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 $4s$ orbital, being lower in energy than the $3d$ orbitals, is occupied by one and two electrons respectively.

A new pattern is followed beginning with scandium (Sc). The $3d$ orbital, being lower in energy than the $4p$ 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 $3d$ orbitals are progressively occupied. We may be puzzled by the fact that chromium and copper have five and ten electrons in $3d$ 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 $3d$ orbitals, the filling of the $4p$ 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 $5s$, $4d$ and $5p$ orbitals are similar to that of $4s$, $3d$ and $4p$ orbitals as discussed above. Then comes the turn of the $6s$ 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 $4f$ and $5d$ orbitals.

After this, filling of $6p$, then $7s$ and finally $5f$ and $6d$ 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 ($4s$ and $3d$) differ slightly in their energies, an electron shifts from a subshell of lower energy ($4s$) to a subshell of higher energy ($3d$), 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.
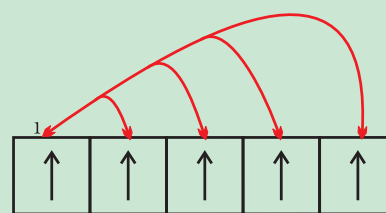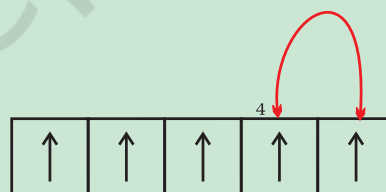
4 exchange by electron 1
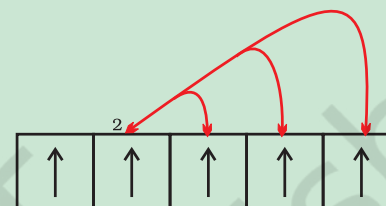
3 exchange by electron 2
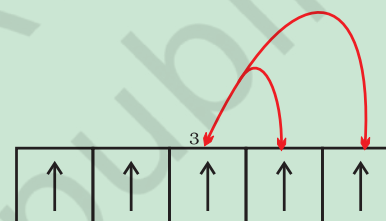
2 exchange by electron 3

1 exchange by electron 4

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

Rationalised 2023-24

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 14C. (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 ?

      $_{6}^{13}C$, $_{8}^{16}O$, $_{12}^{24}Mg$, $_{26}^{56}Fe$, $_{38}^{88}Sr$

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) O2– (d) F–

        (ii) What are the atomic numbers of elements whose outermost electrons are represented by (a) 3s1 (b) 2p3 and (c) 3p5 ?

        (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 ml ?

        (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) $n = 1$,	$1 = 0$,	$ml = 0$,	$ms = -\frac{1}{2}$
(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,   ml = –3,   ms = + ½

(f)   n = 3, l = 1, m_l = 0, m_s = + ½

2.31   How many electrons in an atom may have the following quantum numbers?

(a) n = 4, m_s = – ½   (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 $v = 3.29 \times 10^{15}$ (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 $2p$ orbital, 6 electrons in $3p$ orbital and 5 electron in $4p$ 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) $2s$ and $3s$, (ii) $4d$ and $4f$, (iii) $3d$ and $3p$.

2.65 The unpaired electrons in Al and Si are present in $3p$ 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 $n = 4$?

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

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).

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

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

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

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					

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 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/cm^3)	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	$E\,Cl_3$	$GaCl_3$	ECl_4	$GeCl_4$

PERIODIC SYSTEM OF THE ELEMENTS IN GROUPS AND SERIES

SERIES	0	I	II	III	IV	V	VI	VII	VIII
		GROUPS OF ELEMENTS							
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		
	R	R$_2$O	RO	R$_2$O$_3$	RO$_2$	R$_2$O$_5$	RO$_3$	R$_2$O$_7$	RO$_4$
				HIGHER SALINE OXIDES					
					RH$_4$	RH$_3$	RH$_2$	RH	
				HIGHER GASEOUS HYDROGEN COMPOUNDS					

Fig. 3.1   Mendeleev's Periodic Table published earlier

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

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* *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.*

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.*

a few atoms of them are obtained. Their synthesis and characterisation, therefore, require highly 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	Nh
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 4f- and 5f-**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 4d, 5s and 5p 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.

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

Atomic number	Symbol	Electronic configuration
3	Li	1$s^2$2s^1 **(or)** [He]2s^1
11	Na	1$s^2$2$s^2$2$p^6$3s^1 **(or)** [Ne]3s^1
19	K	1$s^2$2$s^2$2$p^6$3$s^2$3$p^6$4s^1 **(or)** [Ar]4s^1
37	Rb	1$s^2$2$s^2$2$p^6$3$s^2$3$p^6$3d^{10}4$s^2$4$p^6$5s^1 **(or)** [Kr]5s^1
55	Cs	1$s^2$2$s^2$2$p^6$3$s^2$3$p^6$3d^{10}4$s^2$4$p^6$4d^{10}5$s^2$5$p^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

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 and ns^2 outermost electronic configuration belong to the **s-Block Elements**. They are all

s-BLOCK

	1	2
1s		
2s	Li	Be
3s	Na	Mg
4s	K	Ca
5s	Rb	Sr
6s	Cs	Ba
7s	Fr	Ra

H

d-BLOCK

	3	4	5	6	7	8	9	10	11	12
3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5d	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6d	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn

p-BLOCK

	13	14	15	16	17	18
						He
2p	B	C	N	O	F	Ne
3p	Al	Si	P	S	Cl	Ar
4p	Ga	Ge	As	Se	Br	Kr
5p	In	Sn	Sb	Te	I	Xe
6p	Tl	Pb	Bi	Po	At	Rn
7p	Nh	Fl	Mc	Lv	Ts	Og

f-BLOCK

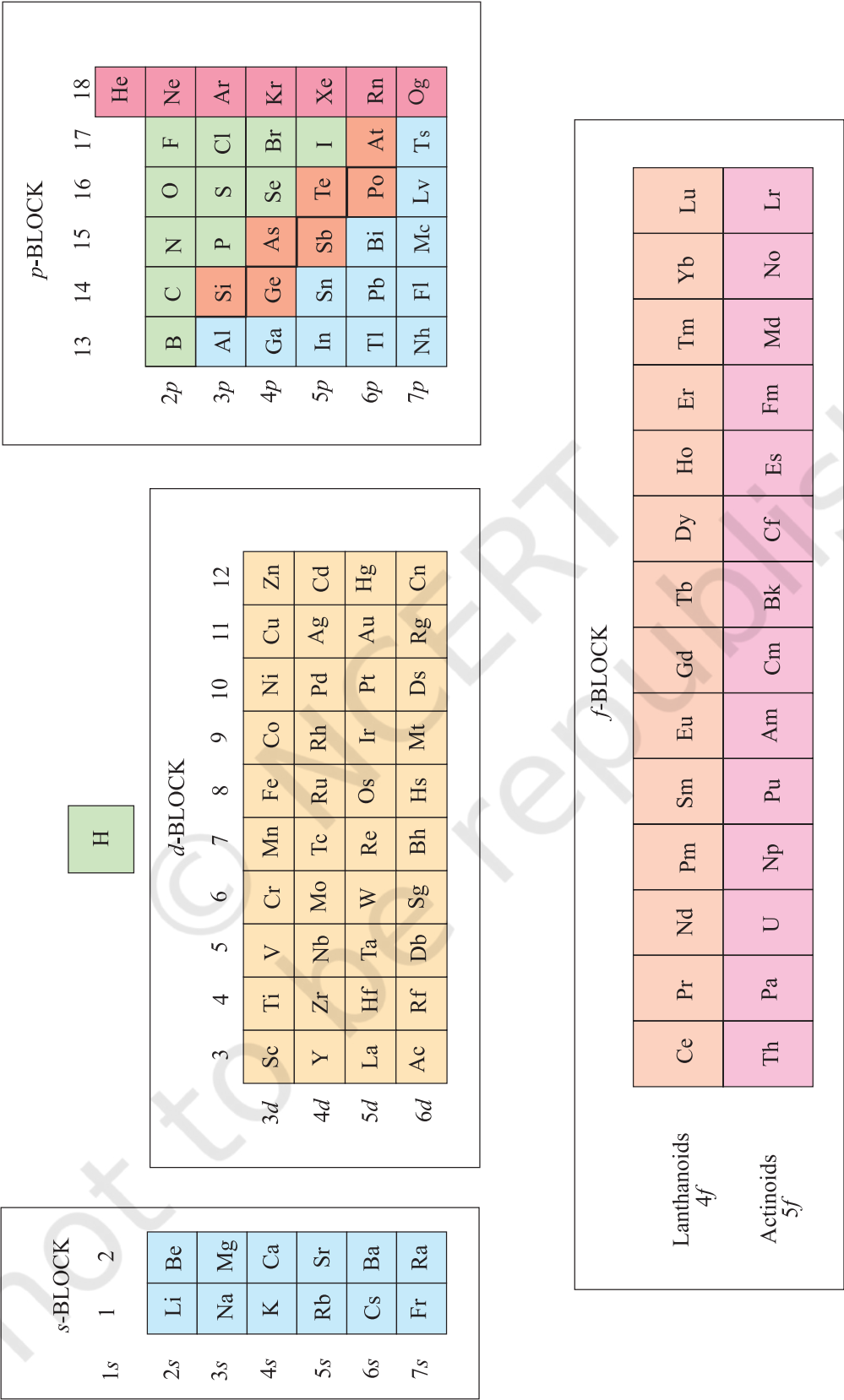| Lanthanoids 4f	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinoids 5f	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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 ( ).*

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 $(n-1)d^{1-10}ns^{0-2}$ except for Pd where its electronic configuration is $4d^{10}5s^0$. 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, $(n-1)d^{10}ns^2$ 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 $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. 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

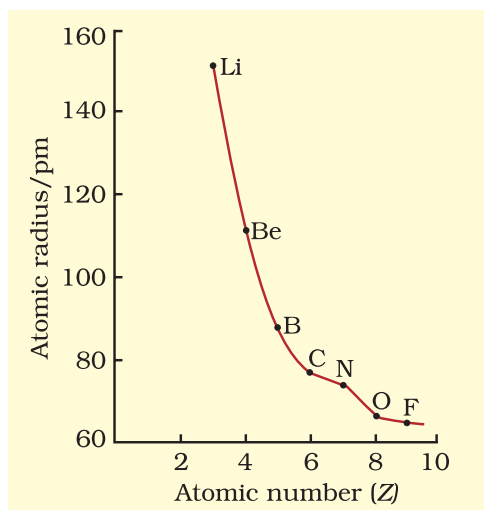| Atom (Group I)	Atomic Radius	Atom (Group 17)	Atomic Radius
Li	152	F	64
Na	186	Cl	99
K	231	Br	114
Rb	244	I	133
Cs	262	At	140

Fig. 3.4 (a) *Variation of atomic radius with atomic number across the second period*
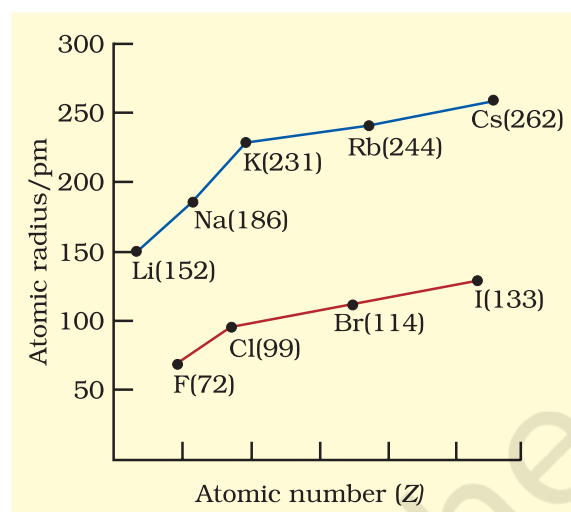

Fig. 3.4 (b) *Variation of atomic radius with atomic number for alkali metals and halogens*

(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.

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* *Two or more species with same number of atoms, same number of valence electrons and same structure, regardless of the nature of elements involved.*

In other words, the first ionization enthalpy for an 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
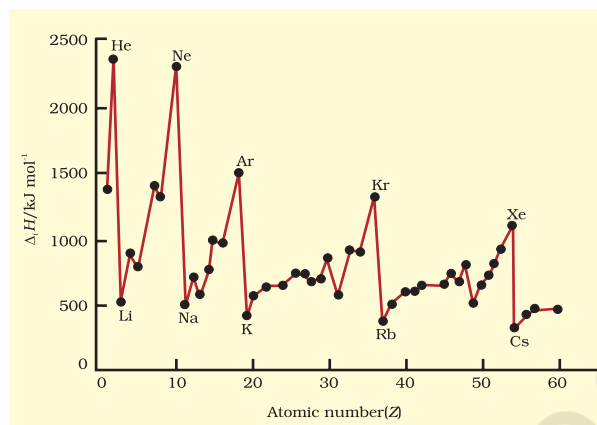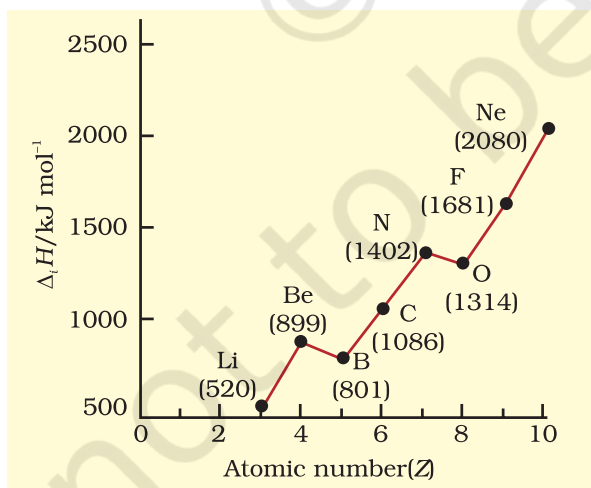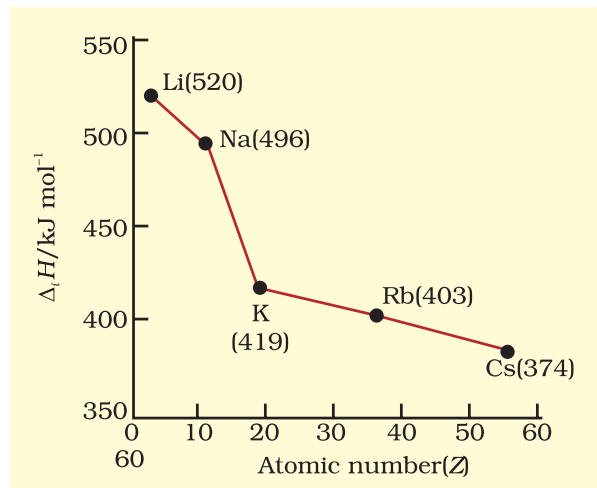

Fig. 3.5 *Variation of first ionization enthalpies ($\Delta_i H$) with atomic number for elements with Z = 1 to 60*

can be correlated 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

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.*