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Structure of Atom

1.1. Introduction

John Dalton was the first to establish the existence of atoms. He defined atom as the smallest part of an element that could exist alone and still be representative of that substance. Later work by physicists was mainly directed to the atom itself and demonstrated the existence of elementary particles (electrons and protons). These elementary particles varied in number with the element concerned. However, the internal arrangement of these particles was inadequately understood and it was not possible to correlate the properties of atoms with their structures. The investigations that followed in the field of spectroscopy amply helped understand the internal structure of atoms and its relationship with the properties of elements.

The spectrometer used in such techniques allowed the light from the source (high temperature flame, gas discharge tube, electric arc, or high frequency spark) to pass through a narrow slit into a collimator, and from there through a prism on to a photographic plate. In many cases the photographic plate could be replaced by observers eye or screen. A series of lines resulted, each corresponding to a particular wave length of radiation emitted. Each of these lines was the image of slit produced by the particular wave-length. The more complex the atom, the more wavelengths were emitted, and thus resulted into greater number of lines. In 1885 Balmer had discovered a relationship between the lines produced in a part of hydrogen spectrum. These lines were called *Balmer series*. This relationship was followed by others known after Lyman, Paschen and Brackett. Rydberg observed that the spectral lines were characterised by certain other properties, quite independent of the atom concerned. Certain of these lines were always sharply defined. These lines were called "*sharp*". Some lines appeared even when the element concerned was present in only small quantity they were called "*principal*". Certain lines were "*diffuse*".

The fourth type of lines was recognized latter and called "*fundamental*". These four lines were referred to as *s*, *p*, *d*, *f*.

1.2. Atomic Models

Atom is presently known to be smallest particle which has the same properties as those of the element which it constitutes. Atom is so small that it can not be observed but can be felt only by its manifestations. The present knowledge of atom has developed through various theories and experiments proposed and performed by several scientists, during the period of 1895 to 1930.

1.2.1. Thompson's Model. J.J. Thompson proposed an atomic model known as plum-pudding model. He proposed that atoms are uniform spheres in which positively charged particles are uniformly distributed over its entire body of 10^{-10} m diameter. The negatively charged particles are embedded in it like plums in a pudding. This model could explain the periodicity in elements, spectral lines, existence of ions and kinetic theory of gases. Fig. 1.1 shows this model. However, this model failed to explain the series of spectral lines. The model had finally to be given up when Rutherford performed his famous experiment in which α particles were scattered from a thin film of gold.

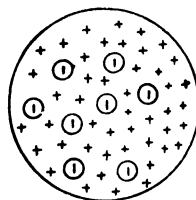


Fig. 1.1. Plum pudding model.

1.2.2. Rutherford Experiments. α -particles are positively charged particles with charge of $2e$ on each (e is the charge on one electron). These particles are emitted from radioactive materials such as the radium. In his experiment, Rutherford directed α particles on a thin gold film. He observed that some α -particles passed through the film, while others were scattered all around. Those passing through the sheet also scattered over a wide area, and produced luminescence on a fluorescent screen of zinc sulphide (Fig. 1.2).

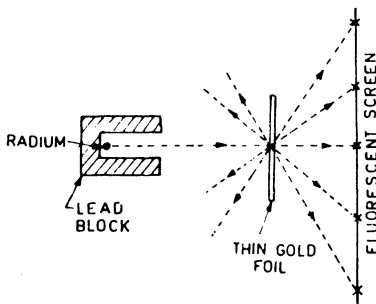


Fig. 1.2. α -particle scattering.

This phenomenon of scattering can be explained only if it is assumed that the positive charge in an atom is concentrated in the centre and the negatively charged particles surround it loosely, leaving enough

space for α -particles to pass through. Further, the positively charged particles will be able to deflect the positively charged α -particles as shown in Fig. 1.3. Those particles which came straight to central positively charged particles are reflected back on the parallel path. The Thompson's model could not explain this α -particles scattering. If positively charged particles were distributed uniformly throughout the body of atom then α -particles would have been only slightly affected because of weak field of such individual particles. Thus Rutherford proposed a strong positive charge and several negative charges surrounding it loosely. He estimated the central positive charge to be of the size of 10^{-14} m, as compared to overall size of atom of 10^{-10} m, thus leaving a large space inside the atom. In fact, he proposed that atom is like a planetary system in which central positive charge, known as nucleus occupies position like sun and the negative particles correspond to planets. The total positive charge of nucleus equals to total negative charge of electrons, making atom a neutral particle.

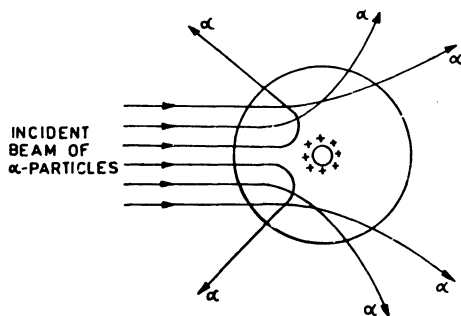


Fig. 1.3. Deflection of α -particles through an atom.

The Rutherford model could explain that all the atoms of any one element have the same nuclear charge which increases regularly from element to element in periodic table. This model also assumed that the electrons will be rotating round the nucleus since otherwise each electron will be pulled towards the nucleus under strong electrostatic force. Thus the electrostatic pull on the electron will balance the outward centrifugal force due to electron rotation. However, this theory also runs into difficulty because of law of electrodynamics. This law states that an accelerated charge must continuously radiate energy. If it is followed then an electron which is essentially an accelerated charge in this model, must radiate energy continuously and thus gradually fall into nucleus. This will also result in a continuous atomic spectrum which is contrary to the experimental evidences.

It was Neil Bohr who postulated an atomic model in 1913 which was much more satisfactory in explaining the known behaviour of atoms and eliminating the above defects.

1.3. Bohr's Atomic Model

In 1913 Bohr proposed following atomic model :

(i) Electrons have stationary orbit. This implies that when an electron is revolving round the nucleus in its stationary orbit it does not radiate any energy. The electrons are permitted to have only such orbits for which angular momentum will be an integral multiple of $h/2\pi$ where h is the Plank's constant. Thus angular momentum of an electron

$$= \frac{nh}{2\pi}$$

where n is the integer known as principal quantum number.

(ii) The energy is radiated by an atom only when an electron jumps from one orbit to another of lower energy. When the electron jumps from an orbit of lower energy to one of higher energy the energy is absorbed by the electron.

(iii) The emission or absorption of energy during transition is not continuous but discrete in form of quantum or bundle each equal to $h\nu$ where ν is the frequency of radiation.

The important conclusions that are drawn from above postulates are :

(a) Centrifugal force on electron = force of attraction between electrons and nucleus. The centrifugal force

$$= \frac{mV^2}{r} = mr\omega^2 \quad \dots(1.1)$$

where V is the velocity of an electron having a mass of m and revolving in a circle of radius r .

ω is the angular velocity or angular frequency of the electron.

If Z is the number of positively charged particles in the nucleus the force of attraction between the electron of charge e and nucleus

$$= \frac{Ze.e}{4\pi\epsilon_0 r^2} \quad \dots(1.2)$$

where ϵ_0 is a constant known as permittivity.

(b) If an electron changes its position from an orbit where its energy is E_1 to another orbit where its energy is E_2 , then

$$E_1 - E_2 = h\nu \quad \dots(1.3)$$

The present day understanding of atom is that nucleus is made up of protons and neutrons. The collective term for both is *nucleons*. The simplest nucleus is that of hydrogen atom and consists of only one proton. The neutron is an uncharged particle with a mass nearly equal to that of a proton. The nature of forces holding protons and neutrons is still not very clear. It is believed that these are very short range forces the range being smaller than nuclear dimensions. The nucleons continuously exchange some constituent particles called **mesons**.

1.3.1. Hydrogen Atom. Hydrogen atom contains a single electron hence its atomic number is 1 i.e. $Z = 1$. From the first conclusion of Bohr's atomic theory the equivalence between the centrifugal force and the force of attraction on the rotating electrons was established.

The centrifugal force of an electron of mass m , rotating with a velocity V

$$F_1 = \frac{mV^2}{r} \quad \dots(i)$$

where r is the radius of the orbit in which electron is rotating.

The force of attraction pulling the electron to the nucleus

$$F_2 = \frac{Ze^2}{4\pi\epsilon_0 r^2} \quad \dots(ii)$$

From (i) and (ii)

$$\frac{mV^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2} = \frac{e^2}{4\pi\epsilon_0 r^2}$$

$$\text{or} \quad mV^2 = \frac{e^2}{4\pi\epsilon_0 r} \quad \dots(iii)$$

From the first postulate of Bohr's Atomic model (sec. 1.3).

$$\text{Angular momentum} = \frac{nh}{2\pi} \quad \dots(iv)$$

For an electron of mass, m , rotating in an orbit of radius, r with a velocity, V .

The angular momentum = mVr .

$$\text{Hence} \quad mVr = \frac{nh}{2\pi}$$

$$mV = \frac{nh}{2\pi r} \quad \dots(v)$$

Dividing (ii) by (v)

$$\frac{mV^2}{mV} = V = \frac{e^2}{4\pi\epsilon_0 r} \cdot \frac{2\pi r}{nh}$$

$$V = \frac{e^2}{2\epsilon_0 nh} \quad \dots(1.4)$$

Substituting V from Eq. (1.4) in (v)

$$\frac{me^2}{2\epsilon_0 nh} = \frac{nh}{2\pi r}$$

or

$$r = \frac{\epsilon_0 h^2 n^2}{me^2 \pi} \quad \dots(1.5)$$

The Eqn (1.5) gives the radius of n th orbit of the electron in the hydrogen atom.

1.3.2. Energy of Electron. The energy of electron rotating in a stationary orbit of a hydrogen atom is composed of two components, *viz.* Kinetic energy and Potential energy

i.e. $E = \text{K.E.} + \text{P.E.} \quad \dots(i)$

$$\text{K.E.} = \frac{1}{2} mV^2 \quad \dots(ii)$$

Using Eq. (1.4) in (ii)

$$\text{K.E.} = \frac{1}{2} \frac{e^4 m}{4\epsilon_0 n^2 h^2} \quad \dots(iii)$$

Potential energy of an electron is due to force of attraction between the nucleus and electron. It is equal to work done by this force over a distance r . Thus if force is F_2 , the P.E. of electron in the orbit of radius r is equal to $F_2 r$. It may also be remembered that K.E. is due to a force which is pulling the atom away from the nucleus. Hence K.E. is taken as positive while P.E. as negative. Thus using (ii) of sec. 1.3.1

$$\text{P.E.} = \frac{-e^4}{4\pi\epsilon_0 r} \quad \dots(iv)$$

Using Eqn. (1.5) in (iv)

$$\text{P.E.} = \frac{e^4 m}{4\epsilon_0^2 n^2 h^2} \quad \dots(v)$$

From (i), (iv) and (v) the energy of an electron

$$E = -\frac{me^4}{8\epsilon_0^2 h^2} \cdot \frac{1}{n^2} \quad \dots(1.6)$$

It can be seen that the energy of an electron in n th orbit of hydrogen atom is inversely proportional to the square of the principal quantum number n . n varies from 1, 2, 3 ∞ .

The constants involved in above equations have the following values.

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ F/m} \quad (\text{Farad per meter})$$

$$h = 6.625 \times 10^{-34} \text{ J-s} \quad (\text{Joule-second})$$

$$m = 9.11 \times 10^{-31} \text{ kg} \quad (\text{Killogramme})$$

$$e = 1.6 \times 10^{-19} \text{ C} \quad (\text{Coulomb})$$

Example 1.1. Calculate the radii of first and second orbits of Bohr hydrogen atom.

Solution. Using Eqn. (1.5) and substituting the values of constant

$$\begin{aligned} r &= \frac{8.854 \times 10^{-12} \times 43.89 \times 10^{-68}}{9.11 \times 10^{-31} \times 2.56 \times 10^{-38} \times \pi} \times n^2 \\ &= 0.53 \times 10^{-10} \times n^2 \end{aligned}$$

For first orbit $n = 1$

Therefore radius of the first Bohr orbit in a hydrogen atom
 $= 0.53 \times 10^{-10} \text{ m}$ or 0.53 \AA (Angstrom)

For second orbit $n = 2$

Therefore the radius of the second Bohr orbit
 $= 2.12 \text{ \AA}$

The orbit for where $n = 1$ is known as ground orbit. [Ans.]

Example 1.2. Calculate the values of kinetic energy, potential energy and total energy of an electron in a hydrogen atom in its ground orbit.

Solution. From Eqn. (1.6) and (iii) of sec. 1.3.2 it can be seen that the kinetic energy and total energy are equal in magnitude but kinetic energy is positive while total energy is negative. Potential energy is the difference of above two.

From Eqn. (1.6) after substitution of the constant total energy of an electron in the ground orbit of the hydrogen atom for which

$$n = 1$$

$$E = - \frac{9.11 \times 10^{-31} \times 6.554 \times 10^{-76}}{8 \times 78.39 \times 10^{-24} \times 43.89 \times 10^{-69}}$$

$$= -2 \times 10^{-18} \text{ J} \quad \dots(1)$$

The energy of an electron is often expressed in eV (electron volts)

where $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$

$$\therefore E = -13.6 \text{ eV} \quad \dots(2)$$

$$\text{K.E.} = 13.6 \text{ eV} \quad \dots(3)$$

$$\text{P.E.} = -27.2 \text{ eV} \quad \dots(4)$$

It was pointed out in sec. 1.3.2 that energy is inversely proportional to n^2 , therefore, energies of electrons in second, third and subsequent orbits can be calculated directly from the results of above examples.

Thus the energy of electron in second orbit of hydrogen atom is

$$= \frac{-13.6}{4} = -3.4 \text{ eV}$$

Energy of the electron in third orbit

$$= \frac{-13.6}{9} = -1.51 \text{ eV}$$

Energy of the electron in fourth orbit

$$= \frac{-13.6}{16} = -0.85 \text{ eV}$$

and so on.

Obviously energy of the orbit for which $n = \infty$ will be zero.

Thus if an electron is excited from ground orbit to second orbit it will absorb energy $= 13.6 - 3.4 = 10.2 \text{ eV}$. Similarly if an electron changes its orbit from 4th to 3rd it will radiate an energy

$$= 1.51 - 0.85 = 0.66 \text{ eV.}$$

This radiant energy which is given out when an electron changes its orbit from higher to lower position appears as spectral line in the spectrum. When

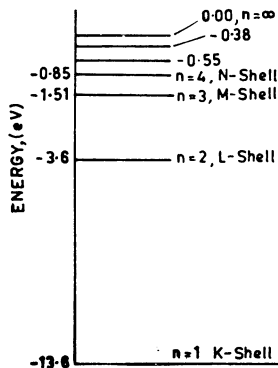


Fig. 1.4. Energy level diagram.

these energy levels are shown on scale as in Fig. 1.4, Energy Level Diagram (ELD) is obtained.

1.4. Quantum Theory of Atom

One modification to Bhor's atomic model was suggested by Sommerfeld by assigning two quantum numbers to an orbit. The second quantum number assigned to an orbit in addition to **principal** quantum number, n was called **azimuthal** quantum number denoted by l . If $n = l$ the orbit is circular. For a given value of n , l can have n values if $n \neq l$, the orbit will be elliptical with ratio of major to minor axes n/l and thus existence of elliptical orbits was conceptualized. Yet Bohr's model failed to explain all atomic phenomena. It gave false idea of definite orbits.

By middle of 1920's enough experimental data, had accumulated which indicated that assumption of applying usual laws of mechanics to such small particles as electron and atom was not correct. These laws could explain the motion of large bodies such as stones, shells or machine parts but not electrons. Flow of small electron through matter is scattered and partially reflected causing interaction among electrons. Such interaction will make certain areas of high density of electrons and certain other regions of low density. The situation is very much similar to wave motion of sound and light. Thus during the second decade of the twentieth century the scientists had started to regard bodies to have dual characteristic. The particle characteristic of the body was well identified, in addition, it was recognized that the bodies of large and small sizes have wave characteristics also. In fact it had already been recognized that light had these two characteristics and as a result two theories, *viz.*, corpuscular theory and wave theory were used to explain several optical behaviours. De-Broglie and Plank had worked in the direction to show that wave like characteristics become very important when the particle is as small as an electron. It was established that a particle of mass m and velocity V could be associated with a wave by following equation.

$$\lambda = \frac{h}{mV} \quad \dots(1.7)$$

where λ = wavelength.

Consider earth for which $m = 6 \times 10^{24}$ kg and $V = 3 \times 10^4$ m/s so that $\lambda = 3.6 \times 10^{-31}$ m. This wavelength is very small and cannot be observed. Even for a stone having $m = 1/10$ kg and $V = 1/10$ m/s, $\lambda = 6.6 \times 10^{-31}$ m. This is also very small. On the other hand for an

electron $m = 9.1 \times 10^{-27}$ kg, $V = 6 \times 10^5$ m/s, $\lambda = 10^{-9}$ m. This approximately corresponds to wavelength of X-rays and can be detected.

The wave characteristic of the electron was verified by observing the diffraction pattern when electrons pass through a crystalline film and when it is reflected from a surface of a simple crystal.

The wave property of an electron limits the number of orbits which it can occupy. Such limitation of orbit is analogous to the fact that a vibrating string can have only a series of distinct modes each consisting of stationary waves, whose wavelength is a simple fraction of the length of the string.

1.4.1. Assumptions of Quantum Theory. Plank and Einstein made following assumptions :

(i) The energy of electromagnetic radiation is discrete in its nature. This implies that light and other forms of radiant energy are not uniformly distributed in a beam or over a wavefront but are separated into discrete packets.

(ii) The basic unit of radiation energy is proportional to the frequency of the radiation. This was also adopted by Bohr and has already been expressed by Eqn. (1.3). Thus one unit of energy is $E = h\nu$, where ν is the frequency and h , the Plank's constant. This basic unit is called a photon or quantum of energy. Photons of large energy constitute waves of high frequency and since

$$\lambda = \frac{C}{\nu} \quad \dots(1.8)$$

where C is the velocity of light, photons of large energy will constitute waves of small wave-lengths. As an example photons of blue light with a wavelength of 4×10^{-7} m are larger than those of red light with a wavelength of 7.5×10^{-7} m. The photons of X-rays having wavelength of 10^{-10} m are considerably larger than those of visible light. By using the equation $E = h\nu$ it can be seen that energy of a photon of visible light lies between 1.5 to 3.0 eV while that of an X-ray photon is 20,000 eV.

(iii) Electrons in an atom can move only in a limited number of possible orbits. In the beginning of this section the wave nature of the electrons has been amply demonstrated to support this statement.

For a given atoms each orbit is associated with a particular energy which depends, among other things, upon the attraction of electron to the nucleus and the kinetic energy of the electron. This

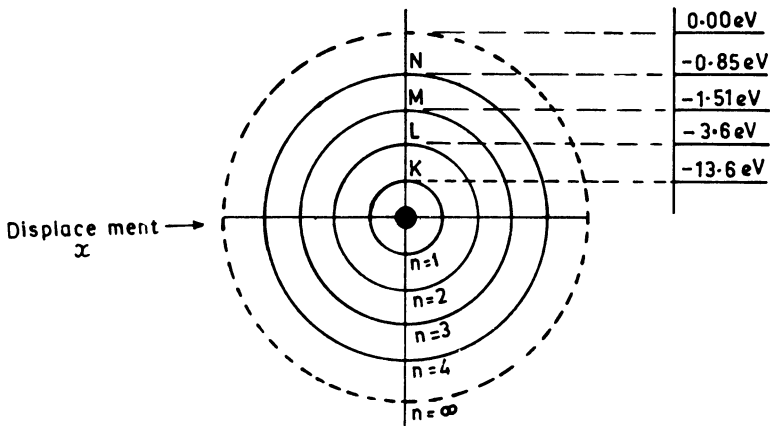


Fig. 1.5. Schematic of orbits in a hydrogen atom.

assumption happens to be same as made by Bohr and is equivalent to saying that there is a limited number of possible energies that an electron can have when it is within a given atom. This is shown schematically in Fig. 1.5 for hydrogen atom. The radii of the orbits and the magnitudes of energy levels differ from one type of atom to another but each type of atom has its own characteristic values. The energies of electron in various shells are proportional to the square of atomic number *i.e.* Z^2 .

The limited number of permissible levels of energy means that while an electron can jump from one level to another, it can never remain between them. It is like a man on a flight of stairs who can remain on any step but never between the two.

The other two assumptions in quantum theory of atom are same as those described in Bohr's theory. They concern the stationary orbits and emission or absorption of energy when electron jumps from one orbit to another [Eqn. (1.3)].

It may appear strange here that even after talking so much about the wave nature of electron, still the quantum theory of atoms is being presented in form of assumptions. It is because without going into complicated mathematical treatment it will not be possible to comprehend the behaviour of electron wave. Such an attempt is postponed for the time being.

1.5. Spectra

Over the last hundred years studies of the interactions of light and matter have played a critical role in formulating ideas of

atomic and molecular structure. These interactions cause rearrangements among the valence electrons, and give rise to line spectra.

1.5.1. Absorption Spectrum. It is well known that if white light is passed through a prism, it is split up into different colours. Each of these colours corresponds to different wave-length. If light from a hot filament lamp is analysed in this way it seems that the spectrum or the wavelengths of light is represented over a wide region and the light is spectrally continuous. However, if the light is first passed through atomic vapour and then through a prism, the emerging light is no longer continuous. Light of different wavelengths is focused on to different areas of the photographic plate. It is because the atoms of gas absorb light of some wavelength and the photographic plate therefore contains light and dark regions. The pattern so obtained is known as absorption spectrum and is characteristic of atomic vapour introduced between the light source and the prism.

1.5.2. Emission Spectrum. If an atomic vapour is subjected to a high potential difference a characteristic glow is produced. This effect has been known for many years, and is familiar in form of sodium street lamps. Such lamps produce orange-yellow light. The light emitted by such lamps can be analysed by a prism or diffraction grating. It is found that emergent light produces a series of lines which appear dark on the photographic plate as is shown in Fig. 1.6. This figure shows a typical pattern using mercury lamp. Such a

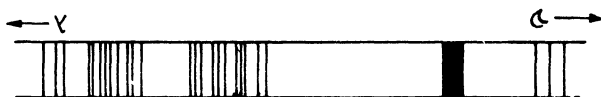


Fig. 1.6. The emission spectrum of mercury.

pattern is called emission spectrum and is characteristic of the atomic vapour used. A further feature of emission spectra is that they frequently contain regions of continuous emission where the intensity of the emission will vary smoothly with the wavelength.

There are important similarities between the absorption and emission spectra of atoms. Emission spectra generally contain far more lines than the corresponding absorption spectra. But there are many lines which are of common wavelength in both.

1.6. Hydrogen Spectrum

When an electric discharge is run in a sample of hydrogen gas, the light emitted by the discharge is found to consist of a series

of discrete wave-lengths and is the emission spectrum of the hydrogen atom. This spectrum consists of several series of lines. The one series lies in the visible region. This is called the *Balmer* series. Other series lies in the ultraviolet region. This is known as *Lyman* series. Several other series lie in the infra-red region and are known after different discoverers.

The lines that appear in the spectrum of hydrogen are due to emission of radiant energy which the electron loses while jumping from a higher orbit (say n_2) to a lower orbit (say n_1). Eqn. (1.6) may be used to write the energies of electron in n_2 and n_1 orbits whereby the radiant energy emitted by the electron when it jumps from n_2 to n_1 orbit may be found. Thus

$$E_{n_2} - E_{n_1} = \frac{me^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \dots(1.9)$$

Using $E = h\nu$ and Eqn. (1.8) in above equation one can write,

$$\frac{1}{\lambda} = \frac{me^4}{8\epsilon_0^2 h^3 C} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \dots(1.10)$$

Eqn. (1.10) can also be written as

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \dots(1.11)$$

where
$$R = \frac{me^4}{8\epsilon_0^2 h^3 C} \quad \dots(1.12)$$

is known as Rydberg's constant.

$\frac{1}{\lambda}$ is also termed as wave number.

1.6.1. Balmer Series. It has already been stated that Balmer series of hydrogen spectrum lies in the visible region. To be specific this series lies between wavelengths of 6,563 Å to 3,646 Å. Balmer has observed that wave number of his series could be written as

$$\frac{1}{\lambda} = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad \dots(1.13)$$

This means [referring to Eqn. (1.11)] that Balmer series lines are obtained when an excited electron falls to second orbit (for which $n = 2$) from any other higher orbits. Thus n can have any value ; 3, 4, 5 etc. Normally when $n = 3, 4, 5, 6$ distinct lines can be seen in the hydrogen spectrum. For n greater than 6 the lines come very close to each other and finally for $n = \infty$ the Balmer series ends in a

hazy region. The lines that can be clearly distinguished are described in Table 1.1 and in Fig. 1.7.

Table 1.1
Balmer Series

<i>Line</i>	<i>n</i>	λ
H_{α}	3	6563 Å
H_{β}	4	4861 Å
H_{γ}	6	4340 Å
H_{δ}	6	4102 Å
Limiting	∞	3646 Å

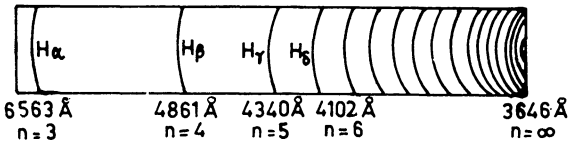


Fig. 1.7. Balmer series of hydrogen spectrum.

1.6.2. Lyman Series. These lines are produced by electrons jumping from any orbit to first orbit (for which $n = 1$).

The equation for these lines can be written

$$\frac{1}{\lambda} = R \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \quad \dots(1.14)$$

n in this case can assume any value from 2, 3, 4 ∞ .

It has already been stated that these lines lie in the ultraviolet region of the spectrum.

1.6.3. Infrared Series. (i) *Ritz Paschen series*

For this series

$$\frac{1}{\lambda} = R \left(\frac{1}{3^2} - \frac{1}{n^2} \right) \quad \dots(1.15)$$

where $n = 4, 5, 6 \dots \infty$

(ii) *Brackett series*

This series is represented by

$$\frac{1}{\lambda} = R \left(\frac{1}{4^2} - \frac{1}{n^2} \right) \quad \dots(1.16)$$

where $n = 5, 6, 7 \dots \infty$

(iii) Pfund series

This series is represented by

$$\frac{1}{\lambda} = R \left(\frac{1}{5^2} - \frac{1}{n^2} \right) \quad \dots(1.17)$$

where

$$n = 6, 7 \dots \infty.$$

Fig. 1.8 describes the various series on ELD.

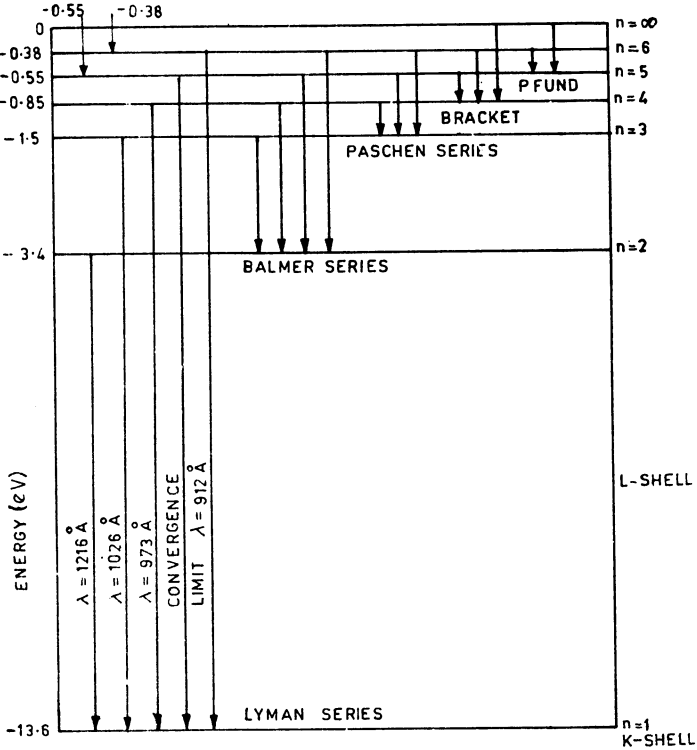


Fig. 1.8. Energy level diagram.

Example 1.3. Calculate the value of Rydbergs constant.

Solution. From Eqn. (1.12)

$$R = \frac{me^4}{8\epsilon_0^2 h^3 C}$$

All constants occurring in above equation are described in sec. 1.3.2. except velocity of light C.

$$C = 3 \times 10^8 \text{ m/s}$$

$$R = \frac{9.11 \times 10^{-31} \times (1.6)^4 \times 10^{-76}}{8 \times (8.854)^2 \times 10^{-24} \times (6.625)^3 \times 10^{-102} \times 3 \times 10^8}$$

$$= 1.09678 \times 10^7 \text{ per m}$$

$$R = 1.09678 \times 10^{-8} \text{ per \AA. [Ans.]}$$

Example 1.4. Calculate the wave-lengths of H_α , H_β , H_γ and H_δ lines of hydrogen spectrum.

Solution. These are the lines of Balmer series whose wave-lengths are given by Eqn. (1.13) and Table 1.1 describes the desired wavelengths. However, in this solution the wavelengths will be calculated by assuming

$$R = 109678 \text{ cm}^{-1}.$$

Using proper values of principal quantum number, n in Eqn. (1.13).

(i) Line H_α is obtained when $n = 3$

$$\text{Hence } \frac{1}{\lambda_\alpha} = 109678 \left(\frac{1}{4} - \frac{1}{9} \right) = 109678 \times \frac{5}{36}$$

$$\text{or } \lambda_\alpha = 6565 \times 10^{-8} \text{ cm} = 6565 \text{ \AA} \quad \dots(i)$$

(ii) Line H_β is obtained when $n = 4$

$$\text{Hence } \frac{1}{\lambda_\beta} = 109678 \left(\frac{1}{4} - \frac{1}{16} \right) = 109678 \times \frac{3}{16}$$

$$\text{or } \lambda_\beta = 4843 \times 10^{-8} \text{ cm} = 4843 \text{ \AA} \quad \dots(ii)$$

(iii) Line H_γ is obtained when $n = 5$

$$\text{Hence } \frac{1}{\lambda_\gamma} = 109678 \left(\frac{1}{4} - \frac{1}{25} \right) = 109678 \times \frac{21}{100}$$

$$\text{or } \lambda_\gamma = 4352 \times 10^{-8} \text{ cm} = 4352 \text{ \AA} \quad \dots(iii)$$

(iv) Line H_δ is obtained when $n = 6$

$$\text{Hence } \frac{1}{\lambda_\delta} = 109678 \left(\frac{1}{4} - \frac{1}{36} \right) = 109678 \times \frac{27}{36}$$

$$\text{or } \lambda_\delta = 4102 \times 10^{-8} \text{ cm} = 4102 \text{ \AA} \quad \dots(iv)$$

(i), (ii), (iii) and (iv) are the required wavelengths. [Ans.]

Example 1.5. Electrons of energies 10.2 eV and 12.09 eV can cause radiation to be emitted from hydrogen atoms. Calculate in each case.

(i) the principal quantum number of the orbit to which electron in the hydrogen atom is raised and

(ii) the wavelengths of the radiation emitted if the electron drops back to ground level. (A.M.I.E. 1976)

Solution. The electron from ground ($n = 1$) state is excited to a higher orbit ($n = ?$). During the process of excitation it acquires energy of 10.2 eV or 12.09 eV.

Using Eq. (1.9) and substituting $En_2 - En_1 = 10.2$ or 12.09 eV, the number n may be calculated.

In the first case,

$$10.20 = 13.61 \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \text{eV}$$

$$= 13.61 - 13.61/n^2$$

or $n^2 = 13.61/3.41 = 4$

Hence $n = 2$

i.e. when an electron of energy 10.2 eV excites the hydrogen electron from ground level it goes to second orbit. ... (i)

When this electron drops back to ground level it will lose same amount of energy *i.e.* 10.2 eV.

Remembering $E = hc/\lambda$ (sec. 1.4.1) and from Eq. (1.8)

$$\lambda = \frac{hc}{E} \quad \dots (ii)$$

Substituting values of h , C and E

$$\lambda = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{10.2 \times 1.6 \times 10^{-19}}$$

$$= 12.16 \times 10^{-10} \text{ m or } 1216 \text{ \AA} \quad \dots (iii)$$

It may be noted that 10.2 eV has been converted in $10.2 \times 1.6 \times 10^{-19} \text{ J}$.

Proceeding as in above case, when energy of exciting electron is 12.09 eV

$$12.09 = 13.61 \left(\frac{1}{1^2} - \frac{1}{n^2} \right)$$

or $\frac{13.61}{n^2} = 1.52$

or $n^2 = 9$ or $n = 3$... (iv)

i.e. when 12.09 eV energy is imparted to ground level electron of hydrogen atom it is excited to third orbits. Thus while coming back to ground level it will lose an energy of 12.09. Using Eq. (ii)

$$\lambda = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{12.09 \times 1.6 \times 10^{-19}}$$

$$= 10.26 \times 10^{-10} \text{ m or } 1026 \text{ \AA} \quad \dots(v)$$

It may also be noted that in hydrogen spectrum the above two drops of electrons from higher orbits for which $n = 2$ and 3 will respectively result into first two lines of Lyman Series. Hence λ may also be calculated by using Eq. (1.14). Thus in first case

$$\frac{1}{\lambda} = 109678 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = 109678 \times \frac{3}{4} \frac{1}{\text{cm}}$$

$$\text{Hence } \lambda = 1216 \text{ \AA}$$

In the second case

$$\frac{1}{\lambda} = 109678 \left(\frac{1}{1^2} - \frac{1}{3^2} \right) = 109678 \times \frac{8}{9}$$

$$\text{Hence } \lambda = 1026 \text{ \AA. [Ans.]}$$

1.7. The Arrangement of Electrons in the Atom

The chemical element which an atom constitutes also depends for its properties upon the positive charge that it carries. This positive charge is equal to the atomic number Z . Since the atom

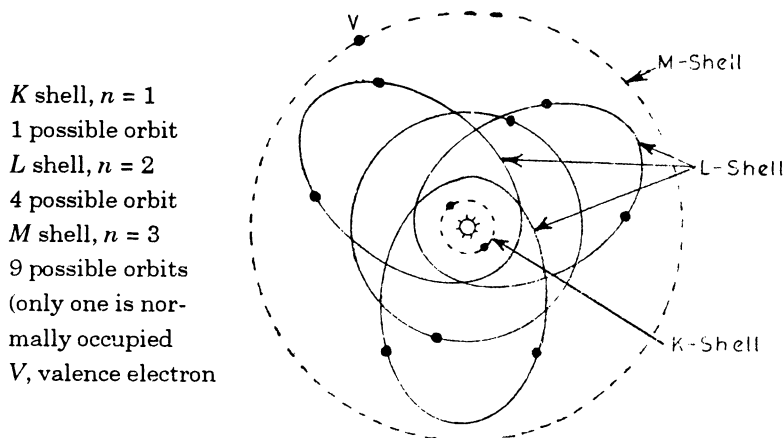


Fig. 1.9. Sodium atom [atomic number = 11] showing orbits normally occupied. The three elliptical orbits in L -shell have equal energies.

as a whole is neutral, the atom will also contain Z electrons. The positive charge of the atom, according to Rutherford's experiment resides in a very small nucleus. However, the above experiment could not indicate how the electrons are distributed. In the Bohr atomic theory it was seen that the assumption of electrons occupying certain well defined orbits or shells was made. Sommerfeld extended Bohr's conception to include elliptical orbits and thus idea of sub-

shells was introduced. Thus a main shell in an atom may be divided into various subshells. This atomic model for sodium atom is shown in Fig. 1.9.

1.7.1. Periodic Table. The properties of the elements are found to vary in a periodic manner if they are arranged in order of increasing atomic number. Each period contains a sequence of element. For each element in one period there are elements at the corresponding point in the other periods that has similar properties. All the elements having similar properties are set to form a family. This is the basis of periodic table. The structure of the atom can be conveniently understood if it is imagined that elements are built up in order of ascending atomic numbers. To begin with one may start with simplest atom *i.e.* hydrogen and add electron one at a time together with the necessary nuclear particles, until the entire list of elements is covered. As the electrons are added they have natural preference for the lowest energy level. This will result filling of shells successively, starting from innermost orbit and progressing outward as the capacity of each shell is reached.

1.7.2. Subshells. It has already been indicated that the atomic shells are further subdivided into subshells. Each shell has a fixed capacity and similarly each subshell, too, can hold a specified number of electrons.

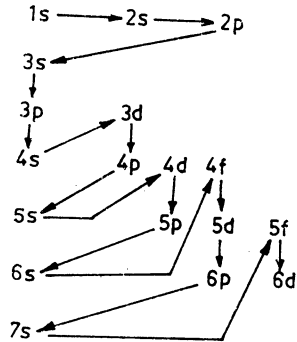
The main electronic shells are designated by letters *K, L, M, N, O, P* and *Q*. These shells correspond to quantum numbers $n = 1, 2, 3, 4, 5, 6$ and 7 . For example the *K* shell has the principal quantum number $n = 1$ and so on. The subshells in each main shell are designated by letters *s, p, d* and *f* with quantum numbers $l = 0, 1, 2$ and 3 respectively. (The idea of quantum number l called azimuthal quantum number was introduced in sec. 1.4). This may be noted that the number of subshells in given main shell is same as its principal quantum number. However, in none of the known elements does any of the last three shells *O, P, Q* contains more than three subshells.

The number of electrons contained in a given main shell is the sum of electrons occupying its subshells. Table 1.2 describes the capacity of main and subshells.

Table 1.2
Electron Capacities of Main and Subshells

Main shell	Quantum No.	Subshell capacity				Main shell capacity
		<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	
K	1	2	—	—	—	2
L	2	2	6	—	—	8
M	3	2	6	10	—	18
N	4	2	6	10	14	32

It may be pointed out the capacity described in Table 1.2 apply only to the inner completed main shell. The outermost main shell never contains more than 8 electrons. Once this number is reached the next electron begins to fill the next main shell, occupying its subshell. Only after both spaces in *s*-subshell are filled does the inner incomplete main shell go on filling up. This process of filling of shells produces what are known as transitional elements. The order in which the electrons fill the subshells is shown in Fig. 1.10.



The electrons possess angular momentum or angular spin which produces a magnetic moment in each electron. The direction of the spin is represented by a spin vector. In most atoms electrons arrange themselves in pairs with parallel but opposite spin vector, resulting into vanishing of net magnetic moment. Thus most materials do not show overall magnetism. However, in a few elements a small number of unpaired electrons may result in magnetism of the bulk material.

A state has been reached now when the development of periodic system can be examined. The first element hydrogen ($Z = 1$) has only 1 electron. This electron occupies the *K* shell. This element is designated by the notation $1s^1$. The "1" refers to the principal quantum number, $n = 1$ and "*s*" refers to *s* subshell (the only subshell present). The superscript "1" represents the number of electrons in the *s*-subshell. If, suppose, another electron is added (plus a proton and two neutrons into the nucleus), the next member

on the periodic table that is *helium* will be obtained. Helium is represented by the notation $1s^2$ indicating that two electrons now occupy the s subshell of the first main shell. From the Table 1.2 it may also be concluded that the first shell now is closed and thus helium is a stable element.

If a third electron is now added it will settle in the L -shell (for which $n = 2$). Further it will settle in the first or s -subshell to produce *lithium*. Thus the electronic configuration of lithium will be $1s^2 2s^1$. Since there is only one electron in the second shell while it can accommodate eight, lithium will be chemically very active. More electrons added will go on filling the L shell through its s and p -subshells until 8 electrons occupy the shell which will result into stable electronic configuration of $1s^2, 2s^2, 2p^6$. This element is neon in which second orbit is closed. All the intermediate elements from lithium through neon are chemically active while neon like helium is stable or inert.

Sodium is the next element with $Z = 11$. In this element the 11th electron settles in the s -subshell of M -shell (For which $n = 3$). This element is designated by $1s^2, 2s^2, 2p^6, 3s^1$. Sodium is unstable like lithium and their properties are similar because both have 1 electron each in the outermost orbit. Manganese with configuration of $1s^2 2s^2 2p^6 3s^2$ has two electrons in the outermost orbit and its properties are similar to those of beryllium which also has 2 electrons in the outermost orbit, though its outermost orbit is L -shell with $n = 2$. Similar comparisons can be made for all the elements which can be arranged in groups or families having same numbers of electron in the outermost orbit. The electrons in the outermost orbit which are not completely filled are known as valence electrons. Table 1.3 describes the electronic configurations of elements in the periodic table. It may be noted from this table that all the alkali metals have one valence electron, the alkali earth elements have two valence electron while carbon family has 4 and the halogens 7. However, since the outermost main shell can never have more than 8 electrons, the number of valence electrons will always be less than this number. If the number of electron in the outermost shell becomes 8, the atom becomes stable. The valence electrons account for most of the chemical properties of the element and also are responsible for forming bonds between two or more atoms. These electrons are not strongly attached to the rest of the atom therefore may be removed by various means.

When an electron is removed from an atom a net positive charge is left on it. Such an atom becomes unstable and is referred

to as an ion. A negative ion is obtained when an atom attracts an additional electron in its outermost orbit thus gaining a net negative charge. The charged ions attract or repel each other if their charges are opposite or same.

Tabel 1.3
The Electronic Configuration of the Elements

	<i>n</i>	<i>Element</i>	<i>K</i>	<i>L</i>	<i>M</i>	<i>N</i>				<i>O</i>				<i>P</i>	
	<i>l</i>		1	2	3	4	5	6	7	8	9	10	11		
						<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>s</i>	
1st Period	1	H	1												
	2	He	2												
2nd Period	3	Li	2	1											
	4	Be	2	2											
	5	B	2	2	1										
	6	C	2	2	2										
	7	N	2	2	3										
	8	O	2	2	4										
	9	F	2	2	5										
	10	Ne	2	2	6										
	3rd Period	11	Na	2	2	6	1								
		12	Mg	2	2	6	2								
13		Al	2	2	6	2	1								
14		Si	2	2	6	2	2								
15		P	2	2	6	2	3								
16		S	2	2	6	2	4								
17		Cl	2	2	6	2	5								
18		Ar	2	2	6	2	6								
	19	K	2	2	6	2	6		1						
	20	Ca	2	2	6	2	6		2						
4th Period Transi- tional elements	21	Sc	2	2	6	2	6	1	2						
	22	Ti	2	2	6	2	6	2	2						
	23	V	2	2	6	2	6	3	2						
	24	Cr	2	2	6	2	6	5	1						
	25	Mn	2	2	6	2	6	5	2						
	26	Fe	2	2	6	2	6	6	2						
	27	Co	2	2	6	2	6	7	2						
	28	Ni	2	2	6	2	6	8	2						
	29	Cu	2	2	6	2	6	10	1						
	30	Zn	2	2	6	2	6	10	2						

	31	Ga	2	2	6	2	2	6	10	2	1			
	32	Ge	2	2	6	2	2	6	10	2	2			
	33	As	2	2	6	2	2	6	10	2	3			
	34	Se	2	2	6	2	2	6	10	2	4			
	35	Br	2	2	6	2	2	6	10	2	5			
	36	Kr	2	2	6	2	2	6	10	2	6			
	37	Rb	2	2	18	2	2	6		2	1			
	38	Sr	2	2	18	2	2	6		2	1			
5th Period Transi- tional elements	39	Y	2	8	18	2	2	6	1	2	2			
	40	Zr	2	8	18	2	2	6	2	2	2			
	41	Nb	2	8	18	2	2	6	4	1	1			
	42	Mo	2	8	18	2	2	6	5	1	1			
	43	Te	2	8	18	2	2	6	6	1	1			
	44	Ru	2	8	18	2	2	6	7	1	1			
	45	Rh	2	8	18	2	2	6	8	1	1			
	46	Pd	2	8	18	2	2	6	10	1	1			
	47	Ag	2	8	18	2	2	6	10	1	1			
	48	Cd	2	8	18	2	2	6	10	1	2			
	49	In	2	8	18	2	2	6	10	2	1			
	50	Sn	2	8	18	2	2	6	10	2	2			
	51	Sb	2	8	18	2	2	6	10	2	3			
	52	Te	2	8	18	2	2	6	10	2	4			
	53	I	2	8	18	2	2	6	10	2	5			
	54	Xe	2	8	18	2	2	6	10	2	6			
6th Period 14 Rare- earth elements	55	Cs	2	8	18	2	2	6	10	2	2		1	1
	56	Ba	2	8	18	2	2	6	10	2	2		1	2
	57	La	2	8	18	2	2	6	10	2	2		2	2
	58	Ce	2	8	18	2	2	6	10	1	2	1		2
	59	Pr	2	8	18	2	2	6	10	2	2	1		2
	60	Nd	2	8	18	2	2	6	10	4	2			2
	61	Pm	2	8	18	2	2	6	10	5	2			2
	62	Sm	2	8	18	2	2	6	10	6	2			2
	63	Eu	2	8	18	2	2	6	10	7	2			2
	64	Gd	2	8	18	2	2	6	10	7	2	1		2
65	Tb	2	8	18	2	2	6	10	8	2	1		2	
66	Dy	2	8	18	2	2	6	10	8	2	1		2	
67	Ho	2	8	18	2	2	6	10	9	2	1		2	
68	Er	2	8	18	2	2	6	10	10	2	1		2	
69	Tm	2	8	18	2	2	6	10	10	2			2	
70	Yb	2	8	18	2	2	6	10	10	2			2	
71	Lu	2	8	18	2	2	6	10	10	14	1		2	

	72	Hf	2	8	18	2	6	10	14	2	6	2		2	
	73	Ta	2	8	18	2	6	10	14	2	6	3		2	
	74	W	2	8	18	2	6	10	14	2	6	4		2	
	75	Re	2	8	18	2	6	10	14	2	6	5		2	
	76	Os	2	8	18	2	6	10	14	2	6	6		2	
	77	Ir	2	8	18	32	2	6	7		2				
	78	Pt	2	8	18	32	2	6	9		1				
	79	Au	2	8	18	32	2	6	10		1				
	80	Hg	2	8	18	32	2	6	10		2				
6th Period	81	Ti	2	8	18	32	2	6	10		2	1			
	82	Pb	2	8	18	32	2	6	10		2	2			
	83	Bi	2	8	18	32	2	6	10		2	3			
	84	Po	2	8	18	32	2	6	10		2	4			
	85	At	2	8	18	32	2	6	10		2	5			
	86	Rn	2	8	18	32	2	6	10		2	6			
	87	Fr	2	8	18	32	2	6	10		2	6		1	
	88	Ra	2	8	18	32	2	6	10		2	6		2	
7th Period Actinide series	89	Ac	2	8	18	32	2	6	10		2	6	1	2	
	90	Th	2	8	18	32	2	6	10		2	6	2	2	
	91	Pa	2	8	18	32	2	6	10		2	6	3	2	
	92	U	2	8	18	32	2	6	10	3	2	6	1	2	
	93	NP	2	8	18	32	2	6	10	5	2	6		2	
	94	Pu	2	8	18	32	2	6	10	6	2	6		2	
	95	Am	2	8	18	32	2	6	10	7	2	6		2	
	96	Cm	2	8	18	32	2	6	10	7	2	6	1	2	
	97	Bk													
	98	Cf													

Example 1.6. Write down the electronic configuration of (i) Li (ii) N (iii) C (iv) Na (v) Ar.

Solution. (i) Li has atomic number of 3, hence 3 electrons. Its configuration $1s^2 2s^1$.

(ii) N, $Z = 7$ hence electronic configuration $1s^2 2s^2 2p^3$.

(iii) C, $Z = 6$ hence electronic configuration $1s^2 2s^2 2p^2$.

(iv) Na, $Z = 11$ hence electronic configuration $1s^2 2s^2 2p^6 3s^1$.

(v) Ar, $Z = 18$ hence electronic configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6.$$

Example 1.7. Find the elements which have the following levels filled in the ground state.

(a) K and L shells, the 3s subshell and one half of 3p subshell

(b) K, L and M shells, the 4s, 4p, 4d and 5s subshells.

Solution.

(a) Refer to Table 1.2 and prepare following table :

Shell	Principal Quantum No.	Subshell	No. of electrons
K	1	s	2
L	2	s	2
		p	6
M	3	s	2
		p	3
			Total = 15

Filling of subshell must follow the rule depicted in Fig. 1.10. In this case, however the subshells $1s$, $2s$, $2p$, $3s$ and $3p$ fill in sequence. Hence the above table is prepared from which total number of electrons is 15.

Hence $Z = 15$.

(b) Following the rule of Fig. 1.10 the subshells will fill in this order :

 $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d$

Table is prepared as under :

Shell	Principal Quantum No.	Subshell	No. of electrons
K	1	s	2
L	2	s	2
		p	6
M	3	s	2
		p	6
		d	10
N	4	s	2
		p	6
		d	10
O	5	s	2
			Total = 48

Total no. of electrons is 48.

Hence $Z = 48$. [Ans.]**1.8. Quantum Numbers**

De Broglie in 1924 had postulated the wave characteristic for electrons. The fact that an electron has wavelength does not necessarily mean that it is a wave. However, it means that the motion of the electron is governed by the same differential equations that

describe wave motions. In 1926 Schrodinger first suggested that electrons obey an equation similar to that of a vibrating string clamped at both ends. Such an equation is

$$\frac{d^2u}{dx^2} + \frac{4\pi^2}{\lambda^2} u = 0 \quad \dots(1.18)$$

Schrodinger modified the above equation for electrons as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - U) \psi = 0 \quad \dots(1.19)$$

where E represents the total energy and U is the potential energy. The three dimensional form of the above equation is

$$\nabla^2\psi \frac{8\pi^2m}{h^2} (E - U) \psi = 0 \quad \dots(1.20)$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \dots(1.21)$$

ψ in these equations is known as *wave function*. The solution of Eqn. (1.20) will give the distributions of electron around a nucleus. These solutions are like the solutions of vibrating string equation in the sense that they are quantized and contain integral numbers of nodes. However, in the case of electron $\psi^2 dv$ represents the probability that the electron will be found in the volume dv or for a spherically symmetric function $4\pi r^2\psi^2 dr$ is the probability that the electron will be found between r and $r + dr$. It may also be remembered that wave function ψ is three-dimensional and hence its nodes (where $\psi = 0$) will be surfaces rather than points as in the case of string. These surfaces around the nucleus represent the locations where probability of finding an electron is zero. The greater the number of nodes in the wave function the higher is the energy of electrons.

The total number of nodes *i.e.* surfaces on which $\psi = 0$, is equal to n . The ground state or lowest energy state will be that with one node located at $r = \infty$. There will be three sets of quantum numbers obtained as solution to three dimensional wave equation. These quantum numbers are presented by letters n , l , and m . Each of these numbers can have only certain values, described in Table 1.4. The principal quantum number n is the measure of how the total energy is quantized. It has values, 1, 2, 3, The quantum numbers l describe the way in which the angular momentum of the electron is quantized. It has small effect on the energy. l can have only the values 0, 1 ($n - 1$). The l states are indicated by letters to avoid

confusion with the values of n . Thus $l = 0$ is represented by s , $l = 1$ is represented by p , $l = 2$ means d while f indicates $l = 3$. The quantum number m is a measure of angle between the electron angular momentum vector and an applied magnetic field. m can have only integral values from $+l$ to $-l$, including zero. Electron in a subshell corresponds to a unique quantum state possessing a combination of n , l and m . This subshell is also known as *orbital*.

Table 1.4
Permissible Values of the Three Quantum Numbers

Quantum Number	Permissible Values
n	1, 2, 3, 4, 5, 6
l	0(s), 1(p), 2(d), 3(f) ($n - 1$)
m	+ l ,, + 1, 0, - 1,, - l

The three quantum numbers described above along with a fourth-one to be described later lay the guidelines for arrangement of electrons in an atom. These electronic configurations have already been described. However, the basis for these configurations was obtained from *Pauli's exclusion principle*. The principle states that each orbital can contain no more than two electrons and these two must have opposite spins. This principle can also be stated that "in any particular atom no two electrons may have same four values for the four quantum numbers". The spins of electrons are designated by fourth quantum number m_s . This number can have values of only $+\frac{1}{2}$ or $-\frac{1}{2}$.

Four quantum numbers are thus required to describe the state of any electron. These are n , l , m and m_s . The Pauli's exclusion principle in other words, states that the group of values of four quantum number must be different for the different electrons.

Table 1.5 describes quantum states in first four orbits. These quantum states have already been described under electronic configuration. To emphasise they are described here again.

- *Principal quantum number*, $n = 1, 2, 3, 4, 5$, represents the nodes obtained from solution of schrodinger equation. Each node is a surface on which the probability of finding an electron is zero ($\psi = 0$).
- *Azimuthal quantum number*, $l = 0, 1, 2, 3, 4$,, represents subshells or orbitals for a give value of n . Thus for $n = 3$, there are three main possible oribts designated by

K, L, M. For K shell only one subshell s with capacity of two electrons which can have opposite spins ($+\frac{1}{2}$ and $-\frac{1}{2}$) is possible. For L shell four possible orbitals exist. They are one s and three p orbitals. These facts are shown in Fig. 1.9.

- *Magnetic quantum number, m .* For each value of l there are $2l + 1$ values of m , having values from l to $-l$.
- *Spin quantum number, m_s .* For each value of n, l and m , there are two values of m_s , viz. $+\frac{1}{2}$ and $-\frac{1}{2}$.

Table 1.5 given on next page.

1.9. More Details on Periodic Table

An element is identified by (1) its atomic number and (2) electronic grouping in outer atomic zone. The factor (2) determines to which group of the periodic table the element will belong and also this factor is related to the valency of the element. The factor (1) determines the position of the element in that group. Both the factors together indicate the chemical nature of the element. The arrangement of the periodic table is shown in Fig. 1.11. The periods are presented horizontally and numbered 1 to 7 in the figure. Under each number the orbitals that are filled in a particular period are also shown. The atomic masses for the elements are depicted below the symbol while atomic numbers are shown above the symbols. For convenience of horizontal length lanthanide (rare earth) series comprising elements of atomic numbers 51 to 70 and Actinide series comprising elements of atomic numbers 89 to 102 have been lifted from 6th and 7th rows and placed below the main body of the table. The vertical columns present the groups and are further subdivided into A and B. Thus group IA, IB etc. can be identified in the Fig. 1.11. The members of same group and particularly subgroups like IA and IB have similar physical and chemical properties. The subgroups are often referred to as families.

For Fig. 1.11 see attached page.

To further understand the property variation from group to group it will be helpful to have energies plotted on a diagram with respect to various subshells like ELD. In this diagram the relative level of energy is also indicative of the fact in which order the subshells will fill. Fig. 1.12 shows such a diagram and on the right side of the various energy levels (subshells) this order can be seen to match with that already shown in Fig. 1.10. It may be noted that

Table 1.5
The Number of Quantum States in First Four Shells

<i>Principal Quantum Number</i>	<i>Shell Designation</i>	<i>Azimuthal Quantum Number</i>	<i>Subshells or Orbitals</i>	<i>Magnetic Quantum Number</i>	<i>Spin Quantum Number</i>	<i>Number of Energy States</i>
1	K	0	s	0	1/2, -1/2	2
2	L	0	s	0	1/2, -1/2	2
		1	p	1, 0, -1	1/2, -1/2	6
3	M	0	s	0	1/2, -1/2	2
		1	p	1, 0, -1	1/2, -1/2	6
		2	d	2, 1, 0, -1, -2	1/2, -1/2	10
4	N	0	s	0	1/2, -1/2	2
		1	p	1, 0, -1	1/2, -1/2	6
		2	d	2, 1, 0, -1, -2	1/2, -1/2	10
		3	f	3, 2, 1, 0, -1, -2, -3	1/2, -1/2	14

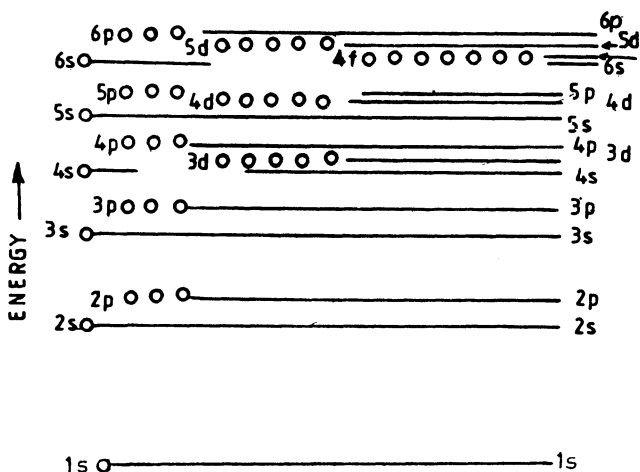


Fig. 1.12. The energy levels of various subshells in an atom.

the electrons at $3p$ level will be excited to higher level $4s$ requiring energy less than that required for exciting electrons of $2p$ to $3s$ level. Such energy is still smaller for transition between $3d$ and $4s$ and between $4p$ and $5s$. It means that with increasing quantum number the transition energy requirement reduces and hence such electrons are more easily excited to higher level whereby the valency increases. For this reason behaviour of elements in different groups are not entirely analogous. Thus while fluorine of 2nd period has only one valency, chlorine of 3rd period by belonging to group of fluorine (VIIA) has more than one valency because $3p$ electrons of chlorine can be more easily excited to $3d$ and $4s$ electrons than $2p$ electrons of fluorine to $3s$ level. The similar situation exists in 4th, 5th and 6th periods.

The chemical properties of the elements depend mainly on the reactivity of the electrons in outermost shells or energy levels. Noble gases having s^2p^6 electron configuration are least reactive. All the noble gases including He (others are Ne, Ar, Xe and Rn) are included in group VIIIA and are known for chemical inactivity.

Electronegativity and Electropositivity. Electronegativity is understood as capability of an atom to attract electrons to itself. On the other hand electropositivity relates to giving up of electrons in a chemical reaction. By losing electron an atom becomes positive ion or **cation**. By gaining electron the atom becomes negative ion or **anion**. Electronegativity is found in non-metallic elements oc-

cupying groups VIA and VIIA. On the other hand the most electropositive elements are found in groups IA and IIA and they are metallic in nature. In periodic table (Fig. 1.11), it can be seen that, atoms from left to right and from bottom to top become more electronegative, meaning their electron affinity increases. Inversely the elements become more electropositive from right to left and top to bottom. The **electron affinity** is the energy given out when an electron is added to an atom and an anion is formed. The energy required to remove the most loosely bound electron from an atom is called **ionization potential**. Lithium, an alkali metal has the highest ionization potential and this gradually decreases downward in group IA. The metallic element francium has the least ionization potential and is most active chemically.

For electronegative elements it is the reverse that is true. They have high values of ionization potential which decreases from top to bottom. Fluorine, having highest ionization potential, is most active chemically. The electronegative elements are described in terms of **electron affinity** rather than ionization potential.

Oxidation Number. It is yet another measure of above two characteristics. The number of electrons given up by an electropositive atom is represented by a **positive oxidation number** whereas a **negative** oxidation number indicates number of electrons accepted by an atom. Carbon, silicon, germanium, arsenic and antimony are some elements belonging to groups IVA and VA which act both as electronegative and electropositive. Thus they show the characteristics of both metal and non metal. Table 1.6 describes oxidation number (both positive and negative) for some elements of periodic table. (See Table 1.6 on next page)

Electronegativity is defined as a degree to which an atom attracts electrons to itself. Each element is assigned an electronegativity number, measuring on scale from zero to 4.1. The electropositive elements like alkali metals belonging to group I A have low electronegativity—Li and Na have 1.0 each while K, Rb and Cs have electronegativity of 0.9. Fluorine has highest electronegativity of 4.1 while oxygen and nitrogen are characterized by 3.5 and 3.1 respectively.

1.10. Atomic and Ionic Sizes

Atomic radii increase in each group from top to bottom for the simple reason that each lower atom has a higher principal quantum number therefore new electrons enter shells further removed from the nucleus. In the same period the principal quantum number remains constant and new electrons enter the existing outer orbit. With increasing number of electrons the force of attraction of the

Table 1.6
Oxidation Numbers

<i>Element</i>	<i>Period</i>	<i>Group</i>	<i>Electronic Configuration</i>	<i>Oxidation Number</i>
H	1	IA	$1s$	+ 1, - 1
Li	2	IA	$1s^2 2s$	+ 1
Na	3	IA	$1s^2 2s^2 2p^6 3s$	+ 1
K	4	IA	$1s^2 2s^2 2p^6 3s^2 3p^6 4s$	+ 1
V	4	VB	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$	+ 5, + 4, + 3, + 2
Cr	4	VIB	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$	+ 6, + 3, + 2
Mn	4	VII B	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$	+ 7, + 6, + 4, + 3, + 2
Fe	4	VIII B	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$	+ 3, + 2
Cu	4	IB	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$	+ 2, + 1
Zn	4	IIB	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$	+ 2
Ge	4	IVA	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$	+ 4, - 4
As	4	VA	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$	+ 5, + 3, - 3
Sb	5	VA	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$	+ 5, + 3, - 3
C	2	IVA	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^1$	+ 4, + 2, - 2
N	2	VA	$1s^2 2s^2 2p^3$	- 1, - 2
O	2	VIA	$1s^2 2s^2 2p^3$	+ 6, + 4, + 2, - 2
S	3	VI A	$1s^2 2s^2 2p^6 3s 3p^4$	

increased positive charge causes electron clouds to be pulled more strongly towards the nucleus and thus reduce overall radius.

A positive ion is smaller than the corresponding atom which loses electrons to become ion. With positive charge remaining same and number of electron reduced the force of attraction will further compact the ion. The same argument will lead to the idea that negative ion which has electron added in the outer shall will cause the radius to increase.

The ions with the same configuration of orbital electrons form a series called **isoelectronic**. In this series the radii decrease rapidly with increasing positive charge. In any vertical group the radii of possible ions increase with increasing atomic number. Table 1.7 describe the size of some atoms and ions.

Table 1.7
Radii of a Few Atoms and Ions (Angstrom Units)

<i>Element (Atom/ion)</i>	<i>Radius (Å)</i>	<i>Element (Atom/ion)</i>	<i>Radius (Å)</i>
Li	1.57	Al	1.43
Li ⁺	0.60	C	0.77
Na	1.92	Si	1.17
Na ⁺	0.95	N	0.71
K	2.38	P	0.11
K ⁺	1.33	O	0.60
Be	1.13	O ²⁻	1.40
Be ²⁺	0.31	S	1.04
Mg	1.60	S ²⁻	1.84
Mg ²⁺	0.65	F	0.71
Ca	1.97	F ⁻	1.36
Ca ²⁺	0.99	Cl	0.99
B	0.97	Cl ⁻	1.81

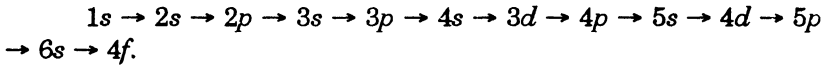
Example 1.8. Write the electronic configuration of Fe atom ($Z = 26$) and Fe²⁺ and Fe³⁺ ions. Use conventional *spdf* notation.

Solution. For writing down the electronic configuration one must remember the capacity of each subshell and the order in which the subshell is to be filled.

For capacity of each subshell see Table 1.2. These are

$$s-2, p-6, d-10 \text{ and } f-14.$$

The order of filling the subshell is shown in Fig. 1.10. It is



For filling in 26 electrons one may start writing the total number of electrons after each subshell is completely filled.

Subshell	1s	2s	2p	3s	3p	4s	3d
Capacity	2	2	6	2	6	2	?
Sum	2	4	10	12	18	20	?

After filling electrons upto 4s the sum of all the electrons is 20 and only 6 electrons remain to be filled whereas the capacity of 3d sub-shell is 10. It means that 3d orbital will remain partially filled with 6 electrons only.

Thus the electronic configuration of Fe atom is



Fe²⁺ ion means the atom of Fe has lost 2 electrons of the outer-most orbit which is 4s. Electronic configuration of Fe²⁺



Fe³⁺ ion means the atom of Fe has lost 3 electrons *i.e.* one more than Fe²⁺. Obviously the loss will occur from 3d electrons. Hence the electronic configuration of Fe³⁺ is



(i), (ii) and (iii) are. [Ans].

EXERCISE 1

- Describe and explain Bohr atomic model.
- Explain : Stationary orbit, ground state and quantum numbers in reference to Bohr's atomic model.
- (a) Derive a mathematical expression for the radius of hydrogen atom.
(b) Show that potential energy = - 2 kinetic energy for a particle in a circular orbit in coulomb potential field. (AMIE, 1978)
- (a) Specify the different quantum numbers describing the state of an electron in an atom. State Pauli's exclusion principle.
(b) Explain how atomic shells and sub-shells are formed. (AMIE, 1979)
- Write brief notes on :
(a) Pauli's exclusion principle,
(b) Non-acceptance of Thompson's model for an atom.

(AMIE, 1980)

6. Explain the terms :
- (a) Electronegativity (b) Electropositivity
 (c) Ionization potential (d) Electron affinity and
 (e) Oxidation numbers.
7. State how the radii of atoms change in a periodic table. Explain while radii of Li atom and its ion are respectively 1.57 \AA and 0.60 \AA those of Oxygen atom and its ion are respectively 0.60 \AA and 1.40 \AA .
8. A hydrogen atom exists with its electron in $n = 3$ state. The electron undergoes a transition to $n = 2$ state. Calculate (a) energy of photon emitted, (b) its frequency (c) its wavelength (d) Is the energy emitted or absorbed.

[Ans. (a) $3.02 \times 10^{-19} \text{ J}$, (b) $4.55 \times 10^{14} \text{ Hz}$, 6590 \AA]

MULTIPLE CHOICE QUESTIONS (1)

1. One eV is equal to
 (a) $1.6 \times 10^{-19} \text{ J}$ (b) $1.6 \times 10^{-13} \text{ J}$
 (c) $1.6 \times 10^{-4} \text{ J}$ (d) $1.6 \times 10^4 \text{ J}$.
2. 1 photon is a quantum of energy equal to
 (a) $h\nu$ (b) $h\nu$
 (c) $1/h\nu$ (d) ν/h .
3. The number of protons in an atom is known as
 (a) atomic weight (b) atomic mass
 (c) atomic number (d) mass number.
4. The nucleons of atom consisting of protons and neutrons are held together by
 (a) magnetic forces (b) electrostatic forces
 (c) centrifugal force
 (d) continuous exchange of sub nucleonic particles.
5. Laws of mechanics are not applicable to electrons moving through matter because
 (a) electrons are very small
 (b) electrons move with very high velocity
 (c) electrons are reflected and interact with others of the same kind
 (d) the density of electron changes during motion.
6. If the atomic number is Z , the energy of an electron in an orbit of radius r is proportional to
 (a) Z (b) Zr
 (c) Z^2 (d) Z^2r .
7. If the energy of an electron of charge e , mass m in n th orbit is $E = (a_1) e^4/n^2$, then

$$(a) a_1 = \frac{m}{8\epsilon_0^2 h^2}$$

$$(b) a_1 = \frac{m}{4\epsilon_0^2 h}$$

$$(c) a_1 = \frac{1}{8\epsilon_0^2 h^2}$$

$$(d) a_1 = \frac{h^2}{8\epsilon_0^2 m}$$

8. Which expression does not represent the angular momentum of an electron in n th orbit
- (a) $m\omega r^2$ (b) $m\omega$
- (c) mVr (d) $\frac{nh}{2\pi}$
9. The energy of X-ray photon is much larger than that of a visible light photon because
- (a) X-ray photon moves with a much higher velocity
- (b) Planck's constant for X-ray is higher than that for visible light
- (c) X-ray photons have higher frequency than visible light photons
- (d) Visible light photons have much smaller wavelength than the X-ray photon.
10. The maximum number of electrons in a shell of quantum number n is
- (a) $\frac{n}{2}$ (b) n
- (c) n^2 (d) $2n^2$
11. A d -sub-shell of M shell will have number of electrons
- (a) less than that in d sub-shell of N shell and this number is 8
- (b) less than that in f sub-shell of N shell and this number is 8
- (c) more than that in p sub-shell of N shell and this number is 8
- (d) same as that in d sub-shell of N shell and this number is 10.
12. Match the list using code given below :
- | I | II |
|---------|-----------------|
| (Shell) | (Energy States) |
| A. K | 1. 8 |
| B. L | 2. 32 |
| C. M | 3. 2 |
| D. N | 4. 18 |
- Code :**
- | A | B | C | D |
|-------|---|---|---|
| (a) 3 | 1 | 4 | 2 |
| (b) 1 | 3 | 4 | 2 |
| (c) 2 | 1 | 3 | 4 |
| (d) 4 | 3 | 2 | 1 |

13. Which combination of quantum numbers is not possible ?
 (a) 1, 1, 1, $-1/2$ (b) 1, 0, 0, $-1/2$
 (c) 3, 1, 1, $+1/2$ (d) 3, 1, 1, $-1/2$.
14. Four quantum numbers of four energy states of p sub-shell of M shell are described below. Select the wrong combination
 (a) $\begin{matrix} 3 & 1 & 1 & 1/2 \\ 3 & 1 & -1 & -1/2 \\ 3 & 1 & 0 & 1/2 \\ 3 & 1 & 0 & -1/2 \end{matrix}$ (b) $\begin{matrix} 3 & 1 & 1 & 1/2 \\ 3 & 1 & -1 & 1/2 \\ 3 & 1 & 0 & 1/2 \\ 3 & 1 & 1 & -1/2 \end{matrix}$
 (c) $\begin{matrix} 3 & 1 & 1 & 1/2 \\ 3 & 1 & 0 & 1/2 \\ 3 & 1 & 1 & 1/2 \\ 3 & 1 & 0 & -1/2 \end{matrix}$ (d) $\begin{matrix} 3 & 1 & 0 & 1/2 \\ 3 & 1 & 1 & 1/2 \\ 3 & 1 & -1 & 1/2 \\ 3 & 1 & -1 & -1/2 \end{matrix}$
15. Correlate the following two statements using the code given below.
 I. After $3p$ sub-shell in atom is filled, the electrons begin to fill the $4s$ sub-shell rather than $3d$ sub-shell.
 II. The difference of energy between $4s$ and $3p$ sub-shells is smaller than that between $3d$ and $3p$ sub-shells.
Code :
 (a) Both I and II are correct and II is the reason for I.
 (b) I and II are independently correct.
 (c) I is correct but II is NOT.
 (d) II is correct but I is NOT.
16. Correlate the following two statements using code given below :
 I. The atoms of elements of smaller atomic number have one valency while those of higher atomic number in the same group have more than one valency.
 II. Chlorine of group VII A has more than one valency while fluorine of the same group has only one valency.
Code :
 (a) Both I and II are correct and II is the reason for I.
 (b) Both I and II are correct and I explains II.
 (c) Both I and II are independently correct.
 (d) Both I and II are NOT correct.
17. The capability of an atom to attract electrons to itself is called
 (a) electropositivity (b) electronic defect
 (c) electronegativity (d) oxidation number.
18. The energy given out when an electron is added to an atom to form anion is called
 (a) electronegativity (b) oxidation number
 (c) ionization potential (d) electron affinity.

19. Choose the correct Statement.

- (a) Atomic size in the same group increases as atomic number increases.
- (b) Atomic size in the same period increases as the atomic number increases.
- (c) Atomic size in the same period decreases as the atomic number increases.
- (d) (a) and (c) are true.

Answers (1)

- | | | | |
|----------------|----------------|----------------|----------------|
| 1. (a) | 2. (b) | 3. (c) | 4. (d) |
| 5. (c) | 6. (c) | 7. (a) | 8. (b) |
| 9. (c) | 10. (d) | 11. (d) | 12. (a) |
| 13. (a) | 14. (c) | 15. (a) | 16. (b) |
| 17. (c) | 18. (d) | 19. (d) | |