Chapter 8

PERIODIC PROPERTIES

8.1 Introduction

The genesis of classification of elements dates back to early 1800s when the German chemist Johann Dobereiner made the first attempt to systematise the study of properties of elements and gave the *Dobereiners law of triads*. This was followed by the *Newlands law of octaves*. The first detailed classification of elements was proposed by Russian chemist Dmitri Mendeleev (1837–1907) and German chemist Lothar Meyer (1830–1895). Both these scientists worked independently and in 1869 proposed that when elements are arranged in the increasing order of their atomic weights, similarities appear in their physical and chemical properties at regular intervals. However, the *Mendeleev's periodic table* had certain anomalies, which were addressed in due course of time. Gradual improvement saw the development of the *modern periodic law* (given by Henry Moseley) in which the elements are arranged in the order of increasing atomic numbers.

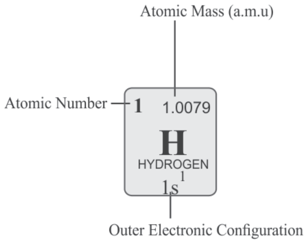
The elements are arranged in the periodic table in the order of increasing atomic numbers. They are divided into 18 vertical columns called groups and seven horizontal rows termed as periods. According to the IUPAC recommendations, the groups are numbered from 1 to 18, replacing the older notations of groups IA…VIIA, IB…VIIB and zero. The seven periods have 2, 8, 8, 18, 18 and 32 elements, respectively. The seventh period is incomplete and will theoretically consist of 32 elements. The properties of the elements vary periodically due to periodic variation in their electronic configuration. In this chapter, we will study the variations in electronic configurations, atomic and ionic sizes, ionisation energies and other related properties.

8.2 Basic Concepts

Before studying the periodicity in properties of elements, it is important to have knowledge of some basic terms and concepts.

- In the atoms, the orbitals are filled in the order of increasing energy (Aufbau principle), that is, an electron will first enter the orbital of lowest energy. The sequence of orbitals in the order of increasing energy is as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s.

Long Form Of The Periodic Table



Main group elements
s–block elements

d–block elements (transition series)

p–block elements
Main group elements

Period Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 1.0079 **H** HYDROGEN $1s^1$																	2 4.0026 **He** HELIUM $1s^2$
2	3 6.941 **Li** LITHIUM $2s^1$	4 9.012 **Be** BERYLLIUM $2s^2$											5 10.811 **B** BORON $2s^2 2p^1$	6 12.011 **C** CARBON $2s^2 2p^2$	7 14.007 **N** NITROGEN $2s^2 2p^3$	8 15.999 **O** OXYGEN $2s^2 2p^4$	9 18.998 **F** FLUORINE $2s^2 2p^5$	10 20.179 **Ne** NEON $2s^2 2p^6$
3	11 22.990 **Na** SODIUM $3s^1$	12 24.305 **Mg** MAGNESIUM $3s^2$											13 26.982 **Al** ALUMINIUM $3s^2 3p^1$	14 28.086 **Si** SILICON $3s^2 3p^2$	15 30.973 **P** PHOSPHORUS $3s^2 3p^3$	16 32.064 **S** SULPHUR $3s^2 3p^4$	17 35.453 **Cl** CHLORINE $3s^2 3p^5$	18 39.948 **Ar** ARGON $3s^2 3p^6$
4	19 39.098 **K** POTASSIUM $4s^1$	20 40.078 **Ca** CALCIUM $4s^2$	21 44.955 **Sc** SCANDIUM $3d^1 4s^2$	22 47.902 **Ti** TITANIUM $3d^2 4s^2$	23 50.942 **V** VANADIUM $3d^3 4s^2$	24 51.996 **Cr** CHROMIUM $3d^5 4s^1$	25 54.938 **Mn** MANGANESE $3d^5 4s^2$	26 55.847 **Fe** IRON $3d^6 4s^2$	27 58.933 **Co** COBALT $3d^7 4s^2$	28 58.699 **Ni** NICKEL $3d^8 4s^2$	29 63.546 **Cu** COPPER $3d^{10} 4s^1$	30 65.70 **Zn** ZINC $3d^{10} 4s^2$	31 69.723 **Ga** GALLIUM $3d^{10} 4s^2 4p^1$	32 72.63 **Ge** GERMANIUM $3d^{10} 4s^2 4p^2$	33 74.922 **As** ARSENIC $4s^2 4p^3$	34 78.971 **Se** SELENIUM $4s^2 4p^4$	35 79.907 **Br** BROMINE $4s^2 4p^5$	36 83.801 **Kr** KRYPTON $4s^2 4p^6$
5	37 85.468 **Rb** RUBIDIUM $5s^1$	38 87.620 **Sr** STRONTIUM $5s^2$	39 88.906 **Y** YTTRIUM $4d^1 5s^2$	40 91.224 **Zr** ZIRCONIUM $4d^2 5s^2$	41 92.906 **Nb** NIOBIUM $4d^4 5s^1$	42 95.95 **Mo** MOLYBDENUM $4d^5 5s^1$	43 98.906 **Tc** TECHNETIUM $4d^5 5s^2$	44 101.07 **Ru** RUTHENIUM $4d^7 5s^1$	45 102.91 **Rh** RHODIUM $4d^8 5s^1$	46 106.42 **Pd** PALLADIUM $4d^9 5s^1$	47 107.87 **Ag** SILVER $4d^{10} 5s^1$	48 112.41 **Cd** CADMIUM $4d^{10} 5s^2$	49 114.82 **In** INDIUM $5s^2 5p^1$	50 118.69 **Sn** TIN $5s^2 5p^2$	51 121.75 **Sb** ANTIMONY $5s^2 5p^3$	52 127.60 **Te** TELLURIUM $5s^2 5p^4$	53 126.90 **I** IODINE $5s^2 5p^5$	54 131.29 **Xe** XENON $5s^2 5p^6$
6	55 132.91 **Cs** CAESIUM $6s^1$	56 137.33 **Ba** BARIUM $6s^2$	57 138.91 **La** LANTHANUM $5d^1 6s^2$	72 178.49 **Hf** HAFNIUM $5d^2 6s^2$	73 180.95 **Ta** TANTALUM $5d^3 6s^2$	74 183.85 **W** TUNGSTEN $5d^4 6s^2$	75 186.20 **Re** RHENIUM $5d^5 6s^2$	76 190.20 **Os** OSMIUM $5d^6 6s^2$	77 192.22 **Ir** IRIDIUM $5d^7 6s^2$	78 195.09 **Pt** PLATINUM $5d^9 6s^1$	79 196.97 **Au** GOLD $5d^{10} 6s^1$	80 200.59 **Hg** MERCURY $5d^{10} 6s^2$	81 204.38 **Tl** THALLIUM $6s^2 6p^1$	82 207.19 **Pb** LEAD $6s^2 6p^2$	83 208.98 **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	87 223.02* **Fr** FRANCIUM $7s^1$	88 226.03* **Ra** RADIUM $7s^2$	89 227.03 **Ac** ACTINIUM $6d^1 7s^2$	104 261.11 **Rf** RUTHERFORDIUM $6d^2 7s^2$	105 262.114 **Db** DUBNIUM $6d^3 7s^2$	106 263.118 **Sg** SEABORGIUM $6d^4 7s^2$	107 262.12* **Bh** BOHRIUM $6d^5 7s^2$	108 265* **Hs** HASSIUM $6d^6 7s^2$	109 268.14* **Mt** MEITNERIUM $6d^7 7s^2$	110 281.16* **Ds** DARMSTADTIUM $6d^8 7s^2$	111 **Rg** ROENTGENIUM $6d^{10} 7s^1$	112 **Cn** COPERNICIUM $6d^{10} 7s^2$	113 **Uut** UNUNTRIUM	114 **Fl** FLEROVIUM	115 **Uup** UNUNPENTIUM	116 **Lv** LIVERMORIUM	117 **Uus** UNUNSEPTIUM	118 **Uuo** UNUNOCTIUM

f–block elements (Inner transition series)

LANTHANOIDS $5f^n 5d^{0-1} 6s^2$	58 140.12 **Ce** CERIUM $4f^2 5d^0 6s^2$	59 140.907* **Pr** PRASEODYMIUM $4f^3 5d^0 6s^2$	60 144.24 **Nd** NEODYMIUM $4f^4 5d^0 6s^2$	61 146.92 **Pm** PROMETHIUM $4f^5 5d^0 6s^2$	62 150.35 **Sm** SAMARIUM $4f^6 5d^0 6s^2$	63 151.97 **Eu** EUROPIUM $4f^7 5d^0 6s^2$	64 157.25 **Gd** GADOLINIUM $4f^7 5d^1 6s^2$	65 158.93 **Tb** TERBIUM $4f^9 5d^0 6s^2$	66 162.50 **Dy** DYSPROSIUM $4f^{10} 5d^0 6s^2$	67 164.93 **Ho** HOLMIUM $4f^{11} 5d^0 6s^2$	68 167.26 **Er** ERBIUM $4f^{12} 5d^0 6s^2$	69 168.93 **Tm** THULIUM $4f^{13} 5d^0 6s^2$	70 173.04 **Yb** YTTERBIUM $4f^{14} 5d^0 6s^2$	71 174.97 **Lu** LUTETIUM $4f^{14} 5d^1 6s^2$
ACTINOIDS $5f^n 6d^{0-2} 7s^2$	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 $5f^{14} 6d^1 7s^2$

***Atomic mass of the isotope of longest half life**

- The other rules governing the filling of orbitals are
  - *Pauli's exclusion principle*: It was given by Austrian scientist Wolfgang Pauli (1925). It states that in an atom, no two electrons can have the same set of all four quantum numbers. If the principal, azimuthal and magnetic quantum numbers are the same, the electrons will have different spins.
  - *Hund's rule of maximum multiplicity:* It states that electrons in the same subshell (*p, d and f*) do not pair until all the orbitals of similar energy gain one electron each.
- *Effective nuclear charge*: The hydrogen atom has only one electron, the energy level of which is determined by its principal quantum number n. All the orbitals inside this shell have the same energy and the only force experienced by the electron is the attractive force towards the positively charged nucleus. The situation is, however, different in case of multielectron atoms. The electrons in such atoms experience not only attractive force of the nucleus but also repulsion among themselves and each of their neighbours. The repulsion of outer-shell electrons by the inner-shell electrons is particularly important, as the outer shell electrons are pushed away from the nucleus due to repulsion of the inner-shell electrons. As a result, the nuclear charge felt by the outer-shell electrons is less than what it would have been if there were no inner electrons. This net charge felt by the valence electrons is termed as the effective nuclear charge, represented by the symbol (Z_{eff}), and the repulsion experienced due to the inner electrons is the shielding effect. The shielding effect is called so because the inner electrons shield/screen the outer electrons from experiencing the actual nuclear charge ($Z_{eff} = Z_{actual}$ – electron shielding).
- Consider the example of fluorine (atomic number = 9); there are two electrons in shell 1 (n=1) and seven electrons in shell 2 (n = 2). The seven electrons in n = 2 will be repelled by two electrons in n = 1 hence they will experience less attraction than what they would have experienced in the absence of these two electrons. Hence, these two inner-shell electrons are shielding or screening the outer electrons from the attractive force of the nucleus, and because of this shielding, the effective attractive force felt by the valence electrons reduces. Shielding effect generally remains the same in the period, as in the period the number of shells is the same and it increases down the group.
- *Penetration effect:* It is the tendency of electrons in an orbital to be attracted towards the nucleus. In a multielectron system, penetration is the electron's relative electron density (probability density) near the nucleus and can also be considered as the presence of electrons inside the shell of other electrons. This can be explained by considering the shapes of orbitals and their radial distribution curves (Fig 8.1). The 1s orbital is spherically symmetrical with no node, hence we can see from the curve (Fig 8.1) that it has maximum probability density near the nucleus. On comparing 2s and 2p orbitals, we see that 2s is spherically symmetrical having a sphere within a sphere. It has two regions of high probability separated by a surface of zero probability called the node, and 2p orbital is dumb-bell shaped with electron distribution in identical lobes on either side of the nucleus and separated by a node cutting through the nucleus. This can be seen in Fig 8.1, which shows that 2s penetrates inside 1s (see the small loop of 2s inside 1s orbital in Fig 8.1). The 2p does not penetrate effectively because its wave function goes to zero at the nucleus. Thus 2s is more tightly bound to the nucleus and has lower energy than the 2p orbital. Thus the penetration of 2s is greater than 2p and the electrons in 2s experience large value of Z_{eff} than the electrons in the 2p orbital. For subshells

within the same shell (n), the penetrating power of electron follow the sequence s > p > d > f. When the value of shell (n) and subshell (l) are different the penetrating power of electrons follows the trend

1s > 2s > 2p > 3s > 3p > 4s > 3d > 4p > 5s > 4d > 5p > 6s > 4f

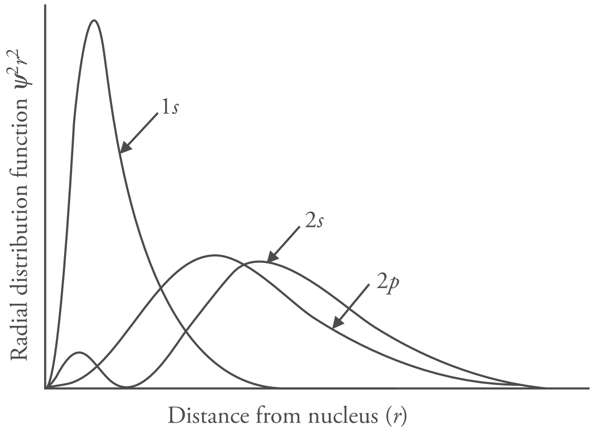


Figure 8.1 *Radial distribution function of orbitals*

Greater the penetration power of an electron, closer it will be to the nucleus, it will experience greater effective nuclear charge and it will be held firmly. Hence the ionisation enthalpy would be high. Table 8.1 gives the effective nuclear charge of the orbitals of a few atoms.

Table 8.1 Effective nuclear charge Z_{eff} of the orbitals of few atoms

	H							**He**
Z	1							2
1s	1.00							1.69
	Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
Z	3	4	5	6	7	8	9	10
1s	2.69	3.68	4.68	5.67	6.66	7.66	8.65	9.64
2s	1.28	1.91	2.58	3.22	3.85	4.49	5.13	5.76
2p			2.42	3.14	3.83	4.45	5.10	5.76
	Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
Z	11	12	13	14	15	16	17	18
1s	10.63	11.61	12.59	13.57	14.56	15.54	16.52	17.51
2s	6.57	7.39	8.21	9.02	9.82	10.63	11.43	12.23
2p	6.80	7.83	8.96	9.94	10.96	11.98	12.99	14.01
3s	2.51	3.31	4.12	4.90	5.64	6.37	7.07	7.76
3p			4.07	4.29	4.89	5.48	6.12	6.76

8.3 Periodicity in Properties

Electronic configuration in period: Each period corresponds to the value of *n* or principal energy level.

First period (n = 1) There are only two elements in this period, hence the electronic configuration of the first element hydrogen is $1s^1$ and that of helium is $1s^2$. With this, the first shell or K shell is completely filled.

Second period (n = 2) It starts with lithium $1s^22s^1$, beryllium with four electrons has the configuration $1s^22s^2$. There are eight elements in this period. The configuration of the last element neon is $1s^22s^22p^6$. The second shell is completely filled.

Third period (n = 3) It starts with Na ($1s^22s^22p^63s^1$). This period also has eight elements. The 3s and 3p orbitals are completely filled; however, the 3d orbitals remain vacant as their energy is higher than the energy of 4s orbitals. The configuration of the last element [Ar] of this period is $1s^22s^22p^63s^23p^6$.

Fourth period (n = 4) It starts with potassium, where the electron is added to the 4s orbital. The electronic configurations of K and Ca are $[Ar]4s^1$ and $[Ar]4s^2$, respectively. After filling of 4s orbital, the filling of 3d orbital becomes energetically favourable. It starts at Sc (Z = 21), which has the configuration $[Ar]3d^14s^2$ and ends at Zn(Z = 30) with electronic configuration $[Ar]3d^{10}4s^2$. There are certain irregularities in filling of 3d orbitals, for example, Cr (Z = 24) and Cu (Z = 29) have the electronic configuration $[Ar]3d^54s^1$ and $[Ar]3d^{10}4s^1$, respectively, against the expected configuration of $[Ar]3d^44s^2$ and $[Ar]3d^94s^2$, respectively. These ten elements from Sc to Zn constitute the *first transition series*. Filling of 4p orbital starts at Ga (Z = 31) and is completed at Kr (Z = 36).

Fifth period (n = 5) It begins with rubidium (Z = 37) where the next electron enters the 5s orbital and this orbital is complete at Sr (Z = 38). After this, ten electrons fill the 4d shell Y (Z = 39) to Cd (Z = 48), where the valence shell configurations are $4d^15s^2$ and $4d^{10}5s^2$, respectively. This is termed as the *second transition series*. However, molybdenum has the configuration $4d^55s^1$ and Ag has the configuration $4d^{10}5s^1$. The filling of 5p orbitals begins at In (Z = 49) and is completed at Xe (Z = 54).

Sixth period (n=6) It contains 32 elements. The orbitals are filled in the order 6s, 4f, 5d and 6p. The filling of 4f orbitals begins with cerium (Z = 58) and ends with lutetium (Z = 71) to give the *4f*-inner transition series termed as the *lanthanoid series*.

Seventh period (n = 7) The filling of orbitals is similar to the sixth period with successive filling of 7s, 5f, 6d and 7p orbitals. The filling of 5f orbitals starts with Th (Z = 90) and is completed at Lw (Z = 103). This series from Th to Lw is called the 5f-inner transition series or the *actinoid series*. The 4f and 5f inner transition series are placed separately below the periodic table to comply with the principle of placing elements with similar properties in a single column.

Table 8.2 gives the IUPAC-recommended names for some groups and sections in the periodic table.

Table 8.2 IUPAC-recommended names of some groups and sections

Group number	IUPAC-recommended name
1 (except H)	Alkali metals
2	Alkaline earth metals
15	Pnictogens
16	Chalcogens
17	Halogens
18	Noble gases
1(except H), 2, 13, 14, 15, 16, 17, 18	Main group elements

8.4 Types of Elements on the Basis of Their Electronic Configuration

Depending on the orbital in which the last electron enters, elements are classified in to four blocks, viz s-block, p-block, d-block and f-block elements.

1. *s-block elements*: They are elements of groups 1 (alkali metals) and 2 (alkaline earth metals) in which the valence electrons enter the s-orbitals. Their outer electronic configuration is ns^1 and ns^2, respectively. They are soft metals with low melting and boiling points, reactive as they have low ionisation enthalpies and strong reducing agents as they lose electrons readily to acquire stable noble gas configuration. Their common oxidation states are +1 and +2, respectively. Their reactivity increases down the group and most of them form ionic compounds, with the exception of lithium and beryllium.
2. *p-block elements*: They are elements of groups 13 to 18, in which the valence electron enters the p-orbitals. Their outermost electronic configuration varies from ns^2np^1 to ns^2np^6. The *p-block elements* together with *s-block elements* are termed as the *representative elements* or the *main group elements*. The p-block elements include both metals and nonmetals. The nonmetallic character increases as we move from left to right across the period and the metallic character increases as we move from top to bottom in the group. Their ionisation enthalpies are higher than that of s block elements. The elements of group 18 (noble gases) with electronic configuration ns^2np^6 are very stable because of completely filled valence electrons. They have very low chemical reactivity. Elements of group 17 (halogens) with electronic configuration ns^2np^5 and group 16 (chalcogens) with electronic configuration ns^2np^4 have highly negative electron gain enthalpies (earlier termed as electron affinity) and they gain one and two electrons, respectively, to acquire the stable noble gas configuration. Some of these elements exhibit more than one oxidation state.
3. *d-block elements*: They are elements of group 3 to 12, in which the last electron enters the d-orbitals of their second last (penultimate) energy level. Their outer electronic configuration is $(n\text{-}1)\ d^{1-10}ns^{0-2}$ These elements are mostly metals, have high melting and boiling points, generally form coloured complexes, exhibit variable valency (oxidation states) and exhibit para magnetism, and many elements like Mn, Ni, Co, Cr, V and Pt and their compounds are used as catalysts. These are termed as transition elements as they act as a bridge between highly reactive elements of groups 1 and 2 and less reactive elements of groups 13 and 14. The d block consists of the following:

First transition series (4th period where 3d orbital is filled), Sc (Z=21) to Zn (Z=30)

Second transition series (5th period where 4d orbitals is gradually filled) Yttrium (Z=39) to Cd (Z=48)

Third transition series (6th period where 5d orbitals are gradually filled) Lanthanum (Z=57), Hafnium (Z=72) and mercury (Z=80)

Fourth transition series (7th period where 6d orbitals are gradually filled) – It is incomplete series.

4. *f-block elements*: *f*-block elements comprises of two rows of elements placed at the bottom of the periodic table. In these elements, the last electron enters the *f*-orbital. However, the last electron is added to the third to the outermost (antepenultimate) energy level; $(n\text{-}2)f$, hence these elements are termed as inner transition element. These elements are characterised by the general electronic configuration $(n\text{-}2)\ f^{1-14}(n-1)d^{0or1}ns^2$
   (a) The first series called *lanthanoid series* extends from from Ce(Z=58) to Lu(Z=71). They are also termed as rare earth elements and have the general electronic configuration is $4f^{1-14}5d^{0or1}\ 6s^2$.
   (b) The second series of elements from Th(Z=90) – Lr(Z=103) is called the *actinoid series;* their general electronic configuration is $5\ f^{1-14}(n-1)d^{0or1}\ 7s^2$

All the f block elements are metals having high melting and boiling points. They exhibit variable oxidation state and form coloured ions. These elements also have the tendency to form complex compounds. Actinoid elements exhibit radioactivity. They have been prepared in nanogram quantities by nuclear reactions and their chemistry is not fully studied. The elements after uranium are called trans-uranium elements.

Note: IUPAC recommends the use of the terms lanthanoids and actinoids over lanthanides and actinide, as 'ide' usually implies negatively charged ions. However, the terms lanthanides and actinides are still commonly used.

8.5 Periodic Trends in Properties of Elements

The physical and chemical properties of elements vary periodically. This has been attributed to similarity in the outer electronic configuration after regular intervals. Let us discuss the periodic trends of some important properties:

Atomic and Ionic Radii

Atomic radius is the distance from the centre of the nucleus to the outermost shell of the electrons. Since it is difficult to obtain an isolated atom, and the electron cloud around an atom does not have a sharp boundary, it is not possible to obtain the atomic radii by direct measurement for an individual atom. For a nonmetal, atomic radius is considered half the distance between the nuclei of two similar atoms bonded together by a single covalent bond (covalent radius) and for a metal it is half the distance between centres of nearest neighbours in a metallic crystal (metallic radius). Both metallic and covalent radii are jointly referred to as the atomic radii.(Table 8.3). For example the inter-nuclear distance between Cl–Cl is 198 pm, hence its atomic radius is taken as 198/2 =

99 pm and the distance between two adjacent copper atoms in solid copper is 256 pm, hence its metallic radius would be 256/2 = 128 pm

$$r_{\text{covalent}} = \frac{\text{Inter-nuclear distance between two similar bonded atoms}}{2}$$

Noble gases do not form covalent bonds, hence their atomic radius is found out by calculating their van der Waals radius, which is defined as half the distance between the nuclei of two non-bonded neighbouring atoms of two adjacent molecules. This can be explained by considering the example of two chlorine molecules in close contact (Fig 8.2)

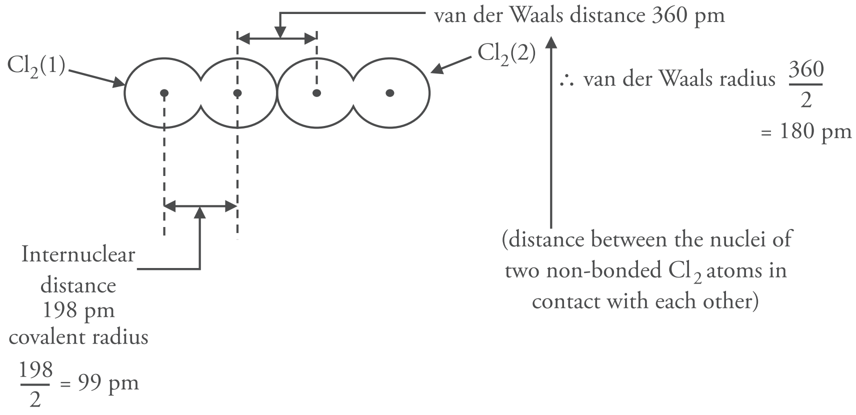


Figure 8.2 *Depiction of van der Waals radii*

Atomic radius can be found by X-ray diffraction, electron diffraction and other spectroscopic techniques.

Trends in atomic and ionic radii: Table 8.3 and Figure 8.3 show the atomic radii of some elements in the period and group, respectively. It is observed that the atomic radii increases down the group and decreases from left to right across the period within s and p block. The atomic radius increases down the group because as one moves down the group the valence electrons occupy the orbitals of successively higher principal quantum number. The valence electrons in Li, Na, K, Rb, Cs, Fr occupy second ($2s^1$), third ($3s^1$), fourth ($4s^1$), fifth ($5s^1$), sixth ($6s^1$), and seventh ($7s^1$), shells, respectively. Since larger shells are occupied, hence the atomic size increases down the group.

The atomic radius decreases across the period, because the valence electrons in a period occupy the same shell but the nuclear charge increases progressively thereby increasing the effective nuclear charge on the valence electrons drawing them closer to the nucleus and decreasing the atomic radii (Fig 8.3). However, it is observed that the atomic radius of second and third rows of d-block elements are almost similar. This is due to lanthanide contraction. The elements of the third row of d block elements (sixth period) are preceeded by 14 lanthanoids where 4f orbitals are occupied. Since these orbitals have poor shielding properties, the valence electrons experience greater attraction towards the nucleus. The repulsions between electrons fails to compensate for the increasing nuclear charge, so Z_{eff} increases from left to right, resulting in the decrease in atomic radii, and the sizes of elements of second and third rows of d-block elements remain almost the same.

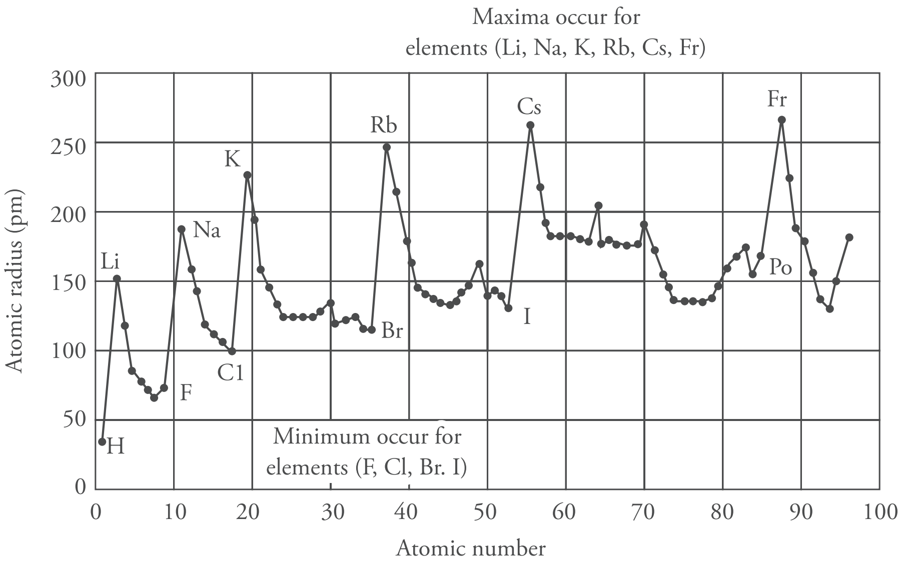


Figure 8.3 *Trends in atomic radius and atomic number*

Table 8.3 Atomic radii of elements in pm

Radius increases ↓

Radius decreases →

H 37																	He
Li 152	Be 112											B 83	C 77	N 75	O 73	F 72	Ne* 160
Na 186	Mg 160											Al 143	Si 117	P 110	S 104	Cl 99	Ar* 191
K 227	Ca 197	Sc 162	Ti 147	V 134	Cr 128	Mn 127	Fe 126	Co 125	Ni 124	Cu 128	Zn 134	Ga 135	Ge 122	As 120	Se 116	Br 114	Kr
Rb	Sr 215	Y 180	Zr 160	Nb 146	Mo 139	Tc 136	Ru 134	Rh 134	Pd 137	Ag 144	Cd 151	In 167	Sn 140	Sb 140	Te 143	I 133	Xe
Cs 248	Ba 222	La 187	Hf 159	Ta 146	W 139	Re 137	Os 135	Ir 136	Pt 138	Au 144	Hg 151	Tl 170	Pb 175	Bi 150	Po 167	At	Rn

*The radii of noble gases are van der Waals radii

Increase in nuclear charge: It results in greater attraction of the orbital electrons towards the nucleus thereby decreasing the atomic radius. As noticed in the Table 8.3, the radius of Ne and Ar is large. This is because it represents the van der Waals radius. The atomic radius increase down the group because while descending in a group two things happen: (i) increase in nuclear charge and (ii) addition of new shells. The second factor outweighs the first, leading to increase in atomic radius from top to bottom.

Variation in ionic radii: It has been observed that the radius of cation (positive ion) is always smaller than that of the parent atom and the radius of anion (negative ion) is always larger than that of the parent atom.

The size of cation decreases not only due to the increase of effective nuclear charge Z_{eff} due to loss of valence electrons thereby decreasing electron–electron repulsions but also due to the fact that generally formation of cation leads to the complete loss of the valence shell. For example the configuration of Li is $1s^2\ 2s^1$ and that of Li ion is $1s^2$. Here the 2s shell is completely lost.

$$\begin{array}{cccc} \text{Li} & \rightarrow & \text{Li}^+ & + \quad e^- \\ (1s^2 2s^1) & & (1s^2) & \\ 123 \text{ pm} & & 60 \text{ pm} & \end{array}$$

Similarly, formation of Mg^{2+} ion (formed by the complete loss of 3s shell) is represented as follows:

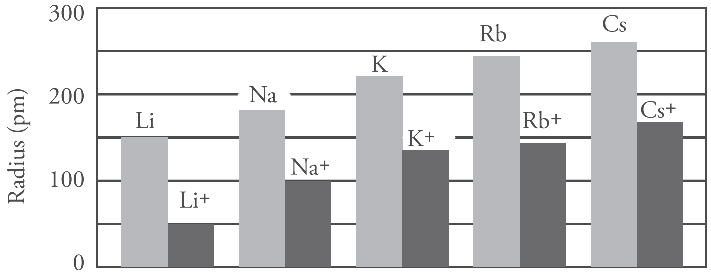
$$\begin{array}{cccc} \text{Mg} & \rightarrow & \text{Mg}^{2+} & + \quad 2e^- \\ (1s^2 2s^2 2p^6 3s^2) & & (1s^2 2s^2 2p^6) & \\ 136 \text{ pm} & & 65 \text{ pm} & \end{array}$$

The radius of cation increases down the group

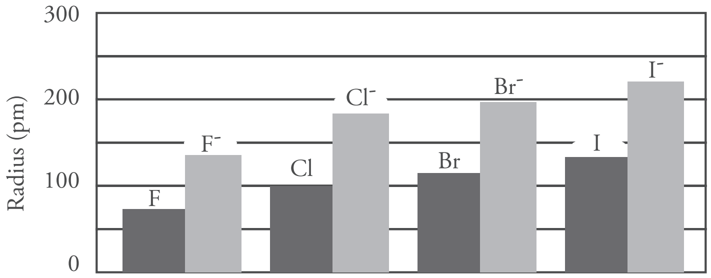
Size of anion increases because addition of electron increases inter-electronic repulsion in the orbital electrons, and hence the electron cloud expands leading to the increase in size. This is also associated with the decrease in Z_{eff}.

For example,

$$\begin{array}{cccc} \text{Cl} \quad + \quad e^- & \rightarrow & \text{Cl}^- \\ (1s^2 2s^2 2p^5) & & (1s^2 2s^2 2p^6) \\ 99 \text{ pm} & & 181 \text{ pm} \end{array}$$



(a)Radius of cation is smaller than the parent atom



(b)Radius of anion is larger than the parent atom

Figure 8.4 *(a) and (b) Comparison of atomic and ionic radii of cations (group 1) and anions (group 17)*

Trends in ionic radii: Like atomic radii, the ionic radii also increases down the group and decreases across the period. However, there are some exceptions to this trend.

8.6 Ionisation Enthalpy

First ionisation energy is defined as the energy required to remove the most loosely bound electron from an isolated gaseous atom in its ground state at 0 K.

$$A(g) \rightarrow A^+(g) + e^-(g) \qquad IE_1 = E(A^+, g) - E(A, g)$$

The second ionisation energy is the energy required to remove the most loosely bound electron from the resulting cation.

$$A^+(g) \rightarrow A^{2+}(g) + e^-(g) \qquad IE_2 = E(A^{2+}, g) - E(A^+, g)$$

Energy required to convert $A^{2+}(g)$ in to $A^{3+}(g)$ is the third ionisation energy and so on. Ionisation energies are expressed in kJ mol^{-1} or electronvolts (eV), where 1 eV = 94.485 kJ mol^{-1}.

However, most chemical reactions occur at constant pressure and at a temperature of 298 K. In such a situation it is more appropriate to use the term ionisation enthalpy. If the gaseous atoms are assumed to be ideal gases then the ionisation enthalpy is larger than ionisation energy by $\frac{5}{2}R\Delta T$, where R is the molar gas constant (8.314 × 10^{-3} kJ K^{-1} mol^{-1} and ΔT is the difference between the two temperatures (0 K and 298 K). The ionisation energies for the removal electrons are of the order of 10^3 kJ mol^{-1} and the ionisation enthalpy is

$$\Delta H(298K) = \Delta H(0K) + \frac{5}{2} \times 8.314 \times 10^{-3} \times 298$$

$$\Delta H(298K) = \Delta H(0K) + 6.2 \text{ kJ mol}^{-1}$$

The difference between ionisation energy and enthalpy is very small (≈ 6 kJ mol^{-1}) and is often ignored. However, the term ionisation enthalpy is commonly used these days.

The ionisation energy depends upon the size of the atom, charge on the nucleus, type of electrons involved (s, p, d, f) on the screening effect of the inner electrons and the penetration effect of electrons. The ionisation enthalpies of elements with Z=1 to 60 are shown in Fig 8.5. From the figure it is clear that alkali metals have low ionisation enthalpies and noble gases have very high ionisation enthalpies. This can be attributed to the fact the alkali metals have only one electron in their valence shell. All the inner shell electrons called core electrons shield this electron from the nucleus thereby reducing Z_{eff}, hence they lose electrons easily and acquire a stable noble gas configuration. Noble gases because of stable electronic configuration do not lose electrons readily, which is reflected in their very high values of ionisation enthalpies.

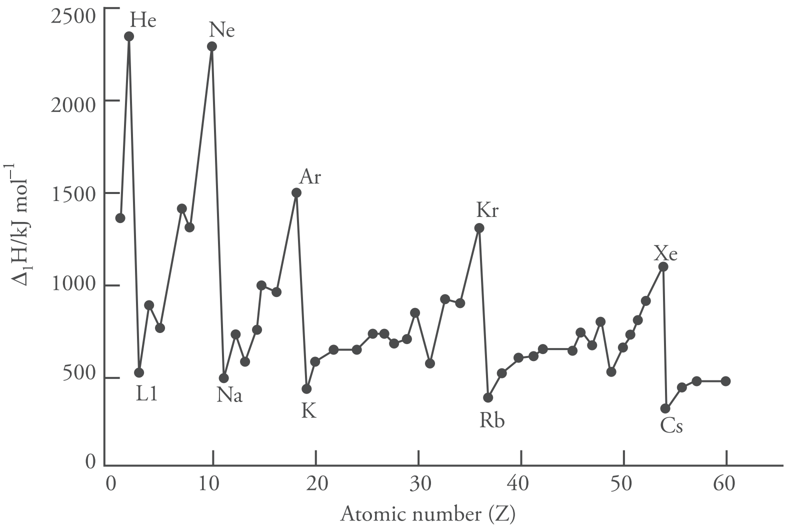


Figure 8.5 *Variation of first ionisation enthalpies ($\Delta_i H$) with atomic number for elements with Z = 1 to 60*

Variation in a group

The ionisation enthalpy decreases as we descend down the group. On moving down the group, the following factors become effective:

- Nuclear charge increases.
- New shells are added.
- The shielding of outermost electrons increases due to increase in the number of inner electrons.

The first factor is outweighed by the second and third factors, as a result of which the ionisation enthalpy decreases on descending down the group. Fig 8.6(b) shows the variation of ionisation enthalpy of the elements of group 1. Table 8.4 gives the first and second ionisation enthalpies of elements.

Variation in a period

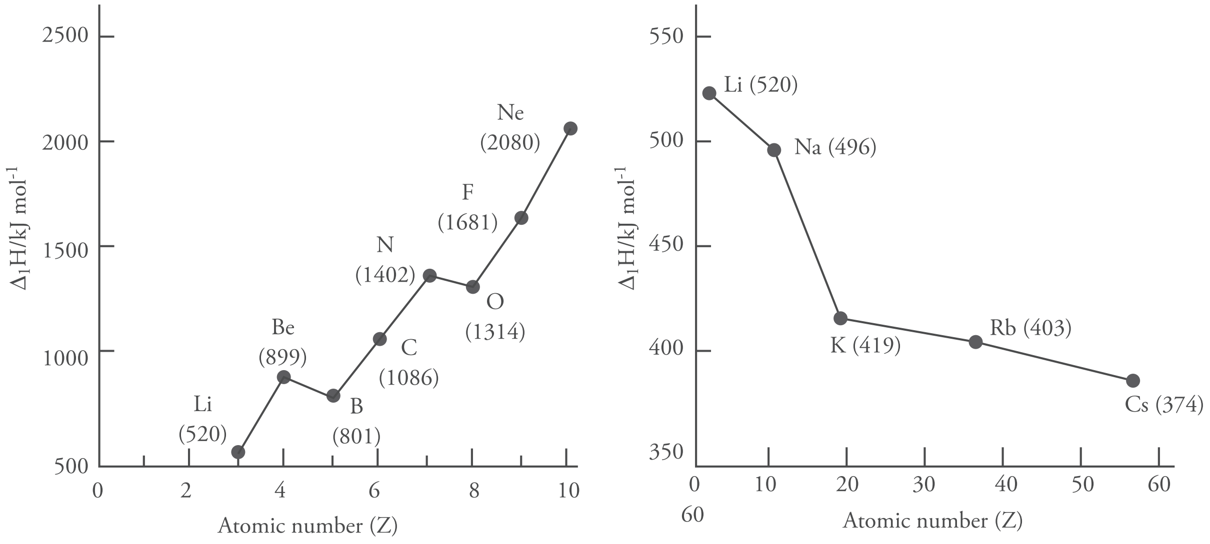
In a period the ionisation enthalpy generally increases from left to right. This is because nuclear charge increases in a period and the successive electrons are added in the orbitals with same principal quantum level resulting in the increase in Z_{eff}. Consequently the electrons are more tightly held by the nucleus, resulting in an increase in ionisation enthalpy. Figure 8.6(a) shows the variation of ionisation enthalpy of the elements of the second period.

However, there are some deviations in this general trend. Although the nuclear charge of B is greater than Be, the first ionisation enthalpy of B (Z=5) is slightly less than Be (Z=4). This is because of the fact that in beryllium the electron is removed from s orbital, whereas in boron the electron is removed from p orbital. Since the penetration of 2s electron to the nucleus is more than that of 2p electron, it is easier to remove electron from 2p orbital, and hence the ionisation enthalpy of boron is less than that of Be.

Similarly O (Z=8) has lesser ionisation enthalpy than N (Z=7). This is because nitrogen has half-filled 2p orbitals which reside in different atomic orbitals whereas in oxygen, two of the four 2p orbitals reside in the same orbital thereby increasing the electron–electron repulsion. Hence it is easier to remove the 2p electron of oxygen. Moreover, the half-filled p orbitals of nitrogen is a stable configuration.

Table 8.4 First and second ionisation enthalpies of elements in kJ mol^{-1}

H 1312							He 2373 5259
Li 520 7297	Be 899 1757	B 801 2426	C 1086 2352	N 1402 2855	O 1314 3386	F 1681 3375	Ne 2080 3952
Na 495 4562	Mg 737 1476	Al 577 1816	Si 786 1577	P 1011 1903	S 1000 2251	Cl 1251 2296	Ar 1520 2665
K 419 3051	Ca 589 1145	Ga 579 1979	Ge 762 1537	As 947 1798	Se 941 2044	Br 1139 2103	Kr 1351 3314
Rb 403 2632	Sr 549 1064	In 558 1821	Sn 708 1412	Sb 834 1794	Te 869 1795	I 1008 1846	Xe 1170 2045
Cs 374 2420	Ba 502 965	Tl 590 1971	Pb 716 1450	Bi 704 1610	Po 812 1800	At 926 1600	Rn 1036



(a) (b)

Figure 8.6 *(a) First ionisation enthalpies ($\Delta_i H$) of elements of the second period as a function of atomic number (Z) and (b) $\Delta_i H$ of alkali metals as a function of Z.*

8.7 Electron Gain Enthalpy

Electron gain enthalpy is defined as the energy change when an electron is added to an isolated gaseous atom in ground state to give an anion represented by the equation

$$A(g) + e^{-}(g) \rightarrow A^{-}(g) \qquad \Delta_{EG} = E(A^{-}, g) - E(A, g)$$

Δ_{EG} is the electron gain enthalpy.

If the energy is released during the addition of an electron, then the electron gain enthalpy is considered negative and if energy is supplied to add electron to the atom, then the electron gain enthalpy is considered as positive. The electron gain enthalpy is measured in kJ mol^{-1} or electronvolts (eV). Table 8.5 gives the electron gain enthalpies for few atoms.

Electron affinity E_a on the other hand is the difference in energy between the gaseous atoms and the gaseous ions at T = 0

$$E_a = E(A, g) - E(A^{-}, g)$$

Hence the sign convention of electron gain enthalpy and electron affinity are opposite $\Delta_{EG} = -E_a$

Note that the sign convention for electron affinity is the reverse of the convention used in thermodynamics. A positive value of electron affinity indicates that the ion A^{-} has a lower energy than the atom A. Although the term electron affinity is widely used in inorganic chemistry, the terms electron gain enthalpy and electron affinity cannot be used interchangeably. In the present text, we shall use the term electron gain enthalpy.

Table 8.5 Electron gain enthalpies (kJ mol^{-1}) of some elements

H –72							He +48
Li –60	Be ≈0	B –27	C –122	N ≈0	O –141 +780	F –328	Ne +116
Na –53	Mg ≈0	Al –43	Si –134	P –72	S –200 +492	Cl –349	Ar +96
K –48	Ca ≈0	Ga –29	Ge –116	As –78	Se –195	Br –325	Kr +96
Rb –47	Sr ≈0	In –29	Sn –116	Sb –103	Te –190	I –295	Xe +77

*The second value given for sulphur and oxygen is for the addition of second electron to the anion

From Table 8.5, it is clear that the electron gain enthalpy increases in a period and decreases down the group. This is because as one moves from left to right in the period the effective nuclear charge increases hence an electron is easily added. Elements of group 17 add electron easily to acquire a stable noble gas configuration; hence they have high negative electron gain enthalpy. Electron gain enthalpy decreases down the group, because on moving down, the group the atomic radius increases and the added electron feels lesser attraction by the nucleus, that is, Z_{eff} decreases.

However, the electron gain enthalpy of S and Cl is larger than O and F. This is because the elements of second period are relatively smaller in size than the elements of the third period. In the second period, the electrons are added in the second shell (n=2), where because of small size, the incoming electron feels greater interelectronic repulsion in the relatively compact 2p subshell. In the third period, because of larger size, the inter-electronic repulsion is less and hence, electron is added easily with the release of energy.

Noble gases have a stable electronic configuration, hence energy has to be supplied to add electron to them, and this is reflected by their high positive values of electron gain enthalpy.

Successive electron gain enthalpies: Except noble gases, the first electron gain enthalpy of most elements is negative. However, the second electron gain enthalpy is positive for all elements, since energy is to be supplied to force the second electron into the anion. Table 8.5 gives the electron gain enthalpies for a few elements.

8.8 Electronegativity

Electronegativity χ (chi) is defined as the ability of a bonded atom to attract the shared pair of electron towards itself.

Consider the formation of a covalent bond between two similar atoms of a molecule like hydrogen. In this case the electron pair participating in bond formation is shared equally by both the atoms, but this is not the case when a covalent bond is formed between two dissimilar atoms, like HCl. In this case, chlorine exerts greater attraction on the electron pair; consequently the electron pair lies closer to the Cl atom. Hence we can say that Cl has greater electronegativity than H. Since the electron pair lies closer to Cl, it develops partial negative charge (δ^-) and the hydrogen atom develops partial positive charge (δ^+) and the covalent bond thus acquires ionic character.

Several scales like Pauling scale, Mulliken–Jaffe scale and Allred–Rochow scale have been developed to express the electronegativity of elements numerically. The most widely accepted among these is the Pauling scale developed by the American scientist Linus Pauling. He computed the values of electronegativity by making use of the concepts related to the energetics of bond formation. For example, consider the formation of AB from diatomic molecules A_2 and B_2

$$\frac{1}{2}A_2(g) + \frac{1}{2}B_2(g) \rightarrow AB(g)$$

The bond energy for AB is

$$E_{AB} = \frac{1}{2}[E_{AA} + E_{BB}] + \Delta_{AB}$$

where E_{AA} and E_{BB} are the bond energies of purely covalent molecules A_2 and B_2, respectively. The bond between A and B is stronger than if the bond was purely covalent; hence Δ_{AB} accounts for this extrastability. Pauling gave a relation to express stability of the bond to the tendency of atoms to attract electrons.

$$\Delta_{AB} = 96.48(\chi_A - \chi_B)^2$$

where χ_A and χ_B are the electronegativities of atoms A and B, respectively. The value of Δ_{AB} in the above equation is expressed in kJ mol^{-1}. If it is expressed in kcal mol^{-1} as done originally by Pauling, the equation becomes

$$\Delta_{AB} = 23.06(\chi_A - \chi_B)^2$$

Pauling arbitrarily assigned a value of 4.0 to fluorine, the most electronegative element in the periodic table.

Robert Mulliken observed that if an atom has high ionisation enthalpy, it means that high energy is required to remove that electron, which in turn means that the electron is tightly bound to the nucleus. Similarly an atom with high electron affinity also has high attraction towards an electron. On the basis of the above arguments, Mulliken proposed that atoms with high ionisation enthalpy and high electron affinity have high electronegativity. He expressed electronegativity as the average value of ionisation enthalpy and electron affinity (both expressed in electronvolts).

$\chi_M = \frac{1}{2}(I + E_a)$ where χ_M is the electronegativity on Mulliken scale.

The Allred and Rochow electronegativity scale is based on the electrostatic attraction between the valence shell electrons and the nucleus. They proposed the equation

$$\chi_{AR} = \frac{35.9Z_{eff}}{r^2} + 0.744$$

where χ_{AR} is electronegativity on Allred Rochow scale, r is the covalent radius in picometers and Z_{eff} is the effective nuclear charge.

According to Allred Rochow scale elements with high Z_{eff} and small covalent radius will have high electronegativity, and these elements lie close to fluorine.

However, Pauling scale is used throughout the chapter.

Table 8.6 Electronegativity values (on Pauling scale) of elements across the periodic table

H 2.1							
Li 1.0	Be 1.5		B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2		Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc……. Zn 1.3…..1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y……. Cd 1.2…...1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La……. Hg 1.1…….1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	As 2.1

Table 8.6 shows that the electronegativity values increase from left to right and decrease down the group. This is because across the period, Z_{eff} increases and hence the nucleus is more likely to attract electron. Similarly down the group, atomic size and Z_{eff} decreases thereby reducing the ability of the nucleus to attract electrons towards itself. Consequently the electronegativity decreases on moving down the group.

Applications of electronegativity

1. *Nature of bond*: The difference in electronegativity of the two bonding atoms helps in predicting the nature of the bond. The bond between A and B will be a non-polar covalent bond if $\chi_A = \chi_B$ and it will have some ionic character if $\chi_A \neq \chi_B$. If $\chi_A > \chi_A$ then the form A^-B^+ will be stable and if $\chi_A < \chi_B$ then A^+B^- will be stable. Greater the difference $\chi_A - \chi_B$ greater will the ionic character in the bond. Pauling predicted the % ionic character on the basis of electronegativity difference of atoms A and B. He calculated that when

   $\chi_A - \chi_B = 1.7$, the bond is approximately 50% ionic and 50% covalent. When

   $\chi_A - \chi_B > 1.7$, then the ionic character will be greater than 50%. Bonds having more than 50% ionic character are termed as ionic bonds and those which are more than 50% covalent are termed as covalent bonds. However, Paulings, results did not hold good when (i) $\chi_A - \chi_B$ values are too large and (ii) Alkali metal hydrides and hydrides of Ca, Sr and Ba are ionic although the value of $\chi_M - \chi_H$ is less than 1.7.

   Hanny and Smith revised the Pauling equation and gave a new equation for the calculation of % ionic character

   $$\begin{aligned}\%\text{ ionic character} &= 100 \times [0.16(\chi_A - \chi_B) + 0.035(\chi_A - \chi_B)^2] \\ &= 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2\end{aligned}$$

   The above equation shows that a bond AB is 50% ionic if $\chi_A - \chi_B = 2.1$. On substituting the electronegativity values of H, F, Cl, Br and I in Hanny and Smith's equation, the % ionic character in HF, HBr, HCl and HI molecules is 43%, 17%, 13% and 7%, respectively. Thus the percentage ionic character decreases in the order HF > HBr > HCl > HI.

2. *Stability and strength of a bond*: Greater the difference in χ_A and χ_B, greater is the stability of the bond. For example, the stability of hydrogen halides decreases in the order HF > HBr > HCl > HI as shown below

   $\chi_{\text{F}} = 4.0 \quad \chi_{\text{Cl}} = 3.0 \quad \chi_{\text{Br}} = 2.8 \quad \chi_{\text{I}} = 2.5 \quad \chi_{\text{H}} = 2.1$

   $H - X$ bond $H - F \quad H - Cl \quad H - Br \quad H - I$

   $\chi_X - \chi_H \qquad 1.9 > 0.9 > 0.7 > 0.4$

   (X = F, Cl, Br I)

Stability of compounds in which $\chi_A - \chi_B$ is very small: Such compounds in which $\chi_A - \chi_B$ is very small tend to be unstable. Examples of such compounds are SiH_4, NCl_3, PH_3, AsH_3, SbH_3 and BiH_3, where $\chi_A - \chi_B$ values are 0.3, 0.0, 0.0, 0.1, 0.2 and 0.2, respectively.

Stability of compounds in which $\chi_A - \chi_B$ is very large: These compounds are generally formed by the combination of metals (whose χ values are very low) and non metals (whose χ values are very large). In such case, $\chi_A - \chi_B$ will be large and these compounds will be stable with large heats of formation, high melting and boiling points.

3. *Acid–base character of normal oxides of elements in a period*: On moving from left to right in a period the acidic character of oxides increases. On moving across the period the electronegativity of the elements increases consequently the difference in electronegativity of element and oxygen $\chi_E - \chi_O$ decreases. This is illustrated in Table 8.7, considering the oxides of elements of the third period.

Table 8.7 Electronegativity difference and nature of oxides

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
χ_E	0.9	1.2	1.5	1.8	2.1	2.5	3.0
$\chi_O - \chi_E$ $\chi_O = 3.5$	2.6	2.3	2.0	1.7	1.4	1.0	0.5
Acid/base character	Strongly basic	Basic	Amphoteric	Weakly acidic	Acidic	Strongly acidic	Very strongly acidic

4. *Metallic and non-metallic character of elements*: The electronegativity values increase from left to right across the period and decrease from top to bottom down the group. Consequently metallic character of elements decreases across the period and increases down the group. Elements on the left of periodic table are metallic in nature and those on the right of the periodic are non-metals.

   The increase in the metallic character down the group is very pronounced in groups 14 and 15, which begin with non-metals (C and N) and end with metals (Pb and Bi).

5. *Acidic and basic character of XOH molecule*: When XOH ionises in aqueous solution (X may be a metal or a non-metal) two case may arise

   (*i*) When $\chi_O - \chi_X < \chi_O - \chi_H$, the polarity of OH bond is more than the polarity of X–O bond, consequently the XOH molecule will ionise in aqueous solution as shown below

$$XOH + H_2O \rightarrow XO^- + H_3O^+$$

   Since H_3O^+ ions are produced, XOH behaves as an acid.

(ii) When $\chi_O - \chi_X > \chi_O - \chi_H$, the polarity of the bond XO is more than the polarity of O–H bond and hence ionisation will occur as follows

$$X - O - H + H_2O \rightarrow [X - OH_2]^+ + OH^-$$

$\because$ XOH molecule gives OH^- ions hence it behaves as a base.

Thus we find that the electronegativity concept helps in predicting the acidic or basic nature of XOH compounds.

Gallais suggested that if χ_X is greater than 1.7, the compound XOH is acidic and if it is lesser than 1.7, the compound XOH shows basic character.

6. *Colour of salts*: Colour of salts is closely related to the percentage ionic character. The relation of ionic character of a bond and colour of a compound has been generalised as given in Table 8.8.

Table 8.8 Variation of colour of compound with % ionic character

S. No	% ionic character	Colour of compound
1.	Less than 20%	Coloured
2.	Greater than 20%	Colourless
3.	Lesser and lesser than 20%	Colour goes on deepening

Example: AgCl (white: 80% ionic character); AgBr (pale yellow: 24% ionic character); AgI (yellow: 15% ionic character); Ag_2S (black: 4% ionic character)

7. *Calculation of bond length*: If two atoms A and B with different electronegativities are bonded together then the bond length of AB is given by the formula

$$d_{A-B} = r_A + r_B - 0.09(\chi_A - \chi_B)$$

where r_A and r_B are the covalent radii of A and B, respectively, and $\chi_A - \chi_B$ is the electronegativity difference. The normal bond length between A and B would be $r_A + r_B$, but the difference in electronegativity reduces the bond length by the factor $0.09(\chi_A - \chi_B)$.

8.9 Polarising Power and Polarisability: Fajan's Rule

When a cation approaches an anion, the positive charge of the cation attracts the electrons of the anion and repels the positively charged nucleus of the anion. As a result of these two effects, the anion is no longer symmetrical but is bulged towards the cation. This is called distortion, deformation or polarisation of the anion and the ability of the cation to polarise the anion is termed as its polarisation power. The anion also exerts a similar effect on the cation, but since the size of cation is less, the effect is less pronounced.

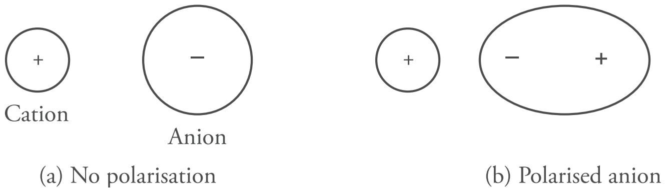


Figure 8.7 *Polarisation of anion by cation*

Greater polarisation implies greater covalent character as the electrons will be drawn from the negative ion towards the positive ion resulting in high concentration of electrons between the two nuclei. Fajan put forward rules summarising the factors that favour polarisation and hence covalency.

(i) *Charge on cation or anion*: The polarising power of the cation increases with an increase in positive charge. This is because a cation with higher charge can attract electron effectively. For example, in NaCl, $MgCl_2$ and $AlCl_3$, the charge on cation is Na^+, Mg^{2+} and Al^{3+}, respectively; thus the polarising power of cation increases from Na^+ to $Al^{3+}$and hence the covalent character of their chlorides increases from NaCl to $AlCl_3$.

Similarly polarisability of anion increases with the increase in negative charge, because with the increase in negative charge the anion will be able to repel its outermost electrons more effectively.

(ii) *Size of cation or anion*: Small cation causes greater polarisation of anion due to concentration of positive charge, in small area. The polarising power of Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Ra^{2+} follows the order $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Ra^{2+}$, because their cation radii increases in the reverse order. On the other hand, large anion is polarised easily, because the effective nuclear charge on outer electrons is less. Example – consider halides of Ca like CaF_2, $CaCl_2$, $CaBr_2$, CaI_2. Their covalent character increases in order $CaF_2 < CaCl_2 < CaBr_2 < CaI_2$, which is reflected by the decrease in melting point (CaF_2 = 1392 °C, $CaCl_2$= 772 °C, $CaBr_2$ = 730 °C and CaI_2 = 575 °C).

(iii) *Electronic configuration of cation*: Cations with noble gas configuration have less polarising power. Polarisation and hence covalency is favoured by cation having non-inert gas configuration ($ns^2p^6d^{10}$). Thus Cu^+ (18 electron structure) causes greater polarisation of Cl^- ion than Na^+ (8 electron structure) in spite of having the same charge and nearly the same size. Hence compounds of Cu^+ are more covalent than compounds of Na^+

Fajan's rule is helpful in predicting the covalent character of compounds in a group and in a period. In a group, the charge on cation remains the same but its size increases hence the tendency to form covalent bond decreases down the group. In a period, the electronic charge increases and size decreases; hence the covalent character increases across the period. However, indiscriminate application of the concept of polarisation may lead to wrong predictions. Other factors should also be considered, for example considering the chlorides of sodium, potassium and rubidium; on the basis of polarisation concept their covalent character should decrease from NaCl to KCl to RbCl, but their melting points are in the order NaCl = 800 °C, KCl = 776 °C and RbCl = 715 °C. Thus RbCl is more covalent. This is because other physical parameters like lattice energy also play on important role in deciding the ionic or covalent character of a compound.

8.10 Oxidation State

The trends in oxidation states can be understood by considering the electronic configuration, ionisation energies, electron affinities, completely and half-filled valence shells. Elements gain or lose electrons to acquire a stable configuration. The common trends in oxidation states of elements are discussed below:

Main group elements

The oxidation state of main group elements generally depends upon the electronic configuration. It is generally equal to the number of electrons in the outermost shell or eight minus the number of electrons in the outermost shell.

Table 8.9 Oxidation state of the main group elements:

Group	1	2	13	14	15	16	17	18
Number of valence electrons	1	2	3	4	5	6	7	8
Oxidation state	1	2	3	4	3, 5	2, 6	1, 7	0, 8

The electronic configuration of groups 1 and 2 is [noble gas]ns^1 and [noble gas]ns^2, respectively, where n represents the valence shell. Hence they lose one and two electrons, respectively, to acquire the stable noble gas configuration. All elements of group I (Li, Na, K, Rb, Cs, Fr) exhibit oxidation state +1 and elements of group II (Be, Mg, Ca, Sr, Ba, Ra) exhibit oxidation state +2.

Group 13 (Boron family): They have three valence electrons, two in s-subshell and one in p-subshell. Therefore, they show a maximum oxidation state +3. However, except boron other elements show +1 oxidation state also and in the last element thallium +1 oxidation state is more stable than +3 oxidation state. This effect in which the stable oxidation number of an element is two less than the oxidation number of the group is termed as the *inert pair effect*. This effect can be explained on the basis ionisation enthalpies and bond energies. Table 8.10 gives the ionisation energies and bond energies of elements of group 13.

Table 8.10 Ionisation energies and bond enthalpies of group 13 elements

Element	**First ionisation enthalpy I_1 kJ/mol**	**I_1+I_2 +I_3 kJ/mol**	**Avg M-Cl bond energy kJ/mol**
B	801	6828	536
Al	578	5139	494
Ga	579	5521	481
In	558	5083	439
Tl	589	5439	373

It is clear from Table 8.10 that the ionisation energy increases from Al to Ga and In to Tl which is contrary to the normal trend. This is because of poor shielding of outer shell electrons by electrons in the d and f orbitals thereby increasing Z_{eff} making it very difficult to remove the ns^2 electrons. Another factor contributing to inert pair effect is the decrease in bond energy down the group. The net result of these two effects is that large amount of energy is required to remove two ns^2 electrons (due to high ionisation enthalpy) but less energy is released during bond formation (low bond energy). Hence oxidation number of an element is two less than the oxidation number of the group (inert pair effect).

Group 14 (Carbon family): The common oxidation state is +4; however, due to inert pair effect Ge, Sn and Pb also show +2 oxidation state. In lead compounds +2 oxidation state is more stable than +4 oxidation state.

Group 15 (Nitrogen family): They have five electrons in their valence shell. It is difficult to lose five electrons due to energy considerations, hence they gain three electrons to complete their octet. Common oxidation state is -3; however, they exhibit +3 and +5 oxidation state also. Nitrogen exhibits oxidation state from -3 to +5 in its hydrates, oxides and oxoacids.

Group 16 (Oxygen family): Common oxidation state of oxygen is +2; however, the oxidation state of oxygen in OF_2 and H_2O_2 is +2 and -1, respectively. Apart from +2 oxidation state other elements like sulphur exhibit higher oxidation states like +4 and +6 due to availability of vacant d orbitals.

Group 17 (Halogen family): The most common oxidation state of the elements of this group is -1. However, due to presence of vacant d orbitals elements (Cl, Br, I)show higher oxidation state like +3, +5 and +7 also. Fluorine, the first member of this group is the most electronegative element in the periodic table.

Group 18 (Noble gases): Although inert, they exhibit oxidation states +2, +4, +6 and +8

Transition elements: Transition metals show variable oxidation states. Table 8.11 gives the oxidation state of elements of the first transition series.

Table 8.11 Oxidation state of elements of the first transition series

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronic configuration	d^1s^2	d^2s^2	d^3s^2	d^5s^1	d^5s^2	d^6s^2	d^7s^2	d^8s^2	$d^{10}s^1$	$d^{10}s^2$
Oxidation state	+2 +3	+2 +3 +4	+2 +3 +4 +5	**+1** **+2** **+3** +4 +5 +6	+2 +3 +4 +5 +6 +7	+2 +3 +4 +5 +6	+2 +3 +4 +5	+2 +3 +4	**+1** **+2** **+3**	+2

Lanthanoids: The most common oxidation state is +3; however, some elements exhibit +2 and +4 oxidation state to acquire the stable noble gas configuration. Example: Cerium gives Ce^{4+} ($4f^0$), europium and terbium gives Eu^{2+} and Tb^{4+} ($4f^7$) and ytterbium forms Yb^{2+} ($4f^{14}$). Few other elements also exhibit +2 and +4 oxidation states.

Actinoids: All actinoids have an oxidation state of +3; however, this is not always the most stable oxidation state.

Summary

- The elements are arranged in the periodic table in the order of increasing atomic number. The electrons occupy the atomic orbitals in the order of increasing energy in the order 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p and 7s.
- Effective nuclear charge is the net attractive force experienced by valence electrons, ($Z_{eff} = Z_{actual}$ – shielding). Shielding effect is the reduction in effective nuclear charge due to repulsion felt by valence electrons due to the presence of electrons in the inner shell.
- Penetration effect is the tendency of electrons to be attracted towards the nucleus. Within the same shell (n) the penetration power of electrons follows the sequence $s > p > d > f$.
- Each period in the periodic table corresponds to the value of n or principal energy level in which the electrons enter into s, p, d and f block elements; the last electrons enter the s, p, d and f orbitals, respectively.
- The atomic and ionic radii decreases in a period and increases down the group. The radii of noble gases is large as it represents the van der Waals radius.
- Ionisation enthalpy is the energy required to remove the most loosely bound electron from an isolated gaseous atom. Its value increases in a period and decreases down the group.
- Electron gain enthalpy is defined as the energy change when an electron is added to an isolated gaseous atom in ground state. Generally energy is released during addition of electron (hence electron gain enthalpy is negative) but in noble gases energy is to be supplied to add electron (positive electron gain enthalpy). Addition of second electron to an anion requires energy, hence second electron gain enthalpy is positive.
- Electronegativity is the ability of a bonded atom to attract the shared electron pair towards itself. It leads to development of ionic character in a bond. It is measured on various scales, the most popular being the Pauling scale in which fluorine, the most electronegative element has been assigned a value of 4.0
- Fajans rule describes polarising power and polarisability. A small cation with high charge and non – inert gas configuration has greater tendency to polarise an anion. A large anion with increase in negative charge have greater polarisability. Greater the polarisation, greater is the ionic character.
- Oxidation state of an element depends upon its electronic configuration. Common oxidation state for various group as:

  Group I = +1. Group II = +2, Group 13 = +3; Group 14 = 4; Group 15 = 3, 5; Group 16 = 2, 6; Group 17 = 1, 7; Group 18 = 0, 8.

- Metals show variable oxidation states. The most common oxidation state of lanthanoids is +3, although some elements show +2 and +4 oxidation state also. The most common oxidation state of actinoids is +3 although it is not always stable.

Review Questions

1. Write the general outer electronic configuration of s, p, d and f block elements. Explain the general properties of elements belonging to these groups.
2. Explain the terms effective nuclear charge, shielding and penetration effect.
3. Differentiate between atomic radius, ionic radius and van der Waals radius. How does atomic radius vary in a group and in a period.
4. Explain why the size of cation is less and that of anion is more than the corresponding atom.
5. What do you understand by the isoelectronic species. Explain the variation in the size of isoelectronic species.
6. Define ionisation enthalpy. In the second period explain why the ionisation enthalpies follow the order Li < B < Be < C < O < N < F < Ne.

   Explain why ionisation enthalpy of Be is higher than B and ionisation enthalpy of oxygen is lower than nitrogen and fluorine.
7. How does ionisation enthalpy vary in a period and in a group. Explain why the first ionisation enthalpy of sodium is lower than that of magnesium but its second ionisation enthalpy is higher than that of magnesium.
8. What is electron gain enthalpy and electron affinity. What is the difference between the two. Except noble gases the first electron gain enthalpy for most elements is negative but the second electron gain enthalpy is positive. Explain with the help of suitable example.
9. What is the difference between the terms electron gain enthalpy and electronegativity. Explain the periodic trends of electronegativity in the periodic table.
10. State and explain the Fajan's rule.

Multiple Choice Questions

1. Which of the following elements will have the outer electronic configuration $(n\text{-}1)d^5ns^1$

   (a) Cr (b) Cu

   (c) Ar (d) Na
2. The number of protons in an element with general electronic configuration of the ultimate and penultimate shell as $(n-1)s^2(n-1)p^6(n-1)d^xns^2$, where $n = 4$ and $x = 5$ will be

   (a) 26 (b) 22

   (c) 25 (d) 28

3. In the following sets of elements the atomic radii will increase in the order

   (a) Mg, K, Na, Rb
   (b) Mg, Na, K, Rb
   (c) Na, K, Rb, Mg
   (d) Na, Rb, K, Mg

4. The correct order for the second ionisation enthalpy of C, N, O and F is

   (a) C > N > O > F
   (b) O > N > F > C
   (c) O > F > N > C
   (d) F > O > N > C

5. The outer electronic configuration of the most electronegative element is

   (a) ns^2np^3
   (b) ns^2np^4
   (c) ns^2np^5
   (d) ns^2np^6

6. The atom having maximum electron gain enthalpy is

   (a) F
   (b) Cl
   (c) Br
   (d) I

7. The electronegativity of the following elements increase in the order

   (a) C, N, Si, P
   (b) N, Si, C, P
   (c) P, Si, N, C
   (d) Si, P, C, N

8. Consider the cations Cr^+, Cr^{2+}, Cr^{3+}, Cr^{4+} and Cr^{6+} and the anions F^-, Cl^-, Br^- and I^-. Which of the above cation has greatest polarising power and which of the anions has maximum polarisability

   (a) Cr^{6+}, F^-
   (b) Cr^{2+}, $C1^-$
   (c) Cr^+, I^-
   (d) Cr^{6+}, I^-

9. The decreasing order of solubility of silver halide is

   (a) AgI > AgBr > AgCl > AgF
   (b) AgF > AgCl > AgBr > AgI
   (c) AgCl > AgF > AgBr > AgI
   (d) AgBr > AgF > AgI > AgCl

10. Which of the following bonds has maximum polarity

    (a) C – O
    (b) C – F
    (c) C – S
    (d) C – Br

11. The % ionic character of a bond between two atoms is calculated from the difference between their

    (a) Electronegativities
    (b) Electron affinities
    (c) Ionisation energies
    (d) Ionic radii

12. Which among the following has the largest size

    (a) Br^-
    (b) I
    (c) I^-
    (d) I^+

Solution

1 (a)	2 (c)	3 (b)	4 (c)	5 (c)	6 (b)	7 (d)	8 (d)
9 (b)	10 (b)	11 (a)	12 (c)				