

## MODULE - 2

Atomic Structure and  
Chemical Bonding



Notes

3

# PERIODIC TABLE AND PERIODICITY IN PROPERTIES

We have seen different heaps of onions and potatoes at vegetable shop. Imagine, they are lying mixed and you want to buy 1 kg of onion. What will happen? You will have to wait for long to sort that and then weigh them. When you possess a variety of material substances, you have to keep them classified for an easy access and quick use. You cannot afford to mix clothes with eatables, cosmetics or books. Classification assures you that your eatbles are in the kitchen, books on the study table or rack and your cosmetics are on the dressing table. Shopkeepers, business houses, storekeepers, administrators, managers, information technology experts and scientists etc. have to keep their materials duly classified.

Chemists faced a similar problem when they were to handle a large number of elements. The study of their physical and chemical properties and keeping a systematic record of them had been a great challenge to chemists. Classification of elements finally could be possible due to pioneering work of a few chemists. In the present lesson we shall discuss the need, genesis of classification and periodic trends in physical and chemical properties of elements.



### OBJECTIVES

After reading this lesson, you will be able to:

- recognise the need for classification of elements;
- recall the earlier attempts on classification of elements;
- define modern periodic law;
- name the elements with atomic number greater than 100 according to IUPAC nomenclature;



- co-relate the sequence of arrangements of elements in periodic table with electronic configuration of the elements;
- recall the designations of the groups (1-18) in the periodic table;
- locate the classification of elements into s-, p-, d- and f- blocks of the periodic table; and
- explain the basis of periodic variations of
  - (a) atomic size
  - (b) ionic size
  - (c) ionization enthalpy
  - (d) electron gain enthalpy within a group or a period.
  - (e) valence

### 3.1 EARLY ATTEMPTS

Attempts were made to classify elements ever since the discovery of metals or may be even earlier. J.W. Dobereiner in 1817 discovered that when closely related elements are grouped in a set of three, the atomic weight of the middle element was almost the arithmetical mean of the other two elements in that group e.g.,

Element	Lithium	Sodium	Potassium
Atomic weight	6.94	22.99	39.10
Mean atomic weight	-----	23.02	-----

He called such a group of three elements a triad. He could group only a few elements due to lack of knowledge of correct atomic weights of the elements at that time.

In 1863, J.A.R. Newlands, developed a system of classification of elements and entitled it as **Law of Octaves**. He arranged the elements in such a way that every eighth element had similar properties, like the notes of music. The law could not apply to a large number of known elements. However, the law indicated very clearly the recurrence of similar properties among the arranged elements. Thus the periodicity was visualised for the first time in a meaningful way.

**Periodicity:** Re-occurrence of properties after regular intervals.

More significant results were obtained when Lothar Meyer's work reflecting the periodicity was found to be based on physical properties of the elements. He clearly showed that certain properties showed a periodic trend.

### 3.2 MENDELEEV'S PERIODIC TABLE

In 1869, Mendeleev, a Russian Chemist made a thorough study of the relation between the atomic weights of the elements and their physical and chemical

## MODULE - 2

### Atomic Structure and Chemical Bonding



#### Notes

### Periodic Table and Periodicity in Properties

properties. He then constructed a table in which elements were arranged in order of their increasing atomic weights. It was also found that every eighth element had properties similar to that of the first element. Thus, there was a periodic occurrence of elements with similar properties.

One of the most striking applications of Mendeleev's classification of elements was that in his periodic table (Table 3.1) he left gaps for elements which were yet to be discovered. He also predicted the properties of these elements. However, Mendeleev's periodic table did not provide any place for isotopes and noble gases which were discovered later on.

**Table 3.1 Mendeleev's Table of 1871**

Group	I	II		III		IV		V		VI		VII		VIII		
Oxide	R <sub>2</sub> O	RO		R <sub>2</sub> O <sub>3</sub>		RO <sub>2</sub>		R <sub>2</sub> O <sub>5</sub>		RO <sub>3</sub>		R <sub>2</sub> O <sub>7</sub>		RO <sub>4</sub>		
Hydride	RH	RH <sub>2</sub>		RH <sub>3</sub>		RH <sub>4</sub>		RH <sub>3</sub>		RH <sub>2</sub>		RH				
Periods	A	B	A	B	A	B	A	B	A	B	A	B	A	B	Transition series	
↓																
1	H 1.008															
2	Li 6.939	Be 9.012		B 10.81		C 12.011		N 14.007		O 15.999		F 18.998				
3	Na 22.99	Mg 24.31		Al 29.98		Si 28.09		P 30.974		S 32.06		Cl 35.453				
4	First series: K 39.102	Ca 40.08		Sc 44.96		Ti 47.90		V 50.94		Cr 50.20		Mn 54.94	Fe 55.85	Co 58.93	Ni 58.71	
	Second series: Cu 63.54	Zn 65.37		Ga 69.72	Ge 72.59		As 74.92	Se 78.96		Br 79.909						
5	First series: Rb 85.47	Sr 87.62		Y 88.91		Zr 91.22		Nb 92.91		Mo 95.94		Tc 99	Ru 101.07	Rh 102.91	Pd 106.4	
	Second series: Ag 107.87	Cd 112.40		In 114.82	Sn 118.69		Sb 121.75	Te 127.60		I 126.90						
6	First series: Cs 132.90	Ba 137.34		La 138.91		Hf 178.49		Ta 180.95		W 183.85		Os 190.2	Ir 192.2	Pt 195.09		
	Second series: Au 196.97	Hg 200.59		Tl 204.37	Pb 207.19		Bi 208.98									

The extent of knowledge regarding the chemical properties of the elements and his insight into the system of periodicity possessed by the elements under certain arrangement have no parallel in the history of chemistry. This work laid strong foundation of the fundamental principles of the periodic law. One of his most important conclusions was that the elements if arranged according to their atomic weights, exhibit an evident systematic reoccurrence of properties (periodicity of properties) and even the properties of some elements were listed much before their discovery. Mendeleev's periodic Table (Table 3.1) was quite useful till the discovery of atomic number. There existed certain inherent defects which opposed the system.

### 3.3 MODERN APPROACH

Atomic number was discovered in 1913 by a team lead by Mosely. The periodic table based on atomic number is termed as Modern Periodic Table. Moseley arranged all the elements according to increasing atomic number and showed that the properties of elements are periodic function of their atomic numbers.

**Modern periodic law:** The properties of the elements are periodic function of their atomic numbers.

### 3.4 LONG FORM OF PERIODIC TABLE

The arrangement of elements in the long form of periodic table is a perfect matching of electronic configuration of the elements on one hand and physical and chemical properties of the elements on the other. Some important considerations of the modern atomic structure applied to the classification of elements are discussed below:

- (i) An atom loses electron(s) from or gains electron(s) in the outermost shell of an atom during a chemical reaction.
- (ii) The sharing of an electron or electrons by an atom with other atom or atoms is largely through the outer most shell. Thus the electrons in the outermost shell of an atom largely determine the chemical properties of the elements.

We may therefore conclude that the elements possessing identical outer electronic configuration should possess similar physical and chemical properties and therefore they should be placed together for an easy and systematic study.

Keeping in mind the reasoning given above, when all the known elements are arranged in a table according to their increasing atomic number, the properties of the elements show periodicity (reappear at definite intervals). The periodicity is shown in Table in 3.2.

### 3.5 STRUCTURAL FEATURES OF THE LONG FORM OF PERIODIC TABLE

- (i) In this table there are 18 vertical columns called **GROUPS**. They are numbered from 1 to 18. Every group has a unique configuration.
- (ii) There are seven horizontal rows. These rows are called **PERIODS**. Thus the periodic table has seven periods, numbered from 1 to 7.
- (iii) There are a total of 114 elements known to us till today. Of all the known elements 90 are naturally occurring and others are made through nuclear transformations or are synthesised artificially. Either way they are **Man-made Elements**, but you will find the term specifically applied to **transuranic elements** (elements listed after uranium) only.



Notes

## MODULE - 2

Atomic Structure and  
Chemical Bonding



Notes

### Periodic Table and Periodicity in Properties

- (iv) First period consists of only two elements (very short period). Second and third periods consist of only eight elements each (short periods). Fourth and fifth periods consist of 18 elements each (long periods). Sixth period consists of 32 elements (long period). Seventh period is yet incomplete and more and more elements are likely to be added as the scientific research advances.
- (v) There are also nick names given to the groups or a cluster of groups on the basis of the similarity of their properties, as given below:

Group 1 elements except hydrogen, are called **Alkali Metals**

Group 2 elements are called **Alkaline Earth Metals**.

Group 3 to 12 elements are called **Transition Metals**.

Group 16 elements are called **Chalcogens**

Group 17 elements are called **Halogens**

Group 18 elements are called **Noble Gases**.

Apart from what has been said above elements with atomic numbers 58 to 71 are called *Lanthanoids* – or Inner Transition elements (First series). Elements from atomic numbers 90 to 103 are called actinoids – Inner Transition elements (Second series). All elements except transition and inner transition elements are also collectively called **Main Group Elements**.

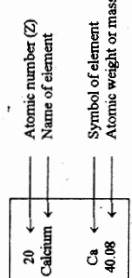
### 3.6 POSITION OF METALS, NON-METALS AND METALLOIDS

In order to locate the position of metals, non-metals and metalloids in the periodic table, you may draw a diagonal line joining the element boron (At. no. 5) with that of tellurium (At. no. 52) and passing through silicon and arsenic. Now we are in a position to make the following observations.

- (i) The elements above the diagonal line and to the far right are non-metals (except selenium which shows slightly metallic character also). The non-metallic character is more marked the farther an element is from the diagonal line and up.
- (ii) The elements below the diagonal line and to the left are metals. (Hydrogen is a non-metal and is an exception) The metallic character is more marked the farther an element is from the diagonal line and down. All lanthanoids and actinoids are metals.
- (iii) The elements along the diagonal line are metalloids and possess the characteristics of metals as well as of non-metals. In addition germanium, antimony and selenium also show the characteristics of metalloids.

# GROUPS REPRESENTATIVE ELEMENTS

Group		TRANSITION ELEMENTS										Noble Gases							
1	2	VIIA										VIII					18		
IA	IIA	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
P	E	R	I	O	D	S											Noble Gases		
1 Hydrogen H 1.0079	2 Helium He 4.00260	21 Scandium Sc 44.9559	22 Titanium Ti 47.88	23 Vanadium V 50.9415	24 Chromium Cr 51.9961	25 Manganese Mn 54.9380	26 Iron Fe 55.847	27 Cobalt Co 58.9332	28 Nickel Ni 58.69	29 Copper Cu 63.546	30 Zinc Zn 65.39	31 Gallium Ga 69.72	32 Germanium Ge 72.59	33 Arsenic As 74.9216	34 Selenium Se 78.96	35 Bromine Br 79.904	36 Krypton Kr 83.80	2	
3 Lithium Li 6.941	4 Beryllium Be 9.01218	39 Yttrium Y 88.9059	40 Zirconium Zr 91.224	41 Niobium Nb 92.9064	42 Molybdenum Mo 95.94	43 Technetium Tc 98.91	44 Ruthenium Ru 101.07	45 Rhodium Rh 102.906	46 Palladium Pd 106.42	47 Silver Ag 107.868	48 Cadmium Cd 112.41	49 Indium In 114.82	50 Tin Sn 118.71	51 Antimony Sb 121.75	52 Tellurium Te 127.60	53 Iodine I 126.905	54 Xenon Xe 131.29	2	
11 Sodium Na 22.9898	12 Magnesium Mg 24.305	57 Lanthanum La 138.906	72 Hafnium Hf 178.49	73 Tantalum Ta 180.948	74 Tungsten (Wolfram) W 183.85	75 Rhenium Re 186.207	76 Osmium Os 190.2	77 Iridium Ir 192.22	78 Platinum Pt 195.08	79 Gold Au 196.967	80 Mercury Hg 200.59	81 Thallium Tl 204.383	82 Lead Pb 207.2	83 Bismuth Bi 208.980	84 Polonium Po (209)	85 Astatine At (210)	86 Radon Rn (222)	2	
19 Potassium K 39.0983	20 Calcium Ca 40.08	88 Radium Ra 226.025	104 Unnilquadium Uuq (261)	105 Unnilpentium Uup (262)	106 Unnilhexium Uuh (263)	107 Unnilseptium Uus (264)	108 Unniloctium Uuo (265)	109 Unnilennium Uue (266)	110 Unnilium Uui (267)	111 Unnilunium Uuu (268)	112 Unnilbium Uub (269)	113 Unniltrium Uut (270)	114 Unnilquadium Uuq (271)	115 Unnilpentium Uup (272)	116 Unnilhexium Uuh (273)	117 Unnilseptium Uus (274)	118 Unniloctium Uuo (276)	2	
37 Rubidium Rb 85.4678	38 Strontium Sr 87.62	55 Cesium Cs 132.905	87 Francium Fr (223)	108 Unniloctium Uuo (265)	109 Unnilennium Uue (266)	110 Unnilium Uui (267)	111 Unnilunium Uuu (268)	112 Unnilbium Uub (269)	113 Unniltrium Uut (270)	114 Unnilquadium Uuq (271)	115 Unnilpentium Uup (272)	116 Unnilhexium Uuh (273)	117 Unnilseptium Uus (274)	118 Unniloctium Uuo (276)	119 Unnilnonium Uun (277)	120 Unnildecium Uud (278)	121 Unnilundecium Uue (279)	122 Unnilduodecium Uud (280)	2



Group		Lanthanide Series 6*										Actinide Series 7**									
18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37		
71 Lutetium	72 Ytterbium	73 Thulium	74 Erbium	75 Thulium	76 Erbium	77 Ytterbium	78 Thulium	79 Erbium	80 Thulium	81 Erbium	82 Ytterbium	83 Thulium	84 Erbium	85 Thulium	86 Ytterbium	87 Thulium	88 Erbium	89 Thulium	90 Erbium	91 Thulium	
103 Lawrencium	104 Nobelium	105 Mendelevium	106 Fermium	107 Mendelevium	108 Fermium	109 Mendelevium	110 Fermium	111 Mendelevium	112 Fermium	113 Mendelevium	114 Fermium	115 Mendelevium	116 Fermium	117 Mendelevium	118 Fermium	119 Mendelevium	120 Fermium	121 Mendelevium	122 Fermium	123 Mendelevium	



Notes



### INTEXT QUESTIONS 3.1

- Classify the elements of group 14, 15 and 16 into metals, non-metals and metalloids.
- Compare the metallic character of aluminium and potassium.
- Name the group number for the following type of elements
  - Alkaline earth metals
  - Alkali metals
  - Transition metals
  - Halogens
  - Noble gases.
- Name five man made elements.

### 3.7 CATEGORISATION OF ELEMENTS INTO 's', 'p', 'd', AND 'f' BLOCKS

Grouping of elements in the periodic table can be done in another way also, which is more related to their electronic configuration. Under this categorisation, the location of the **differentiating electron** (the last electron) is most important. If, for example, the electron has gone to 's-subshell', the elements will fall in 's-block' and if the last electron goes to 'p-subshell', then the element will belong to p-block. Similarly if the differentiating electron enters the 'd-subshell', of an atom, then the elements comprising all such atoms will belong to d-block.

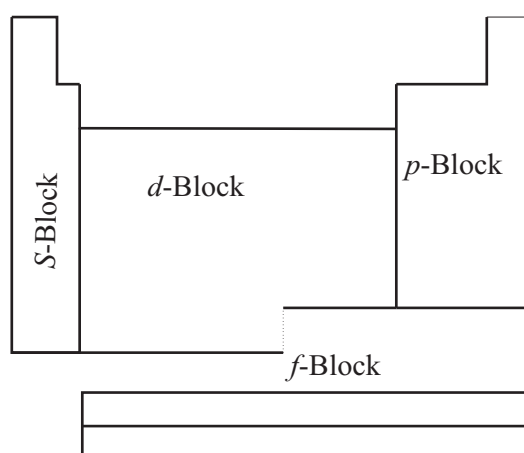


Fig. 3.1 : Blockwise categorization of elements.

There are minor exceptions in Mn and Zn configurations. You will study more about the reasons for such exceptions in Lesson 23.

The grouping of elements explained above can be related to the type of elements discussed earlier:

- (i) *s*-block elements: All alkali metals and alkaline earth metals.
- (ii) *p*-block elements: All elements of group number 13 to group number 18.
- (iii) *d*-block elements: All elements from group no. 3 to group no. 12 except Lanthanoids and Actinoides.
- (iv) *f*-block elements: Lanthanoids (atomic number 58 to 71) and Actinoids (atomic number 90 to 103)

This is shown in Fig. 3.1.

### Nomenclature of Elements with Atomic Numbers greater than 100

The naming of the new elements was earlier left entirely to its discoverer. The suggested names were then later ratified by IUPAC. But due to certain disputes that arose over the original discoverer of some of the elements of atomic numbers greater than 104, the IUPAC in 1994 appointed a Commission on Nomenclature of Inorganic Chemistry (CNIC). After consultation with the Commission and the chemists around the world, the IUPAC in 1997 recommended a nomenclature to be followed for naming the new elements with atomic numbers greater than 103 until their names are fully recognised.

- The names are derived directly from the atomic number of the element using the following numerical roots for 0 and numbers 1–9.

0 = nil	3 = tri	6 = hex	9 = enn
1 = un	4 = quad	7 = sept	
2 = bi	5 = pent	8 = oct	

- The roots are put together in the order of the digits which make up the atomic number and 'ium' is added at the end.
- Names, thus derives, and the IUPAC approved names of some elements with atomic numbers greater than 103 are listed in Table 3.3.



Notes



## MODULE - 2

Atomic Structure and  
Chemical Bonding



Notes

## Periodic Table and Periodicity in Properties

Table 3.3 : Nomenclature of elements with atomic numbers greater than 103

Atomic number	Name	Symbol	IUPAC approved name	IUPAC symbol
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununillium	Uun	–	–
111	Unununnium	Uuu	–	–
112	Ununbium	Uub	–	–
113	Ununtrium	Uul	–	–
114	Ununquadium	Uuq	–	–
115	Ununpentium	Uup	–	–

### 3.8 PERIODICITY IN ATOMIC PROPERTIES

The term periodicity is used to indicate that some characteristic properties occur in the periodic table after definite intervals, however with a varying magnitude. Thus after starting from a certain point on the periodic table, we are almost certain that the movement in a particular direction will show steady increase or decrease of a said property.

### 3.9 ATOMIC SIZE

In homonuclear diatomic molecules the distance from the centre of one nucleus to the centre of another nucleus gives the bond length and half of this bond length is atomic radius (Fig. 3.2). The first member of each period is the largest in size. Thus we can say that the group 1 atoms are the largest in their respective horizontal rows. Similarly, atoms of group 2 elements are large but are definitely smaller than the corresponding atoms of group 1. This is due to the reason that the extra charge on the nucleus draws the electrons inward resulting in smaller size for the atoms under reference. This trend of decrease in size of atoms, continues from left to right. An example is shown in Fig. 3.3. However, there may be some exceptions and there will be other reasons to explain them.

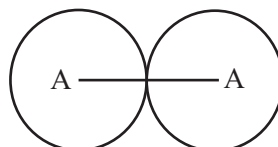


Fig 3.2 : Atomic radius =  $\frac{1}{2}d_{A-A} = r$



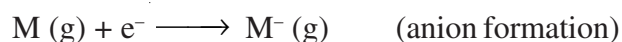
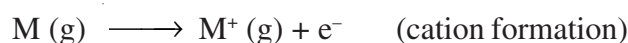
Fig. 3.3: From left to right, size of atoms decrease in the periodic table

In going down the group of elements (in any particular column) the atomic size increases at each step.

This increase may be explained in terms of a new electron shell being added, when we pass from one element to another in a group.

### 3.10 IONIC SIZE

An ion is formed when an atom undergoes a loss or gain of electrons.



A cation is formed when an atom loses the most loosely bound electron from its outermost shell. The atom acquires a positive charge and becomes an ion (a cation). A cation is smaller than its atom. On the removal of an electron, the positive charge of the nucleus acts on lesser number of electrons than in the neutral atom and thus greater pull is exerted by the nucleus, resulting in a smaller size of the cation.

An anion is bigger than its atom because on receipt of an electron in the outermost orbit the number of negative charges increase and it outweighs the positive charges. Thus the hold of the nucleus on the shells decrease resulting in an increase in the size of the anion.

**A cation is always smaller than its atom and an anion is always bigger than its atom e.g.  $\text{Na}^+$  is smaller than  $\text{Na}$ ,  $\text{Cl}^-$  is bigger than  $\text{Cl}$ .**

- In the main groups, the ionic radii increase on descending the group. *e.g.*,  $\text{Li}^+ = 0.76 \text{ \AA}$ ,  $\text{Na}^+ = 1.02 \text{ \AA}$ ,  $\text{K}^+ = 1.38 \text{ \AA}$ , etc. It is due to the addition of extra shell at each step.
- There is a decrease in the ionic radii of the positive ions on moving from left to right across a period in the periodic table. *e.g.*,  $\text{Na}^+ = 1.02 \text{ \AA}$ ,  $\text{Mg}^{2+} = 0.72 \text{ \AA}$ ,  $\text{Al}^{3+} = 0.535 \text{ \AA}$ , etc. It is due to the increase in the number of charges on the nucleus and also due to the increase in the charge on the ion.
- The ionic radii of the negative ions, also decrease on moving from left to right across a period. *e.g.*,  $\text{O}^{2-} = 1.40 \text{ \AA}$ ,  $\text{F}^- = 1.33 \text{ \AA}$ , etc. This is partly due to increase in the number of charges on the nucleus and also due to the decreasing charge on the ion.



## MODULE - 2

Atomic Structure and  
Chemical Bonding

Periodic Table and Periodicity in Properties



Notes

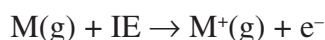


### INTEXT QUESTION 3.2

1. Write the names of the elements with atomic numbers 105, 109, 112, 115 according to IUPAC nomenclature.
2. Arrange the following in the order of increasing size  
 $\text{Na}^+$ ,  $\text{Al}^{3+}$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$
3. How does the size of atoms vary from left to right in a period and on descending a group in the periodic table?

### 3.11 IONIZATION ENTHALPY

Ionization Enthalpy is the energy required to remove the most loosely bound electron from an isolated atom in the gaseous state for one mole of an element. It is expressed in  $\text{kJ mol}^{-1}$  (kilojoules per mole).



As we move from left to right in the periodic table, there is a nearly regular increase in the magnitude of the ionization enthalpy of elements.

Similarly, on moving down a group the magnitude of the ionization enthalpy indicates a regular decline. The ionization enthalpy of the first member of any group is the highest within that group and the ionization enthalpy of the last member in the same group, is the least. This is shown in table 3.4.

Table 3.4: First ionization enthalpies of the elements (in  $\text{kJ mol}^{-1}$ )

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H • 1311																	He • 2372
2	Li • 520	Be • 899											B • 801	C • 1086	N • 1403	O • 1410	F • 1681	Ne • 2081
3	Na • 496	Mg • 737											Al • 577	Si • 786	P • 1012	S • 999	Cl • 1255	Ar • 1521
4	K • 419	Ca • 590	Sc • 631	Ti • 656	V • 650	Cr • 652	Mn • 717	Fe • 762	Co • 758	Ni • 736	Cu • 745	Zn • 906	Ga • 579	Ge • 760	As • 947	Se • 941	Br • 1142	Kr • 1351
5	Rb • 403	Sr • 549	Y • 616	Zr • 674	Nb • 664	Mo • 685	Tc • 703	Ru • 711	Rh • 720	Pd • 804	Ag • 731	Cd • 876	In • 558	Sn • 708	Sb • 834	Te • 869	I • 1191	Xe • 1170
6	Cs • 376	Ba • 503	La • 541	Hf • 760	Ta • 760	W • 770	Re • 759	Os • 840	Ti • 900	Pt • 870	Au • 889	Hg • 1007	Tl • 589	Pb • 1007	Bi • 589	Po • 715	At • 703	Rn • 813
7	Fr • 912	Ra • 1037	Ac • 1037															



Notes

The variation in the magnitude of ionization enthalpy of elements in the periodic table is mainly dependent on the following factors:

- The size of the atom
  - The magnitude of the nuclear charge on the atom,
  - The extent of screening
  - The type of orbital involved (*s*, *p*, *d*, or *f*).
- In small atoms, the electrons are tightly held whereas in large atoms the electrons are less strongly held. Thus, the ionization enthalpy decreases as the size of the atom increases.
  - When an electron is removed from an atom, the effective nuclear charge, i.e., the ratio of the number of charges on the nucleus to the number of electrons, increases. As a result the remaining electrons come closer to the nucleus and are held more tightly. The removal of a second electron, therefore, requires more energy. e.g.,  $\text{Mg}^+$  is smaller than the  $\text{Mg}$  atom. The remaining electrons in  $\text{Mg}^+$  are more tightly held. The second ionisation enthalpy is, therefore, more than the first ionisation enthalpy.
  - Since the orbitals (*s*, *p*, *d* and *f*) have different shapes, the ionization enthalpy depends on the type of electrons removed. e.g. an electron in an *s* orbital is more tightly held as compared to an electron in a *p* orbital. It is because an *s* electron is nearer to the nucleus as compared to a *p* electron. Similarly a *p*-electron is more tightly held than a *d*-electron, and a *d*-electron is more tightly held than a *f*-electron. If all other factors are equal, the ionization enthalpies are in the order  $s > p > d > f$ .

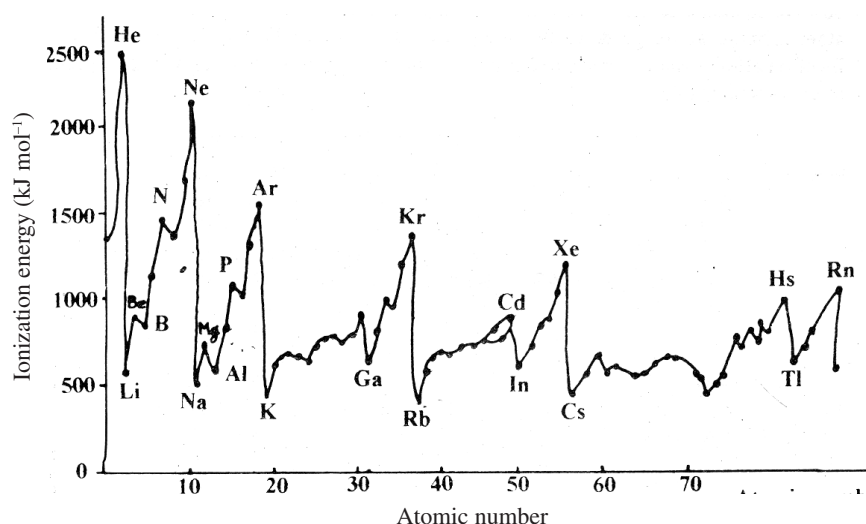


Fig 3.4 : Variation of ionization enthalpy of elements.

These factors taken together contribute largely to decide the extent of the force of attraction between the nucleus and the electrons around it. The resultant of

## MODULE - 2

### Atomic Structure and Chemical Bonding

### Periodic Table and Periodicity in Properties



#### Notes

these factors thus determine the magnitude of ionization enthalpy of any element. You can see the variation in the magnitude of the ionization enthalpy of elements with atomic number in the Fig. 3.4.

It is clear from Fig. 3.4 that

- (i) the metals of group 1 (Li, Na, K, Rb, etc.) have the lowest ionization enthalpies in their respective periods.
- (ii) the noble gases (He, Ne, Ar, Kr, Xe and Rn) have the highest ionization enthalpies in their respective periods. It is because the energy required to remove an electron from a stable fully filled shell is very large.
- (iii) The values of ionization energies do not increase smoothly. e.g. the first ionization enthalpy of B (boron) is lower than that of Be (beryllium); the ionization enthalpy of Al (aluminium) is lower than that of Mg (magnesium); the first ionization enthalpy of O (oxygen) is lower than that of N (nitrogen). It can be explained as follows.

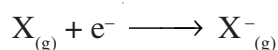
- The first ionization enthalpies of Be and Mg are higher than those of their preceding elements because the electrons are removed from the fully filled  $s$ -orbitals.
- The first ionization enthalpy of N is higher than that of O because from N, the electron is to be removed from a half-filled  $p$ -orbitals

Ionization enthalpy is the energy required to remove the most loosely bound electron from an atom (in the gaseous state) for one mole of an element. It is an absolute value and can be determined experimentally.

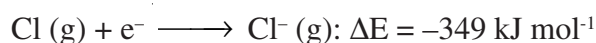
### 3.12 ELECTRON GAIN ENTHALPY

Every atom, in general, has a tendency to gain or lose electrons in order to acquire a noble gas configuration. The atom which have five, six or seven electrons in their outermost shell show tendency to accept electrons and attain the nearest noble gas configuration. Halogens, for example, have seven electrons in their outermost orbit. Thus they show a tendency to accept one more electron and attain the nearest noble gas configuration. The energy change ( $\Delta E$ ) for this process is called **electron gain enthalpy** of that atom.

**Electron gain enthalpy is the energy released for one mole of neutral atoms in a gaseous state when electron is accepted by each atom.**



where X represents an atom.



The negative value shows release of energy and hence tendency to greater stabilisation. The electron gain enthalpy becomes more in negative from left to right in a period. This is because it is easier to add an electron to a smaller atom since the added electron would be closer to the positively charged nucleus. Halogens release maximum energy when they accept an electron. On the other hand, metals do not accept electrons and show a high positive value for  $\Delta E$ . Thus electron gain enthalpy can be positive or negative.

Electron gain enthalpies becomes less in negative as we go down the group showing that the electropositive character of the atoms increases. This is because the size of the atom increases down the group and the electron added goes to the higher shells. Electron affinity values for some elements are shown in table 3.5, along with their position in the periodic table. The electron gain enthalpy of chlorine is more in negative value as compared to that of fluroine. This is due to the small size of the F atom. As the electron approaches the small F atom, it experiences a repulsion from other electrons.

 Table 3.5: Electeron gain enthalpy in  $\text{kJ mol}^{-1}$ 

		Group							
Period	1	2	13	14	15	16	17	18	
1	H							He	
	-73							+98	
2	Li	Be	B	C	N	O	F	Ne	
	-59.6	(0)	-26.7	-154	-7	-111	-328	+116	
3	Na						Cl	Ar	
	-53						-349	+ 96	
4	K						Br	Kr	
	-48						-325	+ 96	
5	Rb						I	Xe	
	-47						-295	+ 77	
6								Rn	
								+ 68	

### 3.13 ELECTRONEGATIVITY

It is an indicator of the extent of attraction by which electrons of the bond pair are attracted by an atom linked by this bond. The value of electronegativity is assigned arbitrarily to one atom such as hydrogen. Then the value of electronegativity is assigned to all other atoms with respect to hydrogen. One such scale is the **Pauling Scale of electronegativity** (Table 3.6).

**Electronegativity is defined as a measure of the ability of an atom to attract the electron pair in a covalent bond to itself.**



Notes

## MODULE - 2

### Atomic Structure and Chemical Bonding



#### Notes

### Periodic Table and Periodicity in Properties

In a homonuclear diatomic molecule such as hydrogen ( $H_2$ ) or fluorine ( $F_2$ ), the electron pair of the covalent bond in each molecule experiences equal attraction by each atom. Thus none of the two atoms is able to shift the bond pair of electrons to itself. However in a heteronuclear diatomic molecule, the bond pair electrons get shifted towards the atom which is more electronegative than the other. For example, in HF or HCl the bond pair of electrons are not shared equally but the more electronegative atom F or Cl is able to shift the bond pair towards itself, resulting in the polarization of the molecule.

A large difference between electronegativities of the two atoms indicates highly ionic character of the bond between them, for example in  $Cs^+F^-$ . On the other hand, zero difference in the electronegativities between the two atoms indicates that the percentage ionic character is zero. Therefore the molecule is purely covalent e.g.  $H_2$ ,  $Cl_2$ ,  $N_2$  etc.

**Table 3.6 : Electronegativities of elements on Pauling scale.**

<b>Li</b>	<b>Be</b>	<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca	Se	Ge	As	Sc	Br
0.8	1.0	1.3	1.7	1.8	2.1	2.5
Cs	Ba					
0.7	0.9					

The most electronegative elements have been placed on the farthest right hand upper corner (noble gases are not included). The value of electronegativity decreases as we go down in any group and increases from left to right in the period. Thus fluorine is the most electronegative and caesium is the least electronegative element. (We have not considered Francium being radioactive).

### 3.14 CONCEPT OF VALENCE OR VALENCY

You that that different elements have different number of electrons in the outermost or the valence shell. These electrons in the outermost shell are known as valence electrons. **The number of valence electrons determines the combining capacity of an atom in an element.** Valence is the number of chemical bonds that an atom can form with univalent atoms. Since hydrogen is a univalent atom, the valence of an element can be taken by the number of atoms of hydrogen with which one atom of the element can combine. For example, in  $H_2O$ ,  $NH_3$ , and  $CH_4$  the valencies of oxygen, nitrogen and carbon are 2, 3 and 4, respectively.

The elements having a completely filled outermost shell in their atoms show little or no chemical activity. In other words, their combining capacity or valency is zero. The elements with completely filled valence shells are said to have stable

electronic configuration. The main group elements can have a maximum of eight electrons in their valence shell. This is called **octet rule**; you will learn more about it in lesson 7. You will learn that the combining capacity or the tendency of an atom to react with other atoms to form molecules depends on the ease with which it can achieve octet in its outermost shell. The valencies of the elements can be calculated from the electronic configuration by applying the octet rule.

- If the number of valence electrons is four or less then the valency is equal to the number of the valence electrons.
- In cases when the number of valence electrons is more than four then generally the valency is equal to 8 minus the number of valence electrons.

Thus,

Valency = Number of valence electrons (for 4 or lesser valence electrons)

Valency = 8 - Number of valence electrons (for more than 4 valence electrons)

The composition and electronic configuration of the elements having the atomic numbers from 1 to 18, along with their valencies is given in Table 3.7.

**Table 3.7: The composition, electron distribution and common valency of the elements with atomic number from 1 to 18**

Name of Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Number of Electrons	Distribution of Electrons				Valency
						K	L	M	N	
Hydrogen	H	1	1	—	1	—	—	—	—	1
Helium	He	2	2	2	2	—	—	—	—	0
Lithium	Li	3	3	4	3	2	1	—	—	1
Beryllium	Be	4	4	5	4	2	2	—	—	2
Boron	B	5	5	6	5	2	3	—	—	3
Carbon	C	6	6	6	6	2	4	—	—	4
Nitrogen	N	7	7	7	7	2	5	—	—	3
Oxygen	O	8	8	8	8	2	6	—	—	2
Fluorine	F	9	9	10	9	2	7	—	—	1
Neon	Ne	10	10	10	10	2	8	—	—	0
Sodium	Na	11	11	12	11	2	8	1	—	1
Magnesium	Mg	12	12	12	12	2	8	2	—	2
Aluminium	Al	13	13	14	13	2	8	3	—	3
Silicon	Si	14	14	14	14	2	8	4	—	4
Phosphorus	P	15	15	16	15	2	8	5	—	3*
Sulphur	S	16	16	16	16	2	8	6	—	2
Chlorine	Cl	17	17	18	17	2	8	7	—	1
Argon	Ar	18	18	22	18	2	8	8	—	0

\*However, the elements in the 3rd and higher periods may show higher valencie, than predicted by octet rule since more than 8 electrons can be accommodate in their outermost shells due to available *d* orbitas,.



Notes





## Notes

## 3.14.1 Electron Configurations and the Periodic Table

By this time you can see a pattern develop among the ground state electron configurations of the atoms. This pattern explains the periodic table. Consider helium, neon, argon, and krypton, elements in Group 18 of the periodic table. Neon, argon, and krypton have configurations in which a p subshell has just filled. (Helium has a filled 1s subshell; no lp subshell is possible.)

helium	$1s^2$
neon	$1s^2 2s^2 2p^6$
argon	$1s^2 2s^2 2p^6 3s^2 3p^6$
krypton	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

These elements are the members of the group called *noble gases* because of their relative unreactivity.

Look now at the configurations of beryllium, magnesium, and calcium, members of the group of *alkaline earth metals* (Group 2), which are similar, moderately reactive elements.

beryllium	$1s^2 2s^2$	or	$[\text{He}]2s^2$
magnesium	$1s^2 2s^2 2p^6 3s^2$	or	$[\text{Ne}]3s^2$
calcium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	or	$[\text{Ar}]4s^2$

Each of these configurations consists of a **noble gas core**, that is, *an inner shell configuration corresponding to one of the noble gases, plus two outer electrons with an  $ns^2$  configuration.*

The elements boron, aluminum, and gallium (Group 13) also have similarities. Their configurations are

boron	$1s^2 2s^2 2p^1$	or	$[\text{He}]2s^2 2p^1$
aluminum	$1s^2 2s^2 2p^6 3s^2 3p^1$	or	$[\text{Ne}]3s^2 3p^1$
gallium	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$	or	$[\text{Ar}]3d^{10} 4s^2 4p^1$

Boron and aluminum have noble-gas cores plus three electrons with the configuration  $ns^2 np^1$ . Gallium has an additional filled 3d subshell. *The noble-gas core together with  $(n - 1)d^{10}$  electrons is often referred to as a **pseudo-noble gas core**, because these electrons usually are not involved in chemical reactions.*

*An electron in a core outside the noble-gas or pseudo-noble-gas core is called a **valence electron**. Such electrons are primarily involved in chemical reactions, and similarities among the configurations of valence electrons (the valence-shell configurations) account for similarities in the chemical properties among the groups of elements.*



## INTEXT QUESTIONS 3.3

- What is the correlation between atomic size and ionization enthalpy.
- Which species, in each pair is expected to have higher ionization enthalpy.
  - ${}_3\text{Li}$ ,  ${}_{11}\text{Na}$
  - ${}_7\text{N}$ ,  ${}_{15}\text{P}$
  - ${}^{20}\text{Ca}$ ,  ${}^{12}\text{Mg}$
  - ${}_{13}\text{Al}$ ,  ${}_{14}\text{Si}$
  - ${}_{17}\text{Cl}$ ,  ${}_{18}\text{Ar}$
  - ${}_{18}\text{Ar}$ ,  ${}_{19}\text{K}$
  - ${}_{13}\text{Al}$ ,  ${}_{14}\text{C}$
- Account for the fact that there is a decrease in first ionization enthalpy from Be to B and Mg to Al.
- Why is the ionization enthalpy of the noble gases highest in their respective periods?
- Name the most electronegative element.



## WHAT YOU HAVE LEARNT

- The classification of elements makes their study systematic.
- The arrangement of elements in the long form of the periodic table depends on their electronic configuration.
- The properties of the elements are the periodic function of their atomic number.
- All the known elements are arranged in 18 groups in the long form of periodic table
- There are seven horizontal rows (periods) in the long form of the periodic table.
- Elements of groups 1 and 2 are known as alkali metals and alkaline earth metals respectively.
- Elements of groups 17 and 18 are known as halogens and noble gases respectively.
- $s$ ,  $p$ ,  $d$  and  $f$  are the four blocks in the periodic table classified on the basis of their outer most electrons residing in  $s$ ,  $p$ ,  $d$  or  $f$  sub-shell.
- The elements can be classified into metals, non-metals and metalloids on the basis of their properties and their position in the periodic table.
- The atomic size, ionic size, ionization enthalpy, electron gain enthalpy and electronegativity and valence show regular trends along a group and a period.
- Valence can be explained.



Notes

## MODULE - 2

Atomic Structure and  
Chemical Bonding



Notes



### TERMINAL EXERCISE

- Define modern periodic law.
- Refer the periodic table given in Table 3.2 and answer the following questions.
  - The elements placed in group number 18 are called .....
  - Alkali and alkaline earth metals are collectively called ..... block metals.
  - The general configuration for halogens is .....
  - Name a *p*-block element which is a gas other than a noble gas or a halogen.
  - Name the groups that comprise the 's' block of elements.
  - Element number 118 has not yet been established, to which block, will it belong?
  - How many elements should be there in total if all the *7s*, *7p*, *6d* and *5f*, blocks are to be full?
- Describe the variation of electron affinity and ionization enthalpy in the periodic table.
- Define the following:
  - Electron gain enthalpy
  - Ionization enthalpy
  - Ionic radius
  - Electronegativity.
- What is electronegativity? How is it related to the type of bond formed?
- Why is the electron gain enthalpy of Cl more in negative value as compared to that of F?



### ANSWERS TO INTEXT QUESTIONS

#### 3.1

- |           |            |            |
|-----------|------------|------------|
| 1. Metals | Non metals | Metalloids |
| Sn, Pb    | C          | Si, Ge     |
| Sb, Bi    | N, P       | As         |
| Te, Po    | O, S       | Se         |

2. Potassium is more metallic than aluminum.
3. (i) 2            (ii) 1            (iii) 3 - 12            (iv) 17    (v) 18
4. Np,            Lr,            No,            Rf,            Hs.

### 3.2

1. (i) Unnilpentium,  
(ii) unnilennium,  
(iii) Ununbium,  
(iv) Ununpentium
2.  $\text{Al}^{3+}$ ,  $\text{Na}^+$ ,  $\text{F}^-$ ,  $\text{O}^{2-}$
3. The atomic size decreases from left to right across a period and increases on moving down the group.

### 3.3

1. Ionization enthalpy decreases with increase in atomic size and vice-versa.
2. (i)  ${}_3\text{Li}$             (ii)  ${}_7\text{N}$             (iii)  ${}_{12}\text{Mg}$   
(iv)  ${}_{14}\text{Si}$             (v)  ${}_{12}\text{Ar}$             (vi)  ${}_{18}\text{Ar}$             (vii)  ${}_6\text{C}$
3. The electronic configuration of Be is  $1s^2 2s^2$  whereas that of B is  $1s^2 2s^2 2p^1$ . In case of Be, the electron is to be removed from completely filled  $s$  orbital whereas in case of B it is to be removed from a singly occupied  $p$  orbital. Fully-filled orbitals are more stable. Hence, ionization enthalpy decreases from Be to B. Similarly it decreases from Mg to Al.
4. The noble gases have fully filled shells and are stable. Hence, they have the highest ionization enthalpies in their respective periods.
5. Fluorine.

## MODULE - 2

### Atomic Structure and Chemical Bonding



### Notes