UNIT 4

Classification of Elements and Periodicity in Properties

SYLLABUS

The need for classification

The significance of (*i*) Mendeleev's periodic law, (*ii*) Atomic number and periodic law

The present form of the periodic table

The IUPAC nomenclature of the elements with Z > 100

Electronic configuration of the elements and periodic table.

Types of elements : *s*-, *p*-, *d*- and *f*- blocks.

Periodic trends in properties : ionization energy, electron affinity, atomic radii and valency.

SECTION – I

PERIODIC TABLE

4.1. General Introduction— Need for Classification of Elements

Before the beginning of eighteenth century, only a few elements were known. Therefore, it was quite easy to study and remember the properties of these elements and their compounds individually. But gradually this number went on increasing and now as many as 112 elements, either *natural* or *synthetic*, have been discovered. It thus became rather difficult to study individually the chemistry of these elements and millions of their compounds. At this stage, scientists felt the need of some simple method to simplify and systematize the study of the properties of various elements and their compounds. This necessity led to the classification of various elements into groups.

Although every element is different from every other element, yet some elements have certain similarities. Based upon these similarities, the scientists after numerous attempts were ultimately successful in arranging the various elements into groups or chemical families in such a way that similar elements were grouped together and dissimilar elements were separated from one another. This arrangement of elements is called classification of elements and this led to the formulation of a periodic table. Thus

Periodic table may be defined as the table which classifies all the known elements in accordance with their properties in such a way that elements with similar properties are grouped together in the same vertical column and dissimilar elements are separated from one another.

4.2. Historical Development of the Periodic Table

In 1808, John Dalton proposed his *Atomic Theory*. According to this theory, atoms of one element can be distinguished from the other on the basis of their atomic weights. Thus, *all earlier attempts on the classification of the elements were based upon their atomic weights.*

1. **Doebereiner's Triads.** The first attempt towards the classification of elements was made by *J. Doebereiner*, a German chemist in 1817.

He arranged similar elements in groups of three and showed that the atomic weights are either nearly the same or the atomic weight of the middle element is approximately the arithmetic mean of the other two. These groups of three elements are called Doebereiner's Triads.

Some examples of these triads are :

1. Triad	**Iron**	**Cobalt**	**Nickel**	
At. wt.	55·85	58·93	58·71	Atomic weights are nearly the same
2. Triad	**Lithium**	**Sodium**	**Potassium**	**Mean of 1st and 3rd**
At. wt.	7	23	39	$\frac{7+39}{2}=23$
3. Triad	**Chlorine**	**Bromine**	**Iodine**	
At. wt.	35·5	80	127	$\frac{35\cdot5+127}{2}=81\cdot25$
4. Triad	**Calcium**	**Strontium**	**Barium**	
At. wt.	40	87·5	137	$\frac{40+137}{2}=88\cdot5$

The major darwback of Dobereiner's classification was that the concept of triads could be applied only to the limited number of elements.

2. Telluric screw (or Helix). The first real periodic classification, in the sense in which the term is now used, was the *Telluric screw (or Helix)* proposed by *de Chancourtois* in 1862. The underlying concept is, however, complex and is beyond the scope of this book.

3. Newlands Law of Octaves. In 1865-66, an English chemist, *John Newlands* observed that

When the lighter elements are arranged in order of their increasing atomic weights, the properties of every eighth element are similar to the first one like the eighth note of a musical scale. This generalization was named as **Newlands law of octaves.**

For example, consider the following elements :

Sr. No.	1	2	3	4	5	6	7
Element	Li	Be	B	C	N	O	F
Sr. No.	8	9	10	11	12	13	14
Element	Na	Mg	Al	Si	P	S	Cl
Sr. No.	15	16					
Element	K	Ca					

Thus, sodium, the eighth element is similar to lithium and so is the next eighth element potassium. The same is true of beryllium, magnesium and calcium ; boron and aluminium and so on. In the beginning this idea was not widely accepted and was actually ridiculed. However, his work was recognized much later by the Royal Society, London by awarding him the Davy Medal in 1887.

This generalization was also discarded since it could not be applied to elements having atomic weights greater than that of calcium, *i.e.* 40 a.m.u. Furthermore, with the discovery of noble gases, the properties of the eighth element were no longer similar to the first one.

4. Lother-Meyer arrangement. In 1869, Lother Meyer, a German chemist, studied the physical properties such as atomic volume, melting point and boiling points of various elements.

He plotted a graph between the atomic volumes (gram atomic weight divided by density) and atomic weights of the elements and observed that the elements with similar properties occupied similar positions on the curve (Fig. 4.1).

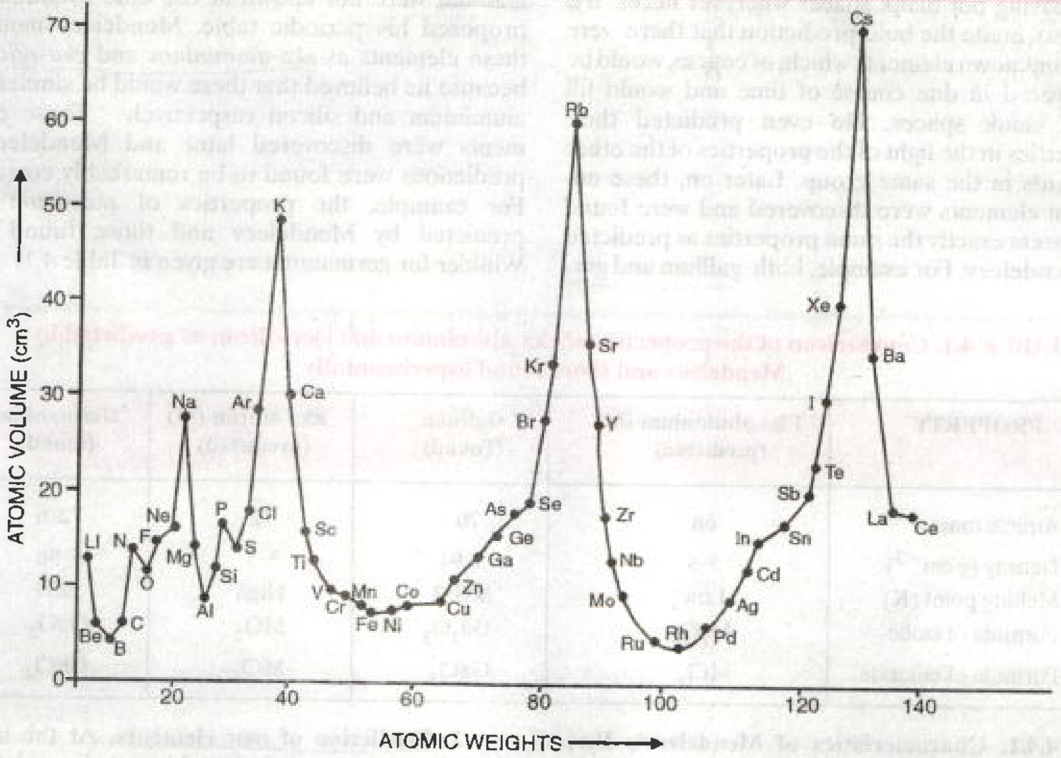

FIGURE 4.1. Lother Meyer's atomic volume curves.

For example,

(i) The most strongly electropositive alkali metals (Li, Na, K, Rb and Cs) occupy the peaks on the curve.

(ii) The less strongly electropositive alkaline earth metals (Be, Mg, Ca, Sr and Ba) occupy the descending positions on the curve.

(iii) The most electronegative elements i.e., halogens (F, Cl, Br and I) occupy the ascending positions on the curve.

On the basis of these observations, Lother Meyer proposed that *the physical properties of the elements are a periodic function of their atomic weights.* He arranged the then known elements in the tabular form in order of their increasing atomic weights.

It may be pointed out that the general pattern of the curve remained the same when atomic numbers were plotted in place of atomic weights as a result of later developments.

4.3. Mendeleev's Periodic Law

In 1869, Dmitri Mendeleev, a Russian chemist, used broader range of physical and chemical properties to classify the elements.

He mainly relied on the similarities in the empirical formulae and properties of the compounds formed by the elements. On the basis of these similarities, Mendeleev proposed his **Periodic Law.** It states that

The physical and chemical properties of elements are a periodic function of their atomic weights, i.e. when the elements are arranged in order of their increasing atomic weights, elements with similar properties are repeated after certain regular intervals.

Although both Lother-Meyer and Mendeleev working independently reported very similar results, the credit for designing the Periodic Table is usually given to Mendeleev because he was certainly the first to fully recognize the significance of periodicity of properties of elements when arranged in increasing order of their atomic weights.

4.4. Mendeleev's Periodic Table

Mendeleev arranged the then known elements in order of their increasing atomic weights, grouping together elements with similar properties and leaving out blank spaces wherever necessary. He also made the bold prediction that there were some unknown elements which, of course, would be discovered in due course of time and would fill these blank spaces. He even predicted their properties in the light of the properties of the other elements in the same group. Later on, these unknown elements were discovered and were found to possess exactly the same properties as predicted by Mendeleev. For example, both gallium and germanium were not known at the time Mendeleev proposed his periodic table. Mendeleev named these elements as *eka-aluminium* and *eka-silicon* because he believed that these would be similar to aluminium and silicon respectively. These elements were discovered later and Mendeleev's predictions were found to be remarkably correct. For example, the properties of *ekasilicon* as predicted by Mendeleev and those found by Winkler for germanium are given in Table 4.1.

TABLE 4.1. Comparison of the properties of eka-aluminium and eka-silicon as predicted by Mendeleev and those found experimentally

PROPERTY	Eka-aluminium (M) (predicted)	Gallium (Found)	Eka-silicon (M) (predicted)	Germanium (found)
Atomic mass	68	70	72	72·6
Density ($g\ cm^{-3}$)	5·9	5·94	5·5	5·36
Melting point (K)	Low	303·2	High	1231
Formula of oxide	M_2O_3	Ga_2O_3	MO_2	GeO_2
Formula of chloride	MCl_3	$GaCl_3$	MCl_4	$GeCl_4$

4.4.1. Characteristics of Mendeleev's Periodic Table. Mendeleev's periodic table consists of :

(*i*) *Eight vertical columns called* **groups.** These are designated as I, II, III, IV, V, VI, VII and VIII. Except for group VIII, each group is further divided into two sub-groups designated as A and B. The elements which lie on the left hand side of each group constitute sub-group A while those placed on the right hand side form sub-group B. This sub-division is made on the basis of the difference in their properties. Group VIII contains nine elements in three sets each containing three elements. Group zero consists of inert gases.

(*ii*) *Six horizontal rows called periods.* These are numbered from 1 to 6.

4.4.2. Significance of Mendeleev's Periodic Table. Some important contributions of the Mendeleev's periodic table are listed below :

1. Systematic study of the elements. The Mendeleev's periodic table simplified and systematized the study of the elements and their compounds since their properties could now be studied as groups or families rather than individuals. Thus, knowing the properties of one element in a group, the properties of the other elements in the group can be easily predicted.

2. Prediction of new elements. At the time when Mendeleev's periodic table was formulated, only 56 elements were known. Therefore, while arranging the elements according to their properties, Mendeleev left some blank spaces or gaps. These gaps represented unknown elements. Further, Mendeleev predicted the properties of these unknown elements on the basis of their positions. For example, he predicted the propeties of gallium (*eka-aluminium*) and germanium (*eka-silicon*) which were unknown at that time. Later when these elements were discovered, their properties were found to be similar to those predicted by Mendeleev (Table 4.1).

3. Correction of doubtful atomic weights. Mendeleev's periodic table has helped in correcting the doubtful atomic weights of some elements. For example, beryllium was assigned an atomic weight of 13·5 on the basis of its equivalent weight (4·5) and valency (wrongly calculated as 3). If beryllium has an atomic weight of 13·5, it should have been placed between carbon (atomic weight 12) and nitrogen (atomic weight 14). But no vacant place was available in between C and N and furthermore properties of beryllium did not justify such a position. Therefore, valency 2 was assigned to beryllium which gave it an atomic weight of $4·5 \times 2 = 9$ and it was placed at its proper position

MENDELEEV'S PERIODIC TABLE†

GROUPS→	I		II		III		IV		V		VI		VII		VIII
Formulae of Oxides	R_2O		RO		R_2O_3		RO_2		R_2O_5		RO_3		R_2O_7		RO_4
Formulae of Hydrides	RH		RH_2		RH_3		RH_4		RH_3		RH_2		RH		
↓PERIODS	A	B	A	B	A	B	A	B	A	B	A	B	A	B	
1	$_{1}$H 1·008														
2	$_{3}$Li 6·919		$_{4}$Be 9·012		$_{5}$B 10·81		$_{6}$C 12·011		$_{7}$N 14·007		$_{8}$O 15·999		$_{9}$F 18·998		
3	$_{11}$Na 22·99		$_{12}$Mg 24·31		$_{13}$Al 26·98		$_{14}$Si 28·09		$_{15}$P 30·974		$_{16}$S 32·06		$_{17}$Cl 35·453		
4	$_{19}$K 39·102	$_{29}$Cu 63·54	$_{20}$Ca 40·08	$_{30}$Zn 65·37	—	$_{21}$Sc 44·96	—	$_{22}$Ti 47·90	$_{33}$As 74·92	$_{23}$V 50·94	$_{34}$Se 78·96	$_{24}$Cr 52·00	$_{35}$Br 79·909	$_{25}$Mn 54·94	$_{26}$Fe 55·85 $_{27}$Co 58·93 $_{28}$Ni 58·71
5	$_{37}$Rb 85·47	$_{47}$Ag 107·87	$_{38}$Sr 87·62	$_{48}$Cd 112·40	$_{49}$In 114·82	$_{39}$Y 85·91	$_{50}$Sn 118·69	$_{40}$Zr 91·22	$_{51}$Sb 121·75	$_{41}$Nb 92·91	$_{52}$Te 127·60	$_{42}$Mo 95·94	$_{53}$I 126·90	$_{43}$Tc (99)	$_{44}$Ru 101.07 $_{45}$Rh 102.91 $_{46}$Pd 106.4
6	$_{55}$Cs 132·90	$_{79}$Au 196·97	$_{56}$Ba 137·34	$_{80}$Hg 200·59	$_{81}$Tl 204·37	* $_{57}$La 138·9	$_{82}$Pb 207·19	$_{72}$Hf 178·49	$_{83}$Bi 208·98	$_{73}$Ta 180·95	$_{84}$Po (210)	$_{74}$W 183·85	—	$_{75}$Re 186·2	$_{76}$Os 190·2 $_{77}$Ir 192·2 $_{78}$Pt 195 —

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†Atomic numbers of elements are given on the left hand lower corner of their symbols while atomic weights are given under their symbols.

between lithium (atomic weight 7) and boron (atomic weight 11).

4.4.3. Defects in the Mendeleev's Periodic Table. In spite of many advantages, Mendeleev's periodic table suffers from many serious defects. Some of these are discussed below :

1. Anomalous position of hydrogen. Hydrogen is placed in group IA. However it resembles the elements of both the group IA (alkali metals) and group VII A (halogens). Therefore, the position of hydrogen in the periodic table is anomalous or controversial.

2. Anomalous pairs of elements. Some elements with higher atomic weight precede the elements with lower atomic weight. For example, Ar (at. weight = 39·9) precedes potassium (at. weight = 39·1) ; Co (at. weight = 58·9) precedes Ni (at. weight = 58·7) and Te (at. weight = 127·6) precedes I (at. weight = 126·9). No justification has been provided for this ambiguity.

3. Position of isotopes. Isotopes are the atoms of the same element having different atomic weights. Therefore, according to Mendeleev's classification, these should be placed at different places in the periodic table according to their atomic weights. For example, isotopes of hydrogen *i.e.*, protium, deuterium and tritium with atomic weights 1, 2 and 3 should be placed at different places. However, isotopes of an element have not been given different places in the periodic table.

4. Some dissimilar elements are grouped together while some similar elements are placed in different groups. For example, alkali metals such as Li, Na, K etc. (group IA) are grouped together with coinage metals such as Cu, Ag and Au (group IB) though their properties are quite different. At the same time, certain chemically similar elements like Cu (group IB) and Hg (group II B) have been placed in different groups.

5. Position of elements of group VIII. No proper place has been allotted to nine elements of group VIII which have been arranged in three triads without any justification.

4.5. Atomic Number and Modern Periodic Law

In 1912, *Moseley*, a young English physicist measured the frequencies of X-rays emitted by a metal when bombarded with high speed electrons. He discovered that the square root of the frequency (ν) of the prominent X-rays emitted by a metal was proportional to the atomic number and not to the atomic weight of the atom of that metal

i.e., $\sqrt{\nu} = a\,(Z - b)$

where 'a' is the proportionality constant and 'b' is a constant for all the lines in a given series of X-rays.

Thus, a plot of $\sqrt{\nu}$ versus Z gave a straight line. This led Moseley to conclude that atomic number was a better fundamental property of an element than its atomic weight. He, therefore, suggested that atomic number (Z) instead of atomic weight should be the basis of classification of the elements. This forms the basis of the *modern periodic law*. Thus,

Modern periodic law *states that physical and chemical properties of the elements are a periodic function of their atomic numbers, i.e., if the elements are arranged in order of their increasing atomic numbers, the elements with similar properties are repeated after certain regular intervals.*

Theoretical Justification of the Modern periodic Law. We know that an atom consists of a nucleus (which contains protons and neutrons) surrounded by electrons. Atomic mass is a nuclear property and depends upon the number of protons and neutrons in the nucleus whereas atomic number implies the number of electrons in the extranuclear part or the number of protons in the nucleus. Now, the chemical properties of the elements depend, among other things, upon the interaction between the atom and the reagent. Since the nucleus is deep seated in an atom and is also shielded by electrons in the extranuclear part so atomic mass has little effect on the chemical properties of elements. Electrons, however, are exposed to the environments and hence can interact with the reagent. As a result, the physical and chemical properties of the elements depend upon their atomic numbers rather than atomic masses. Further, it is understandable that the physical and chemical properties of elements could be different depending upon the number of electrons and their electronic configuration in any atom.

Let us now discuss why the elements with similar properties recur after certain regular intervals.

4.6. Cause of Periodicity

According to the Modern Periodic Law, the properties of the elements are repeated after certain regular intervals when these elements are arranged in order of their increasing atomic numbers. Further, critical examination of the electronic configuration of the various elements (discussed in Unit 3) clearly indicates that with a gradual increase in atomic number there occurs a repetition of similar outer electronic configurations after certain regular intervals. By correlating these two observations, we can say that

The cause of periodicity in properties is the repetition of similar outer electronic configurations at certain regular intervals.

Consider the following examples for illustration.

All the elements of group IA (or 1) *i.e.* alkali metals have the similar outer electronic configuration, *i.e.* ns^1 where n refers to the number of the outermost principal shell. These electronic configurations are given below in Table 4.2.

TABLE 4.2. Electronic configuration of alkali metals

SYMBOL	ATOMIC NUMBER	ELECTRONIC CONFIGURATION
Li	3	$1s^2\ 2s^1$ or [He] $2s^1$
Na	11	$1s^2\ 2s^2\ 2p^6\ 3s^1$ or [Ne] $3s^1$
K	19	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ or [Ar] $4s^1$
Rb	37	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^1$ or [Kr] $5s^1$
Cs	55	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 6s^1$ or [Xe] $6s^1$
Fr	87	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6\ 7s^1$ or [Rn] $7s^1$

Thus, it is because of similarity in electronic configuration that all the elements have similar properties.

In a similar manner all the halogens, *i.e.*, elements of group VII A (or 17) have similar outer electronic configuration *i.e.* $ns^2\ np^5$ and as such possess similar properties. The electronic configurations of halogens are given in Table 4.3.

TABLE 4.3. Electronic configuration of halogens

ELEMENT	ATOMIC NUMBER	ELECTRONIC CONFIGURATION
F	9	$1s^2\ 2s^2\ 2p^5$
Cl	17	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
Br	35	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 4p^5$
I	53	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^5$
At	85	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^5$

Again all the elements of group 0 (or 18) *i.e.*, inert gases have similar outer electronic configuration, *i.e.* $ns^2\ np^6$ and also have similar properties.

Now, it follows from Tables 4.2 and 4.3 that there is a repetition in the electronic configurations of alkali metals and halogens only after certain regular intervals. These regular intervals being 2, 8, 8, 18, 18 and 32. These numbers are also sometimes called **magic numbers.**

4.7. Present Form or Long Form of the Periodic Table — Bohr's Table

Based upon Modern Periodic Law, a number of forms of periodic table have been proposed from time to time but the general plan of the table remained the same as proposed by Mendeleev. The table which is most commonly used these days and which is based upon the electronic configuration of elements is called the Present form or the Long

form of the periodic table. This is also called Bohr's table since it follows Bohr's scheme for the arrangement of various electrons around the nucleus.

Structural Features of the Present (or Long) From of the Periodic Table. The long form of the periodic table consists of eighteen vertical columns and seven horizontal rows. These have been obtained by arranging the elements in order of increasing atomic numbers in such a way that the elements with similar electronic configurations are placed under each other in the same vertical column. *These vertical columns are known as* **groups** or **families** *while the horizontal rows are called* **periods**. These are discussed below :

1. Groups. (*i*) The present (long) form of the periodic table consists of eighteen vertical columns called groups. Each group consists of a number of elements having the same electronic configuration of the outermost shell (valency shell). These groups are numbered from 1 to 18. Earlier in the modified Mendeleev's periodic table, these eighteen vertical columns were divided into sixteen groups designated as IA, II A ... VII A ; IB, II B ..... VII B, VIII and zero. Both these systems of numbering the groups are shown in the long form of the periodic table given on page 4/9.

(*ii*) The elements of the first two groups, *i.e.*, 1 and 2 on the extreme left involve the filling of *s*-orbitals while those of the last six groups, *i.e.*, 13 – 18 lying on the extreme right involve the filling of electrons in the *p*-orbitals of the valence shell.

The elements of these eight groups, *i.e.*, 1, 2, 13, 14, 15, 16, 17 and 18 are collectively called **normal** or **representative elements.** Their outer electronic configurations are ns^1 , ns^2 , $ns^2\,np^1$, $ns^2\,np^2$, $ns^2\,np^3$, $ns^2\,np^4$, $ns^2\,np^5$ and $ns^2\,np^6$ respectively. The elements of group 18 are also called **inert gases** or **noble gases.** As stated above their valence shell electronic configuration is $ns^2\,np^6$.

(*iii*) *The elements of groups 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 are called* **transition elements** *since their properties lie between the properties of the reactive metals (alkali and alkaline earth metals) placed on the extreme left and non-metals (halogens and chalcogens = oxygen family) placed on the extreme right of the periodic table.*

In these elements, both the outermost shell and penultimate shell (next to the outermost) are incompletely filled but filling of the *d*-orbitals of the penultimate shell occurs. As such their general outer electronic configuration is $(n-1)\,d^{1-10}\,ns^{0-2}$.

(*iv*) Two series of elements each containing 14 elements are placed at the bottom of the periodic table. The first series of elements with Z = 58 to Z = 71 which occur in the periodic table after lanthanum are called ***lanthanides*** or ***lanthanoids*** while the second series of elements with Z = 90 to Z = 103 which occur in the periodic table after actinium are called ***actinides*** or ***actinoids***. These elements are also called **inner transition elements.**

In both these series of elements, the outermost shell and the penultimate shell are incompletely filled but the filling of only *f*-orbitals of the ante-penultimate shell occurs. As such their general outer electronic configuration is $(n-2)\,f^{\,0-14}\,(n-1)\,d^{0-1}\,ns^2$.

2. Periods. As stated above, the long form of the periodic table consists of seven horizontal rows called **periods**. These are numbered as 1, 2, 3, 4, 5, 6 and 7 from top to bottom. *Each period consists of a series of elements whose atoms have the same principal quantum number (n) of the outermost shell.* In other words, each period begins with the filling of electrons in a new energy shell. For example,

The **first period** corresponds to the filling of electrons in the first energy shell, *i.e.* $n = 1$. Since this energy shell has only *one orbital, i.e.* 1*s* which can accommodate only two electrons, therefore, *first period has only two elements*. These are hydrogen ($1s^1$) and helium ($1s^2$).

The **second period** corresponds to the filling of electrons in the 2nd energy shell, *i.e.* $n = 2$. Since this shell has *four orbitals* (one 2*s* and three 2*p*) which can accommodate eight electrons, therefore, *second period contains eight elements*. It starts with lithium (Z = 3) in which one electron enters the 2*s*-orbital and ends up with neon (Z = 10) in which the second shell is complete.

The **third period** corresponds to the filling of electrons in the third shell, *i.e.* $n = 3$. This shell has *nine orbitals* (one 3*s*, three 3*p* and five 3*d*). However, we know from energy level diagram for multielectron atoms (Unit 3) that 3*d*-orbitals have even higher energy than 4*s*-orbital. Therefore 3*d*-orbitals are filled only after filling 4*s*-orbitals. Conse-

LONG FORM OF THE PERIODIC TABLE

ATOMIC NUMBER → 26
SYMBOL → Fe
NAME → Iron
ELECTRONIC CONFIGURATION → $3d^6 4s^2$

s-BLOCK (ns^{1-2})

p-BLOCK (np^{1-6})

d-BLOCK (TRANSITION ELEMENTS)
[$(n-1)d^{1-10} ns^{0-2}$]

OLD GROUP NOS.	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
MODERN GROUP NOS.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
GROUPS PERIODS	① (ns^1)	② (ns^2)	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪	⑫	⑬ ($ns^2 np^1$)	⑭ ($ns^2 np^2$)	⑮ ($ns^2 np^3$)	⑯ ($ns^2 np^4$)	⑰ ($ns^2 np^5$)	⑱ ($ns^2 np^6$)
1 (1s)	1 **H** Hydrogen $1s^1$																	2 **He** Helium $1s^2$
2 (2s 2p)	3 **Li** Lithium $2s^1$	4 **Be** Beryllium $2s^2$											5 **B** Boron $2s^2 2p^1$	6 **C** Carbon $2s^2 2p^2$	7 **N** Nitrogen $2s^2 2p^3$	8 **O** Oxygen $2s^2 2p^4$	9 **F** Fluorine $2s^2 2p^5$	10 **Ne** Neon $2s^2 2p^6$
3 (3s 3p)	11 **Na** Sodium $3s^1$	12 **Mg** Magnesium $3s^2$											13 **Al** Aluminium $3s^2 3p^1$	14 **Si** Silicon $3s^2 3p^2$	15 **P** Phosphorus $3s^2 3p^3$	16 **S** Sulphur $3s^2 3p^4$	17 **Cl** Chlorine $3s^2 3p^5$	18 **Ar** Argon $3s^2 3p^6$
4 (4s 3d 4p)	19 **K** Potassium $4s^1$	20 **Ca** Calcium $4s^2$	21 **Sc** Scandium $3d^1 4s^2$	22 **Ti** Titanium $3d^2 4s^2$	23 **V** Vanadium $3d^3 4s^2$	24 **Cr** Chromium $3d^5 4s^1$	25 **Mn** Manganese $3d^5 4s^2$	26 **Fe** Iron $3d^6 4s^2$	27 **Co** Cobalt $3d^7 4s^2$	28 **Ni** Nickel $3d^8 4s^2$	29 **Cu** Copper $3d^{10} 4s^1$	30 **Zn** Zinc $3d^{10} 4s^2$	31 **Ga** Gallium $4s^2 4p^1$	32 **Ge** Germanium $4s^2 4p^2$	33 **As** Arsenic $4s^2 4p^3$	34 **Se** Selenium $4s^2 4p^4$	35 **Br** Bromine $4s^2 4p^5$	36 **Kr** Krypton $4s^2 4p^6$
5 (5s 4d 5p)	37 **Rb** Rubidium $5s^1$	38 **Sr** Strontium $5s^2$	39 **Y** Ytterium $4d^1 5s^2$	40 **Zr** Zirconium $4d^2 5s^2$	41 **Nb** Niobium $4d^4 5s^1$	42 **Mo** Molybdenum $4d^5 5s^1$	43 **Tc** Technetium $4d^5 5s^2$	44 **Ru** Ruthenium $4d^7 5s^1$	45 **Rh** Rhodium $4d^8 5s^1$	46 **Pd** Palladium $4d^{10} 5s^0$	47 **Ag** Silver $4d^{10} 5s^1$	48 **Cd** Cadmium $4d^{10} 5s^2$	49 **In** Indium $5s^2 5p^1$	50 **Sn** Tin $5s^2 5p^2$	51 **Sb** Antimony $5s^2 5p^3$	52 **Te** Tellurium $5s^2 5p^4$	53 **I** Iodine $5s^2 5p^5$	54 **Xe** Xenon $5s^2 5p^6$
6 (6s (4f) 5d 6p)	55 **Cs** Cesium $6s^1$	56 **Ba** Barium $6s^2$	57 **La*** Lanthanum $5d^1 6s^2$	72 **Hf** Hafnium $4f^{14} 5d^2 6s^2$	73 **Ta** Tantalum $5d^3 6s^2$	74 **W** Tungsten $5d^4 6s^2$	75 **Re** Rhenium $5d^5 6s^2$	76 **Os** Osmium $5d^6 6s^2$	77 **Ir** Iridium $5d^7 6s^2$	78 **Pt** Platinum $5d^9 6s^1$	79 **Au** Gold $5d^{10} 6s^1$	80 **Hg** Mercury $5d^{10} 6s^2$	81 **Tl** Thallium $6s^2 6p^1$	82 **Pb** Lead $6s^2 6p^2$	83 **Bi** Bismuth $6s^2 6p^3$	84 **Po** Polonium $6s^2 6p^4$	85 **At** Astatine $6s^2 6p^5$	86 **Rn** Radon $6s^2 6p^6$
7 (7s (5f) 6d)	87 **Fr** Francium $7s^1$	88 **Ra** Radium $7s^2$	89 **Ac**** Actinium $6d^1 7s^2$	104 **Rf** Rutherfordium $5f^{14} 6d^2 7s^2$	105 **Db** Dubnium $6d^3 7s^2$	106 **Sg** Seaborgium $6d^4 7s^2$	107 **Bh** Bohrium $6d^5 7s^2$	108 **Hs** Hassnium $6d^6 7s^2$	109 **Mt** Meitnerium $6d^7 7s^2$	110 **Uun** Ununnillium $6d^8 7s^2$	111 **Uuu** Unununnium $6d^{10} 7s^1$	112 **Uub** Ununbium $6d^{10} 7s^2$	—	114 **Uuq** Ununquadium $7s^2 7p^2$	115 **Uup**• Ununpentium $7s^2 7p^3$	—	—	— NOBLE GASES

REPRESENTATIVE ELEMENTS (groups 1–2)

REPRESENTATIVE ELEMENTS (groups 13–18)

METALS ← → NON-METALS

f-BLOCK/INNER-TRANSITION ELEMENTS (RARE EARTHS)
[$(n-2)f^{0-14} (n-1)d^{0-1} ns^2$]

***LANTHANOIDS (4f-series)** ($4f^{1-14} 5d^{0-1} 6s^2$)	58 **Ce** Cerium $4f^1 5d^1 6s^2$	59 **Pr** Praseodymium $4f^3 5d^0 6s^2$	60 **Nd** Neodymium $4f^4 5d^0 6s^2$	61 **Pm** Promethium $4f^5 5d^0 6s^2$	62 **Sm** Samarium $4f^6 5d^0 6s^2$	63 **Eu** Europium $4f^7 5d^0 6s^2$	64 **Gd** Gadolinium $4f^7 5d^1 6s^2$	65 **Tb** Terbium $4f^9 5d^0 6s^2$	66 **Dy** Dysprosium $4f^{10} 5d^0 6s^2$	67 **Ho** Holmium $4f^{11} 5d^0 6s^2$	68 **Er** Erbium $4f^{12} 5d^0 6s^2$	69 **Tm** Thullium $4f^{13} 5d^0 6s^2$	70 **Yb** Ytterbium $4f^{14} 5d^0 6s^2$	71 **Lu** Lutetium $4f^{14} 5d^1 6s^2$
****ACTINOIDS (5f-series)** ($5f^{0-14} 6d^{0-1} 7s^2$)	90 **Th** Thorium $5f^0 6d^2 7s^2$	91 **Pa** Protactinium $5f^2 6d^1 7s^2$	92 **U** Uranium $5f^3 6d^1 7s^2$	93 **Np** Neptunium $5f^4 6d^1 7s^2$	94 **Pu** Plutonium $5f^6 6d^0 7s^2$	95 **Am** Americium $5f^7 6d^0 7s^2$	96 **Cm** Curium $5f^7 6d^1 7s^2$	97 **Bk** Berkelium $5f^9 6d^0 7s^2$	98 **Cf** Californium $5f^{10} 6d^0 7s^2$	99 **Es** Einsteinium $5f^{11} 6d^0 7s^2$	100 **Fm** Fermium $5f^{12} 6d^0 7s^2$	101 **Md** Mendelevium $5f^{13} 6d^0 7s^2$	102 **No** Nobelium $5f^{14} 6d^0 7s^2$	103 **Lr** Lawrencium $5f^{14} 6d^1 7s^2$

• Discovered most recently by Russian and US scientists by hitting amercium (Z=95) with calcium (Z=20) accelerated in a cyclotron. The calcium nucleus simply fused into the amercium nucleus.

quently, third period involves the filling of only *four orbitals* (one 3*s* and three 3*p*) and thus *contains eight elements* from sodium (Z = 11, $3s^1$) to argon (Z = 18, $3s^2\ 3p^6$).

The **fourth period** corresponding to the filling of electrons in the fourth energy level, *i.e.* $n = 4$. It starts with the filling of 4*s*-orbital. However, after filling 4*s*-orbital, the filling of five 3*d*-orbitals begins since the energy of 3*d*-orbital is lower than those of 4*p*-orbitals but higher than that of 4*s*-orbital. Further, the filling of 4*d* and 4*f*-orbitals does not occur in this period since their energies are higher than that of even 5*s*- orbital. Therefore, in the fourth period, the filling of only *nine orbitals* (one 4*s*, five 3*d* and three 4*p*) occurs which can accommodate at the maximum eighteen electrons. *Therefore, fourth period contains eighteen elements from potassium (Z = 19) to krypton (Z = 36).*

The **fifth period**, like the fourth period also contains eighteen elements since only *nine orbitals* (one 5*s*, five 4*d* and three 5*p*) are available for filling with electrons. It begins with rubidium (Z = 37) in which one electron enters the 5*s*-orbital and ends up with xenon (Z = 54) in which the filling of 5*p*-orbitals is complete.

The **sixth period** corresponds to the filling of sixth energy level, *i.e.*, $n = 6$. Since in this period, only *sixteen orbitals* (one 6*s*, seven 4*f*, five 5*d* and three 6*p*) are available for filling with electrons, therefore, *sixth period contains thirty-two elements*. It begins with caesium (Z = 55) in which one electron enters the 6*s*-orbital and ends up with radon (Z = 86) in which the filling of 6*p*-orbitals is complete. In this period, after the filling of 6*s*-orbital, the next electron (i.e., 57th) enters the 5*d**-orbital against the *aufbau principle* and thereafter, the filling of seven 4*f*-orbitals begins with cerium (Z = 58) and ends up with lutetium (Z = 71). These fourteen elements constitute **the first (or 4f) inner transition series** called **lanthanides** or **lanthanoids**. These are separated from the main frame of the periodic table and are placed at the bottom of the periodic table.

The **seventh period** corresponds to the filling of seventh energy shell, *i.e.* $n = 7$. Like sixth period, it is also expected to contain thirty-two elements corresponding to the filling of *sixteen orbitals* (one 7*s*, seven 5*f*, five 6*d* and three 7*p*). However, this period is still incomplete and only 28 elements are known at present. In this period, after the filling of 7*s*-orbital, the next two electrons (*i.e.*, 89th and 90th) enter the 6*d*** *orbital against aufbau principle* and thereafter the filling of seven 5*f*-orbitals begins with proactinium (Z = 91) and ends up with lawrencium (Z = 103). Although thorium (Z = 90) does not have any electron in the 5*f*-orbital, yet it is considered to be a *f*-block element. Since its properties resemble more the *f*-block elements than the *d*-block elements. These fourteen elements from thorium (Z = 90) to lawrencium (Z = 103).

These fourteen elements constitute the **second (or 5f) inner transition series** which is commonly called as **actinides** or **actinoids**. It mostly includes man-made radioactive elements. In order to avoid the undue expansion of the periodic table actinides like lanthanides, have also been placed separately at the bottom of the periodic table.

The number of elements in a period and the type of orbitals being filled up is given in the Table 4.4.

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*This anomalous behaviour can be explained on the basis of greater stability of the xenon (inert gas) core. After barium (Z = 56), the addition of the next electron (*i.e.*, 57th) should occur in 4*f*-orbital in accordance with *aufbau principle*. This will, however, tend to destabilize the xenon core (Z = 54, [Kr] $4d^{10}\ 4f^0\ 5s^2\ 5p^6\ 5d^0$) since the 4*f*-orbitals lie inside the core. Therefore, the 57th electron prefers to enter 5*d*-orbital which lies outside the xenon core and whose energy is only slightly higher than that of 4*f*-orbital. In doing so, the stability conferred on the atom due to xenon core more than compensates the slight instability caused by the addition of one electron to the higher energy 5*d*-orbital instead of the lower energy 4*f*-orbital. Thus, the outer electronic configuration of La (Z = 57) is $5d^1\ 6s^2$ rather than the expected $4f^1\ 6s^2$. Once 5*d*-orbital has one electron, the next electron (*i.e.* 58th) enters the inner 4*f*-orbital (instead of the outer 5*d*-orbital) due to greater nuclear charge and thereafter the continuous filling of the 4*f*-subshell occurs till it is complete at lutetium (Z = 71, $4f^{14}\ 5d^1\ 6s^2$).

**Here due to (*i*) smaller energy difference between 5*f* and 6*d*-orbitals than between 4*f*- and 5*d*-orbitals, and (*ii*) greater stability of the radon core, the next two electrons (*i.e.* 89th and 90th) after the filling of 7*s*-orbital prefer to enter 6*d*-orbitals before filling of 5*f*-orbitals begins with proactinium (Pa = 91) and continues till it is complete with lawrencium (Lr = 103).

TABLE 4.4. Number of elements in different periods

Period	No. of the energy level being filled	Orbitals being filled	No. of electrons or elements in the period
1	$n = 1$	$1s$	2
2	$n = 2$	$2s, 2p$	$2 + 6 = 8$
3	$n = 3$	$3s, 3p$	$2 + 6 = 8$
4	$n = 4$	$4s, 3d, 4p$	$2 + 10 + 6 = 18$
5	$n = 5$	$5s, 4d, 5p$	$2 + 10 + 6 = 18$
6	$n = 6$	$6s, 4f, 5d, 6p$	$2 + 14 + 10 + 6 = 32$
7	$n = 7$	$7s, 5f, 6d, 7p$	$2 + 14 + 10 + 6 = 32$ (Out of these only 28 elements are known at present)

The first three periods (1st, 2nd and 3rd) containing 2, 8, 8 elements respectively are known as **short periods** while the next three periods (4th, 5th and 6th) containing 18, 18, 32 elements respectively are called **long periods.**

4.8. IUPAC Nomenclature of Elements with Z > 100

All the elements with Z = 101 – 112 and Z = 114 have been identified. Some of these are known since long while others have been discovered only recently. Although names and symbols to many of these elements have been assigned but these are still not universally accepted. Also some of these elements have been assigned two names/symbols. For example, element with Z = 104 is called either Kurchatovium (Ku) or Rutherfordium (R_f) while element with Z = 107 is called Neilsbohrium (Ns) or simply Bohrium (Bh). To overcome all these difficulties, the IUPAC appointed a Commission on Nomenclature of Inorganic Chemistry (CNIC) in 1994 to suggest a rational system of nomenclature for elements with Z > 100 (also collectively called as super heavy elements). After having discussions with chemists around the world, the IUPAC in 1997, approved the official names for elements with Z = 104 to Z = 109 (Table 4.5) and suggested a systematic nomenclature for naming other elements with Z > 100 till their names are officially announced. The main points of this nomenclature are :

(*i*) The names are derived directly from the atomic numbers using numerical roots for 0 and numbers from 1 – 9 and adding the suffix *ium.* A strange mixture of Latin and Greek roots has been chosen to ensure that the symbols are all different. The roots for the numbers 0 – 9 are :

TABLE 4.5. Roots for IUPAC nomenclature of elements

Digit	0	1	2	3	4	5	6	7	8	9
Root	nil	un	bi	tri	quad	pent	hex	sept	oct	enn
Abbreviation	n	u	b	t	q	p	h	s	o	e

(*ii*) In certain cases, the names are shortened. For example, *bi ium* and *tri ium* are shortened to *bium* and *trium* and *enn nil* is shortened to *ennil.*

(*iii*) The symbol of the element is then obtained from the first letters of the roots of numbers which make up the atomic number of the element. The recommended and official names of some super heavy elements are given in Table 4.6 :

4.9. Electronic Configuration of the Elements and the Periodic Table

The present (long) form of the periodic table is based upon electronic configuration of elements. With its help, it is very easy to find out the electronic configuration of any element. The outer electronic configuration of all the elements along with their symbols are given in the present form of the peri-

TABLE 4.6. Recommended and Official names of elements with Z > 100

Z	Recommended name	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	Hassnium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnilium	Uun	*	*
111	Unununium	Uuu	*	*
112	Ununbium	Uub	*	*
113	Ununtrium	Uut	**	—
114	Ununquadium	Uuq	*	*
115	Ununpentium	Uup	*	*
116	Ununhexium	Uuh	**	—
117	Ununseptium	Uus	**	—
118	Ununoctium	Uuo	**	—
119	Ununennium	Uue	**	—
120	Unbinilium	Ubn	**	—

odic table on page 4/9. However, complete electronic configurations of all the elements along with their names and symbols have already been given in unit 3.

4.10. Division of Elements into s, p, d-and f-blocks

Elements in the long form of the periodic table have been divided into four blocks, *i.e.*, *s*, *p*, *d* and *f*. *This division is based upon the name of the orbital which receives the last electron.* These are briefly discussed below.

1. s-Block Elements. *Elements in which the last electron enters the s-orbital* of their respective outermost shells are called *s*-block elements. Since *s*-subshell has only one orbital which can accommodate only two electrons, therefore, there are only two groups of *s*-block elements. Thus, elements of group 1 (hydrogen and the alkali metals) and group 2 (alkaline earth metals) and helium comprise *s*-block elements. Consider, for example, elements of group 1. Hydrogen has only one electron and this enters $1s$ orbital. The rest of the elements, *i.e.* Li, Na, K, Rb, Cs and Fr receive the last electron in $2s$, $3s$, $4s$, $5s$, $6s$ and $7s$- orbitals respectively. These elements are, therefore, said to belong to *s*-block and have ns^1 as the general outer shell electronic configuration.

Now consider He and the elements of group 2, *i.e.* Be, Mg, Ca, Sr, Ba and Ra. The last electron in these elements also enters the *s*-orbitals, *i.e.* $1s$, $2s$, $3s$, $4s$, $5s$, $6s$ and $7s$-orbitals respectively. Hence these elements also belong to *s*-block and have ns^2 as their general outer shell electronic configuration.

Thus the elements of groups 1 and 2, including hydrogen and helium in which the s-orbitals are being progressively filled in are called **s-block elements.** In all there are 14 *s*-block elements in the periodic table.

General outer shell electronic configuration of s-block elements : ns^{1-2}

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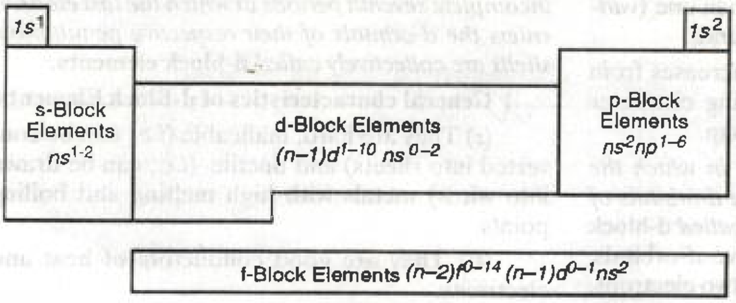
*Elements have been discovered but their official IUPAC names are yet to be announced.

**Elements yet to be discovered.



Division of periodic table into s, p, d- and f-blocks.

General characteristics of s-Block Elements

(*i*) They are soft metals with low melting and boiling points.

(*ii*) They have low ionization ethalpies (energies) and are highly electropositive.

(*iii*) They lose the valence (outermost) electron(s) readily to form +1 (in case of alkali metals) and +2 ions (in the case of alkaline earth metals).

(*iv*) They are very reactive metals. The metallic character and the reactivity increase as we move down the group.

(*v*) The compounds of *s*-block elements with the exception of those of beryllium are predominantly ionic.

(*vi*) Most of the metals of this block impart characteristic colours to the flame.

(*vii*) They are strong reducing agents.

(*viii*) All are good conductors of heat and electricity.

2. p-Block Elements. *Elements in which the last electron enters any one of the three p-orbitals* of their respective outermost shells are called **p-block elements.** Since a *p*- subshell has three degenerate (same energy) *p*-orbitals, each one of which can accommodate two electrons, therefore, in all, there are six groups of *p*-block elements. These are 13, 14, 15, 16, 17 and 18 (excluding helium). The atoms of the elements belonging to these groups receive the last electron in 2*p* , 3*p* , 4*p* , 5*p* and 6*p*-orbitals respectively.

In all these elements, the *s*-orbital of their outermost shells is already complete but their respective *p*-orbitals get progressively filled in by the addition of one electron at a time as we move from group 13 to 14, 15, 16, 17 and 18. Since these elements contain one to six electrons in their respective outermost *p*-orbitals, therefore, their outer shell electronic configurations vary from $ns^2\,np^1$ to $ns^2\,np^6$ as we move from group 13 onwards upto group 18.

Thus, the elements of groups 13, 14, 15, 16, 17, 18 (excluding helium) in which p-orbitals *are being progressively filled in are called* **p-block elements.** Since each group has five elements, therefore, in all, there are 30 *p*-block elements in the periodic table.

General outer shell electronic configuration of p-block elements : $ns^2\,np^{1-6}$

The elements of group 18 are called **noble gases.** Each period ends in a noble gas. Except helium all the elements have closed shell $ns^2\,np^6$ electronic configuration in the outermost shell. Helium, however, has $1s^2$ electronic configuration. *In these elements, all the energy levels which are occupied are completely filled and this stable arrangement of electrons cannot be easily altered by addition or removal of electrons. As a result, these elements are highly stable and hence exhibit very low chemical reactivity.*

The elements of group 17 are called **halogens** (*salt producers*) while those of group 16 are called **chalcogens** (*ore-forming*). These two groups of elements have high negative electron gain enthalpies (or electronegativity) and hence readily add one or two electrons respectively to attain the stable noble gas configuration.

The elements of *s*- and *p*-block are collectively called **representative, or normal or main group elements.** These include elements of group 1 (*alkali metals*), group 2 (*alkaline earth metals*) on the extreme left and elements of groups 13-18 on the right hand side of the periodic table.

General characteristics of p-Block Elements

(*i*) *p*-Block elements include both metals and non- metals but the number of non-metals is much higher than that of metals. Further, *the metallic character increases from top to bottom within a group and non-metallic character increases from left to right along a period in this block.*

(*ii*) Their ionization energies are relatively higher as compared to those of *s*-block elements.

(*iii*) They mostly form covalent compounds.

(*iv*) Some of them show more than one (*variable*) oxidation states in their compounds.

(*v*) Their oxidising character increases from left to right in a period and reducing character increases from top to bottom in a group.

3. d-Block Elements. *Elements in which the last electron enters any one of the five d-orbitals of their respective penultimate shells are called* **d-block elements**. Since a *d*-subshell has five *d*-orbitals, each one of which can accommodate two electrons, therefore, in all there are ten vertical columns comprising ten groups of *d*-block elements, namely 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12.

The atoms of the elements belonging to these groups usually have 1 or 2 (zero in some cases) electrons in the *s*-orbital of the outermost shell, *i.e.*, *ns*-orbital while the electrons are being progressively filled in, one at a time, in the *d*-orbitals of their respective penultimate shells, *i.e.*, $(n-1)$ *d*-orbitals. Thus,

General outer shell electronic configuration of d-block elements : $(n-1)\,d^{1-10}\,ns^{0-2}$.

Since the properties of these elements are midway between those of *s*-block and *p*-block elements, they are also called **transition elements**. All these elements are further divided into four series called *first, second, third, and fourth transition series.*

The first transition series forms a part of the fourth period of the long form of the periodic table. It contains ten elements from scandium to zinc (${}_{21}\text{Sc} - {}_{30}\text{Zn}$) in which 3*d*-orbitals are being progressively filled in.

The second transition series which forms a part of the fifth period also contains ten elements from ytterium to cadmium (${}_{39}\text{Y} - {}_{48}\text{Cd}$) in which 4*d*-orbitals are being progressively filled in.

The third transition series which forms a part of the sixth period also contains ten elements, *i.e.*, lanthanum (${}_{57}\text{La}$) and from hafnium to mercury (${}_{72}\text{Hf} - {}_{80}\text{Hg}$) in which 5*d*-orbitals are being progressively filled in.

The fourth transition series which forms a part of the seventh period also contains ten elements, *i.e.*, actinium (${}_{89}\text{Ac}$) and elements from, rutherfordium (${}_{104}\text{Rf}$), to ekamercury or Ununbium (Z = 112). In all these elements, 6*d*-orbitals are being successively filled in.

Thus the elements of groups, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 belonging to fourth, fifth, sixth and the incomplete seventh periods in which the last electron enters the d-orbitals of their respective penultimate shells are collectively called **d-block elements.**

General characteristics of d-Block Elements.

(*i*) They are hard, malleable (*i.e.*, can be converted into sheets) and ductile (*i.e.*, can be drawn into wires) metals with high melting and boiling points.

(*ii*) They are good conductors of heat and electricity.

(*iii*) Their ionization enthalpies are between *s*-and *p*-block elements.

(*iv*) They show variable oxidation states.

(*v*) They form both ionic and covalent compounds.

(*vi*) Their compounds are generally coloured and paramagnetic.

(*vii*) They form coloured complexes.

(*viii*) Most of the transition metals such as V, Cr, Mn, Fe, Co, Ni, Cu etc. and their compounds are used as catalysts.

(*ix*) Most of the transition metals form alloys.

(*x*) Zn, Cd and Hg which have the $(n-1)\,d^{10}\,ns^2$ electronic configuration, do not show most of the properties of transition elements.

4. f-Block Elements. *Elements in which the last electron enters any one of the seven f-orbitals of their respective ante- penultimate shells are called* ***f-block elements***. In all these elements, the *s*-orbital of the last shell (*n*) is completely filled, the *d*-orbitals of the penultimate $(n-1)$ shell invariably contains zero or one electron but the *f*-orbitals of the antepenultimate $(n-2)$ shell (being lower in energy than *d*-orbitals of the penultimate shell) gets progressively filled in. Hence

General outer shell electronic configuration of f-block elements : $(n-2)\,f^{0-14}\,(n-1)\,d^{0-1}\,ns^2$

There are two series of *f*-block elements each containing 14 elements. Threfore, in all there are 28 *f*-block elements in the periodic table. These are placed at the bottom of the periodic table.

The elements of the first series, i.e., cerium to lutetium (${}_{58}\text{Ce} - {}_{71}\text{Lu}$) which form a part of the sixth period are collectively called as **lanthanides** or **lanthanoids** since all these elements follow lanthanum in the periodic table and also closely resemble lanthanum (La) in their properties. These are also called **rare earth elements** since they occur scarcely in the earth's crust. In lanthanides, 4*f*-orbitals are being progressively filled in.

The elements of the second series, i.e., thorium to lawrencium ($_{90}$Th – $_{103}$Lr) which forms a part of the incomplete seventh period are collectively called **actinides** or **actinoids** since all these elements follow actinium in the periodic table and also closely resemble actinium (Ac) in their properties. In actinides, 5*f*-orbitals are being progressively filled in.

All the actinoids are radioactive elements. The first three elements, *i.e.*, thorium (Th), protoactinium (Pa) and uranium (U) occur in nature but the remaining 11 elements, *i.e.* from neptunium to lawrencium ($_{93}$Np – $_{103}$Lr) have been prepared artificially through nuclear reactions. *These eleven elements are called* ***transuranic*** *or* ***transuranium*** *elements since they follow uranium in the periodic table and also have been derived from it through nuclear reactions.*

All the *f*-block elements, *i.e.*, lanthanides and actinides are also called **inner transition elements** since they form transition series within the transition elements of *d*- block.

General characteristics of f-Block Elements

(*i*) They are heavy metals.

(*ii*) They have generally high melting and boiling points.

(*iii*) They show variable oxidation states.

(*iv*) Their compounds are generally coloured.

(*v*) They have a high tendency to form complexes.

(*vi*) Most of the elements of the actinide series are radioactive.

Metals, non-metals and metalloids. In addition to the division of the elements into *s, p, d* and *f*-block elements, all the elements can be broadly divided into metals and non-metals.

Metals. Metals comprise 75% of all the known elements and appear on the left hand side of the periodic table. With the exception of mercury, gallium and francium which are liquids, all other metals are solids at room temperature. They are good conductors of heat and electricity, malleable (can be converted into thin sheets by hanmering) and ductile (can be drawn into wires).

Non-metals. Non-metals may be gases, liquids or even solids with low melting and boiling points. Most of the non-metallic solids are brittle and are neither malleable nor ductile.

Trends in metallic and non-metallic character. The metallic character increases from top to bottom within a group and non-metallic character increases from left to right along a period. This change from metallic to non-metallic character is not abrupt as shown by thick zig-zag line in the long form of the periodic table given on page 4/9. The elements *silicon, germanium, arsenic, antimony and tellurium* (bordering this line and running diagonally across the periodic table) show the properties of both metals and non-metals. These elements are called **semi-metals** or **metalloids.**

4.11. Advantages of the Present (or Long) form of the Periodic Table

The present form of the periodic table has a large number of advantages since it classifies the elements on the basis of electronic configurations of their atoms. The important advantages are :

(*i*) It relates the position of an element in the table to its electronic configuration more clearly.

(*ii*) It is easy to remember and reproduce. The elements can be reproduced more easily in sequence of atomic numbers.

(*iii*) The elements in the same group show marked similarities due to similar outer electronic configurations. Thus, there is a logical classification of groups in it.

(*iv*) The elements are classified into *normal elements* belonging to 1, 2, 13 – 17 groups and *transition elements* belonging to 3 – 12 groups on the basis of their outer electronic configurations.

(*v*) The elements are also classified as *active metals* placed in groups 1 and 2, heavy metals placed in groups 3 – 12 and *non-metals* placed in the upper right corner (groups 13 – 18) of this periodic table.

(*vi*) Based on their electronic configuration, elements have been grouped into *s, p, d* and *f*-blocks. This has helped us to understand their properties easily.

(*vii*) The transition elements of fourth, fifth, sixth and seventh periods are assigned proper positions in this periodic table.

(*viii*) A satisfactory position has been provided to the elements of groups 8 – 10 consisting of nine elements in three triads (Group VIII of the Mendeleeve's periodic table).

Since long form of the periodic table correlates the position of elements to the electronic configuration of their atoms, it is, therefore, nearly an ideal arrangement.

4.12. Defects of the Present (or Long) form of the Periodic Table

Although the present form of the periodic table has removed most of the shortcomings of Mendeleev's original and modified periodic table, yet it suffers from the following defects :

(*i*) Position of hydrogen is not settled though it has been placed alongwith alkali metals in group 1 and halogens in group 17 since it shows many properties similar to both alkali metals and halogens.

(*ii*) Lanthanides and Actinides have not been accommodated in the main body of this periodic table.

4.13. Prediction of Period, Group and Block of a Given Element

The period, group and block of an element can be easily predicted from its electronic configuration as folows :

(*i*) *The period of an element corresponds to the principal quantum number of the valence shell.*

(*ii*) *The block of an element corresponds to the type of orbital which receives the last electron.*

(*iii*) *The group of an element is predicted from the number of electrons in the valence shell or/and penultimate shell (last but one, i.e. $n - 1$) as follows :*

(*a*) **For *s*-block elements,** *group number is equal to the* **number of valence electrons.**

(*b*) **For *p*-block elements,** *group number is equal to* **10 + number of electrons in the valence shell.**

(*c*) **For *d*-block elements,** *group number is equal to the number of electrons in* **(n – 1) d-subshell + number of electrons in valence shell (nth shell).**

PROBLEMS ON PREDICTING PERIOD, GROUP AND BLOCK OF ELEMENTS

EXAMPLE 4.1. *(a) Write the electronic configurations of the elements given below :*

A (At. No. = 9), B (At. No. = 12), C (At. No. = 29), D (At. No. = 54), and E (At. No. = 58).

(b) Also predict the period, group number and block to which they belong.

(c) Classify them as representative elements, noble gases, transition and inner transition elements.

Solution. (*a*) Electronic configuration of the elements A, B, C, D and E are as follows :

Element	At. No.	Electronic configuration
A	9	$1s^2\ 2s^2\ 2p^5$
B	12	$1s^2\ 2s^2\ 2p^6\ 3s^2$
C	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
D	54	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$
E	58	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 6s^2\ 5d^1\ 4f^1$

(*b*) **Element A** receives the last electron in 2*p*-orbital, therefore, it belongs to **p-block elements** and its **group number** = 10 + No. of electrons in the valence shell = 10 + 7 = 17. Further the **period of the element** = No. of the principal quantum number of the valence shell = **2nd.**

Element B receives the last electron in 3*s*-orbital, therefore, it belongs to **s-block elements** and its **group number** = No. of electrons in the valence shell = 2. Further the **period of the element** = No. of the principal quantum number of the valence shell = **3rd**

Element C receives the last electron in the 3*d*-orbital, therefore, it belongs to **d-block elements** and its **group number** = No. of electrons in the penultimate shell and valence shell = 10 + 1 = 11. Further, the **period of the element** = No. of principal quantum number of the valence shell = **4th.**

Element D receives its last electron in the 5*p*-orbital, therefore, it belongs to **p-block elements** and its **group number** = 10 + No. of electrons in the valence shell = 10 + 8 = 18. Further, the **period of the element** = No. of the principal quantum number of the valence shell = **5th.**

Element E receives its last electron in the 4*f*-orbital, therefore, it belongs to **f-block elements.** It may be noted here that the filling of 4f-orbital occurs only when one electron has already entered 5d-orbital. Therefore, element E belongs to **f-block elements** and not to **d-block elements.** Since it belongs to *lanthanide* series therefore as such it does not have any group number. However, its **period** = No. of the principal quantum number of the valence shell = **6th.**

(*c*) **Elements A and B** are *representative elements* since their last electron entres *p*- and *s*-orbital respectively.

Element C is a *transition element* since it receives its last electron in the *d*-orbital.

Element D is a *p-block element* with completely filled *s*- and *p*-orbitals of the valence shell. Such a type of *p*-block element is called a **noble gas.**

Element E is an *inner transition element* since it receives its last electron in the *f-orbital.*

EXAMPLE 4.2. *The electronic configuration of some elements are given below :*

(*i*) $1s^2\,2s^2\,2p^4$ (*ii*) $1s^2\,2s^2\,2p^6\,3s^1$

(*iii*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$

(*iv*) $1s^2\,2s^2\,2p^6$

(*v*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$

(*vi*) $1s^2\,2s^2\,2p^3$

(*vii*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^5$

(*viii*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^5$

Name these elements and indicate which of them is (a) an alkali metal, (b) an alkaline earth metal, (c) a halogen (d) a noble gas (e) belongs to group 15 (f) belong to second period (g) has lowest chemical reactivity (h) belongs to p-block elements and (i) is a transition element.

Solution. *Names of the elments* :

(*i*) Oxygen (*ii*) sodium (*iii*) calcium (*iv*) neon (*v*) silicon (*vi*) nitrogen (*vii*) managanese and (*viii*) chlorine.

(*a*) (*ii*) *i.e.* sodium is an alkali metal

(*b*) (*iii*) *i.e.* calcium is an alkaline earth metal

(*c*) (*viii*) *i.e.* chlorine is a halogen

(*d*) (*iv*) *i.e.* neon is a noble gas

(*e*) (*vi*) *i.e.* nitrogen belongs to group 15

(*f*) (*i*) *i.e.* oxygen, (*iv*) i.e. neon and (*vi*) *i.e.* nitrogen belong to 2nd period

(*g*) (*iv*) i.e. neon being a noble gas has lowest reactivity

(*h*) (*i*) *i.e.* oxygen, (*iv*) i.e. neon, (*v*) i.e. silicon and (*vi*) i.e.nitrogen are *p*-block elements and

(*i*) Manganese *i.e.* (*vii*) is a transition element.

EXAMPLE 4.3. *Predict the position of the element in the periodic table satisfying the electronic configuration,* $(n-1)\,d^1\,ns^2$ *for* $n = 4$. **(N.C.E.R.T)**

Solution. For $n = 4$, the electronic configuration = $(4-1)\,d^1\,4s^2 = 3d^1\,4s^2$. The element corresponding to this configuration is *scandium which is a d- block element.*

Group number = No. of electrons in $(n-1)$ *d* subshell + No. of electrons in the *n*th shell
$= 1 + 2 = 3$

EXAMPLE 4.4. *Elements A, B, C, D and E have the following electronic configurations.*

$A : 1s^2\,2s^2\,2p^1$

$B : 1s^2\,2s^2\,2p^6\,3s^2\,3p^1$

$C : 1s^2\,2s^2\,2p^6\,3s^2\,3p^3$

$D : 1s^2\,2s^2\,2p^6\,3s^2\,3p^5$

$E : 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$

Which among these will belong to the same group in the periodic table ? **(N.C.E.R.T)**

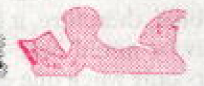
Solution. We know that elements having similar valence electronic configuration belong to the same group of the periodic table. Therefore, elements A and B having three electrons in the valence shell, *i.e.*, $2s^2\,2p^1$ and $3s^2\,3p^1$ respectively belong to the same group, *i.e.*, group 13 of the periodic table.

EXAMPLE 4.5. ***The elements Z = 117 and Z = 120 have not yet been discovered. In what family or group would you place these elements and also give the electronic configuration in each case.*** **(N.C.E.R.T.)**

Solution. In the long form of the periodic table, each period ends with a noble gas. Therefore, the element with Z = 118 will be the noble gas with the configuration $[\text{Rn}]\,4f^{14}\,5d^{10}\,7s^2\,7p^6$ and will lie in group 18 of the periodic table. If this is so, then the element with Z = 117 will belong to the halogen family (group 17) and its electronic configuration would be $[\text{Rn}]\,4f^{14}\,5d^{10}\,7s^2\,7p^5$.

Working on similar lines, the element with Z = 120 will belong to the family of alkaline earth metals (group 2) and its electronic configuration would be $[\text{Rn}]\,4f^{14}\,5d^{10}\,7s^2\,7p^6\,8s^2$ *or* $[\textit{Uuo}]\,8s^2$ since the symbol for the element with Z = 118 is Uuo.

PROBLEMS FOR PRACTICE



1. Write the names and atomic numbers of the following elements :
   - (*i*) The fourth alkali metal
   - (*ii*) The third alkaline earth metal
   - (*iii*) The fifth element of the first transition series
   - (*iv*) The first inner transition element and
   - (*v*) The sixth noble gas.
2. The outer electronic configuration of some elements are given below :
   - (*i*) $3s^2\ 3p^3$ (*ii*) $3d^5\ 4s^1$ (*iii*) $3s^2\ 3p^6\ 4s^2$
   - (*iv*) $5d^1\ 6s^2$ (*v*) $4f^1\ 5d^1\ 6s^1$

   State to which block of the periodic table each of these elements belongs.
3. An element 'X' with atomic number 112 has recently been discovered. Predict its electronic configuration and suggest the group in which this element would be placed.
4. Arrange the following elements in the increasing order of metallic character : B, Al, Mg, K. *(N.C.E.R.T)*
5. Write the electronic configuration and the block to which an element with Z = 90 belongs.
6. How do the electronic configurations of the elements with Z = 107 — 109 differ from one another ?

ANSWERS

1. (*i*) Rb (Z = 37), (*ii*) Ca (Z = 20), (*iii*) Mn (Z = 25) (*iv*) Ce (Z = 58), (*v*) Rn (Z = 86).
2. (*i*) *p*, (*ii*) *d*, (*iii*) *s*, (*iv*) *d*, (*v*) *f*
3. [Rn] $5f^{14}\ 6d^{10}\ 7s^2$, 12th group.
4. B < Al < Mg < K
5. [Rn] $6d^2\ 7s^2$, *f*-block elements.
6. Element with Z = 107 has five, Z = 108 has six while Z = 109 has seven 5 *f*-electrons.

   Thus these elements differ in the number of electrons in the 5 *f*-subshell.

SECTION—II

ATOMIC OR PERIODIC PROPERTIES OF ELEMENTS

The various properties of elements may be divided into the following two categories :

(*i*) **Properties of the individual atoms.** Properties like valency, atomic and ionic radii, ionization enthalpy, electron gain enthalpy and electronegativity are the properties of the individual atoms and are directly related to their electronic configurations.

(*ii*) **Properties of the group of atoms.** Properties like melting point, boiling point, density, atomic volume etc. are the bulk properties, *i.e.*, the properties of a collection or a group of atoms and are only indirectly related to their electronic configurations.

All these properties which are directly or indirectly related to the atomic structure or the electronic configuration of the elements are called **atomic properties.** Since the electronic configurations of the elements are a periodic function of their atomic numbers, (*i.e.*, get repeated after certain regular intervals) therefore, these atomic properties are also a periodic function of atomic numbers of the elements. That is why atomic properties are also called *periodic properties*. Here, the word periodic means that with the rise in the atomic number of the elements in the same period or group, there is a regular gradiation (*i.e.* increase or decrease) in a particular property of the element. Thus,

The properties which are directly or indirectly related to their electronic configuration and which show a regular gradation when we move from left to right in a period or from top to bottom in a group are called **periodic properties.**

In this section, we shall discuss the periodic trends in three physical properties of the elements such as ionization enthalpy, electron gain enthalpy and atomic size and one important chemical property, *viz.*, valence.

4.14. Ionization Enthalpy

4.14.1. Definition. If energy is supplied to an atom, electrons get promoted to the higher energy levels. If sufficient energy is supplied, electron may be removed resulting in the formation of a positively charged ion.

The minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom so as to convert it into a gaseous cation is called its ionization enthalpy or energy.

This process may be represented as

$$M(g) + \text{energy} \longrightarrow M^+(g) + e^-(g)$$

where $M(g)$ and $M^+(g)$ represent the gaseous atom and the resultant gaseous cation (a positive ion).

Ionization enthalpy is also known as ionization potential since it is the minimum potential difference (in a discharge tube) required to remove the most loosely bound electron from an isolated gaseous atom to form gaseous cation.

4.14.2. Units of I.E./I.P. It is measured in units of electron volts (eV) per atom or kilo calories per mole (kcal mol^{-1}) or kilo Joules per mole (kJ mol^{-1}). *One electron volt is the energy acquired by an electron while moving under a potential difference of one volt.*

1 electron volt (eV) per atom

$= 3.83 \times 10^{-20}$ cal per atom

$= 1.602 \times 10^{-19}$ J per atom (1 cal = 4.184 J)

$= 3.83 \times 10^{-20} \times 6.023 \times 10^{23}$ cal mol^{-1}

$= 23.06$ kcal mol^{-1}

$= 1.60 \times 10^{-19} \times 6.023 \times 10^{23}$ J mol^{-1}

$= 96.49$ kJ mol^{-1}

$\therefore$ 1 electron volt (eV) per atom

$= 23.06$ kcal mol^{-1}

$= 96.49$ kJ mol^{-1}

For example, when hydrogen gas under low pressure is taken in the discharge tube, a sudden very large increase in current flow occurs when the voltage is 13.58 volts. Thus, ionization potential of hydrogen is 13.58 electron volts. Therefore, the ionization enthalpy of hydrogen atom is 13.58 eV or $13.58 \times 96.49 = 1310.334$ kJ mol^{-1}

4.14.3. Successive Ionization Enthalpies. The energy required to remove the most loosely bound electron from the isolated gaseous atom is called its first ionization enthalpy and is denoted by IE_1

$$M(g) + IE_1 \longrightarrow M^+(g) + e^-(g)$$

Similarly, the energies required to knock out second and third electrons are called second and third ionization energies respectively *e.g.*

$$M^+(g) + IE_2 \longrightarrow M^{2+}(g) + e^-(g)$$

$$M^{2+}(g) + IE_3 \longrightarrow M^{3+}(g) + e^-(g)$$

where IE_2 and IE_3 are the second and the third ionizaton enthalpies respectively.

The ionization enthalpies required to remove first, second, third etc. electrons from an isolated gaseous atom are called sucessive ionization enthalpies.

The successive ionisation energies of some elements (in kJ mol^{-1}) are given in Table 4.7.

TABLE 4.7. Successive ionization enthalpies of some of elements (kJ mol^{-1})

Element	Electronic configuration	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7	IE_8
H	$1s^1$	1312	—	—	—	—	—	—	—
He	$1s^2$	2372	5250	—	—	—	—	—	—
Li	$1s^2 2s^1$	520	7297	11810	—	—	—	—	—
Be	$1s^2 2s^2$	899	1757	14850	21000	—	—	—	—
B	$1s^2 2s^2 2p^1$	801	2427	3638	25024	32824	—	—	—
C	$1s^2 2s^2 2p^2$	1086	2352	4619	6220	37820	47280	—	—
N	$1s^2 2s^2 2p^3$	1402	2858	4576	7473	9443	53255	64328	—
O	$1s^2 2s^2 2p^4$	1314	3388	5296	7468	10987	13323	15160	84054
F	$1s^2 2s^2 2p^5$	1681	3375	6045	8408	11020	15160	17864	92012
Ne	$1s^2 2s^2 2p^6$	2080	3962	6226	9361	12186	15236	—	—

It may be seen that, IE_2 is always greater than IE_1 and IE_3 is always greater than IE_2, and so on

i.e., $IE_3 > IE_2 > IE_1$

Explanation. This may be explained as follows:

When one electron has been removed from the neutral gaseous atom, the +vely charged ion formed has one electron less than the number of protons in the nucleus. As a result, the electrostatic attraction between the nucleus and the remaining electrons in the cation increases, *i.e.*, effective nuclear charge increases. In other words, the +ve ion holds its remaining electrons more firmly. Therefore, the energy required to remove another electron from this +vely charged ion or second electron from the neutral atom must be higher than the first, *i.e.*, IE_2 must be higher than IE_1.

Further the removal of two electrons from the neutral atom gives a doubly +vely charged ion which will hold its remaining electrons even more tightly. As a result, the energy required to remove third electron from the gaseous atom should be even more than that required for the second electron, *i.e.*, IE_3 must be greater than IE_2. Thus, $IE_3 > IE_2 > IE_1$.

For example,

$$\underset{1s^2\,2s^2\,2p^6\,3s^2\,3p^1}{\mathrm{Al}\,(g)} \quad - e^- \quad \longrightarrow \quad \underset{1s^2\,2s^2\,2p^6\,3s^2}{\mathrm{Al}^+\,(g)}\ ;$$

$$IE_1 = 579 \text{ kJ mol}^{-1}$$

$$\underset{1s^2\,2s^2\,2p^6\,3s^2}{\mathrm{Al}^+\,(g)} \quad - e^- \quad \longrightarrow \quad \underset{1s^2\,2s^2\,2p^6\,3s^1}{\mathrm{Al}^{2+}\,(g)}\ ;$$

$$IE_2 = 1795 \text{ kJ mol}^{-1}$$

$$\underset{1s^2\,2s^2\,2p^6\,3s^1}{\mathrm{Al}^{2+}\,(g)} \quad - e^- \quad \longrightarrow \quad \underset{1s^2\,2s^2\,2p^6}{\mathrm{Al}^{3+}\,(g)}\ ;$$

$$IE_3 = 2758 \text{ kJ mol}^{-1}$$

ADD TO YOUR KNOWLEDGE

The relative stabilities of various oxidation states of an element can be easily predicted on the basis of their successive ionization enthalpies. *If the difference in ionization enthalpies of two successive states is approx. equal to 10—15 eV per atom (or 965—1450 kJ mol^{-1}) or less, the lower oxidation state is not stable. Conversely, if the difference is more than 15 eV, the lower oxidation state is more stable.* For example, in case of Al, $IE_1 = 579$ kJ mol^{-1}, $IE_2 = 1795$ kJ mol^{-1}, $IE_3 = 2758$ kJ mol^{-1} and $IE_4 = 11580$ kJ mol^{-1}.

Difference in successive ionization enthalpies.

$$IE_2 - IE_1 = 1795 - 579 = 1216 \text{ kJ mol}^{-1} \ ; \quad IE_3 - IE_2 = 2758 - 1795 = 963 \text{ kJ mol}^{-1}$$

$$IE_4 - IE_3 = 11580 - 2758 = 8822 \text{ kJ mol}^{-1}$$

Since the difference in successive ionization energies between $IE_2 - IE_1$ and $IE_3 - IE_2$ is less than 1450 kJ mol^{-1} and that of $IE_4 - IE_3$ is much more than 1450 kJ mol^{-1}, therefore, *+ 3 oxidation state of Al is the most stable.*

PROBLEMS ON THE CALCULATION OF IONIZATION ENTHALPIES

EXAMPLE 4.6. *Calculate the energy required to convert all the atoms of magnesium to magnesium ions present in 24 mg of magnesium vapours ? First and second ionization enthalpies of Mg are 737·76 and 1450.73 kJ mol^{-1} respectively.*

Solution. According to the definition of successive ionizaton energies.

$$\mathrm{Mg}\,(g) + IE_1 \longrightarrow \mathrm{Mg}^+\,(g) + e^-\,(g)\ ; \qquad IE_1 = 737{\cdot}76 \text{ kJ mol}^{-1}$$

$$\mathrm{Mg}^+\,(g) + IE_2 \longrightarrow \mathrm{Mg}^{2+}\,(g) + e^-\,(g)\ ; \qquad IE_2 = 1450{\cdot}73 \text{ kJ mol}^{-1}$$

∴ Total amount of energy needed to convert Mg (*g*) atom into $\mathrm{Mg}^{2+}(g)$ ion $= IE_1 + IE_2$

$$= 737{\cdot}76 + 1450{\cdot}73 \text{ kJ mol}^{-1}$$

$$= 2188{\cdot}49 \text{ kJ mol}^{-1}$$

$$24 \text{ mg of Mg} = \frac{24}{1000}\text{ g} = \frac{24}{1000 \times 24}\text{ mole}$$

$$= 10^{-3} \text{ mole}$$

∴ Amount of energy needed to ionize 10^{-3} mole of Mg vapours $= 2188{\cdot}49 \times 10^{-3}$

$$= \mathbf{2{\cdot}188 \text{ kJ.}}$$

PROBLEMS FOR PRACTICE

1. Calculate the energy in joules required to convert all the atoms of sodium to sodium ions present in 2·3 mg of sodium vapours ? Ionization enthalpy of sodium is 495 kJ mol^{-1} (Atomic mass of Na = 23). [Ans. 49.5 J]
2. The ionization potential of hydrogen is 13·60 eV. Calculate the energy in kJ required to produce 0·1 mole of H$^+$ ions. Given, 1 eV = 96·49 kJ mol^{-1}) [Ans. 131·226 kJ]
3. The first and second ionization potentials of helium atoms are 24·58 eV and 54·4 eV respectively. Calculate the energy in kJ required to produce 1 mole of He^{2+} ions. [Ans. 7620·780 kJ]
4. The IE$_1$ and IE$_2$ of Mg (g) are 740 and 1450 kJ mol^{-1}. Calculate the percentage of Mg$^+$ (g) and Mg^{2+} (g) if 1 g of Mg (g) absorbs 50 kJ of energy. [Ans. Mg$^+$ (g) = 68·35% and Mg$^+$ (g) = 31·65%]

HINTS FOR DIFFICULT PROBLEMS

1. No. of moles of Na present is 2·3 mg of Na

$$= \frac{23}{10} \times \frac{1}{1000} \times \frac{1}{23} = 1 \times 10^{-4} \text{ mole}$$

$\therefore$ Required energy $= 1 \times 10^{-4} \times 495 \times 10^3$
$= 49 \cdot 5$ J

2. Required energy $= 0 \cdot 1 \times 13 \cdot 60 \times 96 \cdot 49$
$= 131 \cdot 226$ kJ

3. Required energy $= 1 \times (24 \cdot 58 + 54 \cdot 4) \times 96 \cdot 49$
$= 7620 \cdot 780$ kJ.

4. No. of moles of Mg vapours present in 1 g = 1/24 = 0·0417

Energy absorbed in the ionization of 0·0417 mole of Mg (g) to Mg$^+$ (g)

$= 0 \cdot 0417 \times 740 = 30 \cdot 83$ kJ

Energy left unused = 50—30·83 = 19·17 kJ

Now 19·17 kJ will be used to ionize Mg$^+$ (g) to Mg^{2+} (g)

$\therefore$ No. of moles of Mg$^+$ (g) converted into Mg^{2+} (g) = 19·17/1450 = 0·0132

No. of moles of magnesium ions left as Mg$^+$ (g)

$= 0 \cdot 0417 — 0 \cdot 0132 = 0 \cdot 0285$

$\therefore$ %age of Mg$^+$ (g) $= (0 \cdot 0285 / 0 \cdot 0417) \times 100$
$= 68 \cdot 35\%$

and % age of Mg^{2+} (g) $= 100 - 68 \cdot 35 = 31 \cdot 65\%$.

4.14.4. Factors Governing the Ionization Enthalpy. Ionization enthalpy depends upon the following factors :

(a) Nuclear charge
(b) Atomic size
(c) Penetration effect of the electrons
(d) Screening effect of inner electrons.
(e) Effect of arrangement of electrons, i.e. Effect of exactly half filled or completely filled orbitals.

(a) Nuclear charge. *The ionization enthalpy increases with increase in nuclear charge.* This is due to the fact that with increase in nuclear charge, the electrons of the outer shell are more firmly held by the nucleus and thus greater energy is required to pull out an electron from the atom. For example, the ionization energy increases as we move along a period from left to right due to increased nuclear charge as is evident from Table 4.8.

TABLE 4.8. First ionization enthalpies of 2nd row elements in kJ mol^{-1}

Element	Li	Be	B	C	N	O	F	Ne
Nuclear charge	+3	+4	+5	+6	+7	+8	+9	+10
Ionization enthalpy (kJ mol^{-1})	520	899	801	1086	1402	1314	1681	2080

(b) Atomic size or Radius. *Ionization energy decreases as the atomic size increases.* As the distance of the outer electrons from the nucleus increases with increase in atomic radius, the attractive force on the outer electrons decreases. As a result, outer electrons are held less firmly and hence lesser amount of energy is required to knock them out. Thus, ionization enthalpy decreases with increase in atomic size.

For example, ionization enthalpy is found to decrease on moving down a group as is evident from Table 4.9.

TABLE 4.9. First ionization enthalpies of alkali metals in kJ mol^{-1}

Element	Li	Na	K	Rb	Cs
Ionization enthalpy (kJ mol^{-1})	520	496	419	403	374

(c) Penetration effect of the electrons. *Ionization enthalpy increases as the penetration effect of the electrons increases.* It is a well known fact that in case of multi- electron atoms, the electrons of the *s*-orbital has the maximum probability of being found near the nucleus and this probability goes on decreasing in case of *p, d* and *f*- orbitals of the same shell. In other words, *s*-electrons of any shell are more penetrating towards the nucleus than *p*-electrons of the same shell. Thus, within the same shell, the penetration effect decreases in the order :

$$s > p > d > f$$

Obviously, if the penetration effect of the electron is more, it will be closer to the nucleus and hence will be held more firmly by the nucleus. Consequently, the ionization enthalpy will be high. In other words, ionization enthalpy increases with the increase in the penetration effect of electrons. Thus, *the ionization enthalpy will be more to knock out a s-electron than p-electron of the same shell, which in turn, will be more than that required to remove a d-electron and so on.*

For example, *first ionization enthalpy of aluminium is lower than that of magnesium.* This is due to the fact that in case of aluminium ($1s^2\ 2s^2\ 3s^2\ 3p_x^1$), we have to pull out a *p*-electron to form Al^+ ion whereas in case of magnesium ($1s^2\ 2s^2\ 2p^6\ 3s^2$) we have to remove an *s*-electron of the same energy shell to produce Mg^+ ion. Since the energy required to remove a *p*-electron is lower than that required to knock out a *s*-electron of the same energy shell, therefore, the first ionization enthalpy of aluminium is lower than that of magnesium. Similarly, the first ionization enthalpy of B is lower than that of Be.

(d) Shielding or Screening effect of the inner shell electrons. *As the shielding or the screening effect of the inner electrons increases, the ionization enthalpy decreases.*

In multi-electron atoms, the electrons in the valence shell experience an attractive force from the nucleus and a repulsive force from the electrons in the inner shells. The overall effect of these two opposing forces is that the attractive force exerted by the nucleus on the valence shell electrons is somewhat reduced by the repulsive force exerted by the electrons present in the inner shells. In other words, the valence shell electrons do not feel the full charge of the nucleus. *The actual charge felt by the valence shell electrons is called* **effective nuclear charge** and the repulsive force felt by the valence shell electrons from the electrons present in the inner shells is called the **shielding effect or screening effect.** Therefore, the effective nuclear charge (Z_{eff}) is given by the relation

Z_{eff} = Total nuclear charge (Z) − Screening constant (σ).

where screening constant (σ)* takes into account the screening effect of the electrons present in the inner shells. Obviously greater the number of electrons in the inner shells, larger will be the screening effect. As the screening effect increases, the effective nuclear charge decreases. Consequently, the force of attraction by the nucleus for the valence shell electrons decreases and hence the ionization enthalpy decreases. In other words, *an increase in the number of electrons in the inner shells tends to decrease the ionization enthalpy.*

(e) Electronic configuration i.e. Effect of exactly half-filled or completely filled orbitals. *If an atom contains exactly half-filled or completely filled orbitals, then such an arrangement has extra stability. Therefore, the removal of an electron from such an atom requires more energy than expected, e.g.,*

---

*The screening constant (σ) is calculated by the application of *Slater rules.*

(*i*) Be ($1s^2\,2s^2$) has higher ionization enthalpy than B ($1s^2\,2s^2\,2p^1$). This is because Be has fully filled orbitals which is a stable electronic arrangement. Similarly, Mg ($1s^2\,2s^2\,2p^6\,3s^2$) has higher ionization enthalpy than aluminium ($1s^2\,2s^2\,2p^6\,3s^2\,3p_x^1$).

(*ii*) N($1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$) has higher ionization enthalpy than oxygen ($1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$). This is because N contains exactly half filled p-orbitals. Such an arrangement gives extra stability to the atom. As a result, the removal of electron becomes difficult and hence the ionization enthalpy is high. For similar reasons, ionization enthalpy of P ($1s^2\,2s^2\,2p^6\,3s^2\,3p_x^1\,3p_y^1\,3p_z^1$) is higher than that of S ($1s^2\,2s^2\,2p^6\,3s^2\,3p_x^2\,3p_y^1\,3p_z^1$).

(*iii*) Noble gases have the highest ionization enthalpy in their respective periods. For example, ionization enthalpy of Ne is more than any other element of the second period. So is the case with Ar. This is due to the fact that $ns^2\,np^6$ arrangement which occurs in noble gases is highly stable and hence larger amount of energy is needed to remove an electron from this stable arrangement.

From the above discussion it follows that *more stable the electronic configuration, greater is the ionization enthalpy.*

4.14.5. Variation of Ionization Enthalpy in the Periodic Table. The first ionization enthalpies of the representative elements and noble gases are given in the Table 4.10.

It can be readily noticed that the ionization enthalpy of an element strongly depends upon its electronic configuration and thus shows periodic variation. In each period, the minima are found at the alkali metals and the maxima are found at the noble gases. Thus, alkali metals with one electron in the outermost *s*-orbital have lowest ionization enthalpies and hence are highly reactive. In contrast, noble gases with stable $ns^2\,np^6$ configuration have highest ionization enthalpies and hence are chemically inert. Similar trends are observed for each period as may be seen from the a graph plotted between the first ionization enthalpies along Y-axis and atomic number along X-axis for the first 60 elements (Fig. 4.2). It may be noted that Cs has the lowest first ionization enthalpy. **Hence Cs is the most electropositive element.**

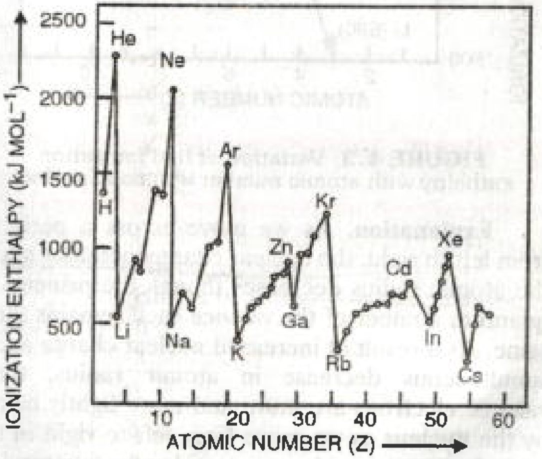


FIGURE 4.2. Variation of first ionization enthalpies of elements with atomic numbers 1 to 60.

(a) Variation along a period. *In general, as we move from left to right in a period, the ionization enthalpy increases with increasing atomic numbers.* This is evident from the values of the first ionization enthalpies of the elements of second period as given in Table 4.8 or 4.10 and Fig. 4.3. *The observed trends can be easily explained on the basis of increased nuclear charge and smaller atomic radii.*

TABLE 4.10. First ionization enthalpies of some elements (kJ mol⁻¹)

H 1312							He 2372
Li 520	Be 899	B 801	C 1086	N 1402	O 1314	F 1681	Ne 2080
Na 496	Mg 737·6	Al 577	Si 786	P 1011	S 999	Cl 1255	Ar 1520
K 419	Ca 590	Ga 579	Ge 760	As 946	Se 941	Br 1142	Kr 1350
Rb 403	Sr 549	In 558	Sn 708	Sb 884	Te 869	I 1009	Xe 1170
Cs 374	Ba 502	Tl 589	Pb 715	Bi 703	Po 813	At 917	Rn 1037

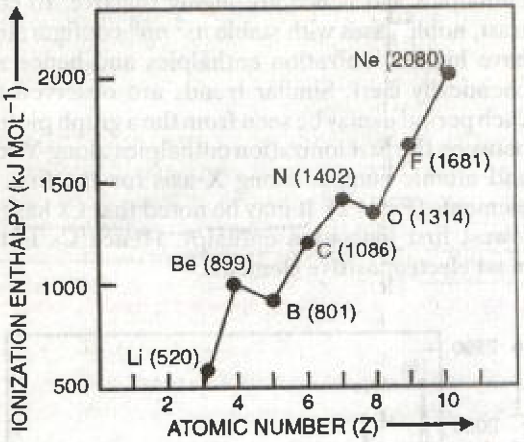


FIGURE 4.3. Variation of first ionization enthalpy with atomic number in second period.

Explanation. As we move across a period from left to right, the nuclear charge increases and the atomic radius decreases though the principal quantum number of the valence shell remains the same. As a result of increased nuclear charge and simultaneous decrease in atomic radius, the valence electrons are more and more tightly held by the nucleus as we move from left to right in a period. Consequently, more and more energy is needed to remove the electron and hence ionization enthalpies keep on increasing. However, some elements show irregularities in this general trend. *These are due to (i) type of electron to be removed and (ii) the extra-stability of the exactly half-filled and completely filled electronic configurations.* To illustrate this, let us consider the first ionization enthalpies of the elements of the second period.

Li to Be. As we move from Li to Be, the ionization enthalpy increases due to increased nuclear charge and smaller atomic radius of Be as compared to that of Li.

Be to B. Although the nuclear charge of B is more than that of Be, yet *the ionization enthalpy of B is lower than that of Be*. This is due to the following reasons.

(*i*) The outermost electron in B is present in 2*p*- orbital while in Be it is present in 2*s*-orbital. Since 2*s*-electrons are more penetrating towards the nucleus than 2*p*-electrons, therefore, lesser amount of energy is required to knock out a 2*p*-electron than a 2*s*- electron. Consequently, the first ionisation enthalpy of B is lower than that of Be.

(*ii*) The electronic configuration of B ($1s^2\,2s^2\,2p^1$) is less stable than that of Be ($1s^2\,2s^2$) which has completely filled orbitals. As a result, 2*p*-electron of B is not as strongly attracted by the nucleus as the 2*s*-electron of Be. Consequently, the first ionization enthalpy of B is lower than that of Be.

B to C to N. As we move from B to C to N, the first ionization enthalpy of these elements keeps on increasing due to progresssively increasing nuclear charge and decreasing atomic radius.

N to O. *The first ionization enthalpy of oxygen is lower than that of N although the nuclear charge of O is higher than that of nitrogen.* This is due to the following reasons :

(*i*) The electronic configuration of N ($1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$) in which the 2*p*-orbitals are exactly half-filled is more stable than the electronic configuration of O ($1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$) in which the 2*p*-orbitals are neither half-filled nor completely filled. Therefore, it is difficult to remove an electron from N than from O. As a result, the first ionization enthalpy of N is higher than that of O.

(*ii*) The removal of an electron from O gives a stable electronic configuration with exactly half-filled 2*p*- subshell, *i.e.*, O^+ ($1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$) while this is not so in case of N, *i.e.* N^+ ($1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_x^0$). Since the removal of an electron from O gives a more stable electronic configuration than that obtainable from N, therefore, the first ionization enthalpy of O is lower than that of N.

O to F to Ne. The first ionization enthalpy increases from O to F to Ne because of the increasing nuclear charge. Neon, the noble gas, however, has the highest first ionization enthalpy amongst the elements of the 2nd period because of its stable ($ns^2\,np^6$) electronic configuration.

Similar variations in the first ionization enthalpies of the elements of the third period have been observed.

(b) Variation down a group. *The ionization enthalpies keep on decreasing regularly as we move down a group from one element to the other.* This is evident from the values of the first ionization enthalpies of the elements of group 1 (alkali metals) as given in Table 4.9 and Fig. 4.4.

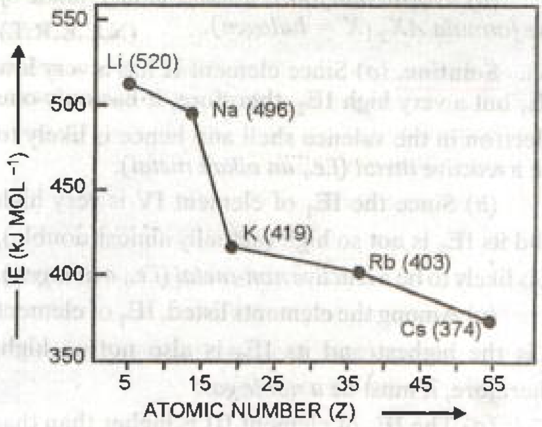


FIGURE 4.4. The variation of first ionization enthalpies with atomic number in group I (alkali metals) of the periodic table.

Explanation. The above *trend can be easily explained on the basis of increasing atomic size and screening effect as follows :*

(*i*) *On moving down the group, the atomic size increases* gradually due to the addition of one new principal energy shell at each succeeding element. As a result, the distance of the valence electrons from the nucleus increases. Consequently, the force of attraction by the nucleus for the valence electrons decreases and hence the *ionization enthalpy should decrease.*

(*ii*) With the addition of new shells, the number of inner electron shells which shield the valence electrons from the nucleus increases. In other words, *the shielding or the screening effect increases*. As a result, the force of attraction of the nucleus for the valence electrons further decreases and hence the *ionization enthalpy should decrease.*

(*iii*) *Nuclear charge increases* with increase in atomic number. As a result, the force of attraction by the nucleus for the valence electrons should increase and accordingly the *ionization enthalpy should increase.*

The combined effect of the increase in the atomic size and the screening effect more than compensates the effect of the increased nuclear charge. Consequently, the valence electrons become less and less firmly held by the nucleus and hence the ionization enthalpies gradually decrease as we move down the group.

PROBLEMS ON PREDICTING RELATIVE IONIZATION ENTHALPIES

EXAMPLE 4.7. *The electronic configuration for the following neutral atoms are given for use in question.*

(*a*) $1s^2, 2s^2, 2p^6, 3s^2$; (*b*) $1s^2, 2s^2, 2p^6, 3s^1$;
(*c*) $1s^2, 2s^2, 2p^4$; (*d*) $1s^2, 2s^2, 2p^5$;
(*e*) $1s^2, 2s^2, 2p^6$.

(i) Which of the electronic configuration given above would you expect for the noble gas ?

(ii) Which of the electronic configurations given above would you expect to have the lowest ionization enthalpy.

(iii) List the above configurations in order of increasing ionization enthalpy.

Solution. (*i*) Arrange the electronic configuration of all the atoms in order of increasing atomic number in such a way that atoms containing the same outer energy shell are grouped together. Thus, we have

$1s^2\,2s^2\,2p^4$ (*c*)	$1s^2\,2s^2\,2p^5$ (*d*)	$1s^2\,2s^2\,2p^6$ (*e*)	**...L-shell**
$1s^2\,2s^2\,2p^6\,3s^2$ (*a*)	$1s^2\,2s^2\,2p^6\,3s^1$ (*b*)		**...M-shell**

Since the M-shell is more distant from the nucleus than L-shell, so lesser amount of energy is required to remove an electron from M-shell than from the L-shell. In other words, ionization enthalpy (IE) of atoms (*a*) and (*b*) should be lower than that of atoms (*c*), (*d*) and (*e*).

Further, in case of atom (*a*), the electron is to be removed from the more stable completely filled 3*s*-orbital whereas in case of atom (*b*) it is not so. Therefore, the IE of atom (*b*) should be lower than that of atom (*a*).

The nuclear charge on atoms (*c*), (*d*) and (*e*) is +8, +9 and +10 respectively. Since the IE increases with increase in nuclear charge so the IEs of atoms (*c*), (*d*) and (*e*) follow the sequence : $c < d < e$.

From the above discussion, we conclude that the ionization enthalpies of the five atoms increase in the following order :

$$b < a < c < d < e$$

i.e.,
$$1s^2\,2s^2\,2p^6\,3s^1 < 1s^2\,2s^2\,2p^6\,3s^2 < 1s^2\,2s^2\,2p^4 < 1s^2\,2s^2\,2p^5 < 1s^2\,2s^2\,2p^6$$

(*ii*) Evidently, atom (*b*) with electronic configuration, $1s^2\,2s^2\,2p^6\,3s^1$ has the lowest ionization enthalpy.

(*iii*) Since the outer electronic configuration of noble gases is $ns^2\,np^6$, therefore, the electronic configuration, $1s^2\,2s^2\,2p^6$ [atom (*e*)] represents an noble gas.

EXAMPLE 4.8. *The first (IE_1) and the second (IE_2) ionization enthalpies (kJ mol^{-1}) of a few elements designated by Roman numerals are shown below :*

Element	IE_1	IE_2
I	*2372*	*5251*
II	*520*	*7300*
III	*900*	*1760*
IV	*1680*	*3380*

Which of the above elements is likely to be

(a) a reactive metal (b) a reactive non-metal

(c) a noble gas

(d) a metal that forms a stable binary halide of the formula AX_2 (X = halogen). (N.C.E.R.T.)

Solution. (*a*) Since element II has a very low IE_1 but a very high IE_2, therefore, it has only one electron in the valence shell and hence is likely to be a *reactive metal (i.e., an alkali metal)*.

(*b*) Since the IE_1 of element IV is very high and its IE_2 is not so high (actually almost double), it is likely to be a *reactive non-metal (i.e., a halogen)*.

(*c*) Among the elements listed, IE_1 of element I is the highest and its IE_2 is also not so high, therefore, it must be *a noble gas*.

(*d*) The IE_1 of element III is higher than that of element II, but unlike element II, its IE_2 is only about twice its IE_1, therefore, it is likely that element III has two electrons in the valence shell (*i.e., alkaline earth metal*). As such it will form a stable binary halide of the formula AX_2 where A is the metal and X is the halogen.

PROBLEMS FOR PRACTICE

1. Arrange the following in the order of increasing ionization enthalpy :
(*i*) $1s^2\,2s^2\,2p^6\,3s^2$ (*ii*) $1s^2\,2s^2\,2p^6\,3s^1$
(*iii*) $1s^2\,2s^2\,2p^6$ (*iv*) $1s^2\,2s^2\,2p^2$
(*v*) $1s^2\,2s^2\,2p^3$
[Ans. (*ii*) < (*i*) < (*iv*) < (*v*) < (*iii*)]

2. The electronic configurations of some neutral atoms are given below :
(*i*) $1s^2\,2s^2$ (*ii*) $1s^2\,2s^2\,2p^1$
(*iii*) $1s^2\,2s^2\,2p^4$ (*iv*) $1s^2\,2s^2\,2p^3$.
Which of these electronic configuration would be expected to have the highest
(*a*) IE_1 (*b*) IE_2 (*c*) IE_3 (*d*) IE_4 ?
[Ans. **(*a*) (*iv*), (*b*) (*iii*), (*c*) (*i*), (*d*) (*ii*)]**

3. Among the elements Li, K, Ca, S and Kr, which one has the lowest first ionization enthalpy ? Which has the highest first ionization enthalpy ? (*N.C.E.R.T.*)
[Ans. **Lowest : K, Highest : Kr]**

4. Which of the following pairs of elements would you expect to have lower first ionization enthalpy ? Explain. (*i*) Cl or F (*ii*) Cl or S
(*iii*) K or Ar (*iv*) Kr or Xe. (*N.C.E.R.T.*)
[Ans. **(*i*) Cl (*ii*) S (*iii*) K (*iv*) Xe]**

5. For each of the following pairs, predict which one has lower first ionization enthalpy ?
(*i*) N or O (*ii*) Na or Na^+ (*iii*) Be^+ or Mg^{2+}
(*iv*) I or I^- [Ans. **(i) O, (ii) Na, (iii) Be^+ (iv) I]**

6. The first (IE_1) and the second (IE_2) ionization enthalpies (kJ mol^{-1}) of three elements I, II, III are given below :

	I	II	III
IE_1	403	549	1142
IE_2	2640	1060	2080

Identify the element which is likely to be (*a*) non-metal (*b*) an alkali metal (*c*) an alkaline earth metal.
(*N.C.E.R.T.*) [Ans. **(*a*) III (*b*) I (*c*) II]**

7. Predict which atom in each of the following pairs has the greater first ionization enthalpy and explain your answer.
(*a*) B and C (*b*) N and O (*c*) F and Ne
(*N.C.E.R.T.*) [Ans. **(*a*) C (*b*) N (*c*) Ne]**

8. From each set, choose the atom which has the largest ionization enthalpy and explain your answer.
(*a*) F, O, N (*b*) Mg, P, Ar (*c*) B, Al, Ga
(*N.C.E.R.T.*) [Ans. **(*a*) F (*b*) Ar (*c*) B]**

HINTS FOR DIFFICULT PROBLEMS

1. In a period, noble gas *i.e.* $1s^2 2s^2 2p^6$ (*iii*) has the highest IE_1. Out of C, $1s^2 2s^2 2p^2$ (*iv*) and N, $1s^2 2s^2 2p^3$ (*v*), N has higher IE_1 due to higher nuclear change and stable exactly half-filled electronic configuration. Because of bigger size both Mg, $1s^2 2s^2 2p^6 3s^2$ (*i*) and Na, $1s^2 2s^2 2p^6 3s^1$ (*ii*) have lower IE_1 than C, N, O. Out (*i*) and (*ii*), (*i*) has higher IE_1 due to higher nuclear charge and completely filled *s*-orbital. Thus, the overall order of increasing IE_1 is (*ii*) < (*i*) < (*iv*) < (*v*) < (*iii*).

2. (*a*)–(*iv*) has highest IE_1 due to stable exactly half-filled electronic configuration. (*b*)–(*iii*) has highest IE_2 since the second electron has to be removed from the stable exactly half filled electronic configuration left after removal of Ist electron, *i.e.*,

$$1s\ 2s^2 2p^4 \xrightarrow{IE_1} 1s^2 2s^2 2p^3 \xrightarrow{IE_2}$$

(*c*)–(*i*) has the highest IE_3 since the third electron has to be removed from the stable inert gas configuration, $1s^2 2s^2 \xrightarrow{IE_1} 1s^2 2s^1 \xrightarrow{IE_2} 1s^2 \xrightarrow{IE_3}$

(*d*)–(*ii*) has the highest IE_4 since the fourth electron has to removed from the stable inert gas configuration,

$$1s^2 2s^2 2p^1 \xrightarrow{IE_1} 1s^2 2s^2 \xrightarrow{IE_2} 1s^2 2s^1 \xrightarrow{IE_3} 1s^2 \xrightarrow{IE_4}.$$

3. Among the elements Li, K, Ca, S and Kr, the elements K, Ca and Kr belong to 4th period. Since in a period, alkali metal has the lowest and inert gas has the highest IE_1, therefore, K has the lowest IE_1 and Kr has the highest IE_1.

4. (*i*) Because of the bigger size and stronger shielding effect, Cl has lower IE_1 than F.

(*ii*) Among S and Cl, S has lower IE_1 due to bigger size and lower nuclear charge.

(*iii*) K has lower IE_1 than Ar because K has one more electron than Ar and hence can easily lose this electron to acquire stable Ar has configuration.

(*iv*) Xe because of its bigger size and stronger shielding effect has lower IE_1 than Kr.

5. (*i*) *O has lower IE_1 than N* because in case of O, loss of an electron gives O^+ which has stable exactly half-filled electronic configuration while in case of N, an electron has to be lost from a stable half-filled electronic configuration.

(*ii*) *Na has lower IE_1 than Na^+* because of the following two reasons :

(*a*) In case of Na^+, an electron has to be lost from a stable inert gas configuration but in case of Na, loss of an electron gives stable inert gas configuration.

(*b*) Na is neutral but Na^+ is +vely charged.

(*iii*) *Be^+ has lower IE_1 than Mg^{2+}* because in case of Be^+, the loss of one electron gives a stable inert gas configuration but in case of Mg^{2+}, the electron has to be lost from the stable inert gas configuration.

(*iv*) *I has lower IE_1 than I^-* because in case of I^-, an electron has to be lost from a stable inert gas configuration.

6. (*a*) IE_1 of element III is the highest of the three elements listed, therefore, *it is a non-metal.*

(*b*) Since IE_2 of element I is very high as compared to its IE_1, therefore, *it is an alkali metal.*

(*c*) Since the IE_1 of element II is higher than that of element I and lower than that of element III, therefore, it is an *alkaline earth metal.*

7. (*a*) C has higher IE_1 than B because of higher nuclear charge.

(*b*) N has higher IE_1 than O because in case of N, the electron has to be lost from a more stable exactly half-filled electronic configuration.

(*c*) Ne has higher IE_1 than F because of stable inert gas configuration.

8. (*a*) F, O, N all belong to 2nd period. Among these, F has the highest IE_1 because of its smallest size and highest nuclear charge.

(*b*) Mg, P, Ar all lie in the 3rd period. Among these, Ar has the highest IE_1 because it has stable inert gas configuration.

(*c*) B, Al, Ga all lie in group 13. B has the highest IE_1 due to its smallest size.

4.15. Electron Gain Enthalpy*

4.15.1. Definition and Units. Just as energy (called ionization enthalpy) is required to remove an electron from an isolated gaseous atom so as to convert it into a positive ion, energy is released when an electron is added to an isolated gaseous atom so as to convert it into a negative ion. This energy is called electron gain enthalpy. Thus, *Electron gain enthalpy of an element may be defined as the energy released when a neutral isolated gaseous atom accepts an extra electron to form the gaseous negative ion, i.e., anion. It is denoted by* $\Delta_{eg} H$.

This process may be represented as :

$$\underset{\text{neutral gaseous atom}}{X(g)} + e^- \longrightarrow \underset{\text{anion}}{X^-(g)};$$

$$\Delta H = \Delta_{eg} H \quad ...(i)$$

Evidently, greater the amount of energy released in the above process, higher is the electron gain enthalpy of the element.

In other words, the *electron gain enthalpy of an element is a measure of the firmness or strength with which an extra electron is bound to it.* Like ionization enthalpy, electron gain enthalpy is measured either in electron volts per atom or kJ per mole.

Depending upon the nature of the element, the process of adding an electron to the atom can be either exothermic or endothermic. For majority of the elements, energy is released when an electron is added to the atom. Therefore, for such elements, *the electron gain enthalpy is* **negative.** For example, the electron gain enthalpy for halogens (*i.e.*, elements of group 17) is highly negative because they can acquire the nearest stable noble gas configuration by accepting an extra electron. In contrast, *noble gases have large* **positive** *electron gain enthalpies* because the extra electron has to be placed in the next higher principal quantum energy level thereby producing highly unstable electronic configuration.

4.15.2 Successive Electron gain enthalpies. Like second and higher ionization enthalpies, second and higher electron gain enthalpies are also possible. However, after the addition of one electron, the atom becomes negatively charged and the second electron is to be added to a negatively charged ion. But the addition of second electron is opposed by electrostatic repulsion and hence *the energy has to be supplied for the addition of second electron. Thus the second electron gain enthalpy of an element is* **positive***. For example, when an electron is added to oxygen atom to form O^- ion, energy is released. But when another electron is added to O^- ion to form O^{2-} ion, energy is absorbed to overcome the strong electrostatic repulsion between the negatively charged O^- ion and the new electron being added. Thus,

First electron gain enthalpy,

$$O(g) + e^-(g) \longrightarrow O^-(g); \qquad \Delta H_{eg} = -141 \text{ kJ mol}^{-1}$$

(Energy is released)

Second electron gain enthalpy :

$$O^-(g) + e^-(g) \longrightarrow O^{2-}(g); \qquad \Delta H_{eg} = +780 \text{ kJ mol}^{-1}$$

(Energy is absorbed)

Similarly, the second electron gain enthalpy of S is also positive. Thus,

First electron gain enthalpy,

$$S(g) + e^-(g) \longrightarrow S^-(g); \qquad \Delta H_{eg} = -200 \text{ kJ mol}^{-1}$$

(Energy is released)

Second electron gain enthalpy,

$$S^-(g) + e^-(g) \longrightarrow S^{2-}(g); \qquad \Delta H_{eg} = +590 \text{ kJ mol}^{-1}$$

(Energy is absorbed)

PROBLEMS ON THE CALCULATION OF ELECTRON GAIN ENTHALPY

EXAMPLE 4.9. *The electron gain enthalpy of chlorine is – 349 kJ mol⁻¹. How much energy in kJ is released when 3·55 g of chlorine is converted completely into Cl⁻ ion in the gaseous state.*

Solution. According to the definition of electron gain enthalpy.

$$Cl(g) + e^-(g) \longrightarrow Cl^-(g) + 349 \text{ kJ mol}^{-1}$$

∴ Energy released when 1 mole (= 35.5 g) of chlorine atoms change completely into $Cl^-(g)$ = 349 kJ

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*In majority of the text books, the negative of the enthalpy change accompanying the addition of an electron to an isolated gaseous atom is defined as **electron affinity** (A_e). The electron affinity is said to be **positive**, *if energy is released when an isolated gaseous atom accepts an electron and it is assigned a* **negative sign** *if energy is to be supplied to add an extra electron to the isolated gaseous atom.* This is, however, contrary to the thermodynamic convention. Further, since electron affinity is defined at absolute zero, therefore, at any other temperature heat capacities instead of electron affinity of the reactants and products should be considered. Therefore, in view of these two reasons, the term electron gain enthalpy is used instead of electron-affinity. The two terms are related to each other as $\Delta H_{eg} = -A_e - \frac{5}{2} RT$

Thus numerically electron gain enthalpy is higher than that of electron affinity by 5/2 RT. Since the value of 5/2 RT at 298 is just 2·477 kJ mol⁻¹, therefore, this small difference is often ignored and the two terms are used indistinguishably with the only difference that **electron gain enthalpy is just the negative of electron affinity.**

Energy relased when 3·55 g of chlorine atoms change completely into Cl^- (g)

$$= \frac{349}{35 \cdot 5} \times 3 \cdot 55 = 34 \cdot 9 \text{ kJ.}$$

EXAMPLE 4.10. *The amount of energy released when 1×10^{10} atoms of chlorine in vapour state are converted to Cl^- ions according to the equation,*

$$Cl(g) + e^- \longrightarrow Cl^-(g) \text{ is } 57 \cdot 86 \times 10^{-10} J.$$

Calculate the electron gain enthalpy of chlorine atom in terms of kJ mol^{-1} and eV per atom.

Solution. The amount of energy released when 1×10^{10} atoms of chlorine in vapour state are converted to Cl^- ions, according to the equation.

$$Cl(g) + e^- \longrightarrow Cl^-(g) \text{ is } 57 \cdot 86 \times 10^{-10} J.$$

∴ The electron gain enthalpy of chlorine, *i.e.*, the amount of energy released when 1 mole ($6 \cdot 023 \times 10^{23}$) atoms of chlorine are converted into Cl^- ions according to the above equation will be

$$= -\frac{57 \cdot 86 \times 10^{-10}}{1 \times 10^{10}} \times 6 \cdot 023 \times 10^{23}$$

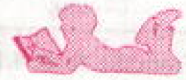
$$= -348 \cdot 49 \times 10^3 \text{ J/mol} = \mathbf{-348 \cdot 49 \text{ kJ/mol}}$$

Now 1 eV/atom = 96·49 kJ mol^{-1}

∴ *Electron gain enthalpy of chlorine*

$$= -\frac{348 \cdot 49}{96 \cdot 49} = \mathbf{-3 \cdot 61 \text{ eV/atom}}$$

PROBLEMS FOR PRACTICE



1. The electron affinity of bromine is 3·36 eV. How much energy in kcal is released when 8g of bromine is completely converted to Br^- ions in the gaseous state ? ($1 eV = 23 \cdot 06$ kcal mol^{-1}). **[Ans. 7·748 kcal]**
2. The amount of energy released when one million atoms of iodine are completely converted into I^- ions in the vapour state according to the equation, $I(g) + e^- \longrightarrow I^-(g)$ is $4 \cdot 9 \times 10^{-13}$ J. Calculate the electron affinity of iodine in (*i*) kJ/mol and (*ii*) in eV per atom. **[Ans. 295 kJ/mol and 3·06 eV/atom]**

HINTS FOR DIFFICULT PROBLEMS

1. No. of moles of Br = 8/80 = 0·1

Required energy = $0 \cdot 1 \times 3 \cdot 36 \times 23 \cdot 06$

$= \mathbf{7 \cdot 748 \text{ kcal}}$

2. Electron affinity

$= 6 \cdot 023 \times 10^{23} \times 4 \cdot 9 \times 10^{-13} \times 10^{-6}$

$= 29 \cdot 5 \times 10^4 \times 10^{-3}$ kJ

$= 295$ kJ mol^{-1}

$= 295/96 \cdot 49$ eV/atom

$= 3 \cdot 06$ eV/atom

4.15.3. Factors on which the Electron Gain Enthalpy depends. Some important factors on which electron affinities depend are discussed below :

(*i*) Atomic size. As the size of the atom increases, the distance between the nucleus and the last shell which receives the incoming electron increases. As a result, the force of attraction between the nucleus and the incoming electron decreases and hence the electron gain enthalpy becomes less negative (Table 4.11).

(*ii*) Nuclear charge. As the nuclear charge increases, the force of attraction between the nucleus and the incoming electron increases and hence the electron gain enthalpy becomes more negative.

(*iii*) Electronic configuration. Elements having exactly half-filled or completely filled orbitals are very stable. As a result, energy has to be supplied to add an electron. Hence their electron gain enthalpies have large positive values since they do not accept the additional electron so easily.

4.15.4. Variation of Electron Gain Enthalpies in the Periodic Table. The electron gain enthalpies of some elements are given in the Table 4.11.

TABLE 4.11. Electron gain enthalpies of some elements in kJ mol^{-1}

Period ↓ Group →	1	2	13	14	15	16	17	18
1.	H −73							He +48
2.	Li −60	Be +66	B −83	C −122	N +31	O −141	F −328	Ne +116
3.	Na −53	Mg +67	Al −50	Si −119	P −74	S −200	Cl −349	Ar +96
4.	K −48	Ca –	Ga −36	Ge −116	As −77	Se −195	Br −325	Kr +96
5.	Rb −47	Sr –	In −29	Sn −120	Sn −101	Te −190	I −295	Xe +77
6.	Cs −46	Ba –	Tl −30	Pb −101	Bi −110	Po −174	At −270	Rn +68

From the Table 4.11, it is evident that electron gain enthalpy does not show a perfectly regular trend along a period or a group because of a number of exceptions. However, *in general, the electron gain enthalpy becomes less negative in going from top to bottom in a group and more negative in going from left to right in a period as discussed below.*

(*a*) **Variation in a group.** (*i*) *In general, the electron gain enthalpy become less negative as we move down a group.* This may be explained as follows.

As we move down a group, both the atomic size and the nuclear charge increase. But the effect of increase in atomic size is much more pronounced than the nuclear charge. Thus, with increase in atomic size, the attraction of the nucleus for the incoming electron decreases and hence the electron gain enthalpy becomes less negative. For example, the electron gain enthalpy of halogens becomes less negative in going from chlorine to bromine to iodine.

(*ii*) *The electron gain enthalpies of some of the elements of second period, i.e., O and F are, however, less negative than the corresponding elements (i.e., S and Cl) of the third period.*

This unexpected behaviour is due to the fact that the elements of second period have smallest atomic size amongst the elements in their respective groups. As a result, there are considerable electron-electron repulsions within the atom itself and hence the additional electron is not accepted with the same ease as is the case with the remaining elements in the same group. For example, electron gain enthalpy of O ($-141\cdot0$ kJ mol^{-1}) is less negative than that of S (-200 kJ mol^{-1}) and the electron gain enthalpy of F (-328 kJ mol^{-1}) is less negative than that of Cl (-349 kJ mol^{-1}). It may be noted that amongst halogens **chlorine has the most negative electron gain enthalpy.**

(*b*) **Variation in a period.** *In general, electron gain enthalpy becomes more and more negative from left to right in a period.* This may be explained as follows :

As we move across a period from left to right, the atomic size decreases and the nuclear charge increases. Both these factors tend to increase the attraction by the nucleus for the incoming electron and hence electron gain enthalpy, in general, becomes more and more negative in a period from left to right.

Some Important Trends in Electron Gain Enthalpies. Some important trends in the electron gain enthalpies of the elements are discussed below :

(*i*) **Halogens have the most negative electron gain enthalpies.** *The electron gain enthalpies of the halogens (Group 17) elements are the most negative.* This is due to the reason that the valence shell electronic configuration of the halogens is $ns^2\,np^5$ and as such they require one more electron to acquire the stable noble gas configuration, *i.e.* $ns^2\,np^6$. As a result, they have a strong tendency to accept an additional electron and hence their electron gain enthalpies are highly negative. However, as we move from Cl to I, the electron gain enthalpies become less and les negative (Fig. 4.5) due to a corresponding increase in their atomic radii. In Cl, the additional electron enters the 3*p*-

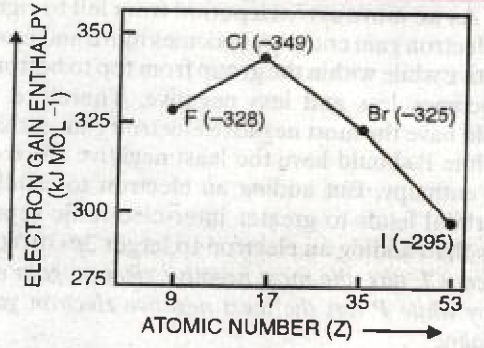


FIGURE 4.5. Variation of electron gain enthalpies of halogens.

subshell ; in Br it goes to the 4*p*-subshell while in I it goes to the 5*p*-subshell. As the distance of the nucleus from the subshell which receives the additional electron increases, the force with which it is attracted by the nucleus decreases and hence the electron gain enthalpies become less negative as we move down the group from Cl ⟶ Br ⟶ I.

The electron gain enthalpy of F is, however, unexpectedly less negative than that of Cl. This is due to its smll size. As a result of its small size, the electron-eledron replusions in the relatively compact 2*p*-subshell are comparatively large and hence the incoming electron is not accepted with the same ease as is the case with Cl. Consequently, the electron gain enthalpy of F is less negative than that of Cl.

(ii) The electron gain enthalpy of noble gases is positive. This is due to the fact that the atoms of these elements have completely filled subshells. As a result, there is no room in their valence orbitals and the additional electron has to be placed in an orbital of next higher shell. As a result, energy has to be supplied to add on additional electron. In other words, the electron gain enthalpy of noble gases is positive. Further, as we move down the group, the size of the atom increases and hence electron gain enthalpies have lower positive values. For example, electron gain enthalpy of Ar (+96) is lower than that of Ne (+116).

The electron gain enthalpy of He is, however, the lowest of all the noble gases. The reason for this unexpected behaviour is that due to its smallest size, it has much higher tendency to accept an additional electron than any other noble gas.

PROBLEMS ON PREDICTING ELECTRON GAIN ENTHALPY

EXAMPLE 4.11. *Which of the following elements has the most negative electron gain enthalpy ? Give reasons.*

(i) [Ne] $3s^2\,3p^3$ *(ii)* [Ne] $3s^2\,3p^4$ *(iii)* [Ne] $3s^2\,3p^5$

Solution. The element (chlorine) corresponding to the electronic configuration *(iii)* will have the the most negative electron gain enthalpy. This is due to the reason that it contains one electron less than the stable noble gas configuration, *i.e.*, [Ne] $3s^2\,3p^6$ and hence, has a strong tendency to accept one electron to acquire the stable noble gas configuration.

EXAMPLE 4.12. *Which of the following pairs of elements would have more negative electron gain enthalpy ? Explain*

(i) N or O (N.C.E.R.T.)

(ii) F or Cl (N.C.E.R.T.)

(iii) S or O *(iv) C or Si*

Solution. (*a*) *The electron gain enthalpy of O is highly negative while that of N is slightly positive.*

Reason. The electronic configuration of N is quite stable since it has exactly half-filled 2*p*-orbitals and hence has no tendency to accept an extra electron. In other words, energy has to be supplied to add an extra electron. Thus, *electron-gain enthalpy of N is slightly positive.* In contrast, the electronic configuration of O is not so stable but it has higher nuclear charge and lower atomic size than N and hence it has a high tendency to accept an extra electron. In other words, *electron gain enthalpy of O is highly negative.*

(*b*) Cl has more negative electron gain enthalpy than F.

Reason. As explained in **Example 4.11.**

(*c*) *S has more negative electron gain enthalpy than O.*

Reason. The size of O is much smaller than that of S. As a result, the electron-electron repulsions in the smaller 2*p*- subshell of O are comparatively larger than those present in the bigger 3*p*-subshell of S. Therefore, S has higher tendency to accept an additional electron than O.

(*d*) *C has more negative electron gain enthalpy than Si.*

Reason. This is because C-atom has smaller size than Si-atom. (Note that the electron-electron repulsions in these atoms are not very large because they contain only 4 electrons in the outermost shell).

EXAMPLE 4.13. *Which of the following will have the most negative electron gain enthalpy and which the least negative ?*

P, S, Cl, F

Explain your answer. **(N.C.E.R.T.)**

Solution. Arranging the given atoms into different groups and periods in order of increasing atomic numbers :

Group No.	15	16	17
2nd Period	–	–	F
3rd Period	P	S	Cl

As we move across a period from left to right, the electron gain enthalpy becomes more and more negative while within the group from top to bottom, it becomes less and less negative. Therefore, F should have the most negative electron gain enthalpy while P should have the least negative electron gain enthalpy. But adding an electron to smaller 2*p*-orbital leads to greater inter-electronic repulsions than adding an electron to larger 3*p*- orbital. *Hence Cl has the most negative electron gain enthalpy while P has the least negative electron gain enthalpy.*

PROBLEMS FOR PRACTICE

1. Arrange the elements with the following electronic configurations in order of increasing electron gain enthalpy.

(*i*) $1s^2\ 2s^2\ 2p^5$ (*ii*) $1s^2\ 2s^2\ 2p^4$ (*iii*) $1s^2\ 2s^2\ 2p^3$

(*iv*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

[Ans. (*i*) < (*iv*) < (*ii*) < (*iii*)]

2. Arrange the following elements in order of decreasing electron gain enthalpy : B, C, N, O.

[Ans. N, B, C, O]

3. Which one (atom/ion) in the following pairs has higher electron gain enthalpy ?

(*i*) O^-, S (*ii*) O, S^- (*iii*) O^-, S^- (*iv*) N^-, P

[Ans. (*i*) $O^- > S$ (*ii*) $S^- > O$ (*iii*) $O^- > S^-$ (*iv*) $N^- > P$]

4. The electron gain enthalpies of halogens decrease in the order F > Cl > Br > I. Comment upon the statement.

[Ans. The statement is wrong. The actual order is I > Br > F > Cl]

HINTS FOR DIFFICULT PROBLEMS

1. Out of F ($1s^2\ 2s^2\ 2p^5$), O ($1s^2\ 2s^2\ 2p^4$) N ($1s^2\ 2s^2\ 2p^3$) and S ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$), only N because of its stable exactly half-filled electron configuration has +ve electron gain enthalpy while all others have –ve electron gain enthalpies. Since F needs only one more electron to acquire the nearest inert gas configuration, therefore, it has the most –ve electron gain enthalpy. Out of O and S, O has less negative electron gain enthalpy than S because of electron-electron repulsions present in its small compact 2*p*-orbital. Thus, overall order of increasing electron gain enthalpy is : (*i*) < (*iv*) < (*ii*) < (*iii*).

2. N has +ve electron gain enthalpy while all others have –ve electron gain enthalpies. Since size decreases in moving from B ⟶ C ⟶ O, therefore, electron gain enthalpies become more and more negative from B ⟶ C ⟶ O. Thus, the overall decreasing order of electron gain enthalpies is N, B, C, O.

3. (*i*) Due to repulsions between the electrons on O^- and the additional incoming electron, the electron gain enthalpy of O^- is positive while that O a –ve.

(*ii*) On similar grounds, the electron gain enthalpy of S^- is +ve while that of O is –ve.

(*iii*) Due to small size, repulsions between O^- and the incoming electron is much more than in S^-. Therefore, electron gain enthalpy of O^- is more +ve than that of S^-

(*iv*) Due to repulsions between N^- and the incoming electron gain enthalpy of N^- is positive while that P is –ve.

4.16. Atomic Radii

4.16.1. Definition. The size of an atom, *i.e.*, the atomic size is a very important property of an atom since many other physical and chemical properties of the atom are related to it. *If an atom is considered to be a sphere, the atomic size is given by the radius of the sphere and is commonly known as* **atomic radius.** It may be defined as

The distance from the centre of the nucleus to the outermost shell containing the electrons.

Or

The distance from the centre of the nucleus to the point upto which the density of the electron cloud (i.e. probability of finding the electron) is maximum.

4.16.2. Difficulties in determining atomic radius. Atomic radius cannot be determined precisely due to the following reasons :

(*i*) The size of an atom cannot be determined precisely since the electron cloud surrounding the atom does not have a sharp boundary. This is due to the reason that the probability of finding an electron never becomes zero even at large distances from the nucleus.

(*ii*) It is not possible to isolate a single atom for the purpose of determination of its radius.

(*iii*) The probability distribution of electrons of an atom is appreciably affected by presence of other atoms within its molecule or in its neighbourhood. Thus, the atomic radius may change in going from one environment to the other.

(*iv*) The atomic radius also changes when the atom is present in different bonded states.

4.16.3. Types of atomic radii. Despite the above limitations, we need some *opertional definition* for the radius of an atom or an ion. This is necessary in order to explain a number of chemical properties of different elements in terms of the size of their atoms or ions. There are three operational concepts whih have been widely used. These are :

(*i*) *Covalent radii* (*ii*) *van der Waals' radii* and (*iii*) *Metallic radii*.

(*a*) Covalent radius.

It is defined as one-half the distance between the nuclei of two covalently bonded atoms of the same element in a molecule (Fig. 4.6).

Thus, for a homonuclear diatomic molecule,

$$r_{\text{covalent}} = \frac{1}{2} \text{ [Internuclear distance between two bonded atoms]}$$

Since the internuclear distance between two bonded atoms is called the bond length. Therefore,

$$\boxed{r_{\text{covalent}} = \frac{1}{2} \text{ [bond length]}}$$

For example, the internuclear distance between two hydrogen atoms in H_2 molecule is 74 *pm* (0·74 Å). Hence the covalent radius of hydrogen is 74/2 = 37 *pm* (0·37 Å). Similarly, the internuclear distance between chlorine atoms in Cl_2 molecule is 198 *pm* (1·98 Å),the covalent radius of chlorine is 198/2 = 99 *pm* (0·99 Å).

(*b*) van der Waals' radius.

***It is defined as one-half the distance between the nuclei of two identical non-bonded isolated atoms or two adjacent identical atoms belonging to two neighbouring molecules of an element in the solid state* (Fig. 4.6).**

The name van der Waals' radius simply means that the forces existing between the non-bonded isolated atoms or neighbouring molecules are the weak van der Waals' forces of attraction. Consequently, the magnitude of the van der Waals' radii depends upon the packing of the atoms when the element is in the solid state. These are obtained from X-ray studies of the various atoms in the solid state. For example, the internuclear distance between the adjacent chlorine atoms of the two neighbouring molecules in the solid state is 360 pm or 3·6 Å (Fig. 4.6). Therefore, the van der Waals' radius of chlorine atom = 360/2 = 180 pm or 1·8 Å. Similarly, the internuclear distance between two adjacent hydrogen atoms of two neighbouring molecules in the solid state = 240 pm. Therefore, its van der Waals' radius = 240/2 = 120 pm or 1·2 Å.

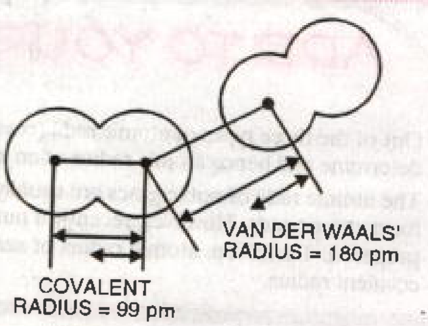


FIGURE 4.6. Covalent and van der Waals' radii of chlorine.

Comparison of covalent radius and van der Waals' radius. van der Waals' radius of an element is always larger than its covalent radius because of the following two reasons :

(*i*) Since the van der Waals' forces of attraction are weak, therefore the internuclear distances in case of atoms held by van der Waals' forces are much larger than those between covalently bonded atoms. Therefore, *van der Waals' radii are always larger than covalent radii.*

(*ii*) Since a covalent bond is formed by overlap of two half-filled atomic orbitals, a part of the electron cloud becomes common (Fig. 4.7). Therefore, *covalent radii are always smaller than the van der Waals' radii.*

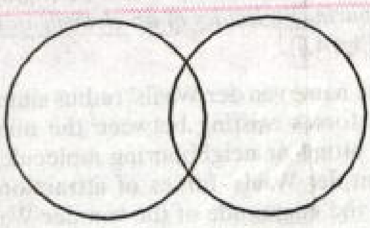


FIGURE 4.7. Overlapping of atomic orbitals to form a covalent bond.

(c) Metallic radius

According to *Electron-sea model*, a metal lattice or crystal consists of positive kernels or metal ions (left after the removal of valence electrons) arranged in a definite pattern in a sea of mobile valence electrons. Thus, each kernel (*i.e.*, metal ion) is simultaneously attracted by a number of mobile electrons and each mobile electron is attracted by a number of metal ions. *This simultaneous force of attraction between the mobile electrons and the positive kernels is called the* **metallic bond.**

It is defined as one-half the internuclear distance between the two adjacent metal ions in the metallic lattice.

The internuclear distances are determined by X-ray studies and the metallic radius is usually expressed in angstrom units or picometers.

Since in a metallic lattice, the valence electrons are mobile, therefore, they are only weakly attracted by the metal ions or kernels. In contrast, in a covalent bond, a pair of electrons are strongly attracted by the nuclei of two atoms. *Thus, a metallic radius is always longer than its covalent radius.* For example, metallic radius of sodium is 186 pm (1·86 Å) whereas its covalent radius as determined from its vapours which exist as Na_2 is 154 pm (1·54 Å). Similarly metallic radius of potassium is 231 pm while its covalent radius is 203 pm. Likewise metallic radius of copper in 128 pm while its covalent radius is 117 pm.

4.16.4. Comparison of Different types of atomic radii. A comparison of three types of atomic radii discussed above reveals that van der Waals' radius is the longest while covalent radius of an atom is the shortest, *i.e., van der Waals' radius > metallic radius > covalent radius.*

ADD TO YOUR KNOWLEDGE

1. Out of the three types of atomic radii (covalent, van der Waals' and metallic) covalent radius is the easiest to determine and hence atomic radius of an atom is usually expressed in terms of its covalent radius.
2. The atomic radii of noble gases are usually expressed in terms of their van der Waals' radii since they do not form compounds. However, recently a number of compounds of xenon with fluorine and oxygen have been prepared. Therefore, atomic radius of xenon can be expressed either in terms of van der Waals' radius or covalent radius.

4.16.5. Variation of Atomic Radii in the Periodic Table

(a) Variation in a period. *In general, the atomic covalent or van der Waals' decrease with increase in atomic number as we move from left to right in a period.* For example, consider the atomic (covalent) radii of the elements of second period (Table 4.12 and Fig. 4.8).

TABLE 4.12. Decrease in atomic (covalent) radii in the second period

Element	Li	Be	B	C	N	O	F	Ne
Nuclear charge	+3	+4	+5	+6	+7	+8	+9	+10
Outer electronic configuration	$2s^1$	$2s^2$	$2s^2 2p^1$	$2s^2 2p^2$	$2s^2 2p^3$	$2s^2 2p^4$	$2s^2 2p^5$	$2s^2 2p^6$
radii (pm)	152	111	88	77	75	74	72	160*

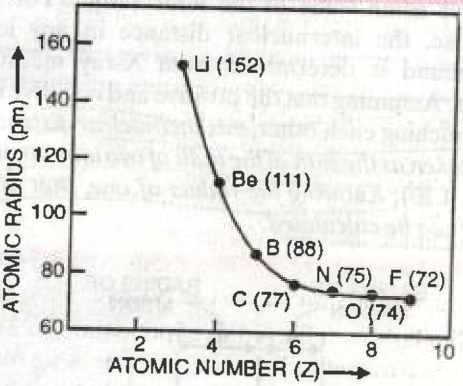


FIGURE 4.8. Variation of atomic radius with atomic number across the second period.

From the above table, it is evident that –

(i) The alkali metals which are at the extreme left of the periodic table have the largest size in a period.

(ii) The halogens which are present at the extreme right of the periodic table have the smallest size.

(iii) The size of the atoms of inert gases are, however, larger than those of the preceding halogens.*

Explanation. As we move from left to right in a period, nuclear charge increases by one unit in each succeding element while the number of the shells remains the same. Due to this enhanced nuclear charge, the electrons of all the shells are pulled little closer to the nucleus thereby making each individual shell smaller and smaller. This results in a decrease of the atomic radius as we move from left to right in a period.

An inspection of the Table 4.12 further reveals that the atomic radius abruptly increases as we move from halogen (F) to the inert gas (Ne). This is due to the reason that in case of inert gases all the orbitals are completely filled and hence the inter-electronic repulsions are maximum. Moreover in case of inert gases, the atomic size is expressed in terms of *van der Waals' radius* since they do not form covalent bonds while in case of all other elements, the atomic size is expressed in terms of *covalent radius*. Since by definition, van der Waals' radii are larger than covalent radii, therefore, the atomic size of an inert gas in a period is much higher than that of the preceding halogen.

Like covalent radii, van der Waals' radii also decrease as we move from left to right in a period. For example, the van der Waals' radii of N, O and F are 150 pm, 140 pm and 135 pm respectively.

(b) Variation in a group. *The atomic (covalent) radii of elements increase with increase in atomic number as we move from top to bottom in a group.* For example, consider the atomic (covalent) radii of the members of the alkali metals group (Table 4.13). These are represented graphically in Fig. 4.9.

TABLE 4.13. Increase in atomic (covalent) radii of the alkali metals.

Element	Li	Na	K	Rb	Cs	Fr
Nuclear charge	+3	+11	+19	+37	+55	+87
Outer electronic configuration	$2s^1$	$3s^1$	$4s^1$	$5s^1$	$6s^1$	$7s^1$
Covalent radii (pm)	152	186	231	244	262	—

From the above table, it is clear that the atomic radii increase as we move down the group from lithium to caesium among alkali metals. Similar trend is followed by halogens from fluorine to iodine as shown graphically in Fig. 4.9.

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*van der Waals' radius.

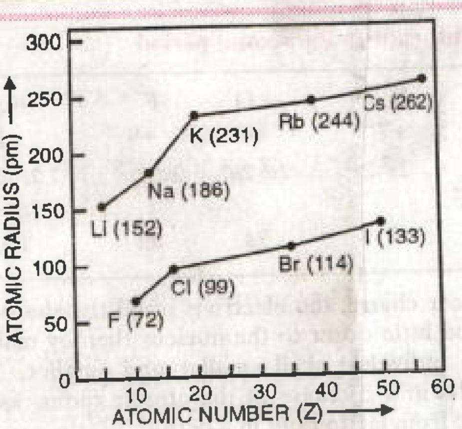


FIGURE 4.9. Variation of atomic radius with atomic number for alkali metals and halogens.

Explanation. As we move down a group, a new energy shell is added at each succeeding element though the number of electrons in the valence shell remains to be the same. In other words, electrons in the valence shell of each succeeding element lie farther and farther away from the nucleus. As a result, the attraction of the nucleus for the electrons decreases and hence the atomic radius increases. However, with increase in atomic number, the nuclear charge also increases. As a result, the force of attraction of the nucleus for the electrons increases and hence the atomic radii should decrease. But the effect of the increased nuclear charge is reduced due to the screening or shielding effect on the valence electrons by the electrons present in the inner shells. Thus, the effect of adding a new energy shell is so large that it outweighs the contractive effect of the increased nuclear charge. Hence, *the increase in atomic radii as we move down the group (from Li to Cs among alkali metals and from F to I among halogens) is primarily due to the addition of a new energy shell.*

Like covalent radii, van der Waals' radii also increase as we move down the group. For example, the van der Waal's radii of Cl, Br and I are 180, 195 and 215 pm respectively.

4.17. Ionic Radii

The ionic radii correspond to the radii of ions in ionic crystals. Ions, in turn, are formed when neutral atoms lose or gain electrons. A *positive ion* or **cation** is formed when a neutral atom loses one or more electrons while a *negative ion* or **anion** is formed when a neutral atom gains one or more electrons. The effective size of these ions is expressed in terms of ionic radius. Ionic radius may be defined in different ways as in the case of atomic radius. However one of the most common definition is as follows :

Ionic radius may be defined as the effective distance from the centre of the nucleus of the ion upto which it exerts its influence on its electronic cloud.

Theoretically, electron cloud may extend up to a large distance. Nevertheless, it is still important to have some value of the ionic radius. For this purpose, the internuclear distance in any ionic compound is determined from X-ray measurements. Assuming that the positive and negative ions are touching each other, *this internuclear distance is then taken as the sum of the radii of two ions involved* (Fig. 4.10). *Knowing the radius of one, that of the other can be calculated.*

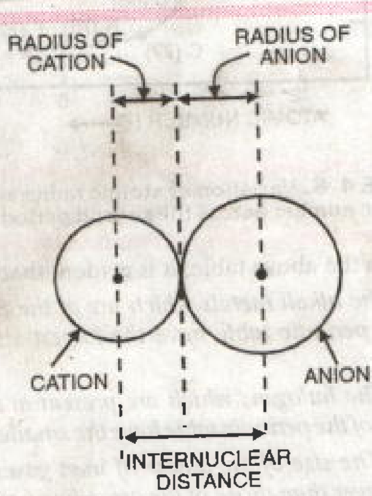


FIGURE 4.10. Internuclear distance and ionic radius.

For example, the internuclear distance between Na^+ and Cl^- ions in sodium chloride crystal has been determined to be 276 pm from X-ray measurements. This distance is then taken as sum of the radii of Na^+ and Cl^- ions. Unless the value of one of them is known that of the other cannot be calculated. Several methods have been used to fix the absolute value of at least one ion (the details of these methods are beyond the scope of this book). However, *Pauling's method* is the most widely accepted and values given here are based upon this method. Once the absolute value of ionic radius of one of the ions is known, that of the other can be easily calculated by subtracting the value of this ion from the measured internuclear distance in its compound. For example, based upon Pauling's method, the absolute value of the ionic radius of Na^+ ion has been determined to be 95 pm. Therefore, the ionic radius of Cl^- ion = 276 − 95 = 181 pm. Further, the radius of Na^+ ion thus obtained may be used to calculate the radii of other anions, such as Br^- and I^- ions, by measuring the internuclear distances in NaBr and NaI. Similarly, the radius of the Cl^- ion may be used to calculate the radii of other cations such as Li^+, K^+ etc. by measuring internuclear distances in LiCl and KCl crystals respectively.

4.17.1. Comparison of the ionic radii with corresponding atomic radii. A study of ionic radii of cations and anions reveals the following two generalizations :

(a) The radius of the cation is always smaller than that of its parent atom. A cation is formed by loss of one or more electrons from the neutral gaseous atom. This generally causes the removal of the whole of the outermost (*valence*) shell of electrons,

e.g.,
$$\underset{1s^2\,2sp^2\,2p^6\,3s^1}{Na} \longrightarrow \underset{1s^2\,2s^2\,2p^6}{Na^+} + e^-$$

Due to the removal of the valence shell, the number of shells in the cation decreases. As a result, the size of the cation is smaller than the parent atom from which it is formed. Further, due to the removal of electrons from the parent atom, the number of electrons in the cation decreases (Fig. 4.11) but its nuclear charge remains the same as that of the atom. As a result, the force of attraction by the nucleus on the electrons increases (i.e. *effective nuclear charge increases*) and hence the size of the atom decreases. Thus, in nutshell,

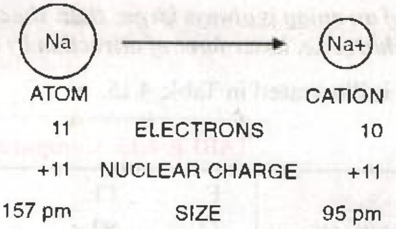


FIGURE 4.11. Relative sizes of Na atom and Na^+ ion.

> ***The size of a cation is always smaller than that of the corresponding atom due to (i) decrease in the number of shells (ii) increase in the effective nuclear charge resulting in greater force of attraction by the nucleus on the electrons.***

This is illustrated in Table 4.14.

TABLE 4.14. Comparative sizes of atoms and their cations

Atom	Li	Na	K	Be	Mg	Al	Mn
Atomic radii (pm)	152	186	231	111	160	143	126
Corresponding cations	Li^+	Na^+	K^+	Be^{2+}	Mg^{2+}	Al^{3+}	Mn^{4+}
Ionic radii (pm)	60	95	133	39	65	50	46

Variation of ionic (cationic) radii within a group. Like covalent radii of atoms, *the ionic radii of cations also increase as we move from top to bottom within a group primarily due to an increase in the number of shells*. For example, the ionic radii of Li^+ is 60 pm, that of Na^+ is 95 pm and that of K^+ is 133 pm.

(*b*) The radius of the anion is always larger than that of its parent atom. An anion is formed when a neutral gaseous atom gains one or more electrons (Fig. 4.12). This increases the number of electrons in the anion while its nuclear charge remains the same as that on the neutral atom. Since the same nuclear charge now attracts greater number of electrons, therefore, the force of attraction by the nucleus on the electrons of all the shells decreases (*i.e., effective nuclear charge decreases*). *Hence the electron cloud of the atom expands*. In other words, the distance between the centre of the nucleus and the last shell that contains electrons increases thereby increasing the ionic radius. Thus,

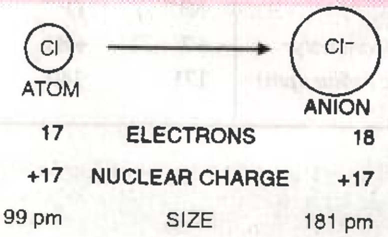


FIGURE 4.12. Relative sizes of Cl atom and Cl^- ion.

The size of an anion is always larger than the corresponding atom mainly because of decrease in the effective nuclear charge i.e. lesser force of attraction by the nucleus on the electrons.

This is illustrated in Table 4.15.

TABLE 4.15. Comparative sizes of atoms and their anions

Atom	F	Cl	Br	I	O	S	N
Atomic radii (pm)	72	99	114	133	74	102	75
Corresponding anion	F^-	Cl^-	Br^-	I^-	O^{2-}	S^{2-}	N^{3-}
Ionic radii (pm)	136	181	196	219	142	184	171

Variation of ionic (anionic) radii within in group. *Like covalent radii, the ionic radii of anions also increase as we move down the group primarily due to an increase in the number of shells.* For example, the ionic radii of F^-, Cl^-, Br^- and I^- ions are 136, 181, 196 and 219 pm respectively.

4.17.2. Isoelectronic ions or species.

Ions of the different elements which have the same number of electrons but different magnitude of the nuclear charge are called isoelectronic ions.

For example, sulphide ion (S^{2-}), chloride ion (Cl^-) and potassium ion (K^+) are isoelectronic ions because each one of them has 18 electrons but have different nuclear charges, *i.e.*, +16, +17 and +19 respectively.

Besides ions, a neutral atom may also have same number of electrons. For example, besides S^{2-}, Cl^- and K^+ ions, argon (Ar) has also 18 electrons. Therefore, Ar is also isoelectronic with S^{2-}, Cl^- and K^+ ions. In order to cover all these species, the term isolectronic species is used. Thus,

Isoelectronic species *may be defined as neutral or ionic species which have the same number of electrons but different nuclear charges.*

Thus, nitride ion (N^{3-}), oxide ion (O^{2-}), fluoride ion (F^-), neon (Ne), sodium ion (Na^+), magnesium ion (Mg^{2+}) and aluminium ion (Al^{3+}) are all isoelectronic species since each one of them contains 10 electrons but different nuclear charges of +7, +8, +9, +10, +11, +12 and +13 respectively.

Variation of ionic size among isoelectronic ions. Within a series of isoelectronic ions, as the nuclear charge increases, the force of attraction by the nucleus on the electrons also increases. As a result, ionic radii decrease. In other words, *the ionic radii of isoelectronic ions decrease with the increase in the magnitude of the nuclear charge*. For example, consider the isoelectronic ions : N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+}. All these ions have 10 electrons but their nuclear charges vary *i.e.* these are +7, +8, +9, +11, +12 and +13 as shown in Table 4.8. Therefore, their ionic radii increase in the order :

$$Al^{3+} < Mg^+ < Na^+ < F^- < O^{2-} < N^{3-}.$$

This is illustrated in Table 4.16.

TABLE 4.16. Variation of ionic radii in an isoelectronic series

Ions	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}
Nuclear charge	+7	+8	+9	+11	+12	+13
Ionic radius (pm)	171	140	136	95	65	50

ADD TO YOUR KNOWLEDGE

The ionic size of isoelectrionic species can be easily compared on the basis of their atomic number/number of electrons, *i.e.* Z/e ratio. *Smaller the value of Z/e, larger the size of the species.* For example,

Ion	Z	e	Z/e	Ionic radius (pm)
N^{3-}	7	10	0·7	171
O^{2-}	8	10	0·8	140
F^{-}	9	10	0·9	136
Ne	10	10	1·0	112
Na^{+}	11	10	1·1	95
Mg^{2+}	12	10	1·2	65
Al^{3+}	13	10	1·3	50

PROBLEMS ON FINDING ISOELECTRONIC SPECIES AND COMPARISION OF THEIR RELATIVE RADII

EXAMPLE 4.14. *Name the species that will be isoelectronic with the following atoms or ions :*

(*i*) *Ne* (*ii*) Cl^-

(*iii*) Ca^{2+} (*iv*) Rb^+

(N.C.E.R.T.)

Solution. Isoelectronic species are those which have same number of electrons.

(*i*) Ne has 10 electrons. Therefore, the species N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+} etc. each of which has also 10 electrons, are isoelectronic with it.

(*ii*) Cl^- has 18 electrons. Therefore, the species P^{3-}, S^{2-}, Ar, K^+ and Ca^{2+}, each one of which contains 18 electrons are isoelectronic with it.

(*iii*) Ca^{2+} has 18 electrons. Therefore, the species P^{3-}, S^{2-}, Ar and K^+, each of which also contains 18 electrons, are isoelectronic with it.

(*iv*) Rb^+ has 36 electrons. Therefore, the species, Br^-, Kr or Sr^{2+} each of which also has 36 electrons, are isolectronic with it.

EXAMPLE 4.15. *Which of following species are isoelectronic ?*

(*i*) O^{2-} (*ii*) *Na*

(*iii*) *F* (*iv*) Mg^{2+}

(*v*) Cl^- (*vi*) Al^{3+}

(*vii*) *Ne.*

Arrange them in decreasing order of their size.

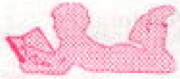
Solution. The number of electrons in these species are :

Atom or ion	No. of electrons
O^{2-}	$8+2 = 10$
Na	$= 11$
F	$= 9$
Mg^{2+}	$12-2 = 10$
Cl^-	$17+1 = 18$
Al^{3+}	$13-3 = 10$
Ne	$= 10$

Thus, O^{2-}, Mg^{2+}, Al^{3+} and Ne (each one of which has 10 electrons) are isoelectronic species. Now nuclear charge on O^{2-} is $+8$, Mg^{2+} is $+12$, Al^{3+} is $+13$ and Ne is $+10$. Since the size of the species decreases as the nuclear charge increases, therefore, their size decreases in the order :

$$O^{2-} > Ne > Mg^{2+} > Al^{3+}.$$

PROBLEMS FOR PRACTICE



1. Which one of the following pairs would have a large size ? Explain.

(i) K or K^+ (ii) Br or Br^-

(iii) O^{2-} or F^- (iv) Li^+ or Na^+

(v) P or As (vi) Na^+ or Mg^{2+}

(N.C.E.R.T.)

[Ans. (i) K, (ii) Br^-, (iii) O^{2-}, (iv) Na^+, (v) As, (vi) Na^+]

2. Arrange the following in order of increasing radii ?

(i) I, I^+, I^- (ii) C, N, Si, P

(iii) O^{2-}, N^{3-}, S^{2-}, F^-

[Ans. (i) $I^+ < I < I^-$ (ii) $N < C < P < Si$ (iii) $F^- < O^{2-} < N^{3-} < S^{2-}$]

3. Select from each group, the species which has the smallest radius stating appropriate reason.

(a) O, O^-, O^{2-} (b) K^+, Sr^{2+}, Ar

(c) Si, P, Cl. (N.C.E.R.T.)

[Ans. (a) O (b) Sr^{2+} (c) Cl]

HINTS FOR DIFFICULT PROBLEMS

1. (i) Due to higher effective nuclear charge, K^+ has lower atomic size than K.

(ii) Due to lower effective nuclear charge, the size of Br^- is higher than that of Br.

(iii) O^{2-} and F^- are isoelectronic species. Since effective nuclear charge of O^{2-} is lower than that of F^-, therefore, O^{2-} has higher atomic size than F^-.

(iv) Li^+ and Na^+ both belong to group 1. Because of greater number of shells (2 in case of Na^+ and 1 in case of Li^+), Na^+ has bigger atomic size than Li^+.

(v) As has four shells while P has three. Therefore, atomic size of As is higher than that of P.

(vi) Na^+ and Mg^{2+} are isoelectronic cations. Therefore, due to lower effective nuclear charge, ionic radius of Na^+ is higher than that of Mg^{2+}.

2. (i) Size of a cation is always smaller while that of an anion is always bigger than the neutral atom, *i.e.*, $I^+ < I < I^-$.

(ii) C and N lie in 2nd period while Si and P lie below them in the 3rd period. Since elements in the 3th period have higher atomic size than those in the 2nd period, therefore, atomic radii of Si and P are higher than those of C and N respectively. Since atomic radii decrease from left to right in a period due to higher nuclear charge, therefore, C has higher atomic radius than N and Si has higher atomic radius than P. Thus, the overall order of increasing atomic radii is : N < C < P < Si.

(iii) Among isoelectronic ions, the size of anions increases as the nuclear charge decreases : $F^- < O^{2-} < N^{3-}$. Since S belongs to third period while F, O, N all belong to the second period, therefore, ionic radius of S^{2-} is bigger than those of F^-, O^{2-} and N^{3-} ions. Thus, the overall order of increasing ionic radii is : $F^- < O^{2-} < N^{3-} < S^{2-}$.

3. (a) Among the different species of the same atom, the size increases as the magnitude of negative charge increases : Therefore, among O, O^- and O^{2-}, O has the smallest radius.

(b) Although Sr^{2+} has Kr gas configuration (*i.e.*, has four shells), but K^+ has Ar gas configuration (*i.e.*, has three shells), nevertheless ionic size of Sr^{2+} is smaller than that of K^+ obviously due to higher nuclear charge which outweighs the effect of an additional shell.

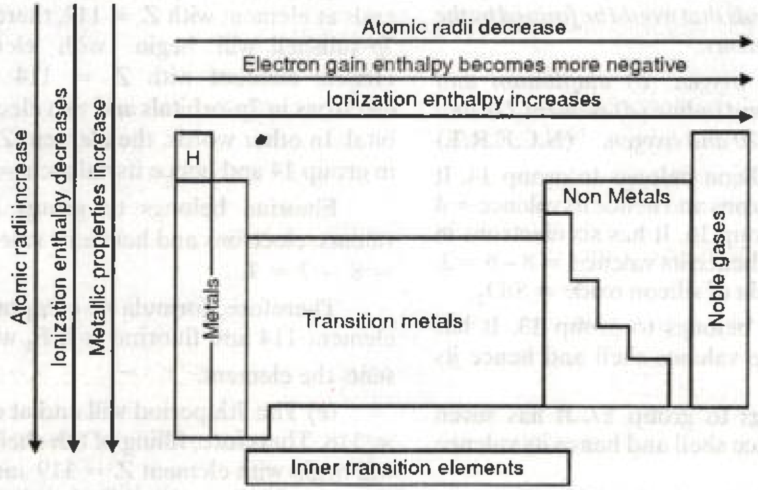
(c) Si, P and Cl all belong to 3rd period. Since atomic size decreases as the nuclear charge increases. Therefore, Cl with the highest nuclear charge has the smallest radius.

4.18. Valency

It has been observed that the chemical properties of the elements depend upon the number of electrons present in the outermost shell of the atom.

> *The electrons present in the outermost shell of an atom are called* **valence electrons** *and the number of these electrons determine the* **valence** *or the* **valency** *of the atom. It is because of this reason that the outermost shell is also called the* **valence shell** *of the atom and the orbitals present in the valence shell the called* **valence orbitals.**

Summary of the Trends in the Periodic Properties of Elements in the periodic Table.



In case of representative elements, the valency of an atom is generally equal to either the number of valence electrons (*s*- and *p*-block elements) or equal to eight minus the number of valence electrons. In contrast, transition and inner transition elements, exhibit variable valence due to involvement of not only valence electrons but *d*- or *f*-electrons as well. However, their most common valence are 2 and 3.

Periodicity of Valence

(*a*) Variation in a period. As we move across a period from left to right, the number of valence electrons increases from 1 to 8. But the valence of elements, *w.r.t.* H or O first increases from 1 to 4 and then decreases to zero. This is illustrated in Table 4.17.

TABLE 4.17. Periodic trends in valence of elements shown by the formulae of their hydrides and oxides.

	Groups → ↓ Periods	1	2	13	14	15	16	17
Formulae of hydrides	2	LiH			CH_4	NH_3	H_2O	HF
	3	NaH			SiH_4	PH_3	H_2S	HCl
	4	KH			GeH_4	AsH_3	H_2Se	HBr
	5	RbH			SnH_4	SbH_3	H_2Te	HI
Formulae of oxides	2	Li_2O	BeO	B_2O_3	CO_2			
	3	Na_2O	MgO	Al_2O_3	SiO_2			
	4	K_2O	CaO	Ga_2O_3	GeO_2			
	5	Rb_2O	SrO	In_2O_3	SnO_2			
	6	Cs_2O	BaO	—	PbO_2			

(*b*) Variation in a group. When we move down the group, the number of valency electrons remains the same, therefore, all the elements in a group exhibit the same valency. For example, all the elements of group 1 (alkali metals) have valency *one* while all the elements of group 2 (alkaline earth metals) exhibit a valency of *two*.

Noble gases present in group 18 are *zerovalent*, *i.e.*, their valency is *zero* since these elements are chemically inert.

PROBLEMS ON VALENCE

EXAMPLE 4.16. *Predict the formulae of the stable binary compounds that would be formed by the following pairs of elements.*

(a) silicon and oxygen (b) aluminium and bromine (c) calcium and iodine (d) element 114 and fluorine (e) element 120 and oxygen. **(N.C.E.R.T.)**

Solution. (*a*) Silicon belongs to group 14. It has four valence electrons and hence its valence = 4 oxygen belongs to group 16. It has six electrons in the valence shell and hence its valence = 8 – 6 = 2. Therefore, the formula of silicon oxide = SiO_2.

(*b*) Aluminium belongs to group 13. It has three electrons in the valence shell and hence its valence = 3.

Bromine belongs to group 17. It has seven electrons in the valence shell and hence its valence = 8 – 7 = 1.

Therefore, formula of aluminium bromide = $AlBr_3$.

(*c*) Calcium belongs to group 2. It has two electrons in the valence shell and hence its valence = 2. Iodine belongs to group 17. It has seven valence electrons and its valence = 8 – 7 = 1.

Therefore, formula of calcium iodide = CaI_2.

(*d*) In the 7th period, the 4th transition series ends at element with Z = 112, therefore, filling of 7*p*-subshell will begin with element Z = 113. Hence, element with Z = 114 will have two electrons in 7*p*-orbitals and two electrons in 7*s*-orbital. In other words, the element Z = 114 will lie in group 14 and hence its valence = 4.

Fluorine belongs to group 17 with seven valence electrons and hence its valence = 8 – 7 = 1.

Therefore, formula of compound formed by element 114 and fluorine is MF_4 where M represents the element.

(*e*) The 7th period will end at element with Z = 118. Therefore, filling of 8th shell *i.e.* 8 *s*-orbital will begin with element Z = 119 and consequently element with Z = 120 will belong to group 2 and its valence will be = 2.

Oxygen belongs to group 16 with six valence electrons and hence its valence = 8 – 6 = 2.

Therefore, formula of compound formed by element Z = 120 and oxygen will be MO where M represents the element.

PROBLEMS FOR PRACTICE

1. Predict the formulae of the stable binary compounds that would be formed by the following pairs of elements :
   (*a*) silicon and bromine (*N.C.E.R.T.*)
   (*b*) aluminium and sulphur (*N.C.E.R.T.*)
   (*c*) calcium and oxygen (*d*) aluminium and carbon.
2. Predict the formulae of the stable binary compounds formed by the following pairs of elements :
   (*a*) element with Z = 116 and hydrogen
   (*b*) element with Z = 113 and fluorine
   (*c*) Uup and sulphur (*d*) Uue and Uus.

ANSWERS

1. (*a*) $SiBr_4$ (*b*) Al_2S_3 (*c*) CaO (*d*) Al_4C_3
2. (*a*) H_2M (*b*) MF_3 (*c*) M_2S_3 where M (Z = 115) (*d*) MX where M (Z = 119) and X (Z = 117) are the elements.

ADD TO YOUR KNOWLEDGE

1. *Addition of first electron to a neutral atom is an* ***exergic process*** *while that of second electron is an* **endoergic process.**
2. *Osmium (Os) has the highest oxidation state (+ 8) or valency (8).*
3. *Among solids, osmium has the highest density of 22·6 while among liquids, mercury has the highest density of 13·6.*
4. *Among metals, tungston (W) has the highest melting point (3683 K) while among non-metals, carbon has the highest melting point (4000 K). Of all the elements, helium, however, has the lowest boiling point (4·2 K).*

Conceptual Questions

Q. 1. Would you regard Zn (Z = 30), Cd (Z = 48) and Hg (Z = 80) as *s*- or *d*-block elements ? Give reasons for your answer.

Ans. The last electron in Zn, Cd and Hg enters the 4*s*, 5*s* and 6*s*-orbitals respectively. Therefore, *on the basis of type of orbital being filled, these three elements should be regarded as s-block elements.* But the properties of these elements resemble more the *d*-block rather than *s*-block elements as listed below:

(*i*) Zn, Cd and Hg like other *d*-block elements form complexes but *s*-block elements usually do not.

(*ii*) Zn, Cd and Hg like other *d*-block elements form many covalent compounds whereas *s*-block elements form only ionic compounds.

(*iii*) Like other *d*-block elements, the first ionization energies of Zn, Cd and Hg are much higher than those of the *s*-block elements of the same period.

(*iv*) Like other *d*-block elements, the atomic radii of Zn, Cd and Hg are much lower than those of the *s*-block elements of the same period.

(*v*) Like other *d*-block elements, the electrode potentials of Zn, Cd and Hg are much less negative than those of *s*-block elements of the same period.

From the above discussion, *it is clear that the properties* of Zn, Cd and Hg resemble more the *d*-block elements rather than the *s*-block elements.

Further, to make the periodic classification of elements more rational, it is better to study them along with the *d*-block elements.

Q. 2. How many elements can be accommodated in the present set up of the long form of the periodic table? Explain.

Ans. In the present set up of the long form of the periodic table, we have seven periods (*i.e.*, principal quantum number, *n* = 7) and four blocks (*s, p, d*- and *f*-block elements). Therefore, the maximum number of elements which can be accommodated in the present set up of the long form of the periodic table in accordance with Aufbau principle is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,5p^6\,6s^2\,4f^{14}\,5d^{10}\,6p^6\,7s^2\,5f^{14}\,6d^{10}\,7p^6 = 118$.

Q. 3. Can an element with atomic number 126, if discovered, be accommodated in the present set up of the long form of the periodic tabel ?

Ans. No. The maximum number of elements which can be accommodated in the present set up of the long form of the periodic table is 118. Thereafter, filling of 8*s*-orbital shall begin which will accommodate only two electrons. After 8*s*-orbitals, the filling of 5*g*-orbitals will begin. Since we do not have any provision for *g*-block elements in the present set up of the long form of the periodic table, therefore, an element with atomic number 126, if discovered, cannot be accommodated in the present set up of the long form of the periodic table.

Q. 4. What would be the atomic number of the next (*i*) alkali metal (*ii*) alkaline earth metal (*iii*) halogen and (*iv*) inert gas, if discovered in future ?

Ans. (*i*) The next alkali metal, if discovered will, have to be placed in the eighth period and hence its outer electronic configuration will be $8s^1$. Therefore, its atomic number will be (118 + 1) = 119.

(*ii*) Similarly, the next alkaline earth metal, if discovered, will have $8s^2$ as its outer electronic configuration and hence its atomic number will be (118 + 2) = 120

(*iii*) The next halogen, if discovered, will have $7s^2\,7p^5$ as its outer electronic configuration. Since the filling of 7*p*-orbitals will begin after 6*d*- orbitals and up to 6*d*-orbitals, in accordance with Aufbau principle, we can accommodate only 112 elements, therefore, the atomic number of the next halogen, if discovered, will be (112 + 5) = 117.

(*iv*) In a similar way, we can easily explain, that the next inert gas, if discovered, will have $7s^2\,7p^6$ as its outer electronic configuration and its atomic number will be (112 + 6) = 118.

Q. 5. What are super heavy elements ?

Ans. Elements with Z > 100 which have high densities are called super heavy elements.

Q. 6. What would be IUPAC names and symbols for elements with atomic numbers 122, 127, 135, 149 and 150 ?

Ans. From the Table 4.5, the roots for 2, 7, 5, 9 and 0 are *bi, sept, pent, enn* and *nil* respectively. Therefore, their names and symbols are :

Z	Name	Symbol
122	Unbibium	Ubb
127	Unbiseptium	Ubs
135	Untripentium	Utp
149	Unquadennium	Uqc
150	Unpetnilium	Upn

Q. 7. Arrange the following elements

(*i*) in the increasing order of metallic character : Si, Be, Mg, Na, P. *(N.C.E.R.T.)*

(*ii*) in the increasing order of non-metallic character : B, C, Si, N, F. *(N.C.E.R.T.)*

Ans. (*i*) Arranging the elements into different groups and periods in order of their increasing atomic numbers, we have,

1	2	13	14	15
—	Be	—	—	—
Na	Mg	—	Si	P

We know that the metallic character increases down a group and decreases along a period as we move from left to right. Therefore, Na is the most metallic element, followed by Mg and Si, while P is the least metallic element. Among Be and Mg, Mg is more metallic than Be. Therefore, the overall increasing order of metallic character is P < Si < Be < Mg < Na.

(*ii*) Arranging the elements into different groups and periods in order of their increasing atomic numbers, we have,

13	14	15	16	17
B	C	N	—	F
—	Si	—	—	—

Since the metallic character increases down the group and non-metallic character increases along a period from left to right, therefore, Si is the most metallic or the least non-metallic element. The overall increasing order of non-metallic character is : Si < B < C < N < F.

Q. 8. The element 119 has not been discovered. What could be the IUPAC name and symbol for this element ? On the basis of the periodic table, predict the electronic configuration of this element and also the formula of its most stable chloride and oxide. *(N.C.E.R.T.)*

Ans. (*i*) The roots for 1 and 9 are *un* and *enn* respectively. Therefore, the name for the element with Z = 119 is un + un + enn + ium = **ununennium** and its symbol is **Uue.**

(*ii*) The maximum number of elements which can be accommodated in the present set up of the long form of the periodic table = 118 (For details refer to **Q. 2** on page 4/43). Since this last element would be an inert gas, therefore, the element with Z = 119 will be an alkali metal and hence its outer electronic configuration will be $8s^1$ or its complete electronic configuration will be $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}$ $5s^2\ 5p^6\ 5d^{10}\ 5f^{14}\ 6s^2\ 6p^6\ 6d^{10}\ 7s^2\ 7p^6\ 8s^1$.

(*iii*) Since the element with Z = 119 will be an alkali metal, therefore, formula of its chloride will be **MCl** and that of its stable oxide will be **M_2O** where M is the alkali metal.

Q. 9. Why has the zero group been placed at the extreme right of the periodic table ?

Ans. This is in accordance with their electronic configurations because each period starts with the fillig of *s*-subshell and is complete after the filling of *p*-subshell of the same principal shell.

Q. 10. Which of the elements Na, Mg, Si and P would have the greatest difference between the first and the second ionization enthalpies. Briefly explain your answer. *(N.C.E.R.T)*

Ans. Among Na, Mg, Si and P, Na is an alkali metal. It has only one electron in the valence shell, therefore, its IE_1 is very low. However, after removal of one electron, it acquires neon gas configuration, *i.e.*, Na^+ $(1s^2\ 2s^2\ 2p^6)$. Therefore, its IE_2 is expected to be very high. Consequently, the difference in first and second ionization enthalpies would be greatest is case of Na.

However, it may be noted here that in case of Mg, Si and P, although their IE_1 will be much higher than that of Na but their IE_2 will be much lower than that of Na. As a result, the difference in their respective IE_1 and IE_2 would be much lower than that of Na.

Q. 11. The first ionization enthalpy of magnesium is higher than that of sodium. On the other hand, the second ionization enthalpy of sodium is much higher than that of magnesium. Explain *(N.C.E.R.T.)*

Ans. The first electron in both the cases has to be removed from the 2*s* orbital but nuclear charge of Na is less than that of Mg. After the loss of first electron, the electronic configuration of Na^+ is $1s^2\ 2s^2\ 2p^6$, *i.e.*, that of noble gas which is very stable and hence the removal of second electron is very difficult. In case of Mg, after the loss of one electron, electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^1$. Here, the second electron is to be removed from 3*s* orbital which is easier.

Q. 12. Arrange the following ions in the order of increasing size ?

Be^{2+}, Cl^-, S^{2-}, Na^+, Mg^{2+}, Br^-. *(N.C.E.R.T.)*

Ans. Arranging the given ions into different groups and periods in order of increasing atomic numbers of their respective elements, we have,

Group No.	1	2	16	17
2nd period	—	Be^{2+}	—	—
3rd period	Na^+	Mg^{2+}	S^{2-}	Cl^-
4th period	—	—	—	Br^-

Consider the following points :

(*i*) The sizes of anions are usually bigger than those of the cations, *i.e.*, the sizes of S^{2-}, Cl^- and Br^- ions are bigger than those of Be^{2+}, Mg^{2+} and Na^+ ions.

(*ii*) Within a group, the ionic size increases from top to bottom, therefore, *ionic size of Mg^{2+} ion is bigger than that of Be^{2+}. Likewise, ionic size of Br^- is bigger than that of Cl^- ion.*

(*iii*) Among isoelectronic ions, higher the +ve charge, smaller is the size. Thus, *ionic size of Na^+ is bigger than that of Mg^{2+}*. Further, among isoelectronic ions, higher the –ve charge, bigger is the size. Thus, *ionic size of S^{2-} is bigger than that of Cl^- ion.*

Further, the increase in ionic size due to addition of one more shell is usually greater than increasing the negative charge by one unit, therefore, *the ionic size of Br^- is expected to be bigger than S^{2-} ion.*

Combining all the above views, the ionic size of all the listed ions increases in the order :

$$Be^{2+} < Mg^{2+} < Na^+ < Cl^- < S^{2-} < Br^-.$$

Q. 13. Among the elements B, Al, C and Si

(*a*) Which has the highest first ionization enthalpy ?

(*b*) Which has the most negative electron gain enthalpy ?

(*c*) Which has the largest atomic radius ?

(*d*) Which has the most metallic character ? *(N.C.E.R.T.)*

Ans. Arranging the given atoms in different periods and groups in order of their increasing atomic numbers, we have,

Group	13	14
2nd period	B	C
3rd period	Al	Si

(*a*) Since IE_1 increases along a period but decreases down a group, Therefore *C has the highest first ionization enthalpy.*

(*b*) Since electron gain enthalpies become more negative along a period and less negative down a group, therefore, *C has the most negative electron gain enthalpy.*

(*c*) Since atomic radii decrease along a period but increase down a group, therefore, *Al has the largest atomic radius.*

(*d*) Since metallic character decreases along a period, but increases down a group, therefore, *Al has the most metallic character.*

Q. 14. Consider the elements N, P, O, S and arrange them in order of

(*a*) increasing first ionization enthalpy

(b) increasing negative electron gain enthalpy

(c) increasing non-metallic character. (N.C.E.R.T.)

Ans. Arranging all the given elements into different groups and periods in order of their increasing atomic numbers, we have,

Group	15	16
2nd period	N	O
3rd period	P	S

(a) Since IE_1 decreases down a group, therefore, IE_1 of N and O are higher than those of P and S. Further since N has more stable exactly half- filled electronic configuration in the 2*p*-subshell, therefore, it is more difficult to knock out an electron from N than from O even though O has higher nuclear charge. Similarly, P has exactly half-filled electronic configuration in the 3*p*-subshell. Therefore, IE_1 of P is higher than that of S.

Thus, the overall increasing order of first ionization enthalpy of these elements follows the order :

$S < P < O < N.$

(b) Since adding an electron to smaller size 2*p*- orbital causes greater repulsion than adding an electron to larger 3*p*-orbital, therefore, electron gain enthalpies of P and S are more negative than those of N and O respectively. Further since S has higher nuclear charge but P has more stable exactly half-filled electronic configuration in the 3*p*-subshell, therefore, it is easier to add an electron to S than to P. In other words, electron gain enthalpy of S is more negative than that of P.

Similarly, N has exactly half-filled electronic configuration in the 2*p*-subshell but O has higher nuclear charge. But the addition of an electron to N causes repulsions to such an extent, that electron gain enthalpy of N is actually positive while that of O as expected is negative.

Combining to above results the increasing order of negative gain enthalpy of these elements follows the order :

$N < P < O < S.$

(c) Since non-metallic character decreases down a group but increases along a period, therefore, O is the most non-metallic element while P is the least non-metallic element. The actual order of increasing non-metallic character is : $P < S < N < O.$

Q. 15. **Which of the following species will have the largest and the smallest size ?**

Mg, Mg^{2+}, Al, Al^{3+} (N.C.E.R.T.)

Ans. (i) Mg and Al belong to the third period. Across a period, atomic radii decrease due to increased nuclear charge. Therefore, *atomic size of Al is smaller than that of Mg.*

(ii) Further, cations are smaller than their parent atoms. Therefore, *Mg^{2+} is smaller than Mg and Al^{3+} is smaller than Al.*

(iii) Mg^{2+} and Al^{3+} are isoelectronic ions. Among isoelectronic ions, higher the +ve charge, smaller the size. Therefore, *atomic radius of Al^{3+} is smaller than that of Mg^{2+}.*

From the above discussion, it follows that *Mg has the largest while Al^{3+} has the smallest size.*

Q. 16. **Arrange the following ions in order of decreasing ionic radii : Li^{2+}, He^{+}, Be^{3+}.**

Ans. He^{+}, Li^{2+} and Be^{3+} are all isoelectronic ions. Among isoelectronic ions, ionic radius decreases as the positive charge increases. Therefore, the ionic radii decrease in the order : $He^{+} > Li^{2+} > Be^{3+}$.

Q. 17. **Arrange the following in order of decreasing *van der Waals'* radii : Cl, H, O, N.**

Ans. The *van der Waals' radii increase* as the number of energy shells increases and decreases as the nuclear charge increases. Since H has only one energy shell, and Cl has three, therefore, the *van der Waals' radius* of H is the smallest while that of Cl is the biggest. Further both N and O have two energy shells but the nuclear charge on O (+ 8) is higher than that on N (+ 7), therefore, the *van der Waals'* radius of N is bigger than that of O. *Thus, the overall decreasing order is :*

$Cl > N > O > H.$

Very Short Answer Questions CARRYING 1 MARK

Q. 1. What are horizontal rows and vertical columns of the periodic table called ?

Ans. Horizontal rows are called periods while vertical columns are called groups.

Q. 2. What is the basis of classification of elements in the long form of the periodic table ?

Ans. Physical and chemical properties of the elements are a periodic function of their atomic numbers.

Q. 3. Name the groups of elements classified as *s*, *p* and *d* blocks.

Ans. *s*-block = 1, 2, *p*-block = 13 to 18, *d*-block = 3 to 12.

Q. 4. What are the atomic numbers of elements which constitute *f*-block (lanthanoids and actinoids) ?

Ans. Lanthanoids = 58 to 71, Actinoids = 90 to 103.

Q. 5. Compare the size of (*a*) Na atom with Na^+ ion (*b*) Cl atom with Cl^- ion.

Ans. (*a*) $Na^+ < Na$ (*b*) $Cl^- > Cl$

Q. 6. Al atom loses electrons successively to form Al^+, Al^{2+} and Al^{3+} ions. Which step will have highest ionization energy ?

Ans. $Al^{2+} \longrightarrow Al^{3+} + e^-$

Q. 7. Why ionization enthalpy of nitrogen is greater than that of oxygen ?

Ans. Nitrogen has exactly half-filled *p*-orbitals.

Q. 8. Why electron gain enthalpies of Be and Mg are positive ?

Ans. They have fully filled *s*-orbitals and hence have no tendency to accept an additional electron. Consequently energy has to be supplied if an extra electron has to be added to the much higher energy *p*-orbitals of the valence shell. That is why electron gain enthalpies of Be and Mg are positive.

Q. 9. Which important property did Mendeleev use to classify the elements in his periodic table ?

Ans. Mendeleev used the atomic masses of the elements in classifying the elements in his preiodic table. According to his law, the properties of elements are a periodic function of their atomic weights.

Q. 10. State the modern periodic law.

Ans. Modern periodic law states that physical and chemical properties of the elements are a periodic function of their atomic numbers.

Q. 11. What would be the IUPAC name and symbol for the element with atomic number 120 ?

Ans. Unbinilium, Ubn.

Q. 12. Which one among the following elements has the lowest first ionisation enthalpy and which one has the highest first ionisation enthalpy ? Li, K, Ca, S and Kr.

Ans. K has the lowest ionisation enthalpy and Kr has the highest ionisation enthalpy.

Q. 13. Lanthanoids and actinoids are placed in separate rows at the bottom of the periodic table. Explain the reason for this arrangement.

Ans. These have been placed separately at the bottom of the periodic table for convenience. If they are placed in the body of the periodic table, the periodic table will become extremely long and cumbersome.

Q. 14. Give four examples of species which are isoelectronic with Ca^{2+}.

Ans. Ar, K^+, Cl^-, S^{2-} or P^{3-} are isoelectronic with Ca^{2+}

Q. 15. State giving clear explanation why argon (atomic weight = 39.9) has been rightly placed before potassium (atomic weight 39.10) in the periodic table.

Ans. This is because argon (Z = 18) has lower atomic number than potassium (Z = 19).

Q. 16. Which has a larger radius ? (*i*) Mg or Ca (*ii*) S or Cl.

Ans. (*i*) Ca (*ii*) S.

Q. 17. In terms of electronic configuration, what the elements of a given period and a group have in common ?

Ans. For elements in a period the number of shells is equal and for elements in a group the number of electrons in the outermost shell (valence shell) is the same.

Q. 18. Which two elements of the following belong to the same period ? Al, Si, Ba and O.

Ans. Al and Si.

Q. 19. Which of the following elements has most positive electron gain enthalpy ? Fluorine, nitrogen, neon.

Ans. Both nitrogen and neon have positive electron gain enthalpies but neon has much higher positive electron gain enthalpy because of its much more stable inert gas configration than the less stable exactly half-filled electronic configuration of nitrogen.

Q. 20. From amongst Be, B and C, choose the element with highest first ionization enthalpy.

Ans. Carbon because of its higher nuclear charge and smaller size has the highest IE_1 amongst the given elements.

Q. 21. Which among the following are transition and which are inner transition elements ?

Sg, Bk, Er, Fm, Fe, Pb, Cr, Ca, Ar, Zr, Ce

Ans. Transition elements : Sg, Fe, Cr, Zr

Inner transition elements : Bk, Er, Fm, Ce

Q. 22. Name the elements in the periodic table which has the highest and lowest first ionization enthalpies.

Ans. Highest : Helium and lowest : Francium

Q. 23. Explain why chlorine can be converted into chloride ion more easily as compared to fluoride from fluorine.

Ans. Electron gain enthalpy of Cl is more negative than that of F.

Q. 24. A monoatomic anion of unit charge contains 45 neutrons and 36 electrons. What is the atomic mass of the element and in which group of the periodic table does it lie ? *(West Bengal J.E.E. 2004)*

Ans. No. of neutrons of the monoatomic anion = 45

No. of electrons of the monoatomic anion = 36

∴ No. of electrons of the monoatomic atom = 36 − 1 = 35

∴ Atomic number of the atom (Z = 35). Therefore, the atom is bromine and it belongs to group 17, *i.e.* ; halogen family.

No. of protons = No. of electrons = 35

∴ Atomic mass = No. of neutrons + No. of electrons = 45 + 35 = 80

Q. 25. To which block (*s, p, d or f*) does the element with atomic number 50 belong ?

Ans. E.C. of Z = 50 is $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^{10}\, 4s^2\, 4p^6\, 4d^{10}\, 5s^2\, 5p^2$. Hence it a *p*-block element

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 4.1. to 4.6.

1. What was the need for classification of elements ?
2. Define Modern Periodic law. Give its theoretical justification.
3. What is the cause of periodicity in properties of the elements ? Explain with two examples.
4. Predict the density of Cs from the density of the following elements

K	0·86 g/cm^3	Ca	1·548 g/cm^3
Sc	2·991 g/cm^3	Rb	1·532 g/cm^3
Sr	2·68 g/cm^3	Y	4·34 g/cm^3
Cs	?	Ba	3·51 g/cm^3
		La	6·16 g/cm^3

[Ans. Between 1·532 and 2·68 g/cm^3 around 1·8 × 2·0 g/cm^3]

Sec. 4.7. to 4.13.

5. Describe the main features of the long form of the periodic table.
6. State modern periodic law. What are the main features of the long form of the periodic table ?
7. Explain briefly 'Groups' and 'Periods'. 'Transition' and 'Normal' elements in the long form of the periodic table.
8. On the basis of electronic configurations, justify that the second and third periods contains 8 elements each, 4th and 5th periods contain 18 elements each and the 6th period contains 32 elemnents.

9. Account for the fact that 4th period has eighteen and not eight elements.

10. Name the four blocks into which the elements of the periodic table have been classified. Why are they named so ? List the groups of periodic table belonging to each block.

11. What do you understand by 'Representative elements' ? Name the groups whose elements are called representative elements.

12. What are transition elements ? Why are they so called ? Name the different transition series.

13. Which elements are called inner transition elements ? Name the different inner transition series. Why are they so named ?

14. Describe the main characteristics of *s, p, d* and *f*-block elements. ***(N.C.E.R.T.)***

15. Name different blocks of elements in the periodic table. Give the general electronic configuration of each block.

16. Though copper, silver and gold atoms have completely filled sets of *d*-orbitals yet they ae called transition metals. Why ? ***(H.S.B. 1998)***

17. The values for three of the quantum numbers for the last electron in A and B are listed below. In what families of the periodic table are these elements present ?

	l	*m*	*s*
A	1	+1	+1/2
B	3	−2	−1/2

[Ans. A = *p*-Block element, B = *f*-Block elements]

18. Elements A, B, C and D have atomic numbers 12, 19, 29, and 36 respectively. On the basis of electronic configuration write to which group of the periodic table each element belongs.

Sec. 4.14. **19.** Define the term ionization enthalpy ? How does it vary along a period and along a group ?

20. What do you understand by the term successive ionization enthalpies ? Explain why second ionization is always greater than the first ionization energy ?

21. Define ionization enthalpy. What are its units ? What is the principle of its measurement ?

22. Discuss briefly the various factors on which ionization enthalpy depends.

23. Why does the first ionization enthalpy increase as we go from left to right across a given period of the periodic table ? ***(N.C.E.R.T.)***

24. Explain why ionization enthalpies decrease down a group of the periodic table ? ***(N.C.E.R.T.)***

25. The first five successive ionization enthalpies of boron atom are 800, 2427, 3658, 25024 and 32824 kJ mol^{-1}. Explain these ionization enthalpies.

26. Explain the following :

(*i*) Ionization enthalpy of Mg is more than that of Na and Al.

(*ii*) Ionization enthalpy of nitrogen is more than that of oxygen.

27. Why is the ionization enthalpy of Be more than that of B ? Explain.

28. If we consider ionization enthalpies of elements in the second period from Li to Ne, they ordinarily increase but Be and N have higher ionization enthalpies than B and O respectively which succeed them. Why is it so ?

Sec. 4.15. **29.** Explain the term electron gain enthalpy ? How does it vary along a group and across a period.

30. Explain the terms ionization enthalpy and electron gain enthalpy ?

31. What do you mean by successive electron gain enthalpies? Why is the second electron enthalpy of an atom positive?

32. Halogens have very high negative electron gain enthalpies. Explain.

33. Electron gain enthalpy of fluorine is less negative than that of chlorine. Explain.

34. Electron gain enthalpy of noble gases in positive. Explain.

35. In each of the following pairs, state which atom/ion has higher ionization enthalpy and more negative electron gain enthalpy ?

(*a*) I, I$^-$ (*b*) Br, Br$^-$ (*c*) Li, Li$^+$ (*d*) Br, I.

36. Arrange the following as stated : Increasing order of ionic size (N^{3-}, Na^+, F^-, O^{2-}, Mg^{2+})

[Ans. $Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$ (All are isoelectrnic ions. Hence greater the nuclear charge, smaller is the size)]

Sec. 4.16. to 4.18. **37.** What do you understand by periodic properties of elements ? Name any three such properties.

38. How do atomic sizes vary in a group and in a period? Give reasons for the variations.

39. What is meant by atomic and ionic radii ? Explain giving reasons why the size of Cl^- ion is greater than that of Cl atom whereas size of Na^+ ion is smaller than that of Na atom ?

40. The size of an anion is larger than that of its parent atom. Give reasons.

41. The size of a cation is smaller than that of its parent atom. Give reasons.

42. Mg^{2+} ion is smaller than O^{2-} ion although both have the same electronic configuration.

43. What are isoelectronic species ? Give examples to illustrate your answer.

44. The valence of representative elements is either equal to the number of the valence electrons or eight minus this number. What is the basis of this rule ?

MISCELLANEOUS QUESTIONS

45. Among the elements of the second period, Li to Ne, pick out the element

(*i*) with the highest first ionization energy (*ii*) with the highest electronegativity

(*iii*) with the largest atomic size (*iv*) that is the most reactive non-metal

(*v*) that is the most reactive metal. **[Ans. (*i*) Ne (*ii*) F (*iii*) Ne (*iv*) F and (*v*) Li]**

46. Among the elements of the third period, Na to Ar, pick out the element

(*i*) with the highest first ionization enthalpy

(*ii*) with the largest atomic radius

(*iii*) that is the most reactive non-metal

(*iv*) that is the most reactive metal. *(N.C.E.R.T.)* **[Ans. (*i*) Ar (*ii*) Ar (*iii*) Cl (*iv*) Na]**

47. For the main group of the periodic table, the metallic properties of the elements vary approximately with their position as shown in the table.

1	2	13	14	15	16	17	18
H							He
A				B			
C				D			

(*i*) Will the most metallic element be found at A, B, C or D ?

(*ii*) Will the most non-metallic element be found at A, B, C or D ? **[Ans. (*i*) C (*ii*) B]**

48. A, B, C are three elements in which B is an inert gas other than helium. With this information complete the following table.

Also explain the following :

Element	Atomic Number	No. of electrons in the valence shell	Group to which the element belongs
A	Z—1	....	....
B	Z	....	....
C	Z+1	....	....

(*i*) Electron affinity of element A is more than that of element C

(*ii*) Ionization energy of element C is less than that of element A

(*iii*) Electron affinity of B is zero. **[Ans. A = F, B = Ne and C = Na]**

49. Name the groups and periods of the elements having atomic numbers 18 and 26. What are possible valencies of the above elements ?

[Ans. E.C. of the element with Z = 18 is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$. It belongs to group 18 and 3rd period. Its valency will be zero.

E.C. of the element with Z = 26 is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$. It belongs to 8th group and 4th period. Its most common valencies are 2 and 3]

Long Answer Questions CARRYING 5 or more MARKS

Sec. 4.1. to 4.13.

1. Describe the main features of the long form of the periodic table. In what respects is it superior to Mendeleev's table ?

2. Name the four blocks of elements in the periodic table and indicate the main difference in their electronic configurations. Give examples of each type. State at least four characteristics of each block.

Sec.4.14. to 4.18.

3. Define ionization enthalpy and successive ionization enthalpies. Discuss the factors that influence the magnitude of ionization enthalpy. What are the general trends of variation of ionization enthalpy in the periodic table ? Explain.

4. Define electron gain enthalpy. Describe the factors which determine the magnitude and sign of electron gain enthalpy. What are the general trends of variation of electron gain enthalpies in periodic table ?

5. Discuss the trends in atomic sizes of elements in the periodic table.

6. Explain what you understand by covalent radius, van der Waal's radius, ionic radius and atomic radius. How do they vary in a period and in a group?

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Bridge elements. In the Mendeleev's Periodic table, the elements of the third period are also called **bridge elements** since the division of each main group into two subgroups A and B starts from these elements. For example, in the second group, Mg acts as the bridge element between Ca of group II A and Zn of group II B. Similarly, Al acts as the bridge element between Ga (III A) and Sc (III B) and Si acts as bridge element between Ge (IV A) and Ti (IV B). The properties of bridge elements are somewhat in between the properties of the elements of the two subgroups. For example, Mg shows similarities with other alkaline earth metals (II A) on one hand and elements of zinc group (II B) on the other hand.

2. Covalent radius and multiplicity of bonds. It may be noted that the relationship that covalent radius of an atom is equal to one-half of the inter-nuclear distance between two bonded atoms is correct only when the two atoms are linked by a single covalent bond and not by double and triple bonds. For example, carbon-carbon single (C—C) bond, double (C = C) bond and triple (C ≡ C) bond distances are 154, 134 and 120 pm respectively but only $154/2 = 77\ pm$ (and not $134/2 = 67\ pm$ or $120/2 = 60\ pm$) represents the covalent radius of carbon atom.

3. Bond length of heteronuclear diatomic molecules.

For a heteronuclear diatomic molecule (AB) in which the atoms A and B are linked by a single covalent bond, the bond length (d_{A-B}) is given by the following relations.

(*i*) *When the atoms A and B have nearly the same electronegativity,*

$$d_{A-B} = r_A + r_B$$

where r_A and r_B are the covalent radii of the atoms A and B respectively.

(*ii*) *When the atoms A and B have different electronegativities,*

$$d_{A-B} = r_A + r_B - 0{\cdot}09\ (x_A - x_B)$$

where x_A and x_B are the electronegativities of the atoms A and B respectively.

This relation was given by **Shoemaker and Stevenson.**

C.B.S.E.-P.M.T. (MAINS) SPECIAL

A. SUBJECTIVE QUESTIONS (Common with I.I.T.)

Q. 1. Arrange the elements of second period in order of increasing second ionization enthalpies.

Ans. The electronic configuration of the ions obtained after removal of first electron from the elements of 2nd period from left to right are : Li^+ ($1s^2$), Be^+ ($1s^2 2s^1$), B^+ ($1s^2 2s^2$), C^+ ($1s^2 2s^2 2p^1$), N^+ ($1s^2 2s^2 2p^2$), O^+ ($1s^2 2s^2 2p^3$), F ($1s^2 2s^2 2p^4$) and Ne^+ ($1s^2 2s^2 2p^5$).

The following conclusions can be drawn from the above configurations :

(*i*) Li^+ has noble gas, *viz.*, He gas configuration, therefore, *IE_2 of Li is the highest in the second period.*

(*ii*) Since in B^+, the electron has to be removed from a more stable fully filled 2 *s*-orbital while in Be^+, it has to be lost from the less stable half-filled 2*s*-orbital and furthermore, the loss of an electron from Be^+ gives more stable Be^{2+} ion with noble gas configuration, therefore, *IE_2 of Be is lower than that of B.*

(*iii*) Since less energy is required to remove an *s*-electron than a *p*-electron of the same energy level, therefore, more energy is required to remove a 2*s*-electron from B^+ ($1s^2 2s^2$) than a 2*p*-electron from C^+ ($1s^2 2s^2 2p^1$). In other words, *IE_2 of C is lower than that of B.*

(*iv*) As we move from C to N to O, the nuclear charge increases by one unit at a time, therefore, their IE_2 also increase accordingly. In other words, *IE_2 of O is higher than that of N which, in turn, is higher than that of C.*

(*v*) In case of O^+ ($1s^2 2s^2 2p^3$) an electron is to be lost from an exactly half-filled 2*p*-orbital but in case of F^+ ($1s^2 2s^2 2p^4$) this is not so. However, loss of an electron from F^+ gives an exactly half-filled 2*p*-orbital (*i.e.*, F^{2+} ($1s^2 2s^2 2p^3$)), therefore, *IE_2 of F should be lower than that of O.*

(*vi*) Lastly due to highest nuclear charge in the 2nd period, *IE_2 of Ne is expected to be much higher than that of Li.*

From the above discussion, it follows that IE_2 of the elements of 2nd period increase in the order : *Be < C < B < N < F < O < Ne < Li.*

Q. 2. The first ionization energy of carbon atom is greater than that of boron whereas the reverse is true for the second ionization energy. Explain. **(*I.I.T. 1989*)**

Ans. E.C. of C-atom is $1s^2 2s^2 2p^2$ and E.C. of B-atom is $1s^2 2s^2 2p^1$. The first electron to be removed in both cases is from a 2*p*-orbital but nuclear charge of C is more than that of B. Therefore, the IE_1 of C is greater than that of B. After the removal of first electron, the second electron to be removed from C-atom is from a 2*p*-orbital whereas that from B-atom is from a 2*s* orbital. Since a *s*-orbital is more penetrating and hence is more strongly attracted by the nucleus than a *p*-orbital, therefore, IE_2 of B is higher than that of C.

Q. 3. Arrange the following ions in order of their increasing ionic radii :

Li^+, Mg^{2+}, K^+, Al^{3+} **(*I.I.T. 1997*)**

Ans. (*i*) The ionic radius of any cation increases as the number of energy shells increases and decreases as the magnitude of the positive charge increases.

(*ii*) Mg^{2+} ($1s^2 2s^2 2p^6$) and Al^{3+} ($1s^2 2s^2 2p^6$) are isoelectronic ions and each one of these has two energy shells. Since the positive charge on Al^{3+} is higher than that on Mg^{2+}, therefore, ionic radius *of Al^{3+} is lower than that of Mg^{2+}.*

(*iii*) Since K^+ ($1s^2 2s^2 2p^6 3s^2 3p^6$) has three shells and Mg^{2+} and Al^{3+} have two shells each, therefore, ionic radius of K^+ is the largest followed by Mg^{2+} and then Al^{3+}.

(*iv*) Now Li^+ ($1s^2$) has one shell and +1 charge but Al^{3+} ($1s^2 2s^2 2p^6$) has two shells and + 3 charge. Since the increase in the ionic radius of Al^{3+} due to the presence of two shells is more than counterbalanced by the decrease in its size due to an increase in charge from + 1 in Li^+ to +3 in Al^{3+}, therefore, *the ionic radius of Al^{3+} is lower than that of Li^+*

Thus, the ionic radii of these four ions increase in the order : $Al^{3+} < Li^+ < Mg^{2+} < K^+$.

B. PROBLEMS

Problem 1. **Classify the elements having atomic numbers as given below into three separate pairs on the basis of similar chemical properties. Give brief electronic explanation : 9, 12, 16, 34, 53, 56.**

(*West Bengal J.E.E. 2003*)

Solution. The second period ends at atomic number 10 while the third period ends at atomic number 18. Therefore, 9, 12 and 16 are the first elements in their respective groups. The atomic numbers of the other elements of the same group can be deduced by adding magic numbers of 8, 18, 18 and 32 to elements of 2nd period and by adding magic numbers of 18, 18 and 32 to the elements of 3rd period. Thus, $9 + 8 + 18 + 18 = 53$

$$12 + 8 + 18 + 18 = 56$$

$$16 + 18 = 34$$

elements with atomic numbers 9 (F) and 53 (I) belong to halogen family (Group 17) ; elements with atomic numbers 12 (Mg) and 56 (Ba) belong to alkaline earth metals (Group 2) while elements with atomic numbers 16(S) and 34 (Se) belong to oxygen family (Group 16) For electronic configurations refer to the text.

Problem 2. **Give the name and atomic number of the inert gas atom in which the total number of *d*-electrons is equal to the difference in numbers of total *p* and *s*-electrons.** ***(West Bengal J.E.E. 2003)***

Solution. The first inert gas which contains *d*-electrons is krypton. Its atomic number is 36 and its electronic configuration is :

$$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6.$$

Total number of *d*-electrons = 10

Total number of *p*-electrons = 6 + 6 + 6 = 18

Total number of *s*-electrons = 2 + 2 + 2 + 2 = 8

∴ Difference in total number of *p*-and *s*-electrons = 18 − 8 = 10.

Thus, the inert gas is krypton.

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. In long from of the periodic table, the properties of the elements are a periodic function of their
(*a*) atomic size (*b*) ionization energy
(*c*) atomic mass (*d*) atomic number.

2. Total number of vertical columns (groups) in the long form of the periodic table is :
(*a*) 8 (*b*) 18
(*c*) 17 (*d*) 16.

3. Number of elements present in the 3rd period is
(*a*) 6 (*b*) 32
(*c*) 18 (*d*) 8.

4. The number of periods in the periodic table is
(*a*) 6 (*b*) 7
(*c*) 8 (*d*) 10.

5. The general outer electronic configuration of transition metals is
(*a*) $ns^2\,nd^{1-10}$ (*b*) $ns^2\,np^1\,(n-1)\,d^{1-10}$
(*c*) $ns^2\,np^6\,(n-1)\,d^{1-10}$ (*d*) $ns^{0-2}\,(n-1)\,d^{1-10}$.

6. An element with atomic number 106 has been discovered recently. Which of the following electronic configurations will it possess ?
(*a*) $[Rn]\,5f^{14}\,6d^4\,7s^2$ (*b*) $[Rn]\,5f^{14}\,6d^5\,7s^1$
(*c*) $[Rn]\,5f^{14}\,6d^6\,7s^0$ (*d*) $[Rn]\,5f^{14}\,6d^1\,7s^2\,7p^3$.

7. Which of the following combinations contains only isoelectronic species ?
(*a*) N^{3-}, O^{2-}, Cl^-, Ne (*b*) F^-, Ar, S^{2-}, Cl^-
(*c*) P^{3-}, S^{2-}, Cl^-, Ar (*d*) N^{3-}, F^-, O^{2-}, Ar.

8. If the ionic radii of K^+ and F^- are about 1·34 Å each, then the expected values of atomic radii of K and F should be respectively :
(*a*) 2·31 and 0·64 Å (*b*) 2·31 and 1·34 Å
(*c*) 0·64 and 2·31 Å (*d*) 1·34 and 1·34 Å

9. Which of the following processes involves absorption of energy ?
(*a*) $Cl + e^- \rightarrow Cl^-$ (*b*) $O^- + e^- \rightarrow O^{2-}$
(*c*) $O + e^- \rightarrow O^-$ (*d*) $S + e^- \rightarrow S^-$.

10. Which of the following elements will have highest electron affinity ?
(*a*) $[Ne]\,3s^1\,3p^2$ (*b*) $[Ne]\,3s^2\,3p^4$
(*c*) $[Ne]\,3s^2\,3p^5$ (*d*) $[Ne]\,3s^2\,3p^6\,3d^5\,4s^1$.

11. In which of the following compounds does the ratio of anion size to cation size has the lowest value ?
(*a*) CsI (*b*) LiI
(*c*) LiF (*d*) CsF.

12. Which of the following represents most electropositive element ?

ANSWERS

1. *d* **2.** *b* **3.** *d* **4.** *b* **5.** *d* **6.** *a* **7.** *c* **8.** *a* **9.** *b* **10.** *c*
11. *d*

(*a*) [He] $2s^1$
(*b*) [He] $2s^2$
(*c*) [Xe] $6s^1$
(*d*) [Xe] $6s^2$.

13. The correct order of electron affinities is
(*a*) O > S > Se
(*b*) O < S < Se
(*c*) O < Se < S
(*d*) S < Se < O.

14. The five successive ionization energies of an element are 800, 2427, 3658, 25024 and 32824 kJ mol^{-1} respectively. The number of valence electrons is
(*a*) 3
(*b*) 5
(*c*) 4
(*d*) 2.

15. Which of the elements whose atomic numbers are given below cannot be accommodated in the present set-up of the long form of the periodic table?
(*a*) 107
(*b*) 118
(*c*) 126
(*d*) 120

16. An element of the 4th period which has maximum number of unpaired electrons is
(*a*) $_{20}Ca$
(*b*) $_{24}Cr$
(*c*) $_{30}Zn$
(*d*) $_{33}As$

17. Which of the following isoelectronic ions has the lowest first ionization energy ?
(*a*) K^+
(*b*) Ca^{2+}
(*c*) Cl^-
(*d*) S^{2-}

18. Which among the following species has the same number of electrons in its outermost as well as penultimate shell ?
(*a*) Mg^{2+}
(*b*) O^{2-}
(*c*) F^-
(*d*) Ca^{2+}

19. The lowest first ionization energy would be associated with which of the following structures ?
(*a*) $1s^2\,2s^2\,2p^6\,3s^1$
(*b*) $1s^2\,2s^2\,2p^5$
(*c*) $1s^2\,2s^2\,2p^6$
(*d*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$
(B.I.T. Ranchi 1990)

20. Which of these does not affect the periodicity of the elements ?
(*a*) Bonding behaviour
(*b*) Electronegativity
(*c*) Ionization energy
(*d*) Neutron/proton ratio.
(B.I.T. Ranchi 1990)

21. The outermost electronic configuration of the most electronegative element is
(*a*) $ns^2\,np^3$
(*b*) $ns^2\,np^4$
(*c*) $ns^2\,np^5$
(*d*) $ns^2\,np^6$. *(I.I.T. 1990)*

22. Amongst the following elements (whose electronic configurations are given below), the one having the highest ionization energy is :
(*a*) [Ne] $3s^2\,3p^1$
(*b*) [Ne] $3s^2\,3p^3$
(*c*) [Ne] $3s^2\,3p^2$
(*d*) [Ar] $3d^{10}\,4s^2\,4p^3$.
(I.I.T. 1990)

23. The statement that is not correct for periodic classification of elements is
(*a*) The properties of elements are a periodic function of their atomic numbers.
(*b*) Non-metallic elements are less in number that metallic elements.
(*c*) The first ionization energies of elements along a period do not vary in a regular manner with increase in atomic number.
(*d*) For transition elements, the *d*-subshells are filled with electrons monotonically with increase in atomic number.
(I.I.T. 1992)

24. Which pair of atomic numbers represents *s*-block elements ?
(*a*) 7, 15
(*b*) 6, 12
(*c*) 9, 17
(*d*) 3, 12
(M.L.N.R. Allahabad 1992)

25. The electronic configuration of the element which is just above the element with atomic number 43 in the same-periodic group is
(*a*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^2$
(*b*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^5$
(*c*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,4s^1$
(*d*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1\,4p^6$.
(M.L.N.R. Allahabad 1992)

26. Which of the following transitions involves maximum amount of energy ?
(*a*) $M^-(g) \longrightarrow M(g)$
(*b*) $M(g) \longrightarrow M^-(g)$
(*c*) $M^+(g) \longrightarrow M^{2+}(g)$
(*d*) $M^{2+}(g) \longrightarrow M^{3+}(g)$.
(A.I.I.M.S. 1992)

27. Which electronic configuration of an element has abnormally high difference between second and third ionization energy ?
(*a*) $1s^2, 2s^2\,2p^6, 3s^1$
(*b*) $1s^2, 2s^2\,2p^6, 3s^2\,3p^1$
(*c*) $1s^2, 2s^2\,2p^6, 3s^2\,3p^2$
(*d*) $1s^2, 2s^2\,2p^6, 3s^2$.
(C.B.S.E. P.M.T. 1993)

28. The correct order of decreasing first ionisation energy is
(*a*) C > B > Be > Li
(*b*) C > Be > B > Li

ANSWERS

12. *c*	**13.** *c*	**14.** *a*	**15.** *c*	**16.** *b*	**17.** *d*	**18.** *d*	**19.** *a*	**20.** *d*	**21.** *c*
22. *b*	**23.** *d*	**24.** *d*	**25.** *a*	**26.** *d*	**27.** *d*				

(c) B > C > Be > Li (d) Be > Li > B > C.
(A.I.I.M.S. 1993)

29. Tick the correct order of second ionisation energy in the following :
(a) F > O > N > C (b) O > F > N > C
(c) O > N > F > C (d) C > N > O > F
(U.P. C.E.E. 1996)

30. Which of the following species has the highest electron affinity ?
(a) F^- (b) O
(c) O^- (d) Na^+
(Haryana C.E.E.T., 1996)

31. The electronic configuration of Gadolinium (At. No. 64) is
(a) [Xe] $4f^8\,5d^0\,6s^2$ (b) [Xe] $4f^7\,5d^1\,6s^2$
(c) [Xe] $4f^3\,5d^5\,6s^2$ (d) [Xe] $4f^6\,5d^2\,6s^2$
(C.B.S.E. P.M.T. 1997)

32. The *incorrect* statement among the following is —
(a) The first ionization potential of Al is less than the first ionization potential of Mg.
(b) The second ionization potential of Mg is greater than the second ionization potenital of Na.
(c) The first ionization potential of Na is less than the first ionization potential of Mg
(d) The third ionization potential of Mg is greater than the third ionization potential of Al.
(I.I.T. 1997)

33. The first ionization potential (eV) of Be and B respectively are
(a) 8·29, 9·32 (b) 9·32, 8·29
(c) 9·32, 9·32 (d) 8·29, 8·29
(C.B.S.E. P.M.T. 1998)

34. In crystals of which of the following ionic compounds, would you expect the maximum distance between centres of cations and anions.
(a) CsF (b) CsI
(c) LiI (d) LiF
(C.B.S.E. P.M.T. 1998 ; J & K C.E.T. 2003)

35. Which of the following configuration represents atoms of the element having the highest second ionization potential ?
(a) $1s^2\,2s^2\,2p^4$ (b) $1s^2\,2s^2\,2p^6$
(c) $1s^2\,2s^2\,2p^6\,3s^1$ (d) $1s^2\,2s^2\,2p^6\,3s^2$.
(Pb. P.M.T. 1998)

36. Which of the following element has the maximum electron affinity ?
(a) Cl (b) Br
(c) I (d) F.
(C.B.S.E. P.M.T. 1999)

37. Which of the following is most electronegative ?
(a) Carbon (b) Silicon
(c) Lead (d) Tin. *(C.P.M.T. 1999)*

38. Which of the following remains unchanged on descending a group in the periodic table
(a) Valence electrons (b) Atomic size
(c) Density (d) Metallic character.
(D.C.E. 1999)

39. The radii of F, F^-, O and O^{2-} are in the order of
(a) $O^{2-} > F^- > F > O$ (b) $F^- > O^{2-} > F > O$
(c) $O^{2-} > O > F^- > F$ (d) $O^{2-} > F^- > O > F$.
(A.I.I.M.S. 1999)

40. Which of the following has maximum ionization potential ?
(a) Be (b) K
(c) Na (d) Mg.
(A.I.I.M.S. 1999)

41. The ionic radius of 'Cr' is minimum in which of the following compounds ?
(a) K_2CrO_4 (b) CrF_3
(c) CrO_2 (d) $CrCl_3$.
(Haryana C.E.E.T. 1999)

42. The species isoelectronic with CN^- ion is
(a) F_2 (b) O_2
(c) Si (d) O_2^{2-}.
(Haryana C.E.E.T. 1999)

43. Point out the *wrong* statement, in a given period of the periodic table, the *s*-block elements has, in general, a lower value of
(a) Electronegativity (b) Atomic radius
(c) Ionization energy (d) Electron affinity.
(D.C.E. 1999)

44. The electron affinities of halogens are :
F = 332, Cl = 349, Br = 324, I = 295 kJ mol^{-1}. The higher value for Cl as compared to that of F is due to
(a) Higher atomic radius of F
(b) Smaller electronegativity of F

ANSWERS

28. *b* 29. *b* 30. *b* 31. *b* 32. *b* 33. *b* 34. *b* 35. *c* 36. *a* 37. *a*
38. *a* 39. *d* 40. *a* 41. *a* 42. *c* 43. *b*

(*c*) Weaker electron-electron repulsion in Cl

(*d*) more vacant *p*-subshell in Cl. *(D.C.E. 1999)*

45. Among the following groupings, which represents the collection of isoelectronic species ?

(*a*) NO^+, C_2^{2-}, CO_2^-, CO

(*b*) N_2, C_2^{2-}, CO, NO

(*c*) CO, NO^+, CN^-, C_2^{2-}

(*d*) NO, CN^-, N_2, O_2^-. *(C.B.S.E. P.M.T. 2000)*

46. Electronic configuration of most electronegative element is

(*a*) $1s^2 2s^2 2p^6 3s^1$ (*b*) $1s^2 2s^2 2p^6 3s^2 3p^5$

(*c*) $1s^2 2s^2 2p^5$ (*d*) $1s^2 2s^2 2p^6 3s^2 3p^6$.

(J.M.S. B.H.U. 2000)

47. The bond length in LiF will be

(*a*) Less than that of NaF

(*b*) Equal to that of KF

(*c*) More than that of KF

(*d*) Equal to that of NaF. *(C.P.M.T. 2000)*

48. The correct sequence of atomic radii is

(*a*) Na > Mg > Al > Si (*b*) Al > Si > Na > Mg

(*c*) Si > Al > Mg > Na (*d*) Si > Al > Na > Mg.

(C.P.M.T. 2000)

49. The first ionization energy will be maximum for

(*a*) Uranium (*b*) Hydrogen

(*c*) Lithium (*d*) Iron.

(C.P.M.T. 2000 ; M.P.C.E.E. 2000)

50. Which of the following has least electron affinity ?

(*a*) Oxygen (*b*) Argon

(*c*) Nitrogen (*d*) Boron.

(A.F.M.C. 2000)

51. Which of the following pairs is isoelectronic ?

(*a*) Ar and Cl (*b*) Na^+ and Ne

(*c*) Na^+ and Mg (*d*) Mg and Ne.

(A.F.M.C. 2000)

52. The elements in which 4*f*-orbitals are progressively filled in are called as

(*a*) Actinides (*b*) Transition elements

(*c*) Lanthanides (*d*) Halogens.

(Haryana C.E.E.T. 2000)

53. Which one of the following is correct order of the size ?

(*a*) $I > I^- > I^+$ (*b*) $I > I^+ > I^-$

(*c*) $I^+ > I^- > I$ (*d*) $I^- > I > I^+$.

(C.B.S.E. P.M.T. 1997, M.P. C.E.E. 2000)

54. The ionic radii of N^{3-}, O^{2-}, F^- and Na^+ follow the order :

(*a*) $N^{3-} > O^{2-} > F^- > Na^+$

(*b*) $N^{3-} > Na^+ > O^{2-} > F^-$

(*c*) $Na^+ > O^{2-} > N^{3-} > F^-$

(*d*) $O^{2-} > F^- > Na^+ > N^{3-}$.

(M.P.P.M.T. 1998, 2000)

55. The first ionization energy of Na, Mg, Al and Si are in the order

(*a*) Na < Mg > Al < Si (*b*) Na > Mg > Al < Si

(*c*) Na > Mg > Al > Si (*d*) Na < Mg < Al < Si.

(M.P.P.M.T. 2000)

56. What is the maximum number of electrons which can be accommodated in an atom in which the highest principal quantum number is 4 ?

(*a*) 10 (*b*) 18

(*c*) 36 (*d*) 54. *(M.P.P.M.T. 2000)*

57. The first ionization energy for Li is 5·4 eV and electron affinity of Cl is 3·61 eV. The ΔH (in kJ/mol) for the reaction,

$$Li\,(g) + Cl\,(g) \longrightarrow Li^+\,(g) + Cl^-\,(g),$$

if the resulting ions do not combine with each other is (1 eV = $1{\cdot}6 \times 10^{-19}$ J)

(*a*) 70 (*b*) 100

(*c*) 170 (*d*) 270.

(M.P.P.M.T. 2000)

58. Which of the following is the smallest cation ?

(*a*) Na^+ (*b*) Mg^{2+}

(*c*) Ca^{2+} (*d*) Al^{3+}.

(M.P.P.M.T. 2000)

59. The *correct* statement about *d*-block elements is

(*a*) they are all metals

(*b*) they show variable valency

(*c*) they form coloured ions and complex salts

(*d*) all the above statements are correct.

(M.P.P.M.T. 2000)

60. The correct order of radii is

(*a*) N < Be < B (*b*) $F^- < O^{2-} < N^{3-}$

(*c*) Na < Li < K (*d*) $Fe^{3+} < Fe^{2+} < Fe^{4+}$

(I.I.T. 2000)

ANSWERS

44. *c* **45.** *c* **46.** *c* **47.** *a* **48.** *a* **49.** *b* **50.** *b* **51.** *b* **52.** *c* **53.** *d*

54. *a* **55.** *a* **56.** *c* **57.** *c* **58.** *d* **59.** *d* **60.** *b*

61. The set representing the correct order of first ionization potential is

(*a*) K > Na > Li (*b*) Be > Mg > Ca

(*c*) B > C > N (*d*) Ge > Si > C

(I.I.T. 2001)

62. The correct order of Ist ionization potential among following elements Be, B, C, N, O is

(*a*) B < Be < C < O < N

(*b*) B < Be < C < N < O

(*c*) Be < B < C < N < O

(*d*) Be < B < C < O < N

(C.P.M.T. 1999 ; C.B.S.E. P.M.T. 2001 ; J & K 2003)

63. The atomic radius increases as we move down a group because

(*a*) effective nuclear charge increases

(*b*) atomic mass increases

(*c*) additive electrons are accommodated in new electron level

(*d*) atomic number increases

(Tamilnadu C.E.T. 2001)

64. The first ionization potential of Mg, Al, P and S follows the order :

(*a*) Mg < Al < P < S (*b*) Al < Mg < P < S

(*c*) Al < Mg < S < P (*d*) Mg < Al < S < P

(G.A.T.E. 2001)

65. Eka-aluminium and Eka-silicon are known as

(*a*) Gallium and germanium

(*b*) Aluminium and silicon

(*c*) Iron and sulphur (*d*) Proton and silicon

(*e*) Neutron and magnesium *(Kerala M.E.E. 2002)*

66. Element with atomic number 56 belongs to which block ?

(*a*) *s* (*b*) *p*

(*c*) *d* (*d*) *f* *(A.F.M.C. 2002)*

67. Identify the least stable ion amongst the following :

(*a*) Li^- (*b*) Be^-

(*c*) B^- (*d*) C^- *(I.I.T. 2002)*

68. According to Periodic Law of elements, the variation in properties of elements is related to their

(*a*) nuclear neutron-proton number ratios

(*b*) atomic masses (*c*) nuclear masses

(*d*) atomic numbers *(A.I.E.E.E. 2003)*

69. Which of the following groupings represents a collection of isoelectronic species ? (At. nos. Cs = 55, Br = 35)

(*a*) Ca^{2+}, Cs^+, Br (*b*) Na^+, Ca^{2+}, Mg^{2+}

(*c*) N^{3-}, F^-, Na^+ (*d*) Be, Al^{3+}, Cl^-

(A.I.E.E.E. 2003)

70. The ions $O^{2-}, F^-, Na^+, Mg^{2+}$ and Al^{3+} are isoelectronic. Their ionic radii show

(*a*) a significant increase from O^{2-} to Al^{3+}

(*b*) a significant decrease from O^{2-} to Al^{3+}

(*c*) an increase from O^{2-} to F^- and then decrease from Na^+ to Al^{3+}

(*d*) a decrease from O^{2-} to F^- and then increase from Na^+ to Al^{3+} *(C.B.S.E. P.M.T. 2003)*

71. The ionic radii of isoelectronic species N^{3-}, O^{2-} and F^- in Å are in the order :

(*a*) 1·36, 1·40, 1·71 (*b*) 1·36, 1·71, 1·40

(*c*) 1·71, 1·40, 1·36 (*d*) 1·71, 1·36, 1·40

(J & K C.E.T. 2003)

72. The arrangement of decreasing sizes of H^+, H^- and H is

(*a*) $H^+ > H > H^-$ (*b*) $H > H^- > H^+$

(*c*) $H^- > H^+ > H$ (*d*) $H^- > H > H^+$

(M.G.I.M.S. Wardha 2003)

73. Arrange the following in proper order of size

(*a*) Mg < Si < Al < P (*b*) P > Al > Mg > Si

(*c*) Al < Mg < Si < P (*d*) Mg < Al > Si > P

(M.G.I.M.S. Wardha 2003)

74. The highly metallic element will have the configuration of

(*a*) 2, 8, 7 (*b*) 2, 8, 8, 5

(*c*) 2, 8, 8, 1 (*d*) 2, 8, 2

(M.G.I.M.S. Wardha 2003)

75. For electron affinity of halogens which of the following is correct ?

(*a*) Br > F (*b*) F > Cl

(*c*) Br > Cl (*d*) F > I

(A.I.I.M.S. 2004)

76. Lanthanoids are

(*a*) 14 elements in the sixth period (atomic no. = 90 to 103) that are filling 4*f*-sublevel

(*b*) 14 elements in the seventh period (atomic no. = 90 to 103) that are filling 5*f*-sublevel

(*c*) 14 elements in the sixth period (atomic no. = 58 to 71) that are filling 4*f*-sublevel

(*d*) 14 elements in the seventh period (atomic no. = 58 to 71) that are filling 4*f*-sublevel

(C.B.S.E. P.M.T. 2004)

ANSWERS

61. *b* **62.** *a* **63.** *c* **64.** *c* **65.** *a* **66.** *a* **67.** *b* **68.** *d* **69.** *c* **70.** *b*

71. *c* **72.** *d* **73.** *d* **74.** *c* **75.** *d* **76.** *c*

77. Ionic radii are

(*a*) inversely proportional to effective nuclear charge

(*b*) inversely proportional to square of effective nuclear charge

(*c*) directly proportional to effective nuclear charge

(*d*) directly proportional to square of effective nuclear charge *(C.B.S.E. P.M.T. 2004)*

78. Which of the following has highest value of ionic radius ?

(*a*) Li^+ (*b*) B^{3+}

(*c*) O^{2-} (*d*) F^- *(A.I.E.E.E. 2004)*

79. The formation of the oxide ion O^{2-} (*g*) requires first an exothermic and then an endothermic step as shown below :

$$O\,(g) + e^- \longrightarrow O^-\,(g)\,;\quad \Delta H^\circ = -\,142\ kJ\ mol^{-1}$$

$$O^-\,(g) + e^- \longrightarrow O^{2-}\,(g)\,;\quad \Delta H^\circ = +\,844\ kJ\ mol^{-1}$$

This is because

(*a*) Oxygen is more electronegative

(*b*) Oxygen has high electron affinity

(*c*) O^- will tend to resist the addition of another electron

(*d*) O^- ion has comparatively larger size than oxygen atom. *(A.I.E.E.E. 2004)*

80. Which one of the following sets of ions represents the collection of isoelectronic species ?

(*a*) K^+, Ca^{2+}, Sc^{3+}, Cl^-

(*b*) Na^+, Ca^{2+}, Sc^{3+}, F^-

(*c*) K^+, Cl^-, Mg^{2+}, Sc^{3+}

(*d*) Na^+, Mg^{2+}, Al^{3+}, Cl^- *(A.I.E.E.E. 2004)*

81. The elements with atomic numbers 9, 17, 35, 53, 85 are all

(*a*) noble gases (*b*) halogens

(*c*) heavy metals (*d*) light metals

(K.C.E.T. 2004)

82. In a given shell, the order of screening effect is

(*a*) $s > p > d > f$ (*b*) $f > d > p > s$

(*c*) $p < d < s < f$ (*d*) $d > f < s < p$

(*e*) $f > p > s > d$ *(Kerala M.E.E. 2004)*

83. Consider the ions : K^+, S^{2-}, Cl^- and Ca^{2+}. The radii of these ionic species follow the order :

(*a*) $Ca^{2+} > K^+ > Cl^- > S^{2-}$

(*b*) $Cl^- > S^{2-} > K^+ > Ca^{2+}$

(*c*) $Ca^{2+} > Cl^- > K^+ > S^{2-}$

(*d*) $K^+ > S^{2-} > Cl^- > Ca^{2+}$

(*e*) $S^{2-} > Cl^- > K^+ > Ca^{2+}$ *(Kerala C.E.E. 2004)*

84. Which of the following have no unit ?

(*a*) electronegativity (*b*) electron affinity

(*c*) ionisation energy (*d*) excitation potential

(A.F.M.C. 2004)

85. The last electron of the '*p*-block' in the present periodic table can be represented by configuration where [In] represents inert gas

(*a*) [In] $7s^2\,7p^6$ (*b*) [In] $7s^2\,5f^{14}\,6d^{10}\,7p^0$

(*c*) [In] $6s^2\,4f^{14}\,5d^{10}\,6p^6$ (*d*) None of these

(C.P.M.T. 2004)

86. Ha is an alphabetical symbol for

(*a*) Hafnium (*b*) Hassnium

(*c*) Hahnium (*d*) Helium

(C.P.M.T. 2004)

HINTS/EXPLANATIONS to Multiple Choice Questions

6. In heavier elements, Hund's rule is not always followed.

8. Since the size of K is larger than K^+ (1·34 Å) and that of F is smaller than that of F^- (1·34 Å), therefore, option (*a*) is correct.

9. The second electron affinity of an element is negative, *i.e.*, energy is absorbed.

11. For ratio of anion size to cation size to be lowest, anion should be smallest (F^-) and cation to be biggest (Cs^+), *i.e.*, option (*d*) is correct.

14. IE abruptly increases (*i.e.* $IE_4 >>> IE_3$) when an electron is knocked out from the noble gas core.

15. From $z \geq 121 \leq 138$, the filling up of *g*- orbitals begins for which there is no provision in he present set-up of the periodic table.

17. Bigger the size, smaller the I.E.

18. Ca^{2+} = 2, 8, 8.

22. Both (*b*) and (*d*) have similar exactly half-filled electronic configuration, but the size of (*b*) is smaller that that of (*d*)

23. In principle, electrons are added one at a time to the penultimate *d*-orbitals but due to extra stability of d^5 and d^{10} configurations, two electrons appear to have entered the *d*- shell due to shifting of one electron from *ns* to (*n*–1) *d* orbital.

ANSWERS

77. *a* **78.** *c* **79.** *c* **80.** *a* **81.** *b* **82.** *a* **83.** *e* **84.** *a* **85.** *c* **86.** *c*

29. IE_2 of O is higher than that of F because in case of O, the second electron has to be removed from a more stable completely half-filled electronic configuration, *i.e.*, $O^+ (1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1)$ while in case of F, this is not so, *i.e.* $F^+ (1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1)$. Instead removal of another electron from F^+ gives a more stable completely half filled electronic configuration, *i.e.*, $F^{2+} (1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1)$.

30. Energy is released when an electron is added to O but energy has to be spent when an electron is added to O^-, F^- and Na^+.

31. The filling of 4*f*-shell begins only when one electron has already been added to 5 *d*-orbital.

32. IE_2 of Na is higher than that of Mg because in case of Na, the second electron has to be removed from the noble gas core while in case of Mg, removal of second electron gives a nobe gas core.

33. Be has higher IE_1 than B.

34. Bigger the size of ions, larger is the distance between the centres of their nuclei.

38. Each group has a fixed number of valence electrons.

39. The size of $O^{2-} > F^-$ and that of $O > F$. Therefore, the overall order is : $O^{2-} > F^- > O > F$

40. Because of smallest size, Be has the highest ionization potential.

41. Amongst K_2CrO_4, CrF_3, CrO_2 and $CrCl_3$, Cr has the maximum oxidation number of + 6 in K_2CrO_4 and hence has the minimum ionic radius.

42. CN^- and Si both have 14 electrons.

43. In any period, *s*-block element has the largest size.

45. All the species have 14 electrons.

46. F $(1s^2 2s^2 2p^5)$ is the most electronegative element.

47. Due to smaller size of Li than Na or K, LiF has smaller bond length than NaF and KF.

48. In a period, atomic radii decrease from left to right.

49. Being smallest, hydrogen has the maximum IE_1.

50. Inert gases have zero electron-affinity.

51. Both Na^+ and Ne have 10 electrons each.

56. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 = 36$.

57. $$\Delta H = (5 \cdot 4 - 3 \cdot 61) \times (1 \cdot 6 \times 10^{-19}\ J) \times (6 \cdot 023 \times 10^{23}) \times 10^{-3} = 172 \cdot 5\ kJ\ mol^{-1}.$$

61. Within a group IE_1 decreases from top to bottom.

62. Because of extra stability of exactly half-filled electronic configuration of N, its IE_1 is higher than that of O. Further because of higher nuclear charge, IE_1 of C is higher than that of Be and B. Amongst Be and B, the IE_1 of Be is higher than that of B because in case of Be a 2 *s*-electron is to removed while in case of B a 2 *p*-electron is to be removed. Thus, the overall order is (*a*) *i.e.*, $B < Be < C < O < N$.

63. As the number of shells increases, atomic radius increases accordingly.

64. Because of extra stability of exactly half-filled electronic configuration of P its IE_1 is higher than that of S. Further the IE_1 of Mg is higher than that of Al because in case of Mg, electron is to be removed from a 3 *s*-orbital while in case of Al, the electron is to be removed from a 3 *p*-orbital. Thus, option (*c*), *i.e.*, $Al < Mg < S < P$ is correct.

67. Be has fully filled 2*s*-subshell $(2s^2)$ and therefore shows little tendency to accept an extra electron to form Be^-.

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The questions given below consist of an 'Assertion' in column 1 and the 'Reason' in column 2. Use the following key to choose the correct answer.

(*a*) If both assertion and reason are CORRECT, and reason is the CORRECT explanation of the assertion.

(*b*) If both assertion and reason are CORRECT, but reason is NOT the CORRECT explanation of the assertion.

(*c*) If assertion is CORRECT, but reason is INCORRECT.

(*d*) If assertion is INCORRECT, but reason is CORRECT.

(*e*) If both assertion and reason are FALSE.

	Assertion (column 1)	Reason (column 2)
1.	The ionization of *s*-electrons requires more energy than that for the ionization of *p*-electrons of the same shell.	*s*-Electrons are closer to the nucleus than *p*-electrons and hence are more strongly attracted by the nucleus.
2.	When transition metal ions ionize, the 4 *s*-orbital electrons are ionized before the 3 *d*-orbital electrons.	The energy of 3 *d*-orbital electron is lower than that of 4 *s*-orbital electrons.
3.	Helium and beryllium have similar outer electronic configuration of the type ns^2.	Both are chemically inert. *(A.I.I.M.S. 1994)*
4.	The element with electronic configuration $[Xe]^{54}\ 4f^1\ 5d^1\ 6s^2$ is a *d*-block element.	The last electron eters the *d*-orbital.
5.	The first ionization energy of aluminium is lower than that of magnesium.	Ionic radius of aluminium is smaller than that of magnesium. *(A.I.I.M.S. 1994)*
6.	Both N_2 and NO^+ are diamagnetic substances.	NO^+ is isoelectronic with N_2. *(A.I.I.M.S. 1997)* *(A.I.I.M.S. 1997)*
7.	Electron affinity of oxygen is less than that of fluorine but greater than that of nitrogen.	Ionization potential is as follows : N > O > F. *(A.I.I.M.S. 1998)*
8.	F atom has a less negative electron affinity than Cl atom.	Additional electrons are repelled more effectively by 3 *p*-electrons in Cl than by 2 *p*-electrons in F atom. *(I.I.T. 1998)*
9.	Zn^{2+} is diamagnetic.	The electrons are lost from 4 *s*-orbital to form Zn^{2+}.
10.	The first ionization energy of Be is greater than that of B.	2 *p*-orbital is lower in energy than 2 *s*-orbital. *(I.I.T. 2001)*

True/False Statements

1. An element with atomic number 47 is a transition element.
2. The second period contains 8 and the third period contains 18 elements.
3. The size decreases as Cu > Cu^+ > Cu^{2+}.
4. The first ionization energy of N is lower than that of oxygen.
5. Second electron affinity is always negative.
6. There are seven periods and eighteen groups in the periodic table.
7. The size of Cl^- ion is smaller than that of S^{2-} ion.
8. The decreasing order of electron affinity of F, Cl, Br is F > Cl > Br. *(I.I.T. 1993)*

Fill In The Blanks

1. An element with atomic number 35 belongs to ..... block.
2. Each series of *d*-block contains ..... elements.
3. The first ionization energy of N is ..... than that of O while the second ionization energy of ..... is higher than that of ..... .
4. The radii of Fe, Fe^{3+} and Fe^{2+} decrease in the order ....
5. In the second period, the most electronegative and electropositive elements are .... and ...... respectively.
6. The general outer shell electronic configuration of *f*-block elements is ..... .
7. Among the isoelectronic ions, the ionic size increases as the ..... charge on the ion ..... .
8. Valency of a *p*-block element is equal to eight ..... the number of electrons present in the ..... shell.
9. When an electron is added to a uninegative ion, energy is ..... .
10. An element which lies right above and below Cd in the preiodic table are .... and .... respectively.
11. On the Pauling electronegativity scale, the element next to F is ..... . *(Roorkee 1989)*
12. Ca^{2+} ion has a smaller radius that K^+ because it has ..... . *(I.I.T. 1993)*
13. The radioactive series consisting of man-made elements is called ..... elements. *(A.I.S.B. 1996)*
14. The electronic configuration of atoms and ....provide a basis for periodic classification.

Matching Type Questions

Match the items in column I with those in column II

Column I	Column II
1. Horizontal rows	(*a*) Ionization energy
2. Elements with electronic configuration as $ns^2\,np^{1-6}$	(*b*) Valence electrons
3. $M(g) + \text{Energy} \longrightarrow M^+(g) + e^-$	(*c*) Electron affinity
4. $X(g) + e^- \longrightarrow X^-(g) + \text{Energy}$	(*d*) *p*-Block elements
5. Electrons present in the outermost shell	(*e*) Periods.

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. (*a*) **2.** (*a*) **3.** (*c*) **4.** (*e*) **5.** (*b*) **6.** (*a*) **7.** (*c*) **8.** (*c*) **9.** (*b*) **10.** (*c*).

TRUE/FALSE STATEMENTS

1. True **2.** False, both contain 8 elements, **3.** True **4.** False, first ionization energy of N is higher than that of O **5.** True **6.** True **7.** True **8.** False, Cl > F > Br.

FILL IN THE BLANKS

1. *p*- **2.** ten **3.** higher, oxygen, nitrogen, **4.** $Fe > Fe^{2+} > Fe^{3+}$ **5.** Fluorine and lithium **6.** $(n-2)f^{1-14}\,(n-1)d^{0-1}\,ns^2$. **7.** negative, increases **8.** minus, valence **9.** absorbed **10.** zinc, mercury **11.** oxygen **12.** higher nuclear charge **13.** transuranic **14.** aufbau principle.

MATCHING TYPE QUESTIONS

1. (*e*) **2.** (*d*) **3.** (*a*) **4.** (*c*) **5.** (*b*).

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

3. *Correct reason* : Although He and Be have similar outer electronic configuration of the type ns^2, only He ($1s^2$) has inert gas configuration and hence is chemically inert but Be ($1s^2\,2s^2$) does not have inert gas configuration and hence is not chemically inert.

4. *Correct assertion* : $Ba(OH)_2$ is more basic than $Mg(OH)_2$

Correct reason : Because of lower IE_1 of Ba than that of Mg, $Ba(OH)_2$ ionises to a greater extent than that of $Mg(OH)_2$ and hence $Ba(OH)_2$ is of stronger base than $Mg(OH)_2$

7. *Correct reason* : Electron affinity of N is essentially zero because of its exactly half-filled electronic configuration.

Further because F has 7 electrons and O has 6 electrons in the valence shell, therefore, the tendency of F to acquire additional electron is higher than that of O, *i.e.* EA of F is higher than that O. In other words, EA decreases as F > O > N.

8. *Correct reason* : Additional electrons are repelled more effectively by 2*p*-electrons in F than 3*p*-electrons in Cl.