UNIT 1

SOME BASIC CONCEPTS OF CHEMISTRY

Objectives

After studying this unit, you will be able to

- appreciate the contribution of India in the development of chemistry understand the role of chemistry in different spheres of life;
- explain the characteristics of three states of matter;
- classify different substances into elements, compounds and mixtures;
- use scientific notations and determine significant figures;
- differentiate between precision and accuracy;
- define SI base units and convert physical quantities from one system of units to another;
- explain various laws of chemical combination;
- appreciate significance of atomic mass, average atomic mass, molecular mass and formula mass;
- describe the terms – mole and molar mass;
- calculate the mass per cent of component elements constituting a compound;
- determine empirical formula and molecular formula for a compound from the given experimental data; and
- perform the stoichiometric calculations.

"Chemistry is the science of molecules and their transformations. It is the science not so much of the one hundred elements but of the infinite variety of molecules that may be built from them."

Roald Hoffmann

Science can be viewed as a continuing human effort to systematise knowledge for describing and understanding nature. You have learnt in your previous classes that we come across diverse substances present in nature and changes in them in daily life. Curd formation from milk, formation of vinegar from sugarcane juice on keeping for prolonged time and rusting of iron are some of the examples of changes which we come across many times. For the sake of convenience, science is sub-divided into various disciplines: chemistry, physics, biology, geology, etc. The branch of science that studies the preparation, properties, structure and reactions of material substances is called chemistry.

DEVELOPMENT OF CHEMISTRY

Chemistry, as we understand it today, is not a very old discipline. Chemistry was not studied for its own sake, rather it came up as a result of search for two interesting things:

i. *Philosopher's stone (Paras)* which would convert all baser metals e.g., iron and copper into gold.

ii. *'Elexir of life'* which would grant immortality.

People in ancient India, already had the knowledge of many scientific phenomenon much before the advent of modern science. They applied that knowledge in various walks of life. Chemistry developed mainly in the form of Alchemy and Iatrochemistry during 1300-1600 CE. Modern chemistry took shape in the 18th century Europe, after a few centuries of alchemical traditions which were introduced in Europe by the Arabs.

Other cultures – especially the Chinese and the Indian – had their own alchemical traditions. These included much knowledge of chemical processes and techniques.

In ancient India, chemistry was called *Rasayan Shastra, Rastantra, Ras Kriya* or *Rasvidya*. It included metallurgy, medicine, manufacture of cosmetics, glass, dyes, etc. Systematic excavations at Mohenjodaro in Sindh and Harappa in Punjab prove that the story of development of chemistry in India is very old. Archaeological findings show that baked bricks were used in construction work. It shows the mass production of pottery, which can be regarded as the earliest chemical process, in which materials were mixed, moulded and subjected to heat by using fire to achieve desirable qualities. Remains of glazed pottery have been found in Mohenjodaro. Gypsum cement has been used in the construction work. It contains lime, sand and traces of $CaCO_3$. Harappans made faience, a sort of glass which was used in ornaments. They melted and forged a variety of objects from metals, such as lead, silver, gold and copper. They improved the hardness of copper for making artefacts by using tin and arsenic. A number of glass objects were found in Maski in South India (1000–900 BCE), and Hastinapur and Taxila in North India (1000–200 BCE). Glass and glazes were coloured by addition of colouring agents like metal oxides.

Copper metallurgy in India dates back to the beginning of chalcolithic cultures in the subcontinent. There are much archeological evidences to support the view that technologies for extraction of copper and iron were developed indigenously.

According to *Rigveda*, tanning of leather and dying of cotton were practised during 1000–400 BCE. The golden gloss of the black polished ware of northen India could not be replicated and is still a chemical mystery. These wares indicate the mastery with which kiln temperatures could be controlled. Kautilya's *Arthashastra* describes the production of salt from sea.

A vast number of statements and material described in the ancient Vedic literature can be shown to agree with modern scientific findings. Copper utensils, iron, gold, silver ornaments and terracotta discs and painted grey pottery have been found in many archaeological sites in north India. *Sushruta Samhita* explains the importance of Alkalies. The *Charaka Samhita* mentions ancient indians who knew how to prepare sulphuric acid, nitric acid and oxides of copper, tin and zinc; the sulphates of copper, zinc and iron and the carbonates of lead and iron.

Rasopanishada describes the preparation of gunpowder mixture. Tamil texts also describe the preparation of fireworks using sulphur, charcoal, saltpetre (i.e., potassium nitrate), mercury, camphor, etc.

Nagarjuna was a great Indian scientist. He was a reputed chemist, an alchemist and a metallurgist. His work *Rasratnakar* deals with the formulation of mercury compounds. He has also discussed methods for the extraction of metals, like gold, silver, tin and copper. A book, *Rsarnavam*, appeared around 800 CE. It discusses the uses of various furnaces, ovens and crucibles for different purposes. It describes methods by which metals could be identified by flame colour.

Chakrapani discovered mercury sulphide. The credit for inventing soap also goes to him. He used mustard oil and some alkalies as ingredients for making soap. Indians began making soaps in the 18th century CE. Oil of *Eranda* and seeds of *Mahua* plant and calcium carbonate were used for making soap.

The paintings found on the walls of Ajanta and Ellora, which look fresh even after ages, testify to a high level of science achieved in ancient India. Varähmihir's *Brihat Samhita* is a sort of encyclopaedia, which was composed in the sixth century CE. It informs about the preparation of glutinous material to be applied on walls and roofs of houses and temples. It was prepared entirely from extracts of various plants, fruits, seeds and barks, which were concentrated by boiling, and then, treated with various resins. It will be interesting to test such materials scientifically and assess them for use.

A number of classical texts, like *Atharvaveda* (1000 BCE) mention some dye stuff, the material used were turmeric, *madder*, sunflower, orpiment, cochineal and lac. Some other substances having tinting property were *kamplcica, pattanga* and *jatuka*.

Varähmihir's *Brihat Samhita* gives references to perfumes and cosmetics. Recipes for hair dying were made from plants, like indigo and minerals like iron power, black iron or steel and acidic extracts of sour rice gruel. *Gandhayukli* describes recipes for making scents, mouth perfumes, bath powders, incense and talcum power.

Paper was known to India in the 17^{th} century as account of Chinese traveller I-tsing describes. Excavations at Taxila indicate that ink was used in India from the fourth century. Colours of ink were made from chalk, red lead and minimum.

It seems that the process of fermentation was well-known to Indians. Vedas and Kautilya's *Arthashastra* mention about many types of liquors. *Charaka Samhita* also mentions ingredients, such as barks of plants, stem, flowers, leaves, woods, cereals, fruits and sugarcane for making *Asavas.*

The concept that matter is ultimately made of indivisible building blocks, appeared in India a few centuries BCE as a part of philosophical speculations. Acharya Kanda, born in 600 BCE, originally known by the name Kashyap, was the first proponent of the 'atomic theory'. He formulated the theory of very small indivisible particles, which he named '*Paramãnu*' (comparable to atoms). He authored the text *Vaiseshika Sutras*. According to him, all substances are aggregated form of smaller units called atoms (*Paramãnu*), which are eternal, indestructible, spherical, suprasensible and in motion in the original state. He explained that this individual entity cannot be sensed through any human organ. Kanda added that there are varieties of atoms that are as different as the different classes of substances. He said these (*Paramãnu*) could form pairs or triplets, among other combinations and unseen forces cause interaction between them. He conceptualised this theory around 2500 years before John Dalton (1766-1844).

Charaka Samhita is the oldest Ayurvedic epic of India. It describes the treatment of diseases. The concept of reduction of particle size of metals is clearly discussed in *Charaka Samhita*. Extreme reduction of particle size is termed as nanotechnology. *Charaka Samhita* describes the use of *bhasma* of metals in the treatment of ailments. Now-a-days, it has been proved that *bhasmas* have nanoparticles of metals.

After the decline of alchemy, Iatrochemistry reached a steady state, but it too declined due to the introduction and practise of western medicinal system in the 20^{th} century. During this period of stagnation, pharmaceutical industry based on Ayurveda continued to exist, but it too declined gradually. It took about 100-150 years for Indians to learn and adopt new techniques. During this time, foreign products poured in. As a result, indigenous traditional techniques gradually declined. Modern science appeared in Indian scene in the later part of the nineteenth century. By the mid-nineteenth century, European scientists started coming to India and modern chemistry started growing.

From the above discussion, you have learnt that chemistry deals with the composition, structure, properties and interection of matter and is of much use to human beings in daily life. These aspects can be best described and understood in terms of basic constituents of matter that are **atoms** and **molecules**. That is why, chemistry is also called the science of atoms and molecules. Can we see, weigh and perceive these entities (atoms and molecules)? Is it possible to count the number of atoms and molecules in a given mass of matter and have a quantitative relationship between the mass and the number of these particles? We will get the answer of some of these questions in this Unit. We will further describe how physical properties of matter can be quantitatively described using numerical values with suitable units.

1.1 IMPORTANCE OF CHEMISTRY

Chemistry plays a central role in science and is often intertwined with other branches of science.

Principles of chemistry are applicable in diverse areas, such as weather patterns, functioning of brain and operation of a computer, production in chemical industries, manufacturing fertilisers, alkalis, acids, salts, dyes, polymers, drugs, soaps, detergents, metals, alloys, etc., including new material.

Chemistry contributes in a big way to the national economy. It also plays an important role in meeting human needs for food, healthcare products and other material aimed at improving the quality of life. This is exemplified by the large-scale production of a variety of fertilisers, improved variety of pesticides and insecticides. Chemistry provides methods for the isolation of life-saving drugs from natural sources and makes possible synthesis of such drugs. Some of these drugs are **cisplatin** and **taxol**, which are effective in cancer therapy. The drug AZT (Azidothymidine) is used for helping AIDS patients.

Chemistry contributes to a large extent in the development and growth of a nation. With a better understanding of chemical principles it has now become possible to design and synthesise new material having specific magnetic, electric and optical properties. This has lead to the production of superconducting ceramics, conducting polymers, optical fibres, etc. Chemistry has helped in establishing industries which manufacture utility goods, like acids, alkalies, dyes, polymesr metals, etc. These industries contribute in a big way to the economy of a nation and generate employment.

In recent years, chemistry has helped in dealing with some of the pressing aspects of environmental degradation with a fair degree of success. Safer alternatives to environmentally hazardous refrigerants, like CFCs (chlorofluorocarbons), responsible for ozone depletion in the stratosphere, have been successfully synthesised. However, many big environmental problems continue to be matters of grave concern to the chemists. One such problem is the management of the Green House gases, like methane, carbon dioxide, etc. Understanding of biochemical processes, use of enzymes for large-scale production of chemicals and synthesis of new exotic material are some of the intellectual challenges for the future generation of chemists. A developing country, like India, needs talented and creative chemists for accepting such challenges. To be a good chemist and to accept such challanges, one needs to understand the basic concepts of chemistry, which begin with the concept of matter. Let us start with the nature of matter.

1.2 NATURE OF MATTER

You are already familiar with the term **matter** from your earlier classes. Anything which has mass and occupies space is called **matter**. Everything around us, for example, book, pen, pencil, water, air, all living beings, etc., are composed of matter. You know that they have mass and they occupy space. Let us recall the characteristics of the states of matter, which you learnt in your previous classes.

1.2.1 States of Matter

You are aware that matter can exist in three physical states *viz.* **solid**, **liquid** and **gas**. The constituent particles of matter in these three states can be represented as shown in Fig. 1.1.

Particles are held very close to each other in **solids** in an orderly fashion and there is not much freedom of movement. In **liquids**, the particles are close to each other but they can move around. However, in **gases**, the particles are far apart as compared to those present in solid or liquid states and their movement is easy and fast. Because of such arrangement of particles, different states of matter exhibit the following characteristics:

(i) Solids have *definite volume* and *definite shape*.

(ii) Liquids have *definite volume* but *do not* have *definite shape*. They take the shape of the container in which they are placed.

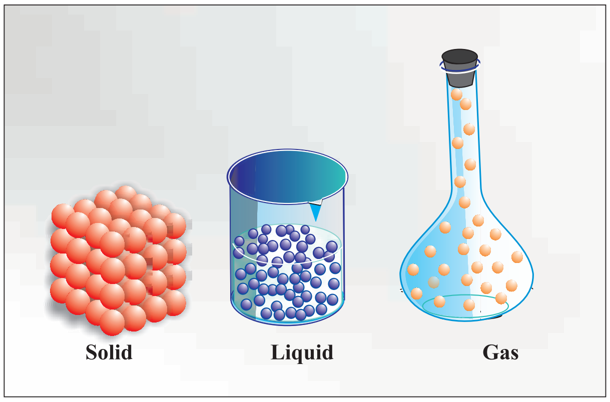


Fig. 1.1 *Arrangement of particles in solid, liquid and gaseous state*

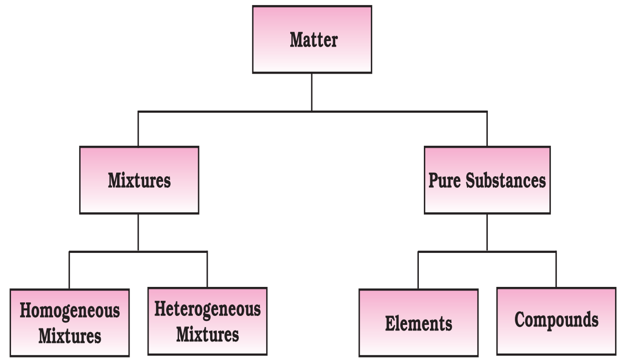


Fig. 1.2 *Classification of matter*

(iii) Gases have *neither definite volume nor definite shape*. They completely occupy the space in the container in which they are placed.

These three states of matter are interconvertible by changing the conditions of temperature and pressure.

$$\text{Solid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{liquid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{Gas}$$

On heating, a solid usually changes to a liquid, and the liquid on further heating changes to gas (or vapour). In the reverse process, a gas on cooling liquifies to the liquid and the liquid on further cooling freezes to the solid.

1.2.2. Classification of Matter

In class IX (Chapter 2), you have learnt that at the macroscopic or bulk level, matter can be classified as **mixture** or **pure substance**. These can be further sub-divided as shown in Fig. 1.2.

When all constituent particles of a substance are same in chemical nature, it is said to be a pure substance. A mixture contains many types of particles.

A mixture contains particles of two or more pure substances which may be present in it in any ratio. Hence, their composition is variable. Pure sustances forming mixture are called its components. Many of the substances present around you are **mixtures**. For example, sugar solution in water, air, tea, etc., are all mixtures. A mixture may be **homogeneous** or **heterogeneous**. In a **homogeneous mixture**, the components completely mix with each other. This means particles of components of the mixture are uniformly distributed throughout the bulk of the mixture and its composition is uniform throughout. Sugar solution and air are the examples of homogeneous mixtures. In contrast to this, in a **heterogeneous mixture**, the composition is not uniform throughout and sometimes different components are visible. For example, mixtures of salt and sugar, grains and pulses along with some dirt (often stone pieces), are heterogeneous mixtures. You can think of many more examples of mixtures which you come across in the daily life. It is worthwhile to mention here that the components of a mixture can be separated by using physical methods, such as simple hand-picking, filtration, crystallisation, distillation, etc.

Pure substances have characteristics different from mixtures. Constituent particles of pure substances have fixed composition. Copper, silver, gold, water and glucose are some examples of pure substances. Glucose contains carbon, hydrogen and oxygen in a fixed ratio and its particles are of same composition. Hence, like all other pure substances, glucose has a fixed composition. Also, its constituents—carbon, hydrogen and oxygen—cannot be separated by simple physical methods.

Pure substances can further be classified into **elements** and **compounds**. Particles of an **element** consist of only one type of atoms. These particles may exist as **atoms** or **molecules**. You may be familiar with atoms and molecules from the previous classes; however, you will be studying about them in detail in Unit 2. Sodium, copper, silver, hydrogen, oxygen, etc., are some examples of elements. Their all atoms are of one type. However, the atoms of different elements are different in nature. Some elements, such as sodium or copper, contain atoms as their constituent particles, whereas, in some others, the constituent particles are molecules which are formed by two or more atoms. For example, hydrogen, nitrogen and oxygen gases consist of molecules, in which two atoms combine to give their respective molecules. This is illustrated in Fig. 1.3.

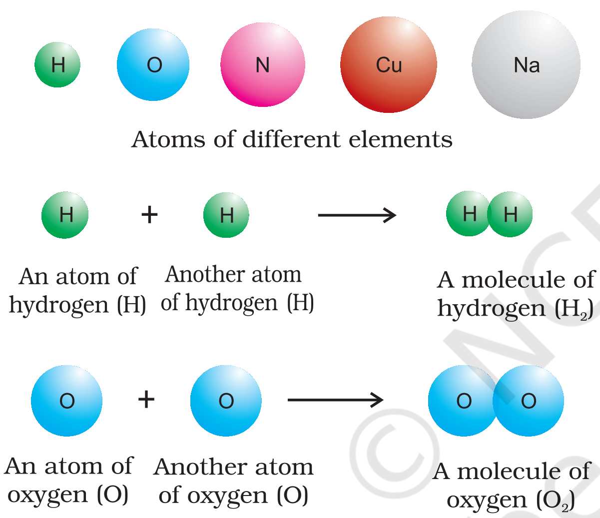


Fig. 1.3 *A representation of atoms and molecules*

When two or more atoms of different elements combine together in a definite ratio, the molecule of a **compound** is obtained. Moreover, the constituents of a compound cannot be separated into simpler substances by physical methods. They can be separated by chemical methods. Examples of some compounds are water, ammonia, carbon dioxide, sugar, etc. The molecules of water and carbon dioxide are represented in Fig. 1.4.

Note that a water molecule comprises two hydrogen atoms and one oxygen atom. Similarly, a molecule of carbon dioxide contains two oxygen atoms combined with one

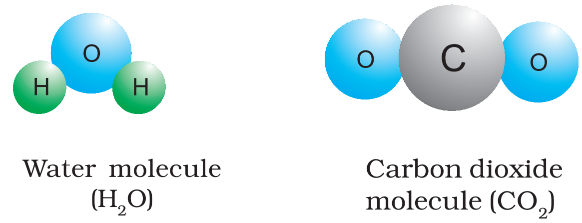


Fig. 1.4 *A depiction of molecules of water and carbon dioxide*

carbon atom. Thus, the atoms of different elements are present in a compound in a fixed and definite ratio and this ratio is characteristic of a particular compound. Also, the properties of a compound are different from those of its constituent elements. For example, hydrogen and oxygen are gases, whereas, the compound formed by their combination i.e., water is a liquid. It is interesting to note that hydrogen burns with a pop sound and oxygen is a supporter of combustion, but water is used as a fire extinguisher.

1.3 PROPERTIES OF MATTER AND THEIR MEASUREMENT

1.3.1 Physical and chemical properties

Every substance has unique or characteristic properties. These properties can be classified into two categories — **physical properties,** such as colour, odour, melting point, boiling point, density, etc., and **chemical properties,** like composition, combustibility, ractivity with acids and bases, etc.

Physical properties can be measured or observed without changing the identity or the composition of the substance. The measurement or observation of **chemical properties** requires a chemical change to occur. Measurement of physical properties does not require occurance of a chemical change. The examples of chemical properties are characteristic reactions of different substances; these include acidity or basicity, combustibility, etc. Chemists describe, interpret and predict the behaviour of substances on the basis of knowledge of their physical and chemical properties, which are determined by careful measurement and experimentation. In the following section, we will learn about the measurement of physical properties.

1.3.2 Measurement of physical properties

Quantitative measurement of properties is reaquired for scientific investigation. Many properties of matter, such as length, area, volume, etc., are quantitative in nature. Any quantitative observation or measurement is represented by a number followed by units in which it is measured. For example, length of a room can be represented as 6 m; here, 6 is the number and m denotes metre, the unit in which the length is measured.

Earlier, two different systems of measurement, i.e., the **English System** and the **Metric System** were being used in different parts of the world. The metric system, which originated in France in late eighteenth century, was more convenient as it was based on the decimal system. Late, need of a common standard system was felt by the scientific community. Such a system was established in 1960 and is discussed in detail below.

1.3.3 The International System of Units (SI)

The International System of Units (in French *Le Systeme International d'Unités* — abbreviated as SI) was established by the 11^{th} General Conference on Weights and Measures (CGPM from *Conference Generale des Poids et Measures*). The CGPM is an inter-governmental treaty organisation created by a diplomatic treaty known as Metre Convention, which was signed in Paris in 1875.

Maintaining the National Standards of Measurement

The system of units, including unit definitions, keeps on changing with time. Whenever the accuracy of measurement of a particular unit was enhanced substantially by adopting new principles, member nations of metre treaty (signed in 1875), agreed to change the formal definition of that unit. Each modern industrialised country, including India, has a National Metrology Institute (NMI), which maintains standards of measurements. This responsibility has been given to the National Physical Laboratory (NPL), New Delhi. This laboratory establishes experiments to realise the *base units* and *derived units* of measurement and maintains National Standards of Measurement. These standards are periodically inter-compared with standards maintained at other National Metrology Institutes in the world, as well as those, established at the International Bureau of Standards in Paris.

The SI system has seven *base units* and they are listed in Table 1.1. These units pertain to the seven fundamental scientific quantities. The other physical quantities, such as speed, volume, density, etc., can be derived from these quantities.

Table 1.1 Base Physical Quantities and their Units

Base Physical Quantity	Symbol for Quantity	Name of SI Unit	Symbol for SI Unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Thermodynamic temperature	T	kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	I_v	candela	cd

The definitions of the SI base units are given in Table 1.2.

The SI system allows the use of prefixes to indicate the multiples or submultiples of a unit. These prefixes are listed in Table 1.3.

Let us now quickly go through some of the quantities which you will be often using in this book.

Table 1.2 Definitions of SI Base Units

Unit of length	**metre**	The *metre* is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second.
Unit of mass	**kilogram**	The *kilogram* is the unit of mass; it is equal to the mass of the international prototype of the kilogram.
Unit of time	**second**	The *second* is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom.
Unit of electric current	**ampere**	The *ampere* is that constant current, which if maintained in two straight parallel conductors of infinite length of negligible circular cross-section and placed 1 metre apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} newton per metre of length.
Unit of thermodynamic temperature	**kelvin**	The *kelvin*, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple* point of water.
Unit of amount of substance	**mole**	1. The *mole* is the amount of substance of a system, which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12; its symbol is 'mol'. 2. When the mole is used, the elementary entities must be specified and these may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.
Unit of luminous intensity	**candela**	The *candela* is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

* *Triple point of water is 0.01 °C or 279.16K (32.01°F)*

Table 1.3 Prefixes used in the SI System

Multiple	Prefix	Symbol
10^{-24}	yocto	y
10^{-21}	zepto	z
10^{-18}	atto	a
10^{-15}	femto	f
10^{-12}	pico	p
10^{-9}	nano	n
10^{-6}	micro	µ
10^{-3}	milli	m
10^{-2}	centi	c
10^{-1}	deci	d
10	deca	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P
10^{18}	exa	E
10^{21}	zeta	Z
10^{24}	yotta	Y

1.3.4 Mass and Weight

Mass of a substance is the amount of matter present in it, while **weight** is the force exerted by gravity on an object. The mass of a substance is constant, whereas, its weight may vary from one place to another due to change in gravity. You should be careful in using these terms.

The mass of a substance can be determined accurately in the laboratory by using an analytical balance (Fig. 1.5).

The SI unit of mass as given in Table 1.1 is kilogram. However, its fraction named as gram (1 kg = 1000 g), is used in laboratories due to the smaller amounts of chemicals used in chemical reactions.

1.3.5 Volume

Volume is the amont of space occupied by a substance. It has the units of $(\text{length})^3$. So in SI system, volume has units of m^3. But again, in chemistry laboratories, smaller volumes are used. Hence, volume is often denoted in cm^3 or dm^3 units.

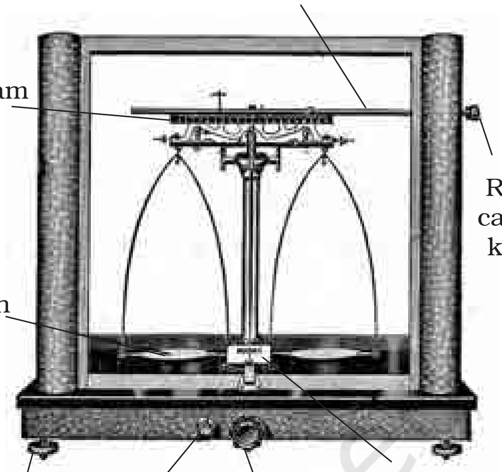


Fig. 1.5 *Analytical balance*

A common unit, litre (L) which is not an SI unit, is used for measurement of volume of liquids.

$$1 \text{ L} = 1000 \text{ mL}, \quad 1000 \text{ cm}^3 = 1 \text{ dm}^3$$

Fig. 1.6 helps to visualise these relations.

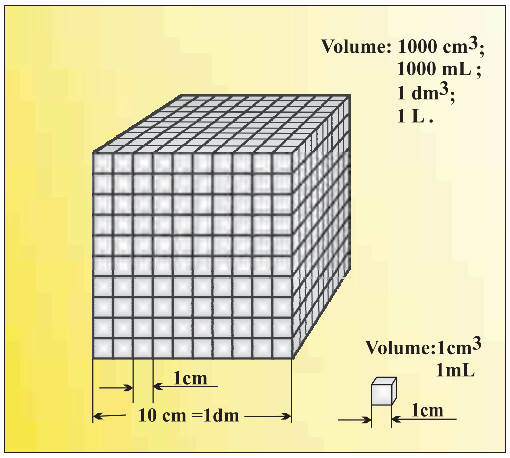


Fig. 1.6 *Different units used to express volume*

In the laboratory, the volume of liquids or solutions can be measured by graduated cylinder, burette, pipette, etc. A volumetric flask is used to prepare a known volume of a solution. These measuring devices are shown in Fig. 1.7.

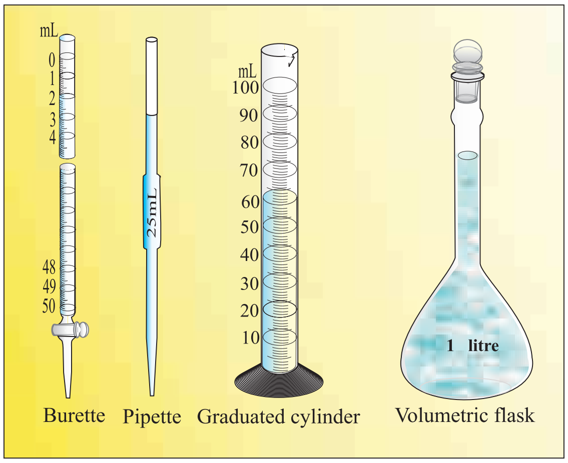


Fig. 1.7 *Some volume measuring devices*

1.3.6 Density

The two properties — mass and volume discussed above are related as follows:

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

Density of a substance is its amount of mass per unit volume. So, SI units of density can be obtained as follows:

$$\text{SI unit of density} = \frac{\text{SI unit of mass}}{\text{SI unit of volume}}$$

$$= \frac{\text{kg}}{\text{m}^3} \text{ or kg m}^{-3}$$

This unit is quite large and a chemist often expresses density in g cm^{-3}, where mass is expressed in gram and volume is expressed in cm^3. Density of a substance tells us about how closely its particles are packed. If density is more, it means particles are more closely packed.

1.3.7 Temperature

There are three common scales to measure temperature — °C (degree celsius), °F (degree fahrenheit) and K (kelvin). Here, K is the SI unit. The thermometers based on these scales are shown in Fig. 1.8. Generally, the thermometer with celsius scale are calibrated from 0° to 100°, where these two temperatures are the freezing point and the boiling point of water, respectively. The fahrenheit scale is represented between 32° to 212°.

The temperatures on two scales are related to each other by the following relationship:

$$°F = \frac{9}{5}(°C) + 32$$

The kelvin scale is related to celsius scale as follows:

$$K = °C + 273.15$$

It is interesting to note that temperature below 0 °C (i.e., negative values) are possible in Celsius scale but in Kelvin scale, negative temperature is not possible.

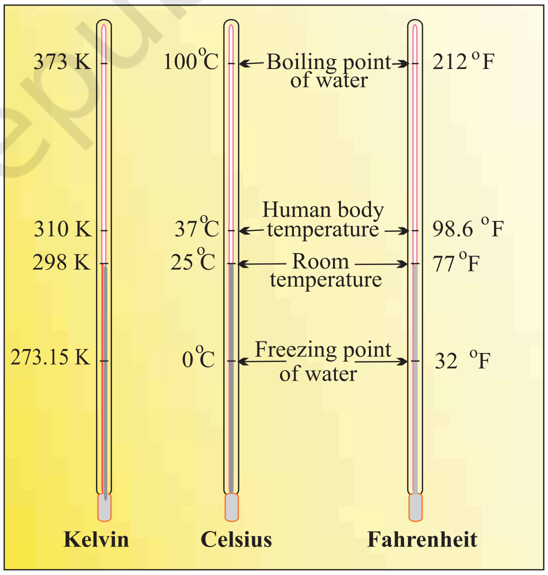


Fig. 1.8 *Thermometers using different temperature scales*

1.4 UNCERTAINTY IN MEASUREMENT

Many a time in the study of chemistry, one has to deal with experimental data as well as theoretical calculations. There are meaningful ways to handle the numbers conveniently and

Reference Standard

After defining a unit of measurement such as the kilogram or the metre, scientists agreed on reference standards that make it possible to calibrate all measuring devices. For getting reliable measurements, all devices such as *metre sticks* and *analytical balances* have been calibrated by their manufacturers to give correct readings. However, each of these devices is standardised or calibrated against some reference. The mass standard is the kilogram since 1889. It has been defined as the mass of platinum-iridium (Pt-Ir) cylinder that is stored in an airtight jar at International Bureau of Weights and Measures in Sevres, France. Pt-Ir was chosen for this standard because it is highly resistant to chemical attack and its mass will not change for an extremely long time.

Scientists are in search of a new standard for mass. This is being attempted through accurate determination of Avogadro constant. Work on this new standard focuses on ways to measure accurately the number of atoms in a well-defined mass of sample. One such method, which uses X-rays to determine the atomic density of a crystal of ultrapure silicon, has an accuracy of about 1 part in 10^6 but has not yet been adopted to serve as a standard. There are other methods but none of them are presently adequate to replace the Pt-Ir cylinder. No doubt, changes are expected within this decade.

The metre was originally defined as the length between two marks on a Pt-Ir bar kept at a temperature of 0°C (273.15 K). In 1960 the length of the metre was defined as 1.65076373×10^6 times the wavelength of light emitted by a krypton laser. Although this was a cumbersome number, it preserved the length of the metre at its agreed value. The metre was redefined in 1983 by CGPM as the length of path travelled by light in vacuum during a time interval of 1/299 792 458 of a second. Similar to the length and the mass, there are reference standards for other physical quantities.

present the data realistically with certainty to the extent possible. These ideas are discussed below in detail.

1.4.1 Scientific Notation

As chemistry is the study of atoms and molecules, which have extremely low masses and are present in extremely large numbers, a chemist has to deal with numbers as large as 602, 200,000,000,000,000,000,000 for the molecules of 2 g of hydrogen gas or as small as 0.00000000000000000000000166 g mass of a H atom. Similarly, other constants such as Planck's constant, speed of light, charges on particles, etc., involve numbers of the above magnitude.

It may look funny for a moment to write or count numbers involving so many zeros but it offers a real challenge to do simple mathematical operations of addition, subtraction, multiplication or division with such numbers. You can write any two numbers of the above type and try any one of the operations you like to accept as a challenge, and then, you will really appreciate the difficulty in handling such numbers.

This problem is solved by using scientific notation for such numbers, i.e., exponential notation in which any number can be represented in the form $N \times 10^n$, where n is an exponent having positive or negative values and N is a number (called digit term) which varies between 1.000... and 9.999....

Thus, we can write 232.508 as 2.32508×10^2 in scientific notation. Note that while writing it, the decimal had to be moved to the left by two places and same is the exponent (2) of 10 in the scientific notation.

Similarly, 0.00016 can be written as 1.6×10^{-4}. Here, the decimal has to be moved four places to the right and (–4) is the exponent in the scientific notation.

While performing mathematical operations on numbers expressed in scientific notations, the following points are to be kept in mind.

Multiplication and Division

These two operations follow the same rules which are there for exponential numbers, i.e.

$$\left(5.6\times10^{5}\right)\times\left(6.9\times10^{8}\right)=\left(5.6\times6.9\right)\left(10^{5+8}\right)$$
$$=\left(5.6\times6.9\right)\times10^{13}$$
$$= 38.64 \times 10^{13}$$
$$= 3.864 \times 10^{14}$$

$$\left(9.8\times10^{-2}\right)\times\left(2.5\times10^{-6}\right)=\left(9.8\times2.5\right)\left(10^{-2+(-6)}\right)$$
$$=\left(9.8\times2.5\right)\left(10^{-2-6}\right)$$
$$= 24.50 \times 10^{-8}$$
$$= 2.450 \times 10^{-7}$$

$$\frac{2.7\times10^{-3}}{5.5\times10^{4}}=\left(2.7\div5.5\right)\left(10^{-3-4}\right)=0.4909 \times 10^{-7}$$
$$=4.909 \times 10^{-8}$$

Addition and Subtraction

For these two operations, first the numbers are written in such a way that they have the same exponent. After that, the coefficients (digit terms) are added or subtracted as the case may be.

Thus, for adding 6.65×10^4 and 8.95×10^3, exponent is made same for both the numbers. Thus, we get $(6.65 \times 10^4) + (0.895 \times 10^4)$

Then, these numbers can be added as follows
$(6.65 + 0.895) \times 10^4 = 7.545 \times 10^4$

Similarly, the subtraction of two numbers can be done as shown below:

$(2.5 \times 10^{-2}) – (4.8 \times 10^{-3})$

$= (2.5 \times 10^{-2}) – (0.48 \times 10^{-2})$

$= (2.5 – 0.48) \times 10^{-2} = 2.02 \times 10^{-2}$

1.4.2 Significant Figures

Every experimental measurement has some amount of uncertainty associated with it because of limitation of measuring instrument and the skill of the person making the measurement. For example, mass of an object is obtained using a platform balance and it comes out to be 9.4g. On measuring the mass of this object on an analytical balance, the mass obtained is 9.4213g. The mass obtained by an analytical balance is slightly higher than the mass obtained by using a platform balance. Therefore, digit 4 placed after decimal in the measurement by platform balance is uncertain.

The uncertainty in the experimental or the calculated values is indicated by mentioning the number of significant figures. **Significant figures** are meaningful digits which are known with certainty plus one which is estimated or uncertain. The uncertainty is indicated by writing the certain digits and the last uncertain digit. Thus, if we write a result as 11.2 mL, we say the 11 is certain and 2 is uncertain and the uncertainty would be ±1 in the last digit. Unless otherwise stated, an uncertainty of ±1 in the last digit is always understood.

There are certain rules for determining the number of significant figures. These are stated below:

(1) All non-zero digits are significant. For example in 285 cm, there are three significant figures and in 0.25 mL, there are two significant figures.

(2) Zeros preceding to first non-zero digit are not significant. Such zero indicates the position of decimal point. Thus, 0.03 has one significant figure and 0.0052 has two significant figures.

(3) Zeros between two non-zero digits are significant. Thus, 2.005 has four significant figures.

(4) Zeros at the end or right of a number are significant, provided they are on the right side of the decimal point. For example, 0.200 g has three significant figures. But, if otherwise, the terminal zeros are not significant if there is no decimal point. For example, 100 has only one significant figure, but 100. has three significant figures and 100.0 has four significant figures. Such numbers are better represented in scientific notation. We can express the number 100 as 1×10^2 for one significant figure, 1.0×10^2 for two significant figures and 1.00×10^2 for three significant figures.

(5) Counting the numbers of object, for example, 2 balls or 20 eggs, have infinite significant figures as these are exact numbers and can be represented by writing infinite number of zeros after placing a decimal i.e., 2 = 2.000000 or 20 = 20.000000.

In numbers written in scientific notation, all digits are significant e.g., 4.01×10^2 has three significant figures, and 8.256×10^{-3} has four significant figures.

However, one would always like the results to be precise and accurate. Precision and accuracy are often referred to while we talk about the measurement.

Precision refers to the closeness of various measurements for the same quantity. However, **accuracy** is the agreement of a particular value to the true value of the result. For example, if the true value for a result is 2.00 g and student 'A' takes two measurements and reports the results as 1.95 g and 1.93 g. These values are precise as they are close to each other but are not accurate. Another student 'B' repeats the experiment and obtains 1.94 g and 2.05 g as the results for two measurements. These observations are neither precise nor accurate. When the third student 'C' repeats these measurements and reports 2.01 g and 1.99 g as the result, these values are both precise and accurate. This can be more clearly understood from the data given in Table 1.4.

Table 1.4 Data to Illustrate Precision and Accuracy

Measurements/g			
	1	2	Average (g)
Student A	1.95	1.93	1.940
Student B	1.94	2.05	1.995
Student C	2.01	1.99	2.000

Addition and Subtraction of Significant Figures

The result cannot have more digits to the right of the decimal point than either of the original numbers.

12.11
18.0
1.012
31.122

Here, 18.0 has only one digit after the decimal point and the result should be reported only up to one digit after the decimal point, which is 31.1.

Multiplication and Division of Significant Figures

In these operations, the result must be reported with no more significant figures as in the measurement with the few significant figures.

$2.5\times1.25 = 3.125$

Since 2.5 has two significant figures, the result should not have more than two significant figures, thus, it is 3.1.

While limiting the result to the required number of significant figures as done in the above mathematical operation, one has to keep in mind the following points for rounding off the numbers

1. If the rightmost digit to be removed is more than 5, the preceding number is increased by one. For example, 1.386. If we have to remove 6, we have to round it to 1.39.
2. If the rightmost digit to be removed is less than 5, the preceding number is not changed. For example, 4.334 if 4 is to be removed, then the result is rounded upto 4.33.
3. If the rightmost digit to be removed is 5, then the preceding number is not changed if it is an even number but it is increased by one if it is an odd number. For example, if 6.35 is to be rounded by removing 5, we have to increase 3 to 4 giving 6.4 as the result. However, if 6.25 is to be rounded off it is rounded off to 6.2.

1.4.3 Dimensional Analysis

Often while calculating, there is a need to convert units from one system to the other. The method used to accomplish this is called **factor label method** or **unit factor method** or **dimensional analysis**. This is illustrated below.

Example

A piece of metal is 3 inch (represented by in) long. What is its length in cm?

Solution

We know that 1 in = 2.54 cm

From this equivalence, we can write

$$\frac{1\ \text{in}}{2.54\,\text{cm}} = 1 = \frac{2.54\,\text{cm}}{1\ \text{in}}$$

Thus, $\frac{1\ \text{in}}{2.54\,\text{cm}}$ equals 1 and $\frac{2.54\,\text{cm}}{1\ \text{in}}$ also equals 1. Both of these are called **unit factors**. If some number is multiplied by these unit factors (i.e., 1), it will not be affected otherwise.

Say, the 3 in given above is multiplied by the unit factor. So,

$$3\ \text{in} = 3\ \text{in} \times \frac{2.54\,\text{cm}}{1\ \text{in}} = 3 \times 2.54\ \text{cm} = 7.62\ \text{cm}$$

Now, the unit factor by which multiplication is to be done is that unit factor ($\frac{2.54\,\text{cm}}{1\ \text{in}}$ in the above case) which gives the desired units i.e., the numerator should have that part which is required in the desired result.

It should also be noted in the above example that units can be handled just like other numerical part. It can be cancelled, divided, multiplied, squared, etc. Let us study one more example.

Example

A jug contains 2 L of milk. Calculate the volume of the milk in m^3.

Solution

Since 1 L = 1000 cm^3

and 1m = 100 cm, which gives

$$\frac{1\ \text{m}}{100\ \text{cm}} = 1 = \frac{100\,\text{cm}}{1\,\text{m}}$$

To get m^3 from the above unit factors, the first unit factor is taken and it is cubed.

$$\left(\frac{1\,\text{m}}{100\,\text{cm}}\right)^3 \Rightarrow \frac{1\,\text{m}^3}{10^6\ \text{cm}^3} = (1)^3 = 1$$

Now 2 L = 2×1000 cm^3

The above is multiplied by the unit factor

$$2 \times 1000\ \text{cm}^3 \times \frac{1\,\text{m}^3}{10^6\ \text{cm}^3} = \frac{2\,\text{m}^3}{10^3} = 2 \times 10^{-3}\,\text{m}^3$$

Example

How many seconds are there in 2 days?

Solution

Here, we know 1 day = 24 hours (h)

or $\frac{1\,\text{day}}{24\,\text{h}} = 1 = \frac{24\,\text{h}}{1\,\text{day}}$

then, 1h = 60 min

or $\frac{1\,\text{h}}{60\,\text{min}} = 1 = \frac{60\,\text{min}}{1\,\text{h}}$

so, for converting 2 days to seconds,

i.e., 2 days – – – – – – = – – – seconds

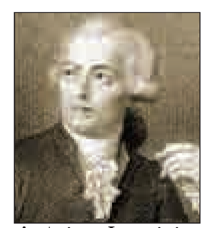
The unit factors can be multiplied in series in one step only as follows:

$$2\,\text{day} \times \frac{24\,\text{h}}{1\,\text{day}} \times \frac{60\ \text{min}}{1\ \text{h}} \times \frac{60\,\text{s}}{1\ \text{min}}$$

$= 2 \times 24 \times 60 \times 60$ s

$= 172800$ s

1.5 LAWS OF CHEMICAL COMBINATIONS



Antoine Lavoisier (1743–1794)

The combination of elements to form compounds is governed by the following five basic laws.

1.5.1 Law of Conservation of Mass

This law was put forth by Antoine Lavoisier in 1789. He performed careful experimental studies for combustion reactions and reached to the conclusion that in all physical and chemical changes, there is no net change in mass duting the process. Hence, he reached to the conclusion that matter can neither be created nor destroyed. This is called 'Law of Conservation of Mass'. This law formed the basis for several later developments in chemistry. Infact, this was the result of exact measurement of masses of reactants and products, and carefully planned experiments performed by Lavoisier.

1.5.2 Law of Definite Proportions


Joseph Proust (1754–1826)

This law was given by, a French chemist, Joseph Proust. He stated that *a given compound always contains exactly the same proportion of elements by weight.*

Proust worked with two samples of cupric carbonate — one of which was of natural origin and the other was synthetic. He found that the composition of elements present in it was same for both the samples as shown below:

	% of copper	% of carbon	% of oxygen
Natural Sample	51.35	9.74	38.91
Synthetic Sample	51.35	9.74	38.91

Thus, he concluded that irrespective of the source, a given compound always contains same elements combined together in the same proportion by mass. The validity of this law has been confirmed by various experiments. It is sometimes also referred to as **Law of Definite Composition**.

1.5.3 Law of Multiple Proportions

This law was proposed by Dalton in 1803. According to this law, *if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers.*

For example, hydrogen combines with oxygen to form two compounds, namely, water and hydrogen peroxide.

Hydrogen + Oxygen $\rightarrow$ Water
2g 16g 18g

Hydrogen + Oxygen $\rightarrow$ Hydrogen Peroxide
2g 32g 34g

Here, the masses of oxygen (i.e., 16 g and 32 g), which combine with a fixed mass of hydrogen (2g) bear a simple ratio, i.e., 16:32 or 1: 2.

1.5.4 Gay Lussac's Law of Gaseous Volumes


Joseph Louis Gay Lussac

This law was given by Gay Lussac in 1808. He observed that *when gases combine or are produced in a chemical reaction they do so in a simple ratio by volume, provided all gases are at the same temperature and pressure.*

Thus, 100 mL of hydrogen combine with 50 mL of oxygen to give 100 mL of water vapour.

Hydrogen + Oxygen $\rightarrow$ Water
100 mL 50 mL 100 mL

Thus, the volumes of hydrogen and oxygen which combine (i.e., 100 mL and 50 mL) bear a simple ratio of 2:1.

Gay Lussac's discovery of integer ratio in volume relationship is actually the law of definite proportions by volume. The law of definite proportions, stated earlier, was with respect to mass. The Gay Lussac's law was explained properly by the work of Avogadro in 1811.

1.5.5 Avogadro's Law

In 1811, Avogadro proposed that *equal volumes of all gases at the same temperature and pressure should contain equal number of molecules.* Avogadro made a distinction between **atoms** and **molecules** which is quite understandable in present times. If we consider again the reaction of hydrogen and oxygen to produce water, we see that two volumes of hydrogen combine with one volume of oxygen to give two volumes of water without leaving any unreacted oxygen.

Note that in the Fig. 1.9 (Page 16) each box contains equal number of molecules. In fact, Avogadro could explain the above result by considering the molecules to be **polyatomic.** If hydrogen and oxygen were considered as **diatomic** as recognised now, then the above results are easily understandable. However, Dalton and others believed at that time that atoms of the


Lorenzo Romano Amedeo Carlo Avogadro di Quareqa edi Carreto (1776–1856)

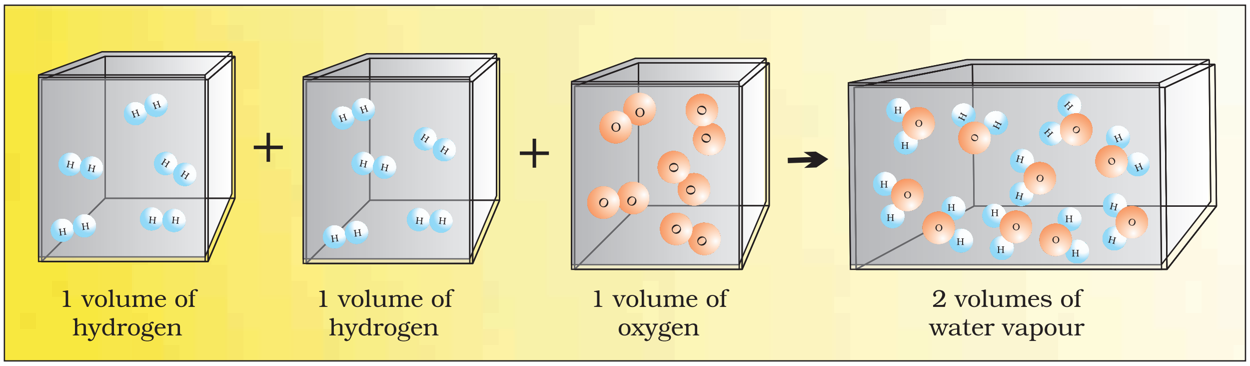


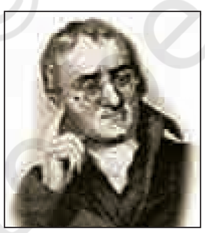
Fig. 1.9 *Two volumes of hydrogen react with one volume of oxygen to give two volumes of water vapour*

same kind cannot combine and molecules of oxygen or hydrogen containing two atoms did not exist. Avogadro's proposal was published in the French *Journal de Physique*. In spite of being correct, it did not gain much support.

After about 50 years, in 1860, the first international conference on chemistry was held in Karlsruhe, Germany, to resolve various ideas. At the meeting, Stanislao Cannizaro presented a sketch of a course of chemical philosophy, which emphasised on the importance of Avogadro's work.

1.6 DALTON'S ATOMIC THEORY

Although the origin of the idea that matter is composed of small indivisible particles called *'a-tomio'* (meaning, *indivisible*), dates back to the time of Democritus, a Greek Philosopher (460–370 BC), it again started emerging as a result of several experimental studies which led to the laws mentioned above.



John Dalton (1776–1884)

In 1808, Dalton published 'A New System of Chemical Philosophy', in which he proposed the following :

1. Matter consists of indivisible atoms.
2. All atoms of a given element have identical properties, including identical mass. Atoms of different elements differ in mass.
3. Compounds are formed when atoms of different elements combine in a fixed ratio.
4. Chemical reactions involve reorganisation of atoms. These are neither created nor destroyed in a chemical reaction.

Dalton's theory could explain the laws of chemical combination. However, it could not explain the laws of gaseous volumes. It could not provide the reason for combining of atoms, which was answered later by other scientists.

1.7 ATOMIC AND MOLECULAR MASSES

After having some idea about the terms atoms and molecules, it is appropriate here to understand what do we mean by atomic and molecular masses.

1.7.1 Atomic Mass

The atomic mass or the mass of an atom is actually very-very small because atoms are extremely small. Today, we have sophisticated techniques e.g., mass spectrometry for determining the atomic masses fairly accurately. But in the nineteenth century, scientists could determine the mass of one atom **relative** to another by experimental means, as has been mentioned earlier. Hydrogen, being the lightest atom was arbitrarily assigned a mass of 1 (without any units) and other elements were assigned masses relative to it. However, the present system of atomic masses is based on carbon-12 as the standard and has been agreed upon in 1961. Here, Carbon-12 is one of the **isotopes** of carbon and can be represented as ^{12}C. In this system, ^{12}C is assigned a mass of exactly 12 atomic mass unit (**amu**) and masses of all other atoms are given relative to this standard. One **atomic mass unit** is defined as a mass exactly equal to one-twelfth of the mass of one carbon - 12 atom.

And 1 amu = 1.66056×10^{-24} g

Mass of an atom of hydrogen

$= 1.6736 \times 10^{-24}$ g

Thus, in terms of amu, the mass

$$\text{of hydrogen atom} = \frac{1.6736 \times 10^{-24}\,\text{g}}{1.66056 \times 10^{-24}\,\text{g}}$$

$= 1.0078$ amu

$= 1.0080$ amu

Similarly, the mass of oxygen - 16 (^{16}O) atom would be 15.995 amu.

At present, **'amu'** has been replaced by **'u'**, which is known as **unified mass**.

When we use atomic masses of elements in calculations, we actually use *average atomic masses* of elements, which are explained below.

1.7.2 Average Atomic Mass

Many naturally occurring elements exist as more than one isotope. When we take into account the existence of these isotopes and their relative abundance (per cent occurrence), the average atomic mass of that element can be computed. For example, carbon has the following three isotopes with relative abundances and masses as shown against

Isotope	Relative Abundance (%)	Atomic Mass (amu)
^{12}C	98.892	12
^{13}C	1.108	13.00335
^{14}C	2×10^{-10}	14.00317

each of them.

From the above data, the average atomic mass of carbon will come out to be:

$(0.98892)\ (12\ u) + (0.01108)\ (13.00335\ u) + (2 \times 10^{-12})\ (14.00317\ u) = 12.011\ u$

Similarly, average atomic masses for other elements can be calculated. In the periodic table of elements, the atomic masses mentioned for different elements actually represent their average atomic masses.

1.7.3 Molecular Mass

Molecular mass is the sum of atomic masses of the elements present in a molecule. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together. For example, molecular mass of methane, which contains one carbon atom and four hydrogen atoms, can be obtained as follows:

Molecular mass of methane,

$(CH_4) = (12.011\ u) + 4\ (1.008\ u)$

$= 16.043\ u$

Similarly, molecular mass of water (H_2O)

$= 2 \times$ atomic mass of hydrogen $+ 1 \times$ atomic mass of oxygen

$= 2\ (1.008\ u) + 16.00\ u$

$= 18.02\ u$

1.7.4 Formula Mass

Some substances, such as sodium chloride, do not contain discrete molecules as their constituent units. In such compounds, positive (sodium ion) and negative (chloride ion) entities are arranged in a three-dimensional structure, as shown in Fig. 1.10.

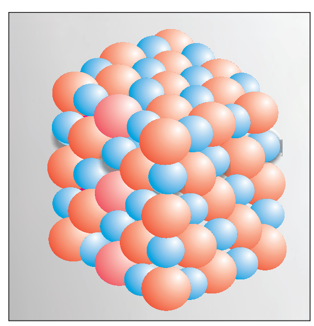


Fig. 1.10 *Packing of Na^+ and Cl^- ions in sodium chloride*

It may be noted that in sodium chloride, one Na^+ ion is surrounded by six Cl^- ion and *vice-versa*.

The formula, such as NaCl, is used to calculate the **formula mass** instead of molecular mass as in the solid state sodium chloride does not exist as a single entity.

Thus, the formula mass of sodium chloride is atomic mass of sodium + atomic mass of chlorine

= 23.0 u + 35.5 u = 58.5 u

Problem 1.1

Calculate the molecular mass of glucose ($C_6H_{12}O_6$) molecule.

Solution

Molecular mass of glucose ($C_6H_{12}O_6$)

= 6(12.011 u) + 12(1.008 u) + 6(16.00 u)

= (72.066 u) + (12.096 u) + (96.00 u)

= 180.162 u

1.8 MOLE CONCEPT AND MOLAR MASSES

Atoms and molecules are extremely small in size and their numbers in even a small amount of any substance is really very large. To handle such large numbers, a unit of convenient magnitude is required.

Just as we denote one dozen for 12 items, score for 20 items, gross for 144 items, we use the idea of mole to count entities at the microscopic level (i.e., atoms, molecules, particles, electrons, ions, etc).

In SI system, **mole** (symbol, mol) was introduced as seventh base quantity for the amount of a substance.

One mole is the amount of a substance that contains as many particles or entities as there are atoms in exactly 12 g (or 0.012 kg) of the ^{12}C isotope. It may be emphasised that the mole of a substance always contains the same number of entities, no matter what the substance may be. In order to determine this number precisely, the mass of a carbon–12 atom was determined by a mass spectrometer and found to be equal to 1.992648×10^{-23} g. Knowing that one mole of carbon weighs 12 g, the number of atoms in it is equal to:

$$\frac{12\,\text{g/mol}\ ^{12}\text{C}}{1.992648 \times 10^{-23}\,\text{g}/^{12}\text{C atom}}$$

$$= 6.0221367 \times 10^{23}\ \text{atoms/mol}$$

This number of entities in 1 mol is so important that it is given a separate name and symbol. It is known as **'Avogadro constant'**, or Avogadro number denoted by N_A in honour of Amedeo Avogadro. To appreciate the largeness of this number, let us write it with all zeroes without using any powers of ten.

602213670000000000000000

Hence, so many entities (atoms, molecules or any other particle) constitute one mole of a particular substance.

We can, therefore, say that 1 mol of hydrogen atoms = 6.022×10^{23} atoms

1 mol of water molecules = 6.022×10^{23} water molecules

1 mol of sodium chloride = 6.022×10^{23} formula units of sodium chloride

Having defined the mole, it is easier to know the mass of one mole of a substance or the constituent entities. **The mass of one mole of a substance in grams is called its molar mass.** The molar mass in grams is numerically equal to atomic/molecular/ formula mass in u.

Molar mass of water = 18.02 g mol^{-1}

Molar mass of sodium chloride = 58.5 g mol^{-1}

1.9 PERCENTAGE COMPOSITION

So far, we were dealing with the number of entities present in a given sample. But many a time, information regarding the percentage of a particular element present in a compound is required. Suppose, an unknown or new compound is given to you, the first question

Fig. 1.11 One mole of various substances

you would ask is: what is its formula or what are its constituents and in what ratio are they present in the given compound? For known compounds also, such information provides a check whether the given sample contains the same percentage of elements as present in a pure sample. In other words, one can check the purity of a given sample by analysing this data.

Let us understand it by taking the example of water (H_2O). Since water contains hydrogen and oxygen, the percentage composition of both these elements can be calculated as follows:

Mass % of an element =

$$\frac{\text{mass of that element in the compound} \times 100}{\text{molar mass of the compound}}$$

Molar mass of water = 18.02 g

$$\text{Mass \% of hydrogen} = \frac{2\times1.008}{18.02}\times100$$
$$= 11.18$$

$$\text{Mass \% of oxygen} = \frac{16.00}{18.02}\times100$$
$$= 88.79$$

Let us take one more example. What is the percentage of carbon, hydrogen and oxygen in ethanol?

Molecular formula of ethanol is: C_2H_5OH

Molar mass of ethanol is:

(2×12.01 + 6×1.008 + 16.00) g = 46.068 g

Mass per cent of carbon

$$= \frac{24.02\,\text{g}}{46.068\,\text{g}}\times100 = 52.14\%$$

Mass per cent of hydrogen

$$= \frac{6.048\,\text{g}}{46.068\,\text{g}}\times100 = 13.13\%$$

Mass per cent of oxygen

$$= \frac{16.00\,\text{g}}{46.068\,\text{g}}\times100 = 34.73\%$$

After understanding the calculation of per cent of mass, let us now see what information can be obtained from the per cent composition data.

1.9.1 Empirical Formula for Molecular Formula

An **empirical formula** represents the simplest whole number ratio of various atoms present in a compound, whereas, the **molecular formula** shows the exact number of different types of atoms present in a molecule of a compound.

If the mass per cent of various elements present in a compound is known, its empirical formula can be determined. Molecular formula can further be obtained if the molar mass is known. The following example illustrates this sequence.

Problem 1.2

A compound contains 4.07% hydrogen, 24.27% carbon and 71.65% chlorine. Its molar mass is 98.96 g. What are its empirical and molecular formulas?

Solution

Step 1. Conversion of mass per cent to grams

Since we are having mass per cent, it is convenient to use 100 g of the compound as the starting material. Thus, in the 100 g sample of the above compound, 4.07g hydrogen, 24.27g carbon and 71.65g chlorine are present.

Step 2. Convert into number moles of each element

Divide the masses obtained above by respective atomic masses of various elements. This gives the number of moles of constituent elements in the compound

$$\text{Moles of hydrogen} = \frac{4.07\,\text{g}}{1.008\,\text{g}} = 4.04$$

$$\text{Moles of carbon} = \frac{24.27\,\text{g}}{12.01\,\text{g}} = 2.021$$

$$\text{Moles of chlorine} = \frac{71.65\,\text{g}}{35.453\,\text{g}} = 2.021$$

Step 3. Divide each of the mole values obtained above by the smallest number amongst them

Since 2.021 is smallest value, division by it gives a ratio of 2:1:1 for H:C:Cl .

In case the ratios are not whole numbers, then they may be converted into whole number by multiplying by the suitable coefficient.

Step 4. Write down the empirical formula by mentioning the numbers after writing the symbols of respective elements

CH_2Cl is, thus, the empirical formula of the above compound.

Step 5. Writing molecular formula

(a) Determine empirical formula mass by adding the atomic masses of various atoms present in the empirical formula.

For CH_2Cl, empirical formula mass is

$12.01 + (2 \times 1.008) + 35.453$

$= 49.48$ g

(b) Divide Molar mass by empirical formula mass

$$\frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{98.96\,\text{g}}{49.48\,\text{g}}$$

$$= 2 = (n)$$

(c) Multiply empirical formula by n obtained above to get the molecular formula

Empirical formula = CH_2Cl, $n = 2$. Hence molecular formula is $C_2H_4Cl_2$.

1.10 STOICHIOMETRY AND STOICHIOMETRIC CALCULATIONS

The word 'stoichiometry' is derived from two Greek words — *stoicheion* (meaning, *element*) and *metron* (meaning, *measure*). Stoichiometry, thus, deals with the calculation of masses (sometimes volumes also) of the reactants and the products involved in a chemical reaction. Before understanding how to calculate the amounts of reactants required or the products produced in a chemical reaction, let us study what information is available from the **balanced** chemical equation of a given reaction. Let us consider the combustion of methane. A balanced equation for this reaction is as given below:

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

Here, methane and dioxygen are called *reactants* and carbon dioxide and water are called *products*. Note that all the reactants and the products are gases in the above reaction and this has been indicated by letter (g) in the brackets next to its formula. Similarly, in case of solids and liquids, (s) and (l) are written respectively.

The coefficients 2 for O_2 and H_2O are called stoichiometric coefficients. Similarly the coefficient for CH_4 and CO_2 is one in each case. They represent the number of molecules (and moles as well) taking part in the reaction or formed in the reaction.

Thus, according to the above chemical reaction,

- One **mole** of CH_4(g) reacts with two **moles** of O_2(g) to give one **mole** of CO_2(g) and two **moles** of H_2O(g)
- One **molecule** of CH_4(g) reacts with 2 **molecules** of O_2(g) to give one **molecule** of CO_2(g) and 2 molecules of H_2O(g)
- 22.7 L of CH_4(g) reacts with 45.4 L of O_2 (g) to give 22.7 L of CO_2 (g) and 45.4 L of H_2O(g)
- 16 g of CH_4 (g) reacts with 2×32 g of O_2 (g) to give 44 g of CO_2 (g) and 2×18 g of H_2O (g).

From these relationships, the given data can be interconverted as follows:

mass $\leftrightharpoons$ moles $\leftrightharpoons$ no. of molecules

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

1.10.1 Limiting Reagent

Many a time, reactions are carried out with the amounts of reactants that are different than the amounts as required by a balanced chemical reaction. In such situations, one reactant is in more amount than the amount required by balanced chemical reaction. The reactant which is present in the least amount gets consumed after sometime and after that further reaction does not take place whatever be the amount of the other reactant. Hence, the reactant, which gets consumed first, limits the amount of product formed and is, therefore, called the **limiting reagent**.

In performing stoichiometric calculations, this aspect is also to be kept in mind.

1.10.2 Reactions in Solutions

A majority of reactions in the laboratories are carried out in solutions. Therefore, it is important to understand as how the amount of substance is expressed when it is present in the solution. The concentration of a solution or the amount of substance present in its given volume can be expressed in any of the following ways.

1. Mass per cent or weight per cent (w/w %)
2. Mole fraction
3. Molarity
4. Molality

Let us now study each one of them in detail.

Balancing a chemical equation

According to the law of conservation of mass, a balanced chemical equation has the *same number of atoms of each element on both sides* of the equation. Many chemical equations can be balanced by *trial and error*. Let us take the reactions of a few metals and non-metals with oxygen to give oxides

$4\,Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ (a) balanced equation

$2\,Mg(s) + O_2(g) \rightarrow 2MgO(s)$ (b) balanced equation

$P_4(s) + O_2(g) \rightarrow P_4O_{10}(s)$ (c) unbalanced equation

Equations (a) and (b) are balanced, since there are same number of metal and oxygen atoms on each side of the equations. However equation (c) is not balanced. In this equation, phosphorus atoms are balanced but not the oxygen atoms. To balance it, we must place the coefficient 5 on the left of oxygen on the left side of the equation to balance the oxygen atoms appearing on the right side of the equation.

$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$ balanced equation

Now, let us take combustion of propane, C_3H_8. This equation can be balanced in steps.

Step 1 Write down the correct formulas of reactants and products. Here, propane and oxygen are reactants, and carbon dioxide and water are products.

$C_3H_8(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$ unbalanced equation

Step 2 *Balance the number of C atoms:* Since 3 carbon atoms are in the reactant, therefore, three CO_2 molecules are required on the right side.

$C_3H_8(g) + O_2(g) \rightarrow 3CO_2(g) + H_2O(l)$

Step 3 *Balance the number of H atoms*: on the left there are 8 hydrogen atoms in the reactants however, each molecule of water has two hydrogen atoms, so four molecules of water will be required for eight hydrogen atoms on the right side.

$C_3H_8(g) + O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

Step 4 *Balance the number of O atoms*: There are 10 oxygen atoms on the right side ($3 \times 2 = 6$ in CO_2 and $4 \times 1 = 4$ in water). Therefore, five O_2 molecules are needed to supply the required 10 CO_2 and $4 \times 1 = 4$ in water). Therefore, five O_2 molecules are needed to supply the required 10 oxygen atoms.

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

Step 5 *Verify that the number of atoms of each element is balanced in the final equation.* The equation shows three carbon atoms, eight hydrogen atoms, and 10 oxygen atoms on each side.

All equations that have correct formulas for all reactants and products can be balanced. Always remember that subscripts in formulas of reactants and products cannot be changed to balance an equation.

Problem 1.3

Calculate the amount of water (g) produced by the combustion of 16 g of methane.

Solution

The balanced equation for the combustion of methane is :

$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g)$

(i) 16 g of CH_4 corresponds to one mole.

(ii) From the above equation, 1 mol of CH_4 (g) gives 2 mol of H_2O (g).

2 mol of water (H_2O) = 2 × (2+16)
= 2 × 18 = 36 g

$$1 \text{ mol } H_2O = 18 \text{ g } H_2O \Rightarrow \frac{18 \text{ g } H_2O}{1 \text{ mol } H_2O} = 1$$

$$\text{Hence, } 2 \text{ mol } H_2O \times \frac{18 \text{ g } H_2O}{1 \text{ mol } H_2O}$$

$$= 2 \times 18 \text{ g } H_2O = 36 \text{ g } H_2O$$

Problem 1.4

How many moles of methane are required to produce 22g CO_2 (g) after combustion?

Solution

According to the chemical equation,

$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g)$

44g CO_2 (g) is obtained from 16 g CH_4 (g).

[∴ 1 mol CO_2(g) is obtained from 1 mol of CH_4(g)]

Number of moles of CO_2 (g)

$$= 22 \text{ g } CO_2\,(g) \times \frac{1 \text{ mol } CO_2\,(g)}{44 \text{ g } CO_2\,(g)}$$

= 0.5 mol CO_2 (g)

Hence, 0.5 mol CO_2 (g) would be obtained from 0.5 mol CH_4 (g) or 0.5 mol of CH_4 (g) would be required to produce 22 g CO_2 (g).

Problem 1.5

50.0 kg of N_2 (g) and 10.0 kg of H_2 (g) are mixed to produce NH_3 (g). Calculate the amount of NH_3 (g) formed. Identify the limiting reagent in the production of NH_3 in this situation.

Solution

A balanced equation for the above reaction is written as follows :

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$

Calculation of moles :

Number of moles of N_2

$$= 50.0 \text{ kg } N_2 \times \frac{1000 \text{ g } N_2}{1 \text{ kg } N_2} \times \frac{1 \text{ mol } N_2}{28.0 \text{ g } N_2}$$

= 17.86×10^2 mol

Number of moles of H_2

$$= 10.00 \text{ kg } H_2 \times \frac{1000 \text{ g } H_2}{1 \text{ kg } H_2} \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2}$$

= 4.96×10^3 mol

According to the above equation, 1 mol N_2 (g) requires 3 mol H_2 (g), for the reaction. Hence, for 17.86×10^2 mol of N_2, the moles of H_2 (g) required would be

$$17.86 \times 10^2 \text{ mol } N_2 \times \frac{3 \text{ mol } H_2\,(g)}{1 \text{ mol } N_2\,(g)}$$

= 5.36×10^3 mol H_2

But we have only 4.96×10^3 mol H_2. Hence, dihydrogen is the limiting reagent in this case. So, NH_3(g) would be formed only from that amount of available dihydrogen *i.e.*, 4.96×10^3 mol

Since 3 mol H_2(g) gives 2 mol NH_3(g)

$$4.96 \times 10^3 \text{ mol } H_2\,(g) \times \frac{2 \text{ mol } NH_3\,(g)}{3 \text{ mol } H_2\,(g)}$$

= 3.30×10^3 mol NH_3 (g)

3.30×10^3 mol NH_3 (g) is obtained.

If they are to be converted to grams, it is done as follows :

1 mol NH_3 (g) = 17.0 g NH_3 (g)

$$3.30 \times 10^3 \text{ mol } NH_3\,(g) \times \frac{17.0 \text{ g } NH_3\,(g)}{1 \text{ mol } NH_3\,(g)}$$

$= 3.30\times10^3\times17$ g NH_3 (g)
$= 56.1\times10^3$ g NH_3
$= 56.1$ kg NH_3

1. Mass per cent

It is obtained by using the following relation:

$$\text{Mass per cent} = \frac{\text{Mass of solute}}{\text{Mass of solution}}\times100$$

Problem 1.6

A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass per cent of the solute.

Solution

$$\text{Mass per cent of A} = \frac{\text{Mass of A}}{\text{Mass of solution}}\times100$$

$$=\frac{2\text{ g}}{2\text{ g of A}+18\text{ g of water}}\times100$$

$$=\frac{2\text{ g}}{20\text{ g}}\times100$$

$=10\%$

2. Mole Fraction

It is the ratio of number of moles of a particular component to the total number of moles of the solution. If a substance 'A' dissolves in substance 'B' and their number of moles are n_A and n_B, respectively, then the mole fractions of A and B are given as:

Mole fraction of A

$$=\frac{\text{No. of moles of A}}{\text{No. of moles of solutions}}$$

$$=\frac{n_A}{n_A+n_B}$$

Mole fraction of B

$$=\frac{\text{No. of moles of B}}{\text{No. of moles of solutions}}$$

$$=\frac{n_B}{n_A+n_B}$$

3. Molarity

It is the most widely used unit and is denoted by M. It is defined as the number of moles of the solute in 1 litre of the solution. Thus,

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}}$$

Suppose, we have 1 M solution of a substance, say NaOH, and we want to prepare a 0.2 M solution from it.

1 M NaOH means 1 mol of NaOH present in 1 litre of the solution. For 0.2 M solution, we require 0.2 moles of NaOH dissolved in 1 litre solution.

Hence, for making 0.2M solution from 1M solution, we have to take that volume of 1M NaOH solution, which contains 0.2 mol of NaOH and dilute the solution with water to 1 litre.

Now, how much volume of concentrated (1M) NaOH solution be taken, which contains 0.2 moles of NaOH can be calculated as follows:

If 1 mol is present in 1L or 1000 mL solution

then, 0.2 mol is present in

$$\frac{1000\text{ mL}}{1\text{ mol}}\times0.2\text{ mol solution}$$

$= 200$ mL solution

Thus, 200 mL of 1M NaOH are taken and enough water is added to dilute it to make it 1 litre.

In fact for such calculations, a general formula, $M_1 \times V_1 = M_2 \times V_2$ where M and V are molarity and volume, respectively, can be used. In this case, M_1 is equal to 0.2M; $V_1 = 1000$ mL and, $M_2 = 1.0$M; V_2 is to be calculated. Substituting the values in the formula:

$0.2 \text{ M} \times 1000 \text{ mL} = 1.0 \text{ M} \times V_2$

$$\therefore V_2=\frac{0.2\text{ M}\times1000\text{ mL}}{1.0\text{ M}}=200\text{ L}$$

Note that the **number of moles of solute** (NaOH) was 0.2 in 200 mL and *it has remained the same*, i.e., 0.2 even after dilution (in 1000 mL) as we have changed just the amount of solvent (i.e., water) and have not done anything with respect to NaOH. But keep in mind the concentration.

Problem 1.7

Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution.

Solution

Since molarity (M)

$$= \frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{\text{Mass of NaOH / Molar mass of NaOH}}{0.250\,\text{L}}$$

$$= \frac{4\,\text{g} / 40\,\text{g}}{0.250\,\text{L}} = \frac{0.1\,\text{mol}}{0.250\,\text{L}}$$

$$= 0.4\,\text{mol}^{-1}$$

$$= 0.4\,\text{M}$$

Note that molarity of a solution depends upon temperature because volume of a solution is temperature dependent.

4. Molality

It is defined as the number of moles of solute present in 1 kg of solvent. It is denoted by m.

$$\text{Thus, Molality (m)} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$

Problem 1.8

The density of 3 M solution of NaCl is 1.25 g mL^{-1}. Calculate the molality of the solution.

Solution

M = 3 mol L^{-1}

Mass of NaCl
in 1 L solution = 3 × 58.5 = 175.5 g

Mass of
1L solution = 1000 × 1.25 = 1250 g
(since density = 1.25 g mL^{-1})
Mass of water in solution = 1250 –75.5
= 1074.5 g

$$\text{Molality} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$

$$= \frac{3\ \text{mol}}{1.0745\,\text{kg}} = 2.79\ \text{m}$$

Often in a chemistry laboratory, a solution of a desired concentration is prepared by diluting a solution of known higher concentration. The solution of higher concentration is also known as stock solution. Note that the molality of a solution does not change with temperature since mass remains unaffected with temperature.

SUMMARY

Chemistry, as we understand it today is not a very old discipline. People in ancient India, already had the knowledge of many scientific phenomenon much before the advent of modern science. They applied the knowledge in various walks of life.

The study of chemistry is very important as its domain encompasses every sphere of life. Chemists study the properties and structure of substances and the changes undergone by them. All substances contain matter, which can exist in three states – solid, liquid or gas. The constituent particles are held in different ways in these states of matter and they exhibit their characteristic properties. Matter can also be classified into elements, compounds or mixtures. An **element** contains particles of only one type, which may be **atoms** or **molecules**. The compounds are formed where atoms of two or more elements combine in a fixed ratio to each other. Mixtures occur widely and many of the substances present around us are mixtures.

When the properties of a substance are studied, measurement is inherent. The quantification of properties requires a system of measurement and units in which the quantities are to be expressed. Many systems of measurement exist, of which

the English and the Metric Systems are widely used. The scientific community, however, has agreed to have a uniform and common system throughout the world, which is abbreviated as SI units (International System of Units).

Since measurements involve recording of data, which are always associated with a certain amount of uncertainty, the proper handling of data obtained by measuring the quantities is very important. The measurements of quantities in chemistry are spread over a wide range of 10^{-31} to 10^{+23}. Hence, a convenient system of expressing the numbers in **scientific notation** is used. The uncertainty is taken care of by specifying the number of **significant figures,** in which the observations are reported. The **dimensional analysis** helps to express the measured quantities in different systems of units. Hence, it is possible to interconvert the results from one system of units to another.

The combination of different atoms is governed by basic laws of chemical combination — these being the **Law of Conservation of Mass, Law of Definite Proportions, Law of Multiple Proportions, Gay Lussac's Law of Gaseous Volumes** and **Avogadro Law**. All these laws led to the **Dalton's atomic theory,** which states that atoms are building blocks of matter. The **atomic mass** of an element is expressed relative to ^{12}C isotope of carbon, which has an exact value of 12u. Usually, the atomic mass used for an element is the **average atomic mass** obtained by taking into account the natural abundance of different isotopes of that element. The **molecular mass** of a molecule is obtained by taking sum of the atomic masses of different atoms present in a molecule. The **molecular formula** can be calculated by determining the mass per cent of different elements present in a compound and its molecular mass.

The number of atoms, molecules or any other particles present in a given system are expressed in the terms of **Avogadro constant** (6.022×10^{23}). This is known as **1 mol** of the respective particles or entities.

Chemical reactions represent the chemical changes undergone by different elements and compounds. A **balanced** chemical equation provides a lot of information. The coefficients indicate the molar ratios and the respective number of particles taking part in a particular reaction. The quantitative study of the reactants required or the products formed is called **stoichiometry**. Using stoichiometric calculations, the amount of one or more reactant(s) required to produce a particular amount of product can be determined and vice-versa. The amount of substance present in a given volume of a solution is expressed in number of ways, e.g., mass per cent, mole fraction, molarity and molality.

EXERCISES

1.1 Calculate the molar mass of the following:
(i) H_2O (ii) CO_2 (iii) CH_4

1.2 Calculate the mass per cent of different elements present in sodium sulphate (Na_2SO_4).

1.3 Determine the empirical formula of an oxide of iron, which has 69.9% iron and 30.1% dioxygen by mass.

1.4 Calculate the amount of carbon dioxide that could be produced when
(i) 1 mole of carbon is burnt in air.
(ii) 1 mole of carbon is burnt in 16 g of dioxygen.
(iii) 2 moles of carbon are burnt in 16 g of dioxygen.

1.5 Calculate the mass of sodium acetate (CH_3COONa) required to make 500 mL of 0.375 molar aqueous solution. Molar mass of sodium acetate is 82.0245 g mol^{-1}.

1.6 Calculate the concentration of nitric acid in moles per litre in a sample which has a density, 1.41 g mL^{-1} and the mass per cent of nitric acid in it being 69%.

1.7 How much copper can be obtained from 100 g of copper sulphate ($CuSO_4$)?

1.8 Determine the molecular formula of an oxide of iron, in which the mass per cent of iron and oxygen are 69.9 and 30.1, respectively.

1.9 Calculate the atomic mass (average) of chlorine using the following data:

	% Natural Abundance	Molar Mass
^{35}Cl	75.77	34.9689
^{37}Cl	24.23	36.9659

1.10 In three moles of ethane (C_2H_6), calculate the following:

(i) Number of moles of carbon atoms.

(ii) Number of moles of hydrogen atoms.

(iii) Number of molecules of ethane.

1.11 What is the concentration of sugar ($C_{12}H_{22}O_{11}$) in mol L^{-1} if its 20 g are dissolved in enough water to make a final volume up to 2L?

1.12 If the density of methanol is 0.793 kg L^{-1}, what is its volume needed for making 2.5 L of its 0.25 M solution?

1.13 Pressure is determined as force per unit area of the surface. The SI unit of pressure, pascal is as shown below:
1Pa = 1N m^{-2}
If mass of air at sea level is 1034 g cm^{-2}, calculate the pressure in pascal.

1.14 What is the SI unit of mass? How is it defined?

1.15 Match the following prefixes with their multiples:

	Prefixes	Multiples
(i)	micro	10^6
(ii)	deca	10^9
(iii)	mega	10^{-6}
(iv)	giga	10^{-15}
(v)	femto	10

1.16 What do you mean by significant figures?

1.17 A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$, supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass).

(i) Express this in per cent by mass.

(ii) Determine the molality of chloroform in the water sample.

1.18 Express the following in the scientific notation:

(i) 0.0048

(ii) 234,000

(iii) 8008

(iv) 500.0

(v) 6.0012

1.19 How many significant figures are present in the following?

(i) 0.0025

(ii) 208

(iii) 5005

(iv) 126,000
(v) 500.0
(vi) 2.0034

1.20 Round up the following upto three significant figures:
(i) 34.216
(ii) 10.4107
(iii) 0.04597
(iv) 2808

1.21 The following data are obtained when dinitrogen and dioxygen react together to form different compounds:

	Mass of dinitrogen	**Mass of dioxygen**
(i)	14 g	16 g
(ii)	14 g	32 g
(iii)	28 g	32 g
(iv)	28 g	80 g

(a) Which law of chemical combination is obeyed by the above experimental data? Give its statement.

(b) Fill in the blanks in the following conversions:
(i) 1 km = ... mm = ... pm
(ii) 1 mg = ... kg = ... ng
(iii) 1 mL = ... L = ... dm^3

1.22 If the speed of light is 3.0×10^8 m s^{-1}, calculate the distance covered by light in 2.00 ns.

1.23 In a reaction

$A + B_2 \rightarrow AB_2$

Identify the limiting reagent, if any, in the following reaction mixtures.
(i) 300 atoms of A + 200 molecules of B
(ii) 2 mol A + 3 mol B
(iii) 100 atoms of A + 100 molecules of B
(iv) 5 mol A + 2.5 mol B
(v) 2.5 mol A + 5 mol B

1.24 Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation:

$N_2 (g) + H_2 (g) \rightarrow 2NH_3 (g)$

(i) Calculate the mass of ammonia produced if 2.00×10^3 g dinitrogen reacts with 1.00×10^3 g of dihydrogen.
(ii) Will any of the two reactants remain unreacted?
(iii) If yes, which one and what would be its mass?

1.25 How are 0.50 mol Na_2CO_3 and 0.50 M Na_2CO_3 different?

1.26 If 10 volumes of dihydrogen gas reacts with five volumes of dioxygen gas, how many volumes of water vapour would be produced?

1.27 Convert the following into basic units:
(i) 28.7 pm
(ii) 15.15 pm
(iii) 25365 mg

1.28 Which one of the following will have the largest number of atoms?

(i) 1 g Au (s)

(ii) 1 g Na (s)

(iii) 1 g Li (s)

(iv) 1 g of Cl_2(g)

1.29 Calculate the molarity of a solution of ethanol in water, in which the mole fraction of ethanol is 0.040 (assume the density of water to be one).

1.30 What will be the mass of one ^{12}C atom in g?

1.31 How many significant figures should be present in the answer of the following calculations?

(i) $\dfrac{0.02856 \times 298.15 \times 0.112}{0.5785}$ (ii) 5×5.364

(iii) $0.0125 + 0.7864 + 0.0215$

1.32 Use the data given in the following table to calculate the molar mass of naturally occuring *argon* isotopes:

Isotope	**Isotopic molar mass**	**Abundance**
^{36}Ar	35.96755 g mol^{-1}	0.337%
^{38}Ar	37.96272 g mol^{-1}	0.063%
^{40}Ar	39.9624 g mol^{-1}	99.600%

1.33 Calculate the number of atoms in each of the following (i) 52 moles of Ar (ii) 52 u of He (iii) 52 g of He.

1.34 A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula, (ii) molar mass of the gas, and (iii) molecular formula.

1.35 Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction, $CaCO_3$ (s) + 2 HCl (aq) $\rightarrow$ $CaCl_2$ (aq) + CO_2(g) + H_2O(l)
What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M HCl?

1.36 Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction
4 HCl (aq) + MnO_2(s) $\rightarrow$ $2H_2O$ (l) + $MnCl_2$(aq) + Cl_2 (g)
How many grams of HCl react with 5.0 g of manganese dioxide?

UNIT 2

STRUCTURE OF ATOM

Objectives

After studying this unit you will be able to

- know about the discovery of electron, proton and neutron and their characteristics;
- describe Thomson, Rutherford and Bohr atomic models;
- understand the important features of the quantum mechanical model of atom;
- understand nature of electromagnetic radiation and Planck's quantum theory;
- explain the photoelectric effect and describe features of atomic spectra;
- state the de Broglie relation and Heisenberg uncertainty principle;
- define an atomic orbital in terms of quantum numbers;
- state aufbau principle, Pauli exclusion principle and Hund's rule of maximum multiplicity; and
- write the electronic configurations of atoms.

"The rich diversity of chemical behaviour of different elements can be traced to the differences in the internal structure of atoms of these elements."

The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter. According to them, the continued subdivisions of matter would ultimately yield atoms which would not be further divisible. The word 'atom' has been derived from the Greek word '*a-tomio*' which means 'uncut-able' or 'non-divisible'. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century.

The atomic theory of matter was first proposed on a firm scientific basis by John Dalton, a British school teacher in 1808. His theory, called **Dalton's atomic theory**, regarded the atom as the ultimate particle of matter (Unit 1). Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failed to explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur get electrically charged.

In this unit we start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms are made of sub-atomic particles, i.e., electrons, protons and neutrons — a concept very different from that of Dalton.

2.1 DISCOVERY OF SUB-ATOMIC PARTICLES

An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Before we discuss these results we need to keep in mind a basic rule regarding the behaviour of charged particles : “Like charges repel each other and unlike charges attract each other”.

2.1.1 Discovery of Electron

In 1830, Michael Faraday showed that if electricity is passed through a solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes. He formulated certain laws which you will study in class XII. These results suggested the particulate nature of electricity.

In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as **cathode ray discharge tubes**. It is depicted in Fig. 2.1. A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. The pressure of different gases could be adjusted by evacuation of the glass tubes. When sufficiently high voltage is applied across the electrodes, current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These were called **cathode rays or cathode ray particles**. The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot is developed on the coating [Fig. 2.1(b)].

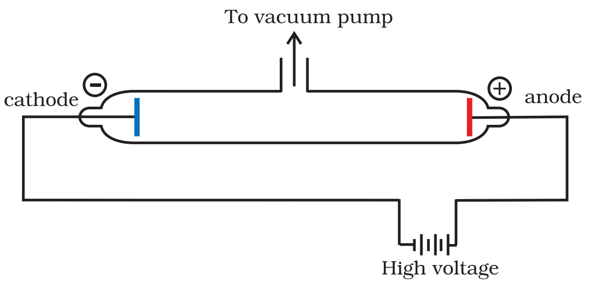


Fig. 2.1(a) *A cathode ray discharge tube*

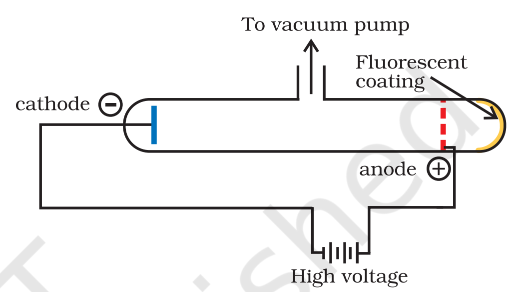


Fig. 2.1(b) *A cathode ray discharge tube with perforated anode*

The results of these experiments are summarised below.

(i) The cathode rays start from cathode and move towards the anode.

(ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.

(iii) In the absence of electrical or magnetic field, these rays travel in straight lines (Fig. 2.2).

(iv) In the presence of electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called **electrons.**

(v) The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube.

Thus, we can conclude that electrons are basic constituent of all the atoms.

2.1.2 Charge to Mass Ratio of Electron

In 1897, British physicist J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (m_e) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons (Fig. 2.2). When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A (Fig. 2.2). Similarly when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path which is followed in the absence of electric or magnetic field and they hit the screen at point B. Thomson argued that the amount of deviation of the particles from their path in the presence of electrical or magnetic field depends upon:

(i) the magnitude of the negative charge on the particle, greater the magnitude of the charge on the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection.

(ii) the mass of the particle — lighter the particle, greater the deflection.

(iii) the strength of the electrical or magnetic field — the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field.

By carrying out accurate measurements on the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson was able to determine the value of e/m_e as:

$$\frac{e}{m_e} = 1.758820 \times 10^{11}\ \mathrm{C\ kg^{-1}} \qquad (2.1)$$

Where m_e is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C). Since electrons are negatively charged, the charge on electron is $-e$.

2.1.3 Charge on the Electron

R.A. Millikan (1868-1953) devised a method known as oil drop experiment (1906-14), to determine the charge on the electrons. He found the charge on the electron to be -1.6×10^{-19} C. The present accepted value of electrical charge is $-1.602176 \times 10^{-19}$ C. The mass of the electron (m_e) was determined by combining these results with Thomson's value of e/m_e ratio.

$$m_e = \frac{e}{e/m_e} = \frac{1.602176 \times 10^{-19}\ \mathrm{C}}{1.758820 \times 10^{11}\ \mathrm{C\ kg^{-1}}}$$

$$= 9.1094 \times 10^{-31}\ \mathrm{kg} \qquad (2.2)$$

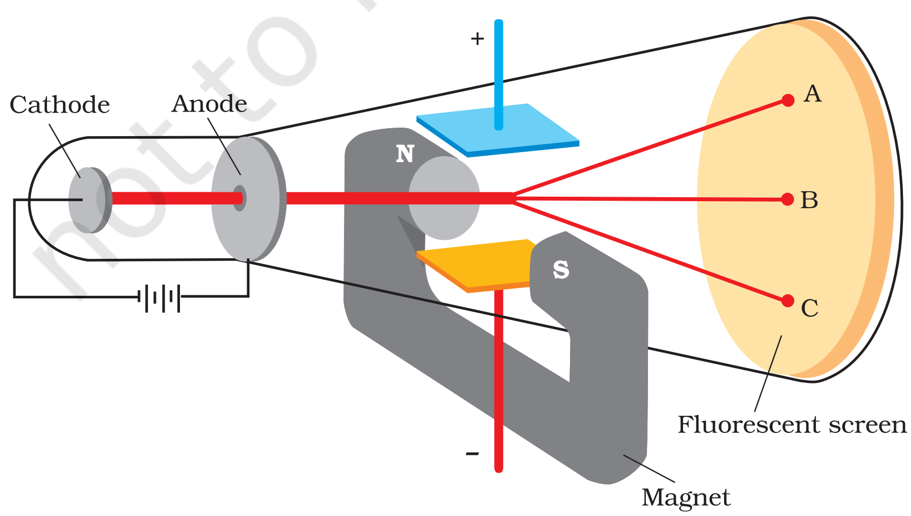


Fig. 2.2 *The apparatus to determine the charge to the mass ratio of electron*

2.1.4 Discovery of Protons and Neutrons

Electrical discharge carried out in the modified cathode ray tube led to the discovery of **canal rays** carrying positively charged particles. The characteristics of these positively charged particles are listed below.

(i) Unlike cathode rays, mass of positively charged particles depends upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.

(ii) The charge to mass ratio of the particles depends on the gas from which these originate.

(iii) Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.

(iv) The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

The smallest and lightest positive ion was obtained from hydrogen and was called **proton**. This positively charged particle was characterised in 1919. Later, a need was felt for the presence of electrically neutral particle as one of the constituent of atom. These particles were discovered by Chadwick (1932) by bombarding a thin sheet of beryllium by α-particles. When electrically neutral particles having a mass slightly greater than that of protons were emitted. He named these particles as **neutrons**. The important properties of all these fundamental particles are given in Table 2.1.

2.2 ATOMIC MODELS

Observations obtained from the experiments mentioned in the previous sections have suggested that Dalton's indivisible atom is composed of sub-atomic particles carrying positive and negative charges. The major problems before the scientists after the discovery of sub-atomic particles were:

- to account for the stability of atom,
- to compare the behaviour of elements in terms of both physical and chemical properties,
- to explain the formation of different kinds of molecules by the combination of different atoms and,
- to understand the origin and nature of the characteristics of electromagnetic radiation absorbed or emitted by atoms.

Millikan's Oil Drop Method

In this method, oil droplets in the form of mist, produced by the atomiser, were allowed to enter through a tiny hole in the upper plate of electrical condenser. The downward motion of these droplets was viewed through the telescope, equipped with a micrometer eye piece. By measuring the rate of fall of these droplets, Millikan was able to measure the mass of oil droplets. The air inside the chamber was ionized by passing a beam of X-rays through it. The electrical charge on these oil droplets was acquired by collisions with gaseous ions. The fall of these charged oil droplets can be retarded, accelerated or made stationary depending upon the charge on the droplets and the polarity and strength of the voltage applied to the plate. By carefully measuring the effects of electrical field strength on the motion of oil droplets, Millikan concluded that the magnitude of electrical charge, q, on the droplets is always an integral multiple of the electrical charge, e, that is, $q = n$ e, where n = 1, 2, 3... .

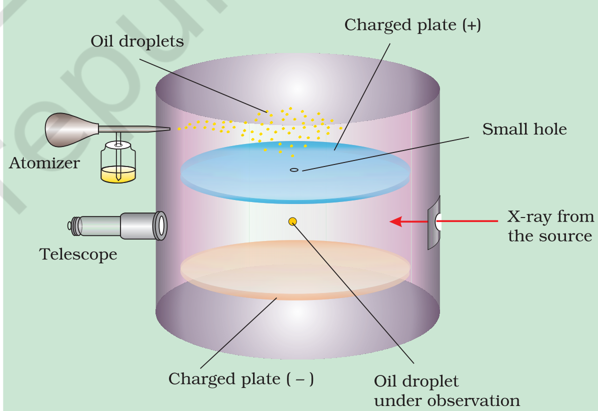


Fig. 2.3 *The Millikan oil drop apparatus for measuring charge 'e'. In chamber, the forces acting on oil drop are: gravitational, electrostatic due to electrical field and a viscous drag force when the oil drop is moving.*

Table 2.1 Properties of Fundamental Particles

Name	Symbol	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx. mass/u
Electron	e	-1.602176×10^{-19}	-1	9.109382×10^{-31}	0.00054	0
Proton	p	$+1.602176\times10^{-19}$	$+1$	1.6726216×10^{-27}	1.00727	1
Neutron	n	0	0	1.674927×10^{-27}	1.00867	1

Different atomic models were proposed to explain the distributions of these charged particles in an atom. Although some of these models were not able to explain the stability of atoms, two of these models, one proposed by J.J. Thomson and the other proposed by Ernest Rutherford are discussed below.

2.2.1 Thomson Model of Atom

J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10^{-10} m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement (Fig. 2.4). Many different names are given to this model, for example, **plum pudding, raisin pudding or watermelon.** This model can be

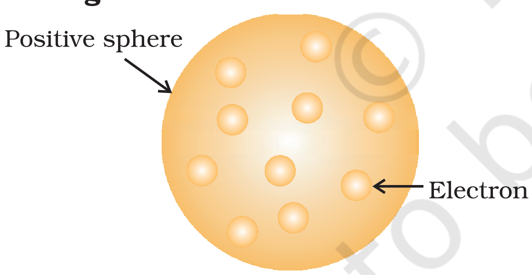


Fig.2.4 *Thomson model of atom*

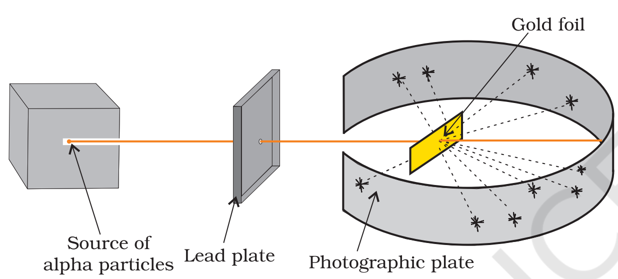
visualised as a pudding or watermelon of positive charge with plums or seeds (electrons) embedded into it. *An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom.* Although this model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments. Thomson was awarded Nobel Prize for physics in 1906, for his theoretical and experimental investigations on the conduction of electricity by gases.

In the later half of the nineteenth century different kinds of rays were discovered, besides those mentioned earlier. Wilhalm Röentgen (1845-1923) in 1895 showed that when electrons strike a material in the cathode ray tubes, produce rays which can cause fluorescence in the fluorescent materials placed outside the cathode ray tubes. Since Röentgen did not know the nature of the radiation, he named them X-rays and the name is still carried on. It was noticed that X-rays are produced effectively when electrons strike the dense metal anode, called targets. These are not deflected by the electric and magnetic fields and have a very high penetrating power through the matter and that is the reason that these rays are used to study the interior of the objects. These rays are of very short wavelengths (~0.1 nm) and possess electro-magnetic character (Section 2.3.1).

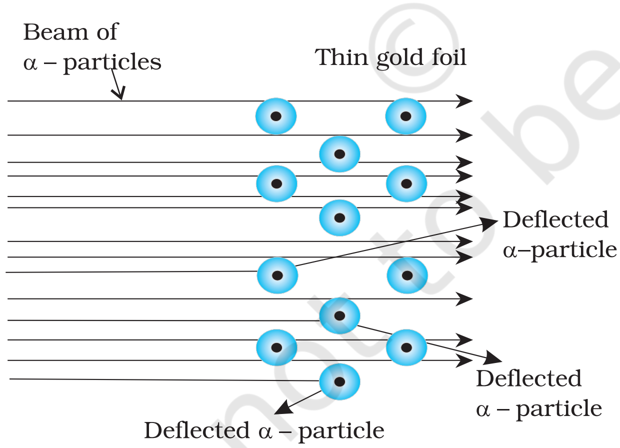
Henri Becqueral (1852-1908) observed that there are certain elements which emit radiation on their own and named this phenomenon as **radioactivity** and the elements known as **radioactive elements.** This field was developed by Marie Curie, Piere Curie, Rutherford and Fredrick Soddy. It was observed that three kinds of rays i.e., α, β- and γ-rays are emitted. Rutherford found that α-rays consists of high energy particles carrying two units of positive charge and four unit of atomic mass. He concluded that α- particles are helium nuclei as when α- particles combined with two electrons yielded helium gas. β-rays are negatively charged particles similar to electrons. The γ-rays are high energy radiations like X-rays, are neutral in nature and do not consist of particles. As regards penetrating power, α-particles are the least, followed by β-rays (100 times that of α–particles) and γ-rays (1000 times of that α-particles).

2.2.2 Rutherford's Nuclear Model of Atom

Rutherford and his students (Hans Geiger and Ernest Marsden) bombarded very thin gold foil with α–particles. Rutherford's famous **α–particle scattering experiment** is



***A.** Rutherford's scattering experiment*



***B.** Schematic molecular view of the gold foil*

***Fig. 2.5** Schematic view of Rutherford's scattering experiment. When a beam of alpha (α) particles is "shot" at a thin gold foil, most of them pass through without much effect. Some, however, are deflected.*

represented in Fig. 2.5. A stream of high energy α–particles from a radioactive source was directed at a thin foil (thickness ~ 100 nm) of gold metal. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever α–particles struck the screen, a tiny flash of light was produced at that point.

The results of scattering experiment were quite unexpected. According to Thomson model of atom, the mass of each gold atom in the foil should have been spread evenly over the entire atom, and α– particles had enough energy to pass directly through such a uniform distribution of mass. It was expected that the particles would slow down and change directions only by a small angles as they passed through the foil. It was observed that:

(i) most of the α–particles passed through the gold foil undeflected.

(ii) a small fraction of the α–particles was deflected by small angles.

(iii) a very few α–particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180°.

On the basis of the observations, Rutherford drew the following conclusions regarding the structure of atom:

(i) Most of the space in the atom is empty as most of the α–particles passed through the foil undeflected.

(ii) A few positively charged α–particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α–particles.

(iii) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m. One can appreciate this difference in size by realising that if a cricket ball represents a nucleus, then the radius of atom would be about 5 km.

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom. According to this model:

(i) The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called **nucleus** by Rutherford.

(ii) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called **orbits**. Thus, Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets.

(iii) Electrons and the nucleus are held together by electrostatic forces of attraction.

2.2.3 Atomic Number and Mass Number

The presence of positive charge on the nucleus is due to the protons in the nucleus. As established earlier, the charge on the proton is equal but opposite to that of electron. The number of protons present in the nucleus is equal to atomic number (Z). For example, the number of protons in the hydrogen nucleus is 1, in sodium atom it is 11, therefore their atomic numbers are 1 and 11 respectively. In order to keep the electrical neutrality, the number of electrons in an atom is equal to the number of protons (atomic number, Z). For example, number of electrons in hydrogen atom and sodium atom are 1 and 11 respectively.

Atomic number (Z) = number of protons in the nucleus of an atom

= number of electrons in a nuetral atom (2.3)

While the positive charge of the nucleus is due to protons, the mass of the nucleus, due to protons and neutrons. As discussed earlier protons and neutrons present in the nucleus are collectively known as **nucleons**. The total number of nucleons is termed as **mass number (A)** of the atom.

mass number (A) = number of protons (Z) + number of neutrons (n) (2.4)

2.2.4 Isobars and Isotopes

The composition of any atom can be represented by using the normal element symbol (X) with super-script on the left hand side as the atomic mass number (A) and subscript (Z) on the left hand side as the atomic number (i.e., ${}^{A}_{Z}X$).

Isobars are the atoms with same mass number but different atomic number for example, ${}^{14}_{6}C$ and ${}^{14}_{7}N$. On the other hand, atoms with identical atomic number but different atomic mass number are known as **Isotopes**. In other words (according to equation 2.4), it is evident that difference between the isotopes is due to the presence of different number of neutrons present in the nucleus. For example, considering of hydrogen atom again, 99.985% of hydrogen atoms contain only one proton. This isotope is called **protium (${}^{1}_{1}H$)**. Rest of the percentage of hydrogen atom contains two other isotopes, the one containing 1 proton and 1 neutron is called **deuterium** (${}^{2}_{1}D$, 0.015%) and the other one possessing 1 proton and 2 neutrons is called **tritium** (${}^{3}_{1}T$). The latter isotope is found in trace amounts on the earth. Other examples of commonly occuring isotopes are: carbon atoms containing 6, 7 and 8 neutrons besides 6 protons (${}^{12}_{6}C$, ${}^{13}_{6}C$, ${}^{14}_{6}C$); chlorine atoms containing 18 and 20 neutrons besides 17 protons (${}^{35}_{17}Cl$, ${}^{37}_{17}Cl$).

Lastly an important point to mention regarding isotopes is that *chemical properties of atoms are controlled by the number of electrons, which are determined by the number of protons in the nucleus.* Number of neutrons present in the nucleus have very little effect on the chemical properties of an element. Therefore, all the isotopes of a given element show same chemical behaviour.

Problem 2.1

Calculate the number of protons, neutrons and electrons in $^{80}_{35}\mathrm{Br}$.

Solution

In this case, $^{80}_{35}\mathrm{Br}$, Z = 35, A = 80, species is neutral

Number of protons = number of electrons = Z = 35

Number of neutrons = 80 – 35 = 45, (equation 2.4)

Problem 2.2

The number of electrons, protons and neutrons in a species are equal to 18, 16 and 16 respectively. Assign the proper symbol to the species.

Solution

The atomic number is equal to number of protons = 16. The element is sulphur (S).

Atomic mass number = number of protons + number of neutrons

= 16 + 16 = 32

Species is not neutral as the number of protons is not equal to electrons. It is anion (negatively charged) with charge equal to excess electrons = 18 – 16 = 2. Symbol is $^{32}_{16}\mathrm{S}^{2-}$.

Note : Before using the notation $^{A}_{Z}\mathrm{X}$, find out whether the species is a neutral atom, a cation or an anion. If it is a neutral atom, equation (2.3) is valid, i.e., number of protons = number of electrons = atomic number. If the species is an ion, determine whether the number of protons are larger (cation, positive ion) or smaller (anion, negative ion) than the number of electrons. Number of neutrons is always given by A–Z, whether the species is neutral or ion.

2.2.5 Drawbacks of Rutherford Model

As you have learnt above, Rutherford nuclear model of an atom is like a small scale solar system with the nucleus playing the role of the massive sun and the electrons being similar to the lighter planets. When classical mechanics* is applied to the solar system, it shows that the planets describe well-defined orbits around the sun. The gravitational force between the planets is given by the expression $\left(\mathrm{G}.\dfrac{m_1m_2}{r^2}\right)$ where m_1 and m_2 are the masses, r is the distance of separation of the masses and G is the gravitational constant. The theory can also calculate precisely the planetary orbits and these are in agreement with the experimental measurements.

The similarity between the solar system and nuclear model suggests that electrons should move around the nucleus in well defined orbits. Further, the coulomb force ($\mathrm{k}q_1q_2/r^2$ where q_1 and q_2 are the charges, r is the distance of separation of the charges and k is the proportionality constant) between electron and the nucleus is mathematically similar to the gravitational force. However, when a body is moving in an orbit, it undergoes acceleration even if it is moving with a constant speed in an orbit because of changing direction. So an electron in the nuclear model describing planet like orbits is under acceleration. According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (This feature does not exist for planets since they are uncharged). Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink. Calculations show that it should take an electron only 10^{-8} s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom. If the motion of an electron is described on the basis of the classical mechanics and electromagnetic theory, you may ask that since the motion of electrons in orbits is leading to the instability of the atom, then why not consider electrons as stationary

* *Classical mechanics is a theoretical science based on Newton's laws of motion. It specifies the laws of motion of macroscopic objects.*

around the nucleus. If the electrons were stationary, electrostatic attraction between the dense nucleus and the electrons would pull the electrons toward the nucleus to form a miniature version of Thomson's model of atom.

Another serious drawback of the Rutherford model is that it says nothing about distribution of the electrons around the nucleus and the energies of these electrons.

2.3 DEVELOPMENTS LEADING TO THE BOHR'S MODEL OF ATOM

Historically, results observed from the studies of interactions of radiations with matter have provided immense information regarding the structure of atoms and molecules. Neils Bohr utilised these results to improve upon the model proposed by Rutherford. Two developments played a major role in the formulation of Bohr's model of atom. These were:

(i) Dual character of the electromagnetic radiation which means that radiations possess both wave like and particle like properties, and

(ii) Experimental results regarding atomic spectra.

First, we will discuss about the duel nature of electromagnetic radiations. Experimental results regarding atomic spectra will be discussed in Section 2.4.

2.3.1 Wave Nature of Electromagnetic Radiation

In the mid-nineteenth century, physicists actively studied absorption and emission of radiation by heated objects. These are called thermal radiations. They tried to find out of what the thermal radiation is made. It is now a well-known fact that thermal radiations consist of electromagnetic waves of various frequencies or wavelengths. It is based on a number of modern concepts, which were unknown in the mid-nineteenth century. First active study of thermal radiation laws occured in the 1850's and the theory of electromagnetic waves and the emission of such waves by accelerating charged particles was developed in the early 1870's by James Clerk Maxwell, which was experimentally confirmed later by Heinrich Hertz. Here, we will learn some facts about electromagnetic radiations.

James Maxwell (1870) was the first to give a comprehensive explanation about the interaction between the charged bodies and the behaviour of electrical and magnetic fields on macroscopic level. He suggested that when electrically charged particle moves under accelaration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called **electromagnetic waves** or **electromagnetic radiation**.

Light is the form of radiation known from early days and speculation about its nature dates back to remote ancient times. In earlier days (Newton) light was supposed to be made of particles (corpuscules). It was only in the 19th century when wave nature of light was established.

Maxwell was again the first to reveal that light waves are associated with oscillating electric and magnetic character (Fig. 2.6).

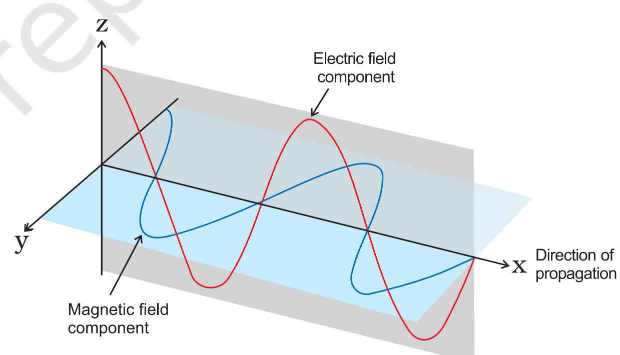


Fig.2.6 *The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.*

Although electromagnetic wave motion is complex in nature, we will consider here only a few simple properties.

(i) The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave. Simplified picture of electromagnetic wave is shown in Fig. 2.6.

(ii) Unlike sound waves or waves produced in water, electromagnetic waves do not require medium and can move in vacuum.

(iii) It is now well established that there are many types of electromagnetic radiations, which differ from one another in wavelength (or frequency). These constitute what is called **electromagnetic spectrum** (Fig. 2.7). Different regions of the spectrum are identified by different names. Some examples are: radio frequency region around 10^6 Hz, used for broadcasting; microwave region around 10^{10} Hz used for radar; infrared region around 10^{13} Hz used for heating; ultraviolet region around 10^{16}Hz a component of sun's radiation. The small portion around 10^{15} Hz, is what is ordinarily called **visible light**. It is only this part which our eyes can see (or detect). Special instruments are required to detect non-visible radiation.

(iv) Different kinds of units are used to represent electromagnetic radiation.

These radiations are characterised by the properties, namely, frequency (ν) and wavelength (λ).

The SI unit for frequency (ν) is hertz (Hz, s^{-1}), after Heinrich Hertz. It is defined as the number of waves that pass a given point in one second.

Wavelength should have the units of length and as you know that the SI units of length is meter (m). Since electromagnetic radiation consists of different kinds of waves of much smaller wavelengths, smaller units are used. Fig.2.7 shows various types of electromagnetic radiations which differ from one another in wavelengths and frequencies.

In vaccum all types of electromagnetic radiations, regardless of wavelength, travel at the same speed, i.e., 3.0×10^8 m s^{-1} (2.997925 $\times 10^8$ m s^{-1}, to be precise). This is called **speed of light** and is given the symbol 'c'. The frequency (ν), wavelength (λ) and velocity of light (c) are related by the equation (2.5).

$$c = \nu \lambda \tag{2.5}$$

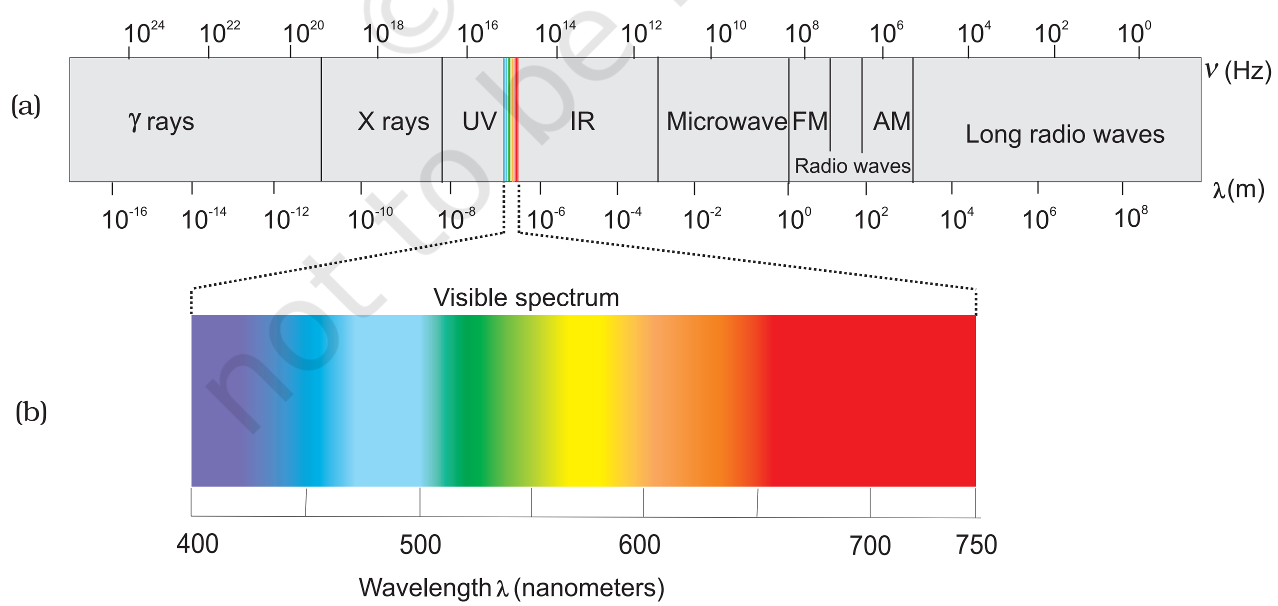


Fig. 2.7 *(a) The spectrum of electromagnetic radiation. (b) Visible spectrum. The visible region is only a small part of the entire spectrum.*

The other commonly used quantity specially in spectroscopy, is the **wavenumber** ($\bar{\nu}$). *It is defined as the number of wavelengths per unit length.* Its units are reciprocal of wavelength unit, i.e., m^{-1}. However commonly used unit is cm^{-1} (not SI unit).

Problem 2.3

The Vividh Bharati station of All India Radio, Delhi, broadcasts on a frequency of 1,368 kHz (kilo hertz). Calculate the wavelength of the electromagnetic radiation emitted by transmitter. Which part of the electromagnetic spectrum does it belong to?

Solution

The wavelength, λ, is equal to c/ν, where c is the speed of electromagnetic radiation in vacuum and ν is the frequency. Substituting the given values, we have

$$\lambda = \frac{c}{\nu}$$

$$= \frac{3.00 \times 10^8 \, m\, s^{-1}}{1368 \text{ kHz}}$$

$$= \frac{3.00 \times 10^8 \, m\, s^{-1}}{1368 \times 10^3 \, s^{-1}}$$

$$= 219.3 \, m$$

This is a characteristic radiowave wavelength.

Problem 2.4

The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz). (1nm = 10^{-9} m)

Solution

Using equation 2.5, frequency of violet light

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \, m\, s^{-1}}{400 \times 10^{-9} \, m}$$

$$= 7.50 \times 10^{14} \, Hz$$

Frequency of red light

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \, m\, s^{-1}}{750 \times 10^{-9} \, m} = 4.00 \times 10^{14} \, Hz$$

The range of visible spectrum is from 4.0×10^{14} to 7.5×10^{14} Hz in terms of frequency units.

Problem 2.5

Calculate (a) wavenumber and (b) frequency of yellow radiation having wavelength 5800 Å.

Solution

(a) Calculation of wavenumber ($\bar{\nu}$)

λ=5800Å = 5800×10^{-8} cm
= 5800×10^{-10} m

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{5800 \times 10^{-10} \, m}$$

$$= 1.724 \times 10^6 \, m^{-1}$$

$$= 1.724 \times 10^4 \, cm^{-1}$$

(b) Calculation of the frequency (ν)

$$\bar{\nu} = \frac{c}{\lambda} = \frac{3 \times 10^8 \, m\, s^{-1}}{5800 \times 10^{-10} \, m} = 5.172 \times 10^{14} \, s^{-1}$$

2.3.2 Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

Some of the experimental phenomenon such as diffraction* and interference** can be explained by the wave nature of the electromagnetic radiation. However, following are some of the observations which could not be explained with the help of even the electromagentic theory of 19th century physics (known as classical physics):

(i) the nature of emission of radiation from hot bodies (black -body radiation)

(ii) ejection of electrons from metal surface when radiation strikes it (photoelectric effect)

(iii) variation of heat capacity of solids as a function of temperature

* *Diffraction is the bending of wave around an obstacle.*

** *Interference is the combination of two waves of the same or different frequencies to give a wave whose distribution at each point in space is the algebraic or vector sum of disturbances at that point resulting from each interfering wave.*

(iv) Line spectra of atoms with special reference to hydrogen.

These phenomena indicate that the system can take energy only in discrete amounts. All possible energies cannot be taken up or radiated.

It is noteworthy that the first concrete explanation for the phenomenon of the black body radiation mentioned above was given by Max Planck in 1900. Let us first try to understand this phenomenon, which is given below:

Hot objects emit electromagnetic radiations over a wide range of wavelengths. At high temperatures, an appreciable proportion of radiation is in the visible region of the spectrum. As the temperature is raised, a higher proportion of short wavelength (blue light) is generated. For example, when an iron rod is heated in a furnace, it first turns to dull red and then progressively becomes more and more red as the temperature increases. As this is heated further, the radiation emitted becomes white and then becomes blue as the temperature becomes very high. This means that red radiation is most intense at a particular temperature and the blue radiation is more intense at another temperature. This means intensities of radiations of different wavelengths emitted by hot body depend upon its temperature. By late 1850's it was known that objects made of different material and kept at different temperatures emit different amount of radiation. Also, when the surface of an object is irradiated with light (electromagnetic radiation), a part of radiant energy is generally reflected as such, a part is absorbed and a part of it is transmitted. The reason for incomplete absorption is that ordinary objects are as a rule imperfect absorbers of radiation. *An ideal body, which emits and absorbs radiations of all frequencies uniformly, is called a black body and the radiation emitted by such a body is called black body radiation.* In practice, no such body exists. Carbon black approximates fairly closely to black body. A good physical approximation to a black body is a cavity with a tiny hole, which has no other opening. Any ray entering the hole will be reflected by the cavity walls and will be eventually absorbed by the walls. A black body is also a perfect radiator of radiant energy. Furthermore, a black body is in thermal equilibrium with its surroundings. It radiates same amount of energy per unit area as it absorbs from its surrounding in any given time. The amount of light emitted (intensity of radiation) from a black body and its spectral distribution depends only on its temperature. At a given temperature, intensity of radiation emitted increases with the increase of wavelength, reaches a maximum value at a given wavelength and then starts decreasing with further increase of wavelength, as shown in Fig. 2.8. Also, as the temperature increases, maxima of the curve shifts to short wavelength. Several attempts were made to predict the intensity of radiation as a function of wavelength.

But the results of the above experiment could not be explained satisfactorily on the basis of the wave theory of light. Max Planck

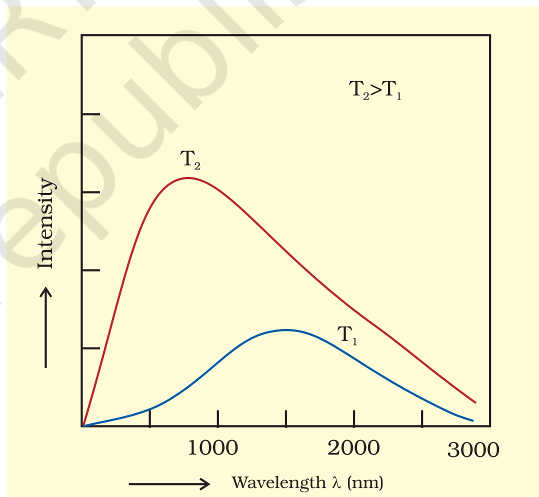


Fig. 2.8 *Wavelength-intensity relationship*

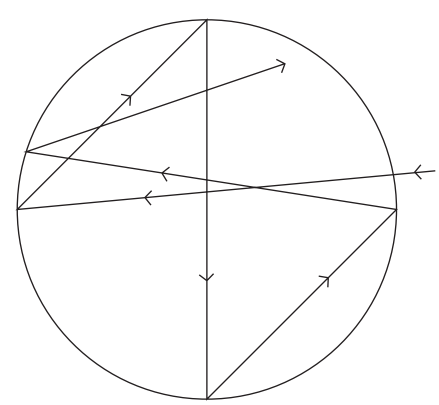


Fig. 2.8(a) *Black body*

arrived at a satisfactory relationship by making an assumption that absorption and emmission of radiation arises from oscillator i.e., atoms in the wall of black body. Their frequency of oscillation is changed by interaction with oscilators of electromagnetic radiation. Planck assumed that radiation could be sub-divided into discrete chunks of energy. He suggested that atoms and molecules could emit or absorb energy only in discrete quantities and not in a continuous manner. He gave the name **quantum** to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation. The energy (E) of a quantum of radiation is proportional to its frequency (ν) and is expressed by equation (2.6).

$$E = h\nu \tag{2.6}$$

The proportionality constant, 'h' is known as Planck's constant and has the value 6.626×10^{-34} J s.

With this theory, Planck was able to explain the distribution of intensity in the radiation from black body as a function of frequency or wavelength at different temperatures.

Quantisation has been compared to standing on a staircase. A person can stand on any step of a staircase, but it is not possible for him/her to stand in between the two steps. The energy can take any one of the values from the following set, but cannot take on any values between them.

E = 0, $h\nu$, $2h\nu$, $3h\nu$....$nh\nu$.....

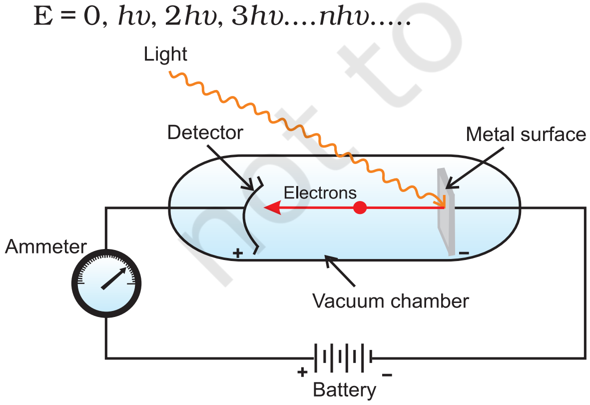


Fig.2.9 *Equipment for studying the photoelectric effect. Light of a particular frequency strikes a clean metal surface inside a vacuum chamber. Electrons are ejected from the metal and are counted by a detector that measures their kinetic energy.*

Max Planck
(1858 – 1947)
Max Planck, a German physicist, received his Ph.D in theoretical physics from the University of Munich in 1879. In 1888, he was appointed Director of the Institute of Theoretical Physics at the University of Berlin. Planck was awarded the Nobel Prize in Physics in 1918 for his quantum theory. Planck also made significant contributions in thermodynamics and other areas of physics.

Photoelectric Effect

In 1887, H. Hertz performed a very interesting experiment in which electrons (or electric current) were ejected when certain metals (for example potassium, rubidium, caesium etc.) were exposed to a beam of light as shown in Fig.2.9. The phenomenon is called **Photoelectric effect**. The results observed in this experiment were:

(i) The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.

(ii) The number of electrons ejected is proportional to the intensity or brightness of light.

(iii) For each metal, there is a characteristic minimum frequency, ν_0 (also known as **threshold frequency**) below which photoelectric effect is not observed. At a frequency $\nu>\nu_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.

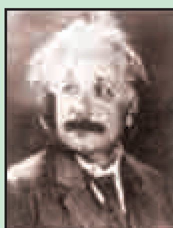
All the above results could not be explained on the basis of laws of classical physics. According to latter, the energy content of the beam of light depends upon the brightness of the light. In other words, number of electrons ejected and kinetic energy associated with them should depend on the brightness of light. It has been observed that though the number of electrons ejected does depend upon the brightness of light, the kinetic energy of the

Table 2.2 Values of Work Function (W_0) for a Few Metals

Metal	Li	Na	K	Mg	Cu	Ag
W_0 /eV	2.42	2.3	2.25	3.7	4.8	4.3

ejected electrons does not. For example, red light [ν = (4.3 to 4.6) × 10^{14} Hz] of any brightness (intensity) may shine on a piece of potassium metal for hours but no photoelectrons are ejected. But, as soon as even a very weak yellow light (ν = 5.1–5.2 × 10^{14} Hz) shines on the potassium metal, the photoelectric effect is observed. The threshold frequency (ν_0) for potassium metal is 5.0×10^{14} Hz.

Einstein (1905) was able to explain the photoelectric effect using Planck's quantum theory of electromagnetic radiation as a starting point.



Albert Einstein (1879-1955)

Albert Einstein, a German born American physicist, is regarded by many as one of the two great physicists the world has known (the other is Isaac Newton). His three research papers (on special relativity, Brownian motion and the photoelectric effect) which he published in 1905, while he was employed as a technical assistant in a Swiss patent office in Berne have profoundly influenced the development of physics. He received the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.

Shining a beam of light on to a metal surface can, therefore, be viewed as shooting a beam of particles, the photons. When a photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision and the electron is ejected without any time lag or delay. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected electron. In other words, kinetic energy of the ejected electron is proportional to the frequency of the electromagnetic radiation. Since the striking photon has energy equal to $h\nu$ and the minimum energy required to eject the electron is $h\nu_0$ (also called work function, W_0; Table 2.2), then the difference in energy ($h\nu - h\nu_0$) is transferred as the kinetic energy of the photoelectron. Following the conservation of energy principle, the kinetic energy of the ejected electron is given by the equation 2.7.

$$h\nu = h\nu_0 + \frac{1}{2} m_e v^2 \qquad (2.7)$$

where m_e is the mass of the electron and v is the velocity associated with the ejected electron. Lastly, a more intense beam of light consists of larger number of photons, consequently the number of electrons ejected is also larger as compared to that in an experiment in which a beam of weaker intensity of light is employed.

Dual Behaviour of Electromagnetic Radiation

The particle nature of light posed a dilemma for scientists. On the one hand, it could explain the black body radiation and photoelectric effect satisfactorily but on the other hand, it was not consistent with the known wave behaviour of light which could account for the phenomena of interference and diffraction. The only way to resolve the dilemma was to accept the idea that light possesses both particle and wave-like properties, i.e., light has dual behaviour. Depending on the experiment, we find that light behaves either as a wave or as a stream of particles. Whenever radiation interacts with matter, it displays particle like properties in contrast to the wavelike properties (interference and diffraction), which it exhibits when it propagates. This concept was totally alien to the way the scientists thought about matter and radiation and it took them a long time to become convinced of its validity. It turns out, as you shall see later, that some microscopic particles like electrons also exhibit this wave-particle duality.

Problem 2.6

Calculate energy of one mole of photons of radiation whose frequency is 5×10^{14} Hz.

Solution

Energy (E) of one photon is given by the expression

$E = h\nu$

$h = 6.626 \times 10^{-34}$ J s

$\nu = 5 \times 10^{14}$ s^{-1} (given)

$E = (6.626 \times 10^{-34}$ J s$) \times (5 \times 10^{14}$ s$^{-1})$

$= 3.313 \times 10^{-19}$ J

Energy of one mole of photons

$= (3.313 \times 10^{-19}$ J$) \times (6.022 \times 10^{23}$ mol$^{-1})$

$= 199.51$ kJ mol^{-1}

Problem 2.7

A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb.

Solution

Power of the bulb = 100 watt

= 100 J s^{-1}

Energy of one photon $E = h\nu = hc/\lambda$

$$= \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^{8} \text{ m s}^{-1}}{400 \times 10^{-9} \text{m}}$$

$= 4.969 \times 10^{-19}$ J

Number of photons emitted

$$\frac{100 \text{ J s}^{-1}}{4.969 \times 10^{-19} \text{J}} = 2.012 \times 10^{20} \text{s}^{-1}$$

Problem 2.8

When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of 1.68×10^{5} J mol^{-1}. What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause a photoelectron to be emitted?

Solution

The energy (E) of a 300 nm photon is given by

$hn = hc / \lambda$

$$= \frac{6.626 \times 10^{-34} \text{ J s} \times 3.0 \times 10^{8} \text{m s}^{-1}}{300 \times 10^{-9} \text{m}}$$

$= 6.626 \times 10^{-19}$ J

The energy of one mole of photons

$= 6.626 \times 10^{-19}$ J $\times 6.022 \times 10^{23}$ mol^{-1}

$= 3.99 \times 10^{5}$ J mol^{-1}

The minimum energy needed to remove one mole of electrons from sodium

$= (3.99 - 1.68)\ 10^{5}$ J mol^{-1}

$= 2.31 \times 10^{5}$ J mol^{-1}

The minimum energy for one electron

$$= \frac{2.31 \times 10^{5} \text{J mol}^{-1}}{6.022 \times 10^{23} \text{ electrons mol}^{-1}}$$

$= 3.84 \times 10^{-19}$ J

This corresponds to the wavelength

$$\therefore \lambda = \frac{hc}{E}$$

$$= \frac{6.626 \times 10^{-34} \text{J s} \times 3.0 \times 10^{8} \text{m s}^{-1}}{3.84 \times 10^{-19} \text{J}}$$

$= 517$ nm

(This corresponds to green light)

Problem 2.9

The threshold frequency ν_0 for a metal is 7.0×10^{14} s^{-1}. Calculate the kinetic energy of an electron emitted when radiation of frequency $\nu = 1.0 \times 10^{15}$ s^{-1} hits the metal.

Solution

According to Einstein's equation

Kinetic energy = ½ $m_e v^2 = h(\nu - \nu_0)$

$= (6.626 \times 10^{-34}$ J s$)\ (1.0 \times 10^{15}$ s$^{-1} - 7.0 \times 10^{14}$ s$^{-1})$

$= (6.626 \times 10^{-34}$ J s$)\ (10.0 \times 10^{14}$ s$^{-1} - 7.0 \times 10^{14}$ s$^{-1})$

$= (6.626 \times 10^{-34}$ J s$) \times (3.0 \times 10^{14}$ s$^{-1})$

$= 1.988 \times 10^{-19}$ J

2.3.3 Evidence for the quantized* Electronic Energy Levels: Atomic spectra

The speed of light depends upon the nature of the medium through which it passes. As a result, the beam of light is deviated or refracted from its original path as it passes from one medium to another. It is observed that when a ray of white light is passed through a prism, the wave with shorter wavelength bends more than the one with a longer wavelength. Since ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of coloured bands called **spectrum**. The light of red colour which has longest wavelength is deviated the least while the violet light, which has shortest wavelength is deviated the most. The spectrum of white light, that we can see, ranges from violet at 7.50×10^{14} Hz to red at 4×10^{14} Hz. Such a spectrum is called **continuous spectrum.** Continuous because violet merges into blue, blue into green and so on. A similar spectrum is produced when a rainbow forms in the sky. Remember that visible light is just a small portion of the electromagnetic radiation (Fig.2.7). When electromagnetic radiation interacts with matter, atoms and molecules may absorb energy and reach to a higher energy state. With higher energy, these are in an unstable state. For returning to their normal (more stable, lower energy states) energy state, the atoms and molecules emit radiations in various regions of the electromagnetic spectrum.

Emission and Absorption Spectra

The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be **"excited"**. To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

An absorption spectrum is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as **spectroscopy**. The spectrum of the visible light, as discussed above, was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called **line spectra** or **atomic spectra** because the emitted radiation is identified by the appearance of bright lines in the spectra (Fig. 2.10 page 45).

Line emission spectra are of great interest in the study of electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as fingerprints are used to identify people. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter, German chemist, Robert Bunsen (1811-1899) was one of the first investigators to use line spectra to identify elements.

Elements like rubidium (Rb), caesium (Cs) thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

Line Spectrum of Hydrogen

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of *discrete frequencies*. The hydrogen spectrum consists of several series of *lines* named after their discoverers. Balmer showed in 1885 on the basis of experimental observations that if

* *The restriction of any property to discrete values is called quantization.*

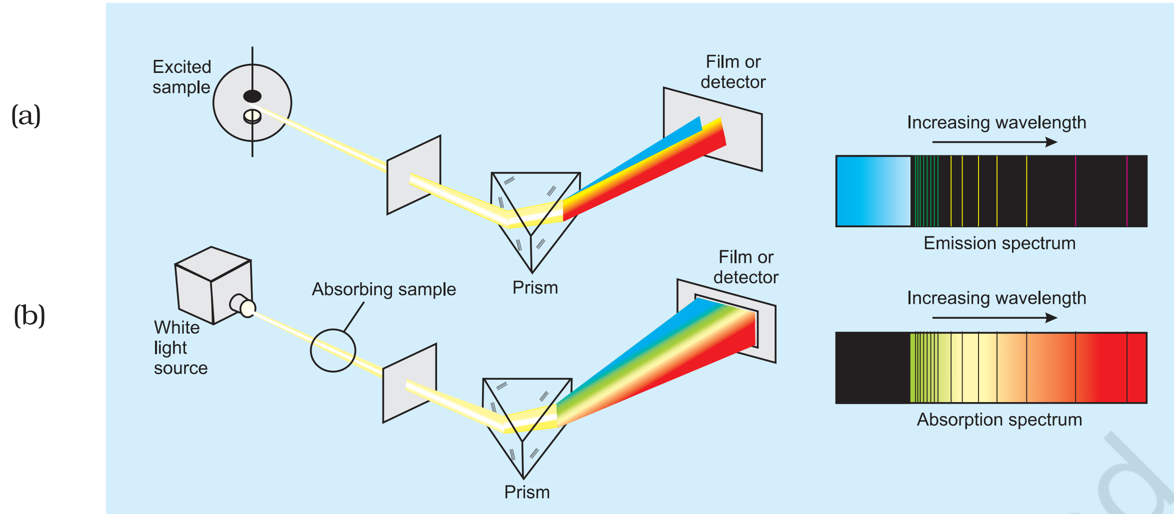


***Fig. 2.10 (a) Atomic emission.** The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus an emission spectrum, which is a photographic recording of the separated wavelengths is called as line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum. **(b) Atomic absorption**. When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a) The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.*

spectral lines are expressed in terms of wavenumber ($\bar{\nu}$), then the visible lines of the hydrogen spectrum obey the following formula:

$$\bar{\nu} = 109{,}677 \left(\frac{1}{2^2} - \frac{1}{n^2}\right) \text{cm}^{-1} \qquad (2.8)$$

where n is an integer equal to or greater than 3 (i.e., $n = 3,4,5,....$)

The series of lines described by this formula are called the **Balmer series**. The Balmer series of lines are the only lines in the hydrogen spectrum which appear in the visible region of the electromagnetic spectrum. The Swedish spectroscopist, Johannes Rydberg, noted that all series of lines in the hydrogen spectrum could be described by the following expression :

$$\bar{\nu} = 109{,}677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{cm}^{-1} \qquad (2.9)$$

where n_1=1,2........

$n_2 = n_1 + 1, n_1 + 2......$

The value 109,677 cm^{-1} is called the **Rydberg constant** for hydrogen. The first five series of lines that correspond to n_1 = 1, 2, 3, 4, 5 are known as Lyman, Balmer, Paschen, Bracket and Pfund series, respectively, Table 2.3 shows these series of transitions in the hydrogen spectrum. Fig 2.11 (page, 46) shows the Lyman, Balmer and Paschen series of transitions for hydrogen atom.

Of all the elements, hydrogen atom has the simplest line spectrum. Line spectrum becomes

Table 2.3 The Spectral Lines for Atomic Hydrogen

Series	n_1	n_2	Spectral Region
Lyman	1	2,3....	Ultraviolet
Balmer	2	3,4....	Visible
Paschen	3	4,5....	Infrared
Brackett	4	5,6....	Infrared
Pfund	5	6,7....	Infrared

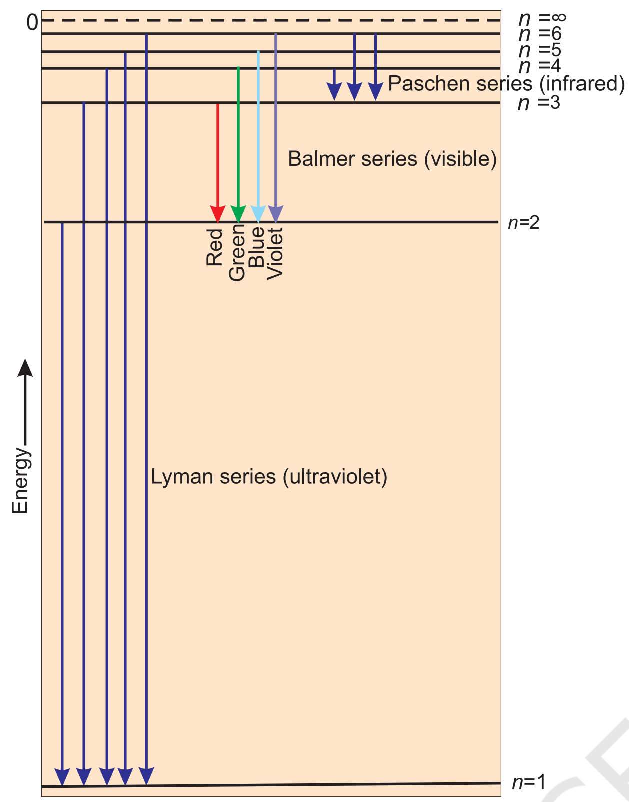


Fig. 2.11 *Transitions of the electron in the hydrogen atom (The diagram shows the Lyman, Balmer and Paschen series of transitions)*

more and more complex for heavier atom. There are, however, certain features which are common to all line spectra, i.e., (i) line spectrum of element is unique and (ii) there is regularity in the line spectrum of each element. The questions which arise are: What are the reasons for these similarities? Is it something to do with the electronic structure of atoms? These are the questions need to be answered. We shall find later that the answers to these questions provide the key in understanding electronic structure of these elements.

2.4 BOHR'S MODEL FOR HYDROGEN ATOM

Neils Bohr (1913) was the first to explain quantitatively the general features of the structure of hydrogen atom and its spectrum. He used Planck's concept of quantisation of energy. Though the theory is not the modern quantum mechanics, it can still be used to rationalize many points in the atomic structure and spectra. Bohr's model for hydrogen atom is based on the following postulates:

i) The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called **orbits**, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.

ii) The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state (equation 2.16). The energy change does not take place in a continuous manner.

Angular Momentum

Just as linear momentum is the product of mass (m) and linear velocity (v), angular momentum is the product of moment of inertia (I) and angular velocity (ω). For an electron of mass m_e, moving in a circular path of radius r around the nucleus,

$$\text{angular momentum} = I \times \omega$$

Since $I = m_e r^2$, and $\omega = \text{v}/r$ where v is the linear velocity,

$$\therefore \text{angular momentum} = m_e r^2 \times \text{v}/r = m_e \text{v} r$$

iii) The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE, is given by:

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} \qquad (2.10)$$

Where E_1 and E_2 are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

iv) The angular momentum of an electron is quantised. In a given stationary state it can be expressed as in equation (2.11)

$$m_e \text{v} r = n.\frac{h}{2\pi} \quad n = 1,2,3..... \qquad (2.11)$$

Where m_e is the mass of electron, v is the velocity and r is the radius of the orbit in which electron is moving.

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$. That means angular momentum is quantised. Radiation is emitted or obsorbed only when transition of electron takes place from one quantised value of angular momentum to another. Therefore, Maxwell's electromagnetic theory does not apply here that is why only certain fixed orbits are allowed.

The details regarding the derivation of energies of the stationary states used by Bohr, are quite complicated and will be discussed in higher classes. However, according to Bohr's theory for hydrogen atom:

a) The stationary states for electron are numbered $n = 1,2,3$.......... These integral numbers (Section 2.6.2) are known as **Principal quantum numbers**.

b) The radii of the stationary states are expressed as:

$$r_n = n^2 a_0 \qquad (2.12)$$

where a_0 = 52.9 pm. Thus the radius of the first stationary state, called the **Bohr orbit**, is 52.9 pm. Normally the electron in the hydrogen atom is found in this orbit (that is n=1). As n increases the value of r will increase. In other words the electron will be present away from the nucleus.

c) The most important property associated with the electron, is the energy of its stationary state. It is given by the expression.

$$E_n = -\mathrm{R}_H\left(\frac{1}{n^2}\right) \qquad n = 1,2,3.... \qquad (2.13)$$

where R_H is called **Rydberg constant** and its value is 2.18×10^{-18} J. The energy of the lowest state, also called as the ground state, is

$E_1 = -2.18\times10^{-18}\ (\frac{1}{1^2}) = -2.18\times10^{-18}$ J. The energy of the stationary state for n = 2, will be : $E_2 = -2.18\times10^{-18}\text{J}\ (\frac{1}{2^2}) = -0.545\times10^{-18}$ J.

Niels Bohr (1885–1962)

Niels Bohr, a Danish physicist received his Ph.D. from the University of Copenhagen in 1911. He then spent a year with J.J. Thomson and Ernest Rutherford in England. In 1913, he returned to Copenhagen where he remained for the rest of his life. In 1920 he was named Director of the Institute of theoretical Physics. After first World War, Bohr worked energetically for peaceful uses of atomic energy. He received the first Atoms for Peace award in 1957. Bohr was awarded the Nobel Prize in Physics in 1922.

Fig. 2.11 depicts the energies of different stationary states or energy levels of hydrogen atom. This representation is called an energy level diagram.

When the electron is free from the influence of nucleus, the energy is taken as zero. The electron in this situation is associated with the stationary state of Principal Quantum number = $n = \infty$ and is called as ionized hydrogen atom. When the electron is attracted by the nucleus and is present in orbit n, the energy is emitted

What does the negative electronic energy (E_n) for hydrogen atom mean?

The energy of the electron in a hydrogen atom has a negative sign for all possible orbits (eq. 2.13). What does this negative sign convey? This negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. A free electron at rest is an electron that is infinitely far away from the nucleus and is assigned the energy value of zero. Mathematically, this corresponds to setting n equal to infinity in the equation (2.13) so that E_∞=0. As the electron gets closer to the nucleus (as n decreases), E_n becomes larger in absolute value and more and more negative. The most negative energy value is given by n=1 which corresponds to the most stable orbit. We call this the ground state.

and its energy is lowered. That is the reason for the presence of negative sign in equation (2.13) and depicts its stability relative to the reference state of zero energy and $n = \infty$.

d) Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^+ Li^{2+}, Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the expression.

$$E_n = -2.18 \times 10^{-18}\left(\frac{Z^2}{n^2}\right)\text{J} \qquad (2.14)$$

and radii by the expression

$$r_n = \frac{52.9(n^2)}{Z}\text{pm} \qquad (2.15)$$

where Z is the atomic number and has values 2,3 for the helium and lithium atoms respectively. From the above equations, it is evident that the value of energy becomes more negative and that of radius becomes smaller with increase of Z. This means that electron will be tightly bound to the nucleus.

e) It is also possible to calculate the velocities of electrons moving in these orbits. Although the precise equation is not given here, qualitatively the magnitude of velocity of electron increases with increase of positive charge on the nucleus and decreases with increase of principal quantum number.

2.4.1 Explanation of Line Spectrum of Hydrogen

Line spectrum observed in case of hydrogen atom, as mentioned in section 2.3.3, can be explained quantitatively using Bohr's model. According to assumption 2, radiation (energy) is absorbed if the electron moves from the orbit of smaller Principal quantum number to the orbit of higher Principal quantum number, whereas the radiation (energy) is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation (2.16)

$$\Delta E = E_f - E_i \qquad (2.16)$$

Combining equations (2.13) and (2.16)

$$\Delta E = \left(-\frac{R_H}{n_f^2}\right) - \left(-\frac{R_H}{n_i^2}\right)$$ (where n_i and n_f stand for initial orbit and final orbits)

$$\Delta E = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = 2.18 \times 10^{-18}\text{J}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad (2,17)$$

The frequency (ν) associated with the absorption and emission of the photon can be evaluated by using equation (2.18)

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= \frac{2.18 \times 10^{-18}\text{J}}{6.626 \times 10^{-34}\text{J s}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad (2.18)$$

$$= 3.29 \times 10^{15}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)\text{Hz} \qquad (2.19)$$

and in terms of wavenumbers ($\bar{\nu}$)

$$\bar{\nu} = \frac{\nu}{c} = \frac{R_H}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad (2.20)$$

$$= \frac{3.29 \times 10^{15}\text{s}^{-1}}{3 \times 10^8\text{m s}^{-s}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= 1.09677 \times 10^7\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)\text{m}^{-1} \qquad (2.21)$$

In case of absorption spectrum, $n_f > n_i$ and the term in the parenthesis is positive and energy is absorbed. On the other hand in case of emission spectrum $n_i > n_f$, ΔE is negative and energy is released.

The expression (2.17) is similar to that used by Rydberg (2.9) derived empirically using the experimental data available at that time. Further, each spectral line, whether in absorption or emission spectrum, can be associated to the particular transition in hydrogen atom. In case of large number of hydrogen atoms, different possible transitions can be observed and thus leading to large number of spectral lines. The brightness or intensity of spectral lines depends upon the number of photons of same wavelength or frequency absorbed or emitted.

Problem 2.10

What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom?

Solution

Since $n_i = 5$ and $n_f = 2$, this transition gives rise to a spectral line in the visible region of the Balmer series. From equation (2.17)

$$\Delta E = 2.18 \times 10^{-18} \text{J}\left[\frac{1}{5^2} - \frac{1}{2^2}\right]$$

$$= -4.58 \times 10^{-19} \text{J}$$

It is an emission energy

The frequency of the photon (taking energy in terms of magnitude) is given by

$$\nu = \frac{\Delta E}{h}$$

$$= \frac{4.58 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}}$$

$$= 6.91 \times 10^{14} \text{ Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^{8} \text{m s}^{-1}}{6.91 \times 10^{14} \text{Hz}} = 434 \text{ nm}$$

Problem 2.11

Calculate the energy associated with the first orbit of He^+. What is the radius of this orbit?

Solution

$$E_n = -\frac{(2.18 \times 10^{-18} \text{J})Z^2}{n^2} \text{ atom}^{-1}$$

For He^+, $n = 1$, $Z = 2$

$$E_1 = -\frac{(2.18 \times 10^{-18} \text{J})(2^2)}{1^2} = -8.72 \times 10^{-18} \text{J}$$

The radius of the orbit is given by equation (2.15)

$$r_n = \frac{(0.0529 \text{ nm})n^2}{Z}$$

Since $n = 1$, and $Z = 2$

$$r_n = \frac{(0.0529 \text{ nm})1^2}{2} = 0.02645 \text{ nm}$$

2.4.2 Limitations of Bohr's Model

Bohr's model of the hydrogen atom was no doubt an improvement over Rutherford's nuclear model, as it could account for the stability and line spectra of hydrogen atom and hydrogen like ions (for example, He^+, Li^{2+}, Be^{3+}, and so on). However, Bohr's model was too simple to account for the following points.

i) It fails to account for the finer details (doublet, that is two closely spaced lines) of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons. Further, Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect).

ii) It could not explain the ability of atoms to form molecules by chemical bonds.

In other words, taking into account the points mentioned above, one needs a better theory which can explain the salient features of the structure of complex atoms.

2.5 TOWARDS QUANTUM MECHANICAL MODEL OF THE ATOM

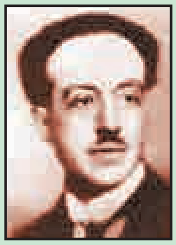
In view of the shortcoming of the Bohr's model, attempts were made to develop a more suitable and general model for atoms. Two important developments which contributed significantly in the formulation of such a model were :

1. Dual behaviour of matter,
2. Heisenberg uncertainty principle.

2.5.1 Dual Behaviour of Matter

The French physicist, de Broglie, in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties. This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength, de Broglie, from this analogy, gave the following relation between wavelength (λ) and momentum (p) of a material particle.

Louis de Broglie (1892 – 1987)



Louis de Broglie, a French physicist, studied history as an undergraduate in the early 1910's. His interest turned to science as a result of his assignment to radio communications in World War I. He received his Dr. Sc. from the University of Paris in 1924. He was professor of theoretical physics at the University of Paris from 1932 untill his retirement in 1962. He was awarded the Nobel Prize in Physics in 1929.

$$\lambda = \frac{h}{mv} = \frac{h}{p} \qquad (2.22)$$

where m is the mass of the particle, v its velocity and p its momentum. de Broglie's prediction was confirmed experimentally when it was found that an electron beam undergoes diffraction, a phenomenon characteristic of waves. This fact has been put to use in making an electron microscope, which is based on the wavelike behaviour of electrons just as an ordinary microscope utilises the wave nature of light. An electron microscope is a powerful tool in modern scientific research because it achieves a magnification of about 15 million times.

It needs to be noted that according to de Broglie, every object in motion has a wave character. The wavelengths associated with ordinary objects are so short (because of their large masses) that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles (with very small mass) can however be detected experimentally. Results obtained from the following problems prove these points qualitatively.

Problem 2.12

What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s^{-1}?

Solution

According to de Brogile equation (2.22)

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34}\,\text{Js})}{(0.1\,\text{kg})(10\ \text{m}\,\text{s}^{-1})}$$

$= 6.626 \times 10^{-34}$ m (J = kg m^2 s^{-2})

Problem 2.13

The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

Solution

Since K. E. = ½ mv^2

$$v = \left(\frac{2\text{K.E.}}{m}\right)^{1/2} = \left(\frac{2 \times 3.0 \times 10^{-25}\,\text{kg m}^2\text{s}^{-2}}{9.1 \times 10^{-31}\,\text{kg}}\right)^{1/2}$$

$= 812$ m s^{-1}

$$\lambda = \frac{h}{m\,\text{v}} = \frac{6.626 \times 10^{-34}\,\text{Js}}{(9.1 \times 10^{-31}\,\text{kg})(812\ \text{m}\,\text{s}^{-1})}$$

$= 8967 \times 10^{-10}$ m = 896.7 nm

Problem 2.14

Calculate the mass of a photon with wavelength 3.6 Å.

Solution

$\lambda = 3.6$ Å $= 3.6 \times 10^{-10}$ m

Velocity of photon = velocity of light

$$m = \frac{h}{\lambda v} = \frac{6.626 \times 10^{-34}\,\text{Js}}{(3.6 \times 10^{-10}\,\text{m})(3 \times 10^{8}\ \text{m}\,\text{s}^{-1})}$$

$= 6.135 \times 10^{-29}$ kg

2.5.2 Heisenberg's Uncertainty Principle

Werner Heisenberg a German physicist in 1927, stated uncertainty principle which is the consequence of dual behaviour of matter and radiation. **It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.**

Mathematically, it can be given as in equation (2.23).

$$\Delta x \times \Delta p_x \geq \frac{h}{4\pi} \qquad (2.23)$$

$$\text{or } \Delta x \times \Delta(mv_x) \geq \frac{h}{4\pi}$$

$$\text{or } \Delta x \times \Delta v_x \geq \frac{h}{4\pi m}$$

where Δx is the uncertainty in position and Δp_x (or Δv_x) is the uncertainty in momentum (or velocity) of the particle. If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain [$\Delta(v_x)$ is large]. On the other hand, if the velocity of the electron is known precisely ($\Delta(v_x)$ is small), then the position of the electron will be uncertain (Δx will be large). Thus, if we carry out some physical measurements on the electron's position or velocity, the outcome will always depict a fuzzy or blur picture.

The uncertainty principle can be best understood with the help of an example. Suppose you are asked to measure the thickness of a sheet of paper with an unmarked metrestick. Obviously, the results obtained would be extremely inaccurate and meaningless, In order to obtain any accuracy, you should use an instrument graduated in units smaller than the thickness of a sheet of the paper. Analogously, in order to determine the position of an electron, we must use a meterstick calibrated in units of smaller than the dimensions of electron (keep in mind that an electron is considered as a point charge and is therefore, dimensionless). To observe an electron, we can illuminate it with "light" or electromagnetic radiation. The "light" used must have a wavelength smaller than the dimensions of an electron. The high momentum photons of such light $\left(p = \frac{h}{\lambda}\right)$ would change the energy of electrons by collisions. In this process we, no doubt, would be able to calculate the position of the electron, but we would know very little about the velocity of the electron after the collision.

Significance of Uncertainty Principle

One of the important implications of the Heisenberg Uncertainty Principle is that **it rules out existence of definite paths or trajectories of electrons and other similar particles.** The trajectory of an object is determined by its location and velocity at various moments. If we know where a body is at a particular instant and if we also know its velocity and the forces acting on it at that instant, we can tell where the body would be sometime later. We, therefore, conclude that the position of an object and its velocity fix its trajectory. Since for a sub-atomic object such as an electron, it is not possible simultaneously to determine the position and velocity at any given instant to an arbitrary degree of precision, it is not possible to talk of the trajectory of an electron.

The effect of Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects. This can be seen from the following examples.

If uncertainty principle is applied to an object of mass, say about a milligram (10^{-6} kg), then

$$\Delta v.\Delta x = \frac{h}{4\pi.m}$$

$$= \frac{6.626 \times 10^{-34}\ \text{J s}}{4 \times 3.1416 \times 10^{-6}\ \text{kg}} \approx 10^{-28}\ \text{m}^2\text{s}^{-1}$$

Werner Heisenberg (1901 – 1976) Werner Heisenberg (1901 – 1976) received his Ph.D. in physics from the University of Munich in 1923. He then spent a year working with Max Born at Gottingen and three years with Niels Bohr in Copenhagen. He was professor of physics at the University of Leipzig from 1927 to 1941. During World War II, Heisenberg was in charge of German research on the atomic bomb. After the war he was named director of Max Planck Institute for physics in Gottingen. He was also accomplished mountain climber. Heisenberg was awarded the Nobel Prize in Physics in 1932.

The value of ΔvΔx obtained is extremely small and is insignificant. Therefore, one may say that **in dealing with milligram-sized or heavier objects, the associated uncertainties are hardly of any real consequence.**

In the case of a microscopic object like an electron on the other hand. Δv.Δx obtained is much larger and such uncertainties are of real consequence. For example, for an electron whose mass is 9.11×10^{-31} kg., according to Heisenberg uncertainty principle

$$\Delta v.\Delta x = \frac{h}{4\pi m}$$

$$= \frac{6.626\times10^{-34}\ \text{Js}}{4\times 3.1416\times9.11\times10^{-31}\ \text{kg}}$$

$$= 10^{-4} m^{2} s^{-1}$$

It, therefore, means that if one tries to find the exact location of the electron, say to an uncertainty of only 10^{-8} m, then the uncertainty Δv in velocity would be

which is so large that the classical picture of electrons moving in Bohr's orbits (fixed) cannot hold good. **It, therefore, means that the precise statements of the position and momentum of electrons have to be replaced by the statements of probability, that the electron has at a given position and momentum. This is what happens in the quantum mechanical model of atom.**

Problem 2.15

A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 Å. What is the uncertainty involved in the measurement of its velocity?

Solution

$$\Delta x\, \Delta p = \frac{h}{4\pi} \quad \text{or} \quad \Delta x\, m \Delta v = \frac{h}{4\pi}$$

$$\Delta v = \frac{h}{4\pi\, \Delta x\, m}$$

$$\Delta v = \frac{6.626\times10^{-34}\ \text{Js}}{4\times3.14\times0.1\times10^{-10}\text{m}\times9.11\times10^{-31}\ \text{kg}}$$

$= 0.579\times10^{7}$ m s^{-1} (1J = 1 kg $m^2 s^{-2}$)

$= 5.79\times10^{6}$ m s^{-1}

Problem 2.16

A golf ball has a mass of 40g, and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position.

Solution

The uncertainty in the speed is 2%, i.e.,

$$45 \quad \frac{2}{100} = 0.9\, \text{m s}^{-1}$$

Using the equation (2.22)

$$\Delta x = \frac{h}{4\pi m \Delta v}$$

$$= \frac{6.626\times10^{-34}\ \text{Js}}{4\times3.14\times40\text{g}\times10^{-3}\ \text{kg g}^{-1}(0.9\,\text{m s}^{-1})}$$

$= 1.46\times10^{-33}$ m

This is nearly ~ 10^{18} times smaller than the diameter of a typical atomic nucleus. As mentioned earlier for large particles, the uncertainty principle sets no meaningful limit to the precision of measurements.

Reasons for the Failure of the Bohr Model

One can now understand the reasons for the failure of the Bohr model. In Bohr model, an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. The wave character of the electron is not considered in Bohr model. Further, an orbit is a clearly defined path and this path can completely be defined only if both the position and the velocity of the electron are known exactly at the same time. This is not possible according to the Heisenberg uncertainty principle. *Bohr model of the hydrogen atom, therefore, not only ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle.* In view of

Erwin Schrödinger _(1887-1961)_

Erwin Schrödinger, an Austrian physicist received his Ph.D. in theoretical physics from the University of Vienna in 1910. In 1927 Schrödinger succeeded Max Planck at the University of Berlin at Planck's request. In 1933, Schrödinger left Berlin because of his opposition to Hitler and Nazi policies and returned to Austria in 1936. After the invasion of Austria by Germany, Schrödinger was forcibly removed from his professorship. He then moved to Dublin, Ireland where he remained for seventeen years. Schrödinger shared the Nobel Prize for Physics with P.A.M. Dirac in 1933.

these inherent weaknesses in the Bohr model, there was no point in extending Bohr model to other atoms. In fact an insight into the structure of the atom was needed which could account for wave-particle duality of matter and be consistent with Heisenberg uncertainty principle. This came with the advent of quantum mechanics.

2.6 QUANTUM MECHANICAL MODEL OF ATOM

Classical mechanics, based on Newton's laws of motion, successfully describes the motion of all macroscopic objects such as a falling stone, orbiting planets etc., which have essentially a particle-like behaviour as shown in the previous section. However it fails when applied to microscopic objects like electrons, atoms, molecules etc. This is mainly because of the fact that classical mechanics ignores the concept of dual behaviour of matter especially for sub-atomic particles and the uncertainty principle. The branch of science that takes into account this dual behaviour of matter is called **quantum mechanics**.

Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties. It specifies the laws of motion that these objects obey. When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics.

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrödinger. Here, however, we shall be discussing the quantum mechanics which is based on the ideas of wave motion. The fundamental equation of quantum mechanics was developed by Schrödinger and it won him the Nobel Prize in Physics in 1933. This equation which incorporates wave-particle duality of matter as proposed by de Broglie is quite complex and knowledge of higher mathematics is needed to solve it. You will learn its solutions for different systems in higher classes.

For a system (such as an atom or a molecule whose energy does not change with time) the **Schrödinger equation** is written as $\hat{H}\Psi = E\Psi$ where $\hat{H}$ is a mathematical operator called Hamiltonian. Schrödinger gave a recipe of constructing this operator from the expression for the total energy of the system. The total energy of the system takes into account the kinetic energies of all the sub-atomic particles (electrons, nuclei), attractive potential between the electrons and nuclei and repulsive potential among the electrons and nuclei individually. Solution of this equation gives E and ψ.

Hydrogen Atom and the Schrödinger Equation

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) (ψ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (**principal quantum number** n, **azimuthal quantum number** l **and magnetic quantum number** m_l) arise as a natural consequence in the solution of the Schrödinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron. The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning. Such wave functions of hydrogen or hydrogen like species with one electron are called **atomic orbitals**. Such wave functions pertaining to one-electron species are called one-electron systems. The probability of finding an electron at a point within an atom is proportional to the $|\psi|^2$ at that point. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

Application of Schrödinger equation to multi-electron atoms presents a difficulty: the Schrödinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above. The principal difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later (in subsections 2.6.3 and 2.6.4), unlike orbitals of hydrogen or hydrogen like species, whose energies depend only on the quantum number n, the energies of the orbitals in multi-electron atoms depend on quantum numbers n and l.

Important Features of the Quantum Mechanical Model of Atom

Quantum mechanical model of atom is the picture of the structure of the atom, which emerges from the application of the Schrödinger equation to atoms. The following are the important features of the quantum-mechanical model of atom:

1. The energy of electrons in atoms is quantized (i.e., can only have certain specific values), for example when electrons are bound to the nucleus in atoms.
2. The existence of quantized electronic energy levels is a direct result of the wave like properties of electrons and are allowed solutions of Schrödinger wave equation.
3. Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously (Heisenberg uncertainty principle). The path of an electron in an atom therefore, can never be determined or known accurately. That is why, as you shall see later on, one talks of only probability of finding the electron at different points in an atom.
4. **An atomic orbital is the wave function ψ for an electron in an atom**. Whenever an electron is described by a wave function, we say that the electron occupies that orbital. Since many such wave functions are possible for an electron, there are many atomic orbitals in an atom. These "one electron orbital wave functions" or orbitals form the basis of the electronic structure of atoms. In each orbital, the electron has a definite energy. An orbital cannot contain more than two electrons. In a multi-electron atom, the electrons are filled in various orbitals in the order of increasing energy. For each electron of a multi-electron atom, there shall, therefore, be an orbital wave function characteristic of the orbital it occupies. All the information about the electron in an atom is stored in its orbital wave function ψ and quantum mechanics makes it possible to extract this information out of ψ.
5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e., $|\psi|^2$ at that point. $|\psi|^2$ is known as **probability density** and is always positive. ***From the value of $|\psi|^2$ at different points within an atom, it is possible to predict the region around the nucleus where electron will most probably be found.***

2.6.1 Orbitals and Quantum Numbers

A large number of orbitals are possible in an atom. Qualitatively these orbitals can be distinguished by their size, shape and orientation. An orbital of smaller size means there is more chance of finding the electron near the nucleus. Similarly shape and orientation mean that there is more probability of finding the electron along certain directions than along others. Atomic orbitals are precisely distinguished by what are known as quantum numbers. Each orbital is designated by three quantum numbers labelled as n, l and m_l.

The principal quantum number '*n*' is a positive integer with value of n = 1,2,3....... The principal quantum number determines the *size and to large extent the energy of the orbital.* For hydrogen atom and hydrogen like species (He^+, Li^{2+}, ... etc.) energy and size of the orbital depends only on 'n'.

The principal quantum number also identifies the **shell**. With the increase in the value of 'n', the number of allowed orbital increases and **are given by 'n^2' All the orbitals of a given value of 'n' constitute a single shell of atom** and are represented by the following letters

n = 1 2 3 4 ....
Shell = K L M N ....

Size of an orbital increases with increase of principal quantum number 'n'. In other words the electron will be located away from the nucleus. Since energy is required in shifting away the negatively charged electron from the positively charged nucleus, the energy of the orbital will increase with increase of n.

Azimuthal quantum number. '*l*' is also known as **orbital angular momentum or subsidiary quantum number.** It defines the three-dimensional shape of the orbital. For a given value of n, l can have n values ranging from 0 to n – 1, that is, for a given value of n, the possible value of l are : l = 0, 1, 2, ... (n–1)

For example, when n = 1, value of l is only 0. For n = 2, the possible value of l can be 0 and 1. For n = 3, the possible l values are 0, 1 and 2.

Each shell consists of one or more **sub-shells** or **sub-levels**. The number of sub-shells in a principal shell is equal to the value of n. For example in the first shell (n = 1), there is only one sub-shell which corresponds to l = 0. There are two sub-shells (l = 0, 1) in the second shell (n = 2), three (l = 0, 1, 2) in third shell (n = 3) and so on. Each sub-shell is assigned an azimuthal quantum number (l). Sub-shells corresponding to different values of l are represented by the following symbols.

Value for l :	0	1	2	3	4	5	....
notation for sub-shell	*s*	*p*	*d*	*f*	*g*	*h*	....

Table 2.4 shows the permissible values of 'l' for a given principal quantum number and the corresponding sub-shell notation.

Table 2.4 Subshell Notations

n	*l*	Subshell notation
1	0	1*s*
2	0	2*s*
2	1	2*p*
3	0	3*s*
3	1	3*p*
3	2	3*d*
4	0	4*s*
4	1	4*p*
4	2	4*d*
4	3	4*f*

Magnetic orbital quantum number. 'm_l' gives information about **the spatial orientation of the orbital with respect to standard set of co-ordinate axis.** For any **sub-shell (defined by '*l*' value)** 2l+1 values of m_l are possible and these values are given by :

$$m_l = -l, -(l-1), -(l-2)... 0, 1... (l-2), (l-1), l$$

Thus for l = 0, the only permitted value of m_l = 0, [2(0)+1 = 1, one s orbital]. For l = 1, m_l can be –1, 0 and +1 [2(1)+1 = 3, three p orbitals]. For l = 2, m_l = –2, –1, 0, +1 and +2, [2(2)+1 = 5, five d orbitals]. It should be noted that the values of m_l are derived from l and that the value of l are derived from n.

Each orbital in an atom, therefore, is defined by a set of values for n, l and m_l. An orbital described by the quantum numbers $n = 2$, $l = 1$, $m_l = 0$ is an orbital in the p sub-shell of the second shell. The following chart gives the relation between the subshell and the number of orbitals associated with it.

Value of l	0	1	2	3	4	5
Subshell notation	*s*	*p*	*d*	*f*	*g*	*h*
number of orbitals	1	3	5	7	9	11

Electron spin 's' : The three quantum numbers labelling an atomic orbital can be used equally well to define its energy, shape and orientation. But all these quantum numbers are not enough to explain the line spectra observed in the case of multi-electron atoms, that is, some of the lines actually occur in doublets (two lines closely spaced), triplets (three lines, closely spaced) etc. This suggests the presence of a few more energy levels than predicted by the three quantum numbers.

In 1925, George Uhlenbeck and Samuel Goudsmit proposed the presence of the fourth quantum number known as the **electron spin quantum number (m_s).** An electron spins around its own axis, much in a similar way as earth spins around its own axis while revolving around the sun. In other words, an electron has, besides charge and mass, intrinsic spin angular quantum number. Spin angular momentum of the electron — a vector quantity, can have two orientations relative to the chosen axis. These two orientations are distinguished by the spin quantum numbers m_s which can take the values of +½ or –½. These are called the **two spin states of the electron** and are normally represented by two arrows, ↑ (spin up) and ↓ (spin down). Two electrons that have different m_s values (one +½ and the other –½) are said to have opposite spins. An orbital cannot hold more than two electrons and these two electrons should have opposite spins.

To sum up, the four quantum numbers provide the following information :

i) ***n*** defines the shell, determines the size of the orbital and also to a large extent the energy of the orbital.

ii) There are n subshells in the n^{th} shell. ***l*** identifies the subshell and determines the shape of the orbital (see section 2.6.2). There are $(2l+1)$ orbitals of each type in a subshell, that is, one s orbital ($l = 0$), three p orbitals ($l = 1$) and five d orbitals ($l = 2$) per subshell. To some extent l also determines the energy of the orbital in a multi-electron atom.

iii) $\boldsymbol{m_l}$ designates the orientation of the orbital. For a given value of l, m_l has $(2l+1)$ values,

Orbit, orbital and its importance

Orbit and orbital are not synonymous. An orbit, as proposed by Bohr, is a circular path around the nucleus in which an electron moves. A precise description of this path of the electron is impossible according to Heisenberg uncertainty principle. Bohr orbits, therefore, have no real meaning and their existence can never be demonstrated experimentally. An atomic orbital, on the other hand, is a quantum mechanical concept and refers to the one electron wave function ψ in an atom. It is characterized by three quantum numbers (n, l and m_l) and its value depends upon the coordinates of the electron. ψ has, by itself, no physical meaning. It is the square of the wave function i.e., $|\psi|^2$ which has a physical meaning. $|\psi|^2$ at any point in an atom gives the value of probability density at that point. Probability density ($|\psi|^2$) is the probability per unit volume and the product of $|\psi|^2$ and a small volume (called a volume element) yields the probability of finding the electron in that volume (the reason for specifying a small volume element is that $|\psi|^2$ varies from one region to another in space but its value can be assumed to be constant within a small volume element). The total probability of finding the electron in a given volume can then be calculated by the sum of all the products of $|\psi|^2$ and the corresponding volume elements. It is thus possible to get the probable distribution of an electron in an orbital.

the same as the number of orbitals per subshell. It means that the number of orbitals is equal to the number of ways in which they are oriented.

iv) $\boldsymbol{m_s}$ refers to orientation of the spin of the electron.

Problem 2.17

What is the total number of orbitals associated with the principal quantum number $n = 3$?

Solution

For $n = 3$, the possible values of l are 0, 1 and 2. Thus there is one 3*s* orbital ($n = 3$, $l = 0$ and $m_l = 0$); there are three 3*p* orbitals ($n = 3$, $l = 1$ and $m_l = -1, 0, +1$); there are five 3*d* orbitals ($n = 3$, $l = 2$ and $m_l = -2, -1, 0, +1+, +2$).

Therefore, the total number of orbitals is 1+3+5 = 9

The same value can also be obtained by using the relation; number of orbitals $= n^2$, i.e. $3^2 = 9$.

Problem 2.18

Using *s*, *p*, *d*, f notations, describe the orbital with the following quantum numbers

(a) $n = 2$, $l = 1$, (b) $n = 4$, $l = 0$, (c) $n = 5$, $l = 3$, (d) $n = 3$, $l = 2$

Solution

	n	l	orbital
a)	2	1	2*p*
b)	4	0	4*s*
c)	5	3	5*f*
d)	3	2	3*d*

2.6.2 Shapes of Atomic Orbitals

The orbital wave function or ψ for an electron in an atom has no physical meaning. It is simply a mathematical function of the coordinates of the electron. However, for different orbitals the plots of corresponding wave functions as a function of *r* (the distance from the nucleus) are different. Fig. 2.12(a), gives such plots for 1*s* ($n = 1$, $l = 0$) and 2*s* ($n = 2$, $l = 0$) orbitals.

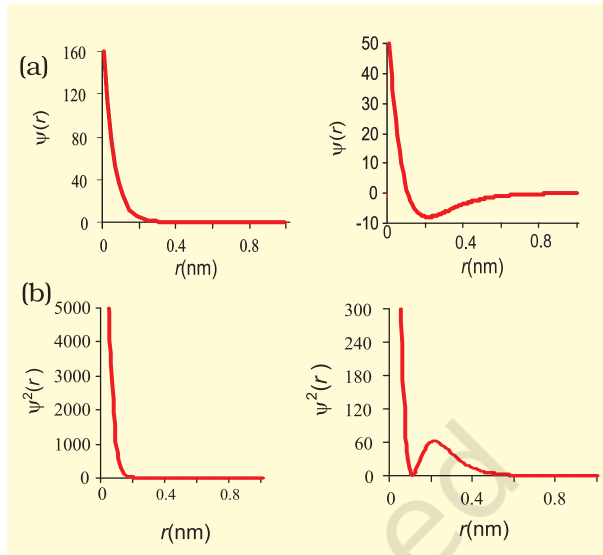


Fig. 2.12 *The plots of (a) the orbital wave function $\psi(r)$; (b) the variation of probability density $\psi^2(r)$ as a function of distance r of the electron from the nucleus for 1s and 2s orbitals.*

According to the German physicist, Max Born, the square of the wave function (i.e., ψ^2) at a point gives the probability density of the electron at that point. The variation of ψ^2 as a function of *r* for 1*s* and 2*s* orbitals is given in Fig. 2.12(b). Here again, you may note that the curves for 1*s* and 2*s* orbitals are different.

It may be noted that for 1*s* orbital the probability density is maximum at the nucleus and it decreases sharply as we move away from it. On the other hand, for 2*s* orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maxima it decreases again and approaches zero as the value of *r* increases further. The region where this probability density function reduces to zero is called **nodal surfaces** or simply **nodes**. In general, it has been found that *ns*-orbital has ($n - 1$) nodes, that is, number of nodes increases with increase of principal quantum number *n*. In other words, number of nodes for 2*s* orbital is one, two for 3*s* and so on.

These probability density variation can be visualised in terms of charge cloud diagrams [Fig. 2.13(a)]. In these diagrams, the density of the dots in a region represents electron probability density in that region.

Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this representation, a boundary surface or contour surface is drawn in space for an orbital on which the value of probability density $|\psi|^2$ is constant. In principle many such boundary surfaces may be possible. However, for a given orbital, only that boundary surface diagram of constant probability density* is taken to be good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high, say, 90%. The boundary surface diagram for 1*s* and 2*s* orbitals are given in Fig. 2.13(b). One may ask a question : Why do we not draw a boundary surface diagram, which bounds a region in which the probability of finding the electron is, 100 %? The answer to this question is that the probability density $|\psi|^2$ has always some value, howsoever small it may be, at any finite distance from the nucleus. It is therefore, not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%. Boundary surface diagram for a *s* orbital is actually a sphere centred on the nucleus. In two dimensions, this sphere looks like a circle. It encloses a region in which probability of finding the electron is about 90%.

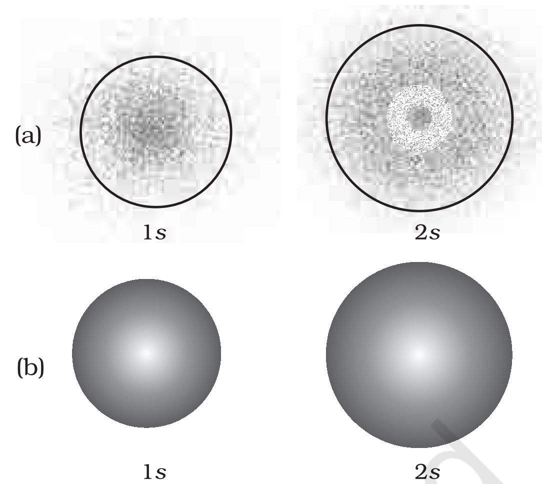


Fig. 2.13 *(a) Probability density plots of 1s and 2s atomic orbitals. The density of the dots represents the probability density of finding the electron in that region. (b) Boundary surface diagram for 1s and 2s orbitals.*

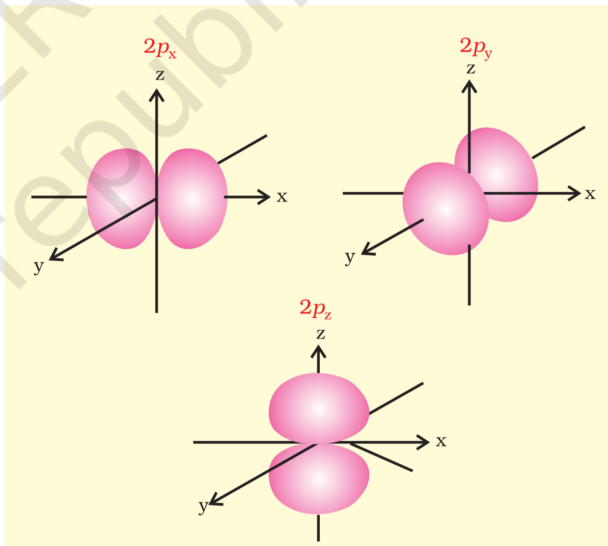


Fig. 2.14 *Boundary surface diagrams of the three 2p orbitals.*

Thus, we see that 1*s* and 2*s* orbitals are spherical in shape. In reality all the *s*-orbitals are spherically symmetric, that is, the probability of finding the electron at a given distance is equal in all the directions. It is also observed that the size of the s orbital increases with increase in *n*, that is, 4*s* > 3*s* > 2*s* > 1*s* and the electron is located further away from the nucleus as the principal quantum number increases.

Boundary surface diagrams for three 2*p* orbitals (l = 1) are shown in Fig. 2.14. In these diagrams, the nucleus is at the origin. Here, unlike *s*-orbitals, the boundary surface diagrams are not spherical. Instead each *p* orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The probability density function is zero on the plane where the two lobes touch each other. The size, shape and

* *If probability density* $|\psi|^2$ *is constant on a given surface,* $|\psi|$ *is also constant over the surface. The boundary surface for* $|\psi|^2$ *and* $|\psi|$ *are identical.*

energy of the three orbitals are identical. They differ however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z axis, they are given the designations $2p_x$, $2p_y$, and $2p_z$. It should be understood, however, that *there is no simple relation between the values of* m_l *(–1, 0 and +1) and the x, y and z directions.* For our purpose, it is sufficient to remember that, because there are three possible values of m_l,

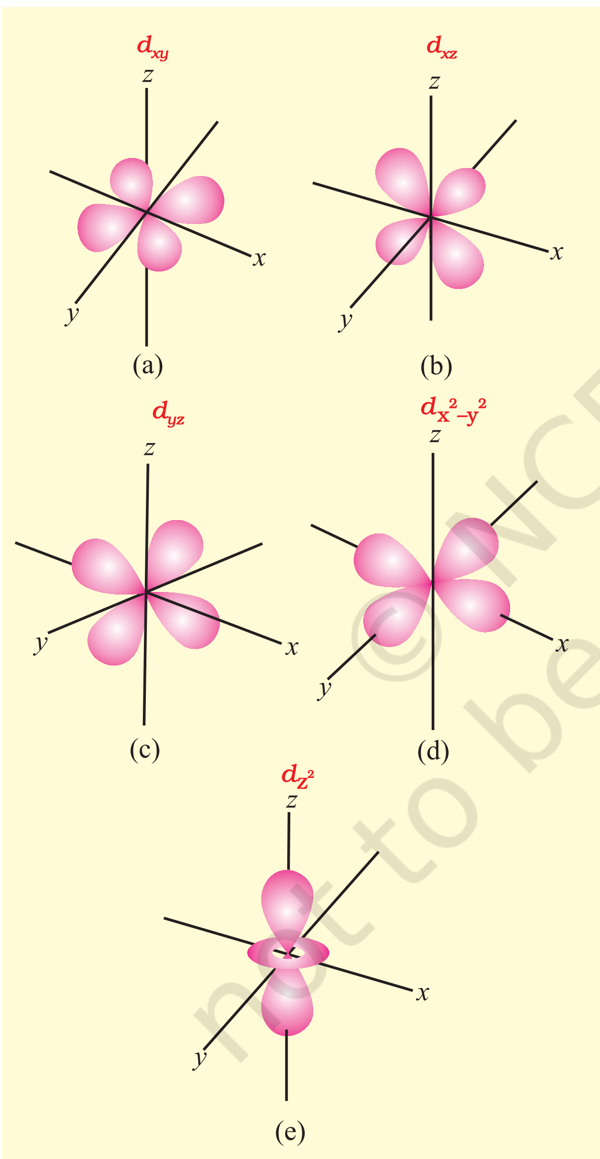


Fig. 2.15 *Boundary surface diagrams of the five 3d orbitals.*

there are, therefore, three *p* orbitals whose axes are mutually perpendicular. Like *s* orbitals, *p* orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various *p* orbitals is $4p > 3p > 2p$. Further, like s orbitals, the probability density functions for *p*-orbital also pass through value zero, besides at zero and infinite distance, as the distance from the nucleus increases. The number of nodes are given by the n–2, that is number of radial node is 1 for 3*p* orbital, two for 4*p* orbital and so on.

For $l = 2$, the orbital is known as *d*-orbital and the minimum value of principal quantum number (*n*) has to be 3. as the value of *l* cannot be greater than n–1. There are five m_l values (–2, –1, 0, +1 and +2) for $l = 2$ and thus there are five *d* orbitals. The boundary surface diagram of *d* orbitals are shown in Fig. 2.15.

The five *d*-orbitals are designated as d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}. The shapes of the first four *d*-orbitals are similar to each other, where as that of the fifth one, d_{z^2}, is different from others, but all five 3*d* orbitals are equivalent in energy. The *d* orbitals for which *n* is greater than 3 (4*d*, 5*d*...) also have shapes similar to 3*d* orbital, but differ in energy and size.

Besides the radial nodes (i.e., probability density function is zero), the probability density functions for the n*p* and n*d* orbitals are zero at the plane (s), passing through the nucleus (origin). For example, in case of p_z orbital, xy-plane is a nodal plane, in case of d_{xy} orbital, there are two nodal planes passing through the origin and bisecting the xy plane containing z-axis. These are called angular nodes and number of angular nodes are given by '*l*', i.e., one angular node for *p* orbitals, two angular nodes for '*d*' orbitals and so on. **The total number of nodes are given by (*n*–1), i.e., *sum of l* angular nodes and (*n* – *l* – 1) radial nodes.**

2.6.3 Energies of Orbitals

The energy of an electron in a hydrogen atom is determined solely by the principal quantum number. Thus the energy of the orbitals in hydrogen atom increases as follows :

$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f <$ (2.23)

and is depicted in Fig. 2.16. Although the shapes of 2*s* and 2*p* orbitals are different, an electron has the same energy when it is in the 2*s* orbital as when it is present in 2*p* orbital. The orbitals having the same energy are called **degenerate.** The 1*s* orbital in a hydrogen atom, as said earlier, corresponds to the most stable condition and is called the **ground state** and an electron residing in this orbital is most strongly held by the nucleus. An electron in the 2*s*, 2*p* or higher orbitals in a hydrogen atom is in **excited state.**

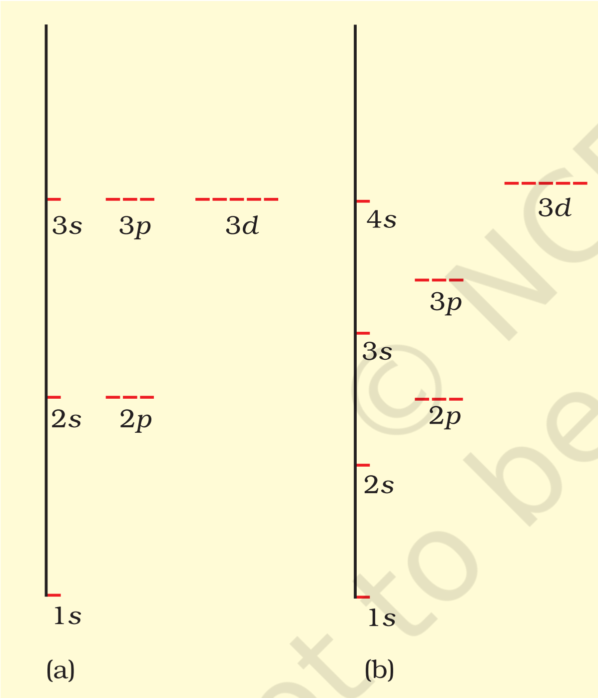


Fig. 2.16 *Energy level diagrams for the few electronic shells of (a) hydrogen atom and (b) multi-electronic atoms. Note that orbitals for the same value of principal quantum number, have the same energies even for different azimuthal quantum number for hydrogen atom. In case of multi-electron atoms, orbitals with same principal quantum number possess different energies for different azimuthal quantum numbers.*

The energy of an electron in a multi-electron atom, unlike that of the hydrogen atom, depends not only on its principal quantum number (shell), but also on its azimuthal quantum number (subshell). That is, for a given principal quantum number, *s*, *p*, *d*, *f* ... all have different energies. Within a given principal quantum number, the energy of orbitals increases in the order $s<p<d<f$. For higher energy levels, these differences are sufficiently pronounced and straggering of orbital energy may result, e.g., $4s<3d$ and $6s<5d$; $4f<6p$. The main reason for having different energies of the subshells is the mutual repulsion among the electrons in multi-electron atoms. The only electrical interaction present in hydrogen atom is the attraction between the negatively charged electron and the positively charged nucleus. In multi-electron atoms, besides the presence of attraction between the electron and nucleus, there are repulsion terms between every electron and other electrons present in the atom. Thus the stability of an electron in a multi-electron atom is because total attractive interactions are more than the repulsive interactions. In general, the repulsive interaction of the electrons in the outer shell with the electrons in the inner shell are more important. On the other hand, the attractive interactions of an electron increases with increase of positive charge (*Ze*) on the nucleus. Due to the presence of electrons in the inner shells, the electron in the outer shell will not experience the full positive charge of the nucleus (*Ze*). The effect will be lowered due to the partial screening of positive charge on the nucleus by the inner shell electrons. This is known as the **shielding of the outer shell electrons from the nucleus by the inner shell electrons,** and the net positive charge experienced by the outer electrons is known as **effective nuclear charge** ($Z_{eff}\, e$). Despite the shielding of the outer electrons from the nucleus by the inner shell electrons, the attractive force experienced by the outer shell electrons increases with increase of nuclear charge. In other words, the energy of interaction between, the nucleus and electron (that is orbital energy) decreases (that is more negative) with the increase of atomic number (***Z***).

Both the attractive and repulsive interactions depend upon the shell and shape of the orbital in which the electron is present. For example electrons present in spherical shaped, *s* orbital shields the outer electrons from the nucleus more effectively as compared to electrons present in *p* orbital. Similarly electrons present in *p* orbitals shield the outer electrons from the nucleus more than the electrons present in *d* orbitals, even though all these orbitals are present in the same shell. Further within a shell, due to spherical shape of *s* orbital, the *s* orbital electron spends more time close to the nucleus in comparison to *p* orbital electron which spends more time in the vicinity of nucleus in comparison to *d* orbital electron. In other words, for a given shell (principal quantum number), the Z_{eff} experienced by the electron decreases with increase of azimuthal quantum number (*l*), that is, the *s orbital electron will be more tightly bound to the nucleus than p orbital electron which in turn will be better tightly bound than the d orbital electron*. The energy of electrons in *s* orbital will be lower (more negative) than that of *p* orbital electron which will have less energy than that of *d* orbital electron and so on. Since the extent of shielding from the nucleus is different for electrons in different orbitals, it leads to the splitting of energy levels within the same shell (or same principal quantum number), that is, energy of electron in an orbital, as mentioned earlier, depends upon the values of *n* and *l*. Mathematically, the dependence of energies of the orbitals on *n* and *l* are quite complicated but one simple rule is that, **the lower the value of (*n* + *l*) for an orbital, the lower is its energy. If two orbitals have the same value of (*n* + *l*), the orbital with lower value of *n* will have the lower energy.** The Table 2.5 illustrates the (*n* + *l*) rule and Fig. 2.16 depicts the energy levels of multi-electrons atoms. It may be noted that different subshells of a particular shell have different energies in case of multi–electrons atoms. However, in hydrogen atom, these have the same energy. Lastly it may be mentioned here that **energies of the orbitals in the same subshell decrease with increase in the atomic number (Z_{eff})**. For example, energy of 2*s* orbital of hydrogen atom is greater than that of 2*s* orbital of lithium and that of lithium is greater than that of sodium and so on, that is, E_{2s}(H) > E_{2s}(Li) > E_{2s}(Na) > E_{2s}(K).

Table 2.5 Arrangement of Orbitals with Increasing Energy on the Basis of (*n*+*l*) Rule

Orbital	Value of *n*	Value of *l*	Value of (*n* + *l*)	
1*s*	1	0	1 + 0 = 1	
2*s*	2	0	2 + 0 = 2	
2*p*	2	1	2 + 1 = 3	2*p* (*n*=2) has lower energy than
3*s*	3	0	3 + 0 = 3	3*s* (*n*=3)
3*p*	3	1	3 + 1 = 4	3*p* (*n* =3) has lower energy than
4*s*	4	0	4 + 0 = 4	4*s* (*n* =4)
3*d*	3	2	3 + 2 = 5	3*d* (*n* =3) has lower energy than
4*p*	4	1	4 + 1 =5	4*p* (*n* =4)

2.6.4 Filling of Orbitals in Atom

The filling of electrons into the orbitals of different atoms takes place according to the *aufbau* principle which is based on the Pauli's exclusion principle, the Hund's rule of maximum multiplicity and the relative energies of the orbitals.

Aufbau Principle

The word '*aufbau*' in German means 'building up'. The building up of orbitals means the filling up of orbitals with electrons. The principle states : **In the ground state of the atoms, the orbitals are filled in order of their increasing energies.** In other words, electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled. As you have learnt above, energy of a given orbital depends upon effective nuclear charge and different type of orbitals are affected to different extent. Thus, there is no single ordering of energies of orbitals which will be universally correct for all atoms.

However, following order of energies of the orbitals is extremely useful:

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 4*f*, 5*d*, 6*p*, 7*s*...

The order may be remembered by using the method given in Fig. 2.17. Starting from the top, the direction of the arrows gives the order of filling of orbitals, that is starting from right top to bottom left. With respect to placement of outermost valence electrons, it is remarkably accurate for all atoms. For example, valence electron in potassium must choose between 3*d* and 4*s* orbitals and as predicted by this sequence, it is found in 4*s* orbital. The above order should be assumed to be a rough guide to the filling of energy levels. In many cases, the orbitals are similar in energy and small changes in atomic structure may bring about a change in the order of filling. Even then, the above series is a useful guide to the building of the electronic structure of an atom provided that it is remembered that exceptions may occur.

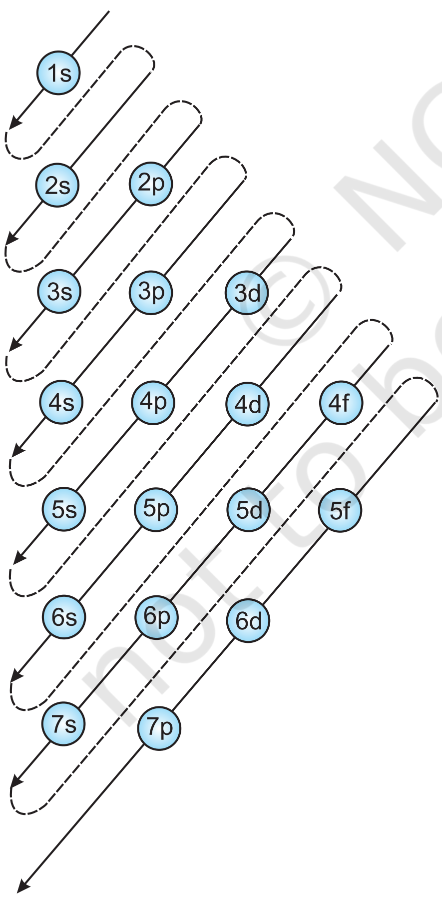


Fig.2.17 *Order of filling of orbitals*

Pauli Exclusion Principle

The number of electrons to be filled in various orbitals is restricted by the exclusion principle, given by the Austrian scientist Wolfgang Pauli (1926). According to this principle : **No two electrons in an atom can have the same set of four quantum numbers.** Pauli exclusion principle can also be stated as : **"Only two electrons may exist in the same orbital and these electrons must have opposite spin."** This means that the two electrons can have the same value of three quantum numbers n, l and m_l, but must have the opposite spin quantum number. The restriction imposed by Pauli's exclusion principle on the number of electrons in an orbital helps in calculating the capacity of electrons to be present in any subshell. For example, subshell 1*s* comprises one orbital and thus the maximum number of electrons present in 1*s* subshell can be two, in *p* and *d* subshells, the maximum number of electrons can be 6 and 10 and so on. This can be summed up as : **the maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$.**

Hund's Rule of Maximum Multiplicity

This rule deals with the filling of electrons into the orbitals belonging to the same subshell (that is, orbitals of equal energy, called

degenerate orbitals). It states : **pairing of electrons in the orbitals belonging to the same subshell (*p*, *d* or *f*) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.**

Since there are three *p*, five *d* and seven *f* orbitals, therefore, the pairing of electrons will start in the *p*, *d* and *f* orbitals with the entry of 4th, 6th and 8th electron, respectively. It has been observed that half filled and fully filled degenerate set of orbitals acquire extra stability due to their symmetry (see Section, 2.6.7).

2.6.5 Electronic Configuration of Atoms

The distribution of electrons into orbitals of an atom is called its **electronic configuration**. If one keeps in mind the basic rules which govern the filling of different atomic orbitals, the electronic configurations of different atoms can be written very easily.

The electronic configuration of different atoms can be represented in two ways. For example :

(i) $s^a p^b d^c$ ...... notation

(ii) Orbital diagram

s *p* *d*

In the first notation, the subshell is represented by the respective letter symbol and the number of electrons present in the subshell is depicted, as the super script, like a, b, c, ... etc. The similar subshell represented for different shells is differentiated by writing the principal quantum number before the respective subshell. In the second notation each orbital of the subshell is represented by a box and the electron is represented by an arrow (↑) a positive spin or an arrow (↓) a negative spin. The advantage of second notation over the first is that it represents all the four quantum numbers.

The hydrogen atom has only one electron which goes in the orbital with the lowest energy, namely 1*s*. The electronic configuration of the hydrogen atom is $1s^1$ meaning that it has one electron in the 1*s* orbital. The second electron in helium (He) can also occupy the 1*s* orbital. Its configuration is, therefore, $1s^2$. As mentioned above, the two electrons differ from each other with opposite spin, as can be seen from the orbital diagram.

	1*s*		1*s*
H	↑	He	↑↓

The third electron of lithium (Li) is not allowed in the 1*s* orbital because of Pauli exclusion principle. It, therefore, takes the next available choice, namely the 2*s* orbital. The electronic configuration of Li is $1s^22s^1$. The 2*s* orbital can accommodate one more electron. The configuration of beryllium (Be) atom is, therefore, $1s^2\ 2s^2$ (see Table 2.6, page 66 for the electronic configurations of elements).

In the next six elements—boron (B, $1s^22s^22p^1$), carbon (C, $1s^22s^22p^2$), nitrogen (N, $1s^22s^22p^3$), oxygen (O, $1s^22s^22p^4$), fluorine (F, $1s^22s^22p^5$) and neon (Ne, $1s^22s^22p^6$), the 2*p* orbitals get progressively filled. This process is completed with the neon atom. The orbital picture of these elements can be represented as follows :

	1*s*	2*s*	2*p*		
Li	↑↓	↑			
Be	↑↓	↑↓			
B	↑↓	↑↓	↑		
C	↑↓	↓↑	↑	↑	
N	↑↓	↑↓	↑	↑	↑
O	↑↓	↑↓	↑↓	↑	↑
F	↑↓	↑↓	↑↓	↑↓	↑
Ne	↑↓	↑↓	↑↓	↑↓	↑↓

The electronic configuration of the elements sodium (Na, $1s^22s^22p^63s^1$) to argon (Ar, $1s^22s^22p^63s^23p^6$), follow exactly the same pattern as the elements from lithium to neon with the difference that the 3*s* and 3*p* orbitals are getting filled now. This process can be simplified if we represent the total number of electrons in the first two shells by the name of element neon (Ne). The electronic configuration of the elements from sodium to argon can be written as (Na, [Ne]$3s^1$) to (Ar, [Ne] $3s^2 3p^6$). The electrons in the completely filled shells are known as core electrons and the electrons that are added to the electronic shell with the highest principal quantum number are called **valence electrons.** For example, the electrons in Ne are the core electrons and the electrons from Na to Ar are the valence electrons. In potassium (K) and calcium (Ca), the 4*s* orbital, being lower in energy than the 3*d* orbitals, is occupied by one and two electrons respectively.

A new pattern is followed beginning with scandium (Sc). The 3*d* orbital, being lower in energy than the 4*p* orbital, is filled first. Consequently, in the next ten elements, scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn), the five 3*d* orbitals are progressively occupied. We may be puzzled by the fact that chromium and copper have five and ten electrons in 3*d* orbitals rather than four and nine as their position would have indicated with two-electrons in the 4s orbital. The reason is that fully filled orbitals and half-filled orbitals have extra stability (that is, lower energy). Thus p^3, p^6, d^5, d^{10}, f^7, f^{14} etc. configurations, which are either half-filled or fully filled, are more stable. Chromium and copper therefore adopt the d^5 and d^{10} configuration (Section 2.6.7)[*caution: exceptions do exist*]

With the saturation of the 3*d* orbitals, the filling of the 4*p* orbital starts at gallium (Ga) and is complete at krypton (Kr). In the next eighteen elements from rubidium (Rb) to xenon (Xe), the pattern of filling the 5*s*, 4*d* and 5*p* orbitals are similar to that of 4*s*, 3*d* and 4*p* orbitals as discussed above. Then comes the turn of the 6*s* orbital. In caesium (Cs) and the barium (Ba), this orbital contains one and two electrons, respectively. Then from lanthanum (La) to mercury (Hg), the filling up of electrons takes place in 4*f* and 5*d* orbitals. After this, filling of 6*p*, then 7*s* and finally 5*f* and 6*d* orbitals takes place. The elements after uranium (U) are all short-lived and all of them are produced artificially. The electronic configurations of the known elements (as determined by spectroscopic methods) are tabulated in Table 2.6 (page 66).

One may ask what is the utility of knowing the electron configuration? The modern approach to the chemistry, infact, depends almost entirely on electronic distribution to understand and explain chemical behaviour. For example, questions like why two or more atoms combine to form molecules, why some elements are metals while others are non-metals, why elements like helium and argon are not reactive but elements like the halogens are reactive, find simple explanation from the electronic configuration. These questions have no answer in the Daltonian model of atom. A detailed understanding of the electronic structure of atom is, therefore, very essential for getting an insight into the various aspects of modern chemical knowledge.

2.6.6 Stability of Completely Filled and Half Filled Subshells

The ground state electronic configuration of the atom of an element always corresponds to the state of the lowest total electronic energy. The electronic configurations of most of the atoms follow the basic rules given in Section 2.6.5. However, in certain elements such as Cu, or Cr, where the two subshells (4*s* and 3*d*) differ slightly in their energies, an electron shifts from a subshell of lower energy (4*s*) to a subshell of higher energy (3*d*), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half filled. The valence electronic configurations of Cr and Cu, therefore, are $3d^5 4s^1$ and $3d^{10} 4s^1$ respectively and not $3d^4 4s^2$ and $3d^9 4s^2$. It has been found that there is extra stability associated with these electronic configurations.

Causes of Stability of Completely Filled and Half-filled Subshells

The completely filled and completely half-filled subshells are stable due to the following reasons:

1. Symmetrical distribution of electrons: It is well known that symmetry leads to stability. The completely filled or half filled subshells have symmetrical distribution of electrons in them and are therefore more stable. Electrons in the same subshell (here *3d*) have equal energy but different spatial distribution. Consequently, their shielding of one-another is relatively small and the electrons are more strongly attracted by the nucleus.

2. Exchange Energy : The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or completely filled (Fig. 2.18). As a result the exchange energy is maximum and so is the stability.

You may note that the exchange energy is at the basis of Hund's rule that electrons which enter orbitals of equal energy have parallel spins as far as possible. In other words, the extra stability of half-filled and completely filled subshell is due to: (i) relatively small shielding, (ii) smaller coulombic repulsion energy, and (iii) larger exchange energy. Details about the exchange energy will be dealt with in higher classes.

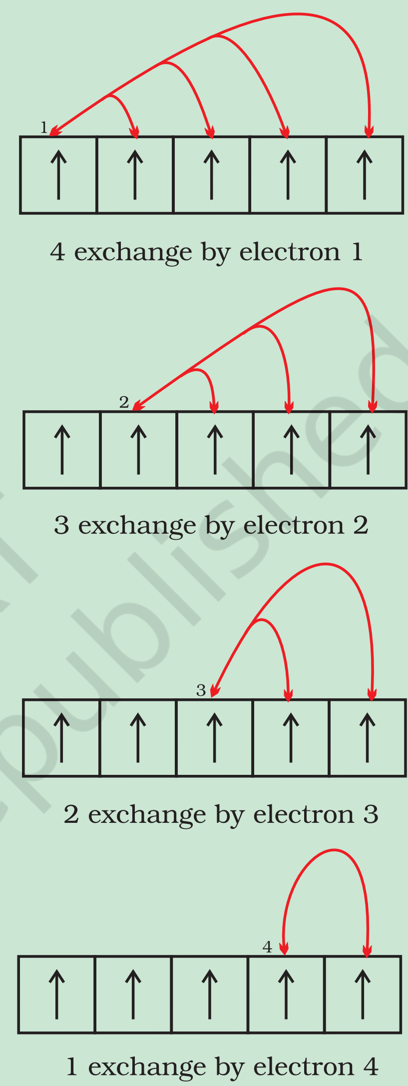


Fig. 2.18 *Possible exchange for a d^5 configuration*

Table 2.6 Electronic Configurations of the Elements

Element	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
H	1	1																	
He	2	2																	
Li	3	2	1																
Be	4	2	2																
B	5	2	2	1															
C	6	2	2	2															
N	7	2	2	3															
O	8	2	2	4															
F	9	2	2	5															
Ne	10	2	2	6															
Na	11	2	2	6	1														
Mg	12	2	2	6	2														
Al	13	2	2	6	2	1													
Si	14	2	2	6	2	2													
P	15	2	2	6	2	3													
S	16	2	2	6	2	4													
Cl	17	2	2	6	2	5													
Ar	18	2	2	6	2	6													
K	19	2	2	6	2	6		1											
Ca	20	2	2	6	2	6		2											
Sc	21	2	2	6	2	6	1	2											
Ti	22	2	2	6	2	6	2	2											
V	23	2	2	6	2	6	3	2											
Cr*	24	2	2	6	2	6	5	1											
Mn	25	2	2	6	2	6	5	2											
Fe	26	2	2	6	2	6	6	2											
Co	27	2	2	6	2	6	7	2											
Ni	28	2	2	6	2	6	8	2											
Cu*	29	2	2	6	2	6	10	1											
Zn	30	2	2	6	2	6	10	2											
Ga	31	2	2	6	2	6	10	2	1										
Ge	32	2	2	6	2	6	10	2	2										
As	33	2	2	6	2	6	10	2	3										
Se	34	2	2	6	2	6	10	2	4										
Br	35	2	2	6	2	6	10	2	5										
Kr	36	2	2	6	2	6	10	2	6										
Rb	37	2	2	6	2	6	10	2	6			1							
Sr	38	2	2	6	2	6	10	2	6			2							
Y	39	2	2	6	2	6	10	2	6	1		2							
Zr	40	2	2	6	2	6	10	2	6	2		2							
Nb*	41	2	2	6	2	6	10	2	6	4		1							
Mo*	42	2	2	6	2	6	10	2	6	5		1							
Tc	43	2	2	6	2	6	10	2	6	5		2							
Ru*	44	2	2	6	2	6	10	2	6	7		1							
Rh*	45	2	2	6	2	6	10	2	6	8		1							
Pd*	46	2	2	6	2	6	10	2	6	10									
Ag*	47	2	2	6	2	6	10	2	6	10		1							
Cd	48	2	2	6	2	6	10	2	6	10		2							
In	49	2	2	6	2	6	10	2	6	10		2	1						
Sn	50	2	2	6	2	6	10	2	6	10		2	2						
Sb	51	2	2	6	2	6	10	2	6	10		2	3						
Te	52	2	2	6	2	6	10	2	6	10		2	4						
I	53	2	2	6	2	6	10	2	6	10		2	5						
Xe	54	2	2	6	2	6	10	2	6	10		2	6						

* *Elements with exceptional electronic configurations*

Element	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
Cs	55	2	2	6	2	6	10	2	6	10		2	6			1			
Ba	56	2	2	6	2	6	10	2	6	10		2	6			2			
La*	57	2	2	6	2	6	10	2	6	10		2	6	1		2			
Ce*	58	2	2	6	2	6	10	2	6	10	2	2	6			2			
Pr	59	2	2	6	2	6	10	2	6	10	3	2	6			2			
Nd	60	2	2	6	2	6	10	2	6	10	4	2	6			2			
Pm	61	2	2	6	2	6	10	2	6	10	5	2	6			2			
Sm	62	2	2	6	2	6	10	2	6	10	6	2	6			2			
Eu	63	2	2	6	2	6	10	2	6	10	7	2	6			2			
Gd*	64	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
Tb	65	2	2	6	2	6	10	2	6	10	9	2	6			2			
Dy	66	2	2	6	2	6	10	2	6	10	10	2	6			2			
Ho	67	2	2	6	2	6	10	2	6	10	11	2	6			2			
Er	68	2	2	6	2	6	10	2	6	10	12	2	6			2			
Tm	69	2	2	6	2	6	10	2	6	10	13	2	6			2			
Yb	70	2	2	6	2	6	10	2	6	10	14	2	6			2			
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
W	74	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
Pt*	78	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
Au*	79	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
At	85	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
Fr	87	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
Pa	91	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
Np	93	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
Pu	94	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
Am	95	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
Cm	96	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
Bk	97	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
Cf	98	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
Es	99	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
Fm	100	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
Md	101	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
No	102	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2
Lr	103	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2
Rf	104	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	2	2
Db	105	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	3	2
Sg	106	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	4	2
Bh	107	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6	5	2
Hs	108	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	6	2
Mt	109	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	7	2
Ds	110	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	8	2
Rg**	111	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	10	1

*** Elements with atomic number 112 and above have been reported but not yet fully authenticated and named.*

SUMMARY

Atoms are the building blocks of elements. They are the smallest parts of an element that chemically react. The first atomic theory, proposed by John Dalton in 1808, regarded atom as the ultimate indivisible particle of matter. Towards the end of the nineteenth century, it was proved experimentally that atoms are divisible and consist of three fundamental particles: **electrons**, **protons** and **neutrons**. The discovery of sub-atomic particles led to the proposal of various atomic models to explain the structure of atom.

Thomson in 1898 proposed that an atom consists of uniform sphere of positive electricity with electrons embedded into it. This model in which mass of the atom is considered to be evenly spread over the atom was proved wrong by Rutherford's famous alpha-particle scattering experiment in 1909. Rutherford concluded that atom is made of a tiny positively charged **nucleus**, at its centre with electrons revolving around it in **circular orbits**. **Rutherford model**, which resembles the solar system, was no doubt an improvement over **Thomson model** but it could not account for the stability of the atom i.e., why the electron does not fall into the nucleus. Further, it was also silent about the electronic structure of atoms i.e., about the distribution and relative energies of electrons around the nucleus. The difficulties of the Rutherford model were overcome by Niels Bohr in 1913 in his model of the hydrogen atom. Bohr postulated that electron moves around the nucleus in circular orbits. Only certain orbits can exist and each orbit corresponds to a specific energy. Bohr calculated the energy of electron in various orbits and for each orbit predicted the distance between the electron and nucleus. **Bohr model**, though offering a satisfactory model for explaining the spectra of the hydrogen atom, could not explain the spectra of multi-electron atoms. The reason for this was soon discovered. In Bohr model, an electron is regarded as a charged particle moving in a well defined circular orbit about the nucleus. The wave character of the electron is ignored in Bohr's theory. An orbit is a clearly defined path and this path can completely be defined only if both the exact position and the exact velocity of the electron at the same time are known. This is not possible according to the Heisenberg uncertainty principle. Bohr model of the hydrogen atom, therefore, not only ignores the dual behaviour of electron but also contradicts **Heisenberg uncertainty principle**.

Erwin Schrödinger, in 1926, proposed an equation called Schrödinger equation to describe the electron distributions in space and the allowed energy levels in atoms. This equation incorporates de Broglie's concept of **wave-particle duality** and is consistent with Heisenberg uncertainty principle. When Schrödinger equation is solved for the electron in a hydrogen atom, the solution gives the possible energy states the electron can occupy [and the corresponding wave function(s) (ψ) (which in fact are the mathematical functions) of the electron associated with each energy state]. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (**principal quantum number** n, **azimuthal quantum number** l and **magnetic quantum number** m_l) arise as a natural consequence in the solution of the Schrödinger equation. The restrictions on the values of these three quantum numbers also come naturally from this solution. The quantum mechanical model of the hydrogen atom successfully predicts all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

According to the quantum mechanical model of the atom, the electron distribution of an atom containing a number of electrons is divided into **shells**. The shells, in turn, are thought to consist of one or more **subshells** and subshells are assumed to be composed of one or more orbitals, which the electrons occupy. While for hydrogen and hydrogen like systems (such as He^+, Li^{2+} etc.) all the orbitals within a given shell have same energy, the energy of the orbitals in a multi-electron atom depends upon the values of n and l: The lower the value of ($n + l$) for an orbital, the lower is its energy. If two orbitals have the same ($n + l$) value, the orbital with lower value of n has the lower energy. In an atom many such orbitals are possible and electrons are filled in those orbitals in order of increasing energy in accordance with **Pauli exclusion principle** (no two electrons in an atom can have the same set of four quantum numbers) and **Hund's rule of maximum multiplicity** (pairing of electrons in the orbitals belonging to the same subshell does not take place until each orbital belonging to that subshell has got one electron each, i.e., is singly occupied). This forms the basis of the electronic structure of atoms.

EXERCISES

2.1 (i) Calculate the number of electrons which will together weigh one gram.
(ii) Calculate the mass and charge of one mole of electrons.

2.2 (i) Calculate the total number of electrons present in one mole of methane.
(ii) Find (a) the total number and (b) the total mass of neutrons in 7 mg of ^{14}C. (Assume that mass of a neutron = 1.675×10^{-27} kg).
(iii) Find (a) the total number and (b) the total mass of protons in 34 mg of NH_3 at STP.
Will the answer change if the temperature and pressure are changed ?

2.3 How many neutrons and protons are there in the following nuclei ?
$^{13}_{6}C$, $^{16}_{8}O$, $^{24}_{12}Mg$, $^{56}_{26}Fe$, $^{88}_{38}Sr$

2.4 Write the complete symbol for the atom with the given atomic number (Z) and atomic mass (A)
(i) Z = 17 , A = 35.
(ii) Z = 92 , A = 233.
(iii) Z = 4 , A = 9.

2.5 Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency (ν) and wavenumber ($\bar{\nu}$) of the yellow light.

2.6 Find energy of each of the photons which
(i) correspond to light of frequency 3×10^{15} Hz.
(ii) have wavelength of 0.50 Å.

2.7 Calculate the wavelength, frequency and wavenumber of a light wave whose period is 2.0×10^{-10} s.

2.8 What is the number of photons of light with a wavelength of 4000 pm that provide 1J of energy?

2.9 A photon of wavelength 4×10^{-7} m strikes on metal surface, the work function of the metal being 2.13 eV. Calculate (i) the energy of the photon (eV), (ii) the kinetic energy of the emission, and (iii) the velocity of the photoelectron (1 eV= 1.6020×10^{-19} J).

2.10 Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

2.11 A 25 watt bulb emits monochromatic yellow light of wavelength of 0.57μm. Calculate the rate of emission of quanta per second.

2.12 Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate threshold frequency (ν_0) and work function (W_0) of the metal.

2.13 What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with n = 4 to an energy level with n = 2?

2.14 How much energy is required to ionise a H atom if the electron occupies $n = 5$ orbit? Compare your answer with the ionization enthalpy of H atom (energy required to remove the electron from $n = 1$ orbit).

2.15 What is the maximum number of emission lines when the excited electron of a H atom in $n = 6$ drops to the ground state?

2.16 (i) The energy associated with the first orbit in the hydrogen atom is -2.18×10^{-18} J atom^{-1}. What is the energy associated with the fifth orbit?
(ii) Calculate the radius of Bohr's fifth orbit for hydrogen atom.

2.17 Calculate the wavenumber for the longest wavelength transition in the Balmer series of atomic hydrogen.

2.18 What is the energy in joules, required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state? The ground state electron energy is -2.18×10^{-11} ergs.

2.19 The electron energy in hydrogen atom is given by $E_n = (-2.18 \times 10^{-18})/n^2$ J. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength of light in cm that can be used to cause this transition?

2.20 Calculate the wavelength of an electron moving with a velocity of 2.05×10^7 m s^{-1}.

2.21 The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

2.22 Which of the following are isoelectronic species i.e., those having the same number of electrons?

Na^+, K^+, Mg^{2+}, Ca^{2+}, S^{2-}, Ar.

2.23 (i) Write the electronic configurations of the following ions: (a) H^- (b) Na^+ (c) O^{2-} (d) F^-
(ii) What are the atomic numbers of elements whose outermost electrons are represented by (a) $3s^1$ (b) $2p^3$ and (c) $3p^5$?
(iii) Which atoms are indicated by the following configurations ?
(a) [He] $2s^1$ (b) [Ne] $3s^2\ 3p^3$ (c) [Ar] $4s^2\ 3d^1$.

2.24 What is the lowest value of n that allows g orbitals to exist?

2.25 An electron is in one of the $3d$ orbitals. Give the possible values of n, l and m_l for this electron.

2.26 An atom of an element contains 29 electrons and 35 neutrons. Deduce (i) the number of protons and (ii) the electronic configuration of the element.

2.27 Give the number of electrons in the species H_2^+, H_2 and O_2^+

2.28 (i) An atomic orbital has $n = 3$. What are the possible values of l and m_l ?
(ii) List the quantum numbers (m_l and l) of electrons for $3d$ orbital.
(iii) Which of the following orbitals are possible?
$1p$, $2s$, $2p$ and $3f$

2.29 Using s, p, d notations, describe the orbital with the following quantum numbers.
(a) $n=1$, $l=0$; (b) $n = 3$; $l=1$ (c) $n = 4$; $l=2$; (d) $n=4$; $l=3$.

2.30 Explain, giving reasons, which of the following sets of quantum numbers are not possible.

(a)	$n = 0,$	$l = 0,$	$m_l = 0,$	$m_s = +\frac{1}{2}$
(b)	$n = 1,$	$l = 0,$	$m_l = 0,$	$m_s = -\frac{1}{2}$
(c)	$n = 1,$	$l = 1,$	$m_l = 0,$	$m_s = +\frac{1}{2}$
(d)	$n = 2,$	$l = 1,$	$m_l = 0,$	$m_s = -\frac{1}{2}$

(e) $n = 3$, $l = 3$, $m_l = -3$, $m_s = +\frac{1}{2}$

(f) $n = 3$, $l = 1$, $m_l = 0$, $m_s = +\frac{1}{2}$

2.31 How many electrons in an atom may have the following quantum numbers?
(a) $n = 4$, $m_s = -\frac{1}{2}$ (b) $n = 3$, $l = 0$

2.32 Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around the orbit.

2.33 What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum ?

2.34 Calculate the energy required for the process

$He^+ (g) \rightarrow He^{2+} (g) + e^-$

The ionization energy for the H atom in the ground state is 2.18×10^{-18} J atom^{-1}

2.35 If the diameter of a carbon atom is 0.15 nm, calculate the number of carbon atoms which can be placed side by side in a straight line across length of scale of length 20 cm long.

2.36 2×10^8 atoms of carbon are arranged side by side. Calculate the radius of carbon atom if the length of this arrangement is 2.4 cm.

2.37 The diameter of zinc atom is 2.6 Å.Calculate (a) radius of zinc atom in pm and (b) number of atoms present in a length of 1.6 cm if the zinc atoms are arranged side by side lengthwise.

2.38 A certain particle carries 2.5×10^{-16}C of static electric charge. Calculate the number of electrons present in it.

2.39 In Milikan's experiment, static electric charge on the oil drops has been obtained by shining X-rays. If the static electric charge on the oil drop is -1.282×10^{-18}C, calculate the number of electrons present on it.

2.40 In Rutherford's experiment, generally the thin foil of heavy atoms, like gold, platinum etc. have been used to be bombarded by the α-particles. If the thin foil of light atoms like aluminium etc. is used, what difference would be observed from the above results ?

2.41 Symbols $^{79}_{35}Br$ and ^{79}Br can be written, whereas symbols $^{35}_{79}Br$ and ^{35}Br are not acceptable. Answer briefly.

2.42 An element with mass number 81 contains 31.7% more neutrons as compared to protons. Assign the atomic symbol.

2.43 An ion with mass number 37 possesses one unit of negative charge. If the ion conatins 11.1% more neutrons than the electrons, find the symbol of the ion.

2.44 An ion with mass number 56 contains 3 units of positive charge and 30.4% more neutrons than electrons. Assign the symbol to this ion.

2.45 Arrange the following type of radiations in increasing order of frequency: (a) radiation from microwave oven (b) amber light from traffic signal (c) radiation from FM radio (d) cosmic rays from outer space and (e) X-rays.

2.46 Nitrogen laser produces a radiation at a wavelength of 337.1 nm. If the number of photons emitted is 5.6×10^{24}, calculate the power of this laser.

2.47 Neon gas is generally used in the sign boards. If it emits strongly at 616 nm, calculate (a) the frequency of emission, (b) distance traveled by this radiation in 30 s (c) energy of quantum and (d) number of quanta present if it produces 2 J of energy.

2.48 In astronomical observations, signals observed from the distant stars are generally weak. If the photon detector receives a total of 3.15×10^{-18} J from the radiations of 600 nm, calculate the number of photons received by the detector.

2.49 Lifetimes of the molecules in the excited states are often measured by using pulsed radiation source of duration nearly in the nano second range. If the radiation source has the duration of 2 ns and the number of photons emitted during the pulse source is 2.5×10^{15}, calculate the energy of the source.

2.50 The longest wavelength doublet absorption transition is observed at 589 and 589.6 nm. Calcualte the frequency of each transition and energy difference between two excited states.

2.51 The work function for caesium atom is 1.9 eV. Calculate (a) the threshold wavelength and (b) the threshold frequency of the radiation. If the caesium element is irradiated with a wavelength 500 nm, calculate the kinetic energy and the velocity of the ejected photoelectron.

2.52 Following results are observed when sodium metal is irradiated with different wavelengths. Calculate (a) threshold wavelength and, (b) Planck's constant.

λ (nm)	500	450	400
$v \times 10^{-5}$ (cm s^{-1})	2.55	4.35	5.35

2.53 The ejection of the photoelectron from the silver metal in the photoelectric effect experiment can be stopped by applying the voltage of 0.35 V when the radiation 256.7 nm is used. Calculate the work function for silver metal.

2.54 If the photon of the wavelength 150 pm strikes an atom and one of tis inner bound electrons is ejected out with a velocity of 1.5×10^7 m s^{-1}, calculate the energy with which it is bound to the nucleus.

2.55 Emission transitions in the Paschen series end at orbit n = 3 and start from orbit n and can be represeted as $\upsilon = 3.29 \times 10^{15}$ (Hz) [$1/3^2 - 1/n^2$]
Calculate the value of n if the transition is observed at 1285 nm. Find the region of the spectrum.

2.56 Calculate the wavelength for the emission transition if it starts from the orbit having radius 1.3225 nm and ends at 211.6 pm. Name the series to which this transition belongs and the region of the spectrum.

2.57 Dual behaviour of matter proposed by de Broglie led to the discovery of electron microscope often used for the highly magnified images of biological molecules and other type of material. If the velocity of the electron in this microscope is 1.6×10^6 ms^{-1}, calculate de Broglie wavelength associated with this electron.

2.58 Similar to electron diffraction, neutron diffraction microscope is also used for the determination of the structure of molecules. If the wavelength used here is 800 pm, calculate the characteristic velocity associated with the neutron.

2.59 If the velocity of the electron in Bohr's first orbit is 2.19×10^6 ms^{-1}, calculate the de Broglie wavelength associated with it.

2.60 The velocity associated with a proton moving in a potential difference of 1000 V is 4.37×10^5 ms^{-1}. If the hockey ball of mass 0.1 kg is moving with this velocity, calcualte the wavelength associated with this velocity.

2.61 If the position of the electron is measured within an accuracy of $\pm$ 0.002 nm, calculate the uncertainty in the momentum of the electron. Suppose the momentum of the electron is $h/4\pi_m \times 0.05$ nm, is there any problem in defining this value.

2.62 The quantum numbers of six electrons are given below. Arrange them in order of increasing energies. If any of these combination(s) has/have the same energy lists:

1. $n = 4,\ l = 2,\ m_l = -2\ ,\ m_s = -1/2$
2. $n = 3,\ l = 2,\ m_l = 1\ ,\ m_s = +1/2$

3. $n = 4,\ l = 1,\ m_l = 0\ ,\ m_s = +1/2$
4. $n = 3,\ l = 2,\ m_l = -2\ ,\ m_s = -1/2$
5. $n = 3,\ l = 1,\ m_l = -1\ ,\ m_s = +1/2$
6. $n = 4,\ l = 1,\ m_l = 0\ ,\ m_s = +1/2$

2.63 The bromine atom possesses 35 electrons. It contains 6 electrons in 2*p* orbital, 6 electrons in 3*p* orbital and 5 electron in 4*p* orbital. Which of these electron experiences the lowest effective nuclear charge ?

2.64 Among the following pairs of orbitals which orbital will experience the larger effective nuclear charge? (i) 2*s* and 3*s*, (ii) 4*d* and 4*f*, (iii) 3*d* and 3*p*.

2.65 The unpaired electrons in Al and Si are present in 3*p* orbital. Which electrons will experience more effective nuclear charge from the nucleus ?

2.66 Indicate the number of unpaired electrons in : (a) P, (b) Si, (c) Cr, (d) Fe and (e) Kr.

2.67 (a) How many subshells are associated with $n = 4$? (b) How many electrons will be present in the subshells having m_s value of $-1/2$ for $n = 4$?

UNIT 3

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Objectives

After studying this Unit, you will be able to

- appreciate how the concept of grouping elements in accordance to their properties led to the development of Periodic Table.
- understand the Periodic Law;
- understand the significance of atomic number and electronic configuration as the basis for periodic classification;
- name the elements with Z >100 according to IUPAC nomenclature;
- classify elements into *s*, *p*, *d*, *f* blocks and learn their main characteristics;
- recognise the periodic trends in physical and chemical properties of elements;
- compare the reactivity of elements and correlate it with their occurrence in nature;
- explain the relationship between ionization enthalpy and metallic character;
- use scientific vocabulary appropriately to communicate ideas related to certain important properties of atoms e.g., atomic/ionic radii, ionization enthalpy, electron gain enthalpy, electronegativity, valence of elements.

"The Periodic Table is arguably the most important concept in chemistry, both in principle and in practice. It is the everyday support for students, it suggests new avenues of research to professionals, and it provides a succinct organization of the whole of chemistry. It is a remarkable demonstration of the fact that the chemical elements are not a random cluster of entities but instead display trends and lie together in families. An awareness of the Periodic Table is essential to anyone who wishes to disentangle the world and see how it is built up from the fundamental building blocks of the chemistry, the chemical elements."

Glenn T. Seaborg

In this Unit, we will study the historical development of the Periodic Table as it stands today and the Modern Periodic Law. We will also learn how the periodic classification follows as a logical consequence of the electronic configuration of atoms. Finally, we shall examine some of the periodic trends in the physical and chemical properties of the elements.

3.1 WHY DO WE NEED TO CLASSIFY ELEMENTS ?

We know by now that the elements are the basic units of all types of matter. In 1800, only 31 elements were known. By 1865, the number of identified elements had more than doubled to 63. At present 114 elements are known. Of them, the recently discovered elements are man-made. Efforts to synthesise new elements are continuing. With such a large number of elements it is very difficult to study individually the chemistry of all these elements and their innumerable compounds individually. To ease out this problem, scientists searched for a systematic way to organise their knowledge by classifying the elements. Not only that it would rationalize known chemical facts about elements, but even predict new ones for undertaking further study.

3.2 GENESIS OF PERIODIC CLASSIFICATION

Classification of elements into groups and development of Periodic Law and Periodic Table are the consequences of systematising the knowledge gained by a number of scientists through their observations and experiments. The German chemist, Johann Dobereiner in early 1800's was the first to consider the idea of trends among properties of elements. By 1829 he noted a similarity among the physical and chemical properties of several groups of three elements (**Triads**). In each case, he noticed that the middle element of each of the **Triads** had an atomic weight about half way between the atomic weights of the other two (Table 3.1). Also the properties of the middle element were in between those of the other two members. Since Dobereiner's relationship, referred to as the **Law of Triads**, seemed to work only for a few elements, it was dismissed as coincidence. The next reported attempt to classify elements was made by a French geologist, A.E.B. de Chancourtois in 1862. He arranged the then known elements in order of increasing atomic weights and made a cylindrical table of elements to display the periodic recurrence of properties. This also did not attract much attention. The English chemist, John Alexander Newlands in 1865 profounded the **Law of Octaves**. He arranged the elements in increasing order of their atomic weights and noted that every eighth element had properties similar to the first element (Table 3.2). The relationship was just like every eighth note that resembles the first in octaves of music. Newlands's Law of Octaves seemed to be true only for elements up to calcium. Although his idea was not widely accepted at that time, he, for his work, was later awarded Davy Medal in 1887 by the Royal Society, London.

The Periodic Law, as we know it today owes its development to the Russian chemist, Dmitri Mendeleev (1834-1907) and the German chemist, Lothar Meyer (1830-1895). Working independently, both the chemists in 1869 proposed that on arranging elements in the increasing order of their atomic weights, similarities appear in physical and chemical properties at regular intervals. Lothar Meyer plotted the physical properties such as atomic volume, melting point and boiling point against atomic weight and obtained a periodically repeated pattern. Unlike Newlands, Lothar Meyer observed a change in length of that repeating pattern. By 1868, Lothar Meyer had developed a table of the

Table 3.1 Dobereiner's Triads

Element	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	**Ca**	40	**Cl**	35.5
Na	23	**Sr**	88	**Br**	80
K	39	**Ba**	137	**I**	127

Table 3.2 Newlands' Octaves

Element	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
At. wt.	7	9	11	12	14	16	19
Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
At. wt.	23	24	27	29	31	32	35.5
Element	**K**	**Ca**					
At. wt.	39	40					

elements that closely resembles the Modern Periodic Table. However, his work was not published until after the work of Dmitri Mendeleev, the scientist who is generally credited with the development of the Modern Periodic Table.

While Dobereiner initiated the study of periodic relationship, it was Mendeleev who was responsible for publishing the Periodic Law for the first time. It states as follows :

The properties of the elements are a periodic function of their atomic weights.

Mendeleev arranged elements in horizontal rows and vertical columns of a table in order of their increasing atomic weights in such a way that the elements with similar properties occupied the same vertical column or group. Mendeleev's system of classifying elements was more elaborate than that of Lothar Meyer's. He fully recognized the significance of periodicity and used broader range of physical and chemical properties to classify the elements. In particular, Mendeleev relied on the similarities in the empirical formulas and properties of the compounds formed by the elements. He realized that some of the elements did not fit in with his scheme of classification if the order of atomic weight was strictly followed. He ignored the order of atomic weights, thinking that the atomic measurements might be incorrect, and placed the elements with similar properties together. For example, iodine with lower atomic weight than that of tellurium (Group VI) was placed in Group VII along with fluorine, chlorine, bromine because of similarities in properties (Fig. 3.1). At the same time, keeping his primary aim of arranging the elements of similar properties in the same group, he proposed that some of the elements were still undiscovered and, therefore, left several gaps in the table. For example, both gallium and germanium were unknown at the time Mendeleev published his Periodic Table. He left the gap under aluminium and a gap under silicon, and called these elements **Eka-Aluminium** and **Eka-Silicon.** Mendeleev predicted not only the existence of gallium and germanium, but also described some of their general physical properties. These elements were discovered later. Some of the properties predicted by Mendeleev for these elements and those found experimentally are listed in Table 3.3.

The boldness of Mendeleev's quantitative predictions and their eventual success made him and his Periodic Table famous. Mendeleev's Periodic Table published in 1905 is shown in Fig. 3.1.

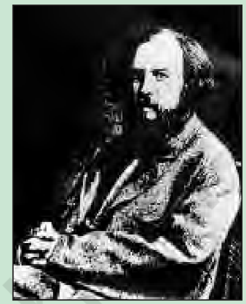
Table 3.3 Mendeleev's Predictions for the Elements Eka-aluminium (Gallium) and Eka-silicon (Germanium)

Property	Eka-aluminium (predicted)	Gallium (found)	Eka-silicon (predicted)	Germanium (found)
Atomic weight	68	70	72	72.6
Density / (g/cm³)	5.9	5.94	5.5	5.36
Melting point /K	Low	302.93	High	1231
Formula of oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
Formula of chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$

PERIODIC SYSTEM OF THE ELEMENTS IN GROUPS AND SERIES

SERIES	GROUPS OF ELEMENTS								
	0	I	II	III	IV	V	VI	VII	VIII
1	-	Hydrogen H 1.008	-	-					
2	Helium He 4.0	Lithium Li 7.03	Beryllium Be 9.1	Boron B 11.0	Carbon C 12.0	Nitrogen N 14.04	Oxygen O 16.00	Fluorine F 19.0	
3	Neon Ne 19.9	Sodium Na 23.5	Magnesium Mg 24.3	Aluminium Al 27.0	Silicon Si 28.4	Phosphorus P 31.0	Sulphur S 32.06	Chlorine Cl 35.45	
4	Argon Ar 38	Potassium K 39.1	Calcium Ca 40.1	Scandium Sc 44.1	Titanium Ti 48.1	Vanadium V 51.4	Chromium Cr 52.1	Manganese Mn 55.0	Iron Fe 55.9, Cobalt Co 59, Nickel Ni 59 (Cu)
5		Copper Cu 63.6	Zinc Zn 65.4	Gallium Ga 70.0	Germanium Ge 72.3	Arsenic As 75	Selenium Se 79	Bromine Br 79.95	
6	Krypton Kr 81.8	Rubidium Rb 85.4	Strontium Sr 87.6	Yttrium Y 89.0	Zirconium Zr 90.6	Niobium Nb 94.0	Molybdenum Mo 96.0	-	Ruthenium Ru 101.7, Rhodium Rh 103.0, Palladium Pd 106.5 (Ag)
7		Silver Ag 107.9	Cadmium Cd 112.4	Indium In 114.0	Tin Sn 119.0	Antimony Sb 120.0	Tellurium Te 127.6	Iodine I 126.9	
8	Xenon Xe 128	Caesium Cs 132.9	Barium Ba 137.4	Lanthanum La 139	Cerium Ce 140	-	-	-	
9		-	-	-	-	-	-	-	
10	-	-	-	Ytterbium Yb 173	-	Tantalum Ta 183	Tungsten W 184	-	Osmium Os 191, Iridium Ir 193, Platinum Pt 194.9 (Au)
11		Gold Au 197.2	Mercury Hg 200.0	Thallium Tl 204.1	Lead Pb 206.9	Bismuth Bi 208	-	-	
12	-	-	Radium Ra 224	-	Thorium Th 232	-	Uranium U 239		
HIGHER SALINE OXIDES	R	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
HIGHER GASEOUS HYDROGEN COMPOUNDS					RH_4	RH_3	RH_2	RH	

Fig. 3.1 *Mendeleev's Periodic Table published earlier*



Dmitri Ivanovich Mendeleev
(1834-1907)

Dmitri Mendeleev was born in Tobalsk, Siberia in Russia. After his father's death, the family moved to St. Petersburg. He received his Master's degree in Chemistry in 1856 and the doctoral degree in 1865. He taught at the University of St.Petersburg where he was appointed Professor of General Chemistry in 1867. Preliminary work for his great textbook "Principles of Chemistry" led Mendeleev to propose the ***Periodic Law*** *and to construct his* ***Periodic Table*** *of elements. At that time, the structure of atom was unknown and Mendeleev's idea to consider that the properties of the elements were in someway related to their atomic masses was a very imaginative one. To place certain elements into the correct group from the point of view of their chemical properties, Mendeleev reversed the order of some pairs of elements and asserted that their atomic masses were incorrect. Mendeleev also had the foresight to leave gaps in the Periodic Table for elements unknown at that time and predict their properties from the trends that he observed among the properties of related elements. Mendeleev's predictions were proved to be astonishingly correct when these elements were discovered later.*

Mendeleev's Periodic Law spurred several areas of research during the subsequent decades. The discovery of the first two noble gases helium and argon in 1890 suggested the possibility that there must be other similar elements to fill an entire family. This idea led Ramsay to his successful search for krypton and xenon. Work on the radioactive decay series for uranium and thorium in the early years of twentieth century was also guided by the Periodic Table.

Mendeleev was a versatile genius. He worked on many problems connected with Russia's natural resources. He invented an accurate barometer. In 1890, he resigned from the Professorship. He was appointed as the Director of the Bureau of Weights and Measures. He continued to carry out important research work in many areas until his death in 1907.

You will notice from the modern Period Table (Fig. 3.2) that Mendeleev's name has been immortalized by naming the element with atomic number 101, as Mendelevium. This name was proposed by American scientist Glenn T. Seaborg, the discoverer of this element, "in recognition of the pioneering role of the great Russian Chemist who was the first to use the periodic system of elements to predict the chemical properties of undiscovered elements, a principle which has been the key to the discovery of nearly all the transuranium elements".

3.3 MODERN PERIODIC LAW AND THE PRESENT FORM OF THE PERIODIC TABLE

We must bear in mind that when Mendeleev developed his **Periodic Table**, chemists knew nothing about the internal structure of atom. However, the beginning of the 20th century witnessed profound developments in theories about sub-atomic particles. In 1913, the English physicist, Henry Moseley observed regularities in the characteristic *X-ray spectra* of the elements. A plot of $\sqrt{\nu}$ (where ν is frequency of X-rays emitted) against atomic number (Z) gave a straight line and not the plot of $\sqrt{\nu}$ *vs* atomic mass. He thereby showed that the atomic number is a more fundamental property of an element than its atomic mass. **Mendeleev's Periodic Law** was, therefore, accordingly modified. This is known as the **Modern Periodic Law** and can be stated as :

> ***The physical and chemical properties of the elements are periodic functions of their atomic numbers.***

The **Periodic Law** revealed important analogies among the 94 naturally occurring elements (neptunium and plutonium like actinium and protoactinium are also found in pitch blende – an ore of uranium). It stimulated renewed interest in Inorganic Chemistry and has carried into the present with the creation of artificially produced short-lived elements.

You may recall that the atomic number is equal to the nuclear charge (*i.e.*, number of protons) or the number of electrons in a neutral atom. It is then easy to visualize the significance of quantum numbers and electronic configurations in periodicity of elements. In fact, it is now recognized that the Periodic Law is essentially the consequence of the periodic variation in electronic configurations, which indeed determine the physical and chemical properties of elements and their compounds.

Numerous forms of Periodic Table have been devised from time to time. Some forms emphasise chemical reactions and valence, whereas others stress the electronic configuration of elements. A modern version, the so-called "**long form**" of the **Periodic Table** of the elements (Fig. 3.2), is the most convenient and widely used. The horizontal rows (which Mendeleev called **series**) are called **periods** and the vertical columns, **groups**. Elements having similar outer electronic configurations in their atoms are arranged in vertical columns, referred to as **groups** or **families**. According to the recommendation of International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18 replacing the older notation of groups IA … VIIA, VIII, IB … VIIB and 0.

There are altogether seven periods. The period number corresponds to the highest principal quantum number (n) of the elements in the period. The first period contains 2 elements. The subsequent periods consists of 8, 8, 18, 18 and 32 elements, respectively. The seventh period is incomplete and like the sixth period would have a theoretical maximum (on the basis of quantum numbers) of 32 elements. In this form of the Periodic Table, 14 elements of both sixth and seventh periods (lanthanoids and actinoids, respectively) are placed in separate panels at the bottom*.

3.4 NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBERS > 100

The naming of the new elements had been traditionally the privilege of the discoverer (or discoverers) and the suggested name was ratified by the IUPAC. In recent years this has led to some controversy. The new elements with very high atomic numbers are so unstable that only minute quantities, sometimes only a few atoms of them are obtained. Their synthesis and characterisation, therefore, require highly

* *Glenn T. Seaborg's work in the middle of the 20th century starting with the discovery of plutonium in 1940, followed by those of all the transuranium elements from 94 to 102 led to reconfiguration of the periodic table placing the actinoids below the lanthanoids. In 1951, Seaborg was awarded the **Nobel Prize** in chemistry for his work. Element 106 has been named Seaborgium (Sg) in his honour.*

Representative elements

GROUP NUMBER

d-Transition elements

Representative elements

GROUP NUMBER

Noble gases

f - Inner transition elements

1 H $1s^1$

PERIOD NUMBER	1 I A	2 II A	3 III A	4 IV A	5 V A	6 VI A	7 VII A	8 ←	9 VIII	10 →	11 I B	12 II B	13 III B	14 IV B	15 V B	16 VI B	17 VII B	18 0
1																		2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10}5s^1$	48 Cd $4d^{10}5s^2$	49 In $5s^25p^1$	50 Sn $5s^25p^2$	51 Sb $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^16s^2$	72 Hf $4f^{14}5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$	81 T*l* $6s^26p^1$	82 Pb $6s^26p^2$	83 Bi $6s^26p^3$	84 Po $6s^26p^4$	85 At $6s^26p^5$	86 Rn $6s^26p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^17s^2$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

*Lanthanoids $4f^n5d^{0-1}6s^2$	58 Ce $4f^25d^06s^2$	59 Pr $4f^35d^06s^2$	60 Nd $4f^45d^06s^2$	61 Pm $4f^55d^06s^2$	62 Sm $4f^65d^06s^2$	63 Eu $4f^75d^06s^2$	64 Gd $4f^75d^16s^2$	65 Tb $4f^95d^06s^2$	66 Dy $4f^{10}5d^06s^2$	67 Ho $4f^{11}5d^06s^2$	68 Er $4f^{12}5d^06s^2$	69 Tm $4f^{13}5d^06s^2$	70 Yb $4f^{14}5d^06s^2$	71 Lu $4f^{14}5d^16s^2$
**Actinoids $5f^n6d^{0-2}7s^2$	90 Th $5f^06d^27s^2$	91 Pa $5f^26d^17s^2$	92 U $5f^36d^17s^2$	93 Np $5f^46d^17s^2$	94 Pu $5f^66d^07s^2$	95 Am $5f^76d^07s^2$	96 Cm $5f^76d^17s^2$	97 Bk $5f^96d^07s^2$	98 Cf $5f^{10}6d^07s^2$	99 Es $5f^{11}6d^07s^2$	100 Fm $5f^{12}6d^07s^2$	101 Md $5f^{13}6d^07s^2$	102 No $5f^{14}6d^07s^2$	103 Lr $5f^{14}6d^17s^2$

Fig. 3.2 *Long form of the Periodic Table of the Elements with their atomic numbers and ground state outer electronic configurations. The groups are numbered 1-18 in accordance with the 1984 IUPAC recommendations. This notation replaces the old numbering scheme of IA–VIIA, VIII, IB–VIIB and 0 for the elements.*

sophisticated costly equipment and laboratory. Such work is carried out with competitive spirit only in some laboratories in the world. Scientists, before collecting the reliable data on the new element, at times get tempted to claim for its discovery. For example, both American and Soviet scientists claimed credit for discovering element 104. The Americans named it Rutherfordium whereas Soviets named it Kurchatovium. To avoid such problems, the IUPAC has made recommendation that until a new element's discovery is proved, and its name is officially recognised, a systematic nomenclature be derived directly from the atomic number of the element using the numerical roots for 0 and numbers 1-9. These are shown in Table 3.4. The roots are put together in order of digits which make up the atomic number and "ium" is added at the end. The IUPAC names for elements with Z above 100 are shown in Table 3.5.

Table 3.4 Notation for IUPAC Nomenclature of Elements

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

Table 3.5 Nomenclature of Elements with Atomic Number Above 100

Atomic Number	Name according to IUPAC nomenclature	Symbol	IUPAC Official Name	IUPAC Symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnillium	Uun	Darmstadtium	Ds
111	Unununnium	Uuu	Rontgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nn
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	Moscovium	Mc
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uuo	Oganesson	Og

Thus, the new element first gets a temporary name, with symbol consisting of three letters. Later permanent name and symbol are given by a vote of IUPAC representatives from each country. The permanent name might reflect the country (or state of the country) in which the element was discovered, or pay tribute to a notable scientist. As of now, elements with atomic numbers up to 118 have been discovered. Official names of all elements have been announced by IUPAC.

Problem 3.1

What would be the IUPAC name and symbol for the element with atomic number 120?

Solution

From Table 3.4, the roots for 1, 2 and 0 are un, bi and nil, respectively. Hence, the symbol and the name respectively are Ubn and unbinilium.

3.5 ELECTRONIC CONFIGURATIONS OF ELEMENTS AND THE PERIODIC TABLE

In the preceding unit we have learnt that an electron in an atom is characterised by a set of four quantum numbers, and the principal quantum number (n) defines the main energy level known as **shell**. We have also studied about the filling of electrons into different subshells, also referred to as **orbitals** (s, p, d, f) in an atom. The distribution of electrons into orbitals of an atom is called its **electronic configuration**. An element's location in the Periodic Table reflects the quantum numbers of the last orbital filled. In this section we will observe a direct connection between the electronic configurations of the elements and the long form of the Periodic Table.

(a) Electronic Configurations in Periods

The period indicates the value of n for the outermost or valence shell. In other words, successive period in the Periodic Table is associated with the filling of the next higher principal energy level ($n = 1$, $n = 2$, etc.). It can be readily seen that the number of elements in each period is twice the number of atomic **orbitals** available in the energy level that is being filled. The first period ($n = 1$) starts with the filling of the lowest level ($1s$) and therefore has two elements — hydrogen ($1s^1$) and helium ($1s^2$) when the first shell (K) is completed. The second period ($n = 2$) starts with lithium and the third electron enters the $2s$ orbital. The next element, beryllium has four electrons and has the electronic configuration $1s^2 2s^2$. Starting from the next element boron, the $2p$ orbitals are filled with electrons when the L shell is completed at neon ($2s^2 2p^6$). Thus there are 8 elements in the second period. The third period ($n = 3$) begins at sodium, and the added electron enters a $3s$ orbital. Successive filling of $3s$ and $3p$ orbitals gives rise to the third period of 8 elements from sodium to argon. The fourth period ($n = 4$) starts at potassium, and the added electrons fill up the $4s$ orbital. Now you may note that before the $4p$ orbital is filled, filling up of $3d$ orbitals becomes energetically favourable and we come across the so called $3d$ **transition series** of elements. This starts from scandium ($Z = 21$) which has the electronic configuration $3d^1 4s^2$. The $3d$ orbitals are filled at zinc (Z=30) with electronic configuration $3d^{10} 4s^2$. The fourth period ends at krypton with the filling up of the $4p$ orbitals. Altogether we have 18 elements in this fourth period. The fifth period ($n = 5$) beginning with rubidium is similar to the fourth period and contains the $4d$ **transition series** starting at yttrium ($Z = 39$). This period ends at xenon with the filling up of the $5p$ orbitals. The sixth period ($n = 6$) contains 32 elements and successive electrons enter $6s$, $4f$, $5d$ and $6p$ orbitals, in the order — filling up of the $4f$ orbitals begins with cerium ($Z = 58$) and ends at lutetium ($Z = 71$) to give the $4f$-**inner transition series** which is called the **lanthanoid series**. The seventh period ($n = 7$) is similar to the sixth period with the successive filling up of the $7s$, $5f$, $6d$ and $7p$ orbitals and includes most of the man-made radioactive elements. This period will end at the element with atomic number 118 which would belong to the noble gas family. Filling up of the $5f$ orbitals after actinium ($Z = 89$) gives the $5f$-**inner transition**

series known as the **actinoid series**. The 4*f*- and 5*f*-**inner transition series** of elements are placed separately in the Periodic Table to maintain its structure and to preserve the principle of classification by keeping elements with similar properties in a single column.

Problem 3.2

How would you justify the presence of 18 elements in the 5th period of the Periodic Table?

Solution

When $n = 5$, $l = 0, 1, 2, 3$. The order in which the energy of the available orbitals 4*d*, 5*s* and 5*p* increases is $5s < 4d < 5p$. The total number of orbitals available are 9. The maximum number of electrons that can be accommodated is 18; and therefore 18 elements are there in the 5th period.

(b) Groupwise Electronic Configurations

Elements in the same vertical column or group have similar valence shell electronic configurations, the same number of electrons in the outer orbitals, and similar properties. For example, the Group 1 elements (alkali metals) all have ns^1 valence shell electronic configuration as shown below.

Atomic number	Symbol	Electronic configuration
3	Li	$1s^2 2s^1$ **(or)** $[He]2s^1$
11	Na	$1s^2 2s^2 2p^6 3s^1$ **(or)** $[Ne]3s^1$
19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ **(or)** $[Ar]4s^1$
37	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ **(or)** $[Kr]5s^1$
55	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ **(or)** $[Xe]6s^1$
87	Fr	$[Rn]7s^1$

Thus it can be seen that the properties of an element have periodic dependence upon its atomic number and not on relative atomic mass.

3.6 ELECTRONIC CONFIGURATIONS AND TYPES OF ELEMENTS: *s*-, *p*-, *d*-, *f*- BLOCKS

The *aufbau* (build up) principle and the electronic configuration of atoms provide a theoretical foundation for the periodic classification. The elements in a vertical column of the Periodic Table constitute a group or family and exhibit similar chemical behaviour. This similarity arises because these elements have the same number and same distribution of electrons in their outermost orbitals. We can classify the elements into four blocks *viz*., ***s*-block**, ***p*-block**, ***d*-block** and ***f*-block** depending on the type of atomic orbitals that are being filled with electrons. This is illustrated in Fig. 3.3. We notice two exceptions to this categorisation. Strictly, helium belongs to the *s*-block but its positioning in the *p*-block along with other group 18 elements is justified because it has a completely filled valence shell ($1s^2$) and as a result, exhibits properties characteristic of other noble gases. The other exception is hydrogen. It has only one *s*-electron and hence can be placed in group 1 (alkali metals). It can also gain an electron to achieve a noble gas arrangement and hence it can behave similar to a group 17 (halogen family) elements. Because it is a special case, we shall place hydrogen separately at the top of the Periodic Table as shown in Fig. 3.2 and Fig. 3.3. We will briefly discuss the salient features of the four types of elements marked in the Periodic Table. More about these elements will be discussed later. During the description of their features certain terminology has been used which has been classified in section 3.7.

3.6.1 The *s*-Block Elements

The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have ns^1

s-BLOCK

	1	2
1*s*		
2*s*	Li	Be
3*s*	Na	Mg
4*s*	K	Ca
5*s*	Rb	Sr
6*s*	Cs	Ba
7*s*	Fr	Ra

H

d-BLOCK

	3	4	5	6	7	8	9	10	11	12
3*d*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4*d*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5*d*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6*d*	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn

p-BLOCK

	13	14	15	16	17	18
						He
2*p*	B	C	N	O	F	Ne
3*p*	Al	Si	P	S	Cl	Ar
4*p*	Ga	Ge	As	Se	Br	Kr
5*p*	In	Sn	Sb	Te	I	Xe
6*p*	Tl	Pb	Bi	Po	At	Rn
7*p*	Nh	Fl	Mc	Lv	Ts	Og

f-BLOCK

Lanthanoids 4*f*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinoids 5*f*	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fig. 3.3 *The types of elements in the Periodic Table based on the orbitals that are being filled. Also shown is the broad division of elements into METALS ( ) , NON-METALS ( ) and METALLOIDS ( ).*

and ns^2 outermost electronic configuration belong to the ***s*-Block Elements**. They are all reactive metals with low ionization enthalpies. They lose the outermost electron(s) readily to form 1+ ion (in the case of alkali metals) or 2+ ion (in the case of alkaline earth metals). The metallic character and the reactivity increase as we go down the group. Because of high reactivity they are never found pure in nature. The compounds of the *s*-block elements, with the exception of those of lithium and beryllium are predominantly ionic.

3.6.2 The *p*-Block Elements

The ***p*-Block Elements** comprise those belonging to Group 13 to 18 and these together with the ***s*-Block Elements** are called the **Representative Elements or Main Group Elements**. The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period. At the end of each period is a noble gas element with a closed valence shell ns^2np^6 configuration. All the orbitals in the valence shell of the **noble gases** are completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons. The noble gases thus exhibit very low chemical reactivity. Preceding the noble gas family are two chemically important groups of non-metals. They are the **halogens** (Group 17) and the **chalcogens** (Group 16). These two groups of elements have highly negative electron gain enthalpies and readily add one or two electrons respectively to attain the stable noble gas configuration. The non-metallic character increases as we move from left to right across a period and metallic character increases as we go down the group.

3.6.3 The *d*-Block Elements (Transition Elements)

These are the elements of Group 3 to 12 in the centre of the Periodic Table. These are characterised by the filling of inner *d* orbitals by electrons and are therefore referred to as ***d*-Block Elements**. These elements have the general outer electronic configuration $(n\text{-}1)d^{1\text{-}10}ns^{0\text{-}2}$. They are all metals. They mostly form coloured ions, exhibit variable valence (oxidation states), paramagnetism and oftenly used as catalysts. However, Zn, Cd and Hg which have the electronic configuration, $(n\text{-}1)\, d^{10}ns^2$ do not show most of the properties of transition elements. In a way, transition metals form a bridge between the chemically active metals of *s*-block elements and the less active elements of Groups 13 and 14 and thus take their familiar name **"Transition Elements"**.

3.6.4 The *f*-Block Elements (Inner-Transition Elements)

The two rows of elements at the bottom of the Periodic Table, called the **Lanthanoids,** Ce(Z = 58) – Lu(Z = 71) and **Actinoids**, Th(Z = 90) – Lr (Z = 103) are characterised by the outer electronic configuration $(n\text{-}2)f^{1\text{-}14}$ $(n\text{-}1)d^{0-1}ns^2$. The last electron added to each element is filled in *f*- orbital. These two series of elements are hence called the **Inner-Transition Elements (*f*-Block Elements)**. They are all metals. Within each series, the properties of the elements are quite similar. The chemistry of the early actinoids is more complicated than the corresponding lanthanoids, due to the large number of oxidation states possible for these actinoid elements. Actinoid elements are radioactive. Many of the actinoid elements have been made only in nanogram quantities or even less by nuclear reactions and their chemistry is not fully studied. The elements after uranium are called **Transuranium Elements**.

Problem 3.3

The elements Z = 117 and 120 have not yet been discovered. In which family / group would you place these elements and also give the electronic configuration in each case.

Solution

We see from Fig. 3.2, that element with Z = 117, would belong to the halogen family (Group 17) and the electronic configuration would be [Rn] $5f^{14}6d^{10}7s^27p^5$. The element with Z = 120, will be placed in Group 2 (alkaline earth metals), and will have the electronic configuration [Uuo]$8s^2$.

3.6.5 Metals, Non-metals and Metalloids

In addition to displaying the classification of elements into ***s*-, *p*-, *d*-**, and ***f*-blocks**, Fig. 3.3 shows another broad classification of elements based on their properties. The elements can be divided into **Metals** and **Non-Metals**. Metals comprise more than 78% of all known elements and appear on the left side of the **Periodic Table**. Metals are usually solids at room temperature [mercury is an exception; gallium and caesium also have very low melting points (303K and 302K, respectively)]. Metals usually have high melting and boiling points. They are good conductors of heat and electricity. They are malleable (can be flattened into thin sheets by hammering) and ductile (can be drawn into wires). In contrast, non-metals are located at the top right hand side of the **Periodic Table**. In fact, in a horizontal row, the property of elements change from metallic on the left to non-metallic on the right. Non-metals are usually solids or gases at room temperature with low melting and boiling points (boron and carbon are exceptions). They are poor conductors of heat and electricity. Most non-metallic solids are brittle and are neither malleable nor ductile. The elements become more metallic as we go down a group; the non-metallic character increases as one goes from left to right across the **Periodic Table**. The change from metallic to non-metallic character is not abrupt as shown by the thick zig-zag line in Fig. 3.3. The elements (e.g., silicon, germanium, arsenic, antimony and tellurium) bordering this line and running diagonally across the **Periodic Table** show properties that are characteristic of both metals and non-metals. These elements are called **Semi-metals** or **Metalloids**.

Problem 3.4

Considering the atomic number and position in the periodic table, arrange the following elements in the increasing order of metallic character : Si, Be, Mg, Na, P.

Solution

Metallic character increases down a group and decreases along a period as we move from left to right. Hence the order of increasing metallic character is: P < Si < Be < Mg < Na.

3.7 PERIODIC TRENDS IN PROPERTIES OF ELEMENTS

There are many observable patterns in the physical and chemical properties of elements as we descend in a group or move across a period in the Periodic Table. For example, within a period, chemical reactivity tends to be high in Group 1 metals, lower in elements towards the middle of the table, and increases to a maximum in the Group 17 non-metals. Likewise within a group of representative metals (say alkali metals) reactivity increases on moving down the group, whereas within a group of non-metals (say halogens), reactivity decreases down the group. But why do the properties of elements follow these trends? And how can we explain periodicity? To answer these questions, we must look into the theories of atomic structure and properties of the atom. In this section we shall discuss the periodic trends in certain physical and chemical properties and try to explain them in terms of number of electrons and energy levels.

3.7.1 Trends in Physical Properties

There are numerous physical properties of elements such as melting and boiling points, heats of fusion and vaporization, energy of atomization, etc. which show periodic variations. However, we shall discuss the periodic trends with respect to atomic and ionic radii, ionization enthalpy, electron gain enthalpy and electronegativity.

(a) Atomic Radius

You can very well imagine that finding the size of an atom is a lot more complicated than measuring the radius of a ball. Do you know why? Firstly, because the size of an atom (~ 1.2 Å i.e., 1.2×10^{-10} m in radius) is very small. Secondly, since the electron cloud surrounding the atom does not have a sharp boundary, the determination of the atomic size cannot be precise. In other words, there is no practical way by which the size of an individual atom can be measured. However, an estimate of the atomic size can be made by knowing the distance between the atoms in the combined state. One practical approach to estimate the size of an atom of a non-metallic element is to measure the distance between two atoms when they are bound together by a single bond in a covalent molecule and from this value, the "**Covalent Radius**" of the element can be calculated. For example, the bond distance in the chlorine molecule (Cl_2) is 198 pm and half this distance (99 pm), is taken as the atomic radius of chlorine. For metals, we define the term "**Metallic Radius**" which is taken as half the internuclear distance separating the metal cores in the metallic crystal. For example, the distance between two adjacent copper atoms in solid copper is 256 pm; hence the metallic radius of copper is assigned a value of 128 pm. For simplicity, in this book, we use the term **Atomic Radius** to refer to both covalent or metallic radius depending on whether the element is a non-metal or a metal. Atomic radii can be measured by *X*-ray or other spectroscopic methods.

The atomic radii of a few elements are listed in Table 3.6 . Two trends are obvious. We can explain these trends in terms of nuclear charge and energy level. The atomic size generally decreases across a period as illustrated in Fig. 3.4(a) for the elements of the second period. It is because within the period the outer electrons are in the same valence shell and the effective nuclear charge increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus. Within a family or vertical column of the **periodic table**, the atomic radius increases regularly with atomic number as illustrated in Fig. 3.4(b). For alkali metals and halogens, as we descend the groups, the principal quantum number (n) increases and the valence electrons are farther from the nucleus. This happens because the inner energy levels are filled with electrons, which serve to shield the outer electrons from the pull of the nucleus. Consequently the size of the atom increases as reflected in the atomic radii.

Note that the atomic radii of noble gases are not considered here. Being monoatomic, their (non-bonded radii) values are very large. In fact radii of noble gases should be compared not with the covalent radii but with the van der Waals radii of other elements.

Table 3.6(a) Atomic Radii/pm Across the Periods

Atom (Period II)	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
Atomic radius	152	111	88	77	74	66	64
Atom (Period III)	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
Atomic radius	186	160	143	117	110	104	99

Table 3.6(b) Atomic Radii/pm Down a Family

Atom (Group I)	**Atomic Radius**	**Atom (Group 17)**	**Atomic Radius**
Li	152	**F**	64
Na	186	**Cl**	99
K	231	**Br**	114
Rb	244	**I**	133
Cs	262	**At**	140

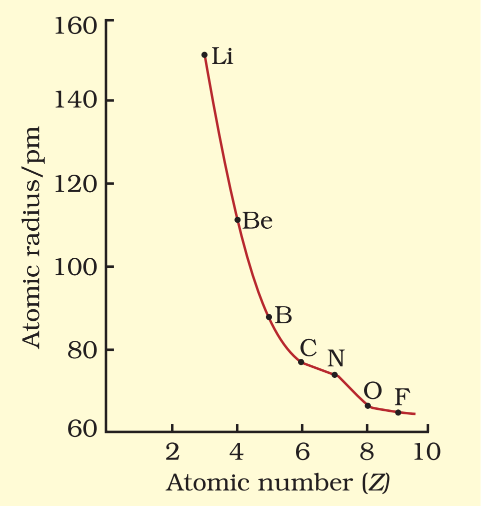


***Fig. 3.4 (a)** Variation of atomic radius with atomic number across the second period*

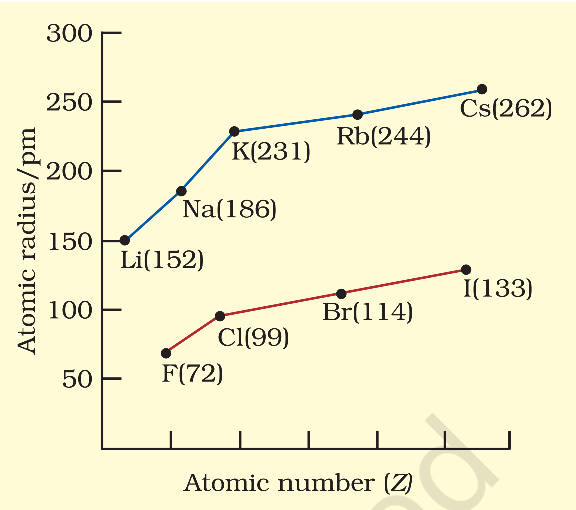


***Fig. 3.4 (b)** Variation of atomic radius with atomic number for alkali metals and halogens*

(b) Ionic Radius

The removal of an electron from an atom results in the formation of a **cation**, whereas gain of an electron leads to an **anion**. The ionic radii can be estimated by measuring the distances between cations and anions in ionic crystals. In general, the ionic radii of elements exhibit the same trend as the atomic radii. A cation is smaller than its parent atom because it has fewer electrons while its nuclear charge remains the same. The size of an anion will be larger than that of the parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge. For example, the ionic radius of fluoride ion (F^-) is 136 pm whereas the atomic radius of fluorine is only 64 pm. On the other hand, the atomic radius of sodium is 186 pm compared to the ionic radius of 95 pm for Na^+.

When we find some atoms and ions which contain the same number of electrons, we call them **isoelectronic species***. For example, O^{2-}, F^-, Na^+ and Mg^{2+} have the same number of electrons (10). Their radii would be different because of their different nuclear charges. The cation with the greater positive charge will have a smaller radius because of the greater attraction of the electrons to the nucleus. Anion with the greater negative charge will have the larger radius. In this case, the net repulsion of the electrons will outweigh the nuclear charge and the ion will expand in size.

Problem 3.5

Which of the following species will have the largest and the smallest size?
Mg, Mg^{2+}, Al, Al^{3+}.

Solution

Atomic radii decrease across a period. Cations are smaller than their parent atoms. Among isoelectronic species, the one with the larger positive nuclear charge will have a smaller radius.

Hence the largest species is Mg; the smallest one is Al^{3+}.

(c) Ionization Enthalpy

A quantitative measure of the tendency of an element to lose electron is given by its **Ionization Enthalpy**. It represents the energy required to remove an electron from an isolated gaseous atom (X) in its ground state. In other words, the first ionization enthalpy for an

* *Two or more species with same number of atoms, same number of valence electrons and same structure, regardless of the nature of elements involved.*

element X is the enthalpy change ($\Delta_i H$) for the reaction depicted in equation 3.1.

$$X(g) \rightarrow X^{+}(g) + e^{-} \qquad (3.1)$$

The ionization enthalpy is expressed in units of kJ mol^{-1}. We can define the second ionization enthalpy as the energy required to remove the second most loosely bound electron; it is the energy required to carry out the reaction shown in equation 3.2.

$$X^{+}(g) \rightarrow X^{2+}(g) + e^{-} \qquad (3.2)$$

Energy is always required to remove electrons from an atom and hence ionization enthalpies are always positive. The second ionization enthalpy will be higher than the first ionization enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom. In the same way the third ionization enthalpy will be higher than the second and so on. The term "ionization enthalpy", if not qualified, is taken as the first ionization enthalpy.

The first ionization enthalpies of elements having atomic numbers up to 60 are plotted in Fig. 3.5. The periodicity of the graph is quite striking. You will find maxima at the noble gases which have closed electron shells and very stable electron configurations. On the other hand, minima occur at the alkali metals and their low ionization enthalpies can be correlated

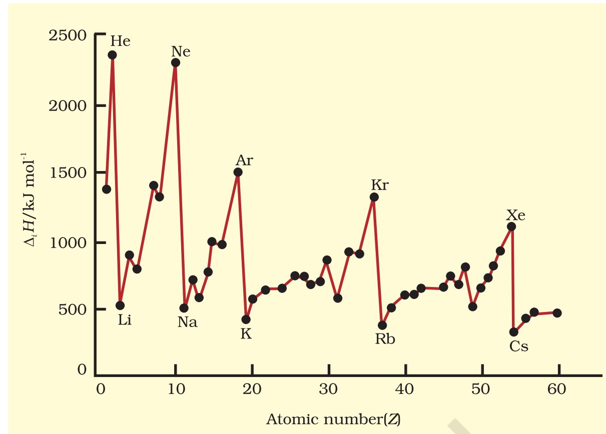
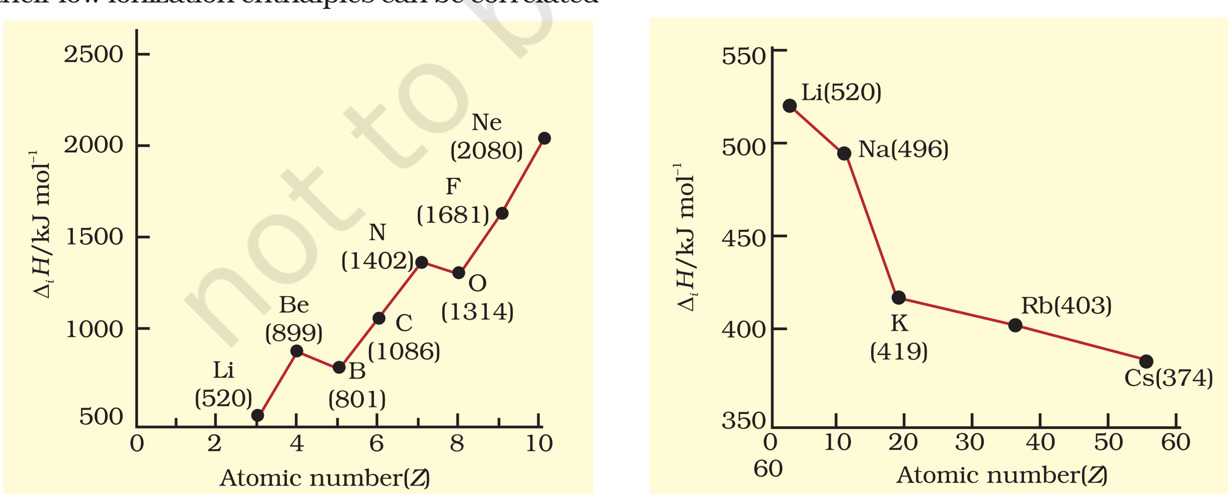


Fig. 3.5 *Variation of first ionization enthalpies ($\Delta_i H$) with atomic number for elements with Z = 1 to 60*

with their high reactivity. In addition, you will notice two trends the first ionization enthalpy generally increases as we go across a period and decreases as we descend in a group. These trends are illustrated in Figs. 3.6(a) and 3.6(b) respectively for the elements of the second period and the first group of the periodic table. You will appreciate that the ionization enthalpy and atomic radius are closely related properties. To understand these trends, we have to consider two factors : (i) the attraction of electrons towards the nucleus, and (ii) the repulsion of electrons from each other. The effective nuclear charge experienced by a valence electron in an atom will be less than



3.6 (a) *3.6 (b)*

Fig. 3.6(a) *First ionization enthalpies ($\Delta_i H$) of elements of the second period as a function of atomic number (Z) and* **Fig. 3.6(b)** *$\Delta_i H$ of alkali metals as a function of Z.*

the actual charge on the nucleus because of **"shielding"** or **"screening"** of the valence electron from the nucleus by the intervening core electrons. For example, the 2*s* electron in lithium is shielded from the nucleus by the inner core of 1*s* electrons. As a result, the valence electron experiences a net positive charge which is less than the actual charge of +3. In general, shielding is effective when the orbitals in the inner shells are completely filled. This situation occurs in the case of alkali metals which have single outermost *ns*-electron preceded by a noble gas electronic configuration.

When we move from lithium to fluorine across the second period, successive electrons are added to orbitals in the same principal quantum level and the shielding of the nuclear charge by the inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus. Thus, across a period, increasing nuclear charge outweighs the shielding. Consequently, the outermost electrons are held more and more tightly and the ionization enthalpy increases across a period. As we go down a group, the outermost electron being increasingly farther from the nucleus, there is an increased shielding of the nuclear charge by the electrons in the inner levels. In this case, increase in shielding outweighs the increasing nuclear charge and the removal of the outermost electron requires less energy down a group.

From Fig. 3.6(a), you will also notice that the first ionization enthalpy of boron ($Z = 5$) is slightly less than that of beryllium ($Z = 4$) even though the former has a greater nuclear charge. When we consider the same principal quantum level, an *s*-electron is attracted to the nucleus more than a *p*-electron. In beryllium, the electron removed during the ionization is an *s*-electron whereas the electron removed during ionization of boron is a *p*-electron. The penetration of a 2*s*-electron to the nucleus is more than that of a 2*p*-electron; hence the 2*p* electron of boron is more shielded from the nucleus by the inner core of electrons than the 2*s* electrons of beryllium. Therefore, it is easier to remove the 2*p*-electron from boron compared to the removal of a 2*s*- electron from beryllium. Thus, boron has a smaller first ionization enthalpy than beryllium. Another "anomaly" is the smaller first ionization enthalpy of oxygen compared to nitrogen. This arises because in the nitrogen atom, three 2*p*-electrons reside in different atomic orbitals (Hund's rule) whereas in the oxygen atom, two of the four 2*p*-electrons must occupy the same 2*p*-orbital resulting in an increased electron-electron repulsion. Consequently, it is easier to remove the fourth 2*p*-electron from oxygen than it is, to remove one of the three 2*p*-electrons from nitrogen.

Problem 3.6

The first ionization enthalpy ($\Delta_i H$) values of the third period elements, Na, Mg and Si are respectively 496, 737 and 786 kJ mol^{-1}. Predict whether the first $\Delta_i H$ value for Al will be more close to 575 or 760 kJ mol^{-1} ? Justify your answer.

Solution

It will be more close to 575 kJ mol^{-1}. The value for Al should be lower than that of Mg because of effective shielding of 3*p* electrons from the nucleus by 3*s*-electrons.

(d) Electron Gain Enthalpy

When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the **Electron Gain Enthalpy** ($\Delta_{eg}H$). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by equation 3.3.

$$X(g) + e^- \rightarrow X^-(g) \qquad (3.3)$$

Depending on the element, the process of adding an electron to the atom can be either endothermic or exothermic. For many elements energy is released when an electron is added to the atom and the electron gain enthalpy is negative. For example, group 17 elements (the halogens) have very high negative electron gain enthalpies because they can attain stable noble gas electronic configurations by picking up an electron. On the other hand, noble gases have

Table 3.7 Electron Gain Enthalpies* / (kJ mol^{-1}) of Some Main Group Elements

Group 1	$\Delta_{eg}H$	Group 16	$\Delta_{eg}H$	Group 17	$\Delta_{eg}H$	Group 0	$\Delta_{eg}H$
H	– 73					**He**	+ 48
Li	– 60	**O**	– 141	**F**	– 328	**Ne**	+ 116
Na	– 53	**S**	– 200	**Cl**	– 349	**Ar**	+ 96
K	– 48	**Se**	– 195	**Br**	– 325	**Kr**	+ 96
Rb	– 47	**Te**	– 190	**I**	– 295	**Xe**	+ 77
Cs	– 46	**Po**	– 174	**At**	– 270	**Rn**	+ 68

large positive electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration. It may be noted that electron gain enthalpies have large negative values toward the upper right of the periodic table preceding the noble gases.

The variation in electron gain enthalpies of elements is less systematic than for ionization enthalpies. As a general rule, electron gain enthalpy becomes more negative with increase in the atomic number across a period. The effective nuclear charge increases from left to right across a period and consequently it will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus. We should also expect electron gain enthalpy to become less negative as we go down a group because the size of the atom increases and the added electron would be farther from the nucleus. This is generally the case (Table 3.7). However, electron gain enthalpy of O or F is less negative than that of the succeeding element. This is because when an electron is added to O or F, the added electron goes to the smaller n = 2 quantum level and suffers significant repulsion from the other electrons present in this level. For the n = 3 quantum level (S or Cl), the added electron occupies a larger region of space and the electron-electron repulsion is much less.

Problem 3.7

Which of the following will have the most negative electron gain enthalpy and which the least negative?

P, S, Cl, F.

Explain your answer.

Solution

Electron gain enthalpy generally becomes more negative across a period as we move from left to right. Within a group, electron gain enthalpy becomes less negative down a group. However, adding an electron to the 2*p*-orbital leads to greater repulsion than adding an electron to the larger 3*p*-orbital. Hence the element with most negative electron gain enthalpy is chlorine; the one with the least negative electron gain enthalpy is phosphorus.

(e) Electronegativity

A qualitative measure of the ability of an atom in a **chemical compound** to attract shared electrons to itself is called **electronegativity**. Unlike ionization enthalpy and electron gain enthalpy, it is not a measureable quantity. However, a number of numerical scales of electronegativity of elements viz., Pauling scale, Mulliken-Jaffe scale, Allred-Rochow scale have been developed. The one which is the most

* *In many books, the negative of the enthalpy change for the process depicted in equation 3.3 is defined as the ELECTRON AFFINITY (A_e) of the atom under consideration. If energy is released when an electron is added to an atom, the electron affinity is taken as positive, contrary to thermodynamic convention. If energy has to be supplied to add an electron to an atom, then the electron affinity of the atom is assigned a negative sign. However, electron affinity is defined as absolute zero and, therefore at any other temperature (T) heat capacities of the reactants and the products have to be taken into account in $\Delta_{eg}H = -A_e - 5/2\ RT$.*

widely used is the Pauling scale. Linus Pauling, an American scientist, in 1922 assigned arbitrarily a value of 4.0 to fluorine, the element considered to have the greatest ability to attract electrons. Approximate values for the electronegativity of a few elements are given in Table 3.8(a)

The electronegativity of any given element is not constant; it varies depending on the element to which it is bound. Though it is not a measurable quantity, it does provide a means of predicting the nature of force that holds a pair of atoms together – a relationship that you will explore later.

Electronegativity generally increases across a period from left to right (say from lithium to fluorine) and decrease down a group (say from fluorine to astatine) in the periodic table. How can these trends be explained? Can the electronegativity be related to atomic radii, which tend to decrease across each period from left to right, but increase down each group ? The attraction between the outer (or valence) electrons and the nucleus increases as the atomic radius decreases in a period. The electronegativity also increases. On the same account electronegativity values decrease with the increase in atomic radii down a group. The trend is similar to that of ionization enthalpy.

Knowing the relationship between electronegativity and atomic radius, can you now visualise the relationship between electronegativity and non-metallic properties?

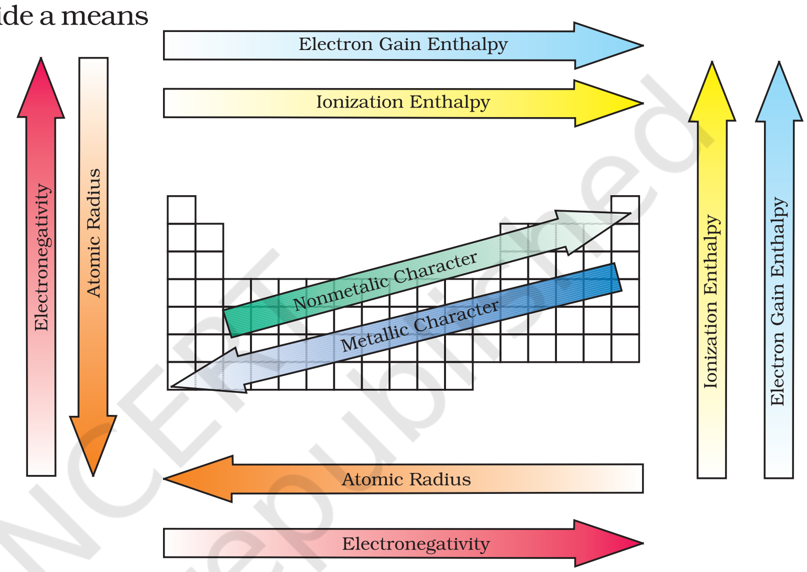


Fig. 3.7 *The periodic trends of elements in the periodic table*

Table 3.8(a) Electronegativity Values (on Pauling scale) Across the Periods

Atom (Period II)	Li	Be	B	C	N	O	F
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

Table 3.8(b) Electronegativity Values (on Pauling scale) Down a Family

Atom (Group I)	Electronegativity Value	Atom (Group 17)	Electronegativity Value
Li	1.0	F	4.0
Na	0.9	Cl	3.0
K	0.8	Br	2.8
Rb	0.8	I	2.5
Cs	0.7	At	2.2

Non-metallic elements have strong tendency to gain electrons. Therefore, electronegativity is directly related to that non-metallic properties of elements. It can be further extended to say that the electronegativity is inversely related to the metallic properties of elements. Thus, the increase in electronegativities across a period is accompanied by an increase in non-metallic properties (or decrease in metallic properties) of elements. Similarly, the decrease in electronegativity down a group is accompanied by a decrease in non-metallic properties (or increase in metallic properties) of elements.

All these periodic trends are summarised in figure 3.7.

3.7.2 Periodic Trends in Chemical Properties

Most of the trends in chemical properties of elements, such as diagonal relationships, inert pair effect, effects of lanthanoid contraction etc. will be dealt with along the discussion of each group in later units. In this section we shall study the periodicity of the valence state shown by elements and the anomalous properties of the second period elements (from lithium to fluorine).

(a) Periodicity of Valence or Oxidation States

The valence is the most characteristic property of the elements and can be understood in terms of their electronic configurations. The valence of representative elements is usually (though not necessarily) equal to the number of electrons in the outermost orbitals and / or equal to eight minus the number of outermost electrons as shown below.

Nowadays the term oxidation state is frequently used for valence. Consider the two oxygen containing compounds: OF_2 and Na_2O. The order of electronegativity of the three elements involved in these compounds is F > O > Na. Each of the atoms of fluorine, with outer electronic configuration $2s^22p^5$, shares one electron with oxygen in the OF_2 molecule. Being highest electronegative element, fluorine is given oxidation state –1. Since there are two fluorine atoms in this molecule, oxygen with outer electronic configuration $2s^22p^4$ shares two electrons with fluorine atoms and thereby exhibits oxidation state +2. In Na_2O, oxygen being more electronegative accepts two electrons, one from each of the two sodium atoms and, thus, shows oxidation state –2. On the other hand sodium with electronic configuration $3s^1$ loses one electron to oxygen and is given oxidation state +1. Thus, the oxidation state of an element in a particular compound can be defined as the charge acquired by its atom on the basis of electronegative consideration from other atoms in the molecule.

Problem 3.8

Using the Periodic Table, predict the formulas of compounds which might be formed by the following pairs of elements; (a) silicon and bromine (b) aluminium and sulphur.

Solution

(a) Silicon is group 14 element with a valence of 4; bromine belongs to the halogen family with a valence of 1. Hence the formula of the compound formed would be $SiBr_4$.

(b) Aluminium belongs to group 13 with a valence of 3; sulphur belongs to group 16 elements with a valence of 2. Hence, the formula of the compound formed would be Al_2S_3.

Some periodic trends observed in the valence of elements (hydrides and oxides) are shown in Table 3.9. Other such periodic trends which occur in the chemical behaviour of the elements are discussed elsewhere in this book.

Group	1	2	13	14	15	16	17	18
Number of valence electron	1	2	3	4	5	6	7	8
Valence	1	2	3	4	3,5	2,6	1,7	0,8

Table 3.9 Periodic Trends in Valence of Elements as shown by the Formulas of Their Compounds

Group	1	2	13	14	15	16	17
Formula of hydride	LiH NaH KH	CaH_2	B_2H_6 AlH_3	CH_4 SiH_4 GeH_4 SnH_4	NH_3 PH_3 AsH_3 SbH_3	H_2O H_2S H_2Se H_2Te	HF HCl HBr HI
Formula of oxide	Li_2O Na_2O K_2O	MgO CaO SrO BaO	B_2O_3 Al_2O_3 Ga_2O_3 In_2O_3	CO_2 SiO_2 GeO_2 SnO_2 PbO_2	N_2O_3, N_2O_5 P_4O_6, P_4O_{10} As_2O_3, As_2O_5 Sb_2O_3, Sb_2O_5 Bi_2O_3 –	– SO_3 SeO_3 TeO_3 –	– Cl_2O_7 – –

There are many elements which exhibit variable valence. This is particularly characteristic of transition elements and actinoids, which we shall study later.

(b) Anomalous Properties of Second Period Elements

The first element of each of the groups 1 (lithium) and 2 (beryllium) and groups 13-17 (boron to fluorine) differs in many respects from the other members of their respective group. For example, lithium unlike other alkali metals, and beryllium unlike other alkaline earth metals, form compounds with pronounced covalent character; the other members of these groups predominantly form ionic compounds. In fact the behaviour of lithium and beryllium is more similar with the second element of the following group i.e., magnesium and aluminium, respectively. This sort of similarity is commonly referred to as **diagonal relationship** in the periodic properties.

What are the reasons for the different chemical behaviour of the first member of a group of elements in the ***s***- and ***p*-blocks** compared to that of the subsequent members in the same group? The anomalous behaviour is attributed to their small size, large charge/radius ratio and high electronegativity of the elements. In addition, the first member of group has only four valence orbitals (2*s* and 2*p*) available for bonding, whereas the second member of the groups have nine valence orbitals (3*s*, 3*p*, 3*d*). As a consequence of this, the maximum covalency of the first member of each group is 4 (e.g., boron can only form $[BF_4]^-$, whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons e.g., aluminium $[AlF_6]^{3-}$ forms). Furthermore, the first member of *p*-block elements displays greater ability to form $p_\pi - p_\pi$ multiple bonds to itself (e.g., C = C, C ≡ C, N = N, N ≡ N) and to other second period elements (e.g., C = O, C = N, C ≡ N, N = O) compared to subsequent members of the same group.

Property	Element		
Metallic radius M/ pm	**Li** 152 **Na** 186	**Be** 111 **Mg** 160	**B** 88 **Al** 143
Ionic radius M^+ / pm	**Li** 76 **Na** 102	**Be** 31 **Mg** 72	

Problem 3.9

Are the oxidation state and covalency of Al in $[AlCl(H_2O)_5]^{2+}$ same ?

Solution

No. The oxidation state of Al is +3 and the covalency is 6.

3.7.3 Periodic Trends and Chemical Reactivity

We have observed the periodic trends in certain fundamental properties such as atomic and ionic radii, ionization enthalpy, electron gain enthalpy and valence. We know by now that the periodicity is related to electronic configuration. That is, all chemical and physical properties are a manifestation of the electronic configuration of elements. We shall now try to explore relationships between these fundamental properties of elements with their chemical reactivity.

The atomic and ionic radii, as we know, generally decrease in a period from left to right. As a consequence, the ionization enthalpies generally increase (with some exceptions as outlined in section 3.7.1(a)) and electron gain enthalpies become more negative across a period. In other words, the ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative (note : noble gases having completely filled shells have rather positive electron gain enthalpy values). This results into high chemical reactivity at the two extremes and the lowest in the centre. Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is exhibited by the loss of an electron leading to the formation of a cation and at the extreme right (among halogens) shown by the gain of an electron forming an anion. This property can be related with the reducing and oxidizing behaviour of the elements which you will learn later. However, here it can be directly related to the metallic and non-metallic character of elements. Thus, the metallic character of an element, which is highest at the extremely left decreases and the non-metallic character increases while moving from left to right across the period. The chemical reactivity of an element can be best shown by its reactions with oxygen and halogens. Here, we shall consider the reaction of the elements with oxygen only. Elements on two extremes of a period easily combine with oxygen to form oxides. The normal oxide formed by the element on extreme left is the most basic (e.g., Na_2O), whereas that formed by the element on extreme right is the most acidic (e.g., Cl_2O_7). Oxides of elements in the centre are amphoteric (e.g., Al_2O_3, As_2O_3) or neutral (e.g., CO, NO, N_2O). Amphoteric oxides behave as acidic with bases and as basic with acids, whereas neutral oxides have no acidic or basic properties.

Problem 3.10

Show by a chemical reaction with water that Na_2O is a basic oxide and Cl_2O_7 is an acidic oxide.

Solution

Na_2O with water forms a strong base whereas Cl_2O_7 forms strong acid.

$Na_2O + H_2O \rightarrow 2NaOH$

$Cl_2O_7 + H_2O \rightarrow 2HClO_4$

Their basic or acidic nature can be qualitatively tested with litmus paper.

Among transition metals (3*d* series), the change in atomic radii is much smaller as compared to those of representative elements across the period. The change in atomic radii is still smaller among inner-transition metals (4*f* series). The ionization enthalpies are intermediate between those of *s*- and *p*-blocks. As a consequence, they are less electropositive than group 1 and 2 metals.

In a group, the increase in atomic and ionic radii with increase in atomic number generally results in a gradual decrease in ionization enthalpies and a regular decrease (with exception in some third period elements as shown in section 3.7.1(d)) in electron gain enthalpies in the case of main group elements.

Thus, the metallic character increases down the group and non-metallic character decreases. This trend can be related with their reducing and oxidizing property which you will learn later. In the case of transition elements, however, a reverse trend is observed. This can be explained in terms of atomic size and ionization enthalpy.

SUMMARY

In this Unit, you have studied the development of the **Periodic Law** and the **Periodic Table**. Mendeleev's **Periodic Table** was based on atomic masses. Modern **Periodic Table** arranges the elements in the order of their atomic numbers in seven horizontal rows (**periods**) and eighteen vertical columns (**groups** or **families**). Atomic numbers in a period are consecutive, whereas in a group they increase in a pattern. Elements of the same group have similar **valence shell** electronic configuration and, therefore, exhibit similar chemical properties. However, the elements of the same period have incrementally increasing number of electrons from left to right, and, therefore, have different valencies. Four types of elements can be recognized in the periodic table on the basis of their electronic configurations. These are ***s*-block, *p*-block, *d*-block** and ***f*-block** elements. **Hydrogen** with one electron in the 1*s* orbital occupies a unique position in the periodic table. **Metals** comprise more than seventy eight per cent of the known elements. **Non-metals**, which are located at the top of the periodic table, are less than twenty in number. Elements which lie at the border line between metals and non-metals (e.g., Si, Ge, As) are called **metalloids** or **semi-metals**. Metallic character increases with increasing atomic number in a group whereas decreases from left to right in a period. The physical and chemical properties of elements vary periodically with their atomic numbers.

Periodic trends are observed in **atomic sizes, ionization enthalpies, electron gain enthalpies**, **electronegativity** and **valence.** The atomic radii decrease while going from left to right in a period and increase with atomic number in a group. Ionization enthalpies generally increase across a period and decrease down a group. Electronegativity also shows a similar trend. Electron gain enthalpies, in general, become more negative across a period and less negative down a group. There is some periodicity in valence, for example, among representative elements, the valence is either equal to the number of electrons in the outermost orbitals or eight minus this number. **Chemical reactivity** is highest at the two extremes of a period and is lowest in the centre. The reactivity on the left extreme of a period is because of the ease of electron loss (or low ionization enthalpy). Highly reactive elements do not occur in nature in free state; they usually occur in the combined form. Oxides formed of the elements on the left are basic and of the elements on the right are acidic in nature. Oxides of elements in the centre are amphoteric or neutral.

EXERCISES

3.1 What is the basic theme of organisation in the periodic table?

3.2 Which important property did Mendeleev use to classify the elements in his periodic table and did he stick to that?

3.3 What is the basic difference in approach between the Mendeleev's Periodic Law and the Modern Periodic Law?

3.4 On the basis of quantum numbers, justify that the sixth period of the periodic table should have 32 elements.

3.5 In terms of period and group where would you locate the element with $Z = 114$?

3.6 Write the atomic number of the element present in the third period and seventeenth group of the periodic table.

3.7 Which element do you think would have been named by
(i) Lawrence Berkeley Laboratory
(ii) Seaborg's group?

3.8 Why do elements in the same group have similar physical and chemical properties?

3.9 What does atomic radius and ionic radius really mean to you?

3.10 How do atomic radius vary in a period and in a group? How do you explain the variation?

3.11 What do you understand by isoelectronic species? Name a species that will be isoelectronic with each of the following atoms or ions.
(i) F^- (ii) Ar (iii) Mg^{2+} (iv) Rb^+

3.12 Consider the following species :
N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+}
(a) What is common in them?
(b) Arrange them in the order of increasing ionic radii.

3.13 Explain why cation are smaller and anions larger in radii than their parent atoms?

3.14 What is the significance of the terms — 'isolated gaseous atom' and 'ground state' while defining the ionization enthalpy and electron gain enthalpy?
Hint : Requirements for comparison purposes.

3.15 Energy of an electron in the ground state of the hydrogen atom is -2.18×10^{-18}J. Calculate the ionization enthalpy of atomic hydrogen in terms of J mol^{-1}.
Hint: Apply the idea of mole concept to derive the answer.

3.16 Among the second period elements the actual ionization enthalpies are in the order Li < B < Be < C < O < N < F < Ne.
Explain why
(i) Be has higher $\Delta_i H$ than B
(ii) O has lower $\Delta_i H$ than N and F?

3.17 How would you explain the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium?

3.18 What are the various factors due to which the ionization enthalpy of the main group elements tends to decrease down a group?

3.19 The first ionization enthalpy values (in kJ mol^{-1}) of group 13 elements are :

B	Al	Ga	In	Tl
801	577	579	558	589

How would you explain this deviation from the general trend ?

3.20 Which of the following pairs of elements would have a more negative electron gain enthalpy?
(i) O or F (ii) F or Cl

3.21 Would you expect the second electron gain enthalpy of O as positive, more negative or less negative than the first? Justify your answer.

3.22 What is the basic difference between the terms electron gain enthalpy and electronegativity?

3.23 How would you react to the statement that the electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds?

3.24 Describe the theory associated with the radius of an atom as it
(a) gains an electron
(b) loses an electron

3.25 Would you expect the first ionization enthalpies for two isotopes of the same element to be the same or different? Justify your answer.

3.26 What are the major differences between metals and non-metals?

3.27 Use the periodic table to answer the following questions.
(a) Identify an element with five electrons in the outer subshell.
(b) Identify an element that would tend to lose two electrons.
(c) Identify an element that would tend to gain two electrons.
(d) Identify the group having metal, non-metal, liquid as well as gas at the room temperature.

3.28 The increasing order of reactivity among group 1 elements is Li < Na < K < Rb <Cs whereas that among group 17 elements is F > CI > Br > I. Explain.

3.29 Write the general outer electronic configuration of *s*-, *p*-, *d*- and *f*- block elements.

3.30 Assign the position of the element having outer electronic configuration (i) ns^2np^4 for n=3 (ii) $(n-1)d^2ns^2$ for n=4, and (iii) $(n-2)f^7(n-1)d^1ns^2$ for n=6, in the periodic table.

3.31 The first (Δ_iH_1) and the second (Δ_iH_2) ionization enthalpies (in kJ mol^{-1}) and the ($\Delta_{eg}H$) electron gain enthalpy (in kJ mol^{-1}) of a few elements are given below:

Elements	ΔH_1	ΔH_2	$\Delta_{eg}H$
I	520	7300	–60
II	419	3051	–48
III	1681	3374	–328
IV	1008	1846	–295
V	2372	5251	+48
VI	738	1451	–40

Which of the above elements is likely to be :
(a) the least reactive element.
(b) the most reactive metal.
(c) the most reactive non-metal.
(d) the least reactive non-metal.
(e) the metal which can form a stable binary halide of the formula MX_2(X=halogen).
(f) the metal which can form a predominantly stable covalent halide of the formula MX (X=halogen)?

3.32 Predict the formulas of the stable binary compounds that would be formed by the combination of the following pairs of elements.
(a) Lithium and oxygen
(b) Magnesium and nitrogen
(c) Aluminium and iodine
(d) Silicon and oxygen
(e) Phosphorus and fluorine
(f) Element 71 and fluorine

3.33 In the modern periodic table, the period indicates the value of :
(a) atomic number
(b) atomic mass
(c) principal quantum number
(d) azimuthal quantum number.

3.34 Which of the following statements related to the modern periodic table is incorrect?
(a) The *p*-block has 6 columns, because a maximum of 6 electrons can occupy all the orbitals in a *p*-shell.

(b) The *d*-block has 8 columns, because a maximum of 8 electrons can occupy all the orbitals in a *d*-subshell.

(c) Each block contains a number of columns equal to the number of electrons that can occupy that subshell.

(d) The block indicates value of azimuthal quantum number (l) for the last subshell that received electrons in building up the electronic configuration.

3.35 Anything that influences the valence electrons will affect the chemistry of the element. Which one of the following factors does not affect the valence shell?

(a) Valence principal quantum number (n)

(b) Nuclear charge (Z)

(c) Nuclear mass

(d) Number of core electrons.

3.36 The size of isoelectronic species — F^-, Ne and Na^+ is affected by

(a) nuclear charge (Z)

(b) valence principal quantum number (n)

(c) electron-electron interaction in the outer orbitals

(d) none of the factors because their size is the same.

3.37 Which one of the following statements is incorrect in relation to ionization enthalpy?

(a) Ionization enthalpy increases for each successive electron.

(b) The greatest increase in ionization enthalpy is experienced on removal of electron from core noble gas configuration.

(c) End of valence electrons is marked by a big jump in ionization enthalpy.

(d) Removal of electron from orbitals bearing lower n value is easier than from orbital having higher n value.

3.38 Considering the elements B, Al, Mg, and K, the correct order of their metallic character is :

(a) B > Al > Mg > K (b) Al > Mg > B > K

(c) Mg > Al > K > B (d) K > Mg > Al > B

3.39 Considering the elements B, C, N, F, and Si, the correct order of their non-metallic character is :

(a) B > C > Si > N > F (b) Si > C > B > N > F

(c) F > N > C > B > Si (d) F > N > C > Si > B

3.40 Considering the elements F, Cl, O and N, the correct order of their chemical reactivity in terms of oxidizing property is :

(a) F > Cl > O > N (b) F > O > Cl > N

(c) Cl > F > O > N (d) O > F > N > Cl