PERIODIC PROPERTIES

Introduction

The basic object of classification is to arrange the facts regarding elements and compounds in such a way so that we may have greatest control over their characteristics with least possible efforts. Such a classification is called as **Periodic table.**

Some of the earlier attempts by scientists are discussed below.

Dobereiner's Triads

In 1829, J. Dobereiner made an important first step towards a systematic classification by arranging elements into groups of three (triads). He observed that the atomic weight of the middle element of the group was midway between the atomic weights of the other two. He also concluded that the same midpoint relation held true for the physical properties of these elements.

Some of his triads were (Li, Na, K), (CI, Br, I), (Ca, Sr, Ba), (S, Se,Te)

Newland's law of Octave

The first attempt to classify all the known elements was made by Newland in 1864.

He proposed that if the elements are arranged according to the increasing atomic weights (beginning with lightest element, excluding Hydrogen), the chemical and physical properties of a particular element would be similar to those of the elements seven places before and seven places after it.

For example, Li, the second element in Newland's list, had properties similar to Na, the ninth element in the list and K, the sixteenth element. Thus these were similar elements represented by numbers 2, 9, 16 which show interval of seven.

Mendeleev's Periodic Law and Classification

In 1869, Mendeleev classified the then known 56 elements on the basis of their physical and chemical properties by giving a law known as the periodic law. The name periodic law stems from the fact that the properties of the elements orderly recur in a cyclic fashion. His periodic law states that **"the physical and chemical properties of the elements are periodic function of their atomic masses."** This means that when the elements are arranged in the order of their increasing atomic masses, the elements with similar properties recur at regular intervals. Based on this law all the known elements were arranged in the form of a table known as periodic table. Elements with similar properties recur at regular intervals and fall in certain groups or families. The elements in each group were similar to each other in many properties.

Merits of Mendeleev's periodic table

Mendeleev's periodic table was one of the greatest achievements in Chemistry with some of its important contributions as follows :

- As the arrangements are classified into groups, it was very useful in studying and remembering the properties of a large number of elements in a systematic way.

- This classification helped in correcting the atomic masses of some of the elements like gold, beryllium and platinum based on their positions in the periodic table.

- Mendeleev could predict the properties of some undiscovered elements like scandium, galliumand germanium. By this intuition, he had left gaps for the undiscovered elements while arranging elements in his periodic table.

Demertis of Mendeleev's periodic table

In spite of the above advantages, Mendeleev's periodic table suffered defects as follows :

- The position of hydrogen was not correctly defined. It was placed in group I although it resembles both the group I elements - the alkali metals and the group VII elements-the halogens, in their properties.

- In some cases Mendeleev placed elements according to their similarities in properties and not in increasing order of their atomic masses. Thus, the position of these elements was not justified e.g. cobalt (atomic mass 58.9) was placed before nickel (atomic mass 58.6).

- Isotopes were not given separate places in the periodic table although Mendeleev's classification is based on the atomic masses.

- Some similar elements were grouped separately while some dissimilar elements were grouped together. For example copper and mercury are similar in their properties but were placed separately. Copper was placed in group I although it did not resemble the elements of this group.

- Mendeleev could not explain the cause of periodicity in the elements.

- the position for lanthanides and actinides were not included in this table.

Long form of periodic table

With developments on the structure of atoms, it was discovered that the atomic number (Z) is the important characteristic of the atom and not the atomic mass. This led to the development of the modern periodic law by Moseley in 1942. The modern periodic law states that **"the physical and chemical properties of the elements are periodic function of their atomic numbers."** Thus, when the elements were arranged in the order of their increasing atomic numbers, the elements of similar properties recur at regular intervals.

The long form of the periodic table or the modern periodic table is based on the general plan of the table as proposed by Mendeleev. This table is the most widely used periodic table of today.

Structural Features of the Modern Periodic Table

This table consists of horizontal rows called as 'periods' and vertical columns called as 'groups'.

Periodic Table of the Elements

H																	He
1																	2
Li	Be											B	C	N	O	F	Ne
3	4											5	6	7	8	9	10
Na	Mg											Al	Si	P	S	Cl	Ar
11	12											13	14	15	16	17	18
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
55	56	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq				
87	88	103	104	105	106	107	108	109	110	111	112		114				

57-70 *
89-102 **

*Lanthanide series

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
57	58	59	60	61	62	63	64	65	66	67	68	69	70

**Actinide series

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
89	90	91	92	93	94	95	96	97	98	99	100	101	102

Periods

There are seven periods in the periodic table and each period starts with a different principal quantum number.

The first period corresponding to 'n' = 1 consists of only two elements hydrogen ($1s^1$) and helium ($1s^2$). This is because the first energy shell has only orbital (1s), which can accommodate only two electrons.

In the second period corresponding to 'n' = 2, there are four orbitals (one '2s' and three '2p') having a capacity of eight electrons and so contains eight elements. This period starts with lithium (Z = 3) with electron entering the '2s' orbital and ends with neon (Z = 10) where the second shell is complete ($2s^2 2p^6$).

In the third period corresponding to 'n' = 3, there are nine orbitals (one '2s' three '2p' and five '3d'). As '3d' orbitals are higher in energy, they are filled after the '4s' orbitals. This period involves filling of only four orbitals ('3s' and '3p') containing eight elements. It starts with sodium (Z = 11) with electron entering the '3s' orbital and ends with argon (Z = 18) where the third shell is partially complete ($3s^2 \ 3p^6$).

The fourth period corresponding to 'n' = 4, consists of filling of one '4s' and three '4p' orbitals. The '4d' and '4f' orbital are higher in energy than the '5s' orbitals and are filled later. The five '3d' orbitals have energies in between '4s' and '4p' orbitals and so are filled accordingly. Totally nine orbitals are filled and therefore, there are eighteen elements in this period starting from potassium with electron entering the '4s' orbital (Z = 19) to krypton (Z = 36) where the third shell gets completed ($4s^2 \ 3d^{10} \ 4p^6$).

In the fifth period there are 18 elements like the fourth period. It begins with rubidium (Z = 37) with the filling of '5s' orbital and ends with xenon (Z = 54) with the filling of '5p' orbital.

The sixth period contains 32 elements (Z = 55 to 86) and the successive electrons enter into '6s', '4f', '5d' and '6p' orbitals in that order. It starts with caesium and ends with radon.

The seventh period, though expected to have 32 elements is incomplete and contains only 19 elements at present.

Number of elements in each period

Period	(n)	Orbital filled up	Number of electron/ elements in the period
First	(1)	1s	2 = 2
Second	(2)	2s 2p	2 + 6 = 8
Third	(3)	3s 3p	2 + 6 = 9
Fourth	(4)	4s 3d 4p	2 + 10 + 16 = 18
Fifth	(5)	5s 4d 5p	2 + 10 + 16 = 18
Sixth	(6)	6s 4f 5d 6p	2 + 14 + 10 + 6= 32
Seventh	(7)	7s 5f 6d 7p	2 + 14 + 10 + 6= 32

There is a periodicitiy occurring at regular intervals of 2, 8, 8, 18 and 32 and so the numbers 2, 8, 18 and 32 are called magic numbers. The first three periods are called short periods while the other three periods are called long periods.

Groups

The vertical column in the periodic table is called as group. There are 18 groups in the long form of the periodic table and they are numbered from 1 to 18 in the IUPAC system. In the old system of naming they are numbered as I to VIII with A and B groups. This convention is followed in many places.

Merits of the long form of the periodic table

- This classification is based on the most fundamental property of the elements - the atomic number, so it is more accurate.
- With the atomic number as the basis of this classification, the position of isotopes in one place is justified.
- The systematic grouping of elements into the four blocks of 's', 'p', 'd' and 'f' has made the study of elements simpler.
- The electronic configuration determines the properties of the elements. The position of elements governed by this feature is useful in studying the properties of elements.
- The position of the element, which were misfit on the basis of atomic mass is now justified on the basis of atomic number.
- The lanthanides and actinides have been placed separately due to their properties different from other groups.
- The whole table is easy to remember and reproduce in terms of electronic configuration and properties of the elements.

Demerits of the long form of the periodic table

Although the long form of the period table has been able to help in systematic studying the elements to a great extent, it has some minor defects.

- Hydrogen resembles both the alkali metals and halogens. But it has been placed with the alkalis.
- The lanthanides and actinides have not been placed in the main body of the table.

Analysis of Table in form of Blocks

With a better understanding of the part that the electron plays great role in the properties of elements, a corresponding understanding of the periodic system came about.

On the basis of electronic configuration the elements may be divided into four groups.

S-block elements

- These are present in the left part of the periodic table.
- These are IA and II A i.e. 1 and 2 group elements.
- These are metals.
- In these elements last electron fills in the s-orbital.
- Electron configuration of valence shell is ns^{1-2} (n = 1 to 7)

P-block elements

- These are present in the right part of the table.
- These constitute the groups III A to VII A and zero groups i.e. groups 13 to 18 of periodic table.
- Most of these elements are metalloids and non-metals but some of them are metals also.
- The last electron fills in p-orbital of valence shell.
- The electronic configuration of valence shell is $ns^2\, np^{1-6}$ (n = 2 to 7)
- $ns^2\, np^6$ is stable noble gas configuration.

s-block elements

These are present in the middle part of the periodic table (between s and p block elements).
- These constitute III B to VII B, VIII, I B and II B i.e., 3 to 12 groups of the periodic table.
- All are metals
- The last electrons fill in (n − 1) d orbital
- The outermost electronic configuration is $i(n-1)\, d^{1-10}\, ns^{1-2}$ (n = 4 to 7)
- There are three series of d-block elements as under :

  3d series – Sc (21) to Zn (30)

  4d series – Y (39) to Cd (48)

  5d series – La (57), Hf (72) to Hg (80)
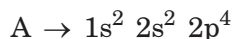
f-block elements

- These are placed separately below the main periodic table.
- These are mainly related to III B i.e, groups of the periodic table.
- There are two series of f-block elements as under :

  4f series – Lanthanides – 14 elements from Ce (58) to Lu (71)

  5f series – Actinides – 14 elements from Th (90) to Lw (103)

- The last electron fills in (n-2)f orbital
- Their outermost electronic configuration is $(n-2)f^{1-14}\, (n-1)s^2\, (n-1)\, p^6\, (n-1)d^{0-1}\, ns^2$ (n = 6 and 7)

Example 1

Predict the period, group number and block of the following elements. A (at. number = 8), B (at. number = 11), C (at. number = 28)

Solution :

Electronic configurations of different elements are

$$A \rightarrow 1s^2\ 2s^2\ 2p^4$$

$$B \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^1$$

$$C \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$$
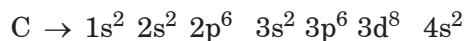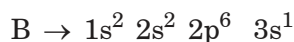
Element A : p – block element

Group number = 10 + number of electron in the valence shell = 10 + 6 = 16

Period of the element = Principal quantum number of the valence shell = 2nd

Element B : s – block element

Group number = number of electrons in valence shell = 1

Period number = 3rd

Element C : d – block element

The Types of Elements

Using electronic configuration as the criterion, we ordinarily recognize some general type of elements.

Typical Elements

Elements of third period are also called as TYPICAL ELEMENTS. These include Na, Mg, Al, Si, P, S, Cl. The properties of all the elements belonging to a particular group resembles the properties of the corresponding typical element of that group. For example, the general properties of Alkali Metals can be predicted from the behaviour of Na, not Li, the first member of the family.

The typical elements (all having n = 3) can take up 18 electrons. Note that, for these elements 3d sub-shell is available, but it is not filled i.e., these have vacant d sub-shell. This is not the case with second period elements, hence they have somewhat different properties than the rest of the group or we can say that it is the typical element, which in true sense represents a group.

Bridge Elements

Elements of second period are also called as BRIDGE ELEMENTS. The properties these elements resemble with the properties of elements belonging to third period placed diagonally. This is illustrated as follows :

2nd Period	Li	Be	B	C	N	O	F
3rd Period	Na	Mg	Al	Si	P	S	Ci

Noble or Inert Gases

Elements of VIII A group or zero group are called as INERT or NOBLE GASES. They have completely filled (2 or 8 electrons in outermost shell) outermost shells, called as stable configuration. Their valency is zero. They are almost inert in their chemical behaviour. They have weak intermolecular forces in them and hence are gases and exists in mono-atomic states.

Transition Elements

- Last two shells of these elements namely outermost and penultimate shells are incomplete.
- The last shell contains one or two electrons and the penultimate shell may contain more than eight up to eighteen electrons.
- Their outermost electronic configuration is similar to d-block elements i.e. $(n-1)d^{1-10} ns^{1-2}$.
- According to latest definition of transition elements those elements which have partly filled d-orbitals in neutral state or in any stable oxidation state are called transition elements. According to this definition Zn, Cu and Hg (II B group) and d-block elements but not transition elements because these elements have d^{10} configuration in neutral as well as in stable +2 oxidation state.

Inner Transition Elements

- In these elements last three shell i.e., last, penultimate and perpenultimate shells are incomplete.
- These are related to III B i.e., group 3
- The last shell contains two electrons. Penultimate shell may contain eight or nine electrons and pre-penultimate shell contains more than 18 upto 32 electrons.
- Their outermost electronic configuration is similar to f-block element i.e., $(n-2)f^{1-14} (n-1)s^2 (n-1)p^6 (n-1)d^{0-1} ns^2$

  Elements of the seventh period after atomic number 93 (i.e. actinides are synthetic elements and are called transuramium elements.

  We can further divide the elements into three classes based on their positions in periodic table.

Metals

This is the largest class of the elements. This includes elements belonging to IA, IIA, IB to VIIIB (i.e., all transition and inner-transition elements) and some elements of groups IIIA to VA lying near the bottom of the table. The metals are characterised by their nature of readily giving up the electron apart from shinning lustre. The oxides of metals are basic in nature.

Non-metals

These do not give up electron, in fact like to take up the electron to form negative ion. These include 10 elements lying to the right side of the table. They are C, N, O, F (2nd period), P, S, Cl (3rd period), Se, Br (4th period) and I (5th period). The oxides of non-metals are acidic in nature.

Metalloid

You are very easily observed that metallic character has decreased when one moves to the right of the table across a row. It is observed that some elements lying at the border of metallic and non-metallic behavior, exhibit both the metallic and non-metallic character, these are called as **metalloids.** These include 8 elements namely; B, Si, Ge, As, Sb, Te, Po and At. The oxides of metalloids are generally amphoteric in nature.

Note : The elements in group VIII A do not behave like metals, nor do they behave like non-metals. So they are classified separately as Noble Gases. Also the element Hydrogen (H) is different from any other element and can not be easily classified into a particular group (however it is placed along with the Alkali Metals, though it does not exhibit metallic character).

Periodic Properties

From the discussion of the periodic table, it is evident that those properties which depend upon the electronic configuration of an atom will vary periodically with atomic number. On the other hand, those properties which depend upon the total number of electrons will show no such variations. Some of the common properties which depend upon electronic configuration are :

Valency

It is defined as combining capacity of an element. It can also be defined in terms of valence electrons (electrons in the outermost shells). The valency is equal to number of valence electrons (or equal to 8 minus the number of valence electrons).

For representative elements, in general, valency of elements belonging to a chemical family i.e., in a group is constant. It is known from its general electronic configuration. To illustrate, for group I A (Alkali metals), valency is 1 (ns^1), for II A (Alkaline earth metals), it is 2 (ns^2) and for group III A, it is 3 ($ns^2 \, np^1$).

For transition elements, no general trend is observed in the valency of elements. The reason is that those elements have variable valencies due to availability of vacant d-subshells in them.

Similar is the case with inner-transition elements (f-block elements) i.e., no general trend is observed due to variable valency.

Effective Nuclear Charge

Between the outer most valence electrons and the nucleus of an atom, there exists finite number of shells containing electrons. Due to the presence of these intervening electrons, the valence electrons are unable to experience the attractive pull of the actual number of protons in the nucleus. These intervening electrons act as shield between the valence electrons and protons in the nucleus. Thus, the presence of intervening (shielding) electrons reduces the electrostatic attraction between the proton in the nucleus and the valence electrons because intervening electrons repel the valence electrons. The concept of effective nuclear charge allows us to account for the effects of shielding on periodic properties.

For example, let us consider a helium atom, which has ground state electron configuration as $1s^2$. Helium has two protons in the nucleus which gives it a charge of +2 but the full attractive force of this charge on the two 1s electrons is partially nullified by electron–electron repulsion. Consequently, the 1s electrons shield each other from the nucleus.

The effective nuclear charge (Z_{eff}) is the charge felt by the valence electron. Z_{eff} is given by $Z_{eff} = Z - \sigma$

where Z is the actual nuclear charge (atomic number of the element) and σ is the shielding (screening) constant. The shielding constant is greater than zero but smaller than Z and depends on the number of intervening electrons and their type of subshell.

To illustrate shielding effect, let us remove both the electrons from a helium atom, one by one. It would take 2370 kJ of energy to remove the first electron from 1 mole of He atoms and 5250 kJ of energy to remove the remaining electron from 1 mole of He^+ ions. The removal of second electrons takes much more energy than the removal of first electron because in He^+ ion, only one electron is present and there would be no shielding and the electron experiences the full effect of +2 nuclear charge.

For atoms with three or more electrons, the electrons in a given shell are shielded by electrons in the same shell and electrons in the inner shells but not by electrons in outer shells. For example, in lithium atom (electron configuration $1s^2 2s^1$), the 2s electron is shielded by the two 1s electrons but 1s electrons are not shielded by 2s electron. In addition, the electrons of the inner shell shield the electrons of outer shell, more effectively than the electrons of the same inner shell.

There are some simple rules for estimating the degree to which electrons in the various types of orbitals shield other electrons from the nucleus & hence for estimating the Z_{eff} experienced by other electrons.

1. After writing the full electron configuration it in the following groupings and order. Group ns and np orbitals together while all other type of orbitals are grouped separated. For example,

    (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p)....

2. Electrons to the right of the group of electrons in question contribute nothing to the shielding of that group of electrons.

3. All other electrons in the same group as the electron in question shield that electron to an extent of 0.35 unit of nuclear charge each.

4. If the electron in question is an s or p electron : (a) All electrons with principal quantum number one less than the electron in question shield it to an extent of 0.85 unit of nuclear charge each (b) All electrons with principal quantum number two or more less than the electron in question shield it completely i.e., to an extent of 1 unit.

5. If the electron in question is a d or f electron : All electrons to the left of the group of the electron in question shield the 'd' or 'f' electron completely (to an extent of 1 unit). This is due to poor penetration effect of 'd' or 'f' electron.

6. Sum the shielding constants from steps 2–5 and subtract them from the actual nuclear charge (Z) of the atom in question to obtain the Z_{eff} felt by the electron in question.

Atomic Radius

Electron clouds do not have sharp edges but when atoms are packed together in solids, their centres are found at definite distances from one another.

For atoms, which link together, to form an extensive three–dimensional network, atomic radius is one–half the distance between the nuclei in two neighbouring atoms. This is called metallic or crystal radius.
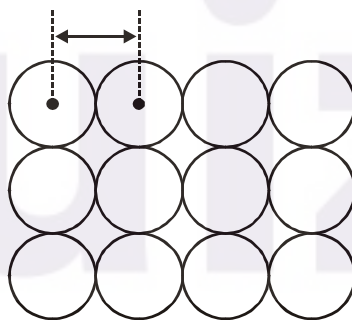
For elements which exist as simple diatomic molecules, the atomic radius is one–half the distance between the nuclei of the two atoms in a particular molecule. This is called covalent radius.
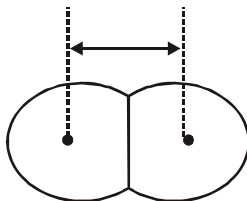
In case of mono atomic gases (like noble gases), the atomic radius is one–half of the distance between the nuclei of two atoms at some distance. This is called van der Waals radius.
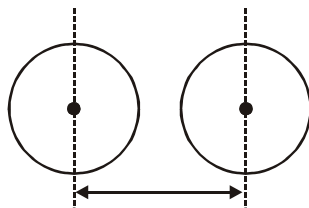
Thus, $r_{covalent} < r_{metallic} < r_{van\ der\ Waals}$

Let us see the variation of atomic radius in a period. For example, consider the second period elements from Li to F. On moving from left to right, we can see that the number of electrons in the inner shell ($1s^2$) remains constant while the nuclear charge increase. The electrons that are added to counter balance the increasing nuclear charge are ineffective in shielding one another. Consequently, the effective nuclear charge increases steadily while the principal quantum number remains constant (n = 2). For example, the outer 2s electron in lithium is shielded from the nucleus (which has 3 protons) by the two 1s electrons. Each 1s electron shields the 2s electron by 0.85 units, so net shielding by two 1s electrons is 1.7 (σ). Thus, the effective nuclear charge of Li is 1.3. The electron configuration of Be is $1s^2 2s^2$. One 2s electron shields other 2s electron by 0.35 unit while each 1s electron shields 2s electron by 0.85. So, the Z_{eff} for Be would be 4–[(2   0.85) + 0.35] = 1.95. Similarly, the Z_{eff} for B would be 5–[(2   0.85)] = 2.6. Thus, it is evident that the effective nuclear charge increases, so progressively the outermost electrons are held more strongly by the nucleus and thus the atomic radius decreases from Li to F.

Now, let us observe the trend of atomic radius in a group. For the alkali metals in group IA (Li, Na, K, Rb, Cs & Fr), the outermost electron resides in the ns orbital. In moving from Li to Na, the increasing principal quantum number n, which superseeds the effect of increasing $Z_{eff.}$ So, thus the size of the metal atoms increase from Li to Na and so on. Thus, atomic radius increases on moving from top to bottom in a group.

Ionic Radius

Ionic radius is the radius of a cation or an anion. When a neutral atom is observed to an ion, these would be change in size, as the Z_{eff} will change but the number of protons in nucleus remains same.

If the atom forms an anions, its size (or radius) increases, since the nuclear charge remains the same but the repulsion resulting from the additional electron(s) enlarges the domain of the electron cloud. On the other hand, if one or more electrons are removed from an atom, it reduces the electron–electron repulsion but the nuclear charge remains the same, so the electron cloud shrinks and the cation is smaller than the atom. When a lithium atom reacts with a fluorine atom to form a LiF unit, the changes in size are very peculiar. Out of Li and F, Li is bigger in size. When lithium changes to Li^+, its size decreases and when F changes to F^-, its size increases. In LiF, Li^+ is smaller than F^- (Note that Li^+ is smaller than F atom and F^- is smaller than Li atom).

Li + F → Li$^+$ F$^-$
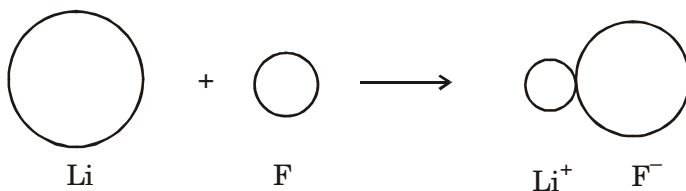
The variation of ionic radii in a period and a group is same as that of atomic radii. Thus, ionic radius decreases in a period while it increases in a group.

For ions derived from elements in different groups, a size comparison is meaningful only if the ions are isoelectronic. If we examine isoelectronic ions, the cations are smaller than anions. Let us compare the radius of Na$^+$ ion and F$^-$ ion. Both ions have same number of electrons (10), but Na (Z = 11) has more protons than F (Z = 9). Thus, Z$_{eff}$ of Na$^+$ is more than that of F$^-$, so Na$^+$ ion is smaller in size than F$^-$ ion. Similarly, for the three isoelectronic ions of third period, Al^{3+}, Mg^{2+} and Na$^+$, they all have the same number of electrons (10) but their number of protons are 13, 12 and 11 respectively. Thus, the electron cloud in Al^{3+} is pulled inward more than that in Mg^{2+} and Mg^{2+} would be smaller than Na$^+$. Thus in general in an isoelectronic cation series, the radii of tripositive ions are smaller than those of dipositive ions, which in turn are smaller than unipositive ions. Similarly, in isoelectronic anions series, the radius increases as we go from uninegative ion to dinegative ion and so on.

Example 2

Compare the size of Cl, Cl$^-$ and Fe^{++} ion.

Solution :

$\dfrac{Z}{e}$ ratio for Cl = $\dfrac{17}{17}$ = 1.00

Cl$^-$ = $\dfrac{17}{18}$ = 0.944

Fe^{++} = $\dfrac{26}{24}$ = 1.08

Cl$^-$ > Cl > Fe^{++}

Example 3

The radii of Ar is greater than the radii of chlorine.

Solution :

In chlorine, the radii means the atomic or covalent radii which is actually half the intermolecular distance between 2 atoms whereas in Argon the radii means the Vanderwaals radii as Argon is not a diatomic molecule. Vanderwaals radii is actually half the distance between adjacent molecule. So Vanderwaal's radii being larger than atomic radii, Argon, has got a larger radii than chlorine.

Ionisation Energy

- Ionisation energy (IE), **sometimes also called ionisation potential (IP),** of an element is defined as the amount of energy required to remove an electron from an isolated gaseous atom of that element resulting in the formation of positive ion. $M(g) \xrightarrow{(IE)} M^+(g) + e^-$

- (IE) is thus a direct measure of the ease with which an atom can change into cation. The smaller the ionisation energy, the easier it is for the neutral atom to change into a positive ion.

- $(IE)_1$, $(IE)_2$, $(IE)_3$... are respectively first, second, third,... ionisation energies required to remove first, second, third, ... electron from the isolated gaseous atoms.

$$M(g) \xrightarrow{(IE)_1} M^+(g) + e^-$$

$$M^+(g) \xrightarrow{(IE)_2} M^{2+}(g) + e^-$$

$$M^{2+}(g) \xrightarrow{(IE)_3} M^{3+}(g) + e^-$$
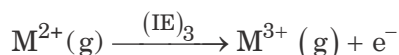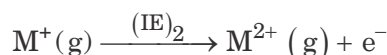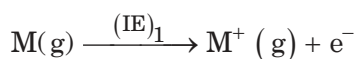
Thus, second ionisation energy, $(IE)_2$, causes ionisation of $M^+(g)$ to form $M^{2+}(g)$ and third ionisation energy, $(IE)_3$ causes ionisation of $M^{2+}(g)$ to form $M^{3+}(g)$ and so on...

- $(IE)_3$ is also called first ionisation energy of $M^{2+}(g)$ and second ionisation energy of $M^+(g)$. $(IE)_2$ is also called first ionisation energy of $M^+(g)$.

- **If an electron has been removed from an atom, it becomes increasingly difficult to remove the second and subsequent electrons from the resulting positively charged ions on account of electrostatic attraction. This is due to the fact that after the removal of an electron, the number of electrons decreases while the nuclear charge remains the same. Consequently, the remaining electrons are held more tightly by the nucleus and it becomes difficult to remove second electron.** Similarly it is further difficult to remove electron from $M^{2+}(g)$. Thus

$$(IE)_1 < (IE)_2 < (IE)_3 < ...$$

Factors Influencing Ionisation Energy

(IE) variation in a period and group may or may not be regular and can be influenced by

(1) Size of the Atom

In a small atom, the electrons are tightly held, while in a larger atom, the electrons are less strongly held, the Coulombic force of attraction F being $F = \dfrac{k\,Ze^2}{r^2}$
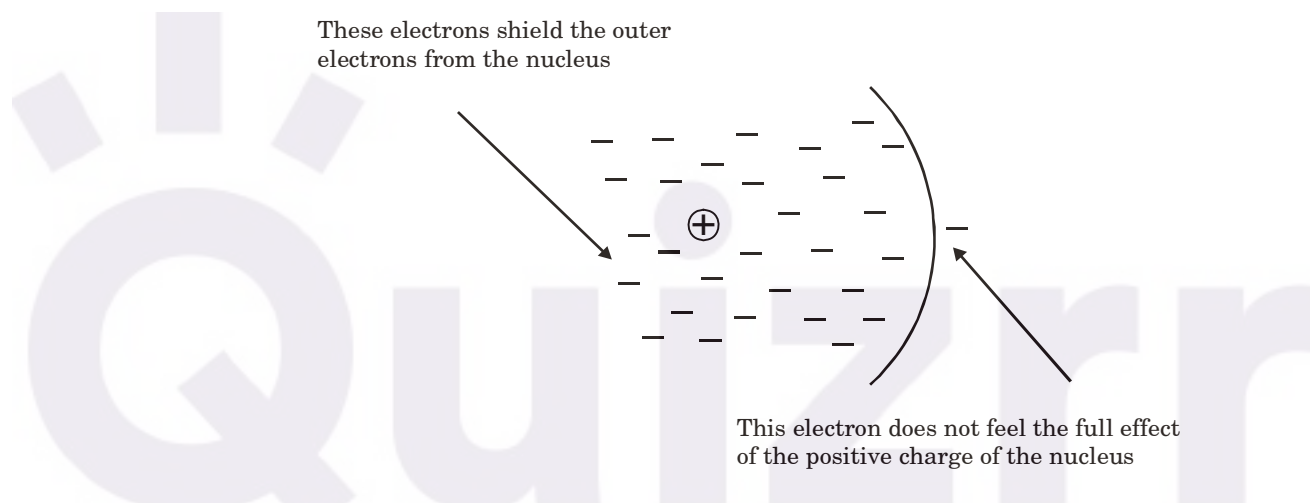
where Ze is charge on nucleus, e the electronic charge, r the atomic size and k the constant. Thus, the ionisation energy decreases as the size of the atom increases.

(2) Nuclear Charge

As given above, the force of attraction between the nucleus and the outermost electron increases with increase in nuclear charge. Greater the nuclear charge, greater the energy required to pull the electron from the atom. Here (IE) increases with increase in nuclear charge.

(3) Shielding Effect

The electrons in the inner-shells act as a screen or shield between the nucleus and the electron in the outermost-shell. This is called **shielding** or **screening** effect. The larger the number of electrons in the inner-shells, greater is the screening effect and smaller the force of attraction and thus (IE) decreases.

These electrons shield the outer electrons from the nucleus

This electron does not feel the full effect of the positive charge of the nucleus

Shielding is most effective whenever there is a full shell (or shells) of electrons between the outermost electron and the nucleus, as in case of noble gases (group VIII A). Hence, there is a sharp decrease in (IE) going from noble gas to alkali metals as given below :

He	$\longrightarrow$	LI	Ne	$\longrightarrow$	Na	Ar	$\longrightarrow$	K
IE	2372		520	2081		513	1521	419

(kJ mol^{-1})

The shielding is not so important across a period as it is down a group. One reason is that an electron in, say, a p_x orbital has little shielding effect on an electron in a py or pz orbital (px, py and pz are mutually at right angles to one another hence as shielding). s-orbitals are spherically symmetrical, hence filling of 1s or 2s will experience shielding effect.

(4) Penetration Effect

The ionisation energy also depends on the type of electron which is removed. s, p, d and f-electrons have orbitals with different shape. An s-electron penetrates nearer to the nucleus, and is therefore more tightly held than a d-electron, and a d electron is more tightly held than an f-electron. Other factors being equal, ionisation energies are in the order s > p > d > f. Thus, the increase in (IE) is not quite smooth on moving from left to right in the periodic table. $(IE)_1$ of group 13 (III A) elements (where a p-electron is being removed) is actuall less than adjacent group 2 (II A) (where an s-electron is being removed).
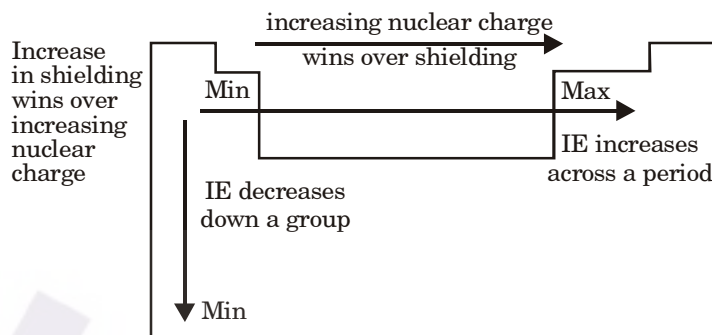
(5) Electronic Configuration

If an atom has fully-filled or half-filled orbitals, its (IE) is higher than expected normally from its position in the periodic table.
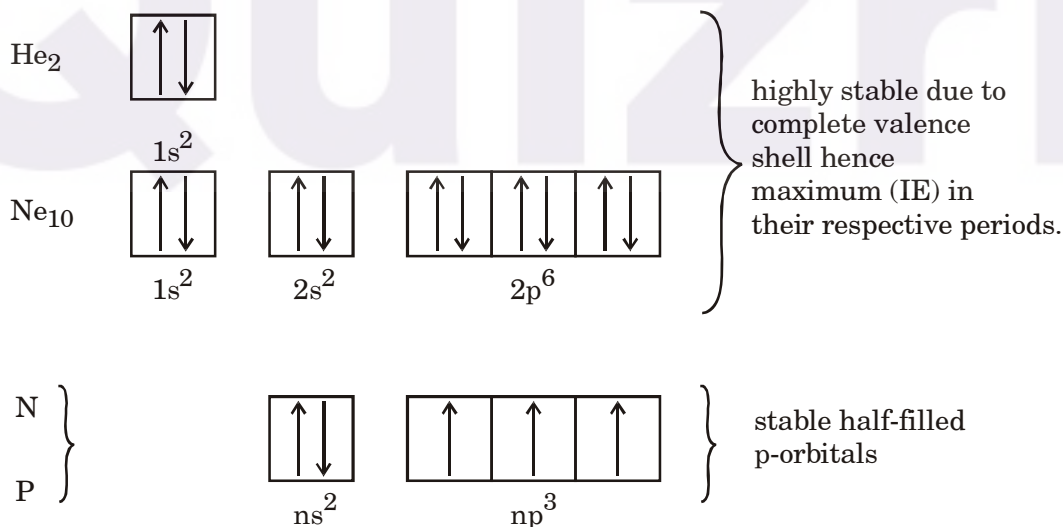
Variation of (IE) in a Group

On moving down a group :

(i)   nuclear charge increases

(ii)   Z* (effective nuclear charge) due to screening is almost constant.

(iii)   number of shells increases, hence atomic size increases.

(iv)   there is increase in the number of inner electrons which shield the valence electrons from the nucleus.

Thus, force of attraction between electrons and nucleus decreases and tendency to remove the valence electron increases. Hence (IE) decreases on moving down the group. Variations of $(IE)_1$ of alkali metals (group I) and boron family (group 13) are given in Fig. 9.6.

In general the first ionisation energy decreases in a regular way on descending the main groups. A departure from this trend occurs in group 13 (boron family), where the expected decrease occurs
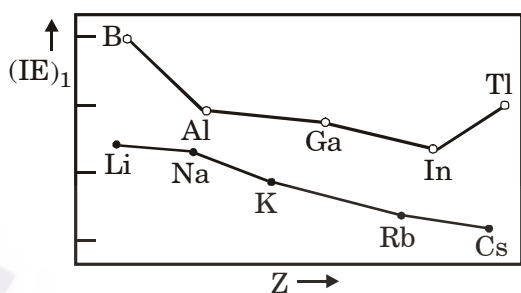
Variation of $(IE)_1$ of groups 1 (•) and 13 (o),
(not according to scale)

between B and A1, but the values for the remaining elements Ga, In and TI do not continue the trend and are irregular. Ga with completely filled 3d-orbitals (no 3d in Al) decreases screening thus Ga is smaller in size than it would otherwise be

(IE) Group 1		in kJ mol^{-1}		$(IE)_1$ Group 13	
Li	520 ↑	B	801	↑	
Na	496	Al	577	↓	decrease
K	419	Ga	579	↑	constant
Rb	403	In	558	↑	decrease
Cs	376	T1	589		increase
	decrease			↓	

As expected the first ionisation energies decrease down the groups in case of the main group elements in the periodic table. But in case of transition elements opposite trends are observed. Thus, $(IE)_1$ of the corresponding elements of 3d and 4d-series are almost similar but these an smaller than the $(IE)_1$ of the 5d-series elements. Certainly, the higher values of ionisation energies of the 5d-transition elements are consistent with the relatively small size of then atoms.

Variation of (IE) in a Period

On moving across a period, the atomic size decreases and nuclear charge increases and therefore the force of attraction exerted by the nucleus on the electron in outer most shell increases. Hence
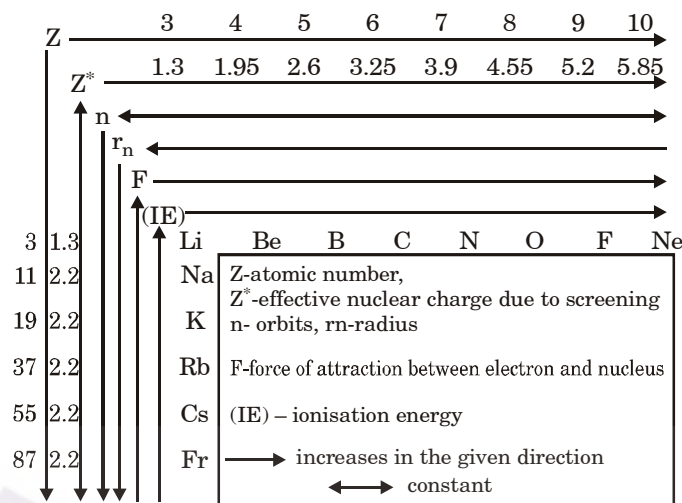

Variation of (IE) in a group and period

(IE) increases along a period from left to right. Fig. above explains general variation of (IE) in a group and period. Fig. below shows the pattern of the ionisation energies of the elements H to Ca.
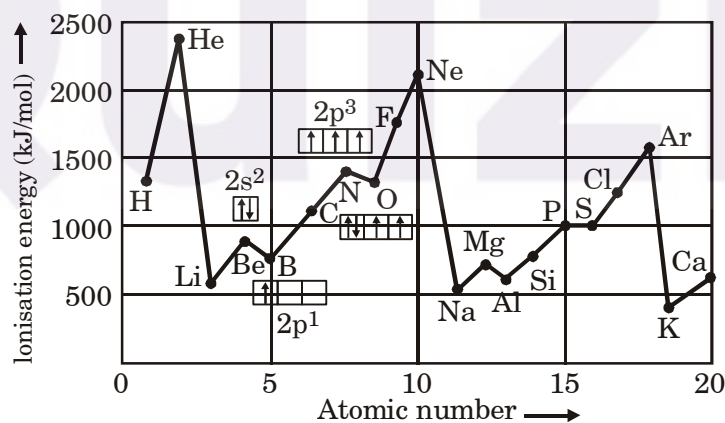
Variation of IE with atomic number showing
apparent anomalies of b and O, and Al and S

- There are two bumps, or dips, around beryllium/boron and nitrogen/oxygen. The dip from beryllium to boron occurs because the extra electron of boron enters a 2p-orbital and this electron will feel the effects of the shielding by the pair of electrons in 2s-orbital. The shielding has the effect of lowering of (IE). The increase from boron to carbon reflects the increased nuclear charge of carbon. Also, because the two 2p-electrons of carbon are in different orbitals, they have little shielding effect on one another. A similar state of affairs accounts for the rise from carbon to nitrogen.
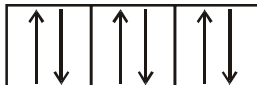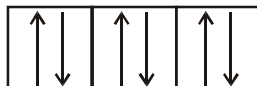
- The dip from nitrogen to oxygen is a different matter. Compared to nitrogen, the oxygen atom's extra electron must go into a 2p-orbital that already has one electron in it. Putting two electrons into the same orbital brings about repulsion between them. For this reason it is easier to remove an electron from 2p-orbital in oxygen containing two electrons than it is from a similar orbital in nitrogen containing only one electron. This effect overweights the effect of nuclear charge from nitrogen to oxygen.

- From oxygen to neon, the increase in ionisation energy reflects the increase in nuclear charge. In a general trend there will be peaks for noble gases for the values of (IE).

- metals have relatively low IE compared to nonmetals.

- The IE, of the metalloids generally fall between those of metals and nonmetals. The difference in IE suggests why metals always form cations and non-metals from anions.

- It is relatively easy to remove an electron from a partially filled valence shell, where Z_{eff} is lower but it is relatively difficult to remove an electron from an atom or ion that has a filled valence shell, when Z_{eff} is higher. In other words, there is a large amount of stability associated with filled s and p-sub-shells (a noble gas electron configuration), which corresponds to having eight electrons (an octet) in the valence shell of an atom or ion. Thus,

  sodium ($[Ne]3s^1$) loses one electron easily

  magnesium (Ne] $3s^2$) loses only two electrons easily,

  aluminium $[Ne]3s^2 3p^1$ loses only three electrons easily, and so on

$$Na(1s^2 2s^2 2p^6 3s^2) = \underbrace{Na^+ (1s^2 2s^2 2p^6)}_{\text{8 electron is valence shells}} + e^-$$
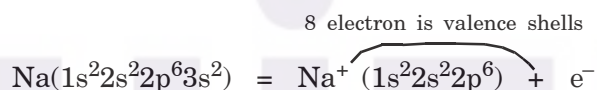
Example 4

Two atoms have the electronic configurations (EC) $1s^2 2s^2 2p^6$ and $1s^2, 2s^2 2p^6 3s^1$. $(IE)_1$ of one is 2080 kJ mol^{-1} and that of the other is 497 kJ mol^{-1}. Match each $(IE)_1$, with one of the given (EC). Justify your choice.

Solution :

Element	(EC)
A	$1s^2 2s^2 2p^6$

$1s^2 \quad 2s^2 \quad 2p^6$

stable inert gas E.C. and removal of
electron requires higher energy

B	$1s^{-2} 2s^2 2p^6 3s^3$

$1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^1$

has unpaired electron, removal of
electron requires lower energy

Thus $(IE)_1$ of A is 2080 kJ mol^{-1} and that of B is 496 kJ mol^{-1}.

Example 5

Arrange the elements Se, Cl and S in increasing order of ionisation energy.

Solution :

Ionisation energy generally increases from left to right across a two of the periodic table and decreases from top to bottom down a group.

(IE) increases →

(IE) decrease

S_{16} Cl_{17}

Se_{34}
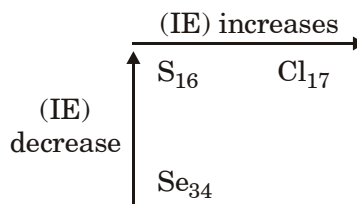
Thus, (IE) of Cl > S

and (IE) of Se < S

Thus, the order is : Se < S < Cl.

Example 6

Which has the larger fifth ionisation energy, Ge or As ?
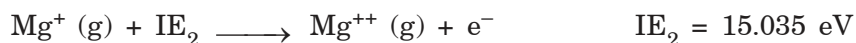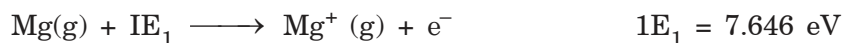
Solution :

			Group
Ge (32)	:	[Ar] $4s^2\ 3d^{10}\ 4p^2$	IVA
As (33)	:	[Ar] $4s^2\ 3d^{10}\ 4p^3$	VA

As their positions in the periodic table indicate, the group IVA element Ge has four valence-shell electrons and thus four relatively low ionisation energies, whereas the group VA element. As has five valence-shell electrons and five low ionisation energies. Ge thus has larger fifth ionisation energy than As.

Example 7

Magnesium has the first and second ionisation potential 7.646 and 15.035 eV respectively. What is the amount of energy required to convert all the magnesium atoms present in 24 mg to magnesium vapours.

Solution :

$$Mg(g) + IE_1 \longrightarrow Mg^+\ (g) + e^- \qquad\qquad 1E_1 = 7.646\ eV$$

$$Mg^+\ (g) + IE_2 \longrightarrow Mg^{++}\ (g) + e^- \qquad\qquad IE_2 = 15.035\ eV$$

So, for the reaction $Mg(g) \longrightarrow Mg^{++}(g) + 2e^-$, energy required

$$= 7.646 \text{ eV} + 15.035 \text{ eV} = 22.681 \text{ eV}$$

$$= 22.681 \times 96.49 \text{ kJ mol}^{-1}$$

$$= 2188.489 \text{ kJ mol}^{-1}$$

24 mg of magnesium $= 1 \times 10^{-3}$ moles of magnesium

∴   Total energy required $= 2188.489 \times 10^{-3} = 2.188 \text{ kJ}$

Electron Affinity

Electron affinity is the energy change that occurs when an electron is accepted by an isolated atom in the gaseous state to form an anion.

$$X(g) + e^- \longrightarrow X^-(g)$$

The sign of electron affinity is opposite to that used for ionization energy. A positive electron affinity signifies that energy is liberated when an electron is added to an atom. To clarify this apparent paradox, let us consider the process in which a gaseous fluorine atom accepts an electron.

$$F(g) + e^- \longrightarrow F^-(g); \quad \Delta H = -328 \text{ kJ/mole}$$
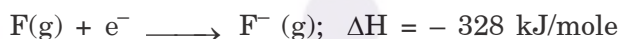
The sign of the enthalpy change indicates that this is an exothermic process. However, the electron affinity of fluorine is assigned a value of + 328 kJ/mole. Thus we can think of electron affinity as the energy that must be supplied to remove an electron from a negative ion. For the removal of an electron from a fluoride ion, we have

$$F^-(g) \longrightarrow F(g) + e^-; \quad \Delta H = +328 \text{ kJ/mole}$$

Do remember two unique features of electron affinity as

(i)   The electron affinity of an element is equal to the enthalpy change that accompanies the ionization process of its anion and

(ii)   a large positive electron affinity means that the negative ion is very stable (i.e. atom has a great tendency to accept an electron), just as a high ionization energy of an atom means that the atom is very stable.

Factors Affecting the Magnitude of Electron Affinity

(i)   **Atomic size :** in general electron affinity value decreases with the increasing atomic radius.

$$\text{Electron affinity } \alpha \frac{1}{\text{Atomic size}}$$

(ii) **Effective nuclear charge :** Electron affinity value of the element increase as the effective nuclear charge on the nucleus increases.

Electron affinity α Effective nuclear charge (Z_{eff})

(iii) **Screening or shielding effect :** Electron affinity value of the elements decreases with the increasing shielding or screening effect. The shielding effect between the outer electrons and the nucleus increases as the number of electrons increases in the inner shells.

$$\text{Electron affinity } \alpha \frac{1}{\text{Shielding effect}}$$

(iv) **Stability of half filled and completely filled orbitals :** The stability of half filled and completely filled degenerate orbitals of a sub shell is comparatively more, so it is difficult to add electron in such orbitals and lesser energy is released on addition of electrons hence the electron affinity value will decrease.

Periodicity in Electron Affinity

(i) In general electron affinity value increases in moving from left to right in a period because effective nuclear change increases.

(ii) In a group moving from top to bottom the electron affinity value of elements decreases because the atomic size increases.

Variation of (EA) in a Period

• On moving across a period, the atomic size decreases and hence the force of attraction exerted by the nucleus on the electrons increases. Consequently, the atom has a greater tendency to attract additional electron, i.e., its electron affinity increases.

• Also (EA) values of metals are low while those of non-metals are high.

• Halogens have high electron affinities. This is due to their strong tendency to gain an additional electron to change into the stable $ns^2 \, np^6$ configuration.

Variation of (EA) in a Group

On moving down a group, the atomic size increases and, therefore, the effective nuclear attraction decreases and thus, electron affinity decreases.

• **The fact that fluorine has a less negative electron affinity than chlorine seems to be due to the relatively greater effectiveness of 2p-electrons in the small F atom to repel the additional electron entering the atom than do 3p-electrons in the larger Cl atom.**

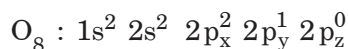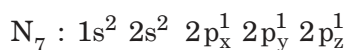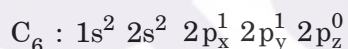• The results have been represented in Fig.
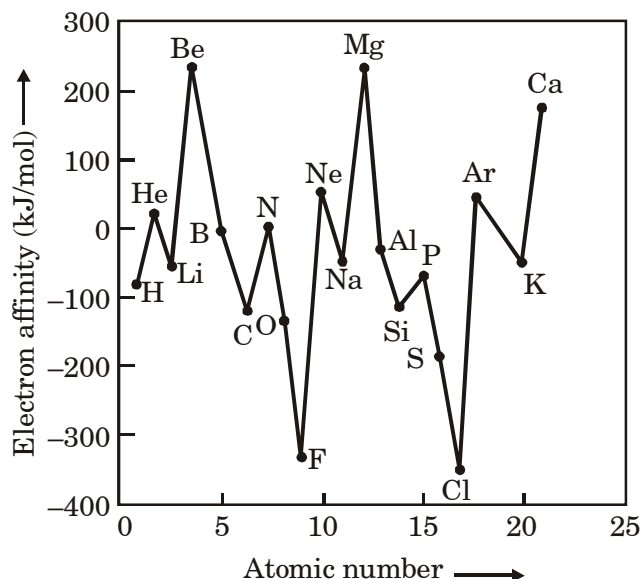
A plot of electron affinity versus atomic number for the first 20 elements. The general horizontal trend is that electron affinities become more negative (more energy is released as an extra electron is added) from group IA (1) through group VIIA (17) for a given period. Exceptions occur at the IIA (2) and VA (15) elements.

Example 8

Why does nitrogen have a less favourable (more positive) electron-affinity than its neighbours on either side, C and O ?

Solution :

Electron configurations of these elements are :

$$C_6 : 1s^2 \; 2s^2 \; 2p_x^1 \; 2p_y^1 \; 2p_z^0$$

$$N_7 : 1s^2 \; 2s^2 \; 2p_x^1 \; 2p_y^1 \; 2p_z^1$$

$$O_8 : 1s^2 \; 2s^2 \; 2p_x^2 \; 2p_y^1 \; 2p_z^0$$

Carbon has only two electrons in its 2 p-subshell and can readily accept another in its vacant $2p_z$-orbital. Nitrogen, however, has a half-filled 2p-subshell and the additional electron must pair up in a 2p-orbital, when it feels a repulsion from the electron already present.

Thus the electron affinity of nitrogen is less favourable than that of carbon. Oxygen also must add an electron to an orbital that already has one electron, but the additional stabilising effect of increased effective nuclear charge (Z_{eff}), across the periodic table counteracts the effect of electron repulsion, resulting in a more favourable electron-affinity for O than for N.

Electronegativity (EN)

Electronegativity is a measure of the tendency of an element to attract electrons to itself.

$$X(g) + e^- \longrightarrow X^- (g)$$

In a molecule, tendency of the atom to attract bonding pair towards itself is its electronegativity. B is said to be more electronegative than A if it pulls bonding pair towards itself.

$$(A)^\bullet (B) \longrightarrow \overset{\delta+}{(A)}\!\!-\!\!\overset{\delta-}{(B)}$$
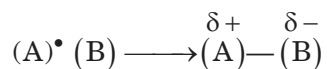
Variation of (EN) in a Group

- On moving down the group
  - Z increases but Zeff. almost remains constant.
  - number of shells (n) increases
  - r_n (atomic radius) increases,
  - force of attraction $\left(F = \dfrac{k\,Ze^2}{r_n^2} \right)$ between added electron and nucleus decreases,
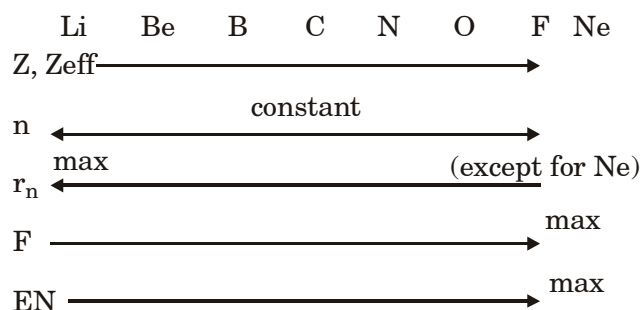
Therefore, (EN) decreases moving down the group.

Element	Z	Zeff	n	r_n	F	(EN)
F	9				max	max
Cl	17					
Br	35					
I	53					
		constant	max	max		

Variation of (EN) in a Period

- While moving across a period left to right
  - Z, Zeff. increases,
  - n number of shells remains constant,
  - r_n decreases
  - $F\left(= k\dfrac{Ze^2}{r_n^2} \right)$ increases

Hence, (EN) increases along a period.

- **Flourine is the most electronegative element in the periodic table.**

  Fig. represents variation of electronegativity of elements with atomic number. In this :

  the **strongest non-metals, the halogens, appear at the peaks;**

  the **alkali metals mark the** troughs. This is largely a result of new shell of electrons starting with noble gases **which have zero values of electronegativities.**
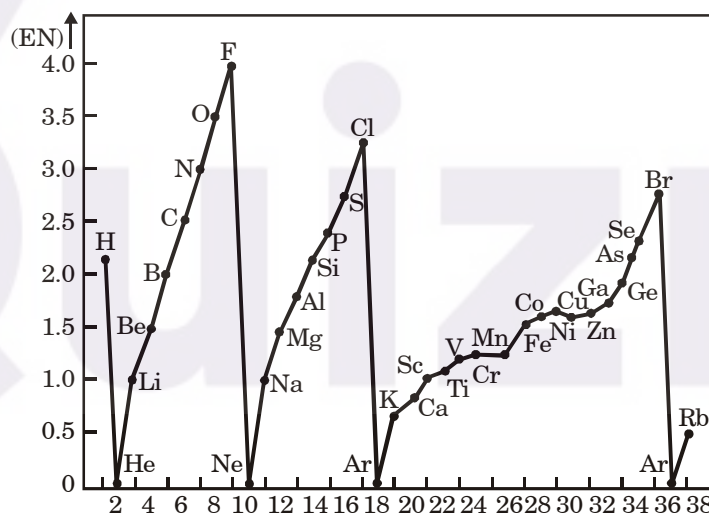

Fig. Electronegativities of the elements H(1) to Rb (37).
The (EN) of the noble gases have been set at zero

- the group 1 (IA) metals have their nuclei quite strongly shielded. Hence they show little tendency to gain new electron.

  the electronegativities of transition metals like their (IE), do not change greatly from one another.

Diagonal Relationship and Electronegativity

- Moving one place to the right across period, the increased nuclear charge holds the electrons more tightly to the atom. Moving down one place in a group, the extra shell of electrons

decreases the attraction of the nucleus for the outer electrons. A **diagonal** move means that these effects tend to compensate for one another.

- The electronegativity increases as we go from Li to Be but it decreases as we move from Be to Mg. As we move diagonally, these two effects partly cancel each other and there is no marked change in electronegativity and thus Li and Mg have close values of electronegativities. Because of this, Li and Mg show similarity in properties— a diagonal relationship (between elements lying diagonally in periodic table).

- Elements' pairs showing this relationship are :

Li—Mg, Be—Al, B—Si
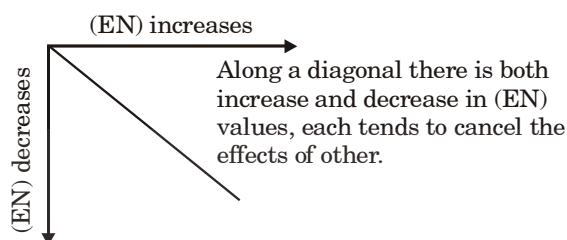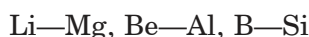
Pauling's Electronegativity

This scale determines electronegativity of the element X w.r.t. hydrogen H

$$\chi_x - X_H = 0.208 \sqrt{\Delta_{H-x}}$$

where χ (chi) represents electronegativity, Δ_{H-x} is the extra bond energy in kcal mol^{-1}.

and

$$\Delta_{H-x} = E_{H-x} - \sqrt{E_{H-H} E_{x-x}}$$

E_{H-x}, E_{H-H} and E_{x-x} represent bond energy of H – X, H – H and X – X bonds respectively. Converting the equation to SI units

$$\chi_x - \chi_H = 0.1017 \sqrt{\Delta_{H-x}}$$

where Δ_{H-x} is measured in kJ mol^{-1}.

- $\chi_H = 2.05$ (and not zero) to avoid any negative value of the element.

Some other elements have following values of electronegativity based on Pauling's scale :

						H
						2.1
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na						Cl
0.9						3.0
K						Br
0.8						2.8
Rb						I
0.8						2.5
Cs						
0.7						

- If two atoms have similar electronegativity, the bond between H and X will be predominantly covalent.

- A large difference in electronegativity leads to a bond with a high degree of polar character, and bond will be predominantly ionic.

- Ionic character of a bond varies with the difference in electronegativity as given in Fig. 9.11. This is based on the ionic character; HI : 4%, HBr : 11%, HCl : 19% and HF : 45% which are known from dipole moment measurements.
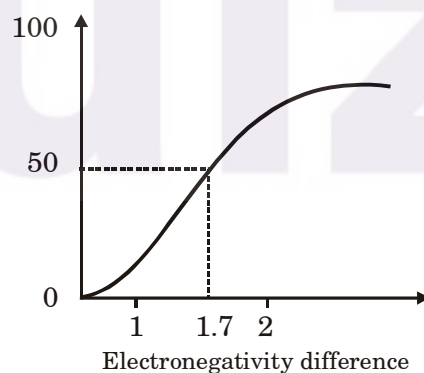
- 50% ionic character is shown in the cases when electronegativity difference is about 1.7. Thus,

$(\chi_x - \chi_H) = 1.7$ 50% ionic

$(\chi_x - \chi_H) > 1.7$ predominantly ionic

$(\chi_x - \chi_H) < 1.7$ predominantly covalent

Mulliken-Jaffe Electronegativity

Electronegativity (EN) can be regarded as the average of the ionisation energy (IE) and the electron affinity (EA) of an atom.

$$(EN) = \frac{IE + EA}{2}$$

If both (EA) and (IE) are determined in eV units then Pauling's electronegativity $(EN)_P$ is related to Mulliken's electronegativity $(EN)_M$ by the equation :

$(EN)_P = 0.336\ [(EN)_M - 0.615]$

- If (EA) and (IE) are in eV, then (EN) in eV is given by

    0.187 (IE + EA) + 0.17

- Mulliken's values were about 2.8 times larger than the Pauling's values.

Allred-Rochow's Electronegativity

Allred and Rochow defined electronegativity as the force exerted by the nucleus of an atom on its valence electrons :

$$(EN)_{A-R} = \frac{0.359 Z_{effective}}{r^2} + 0.744$$

where $Z_{effective}$ is the effective nuclear charge and r the covalent radius (in Å).

METALLIC NATURE

Metals have the tendency to form cations by loss of electrons and this property makes the elements as **electropositive** elements or metals.

$$M(g) \longrightarrow M^+ (g) + e^-$$
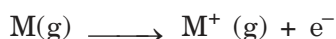
- The tendency of an element to lose electron is closely connected to the (IE) of the element. **The smaller the (IE) of an element, the greater will be its tendency to lose electrons** and **thus greater will be its metallic character.**

- Tendency to oxidise itself provides reducing property to the elements thus, smaller the (IE), greater the metallic character, hence greater the reducing nature : **(IE) increases moving** along a **period left to right** and decreases down the group, hence metallic and reducing nature decrease along the period and increase down the group.

Nuclear Charge	Sheilding		Tendency to make +ve ions	Reducing power	Metallic nature
increases	increases	But the shielding effect wins so ⇒	increases	increases	increases

|	
Nuclear charge	increases
Shielding	increases

But the nuclear charge wins so $\Rightarrow$

**Tendency to form +ve ions** ——— decreases L to R

Reducing power ——— decreases L to R

Metallic nature ——— decreases L to R

Notice that the most reactive metals (the top of the activity series) are on the left of the periodic table, whereas the least reactive metals (the bottom of the activity series) are in the transition metal group closer to the right side of the table as shown in Fig. below

More active metals   Less active metals
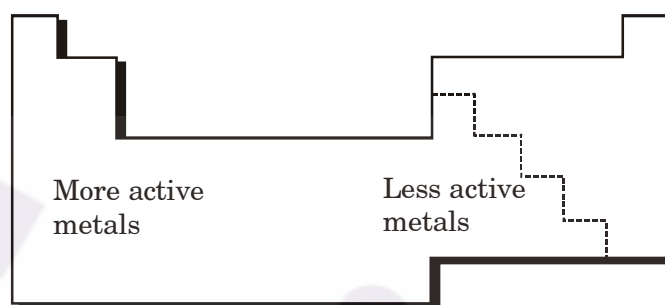
Redox reactions are common for almost every element in the Periodic table except for the noble gas element of group VIIIA (18). In general, metals act as reducing agents, and reactive non-metals such as O_2 and the halogens act as oxidizing agents as given in Fig. below

Oxidizing agents; tend to gain e^-

Reducing agents; tend to lose e^-
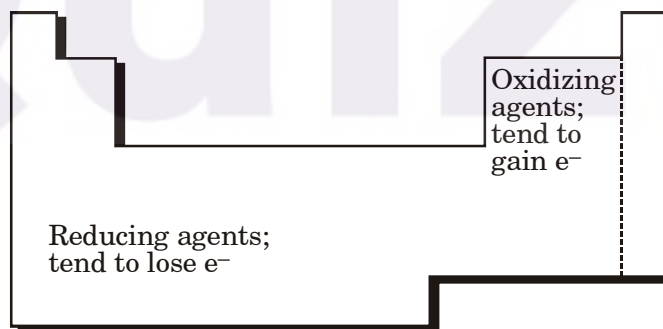
Example 9

The formation of $F_{(g)}^-$ from $F_{(g)}$ is exothermic whereas that of $O^{2-}_{(g)}$ from $O_{2(g)}$ is endothermic. Why ?

Solution :

When F^- is formed from F an e^- is added to an electronegative, neutral atom and energy [E.A.] is released by this process but even through O^- from O is energy releasing process, formation of O^{2-} from O^- is highly energy consuming. So combined effect is O^{2-} formation from O is endothermic.

Diagonal Relationships

A diagonal relationship is a similarity in properties between diagonal neighbours in the main groups of the periodic table. Because these properties lie in a diagonal pattern, it is not surprising to find that the elements within a diagonal band show similar chemical properties. Diagonal relationship helps in making predictions about the properties of elements and their compounds.

Diagonal relationship is exhibited by lithium & magnesium and beryllium & aluminium. For example, lithium and magnesium react directly with nitrogen to form nitrides. Beryllium and aluminium, both are amphoteric i.e., reacts with acids as well as bases.

Properties of Oxides

Properties of the representative elements across a period can be compared by examining the properties of their oxides. Let us see the difference in the behaviour of the oxides of third period elements. Some elements in the third period (P, S and Cl) form several types of oxides but we will consider those oxides in which the elements have the highest oxidation number. The oxides of the elements of third period are Na_2O, MgO, Al_2O_3, SiO_2, P_4O_{10}, SO_3 and Cl_2O_7.

We know that oxygen has a tendency to form the oxide ion. This tendency is greatly favoured when oxygen combines with metals having low ionization energies (like I and II A group elements plus aluminium). Thus, Na2O, MgO and Al_2O_3 are ionic compounds having extensive three–dimensional structures in which each cation is surrounded by a specific number of anions and vice versa. As the ionization energies of the elements increase from left to right, so does the molecular structure of the oxides that are formed. Silicon is a metalloid whose oxide (SiO_2) has a giant three–dimensional network, although no ions are present. The oxides of phosphorous, sulfur & chlorine are molecular compounds composed of small discrete units.

Most oxides can be classified as acidic or basic depending on whether they produce acids or bases when dissolved in water or react as acids or bases in certain processes. Some oxides are amphoteric, which mean they display both acidic and basic properties. The first two oxides of the third period (Na_2O & MgO) are basic oxides. For example, Na_2O reacts with water to form the base ($NaOH$).

$$Na_2O + H_2O \longrightarrow 2NaOH$$
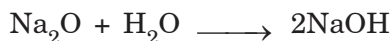
MgO is quite insoluble in H_2O but it reacts with acids showing its basic nature.

$$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$$

Al_2O_3 is even less soluble in H_2O than MgO, it also does not react with water but it shows basic properties by reacting with acids.

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

It also exhibits acidic properties by reacting with bases.

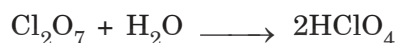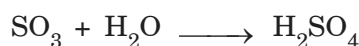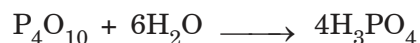$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2NaAl(OH)_4$$

Thus, Al_2O_3 is classified as an amphoteric oxide because it has properties of both acids and bases. Other amphoteric oxides are ZnO, BeO, Bi_2O_3 etc. SiO_2 is insoluble and does not react with water. It has acidic properties as it reacts with very concentrated bases.

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$
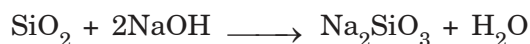
For this reason, concentrated aqueous, strong bases such as NaOH should not be stored in glasswares, which are made of SiO_2.

The remaining oxides are acidic. They react with water to form phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4) and perchloric acid ($HClO_4$).

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$

Thus the oxides of third period elements shows that as the metallic character of the elements decreases from left to right across the period, their oxides changes from basic to amphoteric to acidic. Metallic oxides are usually basic and most oxides of non-metals are acidic. The intermediate properties of the oxides are exhibited by elements which are placed between metals and non-metals. As the metallic character of the elements increases from top to bottom in a group of representative elements, the basic character of oxides also increases from top to bottom. Thus, Na_2O is less basic than K_2O, K_2O is less basic than Rb_2O and so on.

Screening (shielding) Effect

In d-block elements (transition elements), while writing electronic configuration of element, it is seen that the new electrons are being added to the inner shell i.e. penultimate shell (3d after 4s, 4d after 5s & so on). This affects the nuclear attraction of the positive nucleus for the outer electrons. As the differentiating electrons enters the inner shells, they tend to screen or shield the outer shell electrons from the nucleus and hence offset the nuclear attractive force. This is famous as screening or shielding effect. Due to this effect, the atomic size of transition elements (which should have been decreasing across a period) remains nearly same or constant. The same is the case with ionisation energy, electron affinity and other periodic properties when one moves across a period.

Magnetic Properties

In general, the magnetic properties of matter depends upon the atoms contained in them. The magnetic behavior of an atom is the direct consequence of its electronic configuration. Any electron in an atom has two types of motions. One is its motion about the nucleus and other its spin about its own axis. A single electron spinning about its own axis generates a magnetic field. For two electrons in an orbital, the spins are opposite and hence the fields cancel each other.

⇒ Consequently an atom which has a single electron in its orbital generates a magnetic field while an orbital containing two electrons falls to do so. This type of magnetism is called as **paramagnetism.** Any atom or ion or molecule that contains one or more unpaired electrons will be paramagnetic. The substances that contain such type of atoms are weakly attracted by the magnets.

Another kind of magnetism is **diamagnetism.** A diamagnetic substance when placed in an external magnetic field, is weakly repelled in it. This arises due to orbital motion of electrons about nucleus. It is a weak effect and is swamped out if the atom is paramagnetic.

⇒ The strongest kind of magnetism is ferromagnetism. When a paramagnetic substance is placed in a magnetic field, the field will align the unpaired spins & magnetise the substance. If the substance keeps its magnetism after the field is removed, it is called as ferromagnetism. It is much stronger than paramagnetism. The most important example of such types is iron & others are cobalt & nickel.

Hydration And Hydration Energy

Hydration energy is the enthalpy change that accompanies when one mole of the gaseous ion is dissolved in water. For example, reaction of the hydration of Li ion is shown as :

$$Li^+ (g) + nH_2O \longrightarrow [Li(H_2O)_n]^+(aq); \Delta H = -806 \text{ kJ mol}^{-1}$$
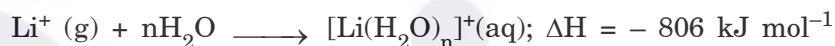
Extent of hydration (means the number of water molecules surrounding a given ion) depends on the size and charge of the ion. If the size of the ion is small and its charge is greater, then there would be greater attraction for water molecules, hence greater the extent of hydration and greater the hydration energy. The total hydration energy of a salt ($M^+ X^-$) is related as

$$\text{Total hydration energy} \propto \left(\frac{1}{r_{M^+}}\right) + \left(\frac{1}{r_{X^-}}\right)$$

The first term in this expression defines the hydration energy due to cation and second term defines the hydration energy due to anion.

Let us take LI^+, Na^+, K^+, Rb^+ and Cs^+ ions for comparison. The charge on all the ions is same but the size increases from Li^+ to Cs^+. Thus the positive charge density increases from Li^+ to Cs^+ and hence Li^+ ion would attract H_2O molecules more strongly than Na^+ and so on. Therefore, hydration energy increases from Li^+ to Cs^+ ion while the size of the hydrated ion decreases from Li^+ ion to Cs^+ ion and thus the ionic mobility decreases from Li^+ to Cs^+ ion.

In a period, on moving from left to right the hydration energy increases. You can very well see this trend in the group of ions Na^+, Mg^{2+} and Al^{3+}.

Hydrides

Hydrogen combines with a number of other elements (metals and non-metals) to form compounds called hydrides. The hydrides can be either ionic or covalent. The ionic hydrides are formed by the elements of I A & II A group while other elements mostly form covalent hydrides.

Covalent nature of hydrides increases across a period and decreases down the group while ionic nature of hydrides decreases across a period and increases down the group.

Ionic hydrides are better reducing agent than covalent hydrides and reducing nature of hydrides decreases across a period and increases down the group.

Example 10

Arrange the following compounds in the order of their decreasing stability if the electro negative values of elements are as follows :

H = 2.1 F = 4, Cl = 3.0, Br = 2.8

I = 2.3, N = 3.0

HF, NCl$_3$, HBr, HI, HCl

Solution :

Electronegativity difference for

$HF = 4.0 - 2.1 = 1.9$

$NCl_3 = 3.0 - 3.0 = 0.0$

$HBr = 2.8 - 2.1 = 0.7$

$HI = 2.3 - 2.1 = 0.2$

$HCl = 3.0 - 2.1 = 0.9$

So their order of their decreasing stability

$HF > HCl > HBr > HI > NCl_3$

1.9   0.9   0.7   0.4   0.0

Example 11

Why are inert gases mono-atomic ?

Solution :

Inert gas have completely octet (ns^2, np^6) and so do not form bonds.

Some Other periodic Properties

(i) **Atomic Volume :** Atomic volume increases in a group from top to bottom. The increase is due to the increases in the number of energy shells.

In period from left to right, atomic volume varies cyclically, i.e., it decreases at first for some elements, becomes minimum in the middle and then increases.

(ii) **Density :** The density of the elements in solid state varies periodically with their atomic numbers. At first, the density increases gradually in a period and becomes maximum somewhere for the central members and then start decreasing afterwards gradually.

Example 12

The sum of first and second ionization energies and those of third and fourth ionization energies in (kJ mol^{-1}) of nickel and platinum are

	$(IE)_1 + (IE)_2$	$(IE)_3 + (IE)_4$
Ni	2.49	8.80
Pt	2.66	6.70

Based on this information; write

(i)   the most common oxidation states of Ni and Pt

(ii) Name of metal (Ni or Pt) which can more easily form compounds in its +4 oxidation state.

Solution :

(i) Ni = +2, Pt = +4 since $(IE)_1 + (IE)_2$ of Ni is less than its $(IE)_3 + (IE)_4$ and reverse is the case in Pt.

(ii) Platinum forms more stable complexes in +4 state due to its higher stability than +2 state.

Example 13

In alkali metal group which is the strongest reducing agent in aqueous solution and why ?

Solution :

Li is the strongest reducing agent. Since I.P. decreases down the group we would expect that Li will have the lowest reducing power in that group. But since it's hydration energy is very high and which in fact decreases down the group, Li will have highest reducing power.

Example 14

**The first ionization energy of carbon atom is greater than that of boron atom, whereas reverse is true for the second ionization energy. Explain.**

Solution :

The electronic configurations of carbon and boron are as follows :

$$C : 1s^2, 2s^2\ 2p_x^1\ 2p_y^1$$

$$B : 1s^2, 2s^2\ 2p_x^1$$
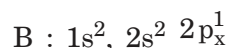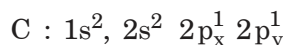
Due to higher nuclear charge in carbon, the force of attraction towards valency electron is more in carbon atom and hence the first ionization energy is greater than boron atom. After loss of one electron, the mono-valent cations have the configurations as follows :

$$B^+ : 1s^2, 2s^2$$

$$C^+ : 1s^2, 2s^2\ 2p_x^1$$
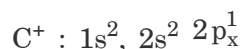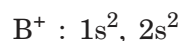
The B^+ configuration is stable one and hence the removal of electron is difficult in comparison to C^+. Hence, second ionization potential of boron is higher than carbon.

Example 15

Calculate the electronegativity of fluorine from the following data :

E_{H-H} = 104.2 kcal mol^{-1}, E_{F-F} = 36.6 kcal mol^{-1}
E_{H-F} = 134.6 kcal mol^{-1}, X_H = 2.1

Solution :

Let the electronegativity of fluorine be X_F.

Applying Pauling's equation

$$X_F - X_H = 0.208[E_{H-F} - (E_{F-F} \quad E_{H-H})^{1/2}]^{1/2}$$

In this equation, dissociation energies are taken in kcal mol^{-1}.

$$X_F - 2.1 = 0.208\ [134.6 - (104.2 \quad 36.6)^{1/2}]^{1/2}$$

$$X_F = 3.87$$