

7. Modern Periodic Table



Can you recall?

- What was the basis of classification of elements before the knowledge of electronic structure of atom?
- Name the scientists who made the classification of elements in the nineteenth century.
- What is Mendeleev's periodic law?
- How many elements are discovered upto now?
- How many horizontal rows and vertical columns are present in modern periodic table?

7.1 Introduction

In the early nineteenth century about 30 elements were known and were classified into three types on the basis of their physical properties as: **metals, nonmetals and metalloids**. Subsequent noteworthy attempts for classification of the increasing number of elements based on **atomic mass** were **Dobereiner's triads** and **Newlands' octaves**.



Just think

- How many days pass between two successive full moon nights?
- What type of motion does a pendulum exhibit?
- Give some other examples of periodic events.

In 1869, **Russian chemist Dmitri Mendeleev** put forth periodic table of the 63 elements known at that time using the atomic mass and properties of elements. Mendeleev's periodic table was based on the as **Mendeleev's periodic law** which is stated as "**The physical and chemical properties of elements are periodic function of their atomic masses**".

Mendeleev arranged the elements known at that time in an increasing order of their atomic masses. The serial or ordinal number of an element in the increasing order of atomic mass was referred to as its atomic number. He folded this list in accordance with recurrence of properties of elements and formed his periodic table consisting of vertical groups and horizontal series (now called periods).

In Mendeleev's periodic table, elements belonging to the same group showed similar properties. Properties of elements in a series/period showed gradual variation from left to right. Mendeleev left some gaps corresponding to certain atomic numbers in the periodic table so as to maintain the periodicity of the properties. Mendeleev's periodic table was accepted by the scientific community since the newly discovered elements fitted well into the gaps with their properties as predicted by Mendeleev's periodic law. Inert gases, not predicted by Mendeleev and discovered in later years also could be accommodated in this periodic table by creating an additional group.

After the discovery of atomic structure, the atomic number, which was an ordinal number assigned to element in Mendeleev's periodic table, was recognized as the proton number, Z , of that element. This was the outcome of **Henry Moseley's work (1913)** on x-ray spectroscopic study of a large number of elements. Moseley showed that the frequency of x-ray emitted by an element is related to atomic number, Z , rather than the atomic mass. The atomic number, Z , was considered as more fundamental property of the atom than the atomic mass. As a result, Mendeleev's periodic law was modified. It is called the **modern periodic law** and is stated as: "**The physical and chemical properties of elements are a periodic function of their atomic numbers**".

Mendeleev’s periodic table was revised in accordance with the modern periodic law. We will look into the final revised version known as the **modern periodic table** also called the **long form of periodic table** in the following sections.

7.2 Structure of the Modern Periodic Table

Over a long period of time many scientists have come up with different forms of periodic table. However, the so called ‘**long form of periodic table**’ or ‘**the modern periodic table**’, which is a revised version of Mendeleev’s periodic table, is the most convenient and widely used form of the periodic table of elements today.

The modern periodic table has horizontal rows intersecting the vertical columns giving rise to a number of boxes. The horizontal rows are called periods (which Mendeleev called series) and the vertical columns are called groups. There are **seven periods** (numbered 1 to 7) and **eighteen groups** (numbered 1 to 18) in the modern periodic table.

This numbering of the periods and groups is recommended by the **International Union of Pure and Applied Chemistry, IUPAC**. The boxes formed at the intersection of the periods and groups are the places for individual elements. Below the main table are placed **two series** containing fourteen elements each. There are in all 118 boxes to accommodate **118 elements** in the modern periodic table. As on today all the 118 boxes are filled as a result of discovery of manmade elements. IUPAC has approved names and symbols of all the 118 elements. (Refer to Fig. 7.1)

The overall shape of the modern periodic table shows that it is divided into four blocks. Two groups on left form the **s-block**, six groups on the right constitute the **p-block**, ten groups in the center form the **d-block** and the two series at the bottom constitute the **f-block** (Fig. 7.2).

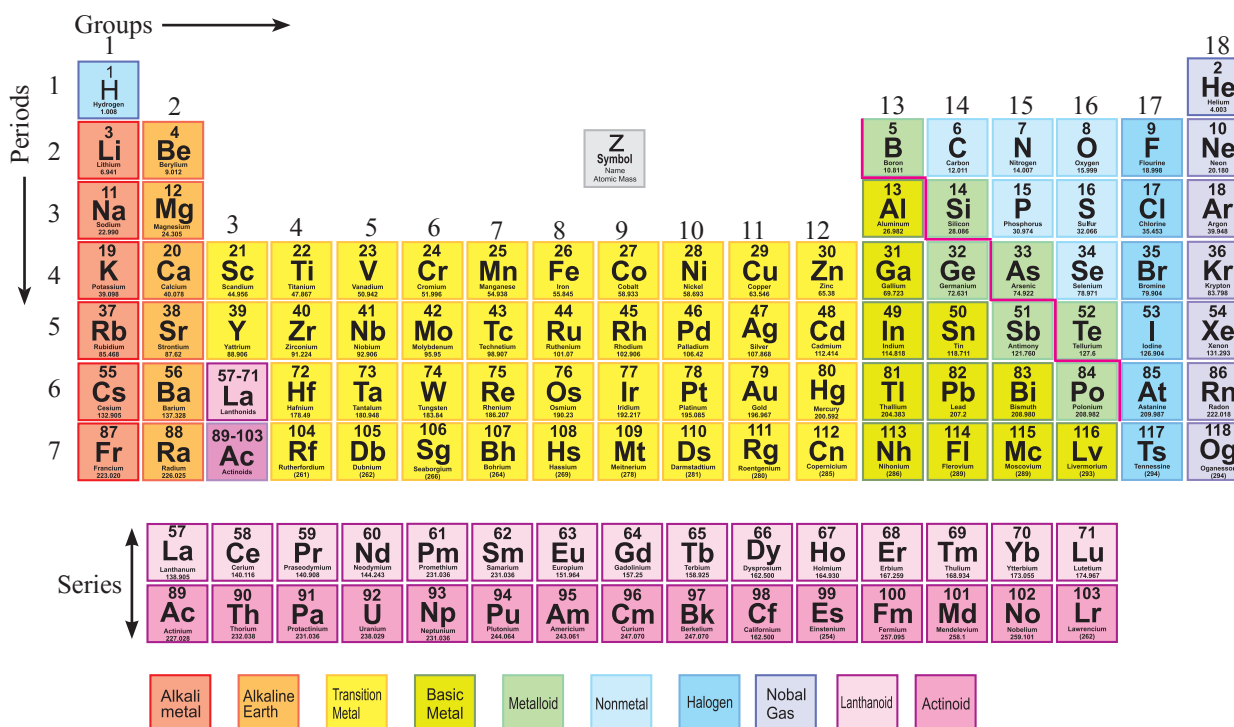


Fig. 7.1 : Modern Periodic Table

(Refer page 271)

7.3 Periodic Table and Electronic configuration



Can you recall?

- What do the principal quantum number 'n' and azimuthal quantum number 'l' of an electron belonging to an atom represent?
- Which principle is followed in the distribution of electrons in an atom?

When Mendeleev put forth his periodic table in 1869, the atomic structure was not known. He observed periodicity in the properties of elements on arranging them in an increasing order of atomic mass. Later, with the advent of quantum mechanical model of atom, the properties of elements were correlated to electronic configuration.

You have learnt in the Chapter 4 that the electrons in atom are distributed in shells and subshells in accordance with the **aufbau principle** which includes **increasing order of energy, Pauli exclusion principle and Hund's rule of maximum multiplicity**. When elements are arranged in an increasing order of atomic number (Z), periodicity is observed in their electronic configuration and which reflects in the characteristic structure of the modern periodic table. The location of elements in the modern periodic table is correlated to quantum numbers of the last filled orbital. Let us have a deeper look into the electronic configuration of the elements and the structure of the modern periodic table.

7.3.1 Electronic configuration in periods

We noted earlier that periods in the modern periodic table are numbered 1 to 7. On inspection of the electronic configurations (see Fig. 7.3) of elements in various periods we understand that the period number is same as the principal quantum number 'n' of the outermost or valence shell of the elements.

Along a period the atomic number increases by one and one electron is added to outermost shell which forms neutral atom of the next element. Every period ends with complete octet configuration (or duplet in the case of the first period) of the valence shell and the next period begins with addition of electron to the next shell of higher energy compared to the previous period. The first shell, thus, gets filled along the **first period**. As the first shell can accommodate only two electrons, there are two elements in the first period, namely, H ($Z=1$): $1s^1$ and He ($Z=2$): $1s^2$. The first period ends at 'He' because 'He' has complete duplet.

Electrons are filled in the second shell along the **second period**. The second period, thus, begins with Li ($Z=3$): $1s^2 2s^1$ and ends up with Ne ($Z=10$): $1s^2 2s^2 2p^6$. 'Ne' with 8 electrons in its outermost second shell has complete octet. The second shell has electron capacity of 8. It gets filled along the second period, as the atomic number increases. Thus there are eight elements in the second period.

Similarly there are eight elements Na ($Z=11$) to Ar ($Z=18$) having the condensed electronic configurations described together as $[\text{Ne}]3s^1-23p^{1-6}$ in the **third period**, as a result of completion of the third shell.

The **fourth period** begins with filling of 4s subshell. The first two elements of the fourth period are K ($Z=19$): $[\text{Ar}] 4s^1$ and Ca ($Z=20$): $[\text{Ar}]4s^2$. According to the aufbau principle the next higher energy subshell is 3d, which can accommodate upto 10 electrons. Filling of the 3d-subshell results in the next 10 elements of the fourth period, from Sc ($Z=21$): $[\text{Ar}] 4s^2 3d^1$ to Zn ($Z=30$): $[\text{Ar}] 4s^2 3d^{10}$. After this the electrons enter the subshell 4p for the next six elements: Ga ($Z=31$): $[\text{Ar}] 4s^2 3d^{10} 4p^1$ to Kr ($Z=36$): $[\text{Ar}] 4s^2 3d^{10} 4p^6$. The fourth period, thus, contains in all 18 elements ($2+10+6=18$).

The **fifth period** accommodates 18 elements as a result of successive filling of electrons in the 5s, 4d and 5p subshells.

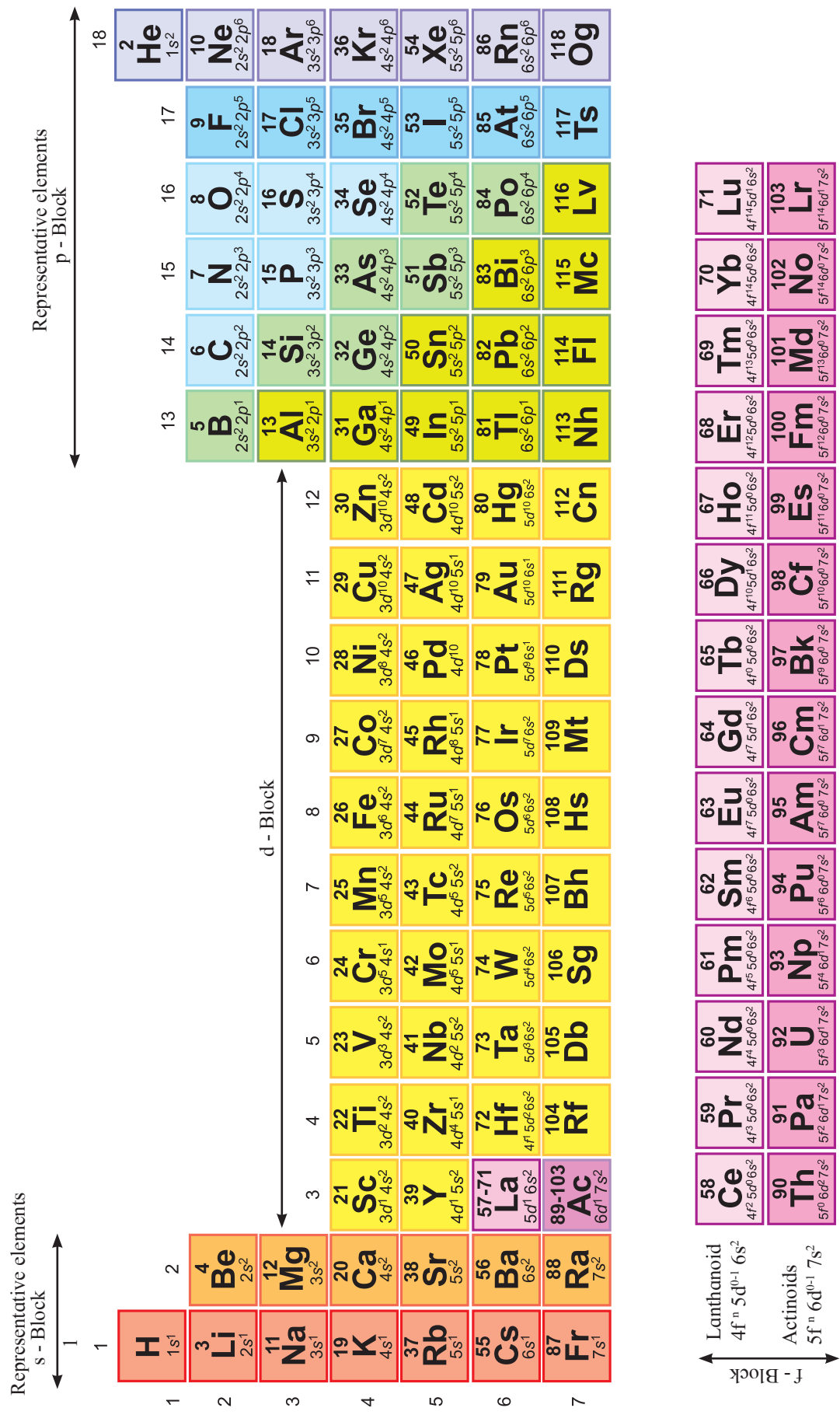


Fig. 7.2 : Outer electronic configuration of elements in the four blocks of the periodic table

Problem 7.1 : What is the subshell in which the last electron of the first element in the 6th period enters ?

Solution :

The 6th period begins by filling the last electron in the shell with $n=6$. The lowest energy subshell of any shell is 's'. Therefore the last electron of the first element in the 6th period enters the subshell '6s'.

Problem 7.2 : How many elements are present in the 6th period? Explain.

Solution :

The 6th period begins by filling the last electron in the subshell '6s' and ends by completing the subshell '6p'. Therefore, the sixth period has the subshells filled in increasing order of energy as $6s < 4f < 5d < 6p$. The electron capacities of these subshells are 2, 14, 10 and 6, respectively. Therefore, the total number of elements in the 6th period are $2+14+10+6 = 32$.

In short, a period begins by filling of one electron to the 's' subshell of a new shell and ends with an element having complete octet (or duplet) corresponding to the same shell. Between these two ends corresponding to 's' and 'p' subshell of the valence shell, the inner subshells 'd' and 'f' are filled successively following the aufbau principle.

7.3.2 Electronic configuration in groups

A new shell is added down a group. The general outer electronic configuration, therefore, is expected to be the same down any particular group. Indeed it is found to be so for the groups 1, 2 and 3. (See Fig. 7.2 and Table 7.1) In the groups 13 to 18 the appropriate inner 'd' and 'f' subshells are completely filled and the general outer electronic configuration is the same down the groups 13 to 18. (see Fig. 7.2 and Table 7.1).

In the groups 4 to 12, however, the 'd' and 'f' subshells are introduced at a later stage (4th period for 'd' and 6th period for 'f') down the group. As a result variation in the general outer configuration is introduced only at the later stage down the groups 4 to 12.

Table 7.1 : General outer electronic configuration in groups 1 to 3 and 13 to 18

Group number	General outer configuration	Examples
Group 1	ns^1	${}^3\text{Li}:2s^1, {}_{11}\text{Na}:3s^1$
Group 2	ns^2	${}^4\text{Be}:2s^2, {}_{12}\text{Mg}:3s^2$
Group 3	$ns^2 (n-1)d^1$	${}_{21}\text{Sc}:4s^23d^1, {}_{39}\text{Y}:5s^24d^1$
Group 13	$ns^2 np^1$	${}^5\text{B}:2s^22p^1, {}_{13}\text{Al}:3s^23p^1$
Group 14	$ns^2 np^2$	${}^6\text{C}:2s^22p^2, {}_{14}\text{Si}:3s^23p^2$
Group 15	$ns^2 np^3$	${}^7\text{N}:2s^22p^3, {}_{15}\text{P}:3s^23p^3$
Group 16	$ns^2 np^4$	${}^8\text{O}:2s^22p^4, {}_{16}\text{S}:3s^23p^4$
Group 17	$ns^2 np^5$	${}^9\text{F}:2s^22p^5, {}_{17}\text{Cl}:3s^23p^5$
Group 18	$ns^2 np^6$	${}_{10}\text{Ne}:2s^22p^6, {}_{18}\text{Ar}:3s^23p^6$

7.3.3 Electronic configuration in the four blocks:

We noted in section 7.2 that structure of the modern periodic table shows four blocks. These blocks are formed in accordance with the subshell in which the last electron enters. Accordingly the four blocks are named as s-block, p-block, d-block and f-block.

s-Block : The last electron in the s-block elements is filled in a s-subshell. There being only one orbital in a s-subshell, the general outer electronic configuration of s-block elements is ns^{1-2} . Thus elements of the group-1 and group-2 belong to the s-block. The s-block is present on the left extreme of the modern periodic table.

p-Block: The last electron in the p-block elements is filled in p-subshell. There being three degenerate p-orbitals in a p-subshell, upto 6 electrons can be filled. Therefore, the elements belonging to six groups, namely, group 13, 14, 15, 16, 17 and 18 constitute the p-block. The p-block appears on the right in the modern periodic table. The p-block ends with the group 18 which represent the family of inert gases. Remarkably, the first element of the group 18, helium (He) does not have the p subshell as its valence shell has $n = 1$ and its configuration is shown as $1s^2$. Yet 'He' is placed in the 18th group of the p-block because its valence shell is completely filled (which is a complete duplet), similar to complete valence shell of the other elements belonging to group 18 (which have complete octets). The general electronic configuration for the p-block (from the second to the seventh period) is $ns^2 np^{1-6}$.

d-Block : The d-block in the modern periodic table is formed as a result of filling the last electron in d-orbital. A d-subshell is present in the shells with $n \geq 3$ and according to the $(n+l)$ rule (refer to Chapter 4) the energy of ns orbital is less than that of the $(n-1)d$ orbital. As a result, the last electron enters a $(n-1)d$ -subshell only after the ns subshell is completely filled. There being five orbitals in a d-subshell, 10 electrons can successively be accommodated. There are

ten groups, namely, groups 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 in the d-block which appears in the centre of the modern periodic table. The general outer electronic configuration of the d-block elements is $ns^{0-2} (n-1)d^{1-10}$. Some variations in the configuration, consequent to the extra stability associated with half-filled and a fully filled subshell, are readily observed. For example, the outer electronic configuration of Cr ($Z = 24$) is $4s^1 3d^5$ instead of $4s^2 3d^4$. This is because both 4s and 3d subshells are half-filled.

f-Block : In the f-block elements the last electron is filled in f-orbital. As there are seven orbitals in a f-subshell, the general outer electronic configuration of the f-block is $ns^2 (n-1)d^{0-1} (n-2)f^{1-14}$. The variations as a result of the extra stability of half-filled and fully filled subshell need to be accounted for. For example, the outer electronic configuration of ${}_{63}\text{Eu}$ is $6s^2 4f^7 5d^0$ because the 4f subshell is half-filled. The f-block constitutes two series of 14 elements called the **lanthanoid** and the **actinoid series**, put one below the other. The f-block is placed separately at the bottom of the periodic table.

Problem 7.3 : Outer electronic configurations of a few elements are given below. Explain them and identify the period, group and block in the periodic table to which they belong.

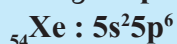
${}_2\text{He} : 1s^2$, ${}_{54}\text{Xe} : 5s^2 5p^6$, ${}_{16}\text{S} : 3s^2 3p^4$, ${}_{79}\text{Au} : 6s^1 5d^{10}$

Solution :

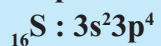
${}_2\text{He} : 1s^2$

Here $n = 1$. Therefore, ${}_2\text{He}$ belongs to the **1st period**. The shell $n = 1$ has only one subshell, namely 1s. The outer electronic configuration $1s^2$ of 'He' corresponds to the maximum capacity of 1s, the **complete duplet**. Therefore, He is placed at the end of the **1st period in the group 18** of inert

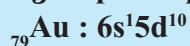
gases, so 'He' belongs to **p-block**.



Here $n = 5$. Therefore, ${}_{54}\text{Xe}$ belongs to the **5th period**. The outer electronic configuration $5s^25p^6$ corresponds to **complete octet**. Therefore ${}_{54}\text{Xe}$ is placed in **group 18** and belongs to **p-block**.



Here $n = 3$. Therefore, ${}_{16}\text{S}$ belongs to the **3rd period**. The 3p subshell in 'S' is partially filled and short of completion of octet by two electrons. Therefore 'S' belongs to $(18-2) = 16^{\text{th}}$ **group** and **p-block**.



Here $n = 6$. Therefore, 'Au' belongs to the **6th period**. The sixth period begins with filling of electron into 6s and then into 5d orbital. The outer configuration of 'Au' : $6s^1 5d^{10}$ implies that $(1+10) = 11$ electrons are filled in the outer orbitals to give 'Au'. Therefore 'Au' belongs to the **group 11**. As the last electron has entered 'd' orbital 'Au' belongs to the **d-block**.

7.4 Blockwise characteristics of elements

We have seen in the previous section that the 118 elements in the modern periodic table are distributed in four blocks having general electronic configuration according to their block. The elemental properties are characteristic of the block they belong.

7.4.1 Characteristics of s-block elements

The s-block contains the elements of **group 1 (alkali metals)** and **group 2 (alkaline earth metals)**. All these elements are **reactive metals**, and occur in nature only in combined state. Their **compounds**, with exception of Li and Be, are **predominantly ionic**. This is because they have only one or two valence electrons which they can lose readily forming M^{\oplus} or $M^{2\oplus}$ ions. They have **low ionization enthalpies**, which decrease down the group resulting in increased reactivity.

7.4.2 Characteristics of p-block elements :

The p-block contains elements of **groups 13 to 18**. The **p-block elements together with s-block elements** are called **main group elements** or **representative elements**. The last group of the p-block, namely, the **18th group**, is the family of **noble/inert gases**. These have closed valence shells (complete duplet in the case of 'He' and complete octet in the case of the other noble gases) and therefore very low chemical reactivity. Elements of **group 17 (halogen family)** and **group 16 (chalcogens)** include **reactive nonmetals**. The **electron gain enthalpies** being **highly negative**, they gain one or two electrons readily and form anions (X^{\ominus} or $X^{2\ominus}$) which have complete octet. The p-block contains **all the three traditional types of elements**. The metals on the left, the nonmetals on the right and the metalloids along a **zig-zag line** (see Fig. 7.1) which separates metals from nonmetals. The nonmetallic character increases as we move from the left to the right, whereas it decreases as we go down a group.

7.4.3 Characteristics of d-block elements

The d-block contains elements of the **groups 3 to 12**. They are **all metals**. The d-block elements are known as **transition elements** or **transition metals**. They form a bridge between chemically reactive s-block elements and less reactive elements of groups 13 and 14. Most of d-block elements possess Partially filled inner d-orbitals. As a result the d-block elements have properties such as **variable oxidation state**, **paramagnetism**, **ability to form coloured ions**. They can be used as **catalysts**. Zn, Cd, and Hg with configuration $ns^2 (n-1) d^{10}$, (completely filled s - and d - subshells) do not show the properties typical of transition metals.

7.4.4 Characteristics of f-block elements

The f-block contains elements **all** of which are **metals** and are placed in the two rows called **lanthanoid series** (${}_{58}\text{Ce}$ to ${}_{71}\text{Lu}$) and **actinoid**

series ($_{90}\text{Th}$ to $_{103}\text{Lr}$). These series are named after their preceding elements lanthanum ($_{57}\text{La}$) and actinium ($_{89}\text{Ac}$) in the third group of the d-block of the 6th and 7th period respectively. The lanthanides are also known as **rare earth elements**. The last electron of the elements of these series is filled in the $(n-2)f$ subshell, and therefore, these are called **inner-transition elements**. These elements have very similar properties within each series. The actinide

Problem 7.4 : Chlorides of two metals are common laboratory chemicals and both are colourless. One of the metals reacts vigorously with water while the other reacts slowly. Place the two metals in the appropriate block in the periodic table. Justify your answer.

Solution

Metals are present in all the four blocks of the periodic table. Salts of Metals in the f-block and p-block (except AlCl_3) are not common laboratory chemicals. Therefore, the choice is between s- and d-block. From the given properties their placement is done as shown below:

s-block: Metal that reacts vigorously with water

d-block: Metal that reacts slowly with water.

The colourless nature of the less reactive metal in the d-block implies that the inner d-subshell is completely filled.

elements beyond $_{92}\text{U}$ are called **transuranium elements**. All the transuranium elements are manmade and radioactive.

7.5 Periodic trends in elemental properties

The original structure of the periodic table was based on empirically observed periodicity in the elemental properties. Thus, elemental properties show similarity in a group and show gradual variation across a period. The quantum mechanical model of atom explains the observed periodic trends of elemental

properties. We will now discuss in this section the periodic trends in some physical and chemical properties of elements, correlating them with electronic configuration and the nuclear charge. These trends are explained in terms of two fundamental factors, namely, attraction of extranuclear electrons towards the nucleus and repulsion between electrons belonging to the same atom. These attractive and repulsive forces operate simultaneously in an atom. This results in two interrelated phenomena called effective nuclear charge and screening effect.

7.5.1 Effective nuclear charge and screening effect :

In a multi-electron atom the positively charged nucleus attracts the negatively charged electrons around it, and there is mutual repulsion amongst the negatively charged extranuclear electrons. The repulsion by inner-shell electrons is particularly important. This results in pushing the outer-shell electrons further away from the nucleus. The outer-shell electrons are, thus, held less tightly by the nucleus. In other words, the attraction of the nucleus for an outer electron is partially cancelled. It means that an outer-shell electron does not experience the actual positive charge present on the nucleus. The net nuclear charge actually experienced by an electron is called the **effective nuclear charge, Z_{eff}** . The effective nuclear charge is lower than the actual nuclear charge, Z . In other words, the inner electrons shield the outer electrons from the nucleus to a certain extent. This effect of the inner electrons on the outer electrons is called **screening effect** or **shielding effect** of the inner/core electrons.

$$\begin{aligned} \text{Effective nuclear charge} &= Z_{\text{eff}} \\ &= Z - \text{electron shielding} \\ &= Z - \sigma \end{aligned}$$

Here σ (sigma) is called **shielding constant** or **screening constant** and the value of σ depends upon type of the orbital that the electron occupies.

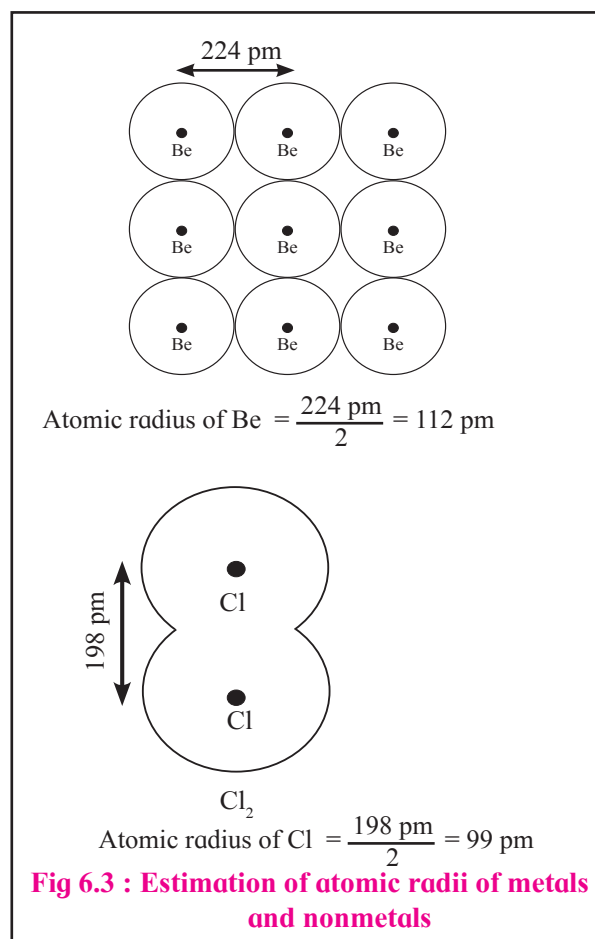
As we move across a period actual nuclear charge increases by +1 at a time, the valence shell remains the same and the newly added electron gets accommodated in the same shell. There is no addition of electrons to the core. Thus, shielding due to core electrons remains the same though the actual nuclear charge, Z , increases. The net result is that **the effective nuclear charge, Z_{eff} , goes on increasing across a period.** On the other hand, the Z_{eff} decreases down a group. This is because, as we move down a group, a new larger valence shell is added. As a result, there is an additional shell in the core. The shielding effect of the increased number of core electrons outweighs the effect of the increased nuclear charge; and thereby **the effective nuclear charge felt by the outer electrons decreases largely down a group.**

7.5.2 Periodic trends in physical properties

Many physical properties of elements such as melting point, boiling point and density show periodicity. In this section we are going to consider the periodic trends in physical properties with reference to atomic radius, ionic radius, ionization enthalpy, electron gain enthalpy and electronegativity.

a. Atomic radius : You have learnt in chapter 4 that the quantum mechanical model of atom describes the extranuclear part of atom as the electron cloud. As a direct implication of this, the atom has no definite boundary. The atomic size or atomic radius, therefore, can be estimated from the internuclear distance under different circumstances. In the case of nonmetals (except noble gases), the atoms of an element are bonded to each other by covalent bonds. (Refer to Chapter 5). Bond length of a single bond is taken as sum of radii of the two single bonded atoms. This is called covalent radius of the atom. For example : (i) Bond length of C-C bond in diamond is 154 pm. Therefore, atomic radius of carbon

is estimated to be 77 pm. (ii) Bond length of Cl-Cl bond in Cl_2 is measured as 198 pm. Therefore, the atomic radius of Cl is estimated to be 99 pm. (see Fig. 6.3)



In the case of metals, distance between the adjacent atoms in metallic sample is measured. One half of this distance is taken as the metallic radius. **Thus, atomic radius is one half of the internuclear distance between two adjacent atoms of a metal or two single bonded atoms of a nonmetal.**



Do you know ?

Atomic radius is estimated in terms of the electron density surface which encloses typically 95 % (or more, which is arbitrary) of the electron density.

Table 7.2 : Atomic radii of some elements

Element symbol (atomic radius / pm)							
Group \ Period	1	2	13	14	15	16	17
2	Li (152)	Be (111)	B (88)	C (77)	N (74)	O (66)	F (64)
3	Na (186)	Mg (160)	Al (143)	Si (117)	P (110)	S (104)	Cl (99)
4	K (231)						Br (114)
5	Rb (244)						I (133)
6	Cs (262)						At (140)

It can be seen from Table 7.2 that atomic radius decreases across a period (upto group 17) and increases down a group. Greater the effective nuclear charge stronger is attraction of the nucleus for the outer electrons and smaller is the atomic radius. As we move across a period, screening effect caused by the core electrons remains the same, on the other hand the effective nuclear charge goes on increasing (see section 6.5.1). The valence electrons are, therefore, more tightly bound and in turn the atomic radius goes on decreasing along a period. The effective nuclear charge decreases and shielding effect increases down a group (see section 7.5.1). The valence electrons are, thus, held by weaker attractive force and the atomic radius increases down a group.

b. Ionic radius: An atom forms a positively charged ion, cation, on the removal of one or more electrons whereas a negatively charged ion, anion, is formed with gain of one or more electrons. Measurements of distances between neighbouring cations and anions in ionic crystals have been useful for estimation of ionic radii. The ionic radii show the same trends as of atomic radii.

A cation is smaller than the atom from which it is formed, because it contains fewer electrons than atom, though the nuclear charge is the same. As a result the shielding effect is less and effective nuclear charge is larger within a cation.

An anion has a larger radius than the corresponding atom, as it has more number of electrons than the atom. These additional electrons result in increased electron repulsion, decreased effective nuclear charge and in turn, the increased size.

Some atoms and ions contain the same number of electrons and are called **isoelectronic species**. (See chapter 4) The actual nuclear charge of the isoelectronic species is, however, different. The radii of isoelectronic species vary according to actual nuclear charge. Larger nuclear charge exerts greater attraction for the electrons and the radius of that isoelectronic species becomes smaller. For example, F^{\ominus} and Na^{\oplus} both have 10 electrons, their radii are 133 pm and 98 pm respectively, as the nuclear charge of F^{\ominus} is + 9 which is smaller than that of Na^{\oplus} which is, + 11.

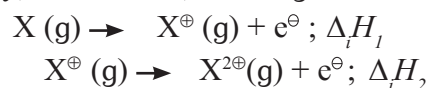
c. Ionization enthalpy : Removal of an electron from the neutral atom X results

Problem 7.5 : Identify the species having larger radius from the following pairs : (i) Na and Na^{\oplus} , (ii) Na^{\oplus} and $Mg^{2\oplus}$

Solution :

(i) The nuclear charge is the same in Na and Na^{\oplus} . But Na^{\oplus} has less number of electrons and less number of occupied shells (two shells in Na^{\oplus} while three shells in Na). Therefore, radius of Na is larger. (ii) Na^{\oplus} and $Mg^{2\oplus}$ are isoelectronic species. $Mg^{2\oplus}$ has larger nuclear charge than Na^{\oplus} . Therefore, Na^{\oplus} has larger radius.

in formation of cation X^{\oplus} . The energy required to remove an electron from the isolated gaseous atom in its ground state is called ionization enthalpy ($\Delta_i H$). Ionization enthalpy is the quantitative measure of tendency of an element to lose electron and expressed in kJ mol^{-1} . Since electrons are lost one at a time, we have first ionization enthalpy, second ionization enthalpy, and so on, for a given element.



Ionization enthalpy is always positive since the energy always need to be supplied to knock out electron from atom.

The second ionization enthalpy, $\Delta_i H_2$, is larger than the first ionization enthalpy, $\Delta_i H_1$, as it involves removal of electron from the positively charged species. Tables 7.3 and 7.4 show the values of first ionization enthalpy down the group 1 and across the period 2 respectively.

It is seen from Table 7.3 that on moving down the group the first ionization enthalpy decreases. This is because electron is to be removed from the larger valence shell. Screening due to core electrons goes on increasing and the effective nuclear charge decreases down the group. (See section 7.5.1) The removal of the outer electron, therefore, becomes easier.

Table 7.3 : First ionization enthalpy values of elements of group 1

Elements of Group 1	Atomic Number Z	Outer electronic configuration	$\Delta_i H_1 / \text{kJ mol}^{-1}$
Li	3	$2s^1$	520
Na	11	$3s^1$	496
K	19	$4s^1$	419
Rb	37	$5s^1$	403
Cs	55	$6s^1$	374

An overall increase of the first ionization enthalpy across the period 2 (see table 7.4) can be notice. This is because the screening is the same and the effective nuclear charge increases across a period. (See section 7.5.1) As a result the outer electron is held more tightly. The first ionization enthalpy, therefore, increases across a period. The alkali metal displays the lowest first ionization enthalpy. The inert gas shows the highest first ionization enthalpy across a period.

Some irregularities are noticed for the first ionization enthalpies as we move across a period. For example, the first ionization enthalpy of 'B' is smaller than that of 'Be'. This is because 'Be' loses the electron from 2s orbital while 'B' loses the electron from 2p orbital which has less penetration (see shapes of orbitals in chapter 4) than the 2s orbital and therefore it is easier to remove a 2p electron than a 2s electron. Similarly, first ionization enthalpy of 'O' is smaller than that of 'N'. This is because 'O' loses the electron from a doubly occupied '2p' orbital. Due to

Table 7.4 : First ionization enthalpy values of elements of period 2

Element of period 2	Li	Be	B	C	N	O	F	Ne
Atomic number Z	3	4	5	6	7	8	9	10
Outer electronic Configuration	$2s^1$	$2s^2$	$2s^2 2p^1$	$2s^2 2p^2$	$2s^2 2p^3$	$2s^2 2p^4$	$2s^2 2p^5$	$2s^2 2p^6$
$\Delta_i H_1 / \text{kJ mol}^{-1}$	520	899	801	1086	1402	1314	1681	2080

electron-electron repulsion it is easier to lose this electron than an electron from the singly occupied 2p orbital in nitrogen atom. (This is a consequence of Hund's rule of maximum multiplicity, described in Chapter 4.)

Problem 7.6 :

The first ionization enthalpy values of Si, P and Cl are 780, 1060 and 1255 kJ mol⁻¹ respectively. Predict whether the first ionization enthalpy of S will be closer to 1000 or 1200 kJ mol⁻¹.

Solution :

As we move across the period 3 from left to right the elements Si, P, S, Cl come in a sequence. Their outer electronic configurations are 3s²3p², 3s²3p³, 3s²3p⁴ and 3s²3p⁵ respectively and 'P' loses an electron from a singly occupied 3p orbital whereas 'S' loses an electron from a doubly occupied 3p orbital. Therefore, the first ionization enthalpy value of 'S' has to be lower than that of 'P'. Thus, first ionization enthalpy of 'S' would be less than 1060 kJ mol⁻¹, and therefore, should be close to 1000 kJ mol⁻¹ and not 1200 kJ mol⁻¹.

d. Electron gain enthalpy: Addition of an electron to a neutral atom (X) results in formation of an anion (X[⊖]). **The enthalpy change that takes place when an electron is added to an isolated gaseous atom in its ground state is called the electron gain enthalpy, $\Delta_{eg}H$.** Electron gain enthalpy is a quantitative measure of the ease with which an atom adds an electron forming the anion and is expressed in units of kJ mol⁻¹.



$\Delta_{eg}H$ may be positive or negative depending upon whether the process of adding electron is endothermic or exothermic. Elements of **group 17** have very high negative values of electron gain enthalpy. This is because of they attain stable noble gas electronic configuration on the addition of one electron. Elements of **group 18**, noble gases have, on

the other the hand, exhibit high positive values for electron gain enthalpy. Since, the added electron has to enter the next higher shell with larger principal quantum number, this is very unstable electronic configuration due to very low effective nuclear charge and high shielding from the core electrons. The **alkali metals** have very low negative electron gain enthalpy values. **In general**, electron gain enthalpies are large negative for elements of the upper right of the periodic table, excluding the group 18 of noble gases.

The trends for electron gain enthalpy values of the elements in the periodic table are less regular than the ionization enthalpies. An **overall trend** reveals that electron gain enthalpy becomes more negative with increase of atomic number along the period upto the second last element, because the effective nuclear charge increases across the period and it is easier to add an electron to a smaller atom. Down the group, the electron has to be added to farther shell and the electron gain enthalpy, thus, becomes less negative.

Problem 7.7 :

Identify the element with more negative value of electron gain enthalpy from the following pairs. Justify.

- (i) Cl and Br (ii) F and O

Solution :

(i) Cl and Br belong to the same group of halogens with Br having higher atomic number than Cl. As the atomic number increases down the group the effective nuclear charge decreases. The increased shielding effect of core electrons can be noticed. The electron has to be added to a farther shell, which releases less energy and thus electron gain enthalpy becomes less negative down the group. Therefore, Cl has more negative electron gain enthalpy than Br.CONTD on next page

(ii) F and O belong to the same second period, with F having higher atomic number than O. As the atomic number increases across a period, atomic radius decreases, effective nuclear charge increases and electron can be added more easily. Therefore more energy is released with gain of an electron as we move to right in a period. Therefore, F has more negative electron gain enthalpy.

e. Electronegativity: When two atoms of different elements form a covalent bond, the electron pair is shared unequally. **The ability of a covalently bonded atom to attract the shared electrons toward itself is called electronegativity (EN).** It is not an experimentally measurable quantity. A number of numerical scales of electronegativity were developed by many scientists. Pauling scale of electronegativity is the one used most widely. **Linus Pauling assigned (1922)** arbitrarily a value of 4.0 for fluorine which is expected to have the highest value of electronegativity. Table 7.5 shows the values of electronegativity assigned to some other elements.

Electronegativity represents attractive force exerted by the nucleus on shared electrons. Electron sharing between covalently bonded atoms takes place using the valence electron. The electronegativity depends upon the effective nuclear charge experienced by

electron involved in formation of the covalent bond. Electronegativity increases as we move across the period. This is because the effective nuclear charge increases steadily across the period. The *EN* decreases down the group. The size of the valence shell goes on increasing, the shielding effect of the core electron goes on increasing and in term the effective nuclear charge decreases down the group.

Electronegativity predicts the nature of the bond, or, how strong is the force of attraction that holds two atoms together. (Refer Chapter 5).

7.5.3 Periodic trends in chemical properties:

The most fundamental chemical property of an element is its combining power. This property is numerically expressed in terms of **valency** or **valence**. Valency of an element indicates the number of chemical bonds that the atom can form giving a molecule. Another frequently used term related to valence is the **oxidation state** or **oxidation number**. Valence does not have any sign associated with it, but oxidation number does, and can be either + or –, which is decided by electronegativities of atoms that are bonded.

The second aspect of chemical property is the **chemical reactivity**. The chemical reactivity is related to the ease with which an element loses or gains the electrons.

The chemical properties of elements are relate to electronic configuration.

Table 7.5 : Electronegativity (EN) values of some elements (Pauling scale)

		Element symbol (EN)					
Group \ Period	1	2	13	14	15	16	17
1	H (2.1)						
2	Li (1.0)	Be (1.5)	B (2.0)	C (2.5)	N (3.0)	O (3.5)	F (4.0)
3	Na (0.9)	Mg (1.2)	Al(1.5)	Si (1.8)	P (2.1)	S (2.5)	Cl (3.0)
4	K (0.8)						Br (2.8)
5	Rb (0.8)						I (2.5)
6	Cs (0.7)						At (2.2)

Table 7.6 : Periodic trends in valency of main group elements

Group	1	2	13	14	15	16	17	18
General outer electronic configuration	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
Number of valence electrons	1	2	3	4	5	6	7	8
Valency	1	2	3	4	3,5	2,6	1,7	0
Formula of hydride	LiH	BeH ₂	B ₂ H ₆	CH ₄	NH ₃	H ₂ O	HF	
	NaH	MgH ₂	AlH ₃	SiH ₄	PH ₃	H ₂ S	HCl	
	KH	CaH ₂	GaH ₃	GeH ₄	AsH ₃	H ₂ Se	HBr	
Formula of oxide	Li ₂ O	BeO	B ₂ O ₃	CO ₂	N ₂ O ₃ N ₂ O ₅		OF ₂	
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₆ , P ₂ O ₅	SO ₂ , SO ₃	Cl ₂ O ₇	
	K ₂ O	CaO	Ga ₂ O ₂	GeO ₂	As ₂ O ₃ , As ₂ O ₅	SeO ₂ , SO ₃	Br ₂ O	

a. Periodic trends in valency: Valency of the main group elements is usually equal to the number of valence electrons (outer electrons) and/or equal to difference between 8 and the number of valence electrons. Table 7.6 shows the periodic trends in the valency of main group elements by taking examples of hydrides and some oxides.

As may be notice form Table 7.6 that the valency remains the same down the group and shows a gradual variation across the period as atomic number increases from left to right.

b. Periodic trends in metallic–nonmetallic character : The metals, nonmetals and metalloids appear in separate regions of modern periodic table: metals on the left, nonmetals on the right and metalloids along a zig-zag line separating the two. Metals are characterized by good electrical conductivity and ability to form compounds by loss of valence electrons. Nonmetals are characterized by their poor electrical conductivities and ability to form compounds by gain of valence electrons in valence shell. This can be explained in terms of ionization enthalpy and electron gain enthalpy.

The ionization enthalpy decreases down the group. The tendency to lose valence electrons, thus, increases down the group and the **metallic character increases down a group**. The ionization enthalpy increases across the period and consequent **metallic character decreases across a period**. Electron gain enthalpy becomes more and more negative across the period, it tends to be less negative down the group. Thus, **nonmetallic character increases across the period and decreases down the group**.

c. Periodic trends in chemical reactivity: Chemical reactivity of elements is decided by how easily it attains electronic configuration of the nearest inert gas by gaining or loosing electrons.

The elements preceding an inert gas react by gaining electrons in the outermost shell, whereas the elements which follow an inert gas in the periodic table react by loss of valence electrons. Thus the chemical reactivity is decided by the electron gain enthalpy and ionization enthalpy values, which in turn, are decided by effective nuclear charge and finally by the atomic size. The ionization enthalpy is smallest for the element on the extreme left in

a period, whereas the electron gain enthalpy is most negative for the second last element on the extreme right, (preceding to the inert gas which is the last element of a period). Thus, the most reactive elements lie on the extreme left and the extreme right (excluding inert gases) of the periodic table.

Apart from the metallic-nonmetallic character the chemical reactivity can be illustrated by comparing their reaction with oxygen to form oxides and the nature of the oxides. The reactive elements on the extreme left (that is, alkali metals) react vigorously with oxygen to form oxides (for example Na_2O) which reacts with water to form strong bases (like NaOH). The reactive elements on the right (that is, halogens) react with oxygen to form oxides (for examples Cl_2O_7) which on reaction with water form strong acids (like HClO_4). The oxides of the elements in the center of the main group elements are either amphoteric (for example Al_2O_3), neutral (for example CO , NO) or weakly acidic (for example CO_2)

The change in atomic radii of transition metals and inner transition elements is rather small. Therefore, the transition metals and inner transition elements belonging to the individual series have similar chemical properties. Their ionization enthalpies are intermediate between those of s-block and p-block.

Problem 7.8 :

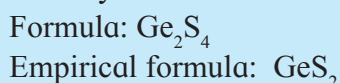
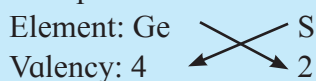
Ge, S and Br belong to the groups 14, 16 and 17, respectively. Predict the empirical formulae of the compounds those can be formed by (i) Ge and S, (ii) Ge and Br.

Solution :

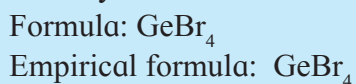
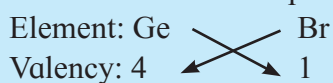
From the group number we understand that the general outer electronic configuration and number of valence electrons and valencies of the three elements are :

Element	Group	Outer electronic configuration	Number of Valence electron	Valency
Ge	14	ns^2np^2	4	4
S	16	ns^2np^4	6	$8 - 6 = 2$
Br	17	ns^2np^5	7	$8 - 7 = 1$

(i) S is more electronegative than Ge. Therefore, the empirical formula of the compound formed by these two elements is predicted by the method of cross multiplication of the valencies :



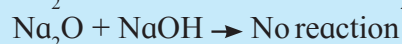
(ii) Br is more electronegative than Ge. The empirical formula of the compound formed by these two elements is predicted by the method of cross multiplication of valencies :



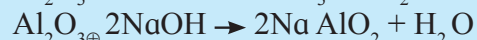
Problem 7.9

Write the chemical equations for reaction, if any, of (i) Na_2O and (ii) Al_2O_3 with HCl and NaOH both. Correlate this with the position of Na and Al in the periodic table, and infer whether the oxides are basic, acidic or amphoteric.

Solution



As Na_2O reacts with an acid to form salt and water it is a basic oxide. This is because Na is a reactive metal lying on the extreme left of the periodic table.



As Al_2O_3 reacts with an acid as well as base to form a salt and water. It is an amphoteric oxide. Al is a moderately reactive element lying in the centre of main group elements in the periodic table.



Exercises

1. Explain the following

- The elements Li , B , C , Be and N have the electronegativities 1.0, 2.0, 1.5 and 3.0, respectively on the Pauling scale.
- The atomic radii of Cl , I and Br are 99, 133 and 114 pm, respectively.
- The ionic radii of F^\ominus and Na^\oplus are 133 and 98 pm, respectively.
- ${}_{13}\text{Al}$ is a metal, ${}_{14}\text{Si}$ is a metalloid and ${}_{15}\text{P}$ is a nonmetal.
- Cu forms coloured salts while Zn forms colourless salts.

2. Write the outer electronic configuration of the following using orbital notation method. Justify.

- Ge (belongs to period 4 and group 14)
- Po (belongs to period 6 and group 16)
- Cu (belongs to period 4 and group 11)

3. Answer the following

- La belongs to group 3 while Hg belongs to group 12 and both belong to period 6 of the periodic table. Write down the general outer electronic configuration of the ten elements from La to Hg together using orbital notation method.
- Ionization enthalpy of Li is 520 kJ mol^{-1} while that of F is 1681 kJ mol^{-1} . Explain.
- Explain the screening effect with a suitable example.

- Why the second ionization enthalpy is greater than the first ionization enthalpy?
- Why the elements belonging to the same group do have similar chemical properties?
- Explain : electronegativity and electron gain enthalpy. Which of the two can be measured experimentally?

4. Choose the correct option

- Consider the elements B , Al , Mg and K predict the correct order of metallic character :
 - $\text{B} > \text{Al} > \text{Mg} > \text{K}$
 - $\text{Al} > \text{Mg} > \text{B} > \text{K}$
 - $\text{Mg} > \text{Al} > \text{K} > \text{B}$
 - $\text{K} > \text{Mg} > \text{Al} > \text{B}$
- In modern periodic table, the period number indicates the :
 - atomic number
 - atomic mass
 - principal quantum number
 - azimuthal quantum number

- C. The lanthanides are placed in the periodic table at
- left hand side
 - right hand side
 - middle
 - bottom
- D. If the valence shell electronic configuration is ns^2np^5 , the element will belong to
- alkali metals
 - halogens
 - alkaline earth metals
 - actinides
- E. In which group of elements of the modern periodic table are halogen placed ?
- 17
 - 6
 - 4
 - 2
- F. Which of the atomic number represent the s-block elements ?
- 7, 15
 - 3, 12
 - 6, 14
 - 9, 17
- G. Which of the following pairs is NOT isoelectronic ?
- Na^{\oplus} and Na
 - $\text{Mg}^{2\oplus}$ and Ne
 - $\text{Al}^{3\oplus}$ and $\text{B}^{3\oplus}$
 - $\text{P}^{3\ominus}$ and $\text{N}^{3\ominus}$
- H. Which of the following pair of elements has similar properties ?
- 13, 31
 - 11, 20
 - 12, 10
 - 21, 33

5. Answer the following questions

- A. The electronic configuration of some elements are given below:
a. $1s^2$ b. $1s^2 2s^2 2p^6$
In which group and period of the periodic table they are placed ?
- B. For each of the following pairs, indicate which of the two species is of large size :
- Fe^{2+} or Fe^{3+}
 - Mg^{2+} or Ca^{2+}
- C. Select the smaller ion form each of the following pairs:
- K^+ , Li^+
 - N^{3-} , F^-

- D. With the help of diagram answer the questions given below:

	Li	Be												O			
														S			

- Which atom should have smaller ionization enthalpy, oxygen or sulfur?
 - The lithium forms +1 ions while beryllium forms +2 ions ?
- E. Define :
- Ionic radius
 - Electronegativity
- F. Compare chemical properties of metals and non metals.
- G. What are the valence electrons ? For s-block and p-block elements show that number of valence electrons is equal to its group number.
- H. Define ionization enthalpy. Name the factors on which ionisation enthalpy depends? How does it vary down the group and across a period?
- I. How the atomic size vary in a group and across a period? Explain with suitable example.
- J. Give reasons.
- Alkali metals have low ionization enthalpies.
 - Inert gases have exceptionally high ionization enthalpies.
 - Fluorine has less electron affinity than chlorine.
 - Noble gases possess relatively large atomic size.
- K. Consider the oxides Li_2O , CO_2 , B_2O_3 .
- Which oxide would you expect to be the most basic?
 - Which oxide would be the most acidic?
 - Give the formula of an amphoteric oxide.



Activity :

Prepare a wall mounting chart of the modern periodic table.