **deuterium oxide**, D_2O. When a sample of water rich in heavy water was electrolysed, a heavy hydrogen with mass twice as that of ordinary hydrogen was obtained. It is referred to as heavy hydrogen.

Preparation : (1) On electrolysis, heavy water gives heavy hydrogen at the cathode. This may be purified by diffusion.

$$2D_2O \rightarrow \underset{\text{cathode}}{2D_2 \uparrow} + \underset{\text{anode}}{O_2 \uparrow}$$

(2) Metals like sodium or potassium react with heavy water displacing heavy hydrogen.

$$2D_2O + 2Na \rightarrow D_2 + 2NaOD$$

Physical properties : (1) It is a colourless, odourless and tasteless gas like ordinary hydrogen. (2) It possesses a density twice that of ordinary hydrogen. (3) It is insoluble in water and is a bad conductor of heat and electricity. (4) Its freezing point is 4·7°C higher and the boiling point 3·2°C higher than that of hydrogen.

Chemical properties : In chemical behaviour it resembles ordinary hydrogen, although the rates of reactions are slower in this case due to its heavy mass.

(1) Combustion :—It burns in air or oxygen forming heavy water.

$$2\,D_2 + O_2 \rightarrow 2\,D_2O$$

(2) Reaction towards metals and non-metals :— It combines with metals and non-metals to form the hydrides.

$$2\,Na + D_2 \rightarrow 2\,NaD \text{ (sodium deuteride)}$$
$$N_2 + 3D_2 \rightarrow 2\,ND_3 \text{ (deuteroammonia)}$$
$$Cl_2 + D_2 \rightarrow 2\,DCl \text{ (deuterium chloride)}$$

(3) It can readily exchange with hydrogen atom in presence of Pt catalyst.

$$H_2O + D_2 \rightarrow D_2O + H_2$$
$$CH_4 + 2D_2 \rightarrow CD_4 + 2H_2$$

Uses : (1) It is used in the preparation of deutero compounds, which are at present used in medicine. (2) Accelerated deuterons are employed in artificial transmutation of elements. (3) It is useful as a tracer element in chemical and biological work.

Tritium

This is a radioactive isotope of hydrogen which occurs in trace amounts. Natural tritium is formed by neutron bombardment of atmospheric nitrogen, the neutrons resulting from the action of cosmic radiation on atmospheric gases. It is prepared by several nuclear reactions.

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{12}_{6}C + ^{3}_{1}H$$

Tritium can be prepared by nuclear reactions.

$$^{7}_{3}Li + ^{1}_{0}n \rightarrow ^{3}_{1}H + ^{4}_{2}He$$

Properties : Tritium is a gas which can be liquefied at 25K. It is radioactive and emits β-rays. Its half-life period is 12·5 years. It emits a β-particle and is changed to a lighter isotope of He (mass 3). It is useful as a tracer.

$$^{3}_{1}T \xrightarrow{\beta} ^{3}_{2}He + ^{0}_{-1}e$$

Heavy Water, D_2O

It has been shown by Urey and his co-workers that ordinary water contains a fraction (about 1 part in 6000) of what is known as heavy water, D_2O. It is made up of 2 atoms of heavy hydrogen and one atom of oxygen.

Preparation : Heavy water is generally prepared by prolonged electrolysis of water containing an alkali (0.5 N strength). The residual liquid is neutralised with carbon dioxide and distilled. The distillate is again made alkaline (0·5 N), and the electrolysis is repeated. With each electrolysis the residual liquid becomes richer in heavy hydrogen. After prolonged electrolysis, a small quantity (0·5 ml from 20 litres of water) of almost pure heavy water can be obtained.

Physical properties : Like ordinary water, heavy water also is a colourless, tasteless and odourless liquid. The physical constants of the two types of water differ.

Property	Ordinary water	Heavy water
Freezing point	0°C	3·82°C
Boiling point	100°C	101·42°C
Density	1	1·108
Specific heat	1·00	1·02
Solubility of NaCl in 100 g H_2O at 25°C	35·9	30·5

Chemical Properties : The reactions of heavy water are similar to those of ordinary water but slow.

1. **Decomposition :** On electrolysis, heavy water yields deuterium and oxygen.

   $2D_2O \rightarrow 2D_2 + O_2$

2. **Reaction towards metals :** Metals like Na or K react with heavy water forming the respective deuteroxide.

   $2Na + 2D_2O \rightarrow 2NaOD + D_2$

3. **Action on oxides :** (a) Acidic oxides dissolve in water forming acids. $SO_3 + D_2O \rightarrow D_2SO_4$ (deutero sulphuric acid)

   (b) Basic oxides dissolve in water forming deuteroxides.

   $Na_2O + D_2O \rightarrow 2NaOD$ (Sodium deuteroxide)

4. **Exchange reactions :** In many exchange reactions with other compounds, deuterium atoms displace hydrogen either wholly or partially.

   $HCl + D_2O \rightarrow DCl + HOD$
   $NaOH + D_2O \rightarrow NaOD + HOD$

5. **Deuterolysis** (similar to hydrolysis) : It undergoes double decomposition with calcium carbide and magnesium nitride.

$CaC_2 + 2D_2O \rightarrow Ca(OD)_2 + C_2D_2$ Deutero acetylene

(d) Uses · (1) Heavy water is used for the preparation of heavy hydrogen. (2) It is used as a moderator in nuclear reaction. (3) It is used as a tracer.

QUESTIONS

Section A

1. Lane's process is a method for the manufacture of ———
2. In Lane's process, steam is passed over hot ———
3. Proton, deuterium and tritium are ——— of H_2.
4. Heavy hydrogen is also known as ———
5. Deuterium atom contains in its nucleus ——— protons and ——— neutrons.
6. Active hydrogen is ——— hydrogen.
7. Atomic hydrogen is ——— active than molecular hydrogen.
8. In the ortho-hydrogen, the spins of protons are in ——— directions.
9. In para-hydrogen, the spins of protons are in ——— directions.
10. Ortho-hydrogen is ——— stable than para-hydrogen.
11. Name the isotopes of hydrogen.
12. What is the name of the radioactivitive isotope of hydrogen?
13. Which is more stable at ordinary temperature ——— ortho or para hydrogen ?

14. What happens when a mixture of ortho and para hydrogen is cooled in liquid air in the presence of activated charcoal?

15. Hydrogen forms salt hydrides by (a) losing an electron to the metal atom (b) gaining an electron from the metal atom (c) sharing of electrons with the metal atom (d) absorption on the surface of the metal.

16. Pick out the correct answer :

The reaction $LiH + H_2O \rightarrow LiOH + H_2$ shows that hydrogen in the hydride possesses (a) a negative character (b) positive character (c) neither positive character nor negative character (d) salt-like character.

17. How is silicon hydride prepared ?

18. Heavy water has (a) higher percentage of oxygen than ordinary water (b) lower percentage of oxygen than ordinary water (c) the same percentage of oxygen than ordinary water (d) no solvent action on alkalis.

19. Which one of the following statements is incorrect ? (a) The density of heavy water is more than that of ordinary water. (b) If ordinary hydrogen is burnt in oxygen, a mixture of H_2O and D_2O is formed.

20. When dilute H_2SO_4 is electrolysed using platinum electrodes (a) H_2 is evolved at the cathode. (b) Oxygen is evolved at the cathode. (c) The cathode dissolves. (d) The anode gains weight. (e) The anode dissolves and the cathode gains weight.

21. Hydrogen is liberated when dilute H_2SO_4 reacts with (a) gold (b) copper (c) aluminium (d) mercury.

22. Hydrogen can be converted into atomic hydrogen by passing it through. (a) finely divided palladium. (b) an electric arc. (c) a suitable catalyst under high pressure. (d) an electrolytic cell.

23. Oxygen is manufactured by the fractional evaporation of (a) water (b) H_2O_2 (c) liquid air.

24. When hydrogen generated in Kipp's apparatus is passed through an acidified solution of $FeCl_3$ no change occurs. However, when zinc pieces are added to the solution, then yellow colour changes to green. This is because, (1) zinc displaces Fe from $FeCl_3$ (2) Ferric ions are reduced to ferrous ions by the nascent hydrogen produced (3) $FeCl_3$ is bleached by the nascent hydrogen produced. (Pick out the correct answer.)

25. Heavy water is made by (1) dissolving salts of heavy metals in distilled water (2) repeated distillation of alkaline water (3) by burning deuterium in oxygen (4) by burning the heavier isotope of oxygen in hydrogen (Indicate the correct answer).

26. Hydrogenation of oils is carried out in the presence ——— as a catalyst.

27. The element produced when steam reacts with coke is———.

28. In Lane's process, H_2 is obtained by (a) the electrolysis of water (b) the action of acid on Mg (c) the action of the steam on red-hot iron (d) the action of steam on red-hot coke.

29. Large quantities of hydrogen are obtained as a by-product during the manufacture of
(a) HCl (b) Na_2CO_3 (c) $NaHCO_3$ (d) NaOH.

30. Deuterium and tritium are ——— of hydrogen.

31. Heavy hydrogen is the other name for———.

32. When the proton spins in the hydrogen molecule are in the same direction, we get ———.

Section B

33 Write notes on (1) Ortho-para hydrogen (2) active hydrogen.

34. Is it possible to prepare pure para-hydrogen ?

35. How is heavy hydrogen prepared ?

36. How is active hydrogen obtained ? How does it differ from molecular hydrogen ?

Section C

37. Describe the preparation of heavy water. What are the differences between the physical properties of heavy and ordinary water ?

38. Give an account of the different types of hydrides formed by hydrogen.

39. How is hydrogen prepared on a large scale ?

CHAPTER III

RARE GASES

Introduction : The Zero Group of the Periodic Table consists of six elements Helium, Neon, Argon, Krypton, Xenon and Radon. They are commonly known as **Noble Gases,** because they are all inactive and chemically inert substances. They are gases at ordinary temperatures. Once they were called '**Inert Gases**', since they are devoid of chemical activity. However, a number of Xenon compounds have been prepared. Hence, the term 'Noble Gases' is to be preferred. These gases are also known as Rare Gases because of their presence in very small amounts in air.

Discovery of Rare Gases : In 1785, Cavendish repeatedly sparked a mixture of air and an excess of oxygen, and absorbed the resulting NO_2 and unused O_2 in alkaline potassium disulphide solution. He found that a small volume, about 1/120th part of the original air did not dissolve. Unfortunately, Cavendish could not draw any conclusion about the nature of the gas, which was later found to be a mixture of rare gases.

In 1868, **Lockyer** and **Frankland** observed a bright yellow line near the D_1 and D_2 lines of sodium in the chromosphere of the sun during a total eclipse. The new line did not coincide with the D lines of sodium, and **Jansen** named it as D_3. They concluded that it was due to the presence of a new element in the sun (not present on earth) and named it as **Helium** (meaning sun).

In 1894, **Rayleigh** noticed that the density of atmospheric nitrogen was 0·5% higher than the density of nitrogen obtained by chemical means. This showed the presence of a heavier constituent in the atmospheric nitrogen.

Density of nitrogen (from atmosphere) = 1·2571

Density of nitrogen (from chemical means) = 1·2520

It was shown by Ramsay that the discrepancy was due to presence of another gas in air, heavier than nitrogen and unknown till then. This made Rayleigh and Ramsay to repeat the forgotten experiment of Cavendish. They isolated this gas from air (freed from CO_2 and moisture) by first removing the oxygen on passing it over heated copper, and then the nitrogen by passing it over heated magnesium.

$$2Cu + O_2 \rightarrow 2CuO$$
$$3Mg + N_2 \rightarrow Mg_3N_2$$

The gas so obtained was spectroscopically examined. The spectrum of the gas did not coincide with nitrogen and indicated the presence of a new gas in the atmosphere. Its vapour density and atomic weight were found to be 20 and 40 respectively. The new gas was named as **Argon** (meaning lazy).

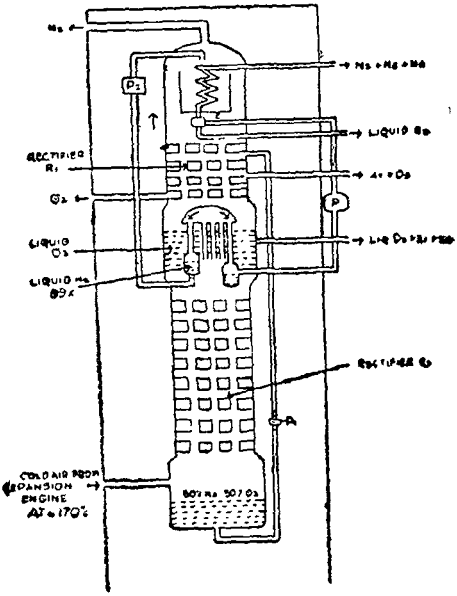


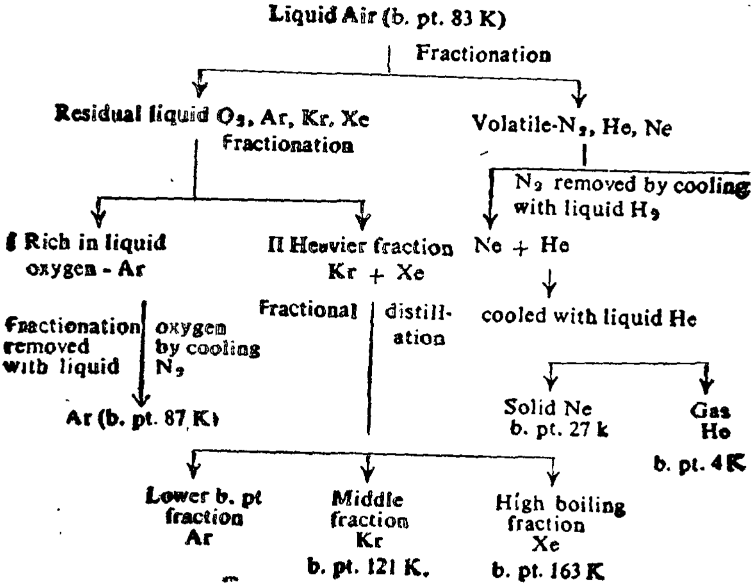
Fig. 57
Rare Gases from Liquid Air

In 1898, Ramsay and Travers carried out fractional distillation of liquid argon under reduced pressure. From the first fraction they isolated besides helium, a new element **neon**, (meaning new), which contained different lines in the spectrum Its atomic weight was found to be 20.

Isolation of Rare Gases From Liquid Air

When liquid air is subjected to fractional distillation, liquid nitrogen first collects as the chief component. This invariably contains helium and neon also, as they are more volatile (lower boiling point) than liquid nitrogen. The distillate is passed through a spiral column surrounded by liquid nitrogen. Nitrogen condenses He and Ne escape liquefaction. They are separated by passing through a bulb surrounded by liquid hydrogen. Ne condenses and He passes over.

On continued distillation, oxygen distills as the chief component. Since the boiling point of argon is very close to that of oxygen, the whole of argon evaporates with it. The oxygen-argon mixture is passed through a rectifying column provided with coils of liquid nitrogen. Liquid oxygen condenses and argon escapes. In liquid oxygen, krypton and xenon accumulate. By fractionation, these two constituents may be separated, since their boiling points are far apart. The following flowsheet diagram illustrates this process :



Uses of Rare Gases

(a) **Uses of Helium** : (1) Owing to its inertness, lightness and non-inflammability, helium is used instead of hydrogen in observation balloons. (2) Deep sea divers use a mixture of helium and oxygen for respiration in preference to air. (3) Liquid helium is used for producing very low temperature.

(b) **Uses of Neon**: (1) Neon lamps give a scarlet-red glow and they are used for advertising signs. The advantage is long life and low current consumption. It can penetrate even fog.

(c) **Uses of Argon** : (1) It is used in discharge tubes for illumination to get lilac to blue colour. (2) It is used in making gas-filled lamps in which it is more efficient than nitrogen.

(d) **Uses of Kripton and Xenon** : They are also useful in making gas-filled lamps.

(e) **Uses of Radon** : It is employed in medical science for treatment of malignancies and also as a substitute for X-ray in industrial radiography.

Position of Rare Gases in the Periodic Table

At the time of enunciation of the periodic law by Mendeleeff, the rare gases were not known. In Mendeleeff's Periodic Table, there was a sharp transition from strongly electronegative elements of group VII (Halogens) to the strongly electropositive elements of group I. When Ramsay discovered the rare gases, he could not properly accommodate them in the periodic table. So, he created a complete group for them in the periodic table known as the **zero group**. He placed the group in between the strongly electropositive alkali metals of group I and strongly electronegative halogens of group VII to form something like a transition group. All the elements in the zero group are gaseous, monoatomic and chemically inert. There are no sub-groups in this group.

Electronegative elements-Monovalent. (Tendency to gain an electron)	Rare Gases-Zero valent (no tendency either to lose or gain electron)	Electropositive elements-Monovalent (Tendency to lose an electron)
	He 2 (2)	Li 3 (2,1)
F 9 (2, 7)	Ne 10 (2,8)	Na 11 (2,8,1)
Cl 17 (2,8,7)	Ar 18 (2,8,8)	K 19 (2,8,8,1)
Br 35 (2,8,18,7)	Kr 36 (2,8,18,8)	Rb 37 (2,8,18,8,1)
I 53 (2,8,18,18,7)	Xe 54 (2,8,18,18,8)	Cs 55 (2,8,18,18,8,1)
	Rn 86 (2,8,18,32,18,8)	Fr 87 (2,8,18,32,18,8,1)

They all have stable electronic configurations (8 electrons in the outermost orbit) in their valency shell except helium in which the outermost orbit contains two electrons. Hence, inert gases have no tendency to form ions (i.e.) to lose or gain electrons or to form ordinary covalent links.

The position of inert gases is further justified from the following facts.

(1) They are all chemically inert, colourless, odourless and tasteless gases. (2) They are monoatomic in character (specific heat ratio is the same for all rare gases 1.66). (3) They display a regular gradation in their physical properties. Their density, boiling point, melting point increase with rise of atomic weight. (4) The electronic configuration shows that they are similar and are rightly placed in the zero group of the periodic table. (5) They form a transition group between highly electronegative halogens and highly electropositive elements. (6) They do not resemble other elements either to their left or to the right.

Fluorides and Oxides of Xenon

Despite the theoretical evidence for the inertness of noble gases, a few chemists predicted the existence of compounds of these gases. Thus, in 1933, Pauling predicted the possibility of formation of Kr F_6, Xe F_6, Xe F_8 and xenic acid H_4XeO_6. Bartlet and Lohman prepared xenon hexafluoroplatinate $Xe^+ (ptF_6)^-$ by reacting xenon and platinum hexafluoride at room temperature. A number of simple compounds, particularly those of xenon have been prepared since then.

Fluorides of Xenon

Xenon forms three different fluorides . XeF_2, XeF_4 and XeF_6.

(a) Xenon Difluoride, Xe F_2

Preparation : (1) By direct interaction of elements (Xe and F_2) in calculated quantities, xenon difluoride is formed. (2) It is prepared quantitatively by interaction of xenon and excess of O_2F_2 at — 118° C.

Physical properties : (1) It is a colourless, crystalline solid. (2) It is less volatile than other fluorides. (3) It melts between 120-140°C. (4) It is stable when pure and dry. It can be stored in a nickel vessel or dry glass vessel. (5) It is soluble in liquid HF without any chemical action.

Chemical properties : (1) It oxidises hydrogen and water.

$$XeF_2 + H_2 \rightarrow Xe + 2HF$$

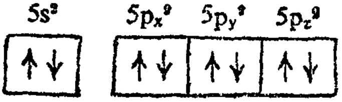
$$2XeF_2 + 2H_2O \rightarrow 2Xe + O_2 + 4HF$$

(2) It is rapidly hydrolysed in aqueous solution of a base

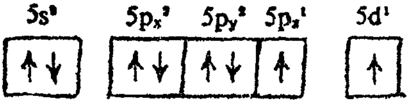
$$2XeF_2 + 4OH^- \rightarrow 2Xe + 4F^- + 2H_2O + O_2$$

(3) It dissolves in molten SbF_6 giving $Xe(SbF_6)_2$

Structure of Xe F_2 : Configuration of Xe.........$5s^2\ 5p^6$



Configuration of Xe in compound XeF_2 $5s^2\ 5p^5\ 5d^1$



As such there are five electron-pairs around xenon in XeF_2. Two of these are involved in Xe-F bonds and the remaining three exist as lone pairs. These five pairs may be

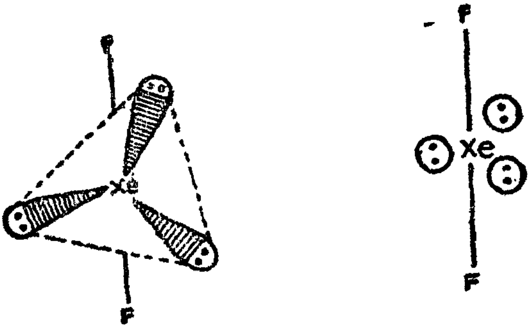


Fig. 58
Xenon difluoride XeF_2

expected to arrange themselves at the corners of a *trigonal* bipyramid. The three equatorial portions are occupied by lone pairs as shown in (Fig. 58)

(b) Xenon Tetrafluoride, XeF_4

Preparation : It is prepared by heating a mixture of xenon and fluorine in the ratio 1 : 5 to 400°C at 6 atmospheric pressures in a nickel container for a few hours and suddenly cooling the vapours.

Physical properties : (1) It is a colourless crystalline solid. (2) It sublimes giving colourless vapours on heating in a current of nitrogen. (3) When pure and dry, it is quite stable. (4) It is stable in liquid HF. (5) It can be stored in a nickel vessel.

Chemical properties : (1) It oxidises iodide to iodine.

$$XeF_4 + 4I^- \rightarrow 2I_2 + 4F^- + Xe$$

(2) It undergoes reduction on treatment with hydrogen.

$$XeF_4 + 2H_2 \rightarrow Xe + 4HF$$

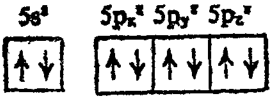
(3) It acts as a fluorinating agent in the following reaction with sulphur tetra fluoride.

$$XeF_4 + 2SF_4 \rightarrow Xe + 2SF_4$$

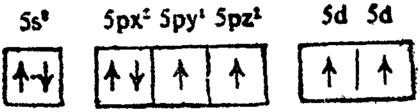
(4) It dissolves in molten SbF_5 to form $Xe(SbF_6)_2$

$$XeF_4 + 2SbF_5 \rightarrow Xe(SbF_6)_2 + F_2$$

Structure of XeF_4 : Configuration of Xe......$5s^2 5p^6$



Configuration of Xe in XeF_4... $5s^2\ 5p^4\ 5d^2$



Hence, in XeF_4 there are six electron pairs around xenon (two d orbitals are used) two of which are lone pairs. Considerations of electron pair repulsion suggest an octahedral geometry with lone pairs projecting along one axis. The fluorine atoms occupy the corners of a square plane having xenon at the centre.

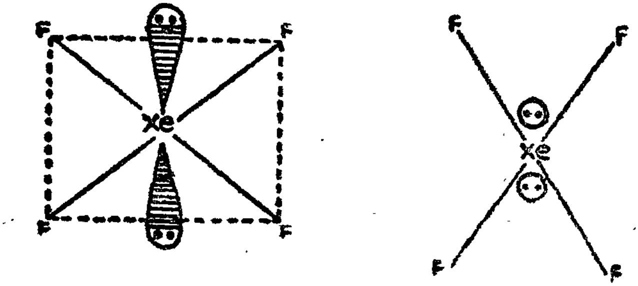


Fig. 59
Xenon Tetrafluoride

(c) Xenon hexafluoride, XeF_6.

Preparation : (1) It is prepared by heating xenon with a large excess of fluorine at 300° C.

$$Xe + 3F_2 \longrightarrow XeF_4 \qquad (F_2/\ Xe\ \text{ratio} = 20)$$

(2) It is also prepared by treating xenon tetrafluoride and dioxygen difluoride at − 130° C.

$$XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$$

Physical properties . (1) At room temperature it is a white solid. (2) It melts at 46°, and its vapour is pale yellow. (3) It is stable at room temperature and hence can be stored in nickel containers indefinitely. It cannot be stored in glass vessels as it reacts with silica.

$$2XeF_4 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$$

Chemical properties : (1) Unlike XeF_2 and XeF_4, it dissolves in liquid HF undergoing a chemical reaction.

$$XeF_4 + HF \rightleftharpoons XeF_5^+ + HF_2^-$$

(2) It undergoes reduction with hydrogen.

$$XeF_6 + 3H_2 \rightarrow Xe + 6\ HF$$

(3) Except Li F, other alkali metal fluorides react with XeF_6. Rubidium and Caesium fluorides form heptafluoro xenates (XeF_6) dissolves in molten rubidium fluoride forming rubidium heptafluoro xenate.

$$XeF_6 + RbF \rightarrow RbXeF_7$$

This decomposes to give octafluoroxenate which is stable.

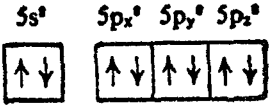
$$2\ Rb\ Xe\ F_7 \xrightarrow{\Delta} Xe\ F_6 + Rb_2\ Xe\ F_8$$

(4) On partial hydrolysis, it forms the oxy flouride $XeOF_4$

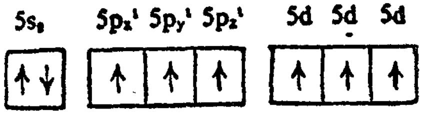
$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$
$$XeOF_4 + H_2O \rightarrow XeO_2F_2 + 2HF$$
$$XeO_2F_2 + H_2O \rightarrow XeO_3 + 2HF$$

Structure :

Configuration of Xe : $5s^2\ 5p^6$



Configuration of Xe in Xe F_6 : $5s^2\ 5p^3 5d^3$



According to valence bond theory, the seven electron airs (one lone pair) around Xenon may be expected to span ap pentagonal bipyramid with one lone pair of electrons (i.e) a distorted octahedron.

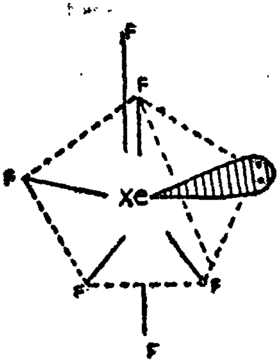


Fig. 60
Xenon hexafluoride

Xenon oxides

Xenon forms two oxides namely xenon trioxide and xenon tetroxide.

(a) Xenon Trioxide XeO_3

Preparation : When XeF_4 or XeF_6 is hydrolysed. It is formed in solution which on evaporation leaves behind a white solid XeO_3.

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

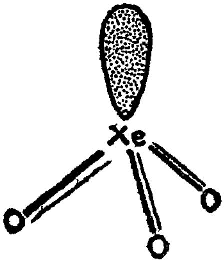


Fig. 61
Xenon trioxide

Physical properties : (1) It is a white non-volatile compound. It is stable in aqueous acid solution. (2) It is explosive when dry.

Chemical properties : (1) In aqueous solution it is weakly acidic and is known as **xenic acid** (H_2XeO_4). Xenic acid is a powerful oxidising agent comparable to O_3. The only by-product of its action is xenon gas.

Structure : It has a trigonal pyramid structure with a non-bonding electron pair at the apex.

(b) Xenon Tetroxide : Xe O_4

Preparation : It is formed when sodium perxenate (Na_4 XeO_4 $6H_2O$) reacts with concentrated sulphuric acid.

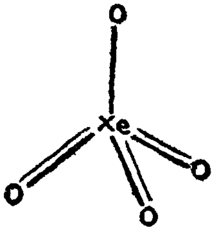


Fig. 62
Xenon tetroxide

Properties : It is an unstable gas at room temperature and is a yellow solid at low temperature. It explodes even at as a low temperature as –40°C.

Structure : XeO_4 has a regular tetrahedral structure with the four oxygen atoms occupying the four corners with Xe at the centre of the tetrahedron.

Impact of inert gases on chemical theory

(1) The discovery of inert gases and their incorporation in the periodic table has clearly explained the position of the most electronegative elements (halogens of VII A group) and the most electropositive elements (alkali metals IA group).

(2) The discovery has led to the formulation of the modern electronic theory of valency. (3) The chemical identification of thorium and actinium emanations as radon contributed to the discovery of isotopes. (4) The alpha particle evolved by a radioactive substance is nothing but a dipositive helium ion. This has influenced our views on radioactivity and atomic structure.

QUESTIONS

PART A

1. The zero group elements of the periodic table form a bridge between———in group VII B and ——— alkali metals in Group IA.

2. The advantage of using He over H_2 in airships is its ——— nature.

3. To prevent the ——— of tungsten filament of electric bulbs ——— gas is used.

4. XeF_2 is a ——— molecule.

5. In the extraction of ———, He is used to give an ——— atmosphere.

6. Match the following :

Symbol	**Electronic Structure**
(a) He	(1) $2s^2 2p^6$
(b) Ne	(2) $1s^2$
(c) Ar	(3) $3s^2\ 3p^6$
(d) Kr	(4) $5d^{10}\ 6s^2\ 6p^6$
(e) Xe	(5) $3d^{10}\ 4s^2\ 4p^6$
(f) Rn	(6) $4d^{10}\ 5s^2\ 5p^6$

7.

Compound	**Structure**
(a) XeF_1	distorted octahedral
(b) XeF_4	linear
(c) XeF_6	square planar

8. The radioactive noble gas is (a) Krypton (q) Xenon (c) Radon (d) Helium.

9. Noble gases are isolated from liquid air by (a) fractional crystallization (b) fractional distillation (c) steam distillation.

10. The noble gas elements exist as single atoms because (a) electron affinity is zero (b) very high electron affinity (c) low ionisation potential.

PART B

11. Why are the noble gases placed in the zero group of the periodic table ?

12. Give the commercial uses of helium and neon.

13. Give the electronic configurations of noble gas elements.

PART C

14. Give a brief history of the discovery of inert gases.

15. Describe the methods employed for the separation of rare gases in the atmosphere.

16. Give an account of the preparation and properties of xenon compounds with fluorine and oxygen.

17. Discuss the orbital structure of XeF_2, XeF_4 and XeF_6.

18. Discuss the position of inert gas elements in the periodic table.

CHAPTER IV

THE HALOGENS

The sub-group B of the group VII of the periodic classification comprises the elements fluorine, chlorine, bromine and iodine. These elements combine with metals to form salts resembling sea-salt. Hence they are called the **halogens,** meaning sea-salt producers. They form a remarkable family of elements and exhibit a gradation of physical properties and chemical activity. They are the most electronegative elements of the periodic table (i.e) they have a great tendency to gain electrons.

FLUORINE

Symbol : F **Valency** : 1

Molecular Formula : F_2

Atomic Weight : 19 **Atomic Number** : 9.

Occurrence : Fluorine is too active to occur in nature in the free state. It occurs in the combined state in the following minerals : Fluoraspar (fluorite) CaF_2 ; Cryolite Na_3AlF_6 and fluorapatite CaF_2, $3Ca_3(PO_4)_2$. It also occurs in traces in sea water and some mineral springs. The bones and teeth of animals also contain compounds of fluorine. Fluorine was prepared in 1886 by the French chemist, **Moissan.**

Isolation of fluorine · The isolation of fluorine was for a long time one of the master problems in inorgranic chemistry. Chlorine, bromine and iodine can be prepared by the oxidation of the respective hydrogen halide. All attempts of isolation of fluorine failed for the following reasons. (1) Hydrogen fluoride is so stable a compound that it cannot be oxidised to give fluorine by any known oxidising agent. (2) When an aqueous solution of hydrofluoric acid is electrolysed, it is only the water present in the solution that gets electrolysed yielding hydrogen and oxygen. On the other hand, if anhydrous HF is used for electrolysis, it is found to be a very poor conductor of electricity. (3) Due to high reactivity of fluorine, it was difficult to find a suitable vessel and electrodes to carry out the electrolysis as it attacked almost all metals. Finally, it was the French Chemist, Henry Moissan, who succeeded in isolating fluorine by the electrolysis of solution of potassium hydrogen fluoride in anhydrous hydrogen fluoride.

(a) **Moissan's method** : As anhydrous HF does not conduct electricity, it was rendered conducting by dissolving it in potassium hydrogen fluoride. The electrolysis is carried out in a U-tube made of platinum-iridium alloy which is less attacked by fluorine than platinum alone. It is fitted with stoppers made of fluorspar and through which are passed electrodes made of an alloy of platinum and iridium. During electrolysis, the electrolytic cell is immersed in a bath of boiling methyl chloride at —23°C (since anhydrous HF has a boiling point of about —19°C). Hydrogen is evolved at the cathode and fluorine at the anode

$$KHF_2 \rightarrow KF + HF$$

$$KF \rightarrow K^+ + F^-$$

Cathode : $K^+ + e^- \rightarrow K$

$$2K + 2HF \rightarrow 2KF + H_2$$

Anode : $F^- - e^- \rightarrow F$

$$F + F \rightarrow F_2$$

The fluorine evolved at the anode is then allowed to pass through a platinum spiral tube, cooled by boiling methyl chloride where the HF coming along with fluorine will condense. The last trace of HF is removed by passing it through platinum vessel packed with fused NaF.

$$NaF + HF \rightarrow NaHF_2$$

The gas is finally collected in a dry platinum jar by upward displacement of air. This method is not very efficient and is expensive. It can be better prepared by the following modern method :

(b) Dennis, Veeder and Rochow Method :—Fluorine is now-a days more easily prepared by electrolysing fused potassium hydrogen fluoride KHF_2. The apparatus consists of a heavy V-shapped copper tube fitted with copper caps into which graphite electrodes are introduced by means of non-conducting materials (Fig. 63). KHF_2 is placed in the tube which is heated. On passing electric current, fluorine is liberated at the anode. It will be contaminated with HF which is removed by passing the fluorine through U-tubes made of copper and containing anhydrous sodium fluoride. It is finally collected in dry platinum jars by upward displacement of air. (Copper also is attacked by fluorine, forming a surface crust of cupric fluoride which protects the tube from being further attacked.)

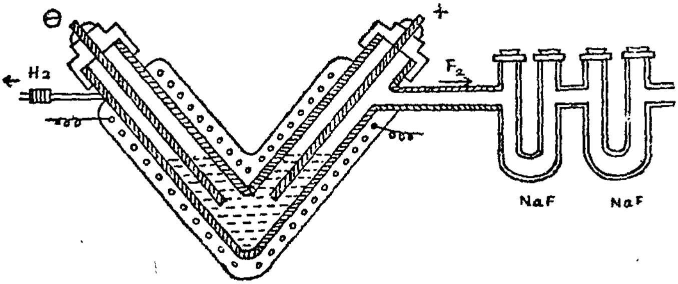


Fig. 63
Isolation of Fluorine

$$KHF_2 \rightarrow KF + HF$$

Anode : $2KF \rightarrow 2K + F_2$

Cathode : $2K + 2HF \rightarrow 2KF + H_2$

Physical properties :—(1) Fluorine is a pale greenish yellow gas. (2) It has a very penetrating odour. (3) It is heavier than air. (4) The solubility of fluorine in water cannot be determined, since fluorine reacts violently with the water and decomposes it. (5) It can be liquefied and solidified under suitable conditions of temperature and pressure.

Chemical properties : Fluorine is the most active member of the halogen family, and forms compounds with most of the elements. The reaction is violent and explosive in many cases.

(1) **Affinity for hydrogen** : It has a great affinity for hydrogen with which it combines even in the dark and even at a low temperature with explosive violence. It also reacts with hydrogen present in other compounds.

$$H_2 + F_2 \rightarrow 2HF$$

(2) **Action on metals** : All metals are attacked by fluorine. Alkali and alkaline earth metals catch fire spontaneously in fluorine while certain others require warming.

$$2Na + F_2 \rightarrow 2NAF$$

(3) **Action on non-metals** : Charcoal burns in fluorine forming the tetrafluoride.

$$C + 2F_2 \rightarrow CF$$

Fluorine has no action on silicon, phosporus, nitrogen, oxygen and sulphur.

(4) **Reaction with water** · Fluorine attacks water, forming ozone and oxygen.

$$2F_2 + 2H_2O \rightarrow 4HF + O_2$$
$$3F_2 + 3H_2O \rightarrow 6HF + O_3$$

(5) **Displacement Reaction** : Being the most powerful electronegative element, it can displace the other halogens from their compounds.

$$2KX + F_2 \rightarrow 2KF + X_2 \; [X = Cl, Br, I]$$

(6) **Action of alkalis** : With dilute alkali (2% NaOH), fluorine monoxide is formed, while with concentrated alkali, oxygen is evolved.

$$2NaOH + 2F_2 \rightarrow 2NaF + F_2O \uparrow + H_2O$$
$$4NaOH + 2F_2 \rightarrow 4NaF + O_2 \uparrow + 2H_2O$$

(7) **As an oxidiser** : It is a powerful oxidising agent. It oxidises chlorate to perchlorate.

$$KClO_3 + F_2 + H_2O \rightarrow KClO_4 + 2HF$$

(8) **Action of organic compounds** : Organic compounds like alcohol, ether catch fire immediately in the gas. Direct fluorination of organic compounds is difficult. However, hydrocarbons like methane undergo fluorination in an atmosphere of nitrogen and in the presence of catalysts.

(9) **Interhalogen compounds formation** : It forms variety of interhalogen compounds with other halogens.

$$Br_2 + 3F_2 \rightarrow 2BrF_3$$
$$I_2 + 5F_2 \rightarrow 2\,IF_5$$

Uses : (1) Fluorine is used in the manufacture of a series of compounds known as **freons**. These non-toxic, non-combustible and volatile liquids are used as refrigerants in refrigerators, deep-freezers and air-conditioners. The most common freon is known as **difluorodichloromethane** CF_2Cl_2. (2) Calcium fluoride is used as a flux in metallurgy. (3) Sodium fluoride is used as a preservative to prevent fermentation and also for preventing dental caries. (4) Sulphur hexafluoride is used as an insulating material in high voltage equipment. (5) **Teflon** (polytetrafluoroethylene) is used as container to store hydrofluoric acid. (6) Uranium hexafluoride is used in the separation of U-235 from U-238.

Differences from other halogens

(1) Fluorine attacks almost all metals, and combines directly even with carbon forming the tetrafluoride.

(2) It reacts with water forming HF and oxygen, while the other halogens form the corresponding hypohalous acids.

(3) Fluorine decomposes cold dilute alkalis liberating fluorine monoxide and with concentrated alkali, oxygen is liberated. Under similar conditions, the other halogens will give rise to the hypohalites and halates respectively.

(4) It has the greatest affinity for hydrogen forming HF, which is associated due to hydrogen bonding. Hydrofluoric acid is a weak acid whereas the other hydrohalic acids are strong acids.

(5) It differs markedly from the other halogens in that it can form two types of salts with metals NaF and $NaHF_2$.

(6) Calcium fluoride is insoluble in water, while the other calcium halides are soluble.

(7) Silver fluoride is soluble in water, while the other silver halides are insoluble.

(8) Being strongly electronegative it can have only a negative oxidation state (oxidation no -1), while the other halogens can have negative as well as positive oxidation states.

(9) Fluorine cannot be prepared by the methods adopted for the preparation of other halogens.

(10) Fluorine attacks glass, while others do not.

(11) Oxyacids of fluorine are unknown, while the other halogens give rise to their oxyacids.

Hydrogen Fluoride

Molecular Formula : HF Molecular Weight : 20

Occurrence : It does not occur free in nature. In the combined state, it occurs as fluorspar (CaF_2) and cryolite (Na_3AlF_6).

Preparation : It is prepared by the action of concentrated sulphuric acid or metallic fluorides.

Aqueous hydrofluoric acid is prepared by warming a mixture of powdered fluorspar (CaF_2) and concentrated sulphuric acid in a lead retort, when HF is given off. The gas evolved is passed into water contained in lead bottles. We get the aqueous acid. It is now sent into the market in polyethylene bottles.

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

Pure and anhydrous hydrofluoric acid is prepared by heating potassium hydrogen fluoride in a platinum retort. The hydrogen fluoride evolved is condensed to liquid in the platinum U tube.

$$KHF_2 \rightarrow K\ F + HF_2$$

Physical properties : Anhydrous hydrofluoric acid is a gas at the ordinary temperature which condenses to a colourless fuming liquid at 19·5°C. It is soluble in water.

Chemical properties : Hydrogen fluoride is very poisonous. It is highly corrosive and attacks many metals as well as organic substances like cotton, silk and gum.

The metal potassium and sodium dissolve in the pure acid forming fluorides and giving off hydrogen. Silver and copper dissolve in the aqueous acid. The acid corrodes glass and porcelain reacting with the silica present to produce silicon tetrafluoride SiF_4 and water.

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

This is the reason why the aqueous solution of the acid cannot be kept in glass bottles and polyethylene bottles are used.

Use : The acid is very extensively used for etching glass.

Etching on glass : The glass article is first covered with a film of wax. The design to be etched is now drawn on the waxed surface and it is then exposed to the action of the acid. The glass is very soon etched. The wax is finally washed off with turpentine.

CHLORINE

Symbol : Cl **Molecular Formula :** Cl_2 **Valency :** 1

Atomic Weight : 35·46 **Atomic Number :** 17

Occurrence :—Chlorine never occurs free in nature on account of its great activity, but it is found in combination with other elements in immense quantities. (1) Common salt, NaCl, is present in sea water, lakes and also in certain rocks. (2) Carnallite $KCl.MgCl_2.6H_2O$.

Preparation of chlorine :—(1) When a strong aqueous solution of hydrochloric acid is electrolysed, hydrogen is liberated at the cathode and chlorine at the anode.

(2) **Laboratory Preparation :**—Chlorine is commonly prepared in the laboratory by the oxidation of hydrochloric acid by manganese dioxide or potassium permanganate. Crystals of potassium permanganate are placed in a conical flask fitted with a dropping funnel and a delivery tube. Concentrated hydrochloric acid, taken in the dropping funnel, is dropped on the potassium permanganate. Chlorine gas is evolved without heating. It contains hydrogen chloride and water vapour as impurities. To get it free from these impurities, it is passed through water contained in a wash-bottle to dissolve hydrogen

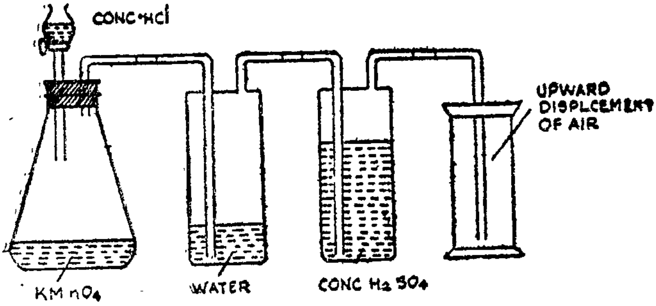


Fig. 64
Preparation of Chlorine

chloride vapour, and through concentrated sulphuric acid in another wash bottle to remove water vapour. It is finally collected by the upward displacement of air. In this reaction, $KMnO_4$ or MnO_2 serves as an oxidising agent and converts hydrogen of the hydrogen chloride into water.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$
$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2\uparrow$$

Chlorine is also made in the laboratory by heating a mixture of sodium chloride and manganese dioxide with concentrated sulphuric acid. Sulphuric acid liberates hydrochloric acid from sodium chloride which is then oxidised by MnO_2 to chlorine.

$$2NaCl + 2H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2\uparrow$$

Commercial production : Electrolysis of brine, a water solution of common salt (NaCl), using graphite anode and mercury cathode produces most of our industrial chlorine. Chlorine is liberated at the anode. Sodium amalgam formed at the cathode reacts with water to form sodium hydroxide and hydrogen.

(1) **Electrochemical** : $NaCl \rightleftharpoons Na^+ + Cl^-$
At the cathode : $2Na^+ + 2e^- \rightarrow 2Na$
At the anode : $2Cl^- - 2e^- \rightarrow Cl_2$

(2) **Chemical** : $2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$

The chlorine is liquefied and stored in steel cylinders,

Physical properties : (1) At ordinary room temperatures chlorine is a greenish yellow gas with a choking odour. (2) It is about 2·5 times as heavy as air and is soluble in cold water. It is because of these properties that chlorine is collected by the upward displacement of air. (3) Chlorine can be easily liquefied. (4) It is poisonous.

Chemical properties : (1) **Combustibility :** Although chlorine does not burn, it supports the combustion of many metals and non-metals.

(2) **Action of metals :** Sodium, ignited in air, continues to burn in a jar of chlorine forming sodium chloride. When warm powdered antimony is sprinkled into a jar of chlorine, it catches fire giving off sparks forming antimony trichloride.

$$2Na + Cl_2 \rightarrow 2NaCl$$
$$2Sb + 3Cl_2 \rightarrow 2SbCl_3$$

(3) **Action of non-metals :** On exposure to sun-light, chlorine and hydrogen unite with explosion to form hydrogen chloride.

$$H_2 + Cl_2 \rightarrow 2HCl$$

White phosphorus burns in chlorine forming phosphorus tri-and penta-chlorides.

$$2P + 3Cl_2 \rightarrow 2PCl_3$$
$$2P + 5Cl_2 \rightarrow 2PCl_5$$

(4) **Oxidising property :** Chlorine possesses oxidising properties in the presence of moisture on account of the ease with which it liberates nascent oxygen from water. It oxidises (1) hydrogen sulphide to sulphur (2) sulphur dioxide to sulphuric acid (3) acidified solution of iron (II) sulphate to iron (III) sulphate. In all these cases, chlorine is reduced to hydrogen chloride.

$$H_2 + Cl_2 \rightarrow 2HCl + S\downarrow$$
$$Cl_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$$
$$2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$$

(5) **Bleaching action:** Chlorine bleaches vegetable colours in the moist condition. Coloured flowers and leaves are made colourless. If the chlorine is dry, the bleaching action is not shown. Chlorine reacts with water to form hypochlorous acid

and hydrochloric acid. Hypochlorous acid being unstable, it is decomposed into hydrochloric acid and nascent oxygen. Nascent oxygen converts the coloured compound into a colourless compound

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$
$$HOCl \rightarrow HCl + [O]$$

(6) **Reaction with alkalis** : When chlorine is passed through a cold and dilute solution of sodium hydroxide, sodium hypochlorite and sodium chloride are formed.

$$Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O$$

It reacts with hot concentrated solution of sodium hydroxide forming sodium chlorate and sodium chloride.

$$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

(7) **Reaction with slaked lime :** When dry chlorine is passed over dry slaked lime, bleaching powder is formed.

$$Ca(OH)_2 + Cl_2 \rightarrow CaCl\,(OCl) + H_2O$$

(8) **Reaction with ammonia** : With excess of ammonia it reacts giving nitrogen.

$$8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$$

But with excess of chlorine, nitrogen trichloride, an explosive substance is obtained.

$$NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$$

(9) **Reaction with carbon monoxide and sulphur dioxide** : Chlorine combines directly with carbon monoxide and sulphur-dioxide to form carbonyl chloride and sulphuryl chloride respectively.

$$CO + Cl_2 \rightarrow COCl_2$$
$$SO_2 + Cl_2 \rightarrow SO_2Cl_2$$

(10) **Reaction with organic compounds** : Chlorine reacts with organic compounds forming chloro derivatives by substitution or addition reactions.

$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$ (Substitution)
Ethane — Ethyl chloride

$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$ (Addition)
Ethylene — Ethylene dichloride

(11) **Displacement of bromine and iodine :** When chlorine water is added to a solution of potassium bromide, the solution turns yellow due to the liberation of bromine.

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$

Chlorine replaces iodine from potassium iodide solution and the solution turns brown.

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

Test for Chlorine : (1) Chlorine is detected by its greenish-yellow colour, peculiar odour and bleaching properties. It turns moist blue litmus paper red and then bleaches it white. (2) It turns potassium iodide starch paper blue.

Uses of chlorine : (1) Chlorine is used for bleaching cotton, linen fabrics and wood pulp. (2) It is employed in the manufacture of bleaching powder, potassium chlorate, carbon tetrachloride and in the extraction of gold. (3) It is used for sterilisation of drinking water. (4) Chlorine is also used for the manufacture of dyes, drugs, disinfectants and poison gases. (5) Chlorine finds application in the production of synthetic rubber.

HYDROGEN CHLORIDE

Molecular Formula : HCl   Molecular Weight : 36·468

Occurrence : Hydrochloric acid occurs in the gases evolved from volcanoes and in the gastric juice.

Preparation : (1) In the presence of sunlight and a trace of moisture, hydrogen combines with chlorine to form hydrogen chloride with explosive violence.

$$H_2 + Cl_2 \rightarrow 2HCl$$

(2) It is also obtained by the action of water on chlorides of non-metals such as phosphorus.

$$PCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_3 \text{ (Phosphorous acid)}$$
$$PCl_5 + 4H_2O \rightarrow 5HCl + H_3PO_4 \text{ (Phosphoric acid)}$$

(3) Laboratory preparation : Hydrogen chloride gas is prepared in the laboratory by the action of concentrated sulphuric acid on common salt. Common salt is taken in a around-bottomed flask fitted with a cork, through which passes dropping funnel and a delivery tube.

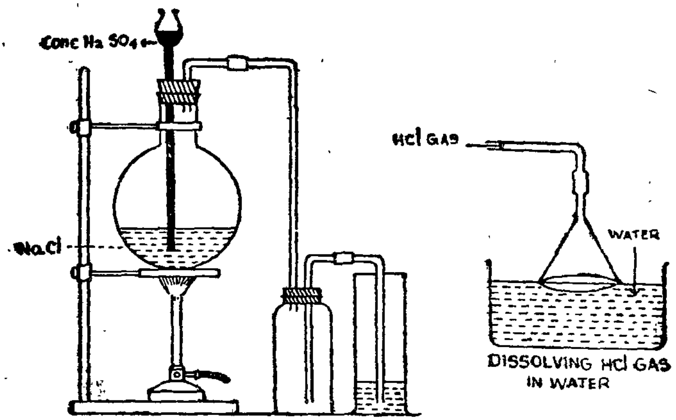


Fig. 65
Preparation of Hydrogen Chloride

Concentrated, sulphuric acid is added to the flask through the funnel. The flask is gently heated on a wire gauze. The hydrogen chloride gas evolved is dried by passing it through a wash bottle containing concentrated sulphuric acid. As the gas is heavier than air, it is collected in dry jars by the upward displacement of air or over mercury.

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$$

Physical properties : (1) Hydrogen chloride is a colourless gas with a pungent odour which affects the membranes of the nose and throat. (2) It is heavier than air. (3) The gas fumes in moist air on account of its extreme solubility in water. The high solubility of the gas is demonstrated by the following experiment. The flask A contains blue litmus solution. The round-bottomed flask B at the top is filled with hydrogen chloride gas. A little air is blown through C to force a little blue litmus solution into the top flask Hydrogen chloride gas dissolves in the solution and a partial vacuum is created. The blue litmus solution rushes into B through the jet tube in the form of a fountain and it turns red due to the acid. (4) It may be liquefied to a colourless liquid at 0°C by applying a pressure of 28 atmospheres. (5) In aqueous solution, it is highly ionised and is a good conductor of electricity. (6) Its aqueous solution is a strong acid and forms a constant-boiling mixture. The solution containing 20-24% of HCl by weight distills over unchanged at 110°C at 760 mm pressure.

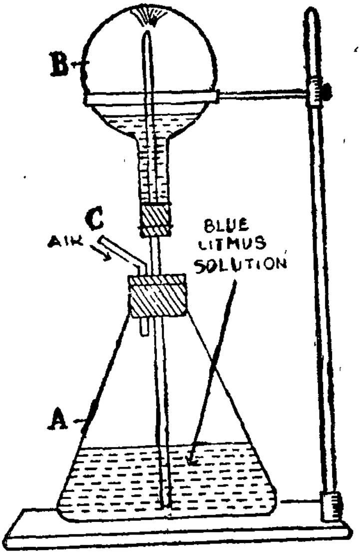


Fig. 66
To show the high solubility of HCl gas in water

Chemical properties : (1) A burning candle is put out in a jar of hydrogen chloride gas and the gas does not catch fire.

It is therefore neither combustible nor a supporter of combustion. But, vigorously burning sodium and potassium continue to burn in it forming metallic chlorides and liberating hydrogen.

$$2Na + 2HCl \rightarrow 2NaCl + H_2 \uparrow$$

(2) **Action of air** :—When a mixture of hydrogen chloride gas and air is passed over heated cupric chloride as a catalyst, hydrogen chloride is oxidised to chlorine. Chlorine may be prepared on a large scale by this method.

$$4HCl + O_2 \rightarrow 2Cl_2 \uparrow + 2H_2O$$

(3) **Action of ammonia** :—In the presence of moisture, it combines with ammonia to form white fumes of ammonium chloride.

$$NH_3 + HCl \rightarrow NH_4Cl$$

(4) With silver nitrate, it gives a white curdy precipitate of silver chloride insoluble in nitric acid but soluble in ammonia. This is employed as a test for the gas.

$$AgNO_3 + HCl \rightarrow AgCl \downarrow + HNO_3$$

HYDROCHLORIC ACID

Preparation : Hydrochloric acid is prepared in the laboratory by dissolving hydrogen chloride gas in water. The gas is prepared as described earlier. It is passedinto an empty flask and then into water. The empty flask guards against any suction of water into the generating flask. The gas is absorbed by the water and hydrochloric acid is obtained. (An inverted funnel may be attached to the end of the delivery tube to prevent back suction. Fig : 65)

Physical properties . (1) Pure hydrochloric acid is a colourless solution. But the yellow colour of commercial acid is due to the presence of iron (III) chloride as an impurity. (2) Concentrated hydrochloric acid has a specific gravity of 1·2. (3) It is a good conductor of electric current. (4) Hydrogen chloride dissolved in water forms a constant-boiling solution. When a strong solution of hydrochloric acid is boiled, hydrogen chloride gas escapes. The solution gets more and more diluted until the concentration of the solution is reduced to 20-24%. On further boiling, the whole solution containing 20-24% of HCl by weight distills over at a temperature of 110°C. On the other hand, when dilute hydrochloric acid is distilled, water escapes and the solution gets more concentrated till it reaches 20-24%. On further heating, the temperature rises to 110°C, when the whole solution distills over unchanged. The liquid having a composition of 20-24% of hydrochloric acid the rest being water boils at 110°C at atmospheric pressure and is called **constant-boiling mixture.**

Chemical properties : (1) Action of metals : Many metals replace hydrogen from hydrochloric acid and the respective chlorides are formed.

$$Mg + 2HCl \rightarrow MgCl_2 + H_2 \uparrow$$
$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2 \uparrow$$

(2) Hydrochloric acid turns blue litmus red. As a molecule of hydrochloric acid contains one replaceable hydrogen atom, it a monobasic acid. It reacts with bases to form salt and water.

$$NaOH + HCl \rightarrow NaCl + H_2O$$

A mixture of concentrated hydrochloric acid and concentrated nitric acid in the ratio 3 : 1 by volume is known as aqua regia, which dissolves noble metals like gold and platinum.

(3) It reacts with carbonates and sulphites, liberating CO_2 and SO_2 respectively.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2 \uparrow$$
$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2 \uparrow$$

(4) It gives a curdy-white precipitate of silver chloride with silver nitrate solution. The precipitate is insoluble in nitric acid, but soluble in ammonium hydroxide.

(5) Hydrochloric acid is oxidised to chlorine by oxidising agents such as MnO_2 and $KMnO_4$.

Uses : (1) Hydrochloric acid is used in the manufacture of chlorides and chlorine. (2) It is used in calico printing and dyeing industry. (3) In the form of aqua regia ($3HCl+HNO_3$) it is used for dissolving noble metals such as gold and platinum. (4) It is used for cleaning iron sheets for 'pickling' before they are galvanised. (5) It is used for extracting glue from bones and for removing scales from the surfaces of metals. (6) It finds use in medicine.

Identification of chlorides: (1) When concentrated sulphuric acid is added to a small quantity of chloride, hydrogen chloride gas is evolved which gives dense white fumes with ammonia. (2) If silver nitrate solution is added to a solution of metallic chloride, a curdy-white precipitate of silver chloride is formed. The precipitate is insoluble in nitric acid but soluble in ammonium hydroxide. HCl also answers this reaction. (3) On treating a solution of metallic chloride with lead nitrate or acetate solution, a white precipitate of lead chloride is formed. When the precipitate is boiled with water, it dissolves to give a clear solution. On cooling, it is reprecipitated.

BROMINE

Symbol : Br. Molecular Formula : Br_2 Valency : 1

Atomic Weight : 80 Atomic Number : 35

Occurrence : Because of its great activity, bromine is not found free in nature. It does however, occur in nature as bromides, chiefly those of sodium, potassium and magnesium. These bromides are found in underground brine lakes, sea water and in salt deposits especially in Stassfurt (Germany).

Laboratory method of preparation : Bromine is prepared in the laboratory by distilling a mixture of potassium or sodium bromide with manganese dioxide and concentrated sulphuric acid in a stoppered retort. The end of this retort is introduced into a small flask kept cooled by means of a stream of water.

Bromine is liberated. It distills over and collects inside the receiver.

$$2KBr + 3H_2SO_4 + MnO_2 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2$$

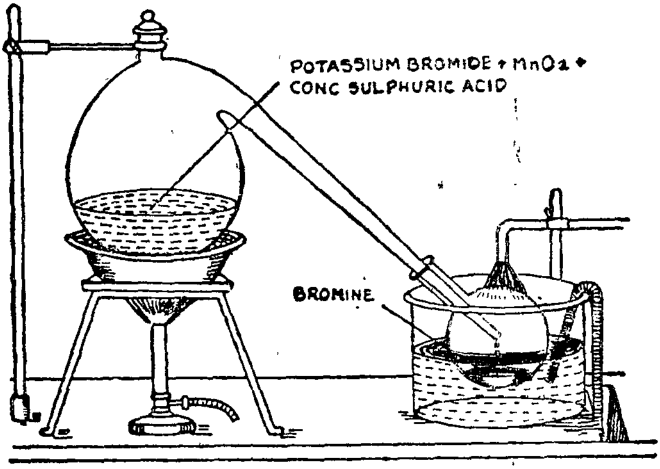


Fig. 67
Laboratory preparation of Bromine

Manufacture of Bromine

(1) **From Carnallite** ($KCl. MgCl_2. 6H_2O$) : Carnallite contains a very small quantity of magnesium bromide as impurity. Bromine of commerce is obtained from this $MgBr_2$. Carnallite is dissolved in water and the solution is concentrated and cooled, when less soluble salts (i.e.) chlorides separate out. The solution (mother liquor) contains magnesium chloride together with magnesium bromide. The hot mother liquor is allowed to slowly percolate down a tower filled with earthenware balls. Chlorine and steam are passed in the tower from the bottom. As chlorine goes up, it reacts with $MgBr_2$ with the formation of $MgCl_2$ and Br_2

$$MgBr_2 + Cl_2 \rightarrow MgCl_2 + Br_2$$

Bromine vapours are carried away with steam, and passed through spiral condensers cooled by water. Bromine condenses.

into a heavy red liquid. The excess of bromine vapours are absorbed in moist iron filings in a separate tower.

$$2Fe + 3Br_2 \rightarrow 2FeBr_3$$

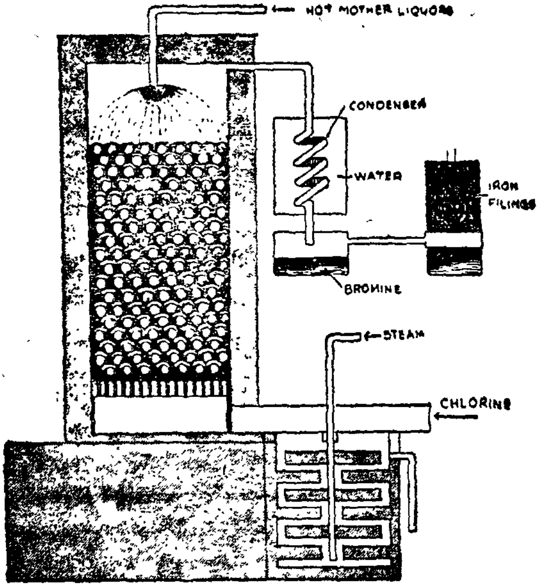


Fig. 68
Manufacture of Bromine from Carnallite

(2) From sea water : Besides other salts in sea water. Bromides are also present in it. Sea water is acidified and chlorinated. Bromine is liberated.

$$Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2$$

The liberated bromine is blown out by a current of air and absorbed in sodium carbonate solution, forming sodium bromide and bromate.

$$3Na_2CO_3 + 3Br_2 \rightarrow 5NaBr + NaBrO_3 + 3CO_2 \uparrow$$

On acidifying the bromide-bromate mixture, the bromine is liberated. It is driven out by steam and condensed to liquid bromine.

$$NaBrO_3 + 5NaBr + 6HCl \rightarrow 6NaCl + 3Br_2 + 3H_2O$$

Physical properties : (1) At the ordinary temperature bromine is a heavy mobile dark-red liquid, possessing an offensive odour. It is the only liquid non-metallic element at ordinary temperatures. (2) It freezes into a dark-red solid. (3) It causes blisters on the skin. (4) It is sparingly soluble in water but readily dissolves in organic solvents like carbon disulphide and ether.

Chemical properties : (1) **Reaction with water** : It reacts with liberation of oxygen.

$$2Br_2 + 2H_2O \rightarrow 4HBr + O_2$$

(2) **Reaction with other elements** : Bromide reacts with the elements P, As, Sb, H_2, Hg and Cu to form bromides

$$2P + 3Br_2 \rightarrow 2PBr_3$$
$$2P + 5Br_2 \rightarrow 2PBr_5$$
$$Hg + Br_2 \rightarrow HgBr_2$$
$$H_2 + Br_2 \rightarrow 2HBr$$

(3) **Reaction with iodides** : Bromine liberates iodine from iodides.

$$2KI + Br_2 \rightarrow 2KBr + I_2$$

(4) **Oxidising property** : Bromine, like chlorine, liberates oxygen in the presence of water with the liberation of nascent oxygen. The nascent oxygen oxidises the compounds.

(a) Oxidises hydrogen sulphide to sulphur
$$Br_2 + H_2S \rightarrow 2HBr + S \downarrow$$

(b) Oxidises sulphur dioxide to sulphuric acid
$$Br_2 + 2H_2O + SO_2 \rightarrow H_2SO_4 + 2HBr.$$

(c) Oxidises sodium sulphite and sodium thiosulphate to sodium sulphate.
$$Na_2SO_3 + Br_2 + H_2O \rightarrow Na_2SO_4 + 2HBr$$
$$Na_2S_2O_3 + Br_2 + H_2O \rightarrow Na_2SO_4 + 2HBr + S \downarrow$$

(5) **Bleaching agent :** It is a bleaching agent. It bleaches litmus solution.

(6) **Reaction with alkalis :** Bromine reacts with alkalis in the same manner as chlorine reacts.

$2NaOH + Br_2 \rightarrow NaBr + NaBrO + H_2O$
(cold and dilute) Sodium + Sodium
bromide hypobromite

$6NaOH + 3Br_2 \rightarrow 5NaBr + NaBrO_3 + 3H_2O$
(hot and conc) (Sodium
bromate)

(7) **Action on ammonia :** Nitrogen gas is evolved

$8NH_3 + 3Br_2 \rightarrow N_2 + 6NH_4Br$

(8) **Reaction with organic compounds :** Saturated and unsaturated organic compounds react with bromine forming substitution and addition products, respectively

$C_2H_6 + Br_2 \rightarrow C_2H_5Br + HBr$ (Substitution)
Ethane Ethyl
bromide

$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$ (Addition)
(Ethylene) Ethylene
dibromide

Test for bromine : (1) It can be recognised by its deep-red colour and irritating odour. (2) It turns starch paste yellow. (3) It dissolves in carbon disulphide giving brown solution.

Uses : (1) It is used in the preparation of bromides, used in medicine and in photography. (2) It is used in the preparation of dyes and other important compounds. (3) It is used as an oxidising agent. (4) It is used as a disinfectant and as a germicide. (5) Xylyl bromide is used as a tear gas.

HYDROGEN BROMIDE

Formula : HBr Molecular Weight : **81**

Laboratory preparation : Hydrogn bromide gas is most conveniently prepared by the action of bromine on a mixture of red phosphorus and water.

The bromine first combines with phosphorus to form the tri-and penta-bromides of phosphorus which are at once decomposed by water.

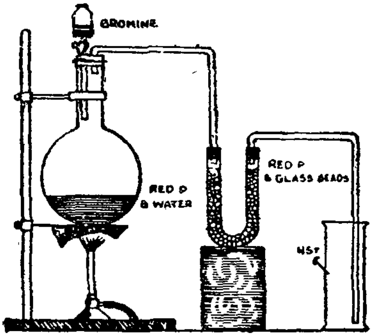


Fig. 69
Preparation of HBr

$2P + 3Br_2 \rightarrow 2Br_3$
$2P + 5Br_2 \rightarrow 2PBr_5$
$PBr_3 + 3H_2O \rightarrow H_3PO_3 + 3HBr$
$PBr_5 + 4H_2O \rightarrow H_8PO_4 + 5HBr$

About 20 gm of red phosphorus and 40 ml of water are placed in a flask fitted with a cork, through which passes a dropping funnel and a delivery tube. The delivery tube is connected to a U-tube containing glass beads smeared with a paste of red P and water. Bromine is poured into the funnel and is added to the flask drop by drop. Hydrogen bromide formed escapes through the delivery tube together with traces of bromine vapour. The bromine is converted into the tribromide by the phosphorus in the U-tube and is decomposed by water there to hydrogen bromide. The gas is collected in dry jars by the upward displacement of air.

Synthetic method : When a mixture of hydrogen and bromine vapour is passed through a heated tube containing either finely divided platinum or platinised asbestos, hydrogen bromide is formed.

$H_2 + Br_2 \rightarrow 2HBr$

Hydrodromic Acid

Unlike hydrochloric acid, hydrobromic acid cannot be prepared by the action of concentrated H_2SO_4 on a bromide. Concentrated H_2SO_4 reacts with a bromide giving HBr. This hydrobromic acid is partially oxidised by concentrated H_2SO_4 into free bromine. Sulphur dioxide is also produced.

$$KBr + H_2SO_4 \rightarrow KHSO_4 + 3HBr$$
$$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$$

If phosphoric acid is used instead of concentrated H_4SO_4, we get hydrogen bromide.

$$3KBr + H_3PO_4 \rightarrow K_3PO_4 + 3HBr$$

Aqueous hydrobromic acid : In order to obtain a sample of aqueous HBr (i.e. a solution of HBr in water) hydrogen bromide gas is passed through an empty flask and then into water. We get a solution of hydrogen bromide gas in water (i.e.) hydrobromic acid. An empty flask is put in to prevent back ward suction.

It may be prepared by passing H_2S or SO_2 gas through bromine water till the colour of the solution is discharged. The precipitated sulphur if any is removed and the filtrate is distilled. The distillate is aqueous HBr.

$$H_2S + Br_2 \rightarrow 2HBr + S \downarrow$$
$$SO_2 + Br_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$$

Physical properties : (1) Hydrogen bromide is a heavy colourless gas. (2) It fumes in moist air and possesses a pungent smell. (3) It can be liquefied. (4) It is highly soluble in water and its aqueous solution is a strong acid forming a constant boiling mixture.

Chemical properties : (1) It is neither combustible nor a supporter of combustion.

(2) An aqueous solution of hydrogen bromide gas in water behaves like an acid similar to hydrochloric acid. It turns blue litmus paper red and forms salts with alkalis which

are called bromides. Hydrobromic acid closely resembles hydrochloric acid in properties but is less energetic.

Action of metals : Many metals dissolve in the acid to form their respective bromides.

$$Fe + 2HBr \rightarrow FeBr_2 + H_2 \uparrow$$
$$Sn + 2HBr \rightarrow SnBr_2 + H_2 \uparrow$$

Action of alkali : It reacts with alkali to form the bromide

$$NaOH + HBr \rightarrow NaBr + H_2O.$$

Action of $NaCO_3$: It liberates CO_2 from carbonate

$$Na_2CO_3 + 2HBr \rightarrow 2\,NaBr + H_2O + CO_2 \uparrow$$

(3) **Stability :** Hydrogen bromide is less stable than hydrogen chloride. It is decomposed into its constituent elements when passed through a tube heated to 800°C.

$$2HBr \xrightarrow{\Delta} H_2 + Br_2$$

(4) Chlorine can displace bromine from hydrobromic acid

$$2HBr + Cl_2 \rightarrow 2HCl + Br_2$$

(5) Unlike HCl, hydrogen bromide is oxidised by concentrated sulphuric acid to bromine

$$2HBr + H_2SO_4 \rightarrow 2H_2O + SO_2 + Br_2$$

Uses : Silver bromide and potassium bromide are used in photography and medicine respectively.

Tests for HBr and bromides

(1) On adding silver nitrate solution to hydrobromic acid or a soluble bromide, a yellowish-white precipitate of silver bromide is formed. It is insoluble in concentrated HNO_3. It dissolves in ammonia with difficulty.

$$KBr + AgNO_3 \rightarrow AgBr \downarrow + KNO_3$$

(2) When chlorine water is added to hydrobromic acid or to a solube bromide and the solution is shaken with carbon disulphide, the CS_2 layer turns brown.

(3) When hydrobromic acid or bromide is treated with concentrated H_2SO_4, red vapours of bromine are given off. The addition of MnO_2 and heat will give better result.

IODINE

Symbol : I Molecular Formula : I_2 Valency : I
Atomic Weight : 126·9 Atomic Number : 53

Occurrence : Iodine does not exist free in nature because of its reactivity. But it is widely distributed in the state of combination with some metals. Iodine compounds are found in sea water and in small amounts in plants and animals living in the sea. Iodine is present in cod-liver oil. in the thyroid gland of animals and in many springs. Chile saltpetre (caliche) contains iodine in the form of sodium iodate.

Laboratory preparation : It is similar to the laboratory preparation of bromine and chlorine. It is obtained by heating a mixture of potassium iodide, manganese dioxide and concentrated sulphuric acid in a retort (diagram similar to bromine). Violet vapours of iodine are evolved. They are condensed to a black shining solid in the receiver kept cooled by water.

$$2KI + 3H_2SO_4 + MnO_2 \rightarrow 2KHSO_4 + 2H_2O + I_2 + MnSO_4$$

Manufacture : (1) **From sea-weeds**. Sea-weeds are first collected, dried and burnt in shallow pits at low temperatures. The ash is found to contain 1% of iodine in the form of iodides together with chlorides, sulphates and other impurities. The ash is treated with water and the solution is concentrated in iron pans, when the soluble chlorides and sulphates present in the ash are deposited as crystals which are separated. The mother liquor containing the iodides in solution is mixed with concentrated sulphuric acid and manganese dioxide and heated in iron retorts provided with earthenware receivers called '**aludels**'. Iodine is liberated and it condenses inside the aludels.

$$2NaI + 3H_2SO_4 + MnO_2 \rightarrow I_2 + 2NaHSO_4 + MnSO_4 + 2H_2O$$

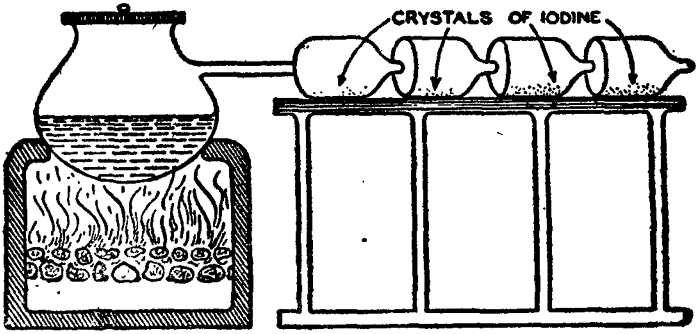


Fig. 70
Manufacture of Iodine from sea-weeds

(2) **From Crude Chile Saltpetre (caliche)**: Nowadays this is the main source of iodine. Caliche contains about 2% of iodine as sodium iodate. The mineral is treated with water and then crystallised when the bulk of sodium nitrate separates out. The sodium iodate, being more soluble, remains in the mother liquor. The mother liquor is treated with the requisite amount of sodium hydrogen sulphite solution which reduces the iodate to iodine. It is washed and pressed into cakes.

Purification of iodine: The chief impurities that are present in crude iodine are chlorine, bromine and cyanogen. It is ground up with solid potassium iodide and the mixture is gently heated in a porcelain dish over a sand bath. The iodine vapours are condensed on the undersurface of a large dish filled with cold water and placed over the porcelain dish.

Physical properties: (1) Iodine is a grey black crystalline solid of metallic lustre. (2) On heating it gives violet vapours with an irritating odour which resembles almost that of chlorine. The solid may sublime going directly from the solid to vapour state. (3) Iodine is not very soluble in water, but easily dissolves in organic solvents (i.e) carbon tetrachloride, chloroform, carbon disulphide. It is also soluble in an aqueous solution of potassium iodide. In alcohol it forms a brown solution called **tincture of iodine**. In carbondi sulphide it forms a violet coloured solution.

Chemical properties : Iodine resembles chlorine in all its chemical properties but it acts less vigorously than chlorine.

(1) Iodine vapour is neither combustible nor ordinarily a supporter of combustion.

(2) **Action of metals** : It combines with mercury, iron filings, zinc and potassium to form the respective iodides,

$$2K + I_2 \rightarrow 2KI_2$$

$$Hg + I_2 \rightarrow HgI_2$$

(3) **Action of non-metals** : Its affinity for hydrogen is much less than that of chlorine. Iodine vapour and hydrogen combine to form hydrogen iodide only when passed through a red hot tube containing the catalyst spongy platinum.

$$H_2 + I_2 \rightarrow 2HI$$

It unites with phosphorus to form tri-and penta-iodides

$$2P + 3I_2 \rightarrow 2PI_3$$

$$2P + 5I_2 \rightarrow 2PI_5$$

It unites with chlorine directly to form iodides of chlorine, ICl and ICl_3. Iodine is not acted upon by oxygen or nitrogen.

(4) **Oxidising property** : It is a less powerful oxidising agent than chlorine. It oxidises

(a) moist hydrogen sulphide to sulphur.

$$H_2S + H_2O + I_2 \rightarrow 2HI + H_2O + S\downarrow$$

(b) Sulphurous acid to sulphuric acid.

$$H_2SO_3 + H_2O + I_2 \rightarrow H_2SO_4 + 2HI$$

(5) **Bleaching action** : It possesses practically no bleaching property.

(6) **Reaction with caustic alkali** : When iodine is treated with a cold dilute solution of NaOH, sodium hypoiodite and sodium iodide are formed. With a hot concentrated solution of NaOH, sodium iodate and sodium iodide are formed.

$$2NaOH + I_2 \rightarrow NaIO + NaI + H_2O$$
$$6NaOH + 3I_2 \rightarrow NaIO_3 + 5NaI + 3H_2O$$

(7) **Reaction with sodium thiosulphate** : Sodium tetrathionate is formed

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4C_6 + 2NaI$$

(8) **Reducing property** : It reduces nitric acid to nitrogen dioxide.

$$10HNO_3 + I_2 \rightarrow 2HIO_3 + 10NO_2\uparrow + 4H_2O$$

(9) **Reaction with organic compounds** It also reacts with organic compounds but very slowly.

Tests for Iodine : (1) Iodine is recognised by the violet colour. (2) It turns starch solution blue. (3) It dissolves in CS_2 forming a violet solution. (4) It produces iodoform (detected by its peculiar smell) when it is treated with alcohol and sodium hydroxide solution.

Uses : (1) It is used in the manufacture of potassium iodide, iodoform and tincture of iodine. (2) It is employed in volumetric analysis for the estimation of sodium thiosulphate. (3) It is used in the manufacture of dyes and drugs. (4) In medicine radio-active iodine (I-131) is used in the diagnosis and treatment of cancer of the thyroid gland. Iodine in the form of tincture of iodine and iodoform (CHI_3) is used as an antiseptic. (5) Silver iodide like silver bromide is employed in making photographic materials.

HHYDROGEN IODIDE

Molecular Formula : **HI** Molecular Weight : 128

Laboratory preparation · Hydrogen iodide is prepared in the laboratory by the action of water on a mixture of red phosphorus and iodine.

$$2P + 3I_2 \rightarrow 2PI_3$$
$$PI_3 + 3H_2O \rightarrow H_3PO_3 + 3HI$$

The mixture of iodine and red phosphorus is taken in a flask fitted with a dropping funnel and a delivery tube. The end of it is connected to a U-tube containing moist red phosphorus to absorb any iodine that may escape from the flask. Now water is dropped very gradually from the dropping funnel over the mixture taken in the flask. Hydrogen iodide gas is evolved. Any iodine vapour coming out with HI is absorbed by moist red P in the U-tube and HI passes on. Hydrogen iodide is collected by the upward displacement of air. The gas may be dried by anhydrous $CaCl_2$ or P_2O_5 and may be collected over mercury very carefully. (Diagram same as that given under hydrogen bromide.)

Aqueous Hydrogen Iodide (1) It is obtained by dissolving the gas in water. The end of the delivery tube is attached to the stem of a funnel dipping just below the surface of water in a beaker. Hydrogen iodide gas dissolves in water in the beaker and aqueous HI is obtained. (2) A solution of HI in water can be prepared by passing H_2S or SO_2 through water containing iodine in suspension

$$H_2S + I_2 \rightarrow 2HI + S \downarrow$$

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$$

The liquid is filtered and the filtrate is distilled. The distillate is aqueous HI.

Physical properties : (1) It is a very heavy colourless gas with penetrating odour. (2) It is extremely soluble in water forming hydroiodic acid. (3) The gas can be easily condensed to a liquid under a pressure of 4 atmospheres and at 0°C.

Chemical properties (1) Hydrogen iodide is neither combustible nor a supporter of combustion.

(2) It is decomposed into hydrogen and iodine when passed through a red-hot tube.

$$2HI \rightarrow H_2 + I_2$$

(3) Solution of hydrogen iodide in water is colourless but turns brown on exposure to sun-light owing to the separation of free iodine

$$4HI + O_2 \rightarrow 2I_2 + 2H_2O$$

(4) **Reducing agent** · On account of its instability and the consequent tendency to produce nascent hydrogen, it acts as a powerful reducing agent.

(a) It reduces sulphuric acid to SO_2 and H_2O getting itself oxidised to iodine. Hence, hydrogen iodide cannot be prepared by the action of concentrated sulphuric acid on an iodide.

$$H_2SO_4 + 2HI \rightarrow I_2 + SO_2 + 2H_2O$$

(b) It reduces chlorine and bromine to the respective hydrogen halides getting itself oxidised to iodine.

$$Cl_2 + 2HI \rightarrow 2HCl + I_2$$
$$Br_2 + 2HI \rightarrow 2HBr + I_2$$

(c) It reduces nitric acid to brown nitrogen dioxide.

$$2HNO_3 + 2HI \rightarrow I_2 + 2NO_2 + 2H_2O$$

(5) With $AgNO_3$ it gives a deep yellow precipitate of silver iodide. This is insoluble in HNO_3 as well as in aqueous ammonia.

Tests for HI and the iodides

(1) Concentrated sulphuric acid liberates iodine from HI or a soluble iodide.

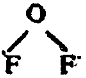
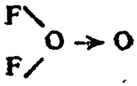
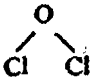
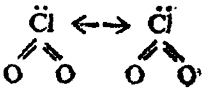
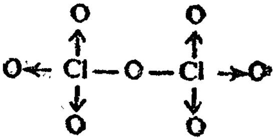
(2) On adding $AgNO_3$ solution to the solution of HI or an iodide in water, a yellow precipitate of AgI insoluble in aqueous ammonia and HNO_3 is formed.

(3) When a solution of HI or an iodide in water is treated with chlorine water and shaken with carbon disulphide,

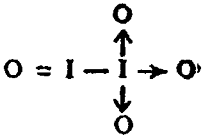
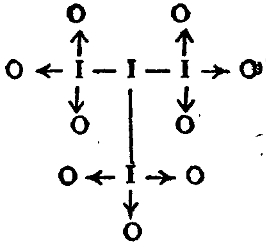
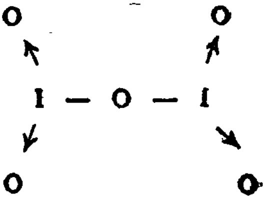
iodine is liberated which turns the carbon disulphide layer violet.

If the above solution is shaken with starch solution, the liberated iodine turns starch solution blue.

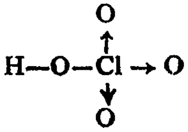
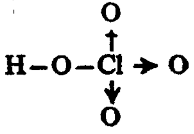
Oxides and oxyacids of Halogens

Oxides		**Molecular Formula**
Fluorine oxides		
(1) Fluorine monoxide	F_2O	
(2) Fluorine dioxide	F_2O_2	
Chlorine Oxides		
(1) Chlorine monoxide	Cl_2O	
(2) Chlorine dioxide	ClO_2	
(3) Chlorine hexoxide	Cl_2O_6	$Cl_2O_6 \rightleftharpoons 2ClO_2$
(4) Chlorine heptoxide	Cl_2O_7	
Bromine Oxides		
(1) Bromine monoxide	Br_2O	
(2) Bromine dioxide	BrO_2	
(3) Bromine octoxide	Br_3O_8	

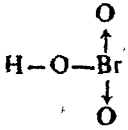
Iodine Oxides

(1) Iodine dioxide	I_2O_4	
(2) Iodine iodate	$(II\ O_3)_3$	
(3) Iodine pentoxide	I_2O_5	

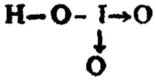
Fluorine forms no oxyacids. Chlorine, bromine and iodine form four series of oxyacids with formulae HXO, HXO_2, HXO_3 and HXO_4. They are known only in solution or as salts.

1. Oxyacids of chlorine	**Formula**	
(1) Hypochlorous acid	HOCl	H–O–Cl
(2) Chlorous acid	$HClO_2$	H–O–Cl = O
(3) Chloric acid	$HClO_3$	
(4) Perchloric acid	$HClO_4$	

2. Oxyacids of bromine

(1)	Hypobromous acid	$HOBr$	$H-O-Br$
(2)	Bromous acid	$HBrO_2$	$H-O-Br=O$
(3)	Bromic acid	$HBrO_3$	 $H-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{Br}}$

3. Oxyacids of iodine

(1)	Hypoiodous acid	HIO	$H-O-I$
(2)	Iodic acid	HIO_3	 $H-O-\underset{\underset{O}{\downarrow}}{I}\rightarrow O$
(3)	Paraperiodic acid		H_5IO_6

Interhalogen Compounds

The binary covalent compounds of halogens with one another called **interhalogen compounds**. The actual product obtained depends on the relative concentrations of the reacting halogens. They are of four types, i.e. AB, AB_3, AB_5 and AB_7.

Type	**Name**	**Molecular Formula**
AB	Chlorine monofluoride	ClF
	Bromine monofluoride	BrF
	Bromine monochloride	$BrCl$
	Iodine monochloride	ICl
	Iodine monobromide	IBr
AB_3	Chlorine trifluoride	ClF_3
	Bromine trifluoride	BrF_3
	Iodine trichloride	ICl_3
AB_5	Bromine pentafluoride	BrF_5
	Iodine pentafluoride	IF_5
AB_7	Iodine heptafluoride	IF_7

Halogen Family

The elements fluorine, chlorine, bromine and iodine (group VII-a) form a remarkable family of elements. They combine with metals to form salts, resembling sea-salt. Hence, they are called the **halogens,** meaning sea-salt producers The fluorides, chlorides, bromides and iodides are called the **halides.** These elements have strong resemblances among themselves, and they exhibit a gradation in their properties with increasing atomic weight

Points of resemblances among the Halogens

(1) **Occurrence** They do not occur in nature in the free state. They occur only in the form of compounds as halides.

(2) **Preparation** Except fluorine they may be all prepared by a similar process. They are prepared in the laboratory by treating the metallic halide with concentrated H_2SO_4 and an oxidising agent such as MnO_2 Fluorine is prepared by a special electrolytic method.

$$2KX+3H_2SO_4+MnO_2 \rightarrow 2KHSO_4+MnSO_4+2H_2O+X_2\uparrow$$

$$(X = Cl, Br, I)$$

(3) **Physical properties** Fluorine and chlorine are gases at ordinary temperature Bromine is a liquid. Iodine is a solid. Fluorine is light-yellow, chlorine is greenish-yellow, bromine is dark-red and iodine is violet in colour. They possess pungent and irritating odour They are heavier than air

(4) **Valency** The common valency of the group is—1 As their atoms have 7 electrons in their outermost orbit, they have a tendency to acquire another electron to give the atom a stable structure.

(5) **Atomicity** . All of them have two atoms in their molecules, Hence, their atomicity is two.

(6) **Reaction with hydrogen** : All the halogens combine directly with hydrogen to form hydrogen halides. Fluorine combines with hydrogen even in the dark and at low temperatures. Chlorine combines in the presence of sun light, bromine only on heating and iodine combines with hydrogen when heated in the presence of a catalyst

$H_2 + F_2 \rightarrow 2HF$

$H_2 + Br_2 \rightarrow 2HBr$

$H_2 + I_2 \rightarrow 2HI$

(7) **Displacement** . Fluorine displaces all the other halogens from their halide. Chlorine displaces bromine from bromide and iodine from iodide. Bromine displaces iodine from the iodide.

$2KCl + F_2 \rightarrow 2KF + Cl_2$

$2KBr + Cl_2 \rightarrow 2KCl + Br_2$

$2KI + Cl_2 \rightarrow 2KCl + I_2$

$2KI + Br_2 \rightarrow 2KBr + I_2$

(8) **Reaction with metals** : All the halogens combine with metals to form metallic halides.

$2Na + Cl_2 \rightarrow 2\,NaCl$

(9)**Reaction with non-metals** : Many non-metals combine wite halogens to form non-metallic halides.

$2P + 3Br_2 \rightarrow 2PBr_3$

$2P + 5Br_2 \rightarrow 2PBr_5$.

Properties showing a gradual change in the properties of chlorine, bromine and iodine with increasing atomic weights are given in the following tabular statement :

Properties of the Halogens

	Property	Fluorine	Chloride	Bromine	Iodine
1.	Symbol	F	Cl	Br	I
2.	Valency	1	1	1	1
3.	Atomic weight	19	35.5	80	127
4.	Atomic number	9 (2, 7)	17 (2,8,7)	35 (2,8,18,7)	53 (2,8,18,18,7)
5.	Physical state	Gas	Gas	Liquid	Solid
6.	Colour of vapour	Pale greenish-yellow	Greenish-yellow	Brownish-red	Violet
7.	Odour	Peculiar irritating odour	Pungent and irritating odour	Smell like that of Cl_2 but more irritating to nose and throat	Smell like that of Cl_2 and intensely irritating to eyes and nose.
8.	Solubility in water	Decomposes water	Fairly soluble	Less soluble	Sparingly soluble
9.	Heaviness or specific gravity	Slightly heavier than air	$2\frac{1}{2}$ times as heavy as air	Specific gravity 3.19	Specific gravity 4.9
10.	Bleaching action	Decomposes organic bodies	Readily bleaches vegetable colouring matter	Bleaches slowly	Slight bleaching action
11.	Reaction with hydrogen	Unites readily with hydrogen in the dark with explosion $H_2 + F_2 \rightarrow 2HF$	Unites readily with H_2 in sunlight with explosion $H_2 + Cl_2 \rightarrow 2HCl$	Unites with H_2 on heating $H_2 + Br_2 \rightarrow 2HBr$	Combines with H_2 on heating and in presence of a catalyst $H_2 + I_2 \rightarrow 2HI$
12.	Reaction with metals	Almost all metals burn in the gas	Most metals burn in the gas	Attacks all metals; but a few burn	Attacks all metals except platinum

Properties of the Halogens—(cont.)

	Property	Fluorine	Chlorine	Bromine	Iodine
13.	Chemical activity	Most active Liberates Cl_2, Br_2, I_2 from chloride, bromide and iodide.	Less active than F_2 Displaces Br_2 from bromide, I_2 from iodide	Less active than Cl_2 Displaces I_2 from iodide	Less active than Br_2
14.	Oxides	Gives the oxide F_2O	Unstable oxides Cl_2O, ClO_2	Unstable oxides Br_2O, Br_3O_8	Stable oxides $I_2O_2 I_2O_5$
15.	Oxyacides	—	HOCl, $HClO_2$, $HClO_3$, $HClO_4$	HOBr, $HBrO_3$	HIO, HIO_3
16.	Reaction with starch solution	Attacks water of the solution	No reaction	It turns yellow	It turns blue
17.	Hydracids	HF (Stable)	HCl (Strong and stable)	HBr (Strong and less stable)	HI (Weak and less stable)
18.	Action on alkalis				
	1. Cold solution	Attacks water of the solution;	1 Chloride and hypochlorite	1. Bromide and hypobromite	1. Iodide and hypoiodite
	2. Hot and concentrated solution	Gives fluorides and F_2O	2. Chlorate and chloride	2. Bromate and bromide	2. Iodate and Iodide

A Comparative study of hydrogen halides

	Property	Hydrochloric acid	Hydrobromic acid	Hydriodic acid
1.	Colour	Colouress	Colourless	Colourless
2.	Odour	Penetrating	Penetrating	Penetrating
3.	Solubility in water	Extremely soluble	Extremely soluble	Extremely soluble
4.	Stability	Most stable	Less stable	Least stable
5.	Acidic nature	Most strong	Strong	Weak
6.	Reaction with NH_3	White fumes of NH_4Cl are formed	White fumes of NH_4Br are formed	White fumes of NH_4I are formed
7.	Reaction with Cl_2	No reaction	Bromine is liberated	Iodine is liberated
8.	Reaction with MnO_2	Cl_2 gas is evolved	Bromine is evolved	Iodine is evolved
9.	Reducing property	Very weak reducing agent	Weak reducing agent	Strong reducing agent
10.	Reaction with $AgNO_3$	White precipitate of AgCl	Yellow precipitate of AgBr	Deep yellow precipitate of AgI
11.	Reaction with $HgCl_2$	No reaction	No reaction	Red precipitate of HgI_2
12.	Reaction with lead-acetate	White precipitate of $PbCl_3$	White precipitate of $PbBr_2$	Yellow precipitate of PbI_2

Distinctions between a fluoride, chloride, bromide and an iodide

	Regent	Fluoride	Chloride	Bromide	Iodide
1.	Concentrated sulphuric acid.	White fumes of HF are evolved	White fumes of HCl given off	Red vapours of bromine given off	Violet vapours of iodine given off
2.	Concentrated H_2SO_4 + MnO_2	—do—	A greenish yellow gas Cl_2 is evolved. It bleaches litmus paper	Red vapours of bromine are evolved. Starch paper turns yellow	Violet vapours of iodine given off. Starch paper turns blue
3.	Silver nitrate solution		White precipate of AgCl soluble in NH_3 and insoluble in conc. HNO_3	Yellowish white precipitate of AgBr. soluble in NH_4OH with difficulty-insoluble in HNO_3	Yellow precipitate of AgI insoluble in NH_4OH and HNO_3

Distinctions between a fluoride, chloride, bromide and an iodide (cont.)

	Reagent	Fluoride	Chloride	Bromide	Iodide
4.	Chlorine water and carbon disulphide	—	—	CS_2 layer is coloured brown	CS_2 layer is coloured violet
5.	Chlorine water + starch	—	—	Yellow colour	Blue colour
6.	**Lead acetate solution**	—	White precipitate of $PbCl_2$ - soluble in hot water	White precipitate of $PbBr_2$ soluble in hot water	Yellow precipitate of PbI_2. Dissolves in hot water. Reprecipitated in the form of golden spangles
7.	Calcium chloride solution	White precipitate of CaF_2	—	—	—

QUESTIONS

PART A

Pick out the correct answer in the following questions

1. The most powerful oxidising agent among the halogens is (a) chlorine (b) iodine (c) fluorine (d) bromine.

2. Chlorine is best freed from HCl by passing it through (a) alkaline solution (b) slaked lime (c) concentrated H_2SO_4 and (d) water

3. The ionisation potential of iodine is lower than that of fluorine, because (a) iodine atom is smaller than fluorine atom (b) iodine atom is larger than fluorine atom. (c) iodine is a solid.

4. Fluorine reacts with water to give oxygen or ozone because (a) fluorine is a reducing agent (b) fluorine is an oxidising agent (c) fluorine is a gas.

5. In solution chlorine displaces bromine from bromide ions because (a) chlorine is a reducing agent (b) chlorine is an oxidising agent (c) chlorine is soluble in water.

6. The thermal stability of halogen hydrides decreases in the order (a) HF, HCl, HBr, HI (b) HI, HBr, HCl, HF (c) HI, HF, HBr, HCl (d) HBr, HCl, HF.

7. The acid strengths of halogen acids increases in the order (a) HF, HCl, HBr, HI. (b) HCl, HBr, HF, HI (c) HBr, HCl, HI, HF (d) HI, HBr, HCl, HF.

8. Concentrated H_2SO_4 is not reduced by (a) HF (b) HBr and (c) HI.

9. HI cannot be prepared by heating KI with concentrated H_2SO_4 because (a) these substances do not react (b) HI dissociates at the temperature of the reaction (c) HI is oxidised by concentrated H_2SO_4 (d) HI dissolves in H_2SO_4.

Fill in the blanks in the following questions

10. Chlorine is liberated from HCl acid in the cold by the action of———.

11. Iodine displaces chlorine from————.

12. The most stable of hydrogen halides is hydrogen ————.

13. HBr is prepared by adding ——— to a paste of ———— and ———— contained in a flask.

14. When KI is heated with concentrated H_2SO_4 ——— are evolved.

15. The extraction of iodine from caliche involves a reaction between sodium ——— and sodium ———.

16. SO_2 reacts with chlorine to form ——— ———.

17. Which of the statements is/are correct (1) Iodine can displace Cl_2 from $KClO_3$. (2) Chlorine bleaches vegetable colouring matter by oxidation (3) Iodine can be melted by heating under pressure (4) Chlorine is displaced from chloride by Br_2.

18. Which of the following statements is true?
    (a) Chlorine converts sulphates into thiosulphates.
    (b) Iodine is a stronger oxidising agent than Br_2.
    (c) HI is a strong oxidising agent.
    (d) HNO_3 oxidises iodine to iodic acid.
    (e) I_2 dissolves in a solution of $Na_2S_2O_3$.
    (f) Oxidising agents turn starch iodide paper blue.

19. Match the following :

(a)	(1) Fluorine	(1) Dark grey solid
	(2) Bromine	(2) Pale yellow gas
	(3) Iodine	(3) Reddish-brown liquid
(b)	(1) Caliche	(1) Liquefaction of air
	(2) Carnallite	(2) Manufacture of hydrogen
	(3) Lane's process	(3) Mineral containing $NaIO_3$
	(4) Claude's process	**(4) Mineral containing $KCl.MgCl_2 6H_2O$.**

Part B

20. Dry chlorine is not a bleaching agent. Why?

21. Why HF is not prepared similar to other hydrogen halides?

22. Why is F_2 not prepared by the electrolysis of HF?

23. Describe the chemistry behind the etching of glass.

24. Give reasons to show that the activity of halogens decreases in the order of increase in atomic number.

25. Show by means of suitable chemical reactions why the halogen atoms are called oxidising agents.

26. What happens when (a) Chlorine is passed into potassium iodide solution (b) NaCl solution is added to $AgNO_3$ solution.

27. Write equations for the oxidation of HCl by (a) MnO_2 (b) $KMnO_4$.

28. How are bromides and iodides detected in qualitative analysis?

29. How would you account for the anomalous behaviour of HF?

Part C

30. Describe the preparation of fluorine, pointing out the difficulties, which confronted the earlier chemists in the isolation of fluorine.

31. What is the action of F_2 on (1) water (2) hydrogen (3) sodium bromide (4) potassium iodide?

32. How is pure dry chlorine prepared in the laboratory? What is the action of chlorine on (a) aqueous solution of H_2S (b) cold and dilute KOH (c) hot and concentrated KOH (d) aqueous solution of SO_2 (e) ethylene.

33. Describe the preparation of bromine on a commercial scale. How does bromine react with solutions of (a) SO_2 (b) H_2S (c) KI.

34. Describe the preparation of iodine on a commercial scale. How does it react with (a) $Na_2S_2O_3$ solution (b) NaOH solution (c) H_2S (d) SO_2 (e) $KClO_3$.

35. Compare the methods of preparation and properties of various halogen acids.

36. How is HF prepared? What is the action of this acid on silica and to what use is this property of the acid put in industry?

37. How is HBr prepared? What is its action on (a) H_2SO_4 (b) chlorine water?

38. With the help of a neat diagram describe the preparation of hydroiodic acid. Give equations for the reducing properties of the acid.

39. Name and give the formulae of the various oxides and oxyacids of halogen and interhalogen compounds.

Section C

ORGANIC CHEMISTRY

CHAPTER I

INTRODUCTION

Organic Chemistry can be considered as the chemistry of compounds produced by 'organisms' All these 'organic' compounds consist of carbon and hence organic chemistry is considered the chemistry of compounds of carbon. Another definition now frequently used is that organic **chemistry is the chemistry of the hydrocarbons and their derivatives.**

It was once believed that the **organic compounds could only be produced by an imaginary 'vital force' which was a property of nature, i.e., organic substances could only be synthesized by living organisms. In 1828, Wohler synthesized urea by heating ammonium cyanate.**

$$NH_4CNO \xrightarrow{\Delta} CO(NH_2)_2$$

Urea was known to be an organic compound which was present in the urine of animals, and it was therefore clear that Wohler had made an organic compound from purely inorganic starting materials. In 1845, acetic acid was synthesized from carbon, hydrogen and oxygen. Organic synthesis is now an everyday affair and the idea of 'vital force' has long since been disregarded.

Carbon is unique amongst the elements in the number of compounds it forms. This can be attributed to the ease with which carbon atoms can link together in long chains or rings. Organic compounds contain only a small number of different atoms, those occurring regularly being carbon, hydrogen, oxygen, nitrogen, halogens and sulphur.

Classification of Organic Compounds

The organic compounds may be broadly divided into the following types :

(1) **Open chain or aliphatic compounds** These compounds have molecules composed of open-chains of carbon atoms The name was derived from the Greek word 'aleiphar' (meaning fat) because the first compounds to be studied in this class were the "**fatty acids**".

CH_4	CH_3-CH_2-CH_2-CH_2-CH_3	$CH_3CH_2CH_2CH_2I$
Methane	n-pentane	n-butyl iodide

(2) **Closed chain or cyclic compounds** Organic compounds with a closed chain of atoms are termed as closed chain or cyclic compounds. When a molecule contains two or more ring systems, it is said to be polycyclic. The cyclic compounds can be further subdivided as follows.

(a) **Homocyclic or carbocyclic compounds** : In these compounds, the ring is made up of only carbon atoms. They may be further subdivided into two types.

(i) **Aromatic compounds** These compounds contain one or more benzene rings. e.g. benzene and naphthalene.

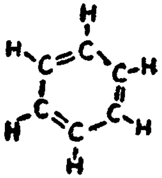


Fig. 71
Benzene

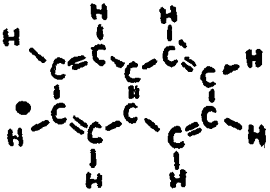


Fig. 72
Naphthalene

(ii) **Alicyclic compounds** : These compounds though having a ring structure, are found to behave more like aliphatic compounds than aromatic, e.g., cyclohexane, cyclopentane, etc.

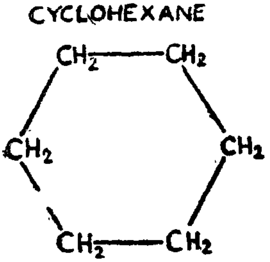


Fig. 73
Cyclohexane

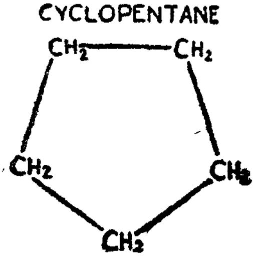


Fig. 74
Cyclopentane

(b) **Heterocyclic compounds** : These are molecules in which other atoms apart from carbon are present in the ring, e.g., pyridine, furan, thiophene, pyrrole.

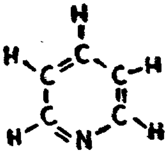


Fig. 75
Pyridine

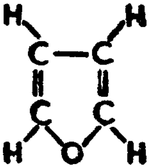


Fig. 76
Furan

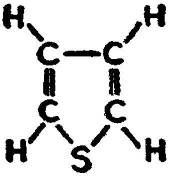


Fig. 77
Thiophene

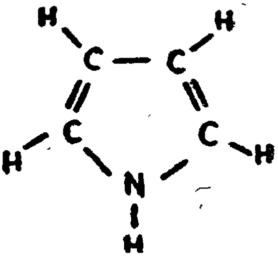
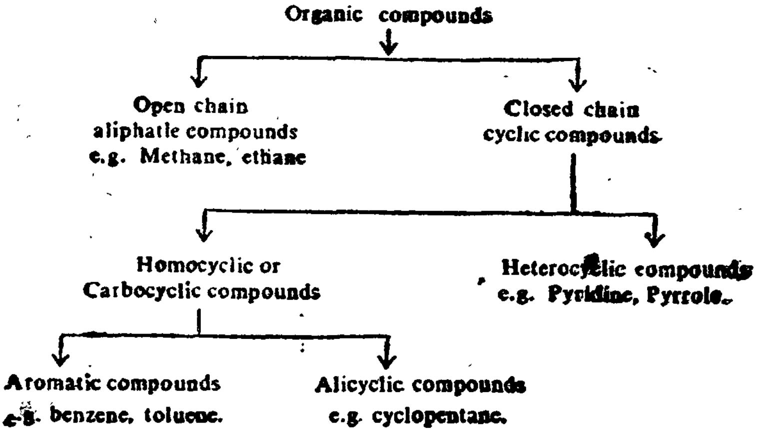


Fig. 78
Pyrrole

The above scheme of classification may be summarised as follows :



Homologous series

A group or class of organic compounds related to each other by a general molecular formula constitutes **homologous** series.

Every homologous series has the following characteristics.

(1) All members of the series have the same general molecular formula.

(2) They can be prepared by similar methods.

(3) They possess similar chemical properties.

(4) There is a regular gradation in their physical properties with increase in molecular weight.

(5) Each member of the series differs from the next member in the series by a difference of CH_2 in their formula.

(6) Every member of the series is said to be a homologue of the other

e.g. CH_4, C_2H_6, C_3H_8. C_4H_{10}, C_5H_{12}.
$CH_8 OH$, C_3H_5OH.C_3H_7OH, C_4H_9OH, $C_5H_{11}OH$.
CH_3COOH, C_2H_5COOH, C_3H_7COOH, C_4H_9COOH.

Functional groups

Each homologous series is characterised by a particular group which is characteristic of that particular series only. This characteristic group is known as the **functional group**. For example, the functional group alcohols is—OH that of aldehydes is—CHO, that of carboxylic acid is—COOH. The properties of the homologues will be of the functional group and the group to which the functional group is attached.

Nomenclature

There are at present more than one million of organic compounds. The organic compounds have '**common names**' given to them from time to time. But a systematised nomenclature has been arrived at by agreement among chemists.

In 1892 the International Commission of Chemists met at Geneva and adopted the Geneva system of nomenclature, which was improved by a committee of the International Union of chemistry which met at Liege in Belgium in 1930.

The revised system is known as I.U.C system of nomenclture. The rules of the I.U.C. system are further revised by **International Union of Pure and Applied Chemistry** called the IUPAC system of nomenclature.

The various homologous series and their IUPAC system of nomenclature are given below

Alkanes

Compounds containing carbon and hydrogen with the general molecular formula C_nH_{2n+2}, are calle alkanes. In alkanes all the carbon atoms are attached to one another by single covalent linkages. CH_4-Methane, C_2H_6-Ethane, C_3H_8-Propane.

Alkenes or Olefines

These are compounds containing carbon and hydrogen with the general molecular formula C_nH_{2n} and are characterised by the presence of a $C{=}C$ bond, called double bond.

The names of olefines are derived from the corresponding alkanes changing the suffix-ane of the alkane into-ene.

$H_2C{=}CH_2$: Ethene. $CH_3\text{-}CH{=}CH_2$ Propene.

Alkynes

These are compounds containing carbon, and hydrogen and have the general molecular formula C_nH_{2n-2}. These are characterised by the presence of a triple bond.

The names of the alkynes are derived from the corresponding alkanes by changing the end-ane of the alkane into "yne".

$HC{\equiv}CH$ Ethyne. $CH_3\text{-}C{\equiv}CH$ Propyne.

Alkyl group

It is a radical obtained from the alkanes by the loss of one hydrogen atom.

If R-H is the alkane, then 'R' represents alkyl group.

CH_3	Methyl
C_2H_5	Ethyl
$CH_2=CH$	Vinyl
$CH_2=CH-CH_2$	Allyl.

Alkyl halides

These are compounds obtained by the replacement of hydrogen atom of an alkane by a halogen atom.

According to IUPAC system, these compounds are named as **haloalkanes**

CH_3Cl	C_2H_5I	$CH_3CH_2CH_2Br$
(methyl chloride)	(Ethyliodide)	(n-Propyl bromide)
Chloromethane	Iodoethane	1-Bromopropane.

Alcohols

If the hydrogen atom of the hydrocarbon is replaced by OH group, then alcohols are obtained.

In IUPAC system, the names of alcohols end with-ol, i.e. by substituting 'e' of the name of the parent hydrocarbon by-**ol**.

CH_3OH	Methanol
C_2H_5OH	Ethanol.

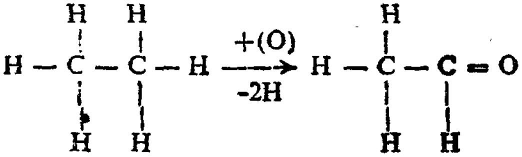
Ethers

When an oxygen atom is flanked by two alkyl groups, then that compound is known as an ether

CH_3OCH_3	Methoxy methane
$CH_3OC_2H_5$	Methoxy ethane
$CH_3OC_3H_7$	Methoxy propane.

Aldehydes

When two hydrogen atoms attached to an end carbon atom of an alkane is replaced by one oxygen atom, aldehydes are obtained.



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H \xrightarrow[-2H]{+(O)} H-\overset{H}{\underset{H}{C}}-\underset{H}{C}=O$$

According to IUPAC system of nomenclature the name of an aldehyde is obtained by changing the end 'e' of the parent hydrocarbon by 'al'

CH_3CHO ethanal

$CH_3\,CH_2CHO$ propanol

Ketones

When two hydrogen atoms attached to a carbon atom, which is not an end carbon atom in an alkane is replaced by an oxygen atom, a ketone is obtained. That is when a $>C=O$ (carbonyl group) is attached to the alkyl group ketone is obtained.

According to IUPAC system, the names of ketones end in " **one** " and the name of a ketone is obtained from the corresponding parent hydrocarbon by adding " **one** " instead of 'e'

CH_3COCH_3	Propanone
$CH_3COCH_2CH_3$	Butanone

Acids

If a hydrogen atom of a hydrocarbon is replaced by a —COOH group, a carboxylic acid is obtained.

According to IUPAC system, fatty acids are called **alkanoic acids** and are named from the present hydrocarbon by replacing the end 'e' by '**oic acid.**'

$HCOOH$	Methanoic acid
CH_3COOH	Ethanoic acid

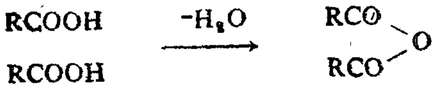
Acid chlorides or Acyl chlorides

If the —OH group of an acid is replaced by Cl atom an acid chloride is obtained. Their names are derived by replacing the suffix-ic acid by - yl chloride as in.

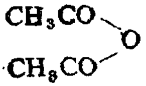
HCOCl	Methanoyl chloride
CH_3 COCl	Ethanoyl chloride

Acid anhydrides

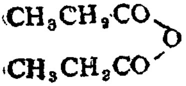
These anhydrides may be regarded theoretically as being derived from an acid by the removal of a molecule of water from the molecules of the acid.



These are named as the anhydrides of the acid radicals present, e.g,



Ethanoic anhydride



Propanoic anhydride

Acid amides

These are compounds in which the hydroxyl group of the acid group has been replaced by an amino group.

These are named according to IUPAC system by replacing the suffix 'e' of the parent alkane by amide

$HCONH_2$	Methanamide
CH_3CONH_2	Ethanamide

Esters

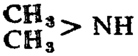
The esters are formed when the hydrogen atom in the carboxyl group is replaced by an alkyl group. These are named as the alkyl salts of the parent acid as given below

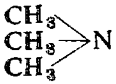
$HCOOCH_3$	Methyl methanoate.
CH_3COOCH_3	Methyl ethanoate.

Amines

These are derivatives of ammonia. If hydrogen atoms of ammonia are replaced by one, two and three alkyl groups then primary, secondary and tertiary amines will be obtained respectively.

$CH_3\text{-}NH_2$ Methylamine (Primary amine)


$\begin{matrix}CH_3\\CH_3\end{matrix} > NH$ Dimethylamine (Secondary amine),


$\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix} > N$ Trimethylamine (Tertiary amine),

Organo metallic compounds

These are compounds in which a metal atom is attached to an alkyl group and a halogen atom.

CH_3MgI Methyl magnesium iodide.
(a Grignard Reagent).

QUESTIONS

1. Discuss briefly the classification of organic compounds.
2. Indicate the classification to which the following compounds belong.
   (a) butane (b) n-propyl iodide (c) benzene (d) phenol (e) cyclohexane (f) pyridine (g) thiophen (h) ethanol.
3. What is a homologous series? Give the characteristic properties of a homologous series.
4. What do you mean by the term functional group? Give examples.
5. What is the functional group of each of the following homologous series ?
   (a) Alkanes (b) Aldehydes (c) Acid amides (d) Alcohols (e) Ethers (f) Acids (g) Amines.
6. What do you understand by IUPAC nomenclature? Give the IUPAC names for the following compounds.
   (a) Acetylene (b) Ethylene (c) Ethyl alcohol (d) $HCOOH$ (e) CH_3COCl (f) CH_3CHO

CHAPTER II

PURIFICATION OF ORGANIC COMPOUNDS

The organic compounds derived from natural sources are seldom pure. They are often mixed with other substances which also occur with them. Similarly the compounds obtained in the laboratory are generally not present alone but are mixed with several substances. In order to study its properties and determine its formula, a given substance must be purified first of all. The methods adopted depend upon the nature of the organic compound and the impurities present in it. The processes of purification commonly used are the following :

(1) Crystallisation (2) Sublimation (3) Distillation (4) Chromatography.

Crystallisation

This is a method of purifying solids. The process is carried out by dissolving the solid to be purified in the minimum quantity of an appropriate solvent, usually by heating. (The suitable solvent is found by taking a portion of the substance in several test tubes and adding a small quantity of each of the common solvents like water, alcohol, ether, chloroform, benzene etc.) Solid impurities, if any, may be filtered and the clear filtrate obtained is allowed to cool slowly when the crystals of the solid are formed. The crystals are then separated, washed and dried.

Sublimation

Certain substances when heated, pass directly from the solid to the vapour state without melting. The vapours when cooled give back the solid substance. This process is known as **sublimation**.

This process may be used to purify a volatile solid from a non-volatile solid. Substances like naphthalene, benzoic acid, camphor can be purified by this method.

The impure substance is placed on a china dish which is gently heated on a sand bath. The china dish is covered with a funnel. The china dish is heated gently at first and then strongly, The vapours arising from the substance will get condensed on the walls of the funnel, which can be removed.

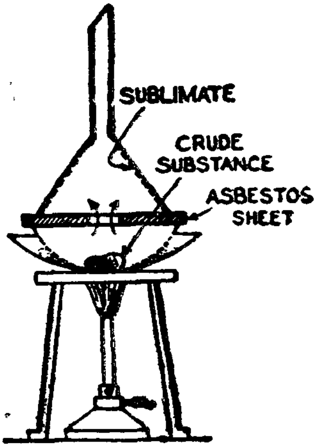


Fig. 79
Sublimation

In the case of substances which readily undergo decompositions sublimation may be carried out under reduced pressure.

Distillation

This is a process used for purifying liquids from non-volatile impurities. The impure liquid is boiled in a distilling flask and the vapours are collected and condensed to give back the pure liquid in another vessel. The non-volatile impurities will be left behind in the flask.

The apparatus used is shown in the figure 79.

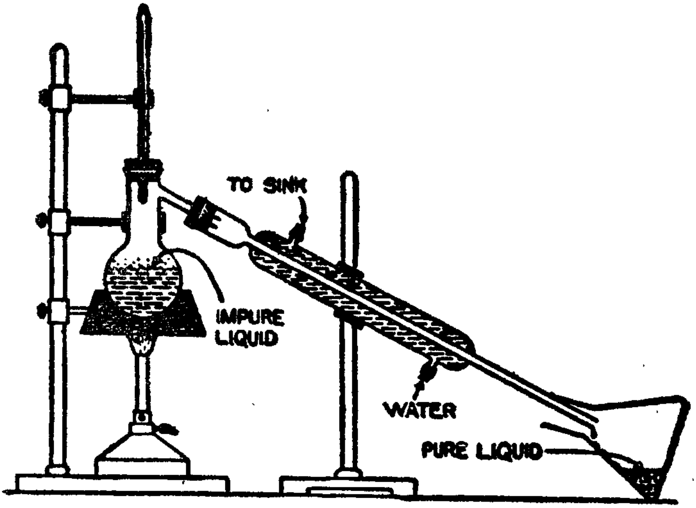


Fig. 80
Distillation

It consists of a distillation flask filled with a thermometer in its neck and a condenser at the side tube. The liquid to be purified is placed in the distillation flask and the thermometer, is adjusted such that its bulb stands just below the opening of the side tube. A suitable vessel is attached to the lower end of the condenser to receive the condensed liquid. On heating the distillation flask, the thermometer first shows an increase in the temperature which then becomes constant. At this point most of the pure liquid passes over, and will be collected in the receiver. In case of liquids having higher boiling points, the water condenser is replaced by means of an air-condenser. To prevent bubbling some porcelain bits are usually added into the distillation flask.

A mixture of two or more volatile liquids may be separeted by fractional distillation, provided their boiling points differ considerably.

In case of organic substances which decompose before the boiling point is reached, distillation under reduced pressure may be used.

Steam distillation

This method is adopted for purification of substances (both solid and liquid) which are immiscible with water and are volatile in steam and are not decomposed by boiling water. When steam is passed through this liquid, the liquid gets heated and its vapour pressure rises. When the sum of the vapour pressures of the liquid and of water become equal to the atmospheric pressure the system begins to boil. The vapour of the liquid and steam that are produced are condensed to a mixture of the liquid and water. The liquid being immiscible with water collects in a separate layer. This can be separated and further distilled.

The substance to be purified is mixed with water and taken in a flask kept in a slightly tilted position. The steam is generated from a tin can or a boiler. The flask is heated first so that the contents boil. When the liquid in the flask boils steam is passed. The vapours are condensed in the Liebig condenser and collect in a receiver. The liquids collects along with water in a separate layer.

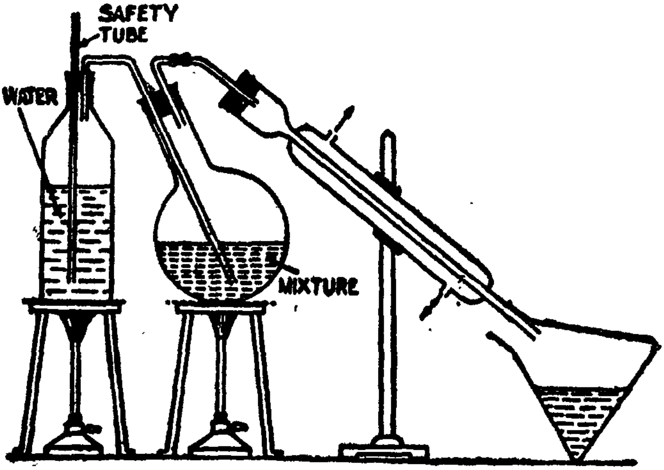


Fig. 81
Steam distillation

This layer is separated and dried and redistilled. The advantage in the steam distillation is that, usually high boiling liquids can bedistilled at low pressure and at low temperature (near 100°C)than their normal boiling points. This is equivalent to distillation under reduced pressure.

Nitrobenzene and aniline can be purified by steam distillation process.

Chromatography

This is an excellent method of separation and purification of complex organic substances. This was developed by the Polish botanist Tswett in 1906. It is based on the principle that when a solution of different substances is allowed to flow down a vertical tube packed with a suitable adsorbent, different substances in the solution get adsorbed in different zones by virtue of the difference in their power of adsorption. The success of this method depends on the selection of the adsorbent and the choice of the solvent. The adsorbents commonly used are alumina, magnesium oxide, silica gel, etc. petroleum ether is the most widely used solvent. Other useful solvents are carbon disulphide, benzene and chloroform.

Separation and recovery of the adsorbed materials are usually effected as described below. A suitable solvent is poured on the developed chromatogram, when the different substances in zones are washed down one by one which are collected separately.

Thin layer chromatography is a special type of chromatography wherein instead of a column, a glass plate with a thin coating of the adsorbent is used.

Paper chromatography is also another type of chromatography wherein the adsorbent column is a paper strip.

Recently the principle of selective adsorption has been applied for the separation and quantitative analysis of mixture of gases and low boiling liquids. This technique known as **vapour phase chromatography** or **gas chromatography** is another excellent tool at the hands of analytical chemists.

QUESTIONS

1. Give an account of the various methods used for purifying an organic compound.

2. Give an account of the methods used to purify a solid organic compound.

3. How will you purify a liquid organic compound ?

4. Give a short account of the chromatographic method used to purify organic compounds.

5. Write short notes on :

   (a) Sublimation

   (b) Recrystallisation

   (c) Distillation

   (d) Steam distillation

CHAPTER III

DETECTION OF ELEMENTS

In addition to carbon, most of the commonly occurring organic compounds contain hydrogen and oxygen. Some of them also contain halogens, sulphur and phosphorus. A few of them may contain metals also. After obtaining an organic compound in a state of purity, the next step is to find the elements present.

Detection of carbon and hydrogen

The presence of carbon and hydrogen in an organic compound is usually assumed, but their presence can be verified by heating the dry powdered compound with copper (II) oxide in a clean dry test tube. The tube is fitted with a bent delivery tube, the other end of which dips into lime water in another test tube. The mixture is heated strongly when the following reactions take place

$$C + 2CuO \xrightarrow{\Delta} CO_2 + 2Cu$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

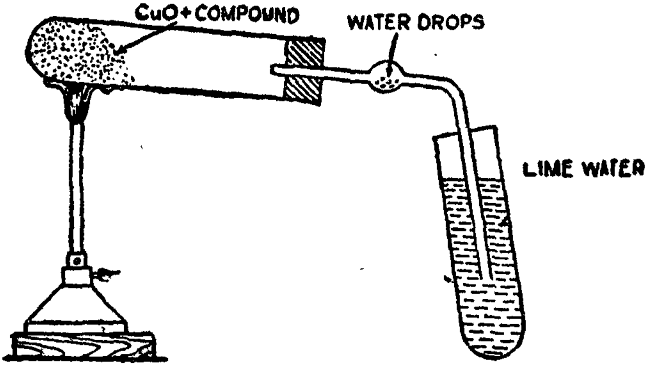


Fig 82.

Thus, if carbon is present it is oxidised to carbon dioxide' which will turn the lime water milky. If hydrogen is also present, it will be oxidised to water, which condenses into small drops on the cooler wall of the test tube and inside the bulb. The formation of water may be further confirmed by testing the condensed liquid with anhydrous copper (II) sulphate (white) which will turn blue.

Detection of nitrogen

(a) Soda-lime test : The given substance is mixed with double the amount of soda-lime ($NaOH + CaO$) and heated in a test tube. The vapours of ammonia evolved show the presence of nitrogen. Several organic substances do not respond to this test.

(b) Lassaigne's test : About 0·2g of sodium metal is placed in a dry ignition tube and the tube is heated till the sodium melts and begins to give vapours. Then about 0·2g of the substance is added to the hot sodium and the heating continued at first gently and then strongly. Then while still red hot it is plunged into about 10ml of distilled water. The liquid is boiled for a short time and filtered.

The extract thus obtained is boiled with iron (II) sulphate solution and then cooled. To the cooled solution is then added a little iron (III) chloride solution and then excess of concentrated hydrochloric acid. The formation of **Prussian blue** indicates the presence of nitrogen.

Sodium combines with carbon and the nitrogen of the organic compound forming sodium cyanide. Sodium cyanide on boiling with iron (II) sulphate forms sodium ferrocyanide, which in acid solution reacts to form ferric ferrocyanide which is called the**Prussian blue.**

$$Na + C + N \rightarrow NaCN.$$
$$2NaCN + FeSO_4 \rightarrow Na_2SO_4 + Fe(CN)_2$$
$$Fe(CN)_2 + 4NaCN \rightarrow Na_4[Fe(CN)_4]$$
$$3Na_4[Fe(CN)_6] + 4FeCl_3 \rightarrow \underset{\text{Prussian blue.}}{Fe_4[Fe(CN)_6]} + 12NaCl$$

Detection of halogens

(a) **Lassaigne's test:** The sodium fusion extract may be prepared as given under detection of nitrogen. The extract is boiled with dilute nitric acid and then a solution of silver nitrate is added. If a white precipitate which is soluble in ammonia is obtained, it indicates that chlorine is present in the compound; a pale yellow precipitate which is sparingly soluble indicates the presence of bromine; an yellow precipitate that is insoluble in ammonia indicates the presence of iodine in the compound.

On fusion with sodium, the halogen if present combines with sodium to give sodium halides. These sodium halides on treatment with silver nitrate precipitate the corresponding silver halides which can be distinguished by using ammonia or by their colour.

$$2Na + X_2 \rightarrow 2Na\,X$$

$$NaX + Ag\,NO_3 \rightarrow AgX \downarrow + Na\,NO_3$$

(b) **Beilstein's test:** A piece of copper gauze, is heated in a Bunsen flame until there is no green colour. It is then dipped into the substance even when hot. A small speck gets stuck to the copper and it is then introduced into the flame again. A green colour shows that one of the halogens may be present.

Detection of sulphur

Lassaigne's test: The sodium fusion extract is prepared as given above. (1) To one portion of the extract a freshly prepared solution of sodium nitroprusside is added. A deep violet colouration indicates sulphur.

(2) Acidify a second portion of the extract with acetic acid and then add lead acetate solution. A black precipitate shows the presence of sulphur.

$$\underset{\text{Lead acetate}}{Pb\,(CH_3\,COO)_2} + Na_2S \rightarrow \underset{\substack{\text{Lead sulphide}\\ \text{(Black)}}}{PbS \downarrow} + 2CH_3\,COONa$$

QUESTIONS

1. Give an account of the principles used to detect the presence of nitrogen, sulphur and chlorine present in an organic compound.

2. How will you detect carbon and hydrogen in an organic compound?

3. How will you detect chlorine and nitrogen if they are present together in an organic compound?

4. How will you detect sulphur and nitrogen if they are present together in an organic compound?

5. Write a short note on "Lassaigne's Test" for nitrogen.

6. Describe briefly how you will detect the following in compounds : (a) Carbon and hydrogen (b) Nitrogen (c) Sulphur (d) Chlorine.

CHAPTER IV

ESTIMATION OF ELEMENTS

Having known the elements present, in compounds the next step is to determine their percentage composition by weight.

Estimation of carbon and hydrogen

A known weight of the organic substance is oxdised with dry copper (II) oxide in a heated furnace. The carbon will be oxidised to carbon dioxide while the hydrogen present will be oxidised to water. Both carbon dioxide and water are collected separately and weighed. From the weight of carbon dioxide and water formed, the percentage of carbon and hydrogen can be calculated.

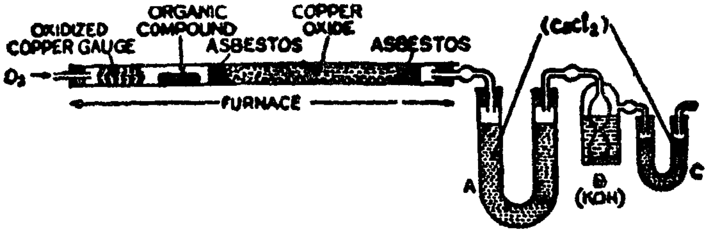


Fig. 83

A quantity of copper (II) oxide in wire form is packed into a combustion tube and is kept in position between two plugs of asbestos wool. A coil of freshly oxidised copper gauze is placed at the inlet end of the combustion tube. The tube is now heated strongly over a furnace while a stream of dry oxygen free from carbondioxide is passed through. This enables the removal of water vapour from the tube and the oxidation of any organic matter present.

The combustion tube is cooled and a boat containing a weighed amount of the organic compound is placed in the combustion tube as shown in the figure Weighed calcium chloride tubes *A* and *C*, and the potash absorption vessel *B* are connected.

The burners at the outlet end are lit first and when the copper (II) oxide is hot the burners under the gauze and then the burners under the boat are lit with a stream of oxygen passing through the tube. The organic compound is vapourised and the vapours are driven into the copper (II) oxide where it is oxidised to carbon dioxide and water The water formed is absorbed in the weighed calcium chloride in *A*. CO_2 is absorbed in the potash in B. Any water vapour removed from the potash bulb by oxygen is trapped in *C*. Increase in weight of *A* gives the weight of water and increase in weight of *B* and *C* together gives the weight of carbon dioxide formed.

Since 18 g of water contains 2 g of hydrogen and 44 g of carbon dioxide contain 12 g of carbon, the weight of these two elements and hence their percentages can be calculated.

Calculations

Weight of the substance taken = x g.

Increase in weight in calcium chloride tube = y g.

Increase in weight in potash bulbs = z g.

18 g of water contains = 2g of hydrogen.

∴ y g of water will contain = $\frac{2}{18} \times y$ g of hydrogen.

y g of water comes from x g of the substance.

∴ x g of the substance contain = $\frac{2}{18} \times y$ g of hydrogen.

Percentage of hydrogen in the compound = $\frac{2}{18} \times \frac{y}{x} \times 100$.

44 g of carbon dioxide contains 12 g of carbon

∴ z g of carbon dioxide will contain $\frac{12}{44} \times z$ of carbon.

z g of carbon dioxide comes from x g of substance.

∴ x g of the substance contain $\frac{12}{44} \times z$ of carbon.

∴ Percentage of carbon in the substance

$$= \frac{12}{44} \times \frac{z}{x} \times 100.$$

Example: 1

0·4280 g of an organic compound on oxidation gave 0·8900 g of CO_2 and 0·1818 g of H_2O. Calculate the percenttage of carbon and hydrogen in the compound.

44 g of carbon dioxide contains = 12 g of carbon.

$$\therefore \left.\begin{array}{r}\text{0·8900 g carbon dioxide}\\ \text{will contain}\end{array}\right\} = \frac{12}{44} \times 0{\cdot}8900 \text{ g of carbon}$$

$$\therefore \text{ \% of carbon in the substance} = \frac{12}{44} \times \frac{0{\cdot}8900}{0{\cdot}4280} \times 100$$

$$= 56{\cdot}71$$

Also, 18 g of water contains = 2 g of hydrogen.

$$\therefore 0{\cdot}1818 \text{ g of water will contain} = \frac{2}{18} \times 0{\cdot}1818 \text{g of hydrogen}$$

$$\therefore \text{ \% of hydrogen in the substance} = \frac{2}{18} \times \frac{0{\cdot}1818}{0{\cdot}4280} \times 100$$

$$= 4{\cdot}72$$

Estimation of Nitrogen by Kjeldahl's method

This method is based upon the fact that organic substances containing nitrogen, when heated with concentrated sulphuric acid are quantitatively decomposed to give ammonium sulphate. The ammonium sulphate is decomposed into ammonia when treated with a strong solution of sodium hydroxide and estimated volumetrically.

About 0·5 g of the substance is accurately weighed and mixed with about 10 ml of potassium sulphate, 20 ml of concentrated sulphuric acid and a drop of copper (II) sulphate as catalyst and heated in a long-necked flask. Potassium sulphate is used so as to raise the boiling point of the liquid. The solution will first turn brown and then will become colourless. The flask is cooled. The contents of the flask are then placed in a round bottomed flask and the apparatus is fitted as shown in the figure.

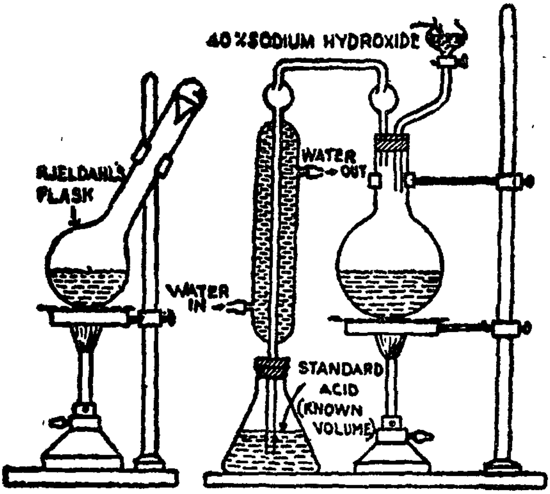


Fig. 84
Kjeldahl's method

Sodium hydroxide solution is added from a dropping funnel and the flask is heated. Ammonia liberated is bubbled through a known volume of standard acid. Some of the standard acid will be neutralised while the remaining acid is back titrated against standard alkali.

Calculation

Let V ml of N acid is used up for neutralisation. Let W be the weight of the substance taken.

V ml of N acid = V ml of N ammonia.

1000 ml of N ammonia contains 17 g of ammonia or 14 g of nitrogen.

∴ Nitrogen present in V ml of N ammonia.

$$= \frac{14}{1000} \times V$$
$$= 0{\cdot}014\ V\ g$$

∴ W g of the substance contain = 0·014 V g of nitrogen.

$$\therefore \text{Percentage of nitrogen} = \frac{0{\cdot}014 \times V}{W} \times 100 = \frac{1{\cdot}4\ V}{W}$$

where

V = Volume of the N acid.

W = Weight of the substance taken.

Example: 2

In Kjeldahl's method of nitrogen estimation, the ammonia resulting from 0·442 g of a substance was distilled into 50 ml of $\frac{N}{10}$ sulphuric acid. The excess of the acid consumed 14 ml of $\frac{N}{10}$ sodium hydroxide. Calculate the percentage of nitrogen in the compound.

Weight of the substance taken = 0·442 g

Volume of $\frac{N}{10}$ sulphuric acid taken = 50 ml.

Let V ml of this acid be left over unused. This unused excess acid required 14 ml of $\frac{N}{10}$ sodium hydroxide.

Now we have,

V_1 ml of $\frac{N}{10}$ sulphuric acid ≡ 14 ml of $\frac{N}{10}$ sodium hydroxide.

$$\therefore V_1 \times \frac{N}{10} = 14 \times \frac{N}{10}$$

$$\therefore V_1 = 14\ \text{ml.}$$

i.e., Volume of acid left over = 14 ml.

∴ Volume of acid used for neutralising ammonia given by the substance

$$= 50-14 = 36 \text{ ml } \frac{N}{10} \text{ sulphuric acid.}$$

$$= 3{\cdot}6 \text{ ml N sulphuric acid.}$$

$$\text{Percentage of nitrogen} = \frac{1{\cdot}4 \times 3{\cdot}6}{0{\cdot}442}$$

$$= 11{\cdot}4$$

Estimation of Halogens

Carius method: The principle of estimation of the halogens in the organic compound by Carius method is as follows.

The organic substance is heated with silver nitrate and fuming nitric acid. The halogen in the organic compound becomes the halide ion and this reacts with silver ion of silver nitrate solution. The silver halide is precipitated. The precipitate is filtered, washed, dried and weighed. From the weight of the precipitate, the weight of the halogen can be calculated.

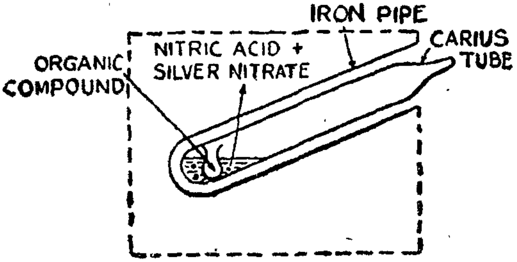


Fig. 85
Carius method

About 0·2 g of the substance is accurately weighed in a small glass tube. This tube is introduced into the Carius tube containing fuming nitric acid and silver nitrate crystals. The upper end of the tube is then sealed and then the tube is heated in a furnace for about 5 to 6 hours. Organic compound breaks up and the halogen present gives a precipitate of silver halide.

The tube is cooled. The tube is then broken and the precipitate of silver halide obtained is washed, dried and weighed.

Let the weight of the substance taken be x g. Let y g be the weight of silver halide obtained. One gram molecular weight of silver chloride (108 + 35·5 = 143·5) contains 35·5 g of chlorine.

$$\therefore \text{ Percentage of chlorine} = \frac{35{\cdot}5}{143{\cdot}5} \times \frac{y}{x} \times 100$$

Similarly,

$$\text{Percentage of bromine} = \frac{80}{188} \times \frac{y}{x} \times 100$$

and

$$\text{Percentage of iodine} = \frac{127}{235} \times \frac{y}{x} \times 100$$

Example : 3

0·3321 g of an organic substance gave 0·5112 g of silver bromide. Calculate the percentage of bromine in the compound.

188 g of silver bromide contains 80 g of bromine.

$\therefore$ 0·5112 g of silver bromide will contain $\frac{80}{188} \times 0{\cdot}5112$ g of bromine.

$$\therefore \left.\begin{array}{r}\text{Percentage of bromine}\\ \text{in the compound}\end{array}\right\} = \frac{80}{188} \times \frac{0{\cdot}5112}{0{\cdot}3321} \times 100$$

$$= 65{\cdot}5$$

Estimation of Sulphur

Carius method : The method used is similar to that for halogens. A known weight of the compound is heated in a sealed tube with fuming nitric acid. The sulphur present in the compound will be oxidised to sulphuric acid. The tube is cooled and broken in dilute hydrochloric acid. Then excess of barium chloride solution is added. The precipitate of barium sulphate obtained is filtered, washed and dried

Let x be the weight of the substance and y be the weight of barium sulphate obtained.

∴ 233·4 g of barium sulphate contains 32 g of sulphur

∴ y g of barium sulphate will contain

$$= \frac{32}{233 \cdot 4} \times y \text{ g of sulphur.}$$

∴ Percentage of sulphur in the compound

$$= \frac{32}{233 \cdot 4} \times \frac{y}{x} \times 100.$$

Example: 4

0·2315 g of an organic compound gave 0·6956 g of barium sulphate by Carius method. Calculate the percentage of sulphur in the substance.

233·4 g of barium sulphate contains 32 g of sulphur.

0·6956 g of barium sulphate will contain $= \frac{32}{233 \cdot 4} \times 0 \cdot 6956$

∴ Percentage of sulphur in the compound $= \frac{32}{233 \cdot 4} \times \frac{0 \cdot 6956}{0 \cdot 2315} \times 100$

$$= 40 \cdot 2$$

Estimation of Oxygen

There is no satisfactory direct method for the direct estimation of the oxygen in an organic compound. After finding the percentage of various elements present other than oxygen, percentage of oxygen can be calculated by difference from 100.

Empirical and Molecular Formulas

The **empirical formula** of a compound is the simplest possible formula. It gives the ratio of the atoms of different elements present in the molecule.

e.g. empirical formula of acetic acid is CH_2O and that of ethylene is CH_2.

The molecular formula of a compound gives the actual number of atoms of different elements present in the molecule of a compound

The molecular formula of acetic acid is $C_2H_4O_2$.

The molecular formula of ethylene is C_2H_4.

Steps to obtain the empirical and molecular formulae from percentage composition are the following

1. Divide the percentage composition of each element by its atomic weight.
2. The ratio obtained is then divided by the smallest number among them.
3. If the ratios are fractional, convert them to the smallest possible whole numbers.
4. Write down the empirical formula.
5. Calculate the empirical formula weight.
6. Molecular formula = (Empirical formula) n

where

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

Example-5

An organic compound contains 71·29% C; 14·86% H; 14% N Calculate the simplest formula

Element	% composition	$\frac{\text{\%composition}}{\text{Atomic weight}}$	$\frac{\text{Previous column}}{\text{Smallest number}}$ among them	Whole number ratio
C	71·29	71·29÷12=5·94	$\frac{5{\cdot}94}{1} = 5{\cdot}94$	6
H	14·86	14·86÷1=14·86	$\frac{14{\cdot}86}{1} = 14{\cdot}86$	15
N	14	14 ÷ 14= 1	1/1 = 1	1

∴ Empirical formula = $C_6H_{16}N_1$

Example - 6

An organic compound contains 31·17% C, and 6·49% H. 0·185 g of the substance in Carius estimation gave 0·280g of barium sulphate. Find the simplest formula of the compound.

Calculation of percentage of sulphur

233·4 g of Barium sulphate contains 32 g of sulphur

∴ 0.280 of Barium sulphate contains $\frac{32}{233{\cdot}4} \times 0{\cdot}280$ g of sulphur

∴ 0·185 g of the substance will contain $\frac{32}{233{\cdot}4} \times 0{\cdot}280$ g of sulphur

$$\therefore \text{Percentage of sulphur} = \frac{32}{233{\cdot}4} \times \frac{0{\cdot}280}{0{\cdot}185} \times 100$$

$$= 20{\cdot}78$$

Percentage of carbon = 31·17
Percentage of hydrogen = 6·49
Percentage of sulphur = 20·74
∴ Percentage of oxygen = 100 - (31·17 + 6·49 + 20·74)
= 100 - 58·44
= 41·6

Element	%composition	$\frac{\text{\%composition}}{\text{Atomic weight}}$	$\frac{\text{Previous column}}{\text{Smallest number among them}}$	Whole number ratio
C	31·17	31·17 ÷ 12 = 2·6	$\frac{2{\cdot}6}{0{\cdot}649} = 4$	4
H	6·49	6·49 ÷ 1 = 6·49	$\frac{6{\cdot}49}{0{\cdot}649} = 10$	10
S	20·78	20·78 ÷ 32 = 0·649	$\frac{0{\cdot}649}{0{\cdot}649} = 1$	1
O	41·6	41·6 ÷ 16 = 2·6	$\frac{2{\cdot}6}{0{\cdot}649} = 4$	4

∴ Empirical formula = $C_4H_{10}SO_4$.

Example - 7

An organic compound contains carbon, hydrogen, oxygen, nitrogen and chlorine. Find its empirical formula from the following data :

(a) 0·3852 g of it gave 0·8012 g of carbon dioxide are 0·1636 g of water. (b) 0·132 g of it gave 9·12 ml of nitrogen 15°C and 768 mm pressure (c) 0·165 g of it gave 0·1307 g of silver chloride. Calculate the percentage of carbon and hydrogen. If the molecular weight is 170, calculate the molecular formula also.

44 g of carbon dioxide contain 12 g of carbon.

∴ 0·8010 g of carbon dioxide will contain $\frac{12}{44} \times 0{\cdot}8010$ g of carbon.

∴ Percentage of carbon in the compound

$$= \frac{12 \times 0{\cdot}8010 \times 100}{44 \times 0{\cdot}3852}$$

$$= 56{\cdot}17$$

Also

18 g of water contain 2 g of hydrogen

∴ 0·1636 g of water will contain $\frac{2}{18} \times 0{\cdot}1636$ g of Hydrogen

∴ Percentage of hydrogen in the compound $= \frac{2 \times 0{\cdot}1636 \times 100}{18 \times 0{\cdot}3852}$

$$= 4{\cdot}72$$

Calculation of percentage of nitrogen

$P_0 = 760$ mm | $P_1 = 768$ mm

$V_0 = ?$ | $V_1 = 9{\cdot}12$ ml

$T_0 = 273°A$ | $T_1 = 273 + 15 = 288°A$

$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

$$\frac{760 \times V_0}{273} = \frac{768 \times 9{\cdot}12}{288}$$

$$\therefore \quad V_0 = \frac{768 \times 9{\cdot}12 \times 273}{760 \times 288}$$

22400 ml of nitrogen at N.T.P will weigh 28 g.

$\frac{768 \times 9{\cdot}12 \times 273}{760 \times 288}$ ml of nitrogen at N.T.P. will weigh

$$\frac{28}{22400} \times \frac{768 \times 9{\cdot}12 \times 273}{760 \times 288} = 0{\cdot}01092 \text{ g}$$

$$\therefore \text{ The percentage of nitrogen} = \frac{0{\cdot}01092}{0{\cdot}132} \times 100 = 8{\cdot}275$$

Calculation of percentage of chlorine :

143·5 g of silver chloride contains 35·5 g of chlorine

0·1397 g of silver chloride contains $\frac{35{\cdot}5}{143{\cdot}5} \times 0{\cdot}1397$ g of Cl.

$$\therefore \text{ Percentage of chlorine} = \frac{35{\cdot}5}{143{\cdot}5} \times \frac{0{\cdot}1397}{0{\cdot}165} \times 100$$

$$= 20{\cdot}95$$

$$\begin{aligned} \text{Percentage of oxygen} &= 100-(56{\cdot}71+4{\cdot}72+8{\cdot}27+20{\cdot}95) \\ &= 100-90{\cdot}65 \\ &= 9{\cdot}35 \end{aligned}$$

Elements	% Composition	% Composition Atomic weight	Previous column Smallest number among them	Whole number ratio
C	56.71	56.71÷12=4.73	$\frac{4.73}{0{\cdot}590} = 8$	8
H	4.72	4.72÷ 1=4.72	$\frac{4.72}{0.590} = 8$	8
N	8.27	8.27÷14=0·585	$\frac{0.584}{0.590} = 1$	1
Cl	20.95	20.95÷35.45 =0.590	$\frac{0.590}{0.590} = 1$	1
O	9.35	9.35÷16=0.590	$\frac{0.590}{0.590} = 1$	1

$\therefore$ Empirical formula C_8H_8ONCl

Empirical formula weight $= (8\times12+(8\times1)+(1\times16)$
$+(1\times14)+(1\times35.45)$
$= 96+8+16+14+35.45$
$= 169{\cdot}45$

$$\therefore \quad n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

$$= \frac{170}{169{\cdot}45} = 1$$

$\therefore$ Molecular formula = (Empirical formula) n
$= C_8H_8ONCl$

EXERCISE

1. Describe a method to estimate the amount of carbon and hydrogen present in an organic compound.
2. Describe Kjeldahl's method of estimating the nitrogen
3. How will you estimate sulphur and halogens using Carius method ?

PROBLEMS

1. A compound gave the following results on analysis. 0·78 g of a substance on combustion yielded 2·64 g of carbon dioxide and 0·54 g of water. Calculate the percentage of carbon and hydrogen in it.
2. 0·1647 g of an organic acid on combustion yielded 0·3418 g of carbon dioxide and 0·0835 g of water. Calculate the percentage of carbon and hydrogen in it.
3. 0·3201 g of an organic substance in a Dumas method of estimation of nitrogen yielded 38·1 ml of nitrogen at 17°C and 769 mm pressure, (Aqueous tension at 17° C = 14·5 mm). Calculate the percentage of nitrogen in it.
4. An organic compound gave the following results on analysis.

   (a) 0·73 g of the substance gave 1·32 g of carbon dioxide and 0·6 g of water. (b) 0·365 g of it gave

56 ml of nitrogen at N.T.P. Calculate the percentage of carbon, hydrogen and nitrogen in it.

5. In Kjeldahl's estimation of nitrogen, 0·305 g of an organic compound was distilled into 50 ml of 0·1 N sulphuric acid. The excess of the acid required 24·9ml of 0·1 N sodium hydroxide for neutralisation Calculate the percentage of nitrogen in it.

6 0·354 g of an organic compound in Kjeldahl's method yielded ammonia which was absorbed in 70 ml of 0·2N sulphuric acid. The excess of the acid required 40 ml of 0·2 N sodium hydroxide for complete neturalisation. Calculate the percentage of nitrogen in the compound.

7 0·4 g of an organic compound in Carius method yielded 0·746 g of barium sulphate. Find the percentage of sulphur in the compound.

8. 0·301 g of an organic compound gave 0.282 g of silver bromide by Carius estimation. Calculate the percentage of bromine in the compound.

9. An organic compound gave the following results on analysis :

Carbon = 70·61%, Hydrogen = 12·90%, Nitrogen = 16·40%. Find the empirical formula of the compound.

10 An organic compound gave the following percentage composition on analysis : Carbon = 26·09, Hydrogen = 4·89, Iodine = 69·02. Find its empirical formula.

11 An organic substance gave the following percentage composition on analysis: Carbon=54·55%. Hydrogen = 9·09%, Oxygen = 36·26%. Find out the molecular formula if the molecular weight of the substance is 88.

12. An organic compound contains carbon 52·17% and hydrogen = 13·05%. The vapour density of the

compound is 23. Arrive at the empirical and molecular formula of the substance.

13. An organic compound containing bromine gave the following results on analysis.

(a) 0·246 g of the compound gave 0·198 g of carbon oxide and 0·1014 g of water on complete combustion. (b) By Carius method 0·37 g of the compound gave 0·638 g of silver bromide.

What is the molecular formula of the compound if its vapour density is 54·5?

14. An organic substance contains carbon 71·29% and hydrogen 14·86%. 0·3201 g of the substance according to Dumas method gave 38·1 ml of nitrogen at 17° and 769 mm pressure. (aqueous tension at 17° is 14·5 mm). Calculate the molecular formula of the substance if the substance contains only one nitrogen atom per molecule.

CHAPTER V

STRUCTURAL AND STEREO ISOMERISM

The molecular formula of a compound may sometimes be represented by more than one structural formula, This phenomenon is called **isomerism**. The compounds which have the same molecular formula but different structural formulae are called **'isomers'**.

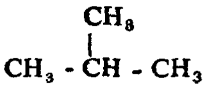
Isomerism can be broadly divided into two types (1) Structural isomerism and (2) Stereoisomerism. Structural isomerism is due to the difference in structure and is classified in many different ways.

Structural Isomerism

(i) **Chain or nuclar isomerism** This is exhibited by compounds which differ in the arrangement of the carbon atoms

e.g. n-butane $CH_3 - CH_2 - CH_2 - CH_3$

Isobutance



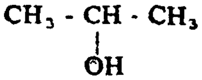
$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - CH_3$

(ii) **Position isomerism** · · It is exhibited by compounds which have the same carbon skeleton, but differ in the position occupied by a substituent group.

e.g. (1) n-propanol

$CH_3CH_2CH_2OH$

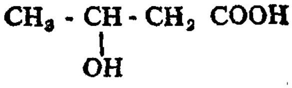
Isopropanol



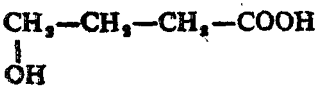
$CH_3 - \underset{\underset{\displaystyle OH}{|}}{CH} - CH_3$

(2) α, β, γ – hydroxybutyric acids

$CH_3 - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - COOH$



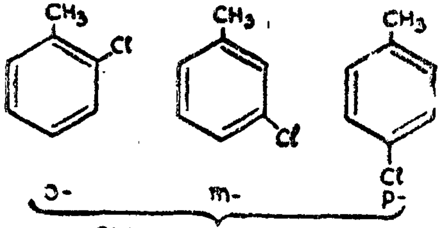
$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2\ COOH$



$\underset{\displaystyle OH}{\underset{|}{CH_2}}—CH_2—CH_2—COOH$

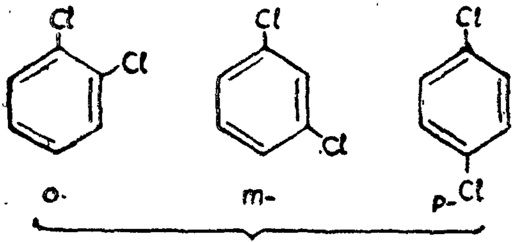
The various di-substituted benzene derivatives : When chlorine and methyl groups are the substituents in a benzene ring, there can be three isomers, depending on the positions of the substituents. They are :

orthochlorotoluene or o-chlorotoluene.
meta chlorotoluene or m-chlorotoluene.
para chlorotoluene or p-chlorotoluene.



CHLOROTOLUENES

Similarly there can be three isomers when two chlorine atoms are present. They are called respectively o-dichloro, m-dichloro or p-dichloro benzenes. Their names are also denoted with numbers for the positions. They are respectively 1 : 2 dichloro, 1 : 3 dichloro, 1 : 4 dichloro benzenes.



DICHLOROBENZENES

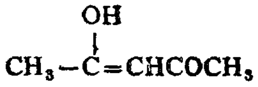
(iii) Functional group isomerism : This is exhibited by compounds having different functional groups. i.e., compounds having the same molecular formula but belonging to different homologous series.

Ethanol $CH_3\ CH_2\ OH$	and	dimethyl ether $CH_3 - O \cdot CH_3$
Acetone $CH_3\ COCH_3$	and	propionaldehyde $CH_3\ CH_2CHO$

(iv) Metamerism : This type of isomerism arises due to the difference in the arrangement of the carbon chain attached to the same polyvalent atom other than carbon atom. Thus diethyl ether $C_2H_5-O-C_2H_5$ and methyl propyl ether $CH_3-O-CH_2\ CH_2CH_3$ are metamers. So also propyl amine $CH_3CH_2CH_2NH_2$, ethyl methyl amine $C_2H_5NHCH_3$ and trimethyl amine $N(CH_3)_3$ are metamers.

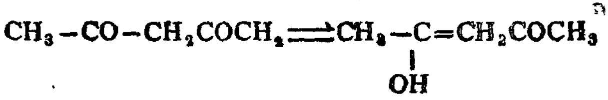
(v) Tautomerism : This type of isomerism results due to a substance exhibiting the properties characteristic of two functional groups (therefore two isomers) but existing as one substance as characterised by its physical properties.

The $CH_3COCH_2COCH_3$ acetyl acetone exists as a mixture of the two isomers $CH_3COCH_2COCH_3$ a ketone and



$$CH_3-\overset{\overset{OH}{|}}{C}=CHCOCH_3$$

an enol. The two forms exist in dynamic equilibrium.



$$CH_3-CO-CH_2COCH_3 \rightleftharpoons CH_3-\underset{\underset{OH}{|}}{C}=CH_2COCH_3$$

This type is known as keto-enol tautomerism.

Stereoisomerism

This is a type of isomerism exhibited by isomers having the same structure but differing in their spatial arrangement.

This stereoisomerism can be broadly divided into two types (1) Optical isomerism (2) Geometrical isomerism. Optical isomers (described later) have their molecular structures such that their mirror images are not superimposable and they rotate differently the plane of polarized light. Geometrical isomers are compounds containing double bonds (or rings) which enable the component parts of the molecules of such compounds to occupy different spatial positions

Optical isomerism

Polarized light and optical activity The wave theory postulates that ordinary light is capable of vibrating in all possible planes perpendicular to the line of the propagation. But if a beam of monchromatic light is passed through a Nicol prism, the emerging light is found to vibrate in one plane only. This beam of light whose vibrations are in only one plane is called as the plane polarized light

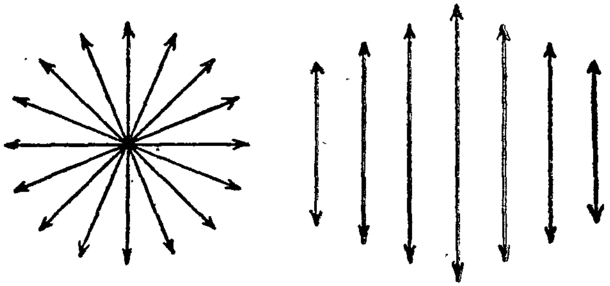


Fig. 86

Unpolarized light Polarized light

Nicol prism is obtained by combining two prisms of Iceland spar suitably cut for the purpose. It is named after **William Nicol** of Edinburgh.

When this plane polarized light is passed through a solution of certain substances like cane sugar, lactic acid, tartaric acid etc, it was found that the plane of the polarized light is rotated through a certain angle either in the clockwise direction or in the anti clockwise direction. Such substances which have the power to rotate the plane of the polarized light are called as **optically active** substances while the phenomenon is called as **optical activity**. Isomers which exhibit this property are called **optical isomers.**

Substances which rotate the plane of plane polarized light to the right (or in the clockwise direction) are called as **dextro rotatory**. The substances that rotate the plane of plane polarized light to the left (or in the anticlockwise direction) are called **laevo rotatory.**

The instrument which is used to measure the angle of rotation of the polarized light is called **a polarimeter**

The extent to which the plane of the polarized light is rotated depends on the following factors

(1) Nature of the compound.
(2) Concentration of the solution.
(3) Length of the tube used.
(4) Nature of the solvent.
(5) Wave length of the light used
(6) Temperature.

The rotating power of a given solution is usually expressed in terms of **specific rotation.**

Specific rotation is defined as the angle of rotation produced by one decimeter length of solution having one gram of the substance per ml. If the measurement is made at temperature t° using sodium light (the D line) then.

$$\text{specific rotation} = \frac{100 \times \text{observed angle of rotation}(\theta)}{\text{Length in decimeter} \times \text{grams of substance present in 100 ml of the solution.}}$$

$$\text{or } [\alpha]_D = \frac{100 \times A}{l \times c}$$

Molecular rotation is given by multiplying specific rotation by molecular weight.

It is found that substances like lactic acid **exist in two forms**. These isomers resemble one another in their chemical properties and in most of their physical properties, but differ in their behaviour towards the polarized light. These isomers are called optical isomers.

To explain the phenomenon of optical isomerism **Van't Hoff** and **Le Bel** proposed that the carbon atom lies at the centre of a regular tetrahedran and its four valencies are directed towards the four corners of the regular tetrahedron. Four different groups attached to a carbon atom gives rise to optical activity. Hence it was suggested that isomerism is due to the different spatial arrangement of the four different atoms or radicals in the molecule around the central carbon atom. Optical isomerism of lactic acid and of tartaric acid are described in their respective chapters.

Geometrical isomerism or cis-trans isomerism

This is a type of isomerism which is due to the difference in spatial arrangements of groups about the doubly bonded carbon atoms.

Such compounds possess molecular symmetry and because of this they are not optically active. The double bond in these compounds prevent free rotation between the two carbons. Hence different groups occupy permanently different positions about the double bond.

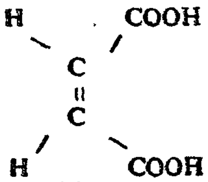
The isomer in which the similar groups lie on the same side of the double bond is called the **cis-isomer** (Latin, cis-same side).

The isomer in which the similar groups lie on the opposite sides of the double bond is called as the **trans-isomer** (Latin trans-across).

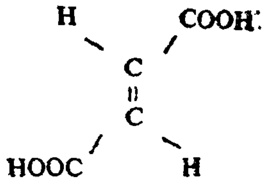
Due to the existence of cis and trans isomers, geometrical isomerism is also called as **cis-trans isomerism.**

Examples

1 Maleic and fumaric acids.



(cis)



(trans)

Both maleic and fumaric acids have the molecular formula $C_4H_4O_4$. They also have same structural formula HOOC CH=CHCOOH. The possible spatial arrangements are as given above. The problem now is to decide which of the above two formulae represents maleic and which fumaric acid. The following evidence indicate that cis isomer is maleic acid and trans isomer is fumaric acid :

(i) Maleic acid (and not fumaric acid) easily forms an anhydride on heating. This is possible only when the two-COOH groups are on the same side. Hence maleic acid should be the cis isomer. The trans isomer must be fumaric acid.

EXERCISE

1. What is isomerism? Mention the types of isomerism. Give an example for each type of isomerism.

2. Give the types of isomerism exhibited by the following compounds :—
   - (a) n-butane and isobutane.
   - (b) 1-propanol and 2-propanol.
   - (c) Ethyl alcohol and dimethylether.
   - (d) n-propyl chloride and isopropyl chloride.
   - (e) Dimethyl benzene.

(f) Dinitrobenzene

(g) Nitro toluene.

3. Define the following :—

   (a) Plane polarized light.

   (b) Optical activity

   (c) Optical isomerism.

4. What is specific rotation? What are the factors on which the specific rotation depends ?

5. Give an account of cis-trans isomerism ?

6. What are geometrical isomers ? Give examples.

7. Give the conditions required for a compound to exhibit optical isomerism and geometrical isomerism.

CHAPTER VI

TYPES OF BONDS

According to the Bohr model of an atom, the atom consists of a tiny nucleus around which the electrons are arranged in definite shells or orbits. But the wave mechanical theory has replaced the orbits by three dimensional orbitals, which represent the shape and size of the space around the nucleus with in which the probability of finding the eletron is high. This has been detailed earlier. Let us now summarise some of the facts presented in earlier.

Quantum numbers

The energy of an electron is considered to be governed by values assumed by its four quantum numbers.

The principal quantum number : (n) This gives an approximate measure of the size of the electron cloud. The bigger the value n, the greater is the volume of the bulk of charge density. The value of n can be 1, 2, 3, 4, 5 etc.

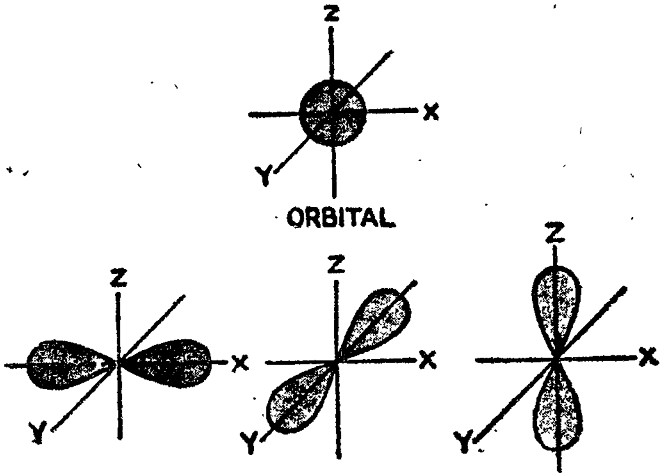
2. **The azimuthal quantum number .** (*l*) This is related to the actual shape of the electron cloud. This *l* can take values of 0 to (n—1). Thus if n = 4, the volues of *l* can be 0, 1, 2, 3.

3. **The magnetic quantum number** (m) This is related to the way in which the electron cloud is oriented in space. m can take values from — *l* . .. . O .... + *l* Thus if *l* = 1, then m = — 1, 0, + 1

4. **The spin quantum number** (s) This is a measure of the direction of the spin of the electron. It can take only two values + ½ and - i.e. a spin can be in clockwise direction or in anticlockwise direction. When *l* = 0, the shape of the electron cloud is spherical and the electron is referred to as s

electron. The spherical orbital which contains the **electron is** called as s **orbital.**

When $l = 1$, the shape of the orbital is like a dumb-bell and the electron is referred to as a p electron. The electrons present in this p-orbital is referred to as p electrons. We have actually three p orbitals which are mutually perpendicular to each other and directed towards the three co-ordinate axes. Each of the p orbital consists of two lobes lying along the axis as shown in the fig. 87. The orbitals along the three axes are referred to as p_x, p_y, p_z.



p_x-orbital p_y-orbital p_z-orbital

Fig. 87

For $l = 2$ and $l = 3$, the shapes of the electron clouds are much more complex and the electrons present in them are said to be d and i respectively.

Molecular orbitals

When atoms combine to form a molecule, the atomic orbitals form each atom overlap to form a molecular orbital.

The electrons will now be held in common between the two nuclei.

For example, when two H atoms combine to form a molecule of hydrogen, the two s orbitals overlap to form a molecular orbital which encloses the two nuclei.

Sigma (σ) bonds

These are bond orbitals which are symmetrical about the line joining the two nuclei. These are formed as a result of maximum overlapping of s-s, s-p or p-p orbitals along their axes.

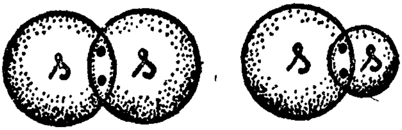


Fig. 88
s.s. overlapping

Thus in the formation of hydrogen molecule two s orbitals from two hydrogens overlap along their axes. The bond formed is a sigma (σ) bond.

Fig. 89
s-s. overlapping in H_2 molecule

Pi (π) bond

The pi (π) bonds are formed by the sideways or lateral overlap of the p orbitals of two atoms. The formation of pi (π) bond is exemplified in the structure of ethylene given under hybridisation.

Hybridisation

The electronic configuration of carbon is $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$ Thus carbon has two unpaired electrons. Hence it should be divalent. But carbon actually exhibits a valency of four in all its compounds. Hence it is postulated that one of the 2s electrons is promoted to $2p_z$ orbital. The carbon atom in this state is said to be excited and now it has four unpaired electrons.

C	1s	2s	2p		
Ground state	↑↑	↑↓	↑	↑	
C	**1s**	**2s**	**2p**		
Excited state	↑↓	↑	↑	↑	↑

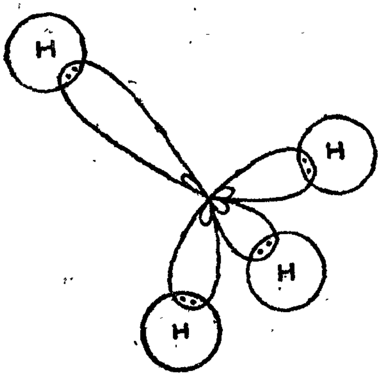
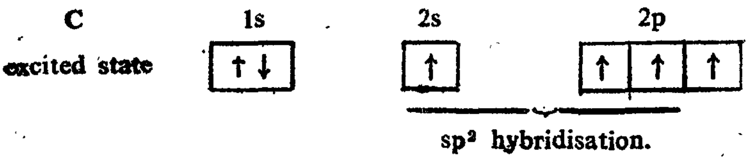


Fig. 90
sp^3 hybridised orbitals

However, it is clear that the four unpaired electrons are of two types—s-electrons and p electrons. Hence, the strength of the bond formed by them must also be different. But actually in methane (CH_4) it is found that the four C-H bonds have equal strength. Therefore, it is proposed that, for the purpose of bonding, these four orbitals combine among themselves or hybridise to give four new identical orbitals, which are inclined at an angle of 109°28' i.e. towards the corner of a regular tetrahedron of 109°28'. This phenomenon is referred to as hybridisation. These hybrid orbitals are now called as sp^3 **hybrid orbitals.**

Now, let us consider the structure of ethylene and acetylene. In ethylene, to form the required number of bonds, each carbon atom contributes one s and two p orbitals which are hybridised to give three sp^2 hybridised orbitals. These hybridised orbitals lie in the same plane and the angle between any two of them is 120°.

In the molecule of ethylene (C_2H_4) two carbons are joined by means of sigma (σ) bonds formed by the overlap of an sp^2 orbital with other sp^2 orbital. Similarly the four C—H bonds are formed by the overlapping of sp^2 orbital of carbon with s-orbitals of hydrogn. All these five bonds are sigma (σ) bonds.



After the formation of sigma (σ) bonds, there remains on each carbon atom one unhybridised p orbital perpendicular to the plane of the C—H and C—C bonds. The second bond between the carbon atoms in ethylene is formed by the sideways overlap of these p-orbitals as shown in the figure.

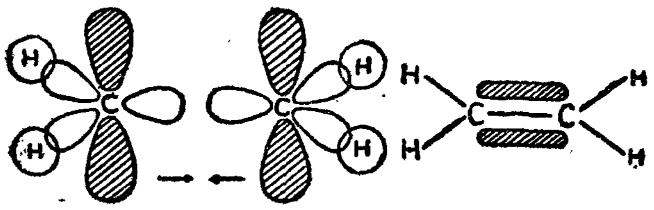
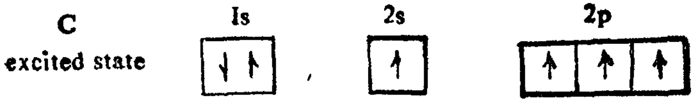


Fig. 91
Bonding in ethylene

The bond formed in this manner is referred to as pi (π) bond. The electron cloud is above and below the plane of the sigma (σ) bond. Thus the double bond in ethylene is made up of one sigma bond and one pi bond.

In the case of acetylene, to form the required bond two orbitals one s and one p orbital of each carbon atom hybridise to give two identical sp orbitals. The two sp orbitals of each carbon forms one sigma (σ) bond with the hydrogen and other sigma (σ) with the neighbouring carbon. These bonds are linear since the two sp orbitals are also linear.



SP$_2$ hydridisation

Thus after the formation of the sigma (σ) bonds there remain on each carbon two unhybridised p orbitals which are mutually perpendicular to one another. Each pair of these p orbitals now overlap in sideways to form two pi (π) bonds. This situation can be represented as below

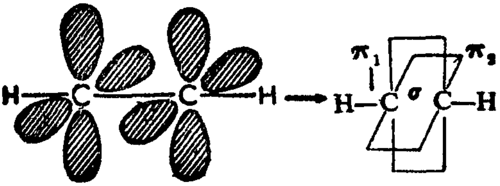


Fig. 92
Two pi bonds in acetylene

Thus the triple bond in acetylene is actually made up of a sigma (σ) bond and two pi (π) bonds.

Delocalisation

In ethylene, the pi bond is localised between the two carbon atoms. Hence, if a compound contains two double bonds it is logical to expect the electrons present to be localised between the doubly bonded carbon atoms. Hence the properties of these two types of compounds should be similar. But in compounds where the double bond and single bonds are present in alternate positions (conjugated systems) the properties are found to be abnormal. This is due to delocalisation of pi electrons in the compounds having conjugated bond. 1 : 3 butadiene is an example where in there is delocalisation of pi electrons.

$H_2C = CH - CH = CH_2$

1, 3, butadiene.

Each carbon atom in 1, 3— butadiene is in a sp^2 hybridised state. Hence each of the carbon in this compound will be having one unhybridised p - orbital as shown in the figure.

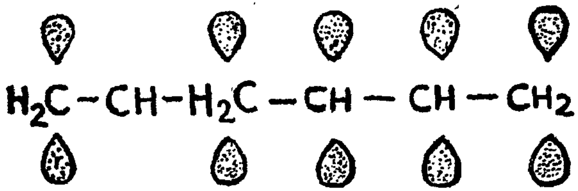


Fig. 93·
Unhybridised p-orbitals

The overlapping of p-orbitals on adjacent carbon atoms leads to two localised pi bonds as shown below

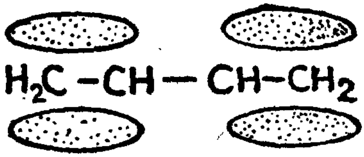


Fig. 94
Formation of localised pi bonds

Interaction is also possible between the p atomic orbitals of the two central carbon atoms, as well as each of these and the p orbitals on out side carbon atoms. Thus an alternative formulation is thus a π orbital covering all the four carbon atoms as shown below, in which the electrons are said to be delocalised as they are now spread over and held in common by all the four carbon atoms. There are however, two such delocalised orbitals each containing one ring above and the other below the plane of the rest of the molecule.

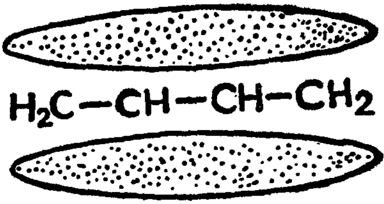


Fig. 95
Electron delocalisation

Benzene is another example wherein delocalisation concept can be invoked. In this each carbon atom is in a sp^2 hybridised state. Hence, each of the carbon atom will be having one unhybridised p-orbital as shown in the figure (Fig. 96).

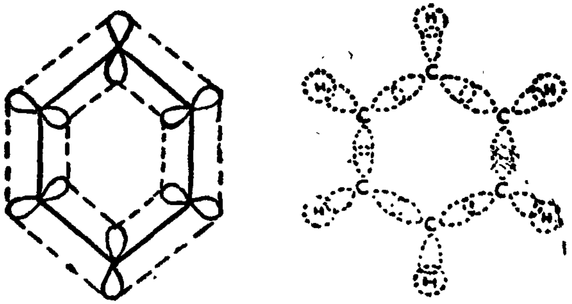


Fig. 96
Unhybridised p-orbital

The overlapping of these p-orbitals leads to the formation of delocalised pi bonds as shown in the figure (Fig. 97).

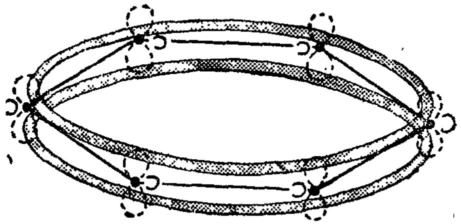


Fig. 97
Delocalisation of pi-bonds

EXERCISE

1. Give the names of the four quantum numbers which govern the energy of an electron present in an orbit.

2. Give the shape of the s and p orbitals.

3. Write a short note on

   (i) Sigma and pi bond. (ii) Hybridisation.

4. What is the kind of hybridisation present in each of the following molecule :

   (i) Methane (ii) Ethylene (iii) Acetylene.

5. Using the concept of hybridisation arrive at the structures of methane, ethylene and acetylene.

6. Explain the concept of delocalisation taking 1, 3-butadiene as an example.

7. Explain with a diagram the slope of the delocalised orbitals in benzene.

CHAPTER VII

REACTION INTERMEDIATES

Introduction

A chemical equation indicates only the reactants and the final products of a reaction. It rarely indicates how the reaction proceeds. Much work has been done in recent years so as to know how actually the reaction proceeds. These actual steps by which the reaction proceeds are known as the **mechanism of the reaction** The main advantage of this mechanistic approach lies in the fact that with the help of these few guide lines we can explain how the reaction actually proceeds and we can even forecast the outcome of changing the conditions of the chemical reaction.

Types of reactions

Organic reactions may be classified into the following types :

1. Substitution

These reactions involve the direct replacement of an atom of group by some other atom or group

$$CH_4 + Cl_2 \rightarrow CH_3 - Cl + HCl \qquad ...(1)$$

$$CH_3Br + H_2O \rightarrow CH_3OH + HBr \qquad ...(2)$$

In (1) one hydrogen of methane is replaced by one chlorine atom. In (2) the bromine of the alkyl halide is replaced by the hydroxyl group.

2. Addition

This is a type of reaction in which a group or radical is added to a compound.

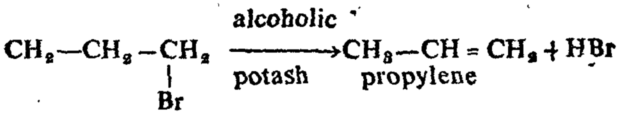
Bromine, on treatment with ethylene, gives ethylene bromide, by the addition of bromine to ethylene.

$$H_2C = CH_2 + Br-Br \rightarrow \underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH_2}}$$

3. Elimination

This is a type of reaction in which there is removal of a molecule of a substance when two substances react with each other.

The reaction between propyl bromide and alcoholic potash resulting in the removal of hydrogen bromide is an elimination reaction.



$$CH_2-CH_2-\underset{Br}{\underset{|}{CH_2}} \xrightarrow[\text{potash}]{\text{alcoholic}} \underset{\text{propylene}}{CH_3-CH=CH_2} + HBr$$

4. Isomerisation

Isomers are compounds that have the same molecular formula but different structural formula. Hence isomerisation is a reaction which involves the rearrangement of atoms in a molecule to form another isomer of the same substance.

For example : 1-butene isomerises to 2-butene on heating to 400–500°C in the presence of a catalyst like $AlCl_3$.

$$\underset{\text{1-butene}}{H_3C-CH_2-CH=CH_2} \xrightarrow[400-500^\circ C]{AlCl_3} \underset{\text{2-butene}}{CH_3-CH=CH-CH_3}$$

5. Polymerisation

This is a reaction in which small molecules combine among themselves in large number to make a large molecule. The compound obtained finally is called a **polymer.** The simple compounds, from which polymers are made are called as **monomers.**

For example: Ethylene molecules combine among themselves at very high temperature and pressure to give polyethylene which is also called "polythene".

$$\underset{\text{ethylene}}{n\,CH_2 = CH_2} \xrightarrow[\text{and high pressure}]{\text{high temp}} \underset{\text{polythene}}{(-CH_2-CH_8-)}.$$

Types of clevages

A chemical reaction occurs with breaking of old bonds and with the formation of new bonds.

For example let us consider the following reaction :

$$R-X+Y \longrightarrow Y-R+X.$$

Here the bond between $R-X$ is broken in the reactant, while a new bond $Y-R$ is formed in the product.

There are actually two ways by which the $R-X$ may be broken depending upon the experimental conditions and the nature of X, Y and R.

(i) The bond breaks in such a way that each atom joined by the bond carries one electron of the shared pair.

This results in the formation of highly reactive species called **free radicals** or **odd electron molecules.**

e.g. $R-X \rightarrow R^{\cdot} + X^{\cdot}$

This type of fission of a covalent bond is termed as **homolytic fission or homolysis**

(ii) One of the two atoms joined by the bond (R or X) may have both the electrons with it. If R is the atom which retains both the shared electrons, then this will result in R acquiring a negative charge while X will attain a positive charge.

$$R - X \rightarrow R\,(^-) + X\,(^+)$$

Breaking of a bond in this manner is known as **heterolysis or, heterolytic fission.**

This type of fission thus results in the formation of charged ions. If the positive charge rests on a carbon atom then it is termed as **carbonium ion.** If the negative charge is on the carbon then it is termed as **carbanion.**

Reaction intermediates

In a chemical reaction, the reactants are converted into the products through the intermediate formation of some species which are termed as **reaction intermediates.** These are in general three types of intermediates (a) Free radicals (b) Carbonium ions (c) Carbanions.

(a) Free radicals

An atom or group of atoms possessing one or more unpaired electrons is called a free radical.

Free radicals are extremely reactive and are present as intermediates in many chemical reactions such as spontaneous decomposition, addition, displacement, rearrangement etc.

These free radicals are produced by the homolytic fission of a covalent bond. This homolytic fission occurs either in the presence of light or on heating or by the action of X-rays on molecules. Reactions which involve free radicals are usually chain reactions. Some free radi cals are given bellow :

CH_3—methl radical

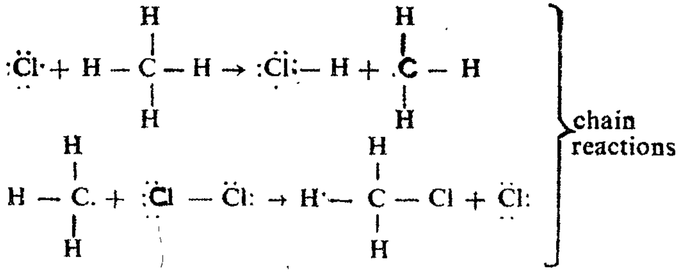
C_2H_5—ethyl radical

C_6H_5—phenyl radical

The reaction of chlorine with methane in the presence of sunlight proceeds by the following chain mechanism—

1. $Cl_2 + \text{light quantum} \rightarrow 2:\ddot{\underset{..}{Cl}}:$

2.



$:\ddot{\underset{..}{Cl}}\cdot + H-\overset{H}{\underset{H}{C}}-H \rightarrow :\ddot{\underset{..}{Cl}}:-H + .\overset{H}{\underset{H}{C}}-H$

3.

$H-\overset{H}{\underset{H}{C}}. + :\ddot{\underset{..}{Cl}}-\ddot{\underset{..}{Cl}}: \rightarrow H^{\cdot}-\overset{H}{\underset{H}{C}}-Cl + \ddot{\underset{..}{Cl}}:$

chain reactions

(b) Carbonium ions

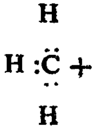
A group of atoms that contain a carbon atom with **only** six electrons around it is termed as a **carbonium ion.**

This is another extremely reactive intermediate in reactions involving hydrolysis, dehydration, dehydrohalogenation etc.

The carbonium ions are formed result by the heterolytic fission of a covalent bond.

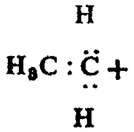
The carbonium ions are further classified as primary, secondary and tertiary carbonium ions depending upon the nature of the carbon atom which has the positve charge.

For example



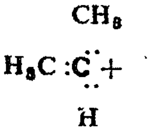
$H:\overset{H}{\underset{H}{\ddot{\underset{..}{C}}}}+$

carbonium ion. Methyl cation



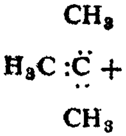
$H_3C:\overset{H}{\underset{H}{\ddot{\underset{..}{C}}}}+$

methyl-carbonium ion. (Primary) Ethylcation



$H_3C:\overset{CH_3}{\underset{H}{\ddot{\underset{..}{C}}}}+$

dimethyl carbonium ion (Secondary) or isopropylcation



$H_3C:\overset{CH_3}{\underset{CH_3}{\ddot{\underset{..}{C}}}}+$

trimethy carbonium ion (Tertiary) t-butyl cation

The order of stability of these, carbonium ions is found to be.

Tertiary > Secondary > Primary > Methyl carbonium ion.

The hydrolysis of an alkyl halide by an alkali proceeds through the formation of a carbonium ion. An alkyl halide first ionises to give carbonium ion

$$R - \underset{..}{\ddot{X}}: \overset{\text{slow}}{\rightleftharpoons} R^+ + :\underset{..}{\ddot{X}}:^-$$

Then the carbonium ion reacts with the hydroxyl ion to form the alcohol.

$$R^+ + {}^-:\underset{..}{\ddot{O}}: - H \xrightarrow{\text{fast}} R - \underset{..}{\ddot{O}} - H$$

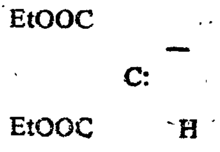
(C) Carbanions

These are negative groups which contain a carbon atom having a pair of unshared electrons in its valence shell.

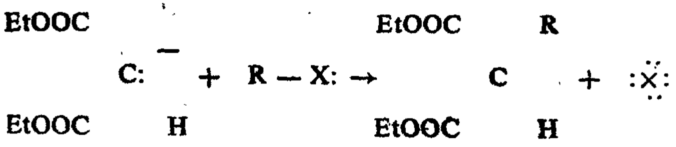
These carbanions are produced by the heterolytic fission of a C - C bond.

e.g. $H_5C_2OOC-\overset{-}{C}H-COOC_2H_5$ Anion of malonic ester.

The malonic ester gives a sodio derivative with sodium ethoxide. This sodio derivative is a carbanion.



This reacts with alkyl halides to give alkyl derivatives of malonic ester :



$$\begin{matrix}\mathrm{EtOOC} & & \\ & \overset{-}{\mathrm{C}}: & \\ \mathrm{EtOOC} & & \mathrm{H}\end{matrix} + \mathrm{R}-\mathrm{X}: \rightarrow \begin{matrix}\mathrm{EtOOC} & & \mathrm{R} \\ & \mathrm{C} & \\ \mathrm{EtOOC} & & \mathrm{H}\end{matrix} + :\underset{\cdot\cdot}{\ddot{\mathrm{X}}}:$$

Types of Reagents

Certain atoms like chlorine and certain groups like—NO_2 and—COOH have a tendency to withdraw electrons towards themselves, while certain groups like methyl have a tendency to donate electrons. Hence, if a molecule contains any of these groups, then there is a possibility to identify electron rich or electron deficient centres in the molecule.

Let us consider a molecule with an electron rich centre. It will be readily attacked by groups or atoms that are electron deficient, because the electron-deficient reagent is looking for a electron rich centre where it can attack. Such reagents are called electrophilic reagents (electron-loving) or electrophiles and the reaction is referred to as electrophilic reaction.

Examples of electrophiles

H^+, H_3O^+, HNO_3, H_2SO_4, Br_2, $AlCl_3$, $FeCl_3$ etc.

Let us consider a molecule with an electron deficient centre. It will be readily attacked by an electron rich reagent. Such reagents are referred to as **nucleophilic reagents** (nucleus-loving) or **nucleophiles** and the reaction is called as nucleophilic reaction.

Examples of nucleophiles

HO^-, HSO_3^-, CN^-

H_2O, NH_3, CH_3OH, etc.

The hydrolysis of an alkyl halide in the presence of alkali ($H-\underset{\cdot\cdot}{\ddot{O}}:^-$) is an example of a nucleophilic reaction.

Thus we can arrive at the following conclusion. An electrophilic reaction is initiated by the attack of an electrophilic reagent and a nucleophilic reaction is initiated by the attack of a nucleophilic reagent.

QUESTIONS

1. What do you understand by the following terms?
   - (1) Homolytic fission
   - (2) Heterolytic fission
   - (3) Carbonium ion
   - (4) Carbanion
   - (5) Free radical

2. What are electrophilic and nucleophilic reagents? Give examples of such reagents.

3. Illustrate what do you understand by "homolysis" and "heterolysis"

4. Explain the terms "electrophilic" and "nucleophilic" reagents.

5. What are carbonium ions and carbanions?

6. Classify the folowing as electrophiles and nucleophiles H^+, OH^-, H_2O^+, HNO_3, HSO_2^-, Br_2, $AlCl_3$, $FeCl_3$ CN^-, H_2SO_4.

7. What do you understand by the following terms?
   - (1) Substitution
   - (2) Elimination
   - (3) Addition
   - (4) Polymerisation

8. Illustrate with examples the different types of reactions which organic compounds undergo.

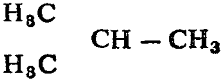
CHAPTER VIII

ALIPHATIC HYDROCARBONS

Compounds containing only carbon and hydrogen are called **hydrocarbons**. Hydrocarbons are classified according to their chemical behaviour and structural relationship. Hydrocarbons such as methane and ethane contain the maximum possible amount of hydrogen in combination with carbon. These molecules are said to be saturated with hydrogen and so they are called saturated hydrocarbons. These are noted for their small chemical activity. They are called **paraffins.** [L-Parum = little; affinis = affinity.] They form a series of compounds called paraffin series. This series is now called by a systematic nomenclature as alkanes. They are represented by the general formula C_nH_{2n+2}. There are other series of hydrocarbons where the carbon atoms do not have their full complement of hydrogen atoms. They are called **unsaturated** hydrocarbons. There are two series of unsaturated hydrocarbons; they are olefine series with the general formula $C_n H_{2n}$ and actylene series with the general formula $C_n H_{2n-2}$

The class name for saturated aliphatic hydrocarbon is alkanes or paraffins. They are represented by the general formula C_nH_{2n+2}. Their names end with ane—

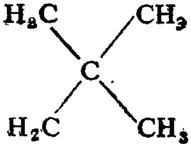
In the trivial system of nomenclature, the straight chain paraffins are termed 'normal' usually abbreviated to **n.** ; those with a branched-chain like



$\begin{matrix} H_3C & \\ & CH-CH_3 \\ H_3C & \end{matrix}$

are termed iso- whereas others containing quarternary carbon atom.

e.g.



are called neo.

Formula	Name
CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
C_5H_{12}	Pentane
C_6H_{14}	Hexane
C_7H_{16}	Heptane
C_8H_{18}	Octane
C_9H_{20}	Nonane
$C_{10}H_{22}$	Decane

In the IUPAC system the alkanes are named according to the following rules :

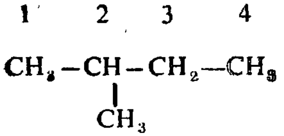
1. From the formula the longest continuous chain of carbon atoms is selected and the compound is considered as the derivative of this n-alkane. The general name of the hydrocarbon with this number of carbon atoms is used.

2. The carbon atoms of this continuous chain (basic chain) is numbered from one end to the other. All other carbon atoms are considered to belong to substituent alkyl groups which have replaced the hydrogen atoms in the basic chain. To each of the alkyl groups the number corresponding to that given in the basic chain is assigned,

3. The numbering of the basic chain must start from that end of the chain which results in the smallest possible numbers being used in the final name.

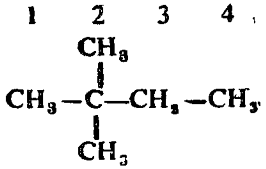
The substituent alkyl groups are named in the alphabetical order.

Examples :



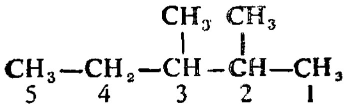
$$\overset{1}{CH_3}-\overset{2}{\underset{\underset{CH_3}{|}}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

2—methyl butane



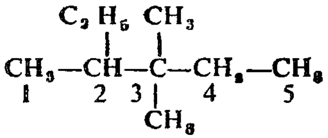
$$\overset{1}{CH_3}-\overset{2}{\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

2, 2—dimethyl butane



$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{\overset{\overset{CH_3}{|}}{CH}}-\underset{2}{\overset{\overset{CH_3}{|}}{CH}}-\underset{1}{CH_3}$$

2, 3, dimethyl pentane



$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{C_2H_5}{|}}{CH}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{4}{CH_2}-\underset{5}{CH_3}$$

2 ethyl, 3, 3 dimethyl pentane

General methods of preparation of alkanes

1. **From alkyl halides :** Compounds containing an alkyl group and a halogen are called **alkyl halide**. From alkyl halides, alkanes can be obtained by reduction and other methods.

(a) Alkanes are formed when an alkyl halide is reduced by hydrogen from zinc-copper couple and alcohol, or aluminium amalgam and alcohol, or zinc dust suspended in alcohol. The iodides are generally used. The reaction is represented as

$$\underset{\text{Methyl Iodide}}{CH_3I} + 2H \rightarrow \underset{\text{Methane}}{CH_4} + HI$$

$$\underset{\text{Ethyl iodide}}{CH_3CH_2I} + 2H \rightarrow \underset{\text{Ethane}}{CH_3CH_3} + HI$$

(b) **Wurtz reaction :** When metallic sodium is refluxed with alkyl halide, two alkyl groups unite to form a higher homologue.

$$CH_3I + 2\,Na + CH_3I \rightarrow CH_3CH_3 + 2\,NaI$$

$$C_2H_5I + 2\,Na + C_2H_5I \rightarrow CH_3CH_2CH_2CH_3 + 2\,NaI$$

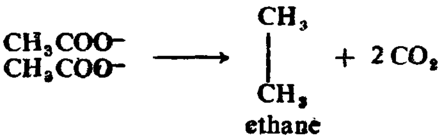
When a mixture of two alkyl halides is used, three different hydrocarbons may be formed. For example a mixture of methyl iodide and ethyliodide with sodium yields ethane, n-butane and propane.

2. **From acids :** (a) The organic acids contain the carboxylic group—COOH as the functional group. When salts sodium of the acids are heated with soda lime, alkanes are formed. This is actully a decarboxylation process.

$$\underset{\text{Sodium acetate}}{CH_3COONa} + NaOH \rightarrow \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

(b) **Kolbe's synthesis :** Electrolysis of an aqueous solution of the salt of a fatty acid produces an alkane. During electrolysis, the negative acid radical ions, the anions, travel towards the anode. There they get decomposed to alkane and carbon dioxide.

$$\underset{\text{Potassium acetate}}{CH_3COOK} \rightarrow K^+ + \underset{\text{Acetate ion}}{CH_3COO^-}$$



$$\begin{matrix} CH_3COO^- \\ CH_3COO^- \end{matrix} \longrightarrow \underset{\text{ethane}}{\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix}} + 2\,CO_2$$

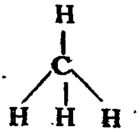
3. **From unsaturated hydrocarbons** : The unsaturated hydrocarbons are mixed with hydrogen and then passed over finely divided nickel catalyst. Alkanes are produced by the reduction of the unsaturated hydrocarbons.

$$\underset{\text{ethylene}}{CH_2 = CH_2} + H_2 \rightarrow \underset{\text{ethane}}{C_2H_6}$$

Methane

It is present in most of the oil wells as a constituent of natural gas. It is also present in marshy places. So it is known as **marsh gas.**

Structural formula



Preparation of Methane

1. It is formed on passing hydrogen over heated carbon at 1200°C.

$$C + 2H_2 \xrightarrow{1200^\circ C} CH_4$$

2. It is prepared by the hydrolysis of aluminium carbide with water or hydrogen chloride.

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

Laboratory method

Methane is prepared in the laboratory by heating anhydrous sodium acetate with soda lime ($NaOH + CaO$) in a hard glass tube.

$$CH_3COONa + NaOH \rightarrow CH_4 \uparrow + Na_2CO_3$$

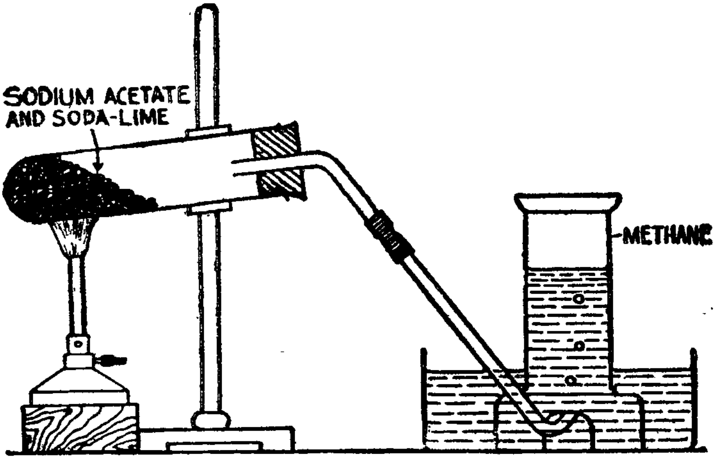


Fig. 98
Preparation of methane

The gas is collected by the displacement of water.

Properties

It is a colourless, odourless, and tasteless gas. It is lighter than air and insoluble in water.

1. Methane is combustible. It forms an explosive mixture with air (or) oxygen. It burns with a non-luminous flame to form carbon dioxide and water.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2\,H_2O.$$

2. When heated to 1200°C it decomposes into elements.

$$CH_4 \xrightarrow{\Delta} C + 2\,H_2\uparrow$$

3. Substitution reaction : Methane is a saturated hydrocarbon and so it undergoes substitution reaction with chlorine (or) bromine in diffused sunlight. All the four hydrogen atoms are replaced one by one by chlorine or bromine atoms. This type of reaction is called **substitution reaction**.

$$CH_4 + Cl_2 \rightarrow \underset{\text{methyl chloride}}{CH_3Cl} + HCl$$

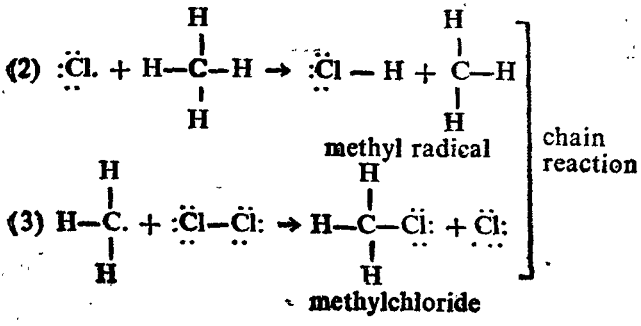
$$CH_3Cl + Cl_2 \rightarrow \underset{\text{methylene chloride}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \rightarrow \underset{\text{chloroform}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \rightarrow \underset{\text{carbon tetrachloride}}{CCl_4} + HCl$$

This reaction proceeds through the formation of radicals and by a chain mechanism.

$$(1)\ :\!\ddot{\underset{\cdot\cdot}{Cl}} - \ddot{\underset{\cdot\cdot}{Cl}}\!: + \text{light quantum} \rightarrow 2\ :\!\ddot{\underset{\cdot\cdot}{Cl}}.$$



$$(2)\ :\!\ddot{\underset{\cdot\cdot}{Cl}}. + H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H \rightarrow :\!\ddot{\underset{\cdot\cdot}{Cl}} - H + \underset{\text{methyl radical}}{\overset{\displaystyle H}{\underset{\displaystyle H}{\dot{C}}}-H}$$

$$(3)\ H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}. + :\!\ddot{\underset{\cdot\cdot}{Cl}}-\ddot{\underset{\cdot\cdot}{Cl}}\!: \rightarrow \underset{\text{methylchloride}}{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\ddot{\underset{\cdot\cdot}{Cl}}\!:} + \ddot{\underset{\cdot\cdot\cdot}{Cl}}\!:$$

4. In direct sunlight, methane reacts with chlorine explosively to form carbon and hydrochloric acid.

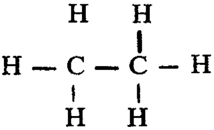
$$CH_4 + 2Cl_2 \xrightarrow[\text{sunlight}]{\text{direct}} C + 4\,HCl$$

5. Methane is resistant to acids and alkali. But nitric acid in the vapour state interacts with methane at 400°C and at a pressure of 10 atmospheres to form nitromethane.

$$CH_4 + HONO_2 \rightarrow CH_3NO_2 + H_2O$$

Uses: 1. Methane is used as a fuel. It is used for the preparation of methyl alcohol, methyl chloride etc.

Ethane



$$\begin{array}{ccccccc} & & H & & H & & \\ & & & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

It is the second member of the alkane family. It is also present in oil wells and in coal gas.

Preparation

1 Ethane is prepared by heating a mixture of anhydrous sodium propionate and soda lime. The gas is collected over water.

$$CH_3CH_2COONa + NaOH \rightarrow C_2H_6 \uparrow + Na_2\,CO_3$$

2. **Wurtz Synthesis**: Ethane is obtained by refluxing equimolecular amounts of methyl iodide with metallic sodium in dry ether,

$$CH_3I + 2\,Na + CH_3I \rightarrow C_2H_6 + 2NaI$$

Manufacture:

Ethane is commercially obtained by the catalytic hydrogenation of ethylene.

$$\underset{\text{ethylene}}{CH_2 = CH_2} + H_2 \xrightarrow{Ni} \underset{\text{ethane}}{C_2H_6}$$

• It is a colourless odourless and tasteless gas. It is slightly heavier than air and slightly soluble in water.

In its chemical properties it resembles methane.

1. It is combustible. It burns with air with a non-luminous flame to form carbon dioxide and water.

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$

2. When heated to 600°C it decomposes to ethylene and hydrogen.

$$C_2H_6 \xrightarrow{\Delta} C_2H_4 + H_2 \uparrow$$

Substitution reaction

3. It undergoes substitution reaction with chlorine or bromine in diffused sunlight.

$C_2H_6 + Cl_2 \rightarrow HCl + C_2H_5Cl$ monochloroethane.
$C_2H_5Cl + Cl_2 \rightarrow HCl + C_2H_4Cl_2$ dichloroethane.
$C_2H_4Cl_2 + Cl_2 \rightarrow HCl + C_2H_3Cl_3$ trichloro ethane.
$C_2H_3Cl_3 + Cl_2 \rightarrow HCl + C_2H_2Cl_4$ tetrachloroethane.

4. Ethane is resistant to acids and alkali. But nitric acid in the vapour state interacts with ethane at 400°C and under high pressure to form nitro methane.

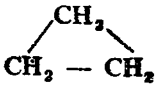
$$CH_3CH_2\boxed{H + HO}NO_2 \rightarrow C_2H_5NO_2 + H_2O$$

Uses

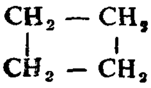
Ethane is used as a fuel.

Cyclo alkanes, cycloparaffins : These are closed chain hydrocarbons with the general formula C_nH_{2n}. They are isomeric with olefins but are saturated. These are named after the corresponding alkanes with the same number of carbon atoms.

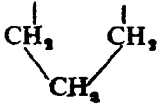
The following are some examples of the cycloalkanes :



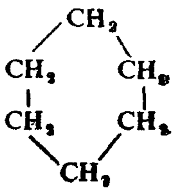
cyclopropane



cyclobutane



cyclopentane



cyclohexane

Cycloparaffins resemble paraffins in their physical properties but have higher boiling points than the corresponding alkanes.

Cyclopropane and cyclobutane are not stable. Cyclopentane and higher members are quite stable.

Cyclohexane exists in chair and boat forms.

Boat configuration   **Chair configuration**

Boat and Chair forms of Cyclohexane

Alkenes or Olefins

The unsaturated hydrocarbons which contain one carbon-double bond are called **olefins** and have the general formula C_nH_{2n}. Ethylene $CH_2 = CH_2$ being the simplest olefin, the double bond is often called **olefinic bond** or ethylenic bond.

Nomenclature

Their names end with ene (or) - ylene.

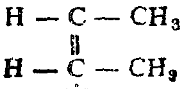
$CH_2 = CH_2$ ethylene (or) ethene.

$CH_3CH = CH_2$ propylene (or) propene.

$\underset{4}{CH_3}\underset{3}{CH_2}\underset{2}{CH} = \underset{1}{CH_2}$ 1-butylene (or) 1-butene.

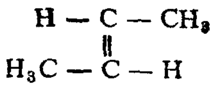
Geometrical Isomerism

Substituted olefins exhibit geometrical isomerism. For example, dimethylethylene exists in two forms. ($CH_3CH = CH\ CH_3$).



$$\begin{array}{c} H - C - CH_3 \\ \| \\ H - C - CH_3 \end{array}$$

cis



$$\begin{array}{c} H - C - CH_3 \\ \| \\ H_3C - C - H \end{array}$$

trans

The isomerism due to the difference in spatial arrangements of groups about the doubly bonded carbon atoms is called **geometrical isomerism.** The isomer in which the similar groups lie on the same side is called the **cis isomer** and the other in which the similar groups lie on the opposite sides are called **trans isomer.** Due to this cis and trans isomers geometrical isomerism is called **cis-trans isomerism.**

General methods of preparation of alkenes

1. **From alcohols**: When a molecule of water is removed from a molecule of an alcohol, by using the dehydrating agent concentrated sulphuric acid or phosphoric acid or alumina the corresponding olefin is formed.

$$C_nH_{2n+1}\,OH \xrightarrow{-H_2O} C_nH_{2n}$$

$$CH_3CH_2OH \longrightarrow CH_2=CH_2$$

ethyl alcohol ethylene

2. **From alkyl halides:** (a) When an alkyl halide is treated with alcoholic potash, hydrogen halide is removed resulting in the formation of an olefin.

$$Cn\;H_{2n+1}\,X \xrightarrow{-HX} C_nH_{2n}$$

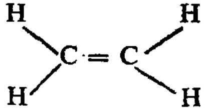
Usually higher members in the series are obtained in good yield.

(b) When dihalides in which the hologen atoms are attached to adjacent carbon atoms are heated with zinc, the two halogen atoms are removed resulting in an olefin.

$$CH_3CHBr\;CH_2Br + Zn \rightarrow CH_3-CH=CH_2 + ZnBr_2.$$

1, 2, dibromopropane propylene

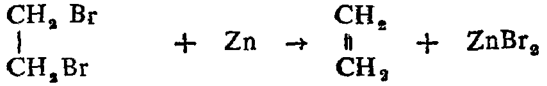
Ethylene



Ethylene is present in natural gas. It also occurs in coal gas and in wood gas.

Preparation

Ethylene is formed when ethylene dibromide is heated with zinc dust.



$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} + Zn \rightarrow \begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + ZnBr_2$$

Laboratory method

Ethylene is prepared by heating ethyl alcohol with an excess of concentrated sulphuric acid to 165° in a flask.

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

$$C_2H_5OH + H_2SO_4 \xrightarrow{100°C} \underset{\text{ethyl hydrogen sulphate}}{C_2H_5HSO_4} + H_2O$$

$$C_2H_5HSO_4 \xrightarrow{165°C} C_2H_4 \uparrow + H_2SO_4$$

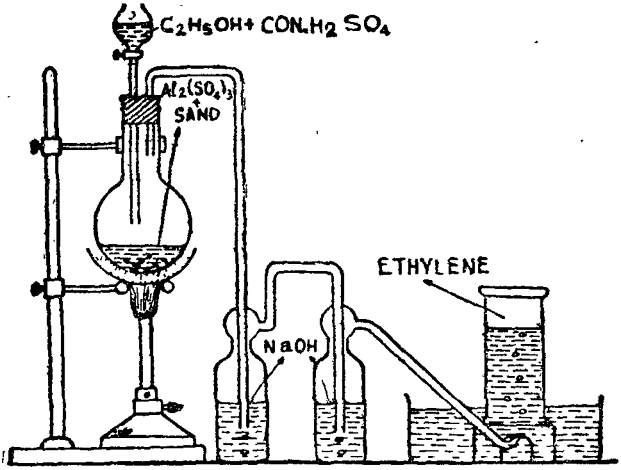


Fig. 99
Preparation of ethylene

A mixture of ethyl alcohol and concentrated sulphuric acid in the ratio 1 : 2 is taken in a round bottomed flask fitted with a dropping funnel and a delivery tube as shown in the figure. A little sand (to mitigate the heat evolved during the reaction) and anhydrous aluminium sulphate (to prevent frothing) are also added and the flask is heated. Ethylene comes out as gas along with sulphur dioxide and carbon dioxide as impurities. The impurities are removed by passing the gas through sodium hydroxide solution and pure ethylene is collected over water.

Ethylene is a colourless gas with a sweet taste and smell. It is slightly lighter than air and sparingly soluble in water.

Unlike paraffins, ethylene is very reactive. The reactivity is due to the unsaturation in the molecule. The properties of ethylene are typical of the properties of alkene series.

1. Ethylene forms explosive mixture with air or oxygen. It burns in oxygen with a luminous flame to form carbon dioxide and water.

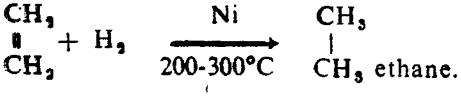
$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

Addition reaction

As ethylene is an unsaturated hydrocarbon with a double bond, it undergoes addition reaction Two univalent atoms or groups are added across the double bond and as a result the double bond is converted into a single bond.

(a) **Addition of Hydrogen**

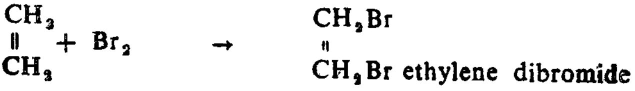
Ethylene combines with a molecule of hydrogen in the presence of nickel catalyst at 200-300°C.



$$\begin{array}{c}CH_2\\ \Vert\\ CH_2\end{array} + H_2 \xrightarrow[200\text{-}300^\circ C]{Ni} \begin{array}{c}CH_3\\ |\\ CH_3\end{array} \text{ ethane.}$$

(b) **Addition of halogens**

Chlorine or bromine readily adds up to ethylene to form the corresponding dihalogen derivative.

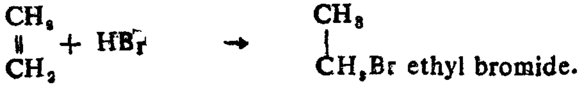


$$\begin{array}{c}CH_2\\ \Vert\\ CH_2\end{array} + Br_2 \rightarrow \begin{array}{c}CH_2Br\\ \Vert\\ CH_2Br\end{array} \text{ ethylene dibromide}$$

Ethylene decolourises bromine water. This is used as a test for unsaturation.

(c) Addition of hydrogen halides

Ethylene reacts with hydrogen chloride or hydrogen bromide to form the corresponding ethyl halide.



$$\begin{array}{l}CH_2\\ \| \\ CH_2\end{array} + HBr \rightarrow \begin{array}{l}CH_3\\ | \\ CH_2Br\end{array}$$

ethyl bromide.

(d) Addition of hypochlorous acid

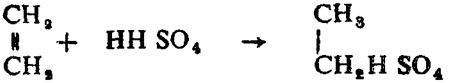
It combines with a molecule of hypochlorous acid to give ethylene chlorohydrin.

$$\begin{array}{l}CH_2\\ \| \\ CH_2\end{array} + \begin{array}{c}OH\\ | \\ Cl\end{array} \rightarrow \begin{array}{l}CH_2OH\\ | \\ CH_2Cl\end{array}$$

Ethylene chlorohydrin.

(e) Addition of sulphuric acid

It combines with concentrated sulphuric acid and forms ethyl hydrogen sulphate.

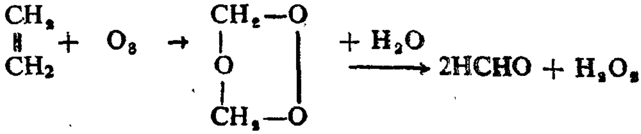


$$\begin{array}{l}CH_2\\ \| \\ CH_2\end{array} + HH\,SO_4 \rightarrow \begin{array}{l}CH_3\\ | \\ CH_2H\,SO_4\end{array}$$

ethyl hydrogen sulphate

(f) Addition of ozone

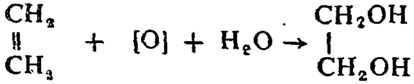
Ethylene reacts with ozone to form etylene ozonide which on warming with water undergoes hydrolysis to give formaldehyde and hydrogen peroxide.



This reaction is called **ozonolysis** and it is used in determining the position of the double bond in an unsaturated compound.

(g) **Oxidation** (addition of—OH groups)

When treated with a dilute alkaline solution of potassium permanganate, ethylene gets oxidised to ethylene glycol and potassium permanganate is decolourised. This is a test for unsaturation.



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + [O] + H_2O \rightarrow \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

ethylene glycol

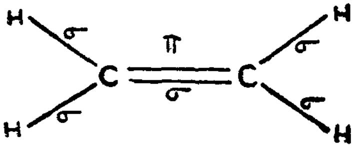
Polymerisation

It is a phenomenon by which two or more molecules condense with one another to form a large single molecule called "**polymer**". Ethylene undergoes polymerisation at high temperature and pressure to give polyethylene also called **polythene**.

$$n\text{-}C_2H_4 \rightarrow (C_2H_4)_n \qquad n = 600 \text{ to } 1000$$

Nature of the double bond in ethylene

In ethylene the two carbon atoms are joined by a double bond. Of these one is sigma (σ) bond (strong bond) and the other is a pi (π) bond (weak bond).



During the addition reactions, the pi bond breaks up. This is the reason why compounds containing ethylenic bond undergo addition reactions easily.

Alkynes or Acetylenes

The unsaturated hydrocarbons that contain one carbon-carbon triple bond are called **alkynes** or acetylenes and have the general formula C_nH_{2n-2}. Acetylene ($HC\equiv CH$) being the simplest alkyne, the homologous series is referred to as the acetylene series. The triple bond is also known as the acetylenic bond.

Nomenclature

The higher homologues are named either as derivatives of acetylene, or after the corresponding paraffin by changing the suffix -ane to-yne. Thus

$HC \equiv CH$ acetylene or ethyne

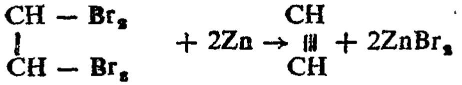
$CH_3C \equiv CH$ methyl acetylene or propyne.

Acetylene $HC \equiv CH$

Acetylene is present in small quantities in coal tar gas. It is produced during the cracking of petroleum

Preparation

Acetylene is prepared by heating an alcoholic solution of tetrabromoethane with zinc.



$$\begin{array}{c} CH-Br_2 \\ | \\ CH-Br_2 \end{array} + 2Zn \rightarrow \begin{array}{c} CH \\ ||| \\ CH \end{array} + 2ZnBr_2$$

It is also obtained by heating ethylene dibromide with an alcoholic solution of potassium hydroxide.

$$CH_2Br - CH_2Br \xrightarrow{\text{alc. KOH}} C_2H_2$$

Laboratory method of preparation

Acetylene is prepared in the laboratory by the action of water on calcium carbide, CaC_2.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \uparrow$$

The apparatus consists of a conical flask fitted with a double holed cork carrying a tap funnel and delivery tube. In the flask a mixture of calcium carbide and sand is taken. The top funnel contains water. The delivery tube leads to a pneumatic trough with water. The gas is arranged to be collected in a gas collecting jar over water. When water is added into the flask acetylene is formed and collects in the gas collecting jar. Sand is added to mitigate the heat evolved during the reaction.

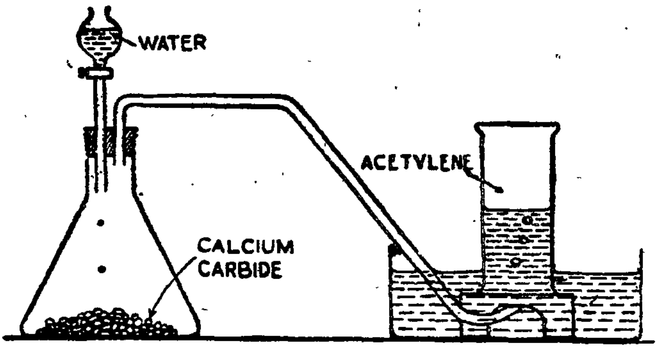


Fig. 100
Preparation of Acetylene

Acetylene is a colourless gas with a pleasant odour. It is slightly lighter than air and is sparingly soluble in water (1 ml of acetylene in 1 ml of water). It is soluble in acetone.

Acetylene forms an explosive mixture with air or oxygen. It burns in air with a sooty luminous flame to form carbon dioxide and water

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

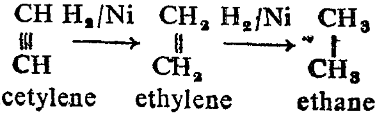
In oxy-acetylene blow pipe, where oxygen is available for the combustion, acetylene burns with a blue flame evolving a lot of heat.

Addition reactions

In acetylene the two carbon atoms are joined by a triple bond. Of these three bonds, one is a sigma bond and the other two are pi bonds. During addition reactions, the weak π bonds break and the carbon atoms get saturated.

Addition of hydrogen

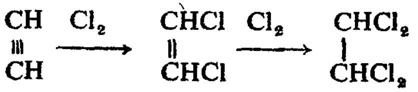
Acetylene adds on hydrogen in the presence of nickel catalyst to form first ethylene and then ethane.



$$\underset{\text{acetylene}}{\begin{matrix}CH\\ |||\\ CH\end{matrix}} \xrightarrow{H_2/Ni} \underset{\text{ethylene}}{\begin{matrix}CH_2\\ ||\\ CH_2\end{matrix}} \xrightarrow{H_2/Ni} \underset{\text{ethane}}{\begin{matrix}CH_3\\ |\\ CH_3\end{matrix}}$$

Addition of halogens

Acetylene adds on chlorine to form **first acetylene dichloride** and then acetylene tetrachloride.



$$\begin{array}{c}\mathrm{CH}\\|||\\\mathrm{CH}\end{array}\xrightarrow{\mathrm{Cl_2}}\begin{array}{c}\mathrm{CHCl}\\||\\\mathrm{CHCl}\end{array}\xrightarrow{\mathrm{Cl_2}}\begin{array}{c}\mathrm{CHCl_2}\\|\\\mathrm{CHCl_2}\end{array}$$

acetylene dichloride (westron)

Acetylene tetrachloride is also known as **westron.** Acetylene decolourises bromine water to give acetylene tetrabromide.

Addition of hydrogen halides

Acetylene reacts with hydrogen halides forming first **vinyl halides** and then ethylidene dihalides.

$$\begin{array}{c}\mathrm{CH}\\|||\\\mathrm{CH}\end{array}\xrightarrow{\mathrm{HBr}}\begin{array}{c}\mathrm{CH_2}\\||\\\mathrm{CHBr}\end{array}\xrightarrow{\mathrm{HBr}}\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{CHBr_2}\end{array}$$

vinyl bromide ethylidene bromide

Addition of water

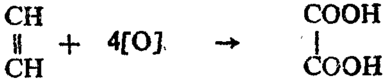
Acetylene adds on water when it is passed into dilute sulphuric acid in the presence of mercury (II) sulphate as catalyst to give acetaldehyde

$$\mathrm{HC \equiv CH} + \mathrm{H_2O} \xrightarrow[\mathrm{HgSO_4}]{\mathrm{H_2SO_4}} \mathrm{CH_3\,CHO}$$

acetaldehyde

Oxidation

An alkaline solution of potassium permanganate oxidises acetylene to oxalic acid



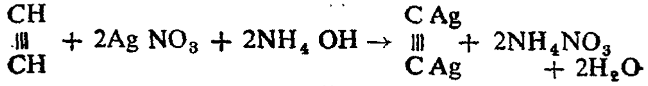
$$\begin{array}{c}\mathrm{CH}\\||\\\mathrm{CH}\end{array} + 4[\mathrm{O}] \rightarrow \begin{array}{c}\mathrm{COOH}\\|\\\mathrm{COOH}\end{array}$$

oxalic acid

Formation of acetylides of acidic properties

The hydrogen atoms of acetylenes are acidic and these can be replaced by metals.

(a) When acetylene is passed through an ammoniacal solution of silver nitrate, a white precipitate of silver acetylide is formed.



$$\begin{array}{c}CH\\ |||\\ CH\end{array} + 2Ag\,NO_3 + 2NH_4\,OH \rightarrow \begin{array}{c}C\,Ag\\ |||\\ C\,Ag\end{array} + 2NH_4NO_3 + 2H_2O$$

silver acetylide.

(b) When acetylene is passed through an ammoniacal solution of copper (I) chloride, a red precipitate of cupper (I) acetylide is formed.

$$C_2H_2 + 2Cucl \rightarrow Cu_2C_2 \downarrow + 2HCl$$
$$2HCl + 2NH_4OH \rightarrow 2NH_4\,Cl + 2H_2O$$

Polymerisation

When acetylene is passed through a red hot tube, 3 molecules of it condense to form one molecule of benzene.

$$3C_2H_2 \rightarrow \underset{\text{benzene.}}{C_6H_6}$$

Uses of acetylene

Acetylene is used in a limited amount as an illuminant. Large amounts of acetylene are used in the oxyacetylene blow pipe for welding purposes. Acetylene is used in the manufacture of many substances like acetic acid, acetic anhydride, acetone and benzene. The chloro derivatives of acetylene (for example Westron) are used as solvents; vinyl chloride is used in making polyvinyl chloride. Vinyl acetylene is used in the production of synthetic rubber.

EXERCISES

1) How are the following prepared ?
(a) Methane (b) Ethylene (c)Acetylene

2) Give 3 typical reactions of (a) alkanes (b) alkenes (c) alkynes.

CHAPTER IX

AROMATIC HYDROCARBONS

A large number of organic compounds obtained from natural sources having a pleasant smell are called aromatic [Gr:aroma= fragrant smell]. These contain higher percentage of carbon than the corresponding aliphatic compounds and contain at least six carbon atoms.

Many chemists isolated some organic compounds from gums, resins and some of the strongly smelling naturally occurring oils like oil of cloves, cinnamon oil, etc. These compounds possess certain characteristics which distinguish them from other organic compounds already isolated. They were richer in carbon, more stable and are not easily oxidised to carbon dioxide and water. One of the substances obtained was from the destructive distillation of gum benzoin; it was called **benzoic acid.** In 1833 **Mitscherlisch** heated the compound with lime and obtained a hydrocarbon. He gave it the name benzin which has since been changed into benzene. This was proved to be the same substance isolated by Farady from a liquid present in the cylinders in which illuminating gas kept under pressure for a long time. In 1845 **Hoffmann** found that this hydrocarbon was a constituent of coal tar. It was found that these more stable organic compounds which were rich in carbon were derivatives of benzene. Because of pleasant smell of some of the derivatives of benzene first obtained, they were called **aromatic compounds.**

It was found that these compounds are closed chain compounds containing at least six carbon atoms and possess certain characteristics (which we shall see presently in benzene). The term 'aromatic' is now retained to signify the structural relationship that exists among these compounds.

These compounds resemble benzene in chemical behaviour. These are also called **benzenoid compounds.**

Benzene is the first member in aromatic series of compounds and all other aromatic compounds are considered to be derived from it. Coal tar obtained during the destructive distillation of coal is the chief source of aromatic substances.

When coal is heated above 1000°C in the absence of air, volatile products are expelled leaving a residue of impure carbon. This process of destructive distillation results in various products such as coal gas, ammoniacal liquor and coal tar. Coke, a solid, is left behind in the retort. Coal gas leaves the retort as a vapour and is condensed in air cooled condensers. The less volatile products are ammoniacal liquor and coal tar. The ammonical liquor is an aqueous mobile liquid while the coal tar is a thick viscous liquid, the two being obtained in separate layers. The coal tar forms the source for many aromatic compounds.

The coal tar is subjected to fractional distillation in wrought iron stills and the vapours are condensed in water cooled iron coil condensers. The distillate is collected in the following fractions.

Fraction	Temperature range	Specific gravity
Light oil [crude naphtha]	upto 170°	0·97
Middle oil [carbolicoil]	170°—230°	1·01
Heavy oil [creosote oil]	230°—270°	1·04
Anthracene oil [green oil]	270°—400°	1·1
Pitch [residue]		

The light oil fraction is washed with sulphuric acid to remove basic impurities and then washed with sodium hydroxide to remove acidic impurities and finally with water. The neutral oil is then subjected to fractional distillation and separated into various fractions. The fraction collecting upto 110° is known as 90 percent benzol. This consists of benzene, toluene and some xylene. This fraction is carefully fractionated when the distillate collecting between 80–82°C is collected as pure benzene.

Benzene, C_6H_6

Benzene is the simplest aromatic compounds; it was discovered by Faraday (1825). The name was given to it by Mitscherlisch. An alternative name phene [Gr pheno = to shine] was suggested by Laurent (1837) as it is inflammable. It is from this name the term 'phenyl' is derived for the radical C_6H_5.

Preparation

1. Benzene can be prepared by distillation of sodium benzoate with soda lime.

$$\underset{\text{Sodium benzoate}}{C_6H_5COONa} + NaOH \rightarrow \underset{\text{benzene}}{C_6H_6} + Na_2CO_3$$

2. When phenol is reduced by heating it with zinc dust benzene is formed.

$$\underset{\text{phenol}}{C_6H_5OH} + Zn \rightarrow C_6H_6 + ZnO$$

3. Benzene can be synthesised by passing acetylene through a red hot pipe. Three molecules of acetylene condense to form one molecules of benzene.

$$3C_2H_2 \rightarrow C_6H_6$$

Benzene is a colourless mobile liquid with a peculiar smell. It boils at 80·4°C and melts at 5·4. It is lighter than water (sp. gr. 0·88) and is immiscible with water. It acts as a good solvent for fats, waxes, resins and many organic substances. It is highly inflammable. It is a poisonous substance affecting the blood. It burns with a sooty flame.

The chemical properties of benzene form a set of characteristic properties and these are generally attributed to aromatic compounds. The molecular formula of benzene is C_6H_6 and this formula indicates a high degree of unsaturation. So it is expected to show addition reactions like decolourising bromine water and adding with hydrogen halides. Under normal conditions benzene shows substitution reactions which are characteristic of saturated compounds. At the same time benzene forms addition compounds under certain conditions.

Halogenation In the presence of a halogen carrier like iron or iodine and in the absence of direct sun light benzene reacts with chlorine and with bromine to give substitution products by successive replacement of hydrogen atoms

$$C_6H_6 \xrightarrow{Cl_2} C_6H_5Cl \xrightarrow{Cl_2} C_6H_4Cl_2 \rightarrow \text{.........}$$

Iodine does not give substiution products.

Nitration When benzene is treated with a mixture of concentrated nitric acid and sulphuric acid at ordinary temperature, nitrobenzene is formed.

$$\underset{\text{benzene}}{C_6H_6} \rightarrow \underset{\text{nitrobenzene}}{C_6H_5NO_2}$$

Sulphonation . Benzene gives benzene sulphonic acid when warmed with concentrated sulphuric acid.

$$C_6H_6 + H_2SO_4 \rightarrow \underset{\substack{\text{benzene}\\ \text{sulphonic}\\ \text{acid}}}{C_6H_5SO_3H} + H_2O$$

Alkylation or acylation (Friedel—Crafts' reaction). When benzene is treated with an alkyl halide or acyl halide in the presence of anhydrous aluminium chloride, one of the hydrogen atoms of benzene is substituted by alkyl or acyl group.

$$C_6H_6 + \underset{\substack{\text{methyl}\\ \text{chloride}}}{ClCH_3} \xrightarrow{AlCl_3} \underset{\text{toluene}}{C_6H_5CH_3} + HCl$$

$$C_6H_6 + \underset{\text{acetyl chloride}}{ClCO\,CH_3} \xrightarrow{AlCl_3} \underset{\text{acetophenone}}{C_6H_5COCH_3} + HCl$$

Addition reactions : When a mixture of benzene vapours and hydrogen is passed over finely divided nickel as catalyst at 200°C, cyclohexane is formed.

$$C_6H_6 + 3H_2 \rightarrow \underset{\text{cyclohexane}}{C_6H_{12}}$$

Chlorine and bromine add to benzene in direct sunlight to form benzene hexachloride and hexabromide.

$$C_6H_6 + 3Cl_2 \rightarrow \underset{\text{benzene hexachloride}}{C_6H_6Cl_6}$$

Ozone slowly reacts with benzene to give benzene triozonide.

$$C_6H_6 + 3O_3 \rightarrow \underset{\text{benzene triozonide}}{C_6H_6O_3}$$

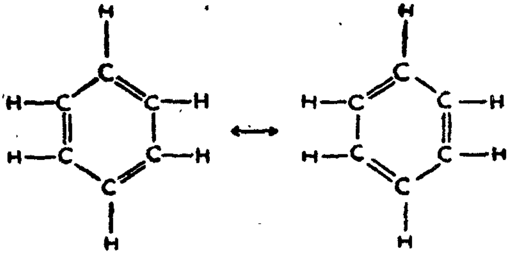
Benzene is used as a solvent for fats, oils, waxes and resins. It is used in dry cleaning and as an ingredient in motor fuel. It is the starting material for the manufacture of dyes, drugs, explosives and perfumes.

Structure of benzene : The structure of benzene had been a complex problem for a long time. Its molecular formula is C_6H_6. This formula indicates a high degree of unsaturation. It does not show readily the properties of an unsaturated compound like addition of hydrogen bromide or decolourisation of bromine water. Many open chain structures have been suggested and one of them is.

$$CH_3-C\equiv C-C\equiv C-CH_3$$

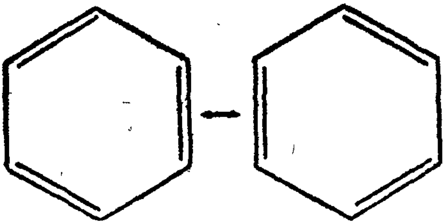
This is the structure of dipropargyl. This is isomeric with benzene but this highly unsaturated and is different from benzene. Reduction of this compound should give n-hexane; but benzene on reduction with hydrogen gives cyclohexane. Therefore benzene cannot be represented by an open chain structure.

Ring structure : Benzene reacts with chlorine to give monochlorobenzene and there is only one monosubstituted product of the type C_6H_5X. Hence all the six hydrogen atoms in benzene should be identically constituted. **Kekule** suggested a ring structure for benzene with alternate double and single bonds in a six membered ring of carbon atoms forming a regular hexagon, each carbon atom carrying a hydrogen atom as given below



Kekule's structure of benzene

In the Kekule formula there are double and single bonds. The bond length of a single bond between two carbon atoms is 1.54A° and the lengh of a double bond between two carbon atoms is 1.34 Å. With such lengths the ring cannot be a regular hexagon. X-ray and electron diffraction methods show that all carbon bonds are of equal length (1.39 A°) and that all the carbon atoms are in the same plane. The structure of benzene is now represented as a resonance hybrid of the structures.

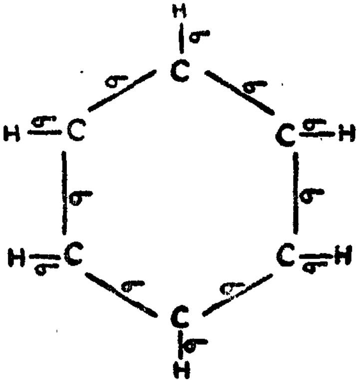


Resonance hybrid structure of benzene

Here the hydrogen atoms are not shown and no C-C bond is wholly single or double.

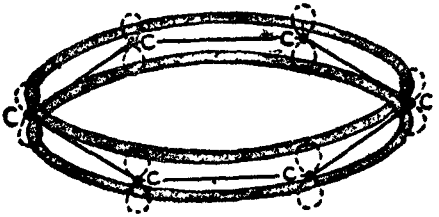
The three double bonds may be in the positions 2—3, 4—5 and 6—1 [as in (I)] or in the position 1—2; 3—4 and 5—6 [as in (II)]. Thus benzene can be represented by the above two structures. This phenomenon is known as resonance. [**Resonance** is a phenomenon by which a structure of compound can be represented by two or more equivalent structures. A double-headed arrow indicates resononce]

In benzene each carbon is bonded to two other carbon atoms by means of sigma (σ) bonds. In addition each carbon is bonded to one hydrogen by a sigma (σ) bond.



σ-bonds in benzene

In benzene there are three double bonds. These three bonds are pi (π) bonds. Because of resonance these π bonds are not localised. The π electrons are delocalised. Actually the benzene ring is sandwitched between the π clouds.



Delocalised pi orbital in benzene

Because of this delocalisation benzene does not undergo addition reactions, but undergoes substitution reactions.

CHAPTER X

PETROLEUM AND COAL

Petroleum is a crude viscous dark coloured fluorescent oil obtained from oil wells. It has often a definite offensive smell. It is generally trapped deep below layers of earth and often floats on salt water. The oil is covered by an atmosphere of the more volatile hydrocarbons the natural gas, which consists of the first six paraffins.

Composition of petroleum

The composition of crude oil varies with places of occurrencc, but all of them contain alkanes, cycloalkanes and aromatic hydrocarbons. The low boiling fractions of petroleum, irrespective of locality of its occurrence, are composed of alkanes. The composition of higher boiling fractions differs according to the sources. Besides hydrocarbons, there are also present certain organic compounds containing oxygen, nitrogen and sulphur

Mining of pertroleum

Petroleum is extracted by drilling holes in the earth's crust and sinking pipes until the drill penetrates the oil bearing sands. Some times the oil rushes out through them due to the pressure exerted by the natural gas inside. As the pressure of the gas diminishes, the oil is obtained by pumping.

Refining of crude oil or petroleum

Crude oil is a mixture of (a) dissolved gases, (b) liquids with low, medium and high boiling points and of widely varying viscosities (c) solids and (d) semisolids. Refining is the process of separation of this mixture by fractional distillation into more useful and therefore more valuable products.

Petroleum is refined by continuous distillation in pipe stills. The essentials of a pipe still process are :

1. The dark coloured fluorescent emulsion of sandy oil and water—crude petroleum—is warmed under pressure with steam coils in iron tanks with conical bases. This breaks the emulsion into two layers. The gas, oil and solids are drawn off separately. The gases evolved are mainly used as fuel, but a portion is liquefied.

2. The upper layer of crude oil, thus removed, is used as cooling agent in the condensers, where it gets heated to about 150°C.

3. This oil at about 150°C is passed through several hundred metres long coils of pipes, heated in a fire box. Here it gets heated to about 400°C.

4. The heated crude oil then enters a large insulated vessel called evaporator. No external heat is applied to the evaporator. All components volatilising upto 400°C vapourise and escape at the top leaving a residue of the fuel oil which is periodically removed from the bottom of the evaporator.

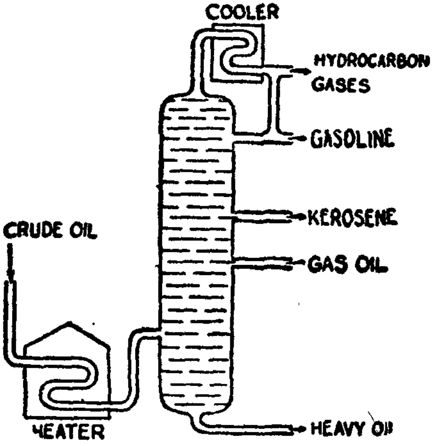


Fig. 101
Refining of petroleum

5. The vapours from the evaporator are passed up a fractionating column. Here fractional condensation occurs. High boiling fractions condense first and low boiling fractions last. These fractions are refractionated and purified to get various products.

Products obtained from petroleum and their uses

Fractions	Boiling range	Uses
1. Gas	Below room temperature	Fuel, manufacture of gasoline and rubber
2. Crude naphtha	18° – 150°	As solvent in varnish
(a) Petroleum ether	18 – 70°	and rubber industries, for dry cleaning
(b) Petrol or gasoline	70 – 90°	*Motor fuel, dry cleaning.* for making petrol
(c) Ligroin or light petroleum	90—120°	As solvent, in dry cleaning
(d) Benzene	120—150°	For varnishes and dry cleaning
3. Kerosene	150 – 300°	As fuel and as illuminant, for making oil gas
4. Gas oil or heavy oil	>300°	As fuel in diesel engines cracked to yield more gasoline
5. Residue from evaporator	>400°	
(a) Paraffin wax	On cooling	For candles and for polishes of leather goods
(b) Lubricating oil		For lubricants
(c) Vaseline		In toilet goods, ointments and for lubricants
(d) Pitch		For paints, varnishes, tarring roads
(e) Petroleum *coke*	On distilling *tar*	As fuel

Petrochemicals

Natural gas is a mixture of alkanes and alkenes. Large volumes of these hydrocarbons are obtained during cracking of petroleum. Theses constitute excellent raw material for numerous compounds which are termed petrochemicals.

Examples : Benzene, alcohols, DDT, Gammexane, halogen compounds, acids etc. are petrochemicals.

Cracking

The thermal decomposition of organic compounds is known as **pyrolysis**. Pyrolysis when applied to paraffins is known as **cracking.**

When heated to about 500—600°, paraffins are decomposed into smaller molecules and the products obtained from a given paraffin depend on (i) the structure of paraffins (ii) the pressure (iii) the presence or absence of catalyst such as silica-alumina, silica-alumina-thoria, etc.

When petroleum is cracked, of all the compounds produced, the most important are those containing upto four carbon atoms (gasoline) namely methane, ethane, propane, ethylene, propylene etc.

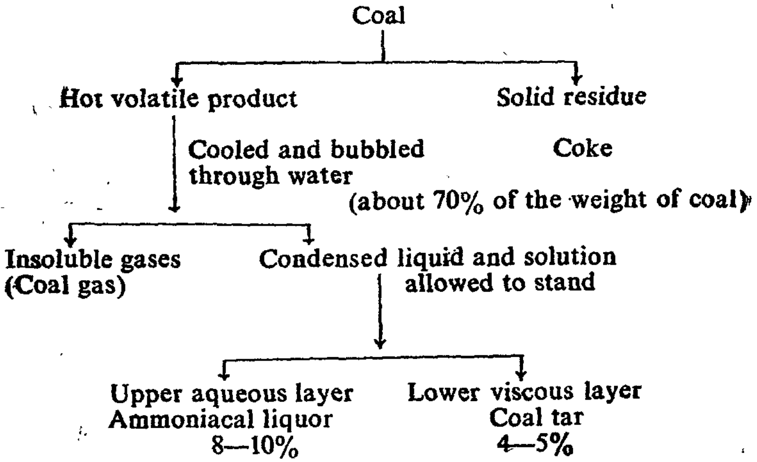
There are two types of cracking : (i) liquid phase and (ii) vapour phase. In the liquid phase, heavy oil is cracked by heating at a suitable temperature (475—530°) under 7 to 68 atmospheres. In the vapour phase cracking, kerosine is heated to 60 °C under 3·5 to 10 atmosphere pressure.

Since the starting materials for these processes are derived from natural gas and the products from petroleum refineries, these are called petrochemicals. The petrochemical industry had made rapid progress in the past thirty years. Petroleum and natural gas now occupy the same position as sources of raw materials for aliphatic chemical industries, that coal tar has long occupied for the aromatic chemical industries.

Coal

Coal is a naturally occurring deposit of carbon formed by the decomposition plants and trees buried under the earth for thousands of years. Due to the heat and pressure the vegetation was converted into carbonaceous matter. Coal is not free carbon; it is a mixture of a number of complex organic compounds. For example, bituminous coal contains about 32% of volatile matter (organic compounds).

When bituminous coal is subjected to distillation at 1000—1400°C, it yields the following chief products :



Gas carbon is also one of the products formed. Coal gas is used as a gaseous fuel and as an illuminant. It is also used to provide an inert or reducing atmosphere in various metallurgical operations.

Coal tar is a thick black liquid, and it is used as the raw material for the production of a large number of organic compounds, e.g., benzene, toluene, naphthalene, phenol, etc. These are used in the manufacture of dyes, drugs, explosives, disinfectants and perfumes.

Ammonical liquor is used for the manufacture of ammonium sulphate.

Coke is used as fuel and as a reducing agent. The gas carbon is used for the manufacture of carbon electrodes.

Fischer-Tropsch Process

The hydrocarbons that constitute petroleum are of natural origin. These are generally of large molecular weights i.e., they are made up of long chain molecules. But the hydrocarbons of the petroleum type can be synthesised by passing carbon monoxide and hydrogen over certain catalysts at temperatures of 180°-250°C and at atmospheric and moderate pressures (upto 10 atmospheres). This is called the **Fischer-Tropsch Synthesis** The best catalyst appears to be a mixture of cobalt and kieselguhr containing small quantites of thoria and magnesia.

$$x\,CO + y\,H_2 \rightarrow \text{saturated and unsaturated hydrocarbons} + H_2O$$

The reactions are complex. The course of the reaction appears to be the formation of cobalt (or iron) carbide and its reaction with hydrogen to produce highly reactive metylene (CH_2) radicals, which rapidly polymerise. Straight chain alkanes and alkenes therefore result. The Fischer-Tropsch process yields a wide range of products, hydrocarbons from propane upto hard waxes (b. pt>450°C) being obtained. Besides hydrocarbons oxygen containing compounds are also produced, some such products being methyl, ethyl, propyl, butyl, and amyl alcohols, acetaldehyde, acetic acid, propionic acid, acetone, and methyl ethyl ketone.

By operating at higher temperatures and pressures (e.g. 450°C and 300 atom) with catalysts such as thoria or thoria-alumina branched chain alkanes are produced in good yield. At lower temperatures branched chain alcohols (e.g. isobutyl alcohol) predominate.

The carbon monoxide for the process is obtained by passing steam over red hot cake. In effect this process amounts to the synthesis of hydrocarbons of the petroleum type and other compounds from the elemental carbon.

CHAPTER XI

HALOGEN COMPOUNDS

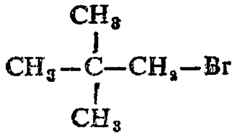
When the hydrogen atoms of the saturated hydrocarbon are substituted by halogen atom, halogen derivatives, are produced. These derivatives are termed the alkyl halides if the halogen atom is attached to alkyl group; they are termed aryl halides if the halogen atom is attached to an aromatic nucleus. Methyl chloride CH_3Cl and ethyl iodide C_2H_5I are examples of alkyl halides. Phenyl chloride or chlorobenzene C_6H_5Cl is an example of an aryl halide. If the halogen atom is present in a side chain in an aryl compound it is called aralkyl halide eg. Benzyl chloride $C_6H_5CH_2Cl$. Different types of halogen substituted derivatives are possible depending on the number of halogen atoms present in the molecule; they are monohalogen, dihalogen, trihalogen, etc derivatives.

The monohalogen derivatives are classified as primary, seconary or tertiary according to the type of the hydrogen atom replaced

RCH_2X	R_2CHX	R_2CX
Primary alkyl halide	Secondary alkyl halide	Tertiary alkyl halide

Nomenclature : In the systematic (IUPAC) method, the halogen compounds are named as substituent products of hydrocarbons, a one word name is obtained by prefixing fluoro, chloro, bromo or iodo directly to the name of the parent hydrocarbon. The names in common use for the simpler (mono and dihalogen) compounds describe them as halides. The name of the group to which the halogen atom is attached being given first CH_2I is methyl iodide, $CH_3CHBrCH_3$ is isopropyl bromide (more correctly secondary propyl bromide). Polyhalogen componds are best given systematic names; when more than one halogen atom is present the alphabetical order is used. The names of some of the compounds are given below, the common names being given within brackets.

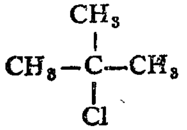
CH_3Cl	Chloromethane	(methyl chloride)
CH_3CH_2I	Iodoethane	(ethyl iodide)
$CH_3CH_2CH_2I$	1-Iodopropane	(n-propyl iodide)
$CH_2CHI\,CH_3$	2-Iodopropane	(iso-propyl iodide)



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-Br$$

1-Bromo 2:2 dimethylpropane (neo-pentyl bromide)

$CH_3CH_2CH_2CH_2Cl$	1-Chlorobutane	(n-butyl chloride)



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}}-CH_3$$

2-Chloro-2 methylpropane (tert-butyl chloride)

General Methods of preparation

From Alkanes : We have seen already with alkanes that chlorine and bromine give substitution products; usually in this method the products will be a mixture of halides. Alkyl iodides cannot be prepared by this method as the hydrodic acid formed reduces the alkyl iodides back to the alkanes.

$$CH_4+I_2 \rightleftharpoons CH_3I+HI$$

From Alcohols : By the action of phosphorus halides, hydrogen halides or thionyl halide on alcohols, the alkyl halides can be prepared.

$$ROH+PX_5 \rightarrow RX+POX_3+HX$$

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + \underset{\substack{\text{phosphorus}\\ \text{pentachloride}}}{PCl_5} \rightarrow \underset{\text{ethyl chloride}}{C_2H_5Cl} + POCl_3 + HCl$$

In the presence of a dehydrating agent, alcohol with a hydrogen halide gives alkyl halide The dehydrating agents can be concentrated sulphuric acid or anhydrous zinc chloride.

$$ROH + HX \rightleftharpoons RX + H_2O$$

$$C_2H_5OH + HCl \rightleftharpoons C_2H_5Cl + H_2O$$

By the action of thionyl chloride on alcohols also the alkyl chlorides can be prepared.

$$ROH + SO_2Cl_2 \rightarrow RCl + SO_2 + HCl$$

From alkenes : Unsaturated hydrocarbons containing double bond when treated with hydrogen halide give alkyl halide as the addition product.

$$CH_2 = CH_2 + HBr \rightarrow CH_3CH_2Br$$

General properties : Ethyl iodide can be taken as a typical member of the alkyl halide series of compounds. The alkyl halides are generally very reactive, the halogen atom being readily replaced by other groups. The iodides are more reactive than bromides and chlorides. Tertiary halides are more reactive than secondary or primary halides.

1. Formation of Alkanes : On reduction by nascent hydrogen alkyl halides give the corresponding alkanes.

$$CH_3CH_2I + 2H \rightarrow C_2H_6 + HI$$

When reduced with metallic sodium, higher homologues of alkanes are formed by Wurtz's synthesis.

$$2CH_3I + 2Na \rightarrow CH_3CH_3 + 2NaI$$

2. Formation of Alkenes : When boiled with alcoholic potash alkyl halides give alkenes by elimination of hydrogen halide. (It should be noted here that ethyl halides do not give this reaction).

$$CH_3CH_2CH_2I \rightarrow CH_3CH = CH_2$$

3. **Formation of Alcohols** - When hydrolysed by aqueous potassium hydroxide or moist silver oxide, the alkyl halides give alcohols.

$$C_2H_5I + aq\ KOH \rightarrow C_2H_5OH$$

4. **Formation of Cyanides** : When heated with potassium cyanide in alcoholic solution, the halogen atom is replaced by a cyanide group forming the corresponding cyanides.

$$CH_3CH_2I + KCN \rightarrow CH_3CH_2CN + KI$$

ethyl cyanide

5. **Formation of Amines** : When boiled with an alcoholic solution of ammonia under pressure, a mixture of amines is formed.

$$C_2H_5I + NH_3 \rightarrow C_2H_5NH_2 + HI$$

ethyl amine

$$C_2H_5I + C_2H_5NH_2 \rightarrow (C_2H_5)_2NH + HI$$

diethyl amine

$$C_2H_5I + (C_2H_5)_2NH \rightarrow (C_2H_5)_3N + HI$$

triethyl amine

$$C_2H_5I + (C_2H_5)_3N \rightarrow N(C_2H_5)_4I$$

tetraethyl ammonium iodide

6. **Formation of Ethers** : When an alkyl halide is boiled with a solution of sodium ethoxide, an ether is formed.

$$C_2H_5-O-Na + I-C_2H_5 \rightarrow C_2H_5-O-C_2H_5 + NaI$$

7. **Formation of an Ester** : On warming with silver acetate in alcohol, an ester, ethyl acetate is formed.

$$C_2H_4I + CH_3COO\ Ag \rightarrow CH_3COOC_2H_5 + AgI$$

ethyl acetate

8. **Formation of organometallic compounds** : When a solution of an alkyl halide in dry ether is heated with dry

magnesium powder in dry ether, magnesium alkyl halides known as **Grignard's reagents** are formed.

$$C_2H_5I + Mg \rightarrow C_2H_5MgI$$

With zinc copper couple, alkyl halides give zinc alkyls.

$$\underset{\text{diethyl zinc}}{2C_2H_5I + Zn \rightarrow Zn\,(C_2H_5)_2} + ZnI_2$$

On heating with lead-sodium alloy under pressure lead tetra alkyl is formed.

$$C_2H_5I \rightarrow \underset{\text{tetraethyl lead}}{Pb\,(C_2H_5)_4}$$

Ethyl Iodine

Preparation : Ethyl iodide is prepared by the action of phosphorus and iodine on ethyl alcohol. Ethyl alcohol is taken in a round bottomed flask. Red phosphorus is placed in the flask and powdered iodine is added into the flask in small quantities with constant shaking. The flask is occasionally cooled under the tap. The flask is fitted with a reflux condenser and left over night. The contents of the flask are refluxed for about two hours. Then the contents are transferred to a distilling flask and distilled over a water bath. The distillate is washed with water and then with sodium thiosulphate to remove any iodine left with and then with sodium carbonate. It is then dried over anhydrous calcium chloride and redistilled.

Ethyliodide is a colourless liquid (boiling point 72°C) heavier than water. On standing, it turns brown due to the separation of iodine. The properties of ethyl iodide are typical of alkyl halides. The properties are already given.

Chloroform $(CHCl_3)$

Preparation : Chloroform is prepared in the laboratory by distilling a mixture of ethyl alcohol or acetone with bleaching powder and water.

In a litre flask a paste of about 50 g of bleaching powder in 150 ml of water is taken. The flask is fitted with a one-holed cork carrying delivery tube connected to water cooled Liebig condenser. An adaptor is connected to the condenser, leading to a conical flask containing water. About 10 grams of ethyl alcohol or acetone are added to the flask and the contents of the flask gently heated, vapours of chloroform collect under water as a separate layer. The lower layer of chloroform is separated, washed with sodium hydroxide, dried with anhydrous calcium chloride and distilled.

Pure chloroform may also be prepared by warming chloral with caustic alkali solution.

$$CCl_3CHO + NaOH \rightarrow CHCl_3 + HCOONa$$

Properties : Chloroform is a sweet smelling liquid (b.pt. 62°C) heavier than water. It is sparingly soluble in water and it is non-inflammable.

Oxidation : When exposed to sunlight and air, chloroform is oxidised to carbonyl chloride, a highly poisonous gas.

$$2CHCl_3 + O_2 \rightarrow 2COCl_2 + 2HCl$$

To prevent this reaction chloroform is kept in dark-coloured bottle and to prevent the decomposition 1% ethyl alcohol is added as preservative.

Reduction : When reduced with zinc dust and hydrochloric acid, chloroform gives methylene chloride.

$$CHCl_3 + 2H \rightarrow CH_2Cl_2 + HCl$$

Hydrolysis : When warmed with alcoholic potash, chloroform is hydrolysed to formic acid, which forms potassium formate.

$$HC(Cl)_3 + 3KOH \rightarrow H-C(OH)_3 \xrightarrow{H_2O} HCOOH$$

Nitration : With concentrated nitric acid, chloroform is nitrated to chloropicrin.

$$Cl_3CH + HONO_2 \rightarrow \underset{\textit{chloropicrin}}{Cl_3CNO_2} + H_2O$$

Carbylamine reaction : On warming with aniline $C_6H_5NH_2$ (or a primary amine) and alcholic potash, a foul smelling liquid phenyl isocyanide (or carbylamine) is formed.

$$C_6H_5NH_2 + 3KOH + CHCl_3 \rightarrow \underset{\text{phenyl isocynide}}{C_6H_5NC} + 3KCl + 3H_2O$$

This reaction is used to identify primary amines.

Halogenation : On treatment with chlorine, chloroform gives carbon tetrachloride.

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

Uses : Chloroform is used as anaesthetic acid sedator. It is used as industrial solvent for fats, iodine and resins.

Iodoform (CHI_3)

Iodoform is prepared by the action of iodine and alkali on ethyl alcohol or acetone.

$$C_2H_5OH + 4I_2 + 3Na_2CO_3 \rightarrow CHI_3 + 5NaI + HCOONa + 3CO_2 + 2H_2O$$

In a beaker about 50 ml of water is taken and 10 gram of sodium carbonate is dissolved in it. About 5 ml of ethyl alcohol is added to this beaker. About 10 gram of iodine is added to the beaker in small amounts with constant shaking. The mixture is heated in a water bath to about 80°C. On cooling, yellow crystals of iodoform separate. The crystals are separated by filtration and washed with a small quantity of water. The crystals are recrystallised from alcohol.

Iodoform is manufactured by the electrolysis of a solution of alcohol, potassium iodide and sodium carbonate.

Properties : Iodoform is a bright yellow crystalline solid (m. pt. 119°C) with a characteristic odour. It is insoluble in water but is readily soluble in alcohol and ether. It is steam volatile.

The properties of iodoform are similar to those of chloroform.

When heated with silver powder, iodoform gives acetylene.

$$2CHI_3 + 6Ag \rightarrow C_2H_2 + 6AgI$$

Uses : Iodoform is used as an antiseptic in dressing wounds. The use of this antiseptic is superseded by new and better antiseptics.

Grignard's reagents

Organic compounds in which a hydrocarbon radical is directly linked to a metal atom are called **organometallic compounds**. Many metals form organometallic compounds. Zinc, cadmium and mercury form dialkyl derivatives such a diethyl zinc, diethyl cadmium and diethyl mercury. Tin and lead form tetra alkyl derivatives like tetraethyl lead or tetramethyl tin. The organometallic compounds are very reactive.

Magnesium forms compounds with alkyl halides and aryl halides. They are called **Grignard's reagents**. They are of immense importance as synthetic reagents. The Grignard's reagents have the general formula R-Mg-X where R is an alkyl or aryl radical and X is a halogen.

Grignard's reagent is prepared by the action of an alkyl halide on magnesium suspended in dry ether. All the reagents used should be pure and dry. Even a trace of moisture present will prevent the reaction on account of the formation of a film of oxide on the surface of magnesium.

Clean dry magnesium ribbon is washed with ether to remove grease and then with dilute acid to remove any oxide and then dried. The ether is kept absolutely dry by distilling it with metallic sodium to remove moisture. The alkyl halide is purified and dried with phosphorus pentoxide.

Clean dry magnesium is cut into pieces and placed in dry ether in a flask fitted with a reflux condenser. Pure dry alkyl halide is added gradually. The flask is heated in a water bath till the reaction starts. Once the reaction starts it becomes violent producing a lot of heat, and so the flask is cooled. The Grignard's reagent formed in solution is used in ether solution.

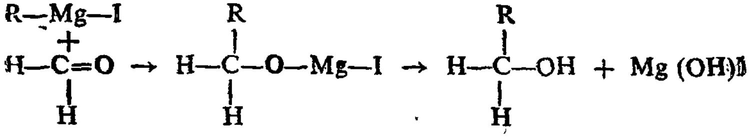
$$C_2H_5I + Mg \rightarrow C_2H_5-Mg-I$$

Grignard's reagents are used in the synthesis of many types of organic compounds.

Hydrocarbons can be synthesised by the hydrolysis of suitable Grignard's reagent with water or alcohol. Thus methyl magnesium iodide on hydrolysis gives methane.

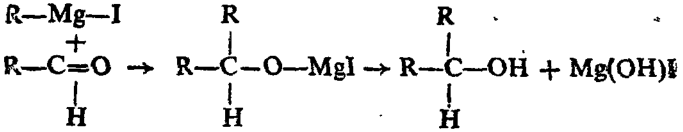
$$CH_3MgI + HOH \rightarrow CH_4 + Mg(OH)I$$
$$CH_3MgI + ROH \rightarrow CH_4 + Mg(OR)I$$

Alcohols : (1) Primary alcohols can be obtained by the action of Grignard's reagent with formaldehyde and subsequent hydrolysis.



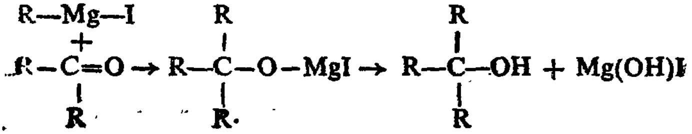
$$\begin{array}{c}R-Mg-I\\+\\H-\underset{\textstyle H}{\overset{}{C}}=O\end{array} \rightarrow H-\underset{\textstyle H}{\overset{\textstyle R}{C}}-O-Mg-I \rightarrow H-\underset{\textstyle H}{\overset{\textstyle R}{C}}-OH + Mg(OH)I$$

(2) With other aldehides, a secondary alcohol is produced.



$$\begin{array}{c}R-Mg-I\\+\\R-\underset{\textstyle H}{C}=O\end{array} \rightarrow R-\underset{\textstyle H}{\overset{\textstyle R}{C}}-O-MgI \rightarrow R-\underset{\textstyle H}{\overset{\textstyle R}{C}}-OH + Mg(OH)I$$

(3) With ketone, a tertiary alcohol is produced.

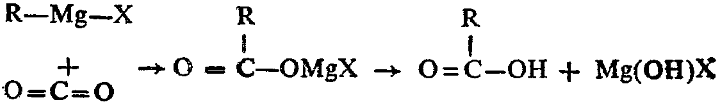


$$\begin{array}{c}R-Mg-I\\+\\R-\underset{\textstyle R}{C}=O\end{array} \rightarrow R-\underset{\textstyle R}{\overset{\textstyle R}{C}}-O-MgI \rightarrow R-\underset{\textstyle R}{\overset{\textstyle R}{C}}-OH + Mg(OH)I$$

Ethers : When a monohalogen derivative of an ether is treated, ether is formed.

$$CH_3-O-CH_2I + I-Mg-R \rightarrow CH_3-O-CH_2R + MgI_2$$

Acids : They are synthesised through absorption of carbondioxide.



$$\begin{matrix} R-Mg-X \\ + \\ O=C=O \end{matrix} \rightarrow O=\overset{\overset{R}{|}}{C}-OMgX \rightarrow O=\overset{\overset{R}{|}}{C}-OH + Mg(OH)X$$

Esters : They are synthesised through esters of lower halogen acids.

$$CH_3\text{-}Mg\text{-}I + ClCH_2COOC_2H_5 \rightarrow CH_3\text{-}CH_2COOC_2H_5 + MgICl$$

Aryl Halides

When the halogen atom is substituted in the place of a hydrogen atom in an aromatic compound, the compound is termed an **aryl halide**. The halogen atom may be connected to the aromatic ring as in chlorobenzene (C_6H_5Cl).

The halogen atom may be connected to carbon atom in the side chain of an aromatic hydrocarbon as in benzyl chloride $C_6H_5CH_2Cl$. Such a compound is termed an **aralkyl halide.**

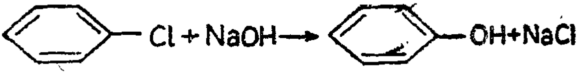
Chlorobenzene

The method of preparation of chlorobenzene can be taken as a general method of preparation of aryl halides.

By direct halogenation of the aromatic hydrocarbon at ordinary temperature in the presence of halogen carrier such as ferric chloride chlorobenzene can be prepared.

$$C_6H_6 + Cl_2 \rightarrow \underset{\text{chlorobenzene or phenyl chloride}}{C_6H_5Cl} + HCl$$

Chlorobenzene is a colourless mobile liquid (b. pt. 130°C) with a pleasant smell. It is immiscible with water but soluble in alcohol and ether. Unlike aliphatic halogen compounds chlorobenzene is not active. The chlorine atom is not easily exchanged for other groups or atoms. Chlorobenzene is hydrolysed to phenol when heated to 300°C with sodium hydroxide under pressure (200 atm)



The chlorine atom is replaced by amino group when chlorobenzene is heated with ammonia in the presence of copper (I) oxide at 200°C under pressure.

$$2C_6H_5Cl + Cu_2O + 2NH_3 \rightarrow 2C_6H_5NH_2 + Cu_2Cl_2 + H_2O$$

When reduced by nickel aluminium alloy and alkali chlorobenzene gives benzene.

$$C_6H_5Cl \xrightarrow{[H]} C_6H_6 + HCl$$

Wurtz-Fittig or Fittig reactions : An ethereal solution of an aryl halide (chlorobenzene) with sodium and an alkyl halide react to give homologues of benzene. These are called **Wurtz-Fitting reaction.**

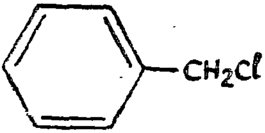
$$C_6H_5Br + C_2H_5Br + 2Na \rightarrow C_6H_5C_2H_5 + 2NaBr$$

Byproducts are formed and the yields are poor. In the absence of alkyl halides, aryl halides in ethereal solution react with sodium to give dinuclear hydrocarbon (Fittig's reaction)

$$2C_6H_5Br + 2Na \rightarrow C_6H_5-C_6H_5 + 2NaBr$$

Chlorobenzene gives the reactions of benzene like nitration, sulphonation and Friedel-Grafts reaction. In the presence of strong sulphuric acid, chlorobenzene reacts with chloral to give what is known as DDT.

Benzyl chloride



Benzyl chloride is a side chain halogen compound. It is prepared by chlorination of boiling toluene.

$$C_6H_5CH_3 + Cl_2 \rightarrow C_6H_5CH_2Cl + HCl$$

It can also be prepared by the action of phosphorus pentachloride on benzyl alcohol.

$$C_6H_5CH_2OH \xrightarrow{PCl_5} C_6H_5CH_2Cl$$

In the laboratory, toluene is taken in a flask fitted with a reflux condenser. The flask is heated on a sand bath, a stream of dry chlorine is passed into the boiling toluene. Since chlorine atom replaces the three hydrogen atoms of the methyl group of toluene successively, the passing of chlorine is continued till the increase in weight corresponds to the substitution of one chlorine atom only.

The benzyl chloride is purified by fractional distillation. Benzyl chloride is a colourless liquid (b. pt. 179°C) with unpleasant irritating smell. It is a lachrymator causing the flow of tears. It is immiscible with water.

In its properties it behaves as an aliphatic halide and it is more active than alkyl halides. Thus when heated with aqueous potassium alkali, aqueous potassium cyanide and alcoholic ammonia it is converted into benzyl alcohol, benzyl cyanide and benzyl amine respectively. All these are nucleophilic substitutions.

$$C_6H_5CH_2Cl \xrightarrow{KOH} \underset{\text{(benzyl alcohol)}}{C_6H_5CH_2OH}$$

$$C_6H_5CH_2Cl \xrightarrow{KCN} \underset{\text{(benzyl cyanide)}}{C_6H_5CH_2CN}$$

$$C_6H_5CH_2Cl \xrightarrow{NH_3} \underset{\text{(benzyl amine)}}{C_6H_5CH_2NH_2}$$

On oxidation by a mild oxidising agent like copper nitrate, benzaldehyde is formed, while alkaline potassium permanganate gives benzoic acid.

$$C_6H_5CH_2Cl \rightarrow H_6H_5CHO$$
(benzaldehyde)

$$C_6H_5CH_2Cl \rightarrow C_6H_6COOH$$
(benzoic acid)

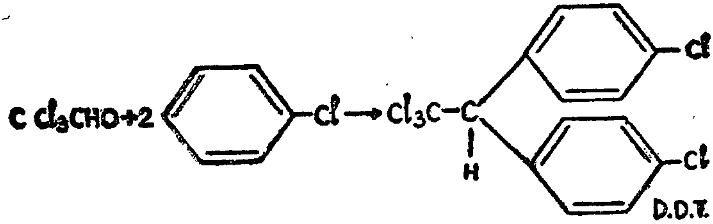
With chlorine it forms benzal chloride and benzotrichloride.

$$CH_3CH_2Cl + Cl_2 \rightarrow C_6H_3CHCl_2 + HCl$$
(benzal chloride)

$$C_2H_5CHCl_2 + Cl_2 \rightarrow C_6H_5CCl_3 + HCl$$
(benzotrichloride)

DDT (Dichlorodiphenyltrichloroethane)

This is an insecticide that had become very popular. Actually it was prepared in 1874 but its insecticide properties were only discovered in 1942. It is prepared by the action of strong sulphuric acid on chlorobenzene and chloral.



The name is p.p.' dichlorodiphenyltrichloroethane or 1-1 bis-p-chlorophenyl-2, 2, 2-trichloro ethane.

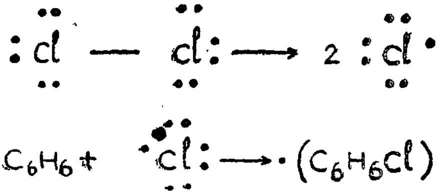
DDT is a solid (m.p. 109-110°C). It has a high and rather specific toxicity for various insects such as the common house fly and mosquito. It was first used on a large scale to control malarial and agricultural pests. DDT is a pernicious Insecticide and it is not easily metabolished nor destroyed by environmental destructive forces. If it is found to remain in the soil, in the plant and in animals for months and years, it causes undesirable effects, for example it causes poor egg formation in birds.

Benzene hexachloride (1, 2, 3, 4, 5, 6 hexachlorocyclohexane)

In the presence of sunlight or ultraviolet light of sufficiently short wavelength, chlorine (and bromine) add to benzene to give crystalline hexachlorides (and hexabromides). These are substituted cyclo-hexanes.

$$C_6H_6 + 3Cl_2 \rightarrow C_6H_6Cl_6$$

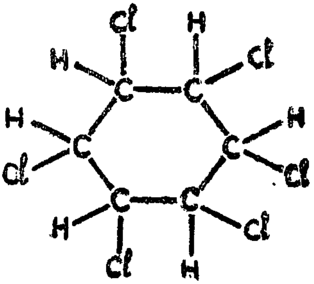
These additions proceed by a free radical process



This free radical on reacting with a chlorine molecule, produces a dichloride and another chlorine atom, this chlorine atom carries on the chain.

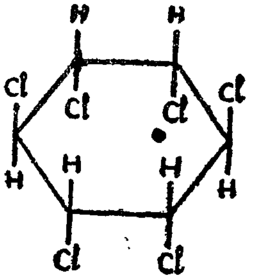
$$(C_6H_6 + {}^{\circ}Cl \rightarrow C_6H_6Cl)^{\circ}$$
$$(C_6H_6Cl)^{\circ} + Cl_2 \rightarrow C_6H_6Cl_2 + Cl^{\circ}$$

A continuation of the substitution process gives finally the hexachloride.



(Benzene hexachloride or 1, 2, 3, 4, 5, 6 hexachloro cyclohexane.)

There are theoretically nine possible stereoisomers. Five of these stereoisomers have been isolated from the mixture obtained in practice. They are called the α, β, γ, δ, and ε forms. The mixture of stereoisomeric hexachlorides is a valuable insecticide It is known commercially as BHC or 666 (abbreviation, of the name and the formula $C_6H_6Cl_6$). The insecticidal properties are due to the γ form which is called gammexane or lindane and has been shown to have the configuration.



Section D—PRACTICAL CHEMISTRY

EXPERIMENT 1

Bunsen Burner

Study of its parts : luminous and non-luminous flames.

Description of Bunsen Burner :

Heating is commonly done in the laboratory by the Bunsen burner. It is so called because it was devised by **Bunsen** in 1895. It consists of three parts : (1) A heavy metallic base with a side tube. The gas enters the base through the side tube and escapes through the pinhole at the top. (2) A burner tube provided with diametrically opposite holes at the bottom of the tube which is screwed on to the base. (3) An air regulator—a short metallic ring with two holes sliding over the burner tube at the bottom. By turning this, it is possible to admit more or less air.

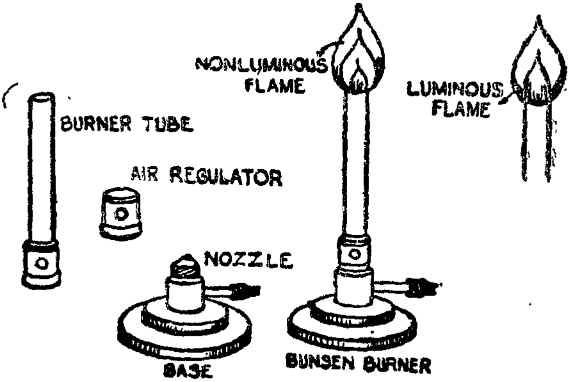


Fig. 102
Bunsen Burner and its parts.

Structure of Flame

(a) **Air holes closed :** Keep the air holes closed, open the gas tap and light the gas. Is the flame luminous or non-luminous ? Expose a china dish to the flame. What is deposited on it? Is this flame suitable for heating substances in the laboratory? How many zones are seen in the flame ? Draw a neat diagram of this flame. Why is the flame luminous ? (Refer Fig. 102).

(b) **Air holes opened :** Now open the air holes. Note the size of the flame. Is the flame luminous or non-luminous ? Hold a china dish over the flame. What is deposited on it? Is this flame suitable for heating substances in the laboratory? How many zones are seen in the flame ? Draw a neat diagram of this flame. (Refer Fig 102).

Experiments to show the hotter and cooler parts of the flame

(1) Place one end of a narrow glass tube in the inner zone of unburnt gas (just above the burner tube) and light the gas coming through the other end of the tube. What does this show ?

(2) Hold a match stick across the flame for a second or two, just above the tube. Account for the phenomenon noticed.

(3) Hold a thread of asbestos about 5 cm long across the flame slightly above the tube. Then slowly raise it vertically till the top of the flame is reached. Ascertain from the quality of the glow produced which parts of the flame are relatively hotter and which cooler ?

Striking back of the flame

Open the air holes completely. Light the burner and reduce the gas supply gradually by slowly closing the gas tap. The flame descends down and burns at the pin hole itself with a roaring sound. This phenomenon is known as 'striking back of the flame'. What is striking back of the flame due to ? How will you prevent the striking back of the flame ?

EXPERIMENT 2

STUDY OF GASES

Preparation of the following gases and a study of their properties

Oxygen

Laboratory Preparation : Make an intimate mixture of potassium chlorate and manganese dioxide in the ratio of 4 : 1. Take the mixture in a hard glass test tube fitted with a one-holed cork carrying a delivery tube as shown in Fig. 103. Place the other end of the delivery tube under the bee-hive shelf in a jar of water. Fill a jar with water and keep it inverted over the bee-hive shelf. Heat the mixture carefully over a low flame so as not to cause too violent an evolution of oxygen. Collect the gas in jars over water by downward displacement of water. [The delivery tube should be removed from the water as soon as the jars are filled].

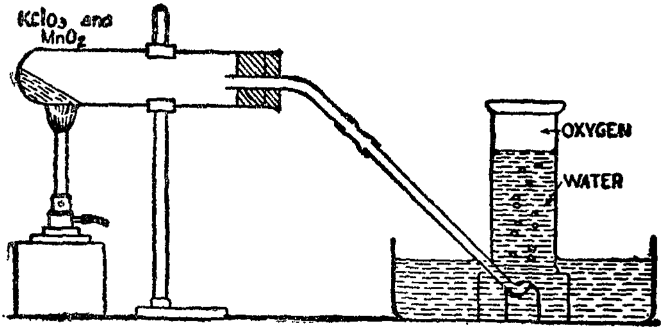


Fig. 103
Preparation of oxygen in the laboratory

Properties : (1) Make a list of the physical properties of gas observed such as colour, odour etc.

(2) Take a pinch of sulphur in a deflagrating spoon, burn it and lower it into a jar of oxygen. Remove the spoon and note the smell of the gas. Add some water to the jar,

close it with a greased plate and shake well. Test the solution with litmus paper.

(3) Repeat the experiment with phosphorus.

(4) Wrap the end of a piece of copper wire round a bit of charcoal and hold it in a flame till the charcoal glows. Lower the glowing charcoal into a jar of oxygen. Remove the charcoal, add some water and shake. Test the solution in the jar with a litmus paper. Add some clear lime water and shake.

(5) Burn a piece of magnesium ribbon held by the songs. Catch the ash in a test tube and shake with water. Test the solution with a litmus paper. Tabulate your results as shown below ·

Name of the element	Name of the oxide produced	Nature of oxide produced

Hydrogen

Preparation: Prepare hydrogen by the action of dilute H_2SO_4 on granulated zinc taken in a Kipp's apparatus shown in the diagram. Lead the delivery tube to a pneumatic through containing water and collect the gas in test tubes over water.

Properties (1) Using a test tube filled with hydrogen and a similar test tube filled with air show that hydrogen is lighter than air.

Fill a test tube with hydrogen and a similar test tube filled with air. Close the mouth of the test tube containing hydrogen with the thumb and bring it under the mouth of another test tube held inverted. Wait a minute and bring the mouth of the upper tube in contact with a flame. What happens ?

(2) Take a test tube of hydrogen and apply it closely with mouth downward to a test tube containing air held mouth upward. Allow the tubes to remain in this position for some time. Then bring first the lower and then the upper tube quickly to the flame or test the tubes with a burning splinter? What fact about diffusion does the result illustrate?

(3) To a test tube of hydrogen add some water, close the mouth of the tube with the thumb and shake vigorously. See if hydrogen is soluble. If the gas is soluble, the pressure within the tube is reduced owing to the disappearance of gas and consequently the thumb would adhere to the tube slightly. In the case of hydrogen, the finger comes off easily showing that none of the gas has dissolved.

(4) Fill a test tube with hydrogen, and holding it mouth downwards, thrust in to the gas a burning splinter. Is hydrogen a supporter of combustion? Is it a combustible gas?

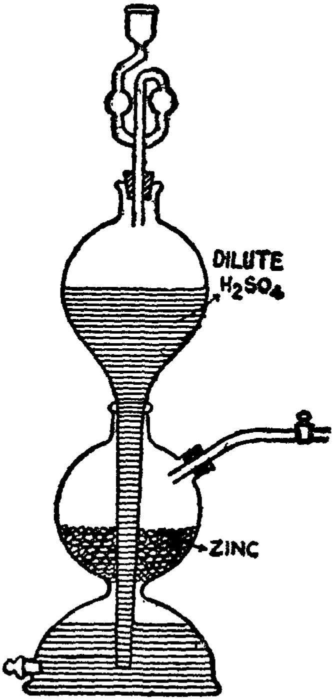


Fig. 104
Preparation of hydrogen in the laboratory

(5) Nascent hydrogen : Take a drop of potassium permanganate solution and acidify it with dilute sulphuric acid. Pass hydrogen through this solution. Is their any change? Add a little zinc dust to the acidified potassium permanganate solution and shake well. What do you observe? Explain the changes now seen.

Carbon dioxide

Preparation : Set up Kipp's apparatus or any other gas generator for generating carbon dioxide using marble chips and dilute hydrochloric acid. (It is not advisible to use dilute sulphuric acid. Why?) Arrange a gas washing bottle containing water to wash the gas. If necessary, dry the gas by passing it through another bottle containing conc. H_2SO_4. Collect the gas by the downward displacement and study the following properties.

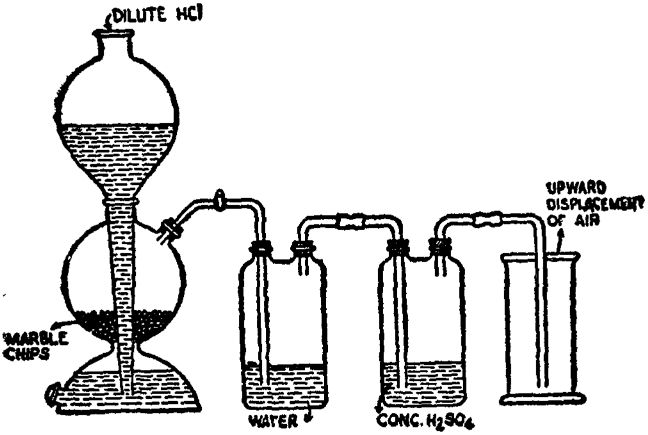


Fig. 105
Laboratory preparation of CO_2

1. Show that carbon dioxide is a heavy gas—heavier than air—by pouring it from one tube into another tube containing some lime water and shaking.

2. Add some water to a test tube of the gas, close the mouth quickly with the thumb and shake vigorously. Is the gas soluble in water or not ?

3. Test the aqueous solution of the gas with litmus paper. Boil the solution and test again with litmus.

4. Place a test tube of air with mouth downward over a test tube of carbon dioxide held mouth upward. Keep the two in this position for sometime. Remove the

upper tube add some lime water and shake. **What** property of gases is illustrated by this ?

5. Thrust a burning splinter into a test tube of the gas.

6. Fill a beaker with carbon dioxide and pour it on the flame.

7. Pass carbon dioxide through 2 ml. of lime water continuously?

Ammonia

Preparation : Make a mixture of powdered quick lime and ammonium chloride. Take the mixture in a hard glass test tube and close it with a cork carrying an elbow tube turned upwards. Heat the tube gently, holding it horizontally.

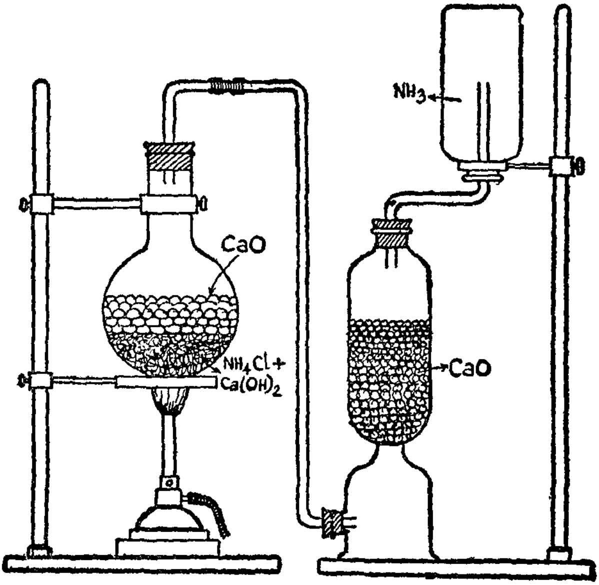


Fig. 106
Laboratory Preparation of Ammonia

Collect the ammonia in test tubes by downward displacement of air. For getting its aqueous solution, pass it into some water in a test tube. Study the properties of the gas and its aqueous solution by performing the following tests.

1. Smell.
2. See the action of ammonia under water.
3. Open a test tube of ammonia under water.
4. Devise a way of showing that ammonia is lighter than air.
5. Introduce a burning splinter into ammonia.
6. Dip a glass rod in strong hydrochloric acid and bring it to the mouth of a test tube containing ammonia.
7. Bring a drop of mercury (I) nitrate solution on a glass rod into ammonia.
8. Boil a little aqueous solution of ammonia and note the odour from time to time.
9. Add potassium iodide solution in drops to a small quantity of mercury (II) chloride solution until the scarlet precipitate formed just dissolves to a colourless solution. Make the solution alkaline by adding some KOH. This gives Nessler's reagent. Add some ammonia to this. · This is a delicate test for ammonia and ammonium compounds.
10. See the action of (a) a little ammonium hydroxide and (b) excess of it, on solutions of copper (II) sulphate silver nitrate, zinc sulphate, aluminium sulphate and magnesium sulphate.

Sulphur dioxide

Laboratory Preparation : Take copper turnings in a round bottomed flask fitted with a thistle funnel and a delivery tube. Drop concentrated sulphuric acid into the flask through the funnel and heat the flask on the wire gauze. Copper reduces sulphuric acid to sulphur dioxide, getting itself oxidised to copper sulphate. Collect the gas by the upward displacement of air. Study the following properties.

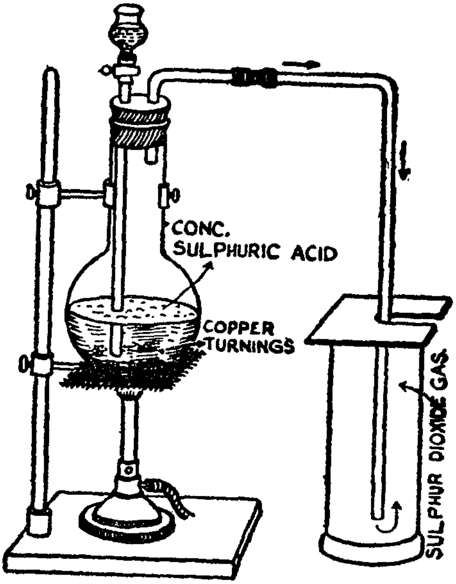


Fig. 107
Preparation of SO_2 in the lab.

1. Show that sulphur dioxide is a heavy gas by pouring it into another tube containing some potassium permanganate and shaking it.

2. Invert a test tube of the gas under water or add some water to the gas in a test tube and shake. What do you infer about the solubility of the gas?

3. Pass SO_2 into some water in a test tube. Note the smell of the solution. Divide the solution into five portions :

   (a) Test one portion with litmus paper.

   (b) Boil another portion, noting now and then the smell of the vapours. What is the effect of boiling the aqueous solution ?

   (c) Keep some rose flowers or some other coloured flowers or green leaves in contact with another portion of the solution. After the bleaching has taken place, expose the bleached flower to air or wash it with some dilute acid or alkali. Is the bleaching by sulphurous acid permanent? What is the difference between bleaching by sulphur dioxide and bleaching by chlorine?

   (d) Test a little of the sulphurous acid with barium chloride. Add to the precipitate dilute hydrochloric acid.

   (e) Expose the sulphurous acid to air for some days and then test with barium chloride and dilute hydrochloric acid.

4. Pass SO_2 through barium hydroxide solution. What is the precipitate formed? What happens if excess of SO_2 is passed?

5. Pass SO_2 through (a) dilute bromine water (b) dilute potassium permanganate solution. (c) warm dilute ferric chloride solution (d) acidulated potassium dichromate. Note and explain what happens in each case. What property of sulphur dioxide is illustrated by the above reactions?

Hydrogen chloride

Laboratory Preparation : Take common salt in a round-bottomed flask, fitted with a cork through which pass a dropping funnel and a delivery tube. Add concentrated H_2SO_4 to the flask through the funnel. Heat the flask gently on a wire gauze. Collect the gas in dry jars by the upward displacement of air. If hydrochloric acid is required, pass the gas into water taken in a test tube. (An inverted funnel is attached to the end of the delivery tube to prevent back suction).

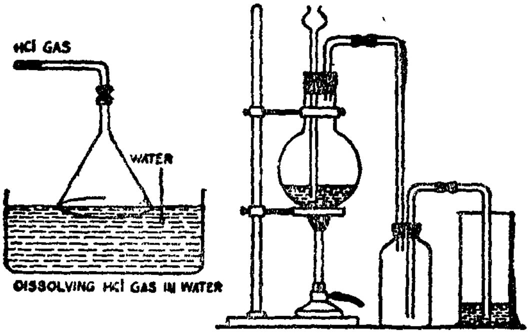


Fig. 108
Preparation of HCl gas

Properties

1. Show that the gas is heavier than air, by pouring it from one tube into another.

2. To a test tube of the gas, add a little water and quickly close the mouth of the tube with the thumb. Shake well. Try to lift the thumb off the mouth of the tube. What do you infer about the solubility of the gas? Repeat the experiment by inverting another tube of the gas into a dish of water. How is an aqueous solution of the gas prepared? What precautions are necessary and why?

3. See if the gas is combustible or a supporter of combustion.

4. Pour a little ammonium hydroxide into a test tube, shake up and pour out the liquid. Bring the tube mouth to mouth with a test tube of hydrogen chloride. Study the following properties of the aqueous solution. (Use dilute hydrochloric acid from the side shelf.)

5. To a part of solution add some zinc or Mg dust.

6. Treat the solution with a pinch of sodium carbonate. Test the escaping gas with lime water taken on the end of a glass rod.

7. See the action of the acid solution on zinc oxide.

8. What is the action of concentrated HCl on manganese dioxide?

9. Treat some of the acid solution with mercury (II) nitrate solution.

10. To another portion of the solution add some silver nitrate solution. Warm, allow the precipitate to settle and decant. Divide the precipitate into two parts, add dilute nitric acid to one and ammonia solution to the other and shake.

11. Treat the acid solution with lead nitrate solution. Allow the precipitate to settle, pour away the supernatant liquid, add some water and boil. Cool the hot liquid under the tap.

N.B. The reactions studied in reactions 9, 10, 11 are answered not only by hydrochloric acid but also by a solution of any chloride. These are employed as tests for chlorides.

EXPERIMENT 3

REACTIONS OF ANIONS AND CATIONS

Reactions of Anions

Reactions of Carbonate

1. Heat a little of solid zinc carbonate in a test tube. Test the gas evolved with lime water taken on a glass rod.

2. Take a little sodium carbonate (any carbonate) in a test tube, and add a few drops of dilute HCl. Test the gas evolved with lime water.

Reactions of Sulphide

1. Add dilute hydrochloric acid to a little of sodium sulphide or powdered iron (II) sulphide in a test tube and warm. Note the colour and odour of the gas evolved. Test the gas evolved with a filter paper dipped in lead acetate solution.

2. To a little ammonium sulphide solution, add silver nitrate solution. Add dilute nitric acid to the precipitate and heat.

3. To a little sulphide solution, add lead acetate solution. Add dilute nitric acid to the above precipitate.

Reaction of Sulphate

1. To a little sodium sulphate solution add barium chloride solution. Add a little dilute HCl to the above precipitate.

2. To a little sulphate solution, add lead acetate solution.

Reactions of Nitrate

1. Heat a little of solid sodium nitrate in a dry test tube. Note the colour and odour of the gas evolved. Test the gas evolved with a glowing splinter.

2. Heat a little of solid lead nitrate in a test tube. Note the colour and odour of the gas evoled. Test the gas evolved with (a) a filter paper dipped fluorescein solution (b) glowing splinter.

3. Take some potassium nitrate in a dry test tube. Add a few drops of concentrated H_2SO_4 just enough to cover the solid warm. Then add a bit of copper and heat.

4. **Brown ring test for nitrate** : To a solution of potassium nitrate in a test tube, add an equal volume of freshly prepared iron (II) sulphate solution. Then add carefully a few drops of concentrated H_2SO_4 along the inner sides of the tube.

Reactions of Chloride

1. To a little sodium chloride taken in a test tube add concentrated H_2SO_4 and warm. Note the colour and odour of the gas evolved. Test the gas evolved with (a) moist blue litmus (b) a glass rod dipped in ammonia (c) a glass rod dipped in silver nitrate solution.

2. Heat a little of solid sodium chloride with a little of manganese dioxide and a few drops of concentrated H_2SO_4. Note the colour and odour of the gas evolved. Test the gas evolved with (1) starch iodide paper and (2) blue litmus paper.

3. Mix a little of solid sodium chloride with potassium dichromate and heat the mixture with a few drops of concentrated sulphuric acid. Pass the vapours into

water. To the solution add dilute acetic acid and lead acetate solution.

4. To a little sodium chloride solution add a few drops of silver nitrate solution. Divide the precipitate into two parts. To one part add (l) ammonium hydroxide solution and to the other part add dilute nitric acid.

5. To a little·chloride solution add lead nitrate solution. To a little of the precipitate add more water and heat; then cool the solution.

Reactions of Cations

Reactions of lead (Pb^{2+}) Group I.

1. **Charcoal Test :** Heat a mixture of lead salt ($PbCO_3$) with sodium carbonate in a charcoal cavity in a reducing below pipe flame.

2. To a little lead nitrate solution add dilute HCl. Heat the precipitate with more water and then cool.

3. To another portion of lead nitrate solution add potassium iodide solution. Heat the precipitate obtained with more water and then cool.

4. To a third portion of the solution add potassium chromate solution.

5. Pass hydrogen sulphide gas through another portion of the solution. Test the solubility of the precipitate in dilute nitric acid. Then add dilute sulphuric acid.

6. To another portion of the solution add dilute sulphuric acid.

Reactions of Copper, Cu^{2+} (Group II)

1. **Flame Test :** Moisten the substance (copper (II) sulphate solid) with a few drops of concentrated HCl on a watch glass. Take the paste on the end of a

charred splinter and introduce it into the non-luminous flame.

2. Take little copper (II) sulphate solution in a test tube, acidify it with dilute HCl and pass hydrogen sulphide gas through the solution. To the precipitate add dilute HNO_5 and heat.

3. To a portion of copper (II) sulphate solution add ammonium hydroxide solution drop by drop to excess.

4. To a portion of copper (II) sulphate solution, add sodium hydroxide solution drop by drop to excess.

5. To a portion of the solution add acetic acid and potassium ferrocyanide solution.

Reactions of Aluminium, Al^{3+} (Group III)

1. **Charcoal Test**: Heat a mixture of aluminium sulphate and sodium carbonate in a charcoal cavity in a reducing blow pipe flame, cool and add a drop of cobalt nitrate solution to the residue and reheat.

2. To a portion of aluminium sulphate solution add ammonium chloride solution and then ammonia in excess.

3. To another portion of the solution, add sodium hydroxide solution drop by drop to excess.

Reactions of Iron (II) ion, Fe_2+ (III) Group

Take iron (II) sulphate solution, and divide it into five portions. To portions of the solution add

(a) Ammonium chloride solution and then ammonium hydroxide in excess.

(b) Sodium hydroxide solution drop by drop to excess.

(c) Potassium permanganate solution in drops.

(d) Ammonium thiocyanate solution.

(e) Potassium ferricyanide solution.

Reactions of Iron (III) ion, Fe^{2+} (Group III)

Take iron (II) chloride solution, and divide it into five portions. To portions of the solutions add

(a) Ammonium chloride solution and then ammonium hydroxide in excess.

(b) Sodium hydroxide solution drop by drop to excess.

(c) Potassium permanganate solution in drops.

(d) Ammonium thiocyanate solution.

(e) Potassium ferrocyanide solution.

Reactions of Zinc, Zn^{2+} (Group IV)

(a) **Charcoal Test**. Heat a mixture of $ZnSO_4$ and Na_2CO_3 in a charcoal cavity in a reducing blowpipe flame; cool, add a drop of cobalt nitrate solution to the residue and heat.

(b) To portions of zinc sulphate solution, add

1. Ammonium chloride solution, ammonium hydroxide in excess and then pass hydrogen sulphide gas. To the precipitate add dilute HCl.
2. Sodium hydroxide solution drop by drop to excess.
3. Potassium ferrocyanide solution.

(c) **Rinmann's green test**: To 1 ml of zinc sulphate solution add cobalt nitrate solution. Dip a filter paper in the solution and burn it to an ash. Note the colour of the ash.

Reactions of Calcium, Ca^{2+} (Group V)

(a) **Flame Test :** Make a paste of calcium salt with concentrated HCl. Take a little of the paste on the end of a charred splinter, and introduce it into the non-luminous part of the flame.

(b) To separate portions of calcium chloride solution add.

1. Ammonium chloride solution, ammonia solution and then ammonium carbonate solution.
2. Potassium chromate solution.
3. Calcium sulphate solution or dilute H_2SO_4
4. Ammonium oxalate solution. Add dilute acetic acid to the precipitate obtained.

Reactions of Magnesium, Mg^{2+} (VI Group)

(a) Charcoal cavity test : Heat a mixture of magnesium sulphate and sodium carbonate in a charcoal cavity in a reducing blow pipe flame. Cool, add a drop of cobalt nitrate solution to the residue and heat.

(b) To magnesium sulphate solution, add ammonium chloride solution, ammonium hydroxide solution and then sodium phosphate solution,

(c) To magnesium sulphate solution, add ammonium chloride solution and then ammonium carbonate solution.

(d) To another portion of magnesium sulphate solution, add sodium hydroxide solution drop by drop to excess.

Reactions of Ammonium, NH_4^+

(a) Heat a little of solid ammonium chloride in a test tube. Test the gas evolved with (1) moist red litmus paper and (2) a glass rod dipped in HCl.

(b) Add a few ml of sodium hydroxide solution to ammonium chloride solution and warm. Test the gas evolved with moist red litmus paper.

(c) **Nessler's test** : To a little mercury (II) chloride solution, add potassium iodide solution drop by drop to excess until the red precipitate formed first, nearly redissolved to give a colourless solution. Add a few ml of potassium or sodium hydroxide solution. The resulting solution is Nessler's reagent. Add Nessler's reagent to an ammonium salt solution.

EXPERIMENT 4

Use of a chemical balance

(Weight by using a rider and determination of the solubility of a salt)

Description of a chemical balance : The analytical balance is a sensitive instrument in which weighing can be done with accuracy upto the fourth decimal place. The beam is supported at the centre (fulcrum) on an agate knife edge which rests on a plate of agate. On the ends of the beam, pans are suspended. If the pans are of equal weights and the distance of suspension from the centre (fulcrnm) is identical, the beam will be horizontal. A long pointer beam is attached to the centre of the beam to indicate any displacement of the beam from a horizontal position. In the rider balance, the beam is graduated in equal divisions on either side of the fulcrum. The graduations on the beam start with the zero mark at the centre and finish with 10 on either end of the beam. The rider (made of aluminium wire bent into a U-shape) is placed and moved on the beam to any position with the help of a 'rider carrier' which can be manipulated from the outside of the balance cabinet. The weight of a rider is generally 10 mg. (Fig. 109).

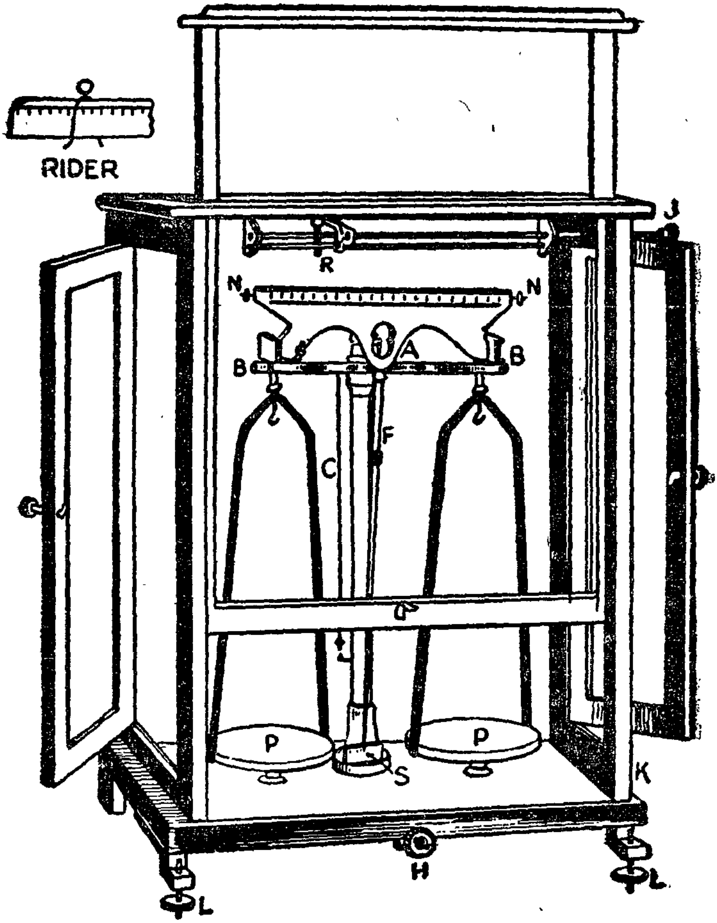


Fig. 109
Chemical balance

Method of weighing : The article to be weighed is carefully placed in the centre of the left pan, and weights a little greater than estimated of the article are placed on the centre of the right pan with the help of the forceps. Then carefully allow the pointer to swing freely by turning the key. See which way the pointer swings. If the pointer swings more to the left than to the right, it means the weights placed in the pan are heavier than the actual weight of the article. Now arrest the beam by turning the lever clockwise. If the weights in the pan are too heavy then replace it by the small weights. This process is continued until the difference of weights is less than 10 mg. The fractional weights are added in a decreasing order. Adjustments below 10 mg. is made by placing rider on a suitable point of the beam scale by means of 'rider carrier'. When the pointer swings equally on either sides of the zero, the article is exactly counter-balanced. Note the weights by actually counting the weights placed on the pan. If the rider is located at the 7·8 graduation mark on the right hand side of the beam, 0·0078 gm should be added to the weight in the right hand pan.

The record of weighing is given in Tabular Column.

	Article weighed	Weights added			Total wt. added
		Grams	Milli grams	Rider at	
1.	China dish				
2.	China dish + Solution				
3.	China dish+salt				

Determination of the solubility of a salt in water at room temperature

Solubility at a temperature is expressed as the weight in gms. of the solubility dissolved by 100 gms. of the solvent to give a saturated solution at the given temperature.

Prepare a saturated solution of the given salt, say, potassium chloride in water at room temperature by adding small amounts of KCl to water in a beaker with constant stirring. Continue stirring till some added salt remains undissolved. Leave the solution aside for about 15 minutes to attain saturation at room temperature. Note the room temperature.

Pipette out the supernatant solution into a weighed china dish of weight (W_1 gm). Find the weight of the dish with the solution (W_2 gm). Evaporate the solution to dryness over the wire gauze. Then translates the dish to a sand bath and heat it for a few minutes to drive away the last traces of moisture. Cool the dish and weigh. Repeat heating over the sand bath, cooling and weighing until constant weights are obtained (W_3 gm).

Calculations

Weight of empty dish …………… W_1gm.

Weight of the dish with solution …W_2gm.

Weight of the dish with salt …… W_3gm.

Weight of solvent = $W_2 - W_3$

Weight of solute = $W_3 - W_1$

$$\left.\begin{array}{r}\text{Solubility of KCl at}\\ \text{room temperature}\end{array}\right\} = \frac{\text{Wt. of solute}}{\text{Wt. of solvent}} \times 100$$

$$= \frac{W_3 - W_1}{W_2 - W_3} \times 100.$$

EXPERIMENT 5

Aim : Determination of the equivalent weight of magnesium by displacement of hydrogen from acids.

Principle : The number of parts by weight of the metal which can displace 1.008 parts by weight of hydrogen is the equivalent of the metal with respeat to hydrogen. A known weight of the metal is allowed to react with a dilute acid. The volume of hydrogen liberated is measured under the laboratory conditions. The volume is reduced to N.T.P. and the weight of hydrogen liberated is calculated knowing that 1000 ml of hydrogen at N.T.P. will weigh 0.09 gm. From the weight of the hydrogen liberated the equivalent weight of the metal is computed.

Apparatus : The apparatus consists of an aspirator bottle containing water. It is fitted with a two-holed rubber stopper carrying two bent glass tubes. One of them is connected to a conical flask through a rubber stopper. The other glass tube which is a long one acts as a syphon tube. It carries with it a pinch clip and one of its ends is placed in a measuring cylinder. The other end almost reaches the bottom of the aspirator bottle.

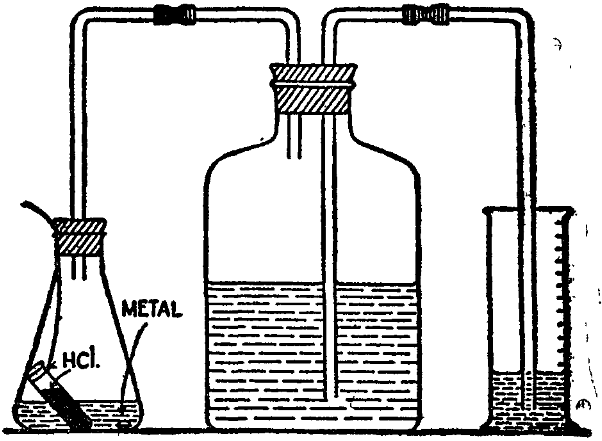


Fig. 110
Determination of the equivalent weight of Mg by displacement of hydrogen from acids

Experimental details : Test the apparatus for air tightness. Place a small piece of accurately weighed metal in a small test tube. In the conical flask take 1 : 1 HCl. Keep the test tube suspended inside the flask by means of a thread. Care is taken to see that the acid in the flask will not come into contact with the metal in the test tube before the apparatus set up is complete and ready for hydrogen collection. Blow air through the glass tube attached to the conical flask. Water comes out of the syphon tube. Replace the stopper. Water flows for a while through the delivery tube and then stops if the apparatus is air tight. Adjust the levels of the water in the jar and the aspirator bottle and read off the volume of the water in the jar.

Tilt the flask gently to bring the metal in contact with the acid. The hydrogen evolved will displace its own volume of water into the jar. When all the metal is dissolved, allow to cool, make the level of water in the jar the same as that in the bottle by raising or lowering the jar, and close the pinch cock. Note the volume of the water in the jar. The difference between this and the initial volume of water in the jar gives the volume of hydrogen liberated. Note the room temperature and pressure.

Calculations

Weight of the metal taken.........W gms

Volume of hydrogen liberated = Volume of water collected

Atmospheric pressure .... P mm

Laboratory temperature = t_1°C; Aqueous tension = p mm

This volume is reduced to N.T.P.

$$\frac{(P-p)\,V_1}{(273+t_1)} = \frac{760 \times V_2}{273}$$

V_2 the volume of hydrogen at N.T.P. is calculated.

1000 ml of hydrogen at N.T.P. weigh 0·09 gms

V_2 of hydrogen at N.T.P. weigh $\frac{0.09}{1000} \times V_2$ gms.

$\frac{0.09 \times V_2}{1000}$ gms of hydrogen is displaced by W gms of the metal.

1·008 gms ,, ... ,, $\frac{W \times 1000}{0{\cdot}09 \times V_2} \times 1{\cdot}008 =$ Equivalent weight of the metal.

EXPERIMENT 6

Preparation of Crystalline Salts

(a) Copper(II) Sulphate from Copper(II) Carbonate

Principle . Copper(II) sulphate is prepared by dissolving copper(II) carbonate in hot dilute sulphuric acid.

$$CuCO_3 + H_2SO_4 \rightarrow CuSO_4 + H_2O + CO_2 \uparrow$$

(i.e.) 98 gms of sulphuric acid give 250 gms of copper (II) sulphate, $CuSO_4, 5H_2O$.

(i.e.) 40cc of 2N sulphuric acid give 10 gms of copper (II) sulphate.

Procedure : Take about 40 cc of dilute sulphuric acid (2N, i.e., 1 : 16 acid) in a beaker and heat it over the wire gauze. To the hot acid, add copper (II) carbonate little by little with constant stirring till no more of it dissolves. Remove the excess of the solid by filtering the solution into an evaporating dish. Concentrate the filtrate by heating till the crystallisation point is reached. To know this, dip a glass rod in the hot solution and take it out. See if crystals appear on the glass rod. If they appear, then stop heating the solution. On cooling it, crystals of copper (II) sulphate will be formed. Collect the crystals ; dry them in the folds of a filter paper and submit the sample.

(b) Iron (II) Sulphate from iron filings

Principle : Iron (II) sulphate is prepared by dissolving iron filings or pure iron wire in hot dilute sulphuric acid out of contact with air. The undissolved iron is filtered off and the filtrate is concentrated to crystallisation.

$$Fe + \underset{98}{H_2SO_4} + 7H_2O \rightarrow \underset{278}{FeSO_4\,7H_2O} + H_2 \uparrow$$

To prepare 278 gms of iron (II) sulphate, 98 gms of sulphuric acid air required = 2 litres of 1N H_2SO_4 is needed.

To prepare 11 gms of iron (II) sulphate, about 40 ml of 2N H_2SO_4 is needed.

Procedure : Take a round bottomed flask fitted with a stopper carrying a small glass tube. Attach a short rubber tube having a vertical slit and close the other end of the tube with a small glass rod. This arrangement is known as a **Bunsen Valve.** Take about 40 ml of 2N H_2SO_4 (1 : 16 acid) in the flask and place an excess of pure iron wire (about 5gms). Replace the stopper carrying the Bunsen Valve, and heat the flask gently. When the pressure inside increases, the slit gets opened and hydrogen escapes. This arrangement prevents atmospheric oxygen from entering the flask and thus oxidation is prevented. When the reaction ceases, filter the solution. Take the clear filtrate in an evaporating dish, concentrate the filtrate to the crystallisation point and cool. Iron (II) sulphate crystallises out of the solution. Pour away the supernatant liquid, transfer the crystals to a filter paper and dry them. Submit the weighed sample.

(c) Magnesium Sulphate from Magnesium Carbonate

Principle : Magnesium sulphate is prepared by dissolving magnesium carbonate in hot dilute sulphuric acid.

$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2O + CO_2 \uparrow$$

98 gms of sulphuric acid give 246 gms of $MgSO_4 . 7H_2O$

(i.e) 40 ml of 2N H_2SO_4 give 9·8 gms of magnesium sulphate crystals.

Procedure : Same as given under (a)

EXPERIMENT 7

VOLUMETRIC ANALYSIS

Introduction : Volumetric analysis is a branch of quantitative analysis involving measurement of the volumes of the solutions reacting with each other. The process of determining the strength of an unknown solution by allowing it to react with a standard solution (solution of known strength) is known as **titration.**

The process consists in taking exactly 10 ml or 20 ml of one solution using a pipette. An indicator is added to know the end point. The other solution is added from a burette slowly till the reaction is just complete. The volume required is noted. **Normal solution** is defined as a solution which contains 1 gm equivalent of the substance dissolved in one litre of the solution. It is represented as 1 N solution. If strengths are expressed in terms of normal solution, then $V_1N_1 = V_2N_2$ where V_1 and V_2 are the volumes of the two solutions, and N_1 and N_2 are their strengths or normalities. Since V_1, V_2 and N_1 are known, N_2 can be calculated. From the above, it is clear that **'equinormal solutions interact in equal volumes'**, which is the fundamental law of volumetric **analysis.**

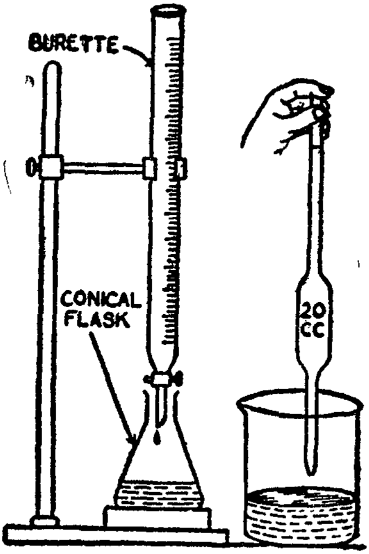


Fig 111
Burette and Pipette

In the titration of acids against bases, phenolphthalein and methyl orange are generally used as indicators. Phenolphthalein is pink in alkaline solution and colourless in acid.

solution. Methyl orange is yellow in alkaline solution and red in acid solution. For titrations of weak acids (organic acid like acetic acid, oxalic acid) against strong bases (NaOH,KOH), phenolphthalein should be used. In the case of titrations of weak bases (NH_4OH, $Ca(OH)_2$) against strong acids (mineral acids like HCl, H_2SO_4), methyl orange should be used.

$$\text{Equivalent weight of an acid} = \frac{\text{Molecular weight of acid}}{\text{Basicity of acid}}$$

For example, HCl : $\frac{36\cdot5}{1} = 36\cdot5$; H_2SO_4 : $\frac{98}{2} = 49$

$$\text{Equivalent weight of a base} = \frac{\text{Molecular weight of base}}{\text{Acidity}}$$

For example NaOH : $\frac{40}{1} = 40$, $Ba(OH)_2$: $\frac{171\cdot36}{2} = 85.68$

40 gms of NaOH (gm equivalent) dissolved in one litre of the solution will be I N solution of sodium hydroxide.

4·4 gms of NaOH are dissolved in one litre of the solution. the strength of the solution is

$$\frac{4\cdot4}{40} = 0\cdot11\text{N}$$

$$\text{Strength} = \frac{\text{Amount in one litre}}{\text{Equivalent weight}}$$

or Amount in one litre = Equivalent weight × Strength

So, if the equivalent weight of the substance is known, and the strength of the solution is found out, its amount dissolved in one litre of the solution can be calculated. If the amount of the substance dissolved in 1 litre of the solution and the strength of the solution are known, the equivalent weight can be calculated.

Acids are usually taken in the burette, and bases in the conical flask. If methyl orange is used as indicator, yellow colour must just turn red at the end point. In the case of phenolphthlein pink colour must just be discharged at the end point.

[A] Titration of strong acid against strong base.

Aim : To find the weight in grams of sodium hydroxide present in one litre of the solution. You are given a solution of hydrochloric acid of strength 0·12 N.

Principle : Sodium hydroxide reacts with hydrochloric acid as follows :

$$NaOH + HCl \rightarrow NaCl + H_2O$$

Since one equivalent of sodium hydroxide reacts with one equivalent of HCl, the equivalent weight of NaOH is the same as its molecular weight. A known volume of NaOH solution is titrated against HCl in the burette using methyl orange or phenolphthalein as indicator. The normality of hydrochloric acid is calculated from the titrate values.

Volume of NaOH × Normality of NaOH = Volume of HCl × Normality of HCl.

Weight of NaOH in 1 litre of the solution = Normality of NaOH × Equivalent weight of NaOH

Procedure : Wash the apparatus first with tap water, and then with distilled water. Rinse the burette with the standard HCl solution and the pipette with the NaOH solution. Reject the rinsed solutions. Completely fill the burette including its nozzle portion with the acid without any air bubbles. Pipette out 20ml of the NaOH solution into a conical flask which has been previously washed with distilled water. Add one or two drops of the indicator methyl orange to the alkali solution taken in the conical flask. The solution turns yellow. Adjust the level of the acid in the burette till it coincides with the zero mark.

Place the conical flask underneath the burette on a glazed tile. Run down the acid from the burette drop by drop, shaking the contents of conical flask after each addition. Acid is added till the yellow colour of the solution in the conical flask just turns pale red (pale pink). Note the final reading of the burette. Repeat the experiment till at least two readings agree.

Note : (a) Before each titration, it is always better to start from the zero mark on the burette.

(b) Phenolphthalein can also be used as an indicator in this experiment. Then the colour change at the end point will be from pink to colourless.

Record the reading in a tabular form as shown below. Volume of NaOH taken (i.e. capacity of pipette) = 20 ml.

Serial No.	Volume of NaOH (ml)	Initial reading of burette (ml)	Final reading of burette (ml)	Volume of acid run down (ml)
1	20 ml			
2	20 ml			
3	20 ml			

Volume of NaOH = 20 ml (V_1) Normality of NaOH=(N_2)

Volume of HCl = (V_2) Normality of HCl =(N_2)

$$V_1 \times N_1 = V_2 \times N_2$$

$$20 \times ? = V_2 \times 0{\cdot}12$$

$$N_1 = \frac{V_2 \times 0{\cdot}12}{20}$$

Weight of NaOH in one litre = Normality of NaOH × Equivalent Weight of NaOH

$$= \frac{V_2 \times 0{\cdot}12}{20} \times 40$$

[B] Titration of strong acid against weak base

Aim : To determine the weight of anhydrous sodium carbonate in a litre of the given solution. You are provided with decinormal sulphuric acid.

Principle : Sodium carbonate reacts with sulphuric acid as follows :

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2\uparrow$$

106	98
53	49 (Equivalent weight)

The equivalent weight of Na_2CO_3 is that weight of it which reacts with one equivalent of an acid. Hence, the equivalent weight of Na_2CO_3 is 53. A known volume of Na_2CO_3 solution is titrated against H_2SO_4, using methyl orange as an indicator. The normality of Na_2CO_3 solution is calculated from the titre values.

Volume of Na_2CO_3 solution × Normality of Na_2CO_3 solution =

Volume of H_2SO_4 solution × Normality of H_2SO_4 solution

$$\left.\begin{array}{l}\text{Weight of } Na_2CO_3 \text{ in one}\\ \text{litre of the solution}\end{array}\right\} = \begin{array}{l}\text{Normality of } Na_2CO_3 \times\\ \text{its equivalent weight}\end{array}$$

Procedure : Rinse the burette with the standard H_2SO_4 solution and the pipette with the Na_2CO_3 solution. Reject the rinsed solutions. Completely fill the burette with the acid, Pipette out 20 ml of Na_2CO_3 solution into a conical flask which has been previously washed with distilled water. Add one or two drops of the indicator methyl orange to the sodium carbonate solution taken in the conical flask. The solution is yellow. Adjust the level of the acid in the burette till it coincides with the zero mark.

Place the conical flask underneath burette on a glazed tile. Run down the acid from the burette drop by drop shaking the contents of conical flask after each addition. Acid is added till the yellow colour of the solution in the conical flask just turns pale red (pale pink). Note the final reading of the burette. Repeat the experiment till atleast two readings agree. [Phenolphthalein should not be used as an indicator in the titration of weak base like Na_2CO_3 against a mineral acid, as it shows the end point at the bicarbonate stage.] Record the reading in a tabular from as shown below :

Serial No.	Volume of Na_2CO_3 (ml)	Initial reading of burette (ml)	Final reading of burette (ml)	Volume of H_2SO_4 (ml)
1	20 ml			
2	20 ml			
3	20 ml			

$$\begin{array}{ccccccc} \text{Volume of} & & \text{Normality of} & & \text{Volume of} & & \text{Normality} \\ Na_2CO_3 & \times & Na_2CO_3 & = & H_2SO_4 & \times & \text{of } H_2SO_4 \\ 20 & \times & N & = & V_2 & \times & N/10 \end{array}$$

$$N = \frac{V_2}{20} \times \frac{N}{10}$$

$$\left.\begin{array}{l}\text{Weight of } Na_2CO_3 \text{ in 1 litre} \\ \text{of the solution.}\end{array}\right\} = \begin{array}{l}\text{Normality of} \\ Na_2CO_3\end{array} \times \begin{array}{l}\text{Equivalent} \\ \text{Wt. of } Na_2CO_3\end{array}$$

[C] Titration of weak acid against strong base

Aim : *To determine the weight of crystaline oxalic acid in one litre of the given solution. You are supplied with 0·12 N sodium hydroxide.*

Principle : NaOH reacts with oxalic acid according to the equation

$$\begin{array}{lll} 2NaOH & + \; H_2C_2O_4 \rightarrow Na_2C_2O_4 + 2H_2O \\ 2 \times 40 & \quad 126 \\ \quad 40 & \quad 63 \end{array}$$

$$\left.\begin{array}{l}\text{Equivalent weight of} \\ \text{crystalline oxalic acid}\end{array}\right\} \frac{H_2C_2O_4.2H_2O}{2} = 63$$

A known volume of sodium hydroxide solution is titrated against oxalic acid solution using phenolphthalein as indicator.

The normality of oxalic acid solution is calculated from the titre values. The weight of crystalline oxalic acid can be calculated knowing that the equivalent weight of crystalline oxalic acid is 63.

Procedure : Rinse the burette with the oxalic acid solution and the pipette with standard NaOH solution. Reject the rinsed solution. Completely fill the burette with the acid. Pipette out 20 ml of NaOH solution into a conical flask which has been previously washed with distilled water. Add one or two drops of the indicator phenolphthalein to the sodium hydroxide solution taken in the conical flask. The solution turns pink in colour. Adjust the level of the acid in the burette till it coincides with the zero mark.

Place the conical flask underneath the burette on a glazed tile. Run down the acid from the burette drop by drop shaking the contents of conical flask after each addition. Acid is added till the pink colour of the solution in the flask just becomes colourless. Note the final reading of the burette. Repeat the experiment till atleast two readings agree. Record the reading in a tabular from as shown below :

Serial No.	Volume of NaOH (ml)	Initial reading of the burette (ml)	Final reading of the burette (ml)	Volume of $H_2C_2O_4$ (ml)
1	20 ml			
2	20 ml			
3	20 ml			

$$\begin{array}{ccccccc} \text{Volume of} & & \text{Normality of} & & \text{Volume of} & & \text{Normality of} \\ \text{NaOH} & \times & \text{NaOH} & = & H_2C_2O_4 & \times & H_2C_2O_4 \\ 20 & \times & 0{\cdot}12\text{N} & = & V_2 & \times & N_2 \end{array}$$

$$N_2 = \frac{20}{V_2} \times 0{\cdot}2\text{N}$$

$$\left.\begin{array}{l}\text{Weight of crystalline oxalic acid} \\ \text{in one litre of the solution}\end{array}\right\} = \frac{20 \times 0{\cdot}12}{V_2} \times 63$$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