(*iii*) Though atomic radii decrease along a period but at the end of each period, there is increase in the atomic radii of noble gases. It is because in case of noble gases the atomic radii are van der Waal radii.

Trend in atomic and ionic radii down a group in the periodic table. **As we move down the group in the periodic table,** we observe that :

The atomic number, *i.e.*, the nuclear charge goes on increasing. The electrons get added in the new shells which screen the nucleus. The screening effect of the new shells goes on increasing. Thus, the attraction of the nucleus for the outermost electrons goes on decreasing.

As a result : **"The atomic as well as ionic radii go on increasing"** see (Table 2.17).

Table 2.17.

Period 2 elements	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
Atomic radii (pm)	123	90	85	77	75	73	72
Ionic radii (pm)	$Li^+ = 68$	$Be^{2+}=31$	$B^{3+}=20$	$C^{4+} = 15$	$N^{5+} = 11$ $N^{3-} = 171$	$O^{6+} = 9$	$F^{7+} = 7$ $F^- = 136$
I.E. (kJ mol$^-$)	520.3	899.5	800.6	1086.4	1402.3	1314.0	1681.0
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Electron affinity (kJ mol$^-$)	59.8	< 0	26.8	122.3	≤ 0	141.1	328
Period 3 elements	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
Atomic radii (pm)	154	136	143	111	106	102	99
Ionic radii (pm)	$Na^+ = 95$	$Mg^{2+}=65$	$Al^{3+}=50$	$Si^{4+} = 41$ $Si^{4-} = 271$	$P^{5+}=34$ $P^{3-}=212$	$S^{6+}=29$ $S^{2-}=184$	$Cl^{7+} = 26$ $Cl^- = 171$
I.E. (*k* J mol$^-$)	495.8	737.7	577.6	786.5	1011.8	999.62	1251.1
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0
Electron affinity (kJ mol^{-1})	52.7	< 0	< 0	133.6	71.7	200.43	348.8
Period 4 elements	**K**	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**
Atomic radii (pm)	203	174	135	122	120	116	114
Ionic radii (pm)	$K^+ = 133$	$Ca^{2+}=99$	$Ga^{3+}=62$	$Ge^{2+}=93$	$As^{5+}=47$ $As^{3-}=222$	$Se^{6+}=42$ $Se^{2-}=198$	$Br^{7+}=39$ $Br^-=195$
I.E. (kJ mol$^-$)	418.9	589.8	578.8	762.2	944	940.9	1139.9
Electronegativity	0.8	1.0	1.6	2.0	2.0	2.4	2.8
Electron affinity (kJ mol$^-$)	48.36	< 0	< 0	116	77	194.97	324.6

IONISATION ENERGY (I.E.) or IONISATION POTENTIAL (I.P.)* or IONISATION ENTHALPY

First I.E. (E_1). *It is the amount of energy required to remove one valence electron from an isolated neutral gaseous atom to make it unipositive gaseous ion.*

Units. It is measured in kJ mol^{-1}, kcals/mole or electron volt **(e. V.) 1 eV = 23.06 kcals.

e.g.

$$A\,(g) + E_1 \longrightarrow A^+\,(g) + e^- \;;\; E_1 = \text{First I.E.}$$

$$Na\,(g) + 118\text{ kcal/mole} \longrightarrow Na^+\,(g) + e^-$$

*Because energy is supplied in the form of potential, the ionisation energy is also expressed as I.P. ; 1*k* . cal = 4.184 kJ.

**e.V. It is the unit of electrical work. It is the kinetic energy acquired by one electron (Charge $= -1.6 \times 10^{-19}$ coulomb) when it is accelerated in an electric field produced by a potential difference of one volt.

Factors on which ionisation potential depends

1. **Size of atom.** Greater the size of an atom, lesser will be the force of attraction of its nucleus for the valence electrons. Thus, less energy will be required to remove an electron from such atoms. Hence, I.E. will be less. The size of an atom increases down the group but decreases along a period. Hence, I.E. decreases down a group but increases along a period.

2. **Magnitude of nuclear charge.** Greater the magnitude of nuclear charge (along a period), greater will be the force of attraction of the nucleus for the valence electrons. Thus, greater energy will be required to remove the valence electrons. Hence, greater will be the ionisation energy, *e.g.*, in the second period, Be (At. No. 4) has greater ionisation energy (214.9 kcal/mole) than Li (At. No. 3) with I.E., 124 kcal/mole.

   When size of the atom and nuclear charge increase simultaneously, (*e.g*, down a group), the size of atom dominates the magnitude of nuclear charge. As a result, the I.E. generally decreases.

3. **Screening effect.** The shells between the nucleus and the valence electrons reduce the force of attraction between the nucleus and valence electrons. *The effect of reduction of force of attraction by the shells present between nucleus and valence electrons is called screening or shielding effect.* Greater the number of shells between nucleus and valence electron, lesser will be the electron-nucleus attraction and lesser will be the ionisation potential.

4. **Penetration of sub-shell.** The order of increase in energy of different sub shells is $s < p < d < f$. Thus, the order of penetration of different sub-shells is $s > p > d > f >$. *s*-sub-shell is more penetrated towards nucleus than *p*. Thus, greater energy (I.E.) will be required to remove an electron from *s*-sub shell than *p*-sub-shell. Similarly, it can be explained that lesser energy will be required to remove an electron from *f*-sub-shell than in case of *d*-sub-shell.

   Example. I.E. of Al is less than that of Mg. **Reason.** In case of Al ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1$), the electron is to be removed from *p*-sub-shell. In case of Mg ($1s^2\ 2s^2\ 2p^6\ 3s^2$), the electron is to be removed from *s*-sub shell. Since *s*-sub shell is more penetrated towards nucleus (and strongly attracted) than *p*, thus I.E. of Mg is more than that of Al.

5. **Stable electronic configuration.** Atoms with stable configuration have high value of first I.E. The electronic configuration of an atom is stable if :

   (*i*) The available orbital is fully filled, *e.g.*, in beryllium atom (Z = 4, $1s^2\ 2s^2$), 2*s*-orbital is fully filled. Thus, Be-atom has stable configuration.

   (*ii*) The available orbitals are half-filled, *e.g.*, in N-atom, (Z = 7 ; $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$), 2*p* sub-shell is half filled. Thus, N-atom has stable configuration.

   (*iii*) The atom or ion has inert gas configuration, *i.e.*, 8 electrons (except helium which has $2e^-s$) in their outermost orbit,

   e.g., Ne (Z = 10, e^-s = 10 $1s^2\ 2s^2\ 2p^6$), Na^+ (Z = 11, e^-s = 10 ; $1s^2\ 2s^2\ 2p^6$).

Trend in ionisation energy of elements in a group. As we go down the group in a periodic table, their first ionisation energy goes on decreasing. It is due to the combined effect of size and shielding. On moving down the group, the electrons, are added in new shells and size of atom goes on increasing. The new shells screen the nucleus appreciably. As a result, the effective nuclear charge (Z*) becomes less than the combined effect of size and shielding. The force of attraction of nucleus for the outermost electron decreases. Thus the ionisation energy goes on decreasing down the group (Table 2.17).

Trend in ionisation energy of elements along a period. As we go from left to right along a period in the periodic table, there is a general tendency for the ionisation energy to increase with increase in atomic number. It is due to the tendency for Z* (effective atomic number or nuclear charge) to increase progressively from left to right in the periodic table. But the increase in ionisation energy is not regular (Table 2.17). There are two factors which prevent the regular increase

*Effective nuclear charge = Nuclear charge – shielding constant.

(i) **Type of orbital.** The type of orbital changes from IIA group (*s*-orbital) to IIIA group (*p*-orbital).

(ii) **Exchange energy.** The exchange energy between electrons of like spin stabilizes a system of parallel electron spins. It is because the electrons having the same spin tend to avoid each other as a result of Pauli's exclusion principle. Thus the electrostatic force of repulsion between electrons is reduced. This tends to increase the number of unpaired electrons to maximum extent and makes it difficult to remove an electron from, say, nitrogen atom ($1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$) with half filled orbitals. Due to this stabilisation, the first **ionisation energy of nitrogen is greater than that of oxygen** although atomic number of nitrogen (= 7) is less than that of oxygen (= 8).

Successive ionisation energies. In order to understand successive ionisation energies, let us study first, second and third ionisation energies of Al atom.

First I.E. (E_1). For definition, previous pages.

Example. $Al(g) + E_1 \longrightarrow \underset{\text{(unipositive ion)}}{Al^+(g)} + e^-(g)$ (E_1 or ΔH_1 = + 138 kcal/mole)

Second I.E. (E_2). It is the amount of energy required to remove the outermost electron from unipositive gaseous ion to form dipositive gaseous ion

$$Al(g) + E_2 \longrightarrow \underset{\text{Dipositive ion}}{Al^{+2}(g)} + e^- \qquad E_2 = \Delta H_2 = +\ 438 \text{ kcal mole}^-.$$

Third I.E (E_3). It is the amount of energy required to remove the outermost electron from dipositive gaseous ion to make it tripositive gaseous ion.

$$Al^{+2}(g) + E_3 \longrightarrow \underset{\text{Tripositive ion}}{Al^{+3}(g)} + e^- \qquad E_3 = \Delta H_3 = +\ 646 \text{ kcal/mole}$$

From above we see that the electrons get removed from gaseous atoms one after the other and not simultaneously. **The phenomenon of removing the electrons from gaseous atoms one after the other, *i.e.*, in succession is called successive ionisation energies (or potentials).**

$$E_3 > E_2 > E_1$$

In order to explain that third I.P. (E_3) is greater than second I.P. (E_2) and E_2 is greater than first I.P. (E_1) (Table 2.18), let us consider sodium atom.

(i) $Na(g) + E_1 \longrightarrow Na^+(g) + e^-$ E_1 = 1st I.P. = 118 kcal/mole.

(ii) $Na^+(g) + E_2 \longrightarrow Na^{+2}(g) + e^-$ E_2 = 2nd I.P. = 1091 kcal/mole.

(iii) $Na^{+2}(g) + E_3 \longrightarrow Na^{+3}(g) + e^-$ E_3 = 3rd I.P. = 1653 kcal/mole.

Table 2.18.

	Na-atom	Na^+ – ion	Na^{+2} –ion
No. of protons	11	11	11
No. of electrons	11	10	9
Force of attraction of 11 protons for e^- s	Less	More than Na-atom	More than Na^+-ion
I.P.	E_1 = 118 kcal/mole	E_2 = 1091 kcal/mole	E_3 = 1653 kcal/mole.

(i) The force of attraction of 11 protons for 11 electrons in Na-atom is less than that for 10 electrons in Na^+ ion. Thus, the energy required to remove an electron from Na-atom is less as compared to that from Na^+-ion. Hence, second I.E. is greater than first I.E.

(*ii*) The force of attraction of 11 protons for 10 electrons in Na^{+}-ion is less than that for 9 electrons in Na^{+2}-ion. Thus, the energy required to remove an electron from Na^{+}-ion is less as compared to Na^{+2}-ion. Hence, third I.E. is greater than second I.E. (Table 2.19).

Table 2.19 Successive ionisation energies

Element with At. No.	Successive I.E. (kcal/mole)		
	E_1	E_2	E_3
$_{11}Na$	118	1091	1653
$_{12}Mg$	176	345	1838
$_{13}Al$	138	438	656

Trend of first I.E. for elements of second period, (fig. 2.18).

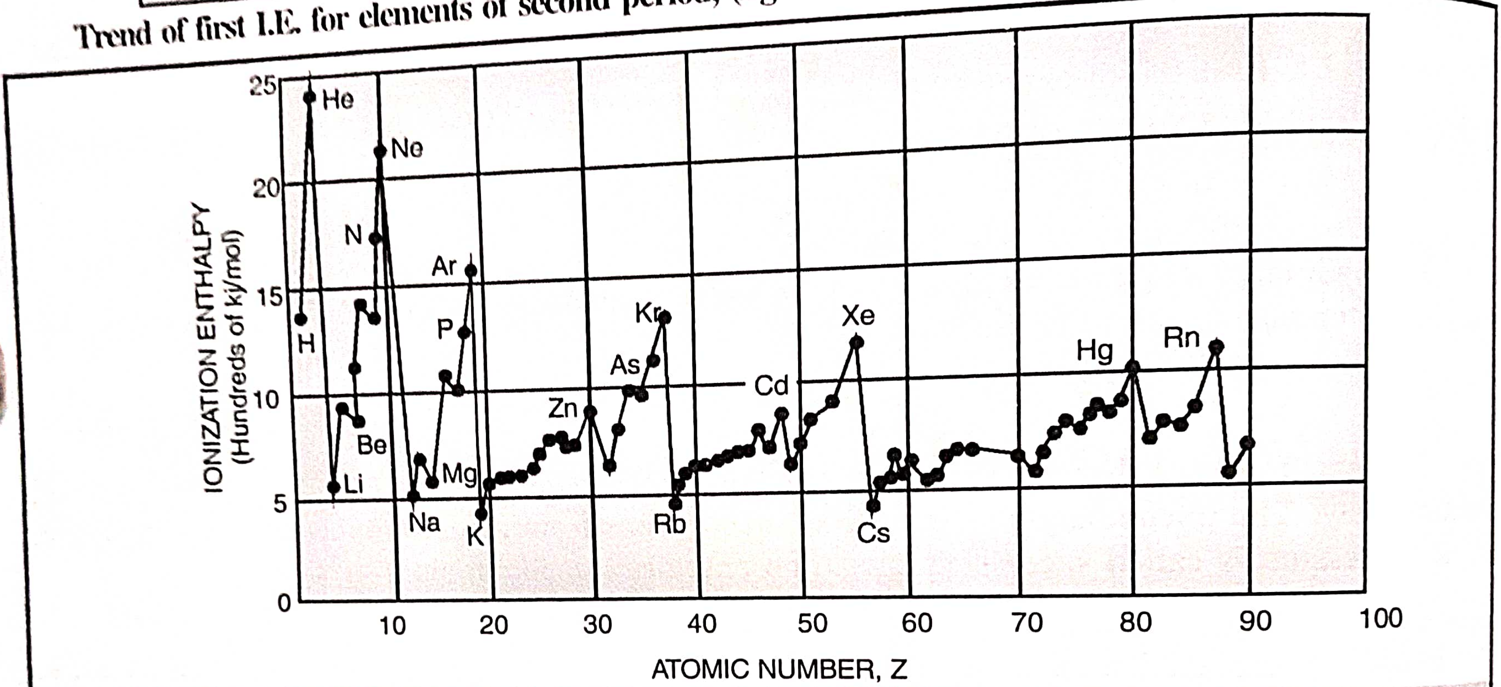

Fig. 2.18. Curve of ionisation potential versus atomic number.

1. I.E. of Be (At. No. 4) is greater than that of Li (At. No. 3). Reasons. (*i*) The nuclear charge of Be (Z = 4) is greater than Li (Z = 3). Greater the nuclear charge, greater the force of attraction between nucleus and outermost electron. Hence, the first I.E. of Be is greater than that of Li.

(*ii*) 2*s* sub-shell of Be ($1s^2\ 2s^2$) is fully filled. Fully filled subshells are most stable due to symmetry and high exchange energy. Thus, more energy is required to remove the electron. Hence, more I.E.

(*iii*) **Pairing energy.** Two electrons in 2*s*-sub shell of Be-atom are paired. Thus, firstly pairing energy is required to unpair the paired electrons. This energy is in addition to the energy required to remove the unpaired electron. Hence, first I.E. of Be is more than that of Li.

2. I.E. of Be is more than that of B. *Although the nuclear charge of boron atom (Z = 5) is greater than that of beryllium atom (Z = 4) yet first I.E. of Be is greater than that of boron. The reasons are :*

(*i*) Boron atom (Z = 5 ; $1s^2\ 2s^2\ 2p_x^1\ 2p_y^0\ 2p_z^0$) has one unpaired electron in the 2*p*-sub-shell. Be-atom (Z = 4, $1s^2\ 2s^2$) has paired electrons in the 2*s*-sub-shell. Thus, pairing energy is required in addition to I.E. to remove an electron in Be-atom. Pairing energy is not required in case of B-atom.

(*ii*) *s*-orbital penetrates more towards nucleus than *p*-orbital. Thus, *s*-orbital feels more attraction towards nucleus than *p*-orbital. In case of Be atom, electrons are removed from 2*s*-orbital. Hence more energy is required to remove an electron from 2*s*-orbital than from 2*p*-orbital in boron atom.

(*iii*) Fully filled 2*s*-sub shell in Be-atom is more stable than B-atom due to symmetry and high exchange energy. Thus, more energy is required to remove an electron from Be-atom. Hence, high I.P.

3. The I.E. of carbon (At. No. 6) is more than that of boron (At. No. 5). Reason. Carbon (Z = 6) ; $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$) has more nuclear charge than boron (Z = 5 ; $1s^2\ 2s^2\ 2p_x^1\ 2p_y^0\ 2p_z^0$). In both the cases, the electron is to be removed from same 2*p* sub- shell. Carbon has more nuclear charge than boron. The nucleus of carbon thus attracts the outer 2*p* electron more strongly than does boron. Hence first I.E. of carbon is more than that of boron.

4. I.E. of nitrogen (At. No. 7) is more than that of carbon (At. No. 6). Reasons. (*i*) N (Z = 7; $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$) has greater nuclear charge than carbon (Z = 6 ; $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$). Greater the nuclear charge, greater the force of attraction of nucleus for electron. Hence, greater is the I.E.

(*ii*) All the 2*p*-orbitals in nitrogen are half filled. Half filled orbitals are most stable due to symmetry and high exchange energy. It is not the case in carbon. (For stability of half-filled orbitals, see chapter 1).

5. I.E. of nitrogen is more than that of oxygen. Reasons. (*i*) N (Z = 7 ; $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$) atom has stable configuration due to its half-filled 2*p*-orbital. Half-filled orbitals are most stable due to symmetry and high exchange energy.

(*ii*) In case of oxygen atom (Z = 8 ; $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$), two electrons in $2p_x$ sub-shell are paired. These paired electrons cause inter-electronic repulsions. Thus electronic configuration becomes less stable. Hence less energy is required to remove an electron from 2*p*-subshell of oxygen atom than more stable half-filled 2p-subshell of nitrogen atom.

6. I.E. of fluorine is more than that of oxygen. Reasons.

(*i*) F (Z = 9, $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$) has more nuclear charge than oxygen (Z = 8 ; $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$). In both the cases, the electron is to be removed from the same 2*p* sub-shell. Fluorine has more nuclear charge than oxygen. The nucleus of fluorine will thus attract the outer 2*p*-electrons more firmly than oxygen. Hence, first I.E. of fluorine is more than that of oxygen.

7. I.E. of neon (Ne) is more than that of fluorine. Reasons. (*i*) The nuclear charge of Ne (Z = 10) is greater than that of F (Z = 9). Greater the nuclear charge, greater is the force of attraction between nucleus and outermost electron. Hence, the first I.E. of neon is greater than that of fluorine.

(*ii*) 2*p*-sub shell of Ne ($1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$) is fully filled. Fully filled sub-shells are more stable due to symmetry and high exchange energy. Hence, more energy is required to remove the electron in case of Ne than in case of F. Thus, I.E. of Ne is more than that of F.

(*iii*) **Pairing energy.** All the electrons in 2*p*-sub-shell in neon are paired. Thus, firstly pairing energy is required to unpair the paired electrons. This energy is in addition to the energy required to remove the unpaired electron. Hence, first I.E. of neon is more than that of fluorine.

Some other examples are :

(*i*) **I.E. of Li > Na > K**

$$_3Li = 1s^2\ 2s^1$$
$$_{11}Na = 1s^2\ 2s^2\ 2p^6\ 3s^1$$
$$_{19}K = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$$

Lithium, sodium and potassium belong to IA group of the periodic table. As we move down the group, the nuclear charge goes on increasing. The electrons are added in the new shells. These new shells shield the nucleus appreciably. As a result, the effective nuclear charge, *i.e* force of attraction between nucleus and the outermost electrons, decreases. Thus, less energy is required to remove the outermost electrons.

Hence, first I.E. of Li > Na > K.

(*ii*) **I.E. of Li⁺ > I.E. of He (helium)**

$$_3Li^+ = 1s^2\ ;\ _2He = 1s^2$$

The I.E. of Li^+ is greater than that of helium. It is because the nuclear charge of Li (Z = 3) is more than that of He (Z = 2). High nuclear charge will attract the same number of electrons (= 2) with greater force. Thus, high energy is required to remove electron from Li^+ ion.

(*ii*) **Alkaline earth metals always form dipositive ions.** Alkaline earth metals always form dipositive ions, *e.g.*, $CaCl_2$ is formed and not CaCl. It is because of the fact that **aqueous Ca^{+}(aq)** where hydration energy plays the role" is energetically unstable with respect to Ca^{2+} (*aq*) and Ca (*g*).

It is clear from the positive value of ΔH in the following reaction :

(*a*)	$2Ca^+ (g) + (aq) \longrightarrow 2Ca^+ (aq)$	ΔH = –152 kcal
(*b*)	$Ca (s) \longrightarrow Ca (g)$	ΔH = + 42 kcal
(*c*)	$Ca^{2+} (aq) \longrightarrow Ca^{2+} (g) + (aq)$	ΔH = +395 kcal
(*d*)	$Ca (g) + Ca^{2+} (g) \longrightarrow 2Ca^+ (g)$	ΔH = –135 kcal
Adding :	$Ca (s) + Ca^{2+} (aq) \longrightarrow 2Ca^+ (aq)$	ΔH = + 150 kcal

However, Ca^+ (*g*) is stable as is clear from the negative value of ΔH in the following reaction :

(*a*)	$Ca (g) \longrightarrow Ca^+ (g) + e^-$	ΔH = + 140 kcal
(*b*)	$Ca^{2+} (g) + e^- \longrightarrow Ca^+ (g)$	ΔH = – 274 kcal
Adding :	$Ca (g) + Ca^{2+} (g) \longrightarrow 2Ca^+ (g)$	ΔH = –134 kcal

ELECTRON AFFINITY (E.A.) or ELECTRON GAIN ENTHALPY

The amount of energy released when an extra electron is added to a neutral gaseous atom of an element to form a uninegative gaseous ion is called **electron affinity** or **first electron affinity**. Since energy is released, first electron affinity is always given a *negative sign*. Electron affinities of elements cannot be measured directly. These are obtained with the help of Born-Haber cycle.

These are measured in kcal $mole^-$ or electron volts (e.V) (one e.V. = 23.06 kcal $mole^-$) or kJ mol^- (1 kcal = 4.184 kJ). For example, when one mole of F-atoms are converted into one mole of F^- gaseous ions, 333 kJ mol^- energy is released.

$$F (g) + e^- \longrightarrow F^- (g) + 333 \text{ kJ (or E.A.} = -333 \text{ kJ mol}^-)$$

So, the first electron affinity of fluorine is – 333 kJ mol^-. The negative value of electron affinity indicates that energy is given out when an atom accepts an electron. The electron affinities of some elements are given in the following table 2.20 in kJ mol^-.

Table 2.20.

Elements		Uni and dinegative ion	E.A. In kJ mol^-	Elements		Uni and dinegative ion	E.A. in kJ mol^-
H	→	H^-	– 72	Mg	→	Mg^-	+ 67
He	→	He^-	+ 54	Al	→	Al^-	– 26
Li	→	Li^-	– 57	Si	→	Si^-	– 135
Be	→	Be^-	+ 66	P	→	P^-	– 60
B	→	B^-	– 15	S	→	S^-	– 200
C	→	C^-	– 121	S	→	S^{2-}	+ 332
N	→	N^-	+ 31	Cl	→	Cl^-	– 348
O	→	O^-	– 142	Br	→	Br^-	– 324
O	→	O^{-2}	+ 702	I	→	I^-	– 295
F	→	F^-	– 333				
Ne	→	Ne^-	+ 99				
Na	→	Na^-	– 21				

Successive electron affinities. When an electron is added to a neutral gaseous O or S atom, energy is evolved. As a result O^- and S^- are formed. So, the first electron affinities of O and S atoms are negative. When two electrons are added to O and S atoms, energy is absorbed. As a result, O^{2-} and S^{2-} are formed. So, the second electron affinity of O and S atoms is positive. *The amount of energy absorbed to add an electron to uninegative gaseous ion to form dinegative gaseous ion is called* **second electron affinity.** Following examples are given for clarity.

1. $O(g) + e^- \longrightarrow O^-(g) + 142$ kJ (E.A = – 142 kJ mol⁻)

$O^-(g) + e^- + 702$ k $\longrightarrow O^{2-}(g)$ (E.A = +702 kJ mol⁻)

2. $S(g) + e^- \longrightarrow S^-(g) + 200$ kJ (E.A = –200 kJ mol⁻)

$S^-(g) + e^- + 332$ kJ $\longrightarrow S^{2-}(g)$ (E.A. = + 332 kJ mol⁻)

From above it is clear that the electrons get added to gaseous atoms one after the other and not simultaneously. The *phenomenon of adding the electrons to an atom one after the other, i.e., in succession, is called* **successive electron affinities.**

Factors on which electron affinity depends

The electron affinity of elements depends on the following factors.

1. **Size of the atom.** Smaller the size of the atom, greater will be the attraction of its nucleus for electron to be added. So, greater energy is released and greater is its electron affinity. For example, in the second period elements of *p*-block, the size of carbon atom is smaller than that of boron atom. Thus, the electron affinity of carbon atom (– 121 kJ mol⁻) is greater than that of boron atom (= – 15 kJ mol⁻). In other words, the energy released in the conversion $C(g) + e^-(g) \rightarrow C^-(g)$ is greater (121 kJ mol⁻) than that released (15 kJ mol⁻) in the conversion,

$$B(g) + e^-(g) \longrightarrow B^-(g).$$

It may be noted that the above rule is not a general rule. There are certain exceptions which will be described later on.

2. **Magnitude of the effective nuclear charge.** Greater the magnitude of effective nuclear charge of atom of an element, stronger is the attraction of its nucleus for the electron to be added. So, greater energy is released and greater is its electron affinity. For example, in the second period elements of *p*-block, the nuclear charge (+6) of carbon atom being more than that of boron atom (+5), so the energy released (121 kJ mol⁻ in the conversion $C(g) + e^-(g) \longrightarrow C^-(g)$ is greater than that released (15 kJ mol⁻) in the conversion,

$$B(g) + e^-(g) \longrightarrow B^-(g).$$

3. **Electronic configuration.** An atom with stable configuration has little tendency to gain an electron. So, energy has to the supplied to add an electron to such elements to form uninegative ions. So, their electron affinity has a positive sign. An atom has stable configuration which has :

(*i*) fully filled orbitals

(*ii*) half filled orbitals of the same sub shell

(*iii*) noble gas configuration *i.e.* 8 electrons in the valence shell (or $1s^2$ configuration *i.e.*, helium gas atom).

For clarity, consider neon atom. It has stable configuration, $1s^2\,2s^2\,2p^6$. When a negatively charged electron is added to it, it faces repulsion from the negatively charged electrons present in the valence shell. So, 99 kJ per mole energy has to be supplied to overcome the repulsive forces to make the reaction, $Ne(g)\ e^-(g) \longrightarrow Ne^-(g)$ possible. So the first electron affinity of neon atom is +99 kJ mol⁻.

Variations of electron affinity of elements down a group. The electron affinity of elements decreases down a group due to the simultaneous increase in atomic size and nuclear charge. However, the effect of increase in size is greater than the increase in nuclear charge. As a result, the incoming electron feels less attraction by the large sized atom and hence the electron affinity decreases.

It may, however, be noted that the first member of every family has a lower electron affinity than the next heavier member of the group. This unexpected behaviour is related to very small size of those elements. A large repulsion between the electrons already present in the valence shell and the electrons being added, accounts for a lower attraction for the new electron. Hence first member of each group has a low electron affinity.

Variation of electron affinity of elements along a period

The electron affinity of elements usually increase along a period due to increase in effective nuclear charge and decrease in the size of atoms. But this increase is not regular because of either fully filled or half filled orbitals in their valence shell. For example, the first electron affinity of elements in the second period is, Li ($1s^2\ 2s^1$; – 57 kJ mol⁻), Be ($1s^2\ 2s^2$; fully filled 2s-orbital ; + 66 kJ mol⁻), B($1s^2\ 2s^2\ 2p^1$; – 15 kJ mol⁻) etc, which is not regular. Its detailed description is given later on.

1. Electron affinity of Be, Mg, N and noble gases is positive*. $_4$Be ($1s^2\ 2s^2$) and $_{12}$Mg ($1s^2\ 2s^2\ 2p^6\ 3s^2$) have fully filled *s*-orbital in their valence shell. Fully filled orbitals are most stable due to symmetry. Hence substantial amount of energy is absorbed to add an electron to overcome the repulsion between negatively charged electron being added and the negatively charged valence electrons. Their electron affinity is hence positive (Be = + 66 kJ mol⁻ ; Mg = + 67 kJ mol⁻).

2. Electron affinity of nitrogen is positive. $_7$N ($1s^2\ 2s^2\ 2px^1\ 2py^1\ 2pz^1$) has half filled 2*p*-orbitals. Half filled orbitals are most stable due to symmetry. Hence substantial amount of energy is absorbed to add an electron to overcome the repulsion between negatively charged electron being added and the negatively charged valence electrons. Its electron affinity is hence positive (= + 31 kJ mol⁻).

3. Electron affinity of noble gases is positive. Consider helium gas ($1s^2$) and neon gas ($1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$). These have fully filled orbitals in their valence shell. Fully filled orbitals are most stable due to symmetry. Hence substantial amount of energy is absorbed to add an electron to overcome the repulsion between negatively charged electron being added and negatively charged valence electrons. Their electron affinity is hence positive (He = + 54 kJ mol⁻ ; Ne = + 99 kJ mol⁻).

4. Halogens have the highest electron gain enthalpies. Halogens have the general electronic configuration of $ns^2\ np^5$. Thus, these have only one electron less than the stable noble gas ($ns^2\ np^6$) configuration. In order to acquire the noble gas configuration, halogens have maximum tendency to accept an additional electron and their electron gain enthalpies are, therefore, high.

5. Electron gain enthalpy of fluorine is less than that of the chlorine. This is because of very compact size of fluorine. It has only two shells as compared to three in chlorine. When an electron is added to a relatively compact 2*p*-subslell, there are strong repulsions between the electrons already present and the one being added. Thus, the incoming electron does not feel much attraction. Hence, the electron gain enthalpy of fluorine is small. On the other hand, the electron is added to relatively large sized 3*p*-subshell in case of chlorine which can easily accommodate the additional electron. Thus, electron gain enthalpy of chlorine atom is large.

Determination of electron affinity. Although the formation of O → O^{2-} and S → S^{2-} involves absorption of energy yet compounds containing these ions are known. It follows that the energy required to form these ions must come from other processes like lattice energy (when ions are packed to-gether in a regular way to form a crystalline solid) or from solvation energy in solution. One must not consider one energy term in isolation and a complete energy cycle (Born-Haber cycle) should be used wherever possible.

Hess's law relates the lattice energy of a crystal to other thermochemical data as given below.

$$\Delta H_f = \Delta H_s + IE + 1/2\ \Delta H_d + EA + U$$

*In certain books, the electron affinity values of Be, Mg, N, P, noble gases are shown as zero. But, recently, their values have been reported as positive (See table 2.20).

where
ΔH_f = Enthalpy of formation
ΔH_s = Enthalpy of sublimation
I.E. = Ionisation energy
ΔH_d = Enthalpy of dissociation
E.A = Electron affinity
U = Lattice energy

All the terms except lattice energy and electron affinity can be measured. Originally, this cycle was used to calculate electron affinities. With the help of known crystal structures, it was possible to calculate the lattice energy and hence values were obtained for the electron affinity.

$$\Delta H_f = + \Delta H_s + I.E + 1/2 \ \Delta H_d + E.A + U$$

For NaCl : $381.2 = + 108.4 + 495.4 + 120.9 + E.A. - 757.3$

Hence E.A. = – 348.6 kJ mol^{-}

Now, that some electron affinity values are known, the cycle is used to calculate the lattice energy for unknown crystal structures.

Difference between Electron affinity and Electronegativity

	Electron affinity	Electronegativity
1.	It is the tendency of an isolated gaseous atom to attract an electron.	1. It is the tendency of an atom in a molecule to attract the shared pair of electrons.
2.	It is measured in electron volts or kcal/mol or kJ/mol.	2. It is a number and has no units.
3.	It is a property of a isolated atom. *i.e.*, it is an atomic property.	3. It is the property of a bonded atom *i.e.*, it is a molecular property.
4.	An atom has an absolute value of electron affinity.	4. An atom has a relative value of electronegativity depending upon its bonding state. For example, sp-hybridized carbon is more electro-negative than sp^2\-hybridized carbon which, in turn, is more electro-negative than sp^3– hybridized carbon.
5.	It does not change regularly in a period or a group.	5. It changes regularly in a preiod or a group.

Example

Example 18. How much energy is kilo calories is released when 3.55 g of chlorine are completely converted to Cl^- ions in the gaseous state ? The electron affinity of Cl(g) is – 3.7 eV.

Solution.

$$\underset{35.5\,g}{Cl(g)} + e^- \longrightarrow Cl^-\ (g) \quad \text{ion} + 3.7 \text{ eV}$$

From above equation, it is clear that 35.5 g of

$$Cl\ (g) \equiv -3.7 \text{ e.V.}$$

$$3.55 \text{ g of Cl } (g) \equiv -\frac{3.7}{35.5} \times 3.55 = -0.37 \text{ eV} \qquad [\because 1 \text{ eV} = 23.06 \text{ kcal}]$$

$$= -0.37 \times 23.06 \text{ kcal}$$

$$= -8.53 \text{ kcal/mole}$$

Hence, energy released = 8.53 kcal/mole

ELECTRONEGATIVITY

We know that a covalent bond is formed by the mutual sharing of electrons between two atoms. If the two covalently bonded atoms are identical, the shared electron pair (or pairs) is equally attracted by the nuclei of the two atoms. Therefore, the electron distribution around the two nuclei is similar as in case of H_2 or F_2. Hence, bond between two identical atoms is non-polar. On the other hand, bond between two dissimilar atoms such as hydrogen and fluorine in HF is polar, *i.e.*, one of the atoms acquires some partial positive charge while the other atom acquires the same amount of negative charge. This is because, the two atoms have unequal attraction for the shared pair of electrons.

The tendency or power of an element in a molecule to attract the shared pair of electrons towards itself is known as its electronegativity.

The element having higher electronegativity withdraws the shared pair of electron, more towards itself. Hence, it acquires some partial negative charge. On the other hand, the element with lower electronegativity acquires the same amount of positive charge because molecule as a whole is electrically neutral, *e.g.*, in HF, fluorine atom acquires some partial negative charge while the hydrogen atom acquires the same amount of positive charge as shown below :

$$\overset{\delta^+}{H} : \overset{\delta^-}{F} \qquad \overset{\delta^+}{H} - \overset{\delta^-}{F}$$

The above definition of electronegativity is purely qualitative. However, various attempts have been made to give quantitative meaning to the electronegativity.

Trend in electronegativity of elements along a period. As we move along a period in the periodic table, the nuclear charge goes on increasing. The electrons are added in the same shell. These electrons hence do not screen the nucleus appreciably. The force of attraction of the nucleus for the valence electrons goes on increasing.

As a result : the effective nuclear charge > screening effect

Hence the electronegativity of elements goes on increasing.

For example, in the second period elements, the electro-negativity of Li-atom (revised = 0.98 ; original = 1.0) is least while that of fluorine atom (revised = 3.98 ; original = 4.0) is the maximum in Pauling scale.

Trend in electronegativity of elements down a group. As we move down a group in the periodic table, the nuclear charge goes on increasing. The electrons are added in the new shells. These electrons hence, screen the nucleus appreciably. The force of attraction of the nucleus for the valence electrons goes on decreasing.

As a result : the effective nuclear charge < screening effect

Hence electronegativity of elements goes on decreasing. For example in the IA group elements, the electronegativity of Li-atom (revised = 0.98, original = 1.0) is highest while that of cesium atom (revised = 0.79, original = 0.7) is the least on the Pauling scale.

Factors determining electronegativity

The tendency of an atom, in a molecule to attract covalent electrons to-wards itself depends upon the nature of the other atom with which it is bonded in the molecule. The various factors which largely determine the electronegativity of an atom are described below:

1. **Size of the atom.** The smaller the size of an atom, the greater is the attraction for bonding electrons. Thus, atoms with smaller size are more electronegative.
2. **Type of the ion.** (*a*) Cations are more electronegative than the atoms from which these are formed. It is because the cations are smaller in size than the corresponding atoms, *e.g.*, the electronegativity of Li^+ is 2.5 while that of Li is 1.0.

(*b*) **Anions** are less electronegative than the atoms from which these are formed. It is because the anions are larger in size than the corresponding atoms, *e.g.* the electronegativity of fluoride ion (F^-) is 0.78 while that of fluorine atom is 4.0.

3. **Hybridisation.** The basicity of an amine depends upon the type of hybridisation of the nitrogen atom. Greater the *s*-character of hybrid orbital, greater will be the electronegativity of N-atom. It lowers the donating power of electrons to N-atom and hence lowers the basicity of the amine. For example, let us consider the relative basicity of alkyl cyanide (R–C ≡ N), pyridine (C_5H_5N :) and aniline ($C_6H_5NH_2$). The N-atom in these compounds is *sp*, sp^2 and sp^3 hybridised respectively. Thus *s*-character of hybrid orbital is 50% in RCN, 33.3% in C_5H_5N and 25% in $C_6H_5NH_2$. Thus the decreasing order of the basicity of these amines is RCN > C_5H_5N > $C_6H_5NH_2$.

4. **Effect of substituents.** The electronegativity of an element depends upon the nature of the substituent to which it is bonded. The element acquires greater positive charge if the electronegativity of the substituent is higher than that of the element. Greater positive charge makes the element more electron attracting. Thus the chemical behaviour of the element changes. For example, C-atom in CF_3I has more positive charge than C-atom in CH_3I. It is because electronegativity of F-atom (= 4) is greater than that of I-atom (2.8).

   Because of the difference in the electronegativities of substituents, CH_3I and CF_3I give different products on hydrolysis.

$$CH_3I + OH^- \longrightarrow CH_3OH + I^- \; ; \; CF_3I + OH^- \longrightarrow CF_3H + IO^-$$

5. **Electron affinity and ionisation energies.** According to Mulliken, electronegativity of an element is one half of the sum total of its electron affinity and first ionisation energy. It means that higher the value of ionisation energy and electron affinity, greater will be the electronegativity.

6. **Effective nuclear charge.** According to Allred and Rochow, the electronegativity of an element is proportional to the effective nuclear charge, Z_{eff}. As we go down the group, Z_{eff} **decreases** because with increase in atomic number, the size of atom increases. Hence electronegativity decreases down the group. It is clear from the electronegativity of the halogens

[F (4.0) > Cl (3.0) > Br (2.8) > I (2.5)].

As we move along a period, Zeff increases because of decrease in size of the elements. Hence electronegativity increases along a period. It is clear from the electronegativity of second period elements

[Li(1.0) < Be (1.5) < B (2.0) < C (2.5) < N (3.0) < O (3.5) < F (4.0)].

Z_{eff} decreases with greater screening effect of larger number of inner electrons. Thus electronegativity would decrease with increase in the number of inner electrons in atoms of elements in the same group. It is another reason which explains why the electronegativity of alkali metals decreases in the order,

Li (1.0) > Na(0.9) > K (0.8) > Rb (0.8) > Cs (0.7).

MEASUREMENT OF ELECTRONEGATIVITY OF AN ATOM– DIFFERENT ELECTRONEGATIVITY SCALES

Following methods are used to measure the electro-negativity of an atom in a molecule.

1. **Mulliken's scale.** Mulliken (1934) suggested electronegativity scale which was based upon the first ionisation potential (I.P.) and first electron affinity (E.A.) of an element. He determined the electronegativity of an element, (X_A) with the use of following relations.

(*i*) **When I.P. and E.A. are measured in electron volts**

$$X_A = \frac{(I.P.)_A + (E.A.)_A}{2}$$

(*ii*) **When I.P. and E.A. are measured in kcal per mole**

$$X_A = \left[\frac{(I.P.)_A + (E.A.)_A}{2}\right] \times \frac{1}{62.5}$$

(*iii*) **Relation between Pauling's values and Mulliken's values.** In order to make Mulliken's values approximately equal to Pauling's values of electronegativity, following relations are used.

(*i*) $X_{Pauling} = X_{Mulliken}/2.8$

or $$X_A = \left(\frac{(I.P.)_A + (E.A.)_A}{2}\right) \times \frac{1}{2.8} = [(I.P.)_A + (E.A.)_A] \times \frac{1}{5.6}$$

The constant $\frac{1}{5.6}$ is called scale adjustment factor. In this relation, I.P. and E.A. are measured in *electron volts*.

(*ii*) $X_{Pauling} = X_{Mulliken}/3.15 = [(I.P.)_A + (E.A.)_A] \times \frac{1}{3.15}$

where $\frac{1}{3.15}$ is called scale adjustment factor. In this relation, I.P. and E.A. are measured in *kcal per mole.*

Limitations. (*i*) It is difficult to get reliable values of electron affinities.

(*ii*) The electron affinities of all the elements are not known.

(*iii*) The values of E.A. and I.P. change with the change in the valence state of an element.

2. Pauling method. According to Pauling :

Electronegativity difference between two atoms $= 0.18\sqrt{\text{Resonance energy in kcal mol}^{-}}$ ...(*i*)

where Resonance energy = Actual bond energy – Energy for 100% covalent bond ...(*ii*)

Actual bond energy can be measured experimentally. 100% covalent bond energy can be calculated as follows :

$$E_{100\%} \text{ covalent bond } A-B = \sqrt{E_{A-A}\, E_{B-B}}$$

where E_{A-B} = Bond energy of covalent bond A – B

E_{A-A} = Bond energy of bond A – A

E_{B-B} = Bond energy of bond B – B.

After finding resonance energy, electronegativity difference between two bonded atoms A and B can be found by using relation (*i*). If atom B is hydrogen and electronegativity of hydrogen atom (2.05) is taken as origin of scale, then :

Electronegativity of atom A in A – H bond = 2.05 + electronegativity difference of A-H bond.

Example

EXAMPLE 19. Calculate the electronegativity of carbon in C – H bond if E_{C-H}, E_{H-H} and E_{C-C} bonds are 98.8, 104 and 83 kcal mol⁻ respectively.

SOLUTION. (*a*) To find resonance energy.

$$\text{Resonance energy} = \left[\begin{array}{c}\text{Actual bond}\\ \text{energy of}\\ \text{C – H bond}\end{array}\right] - \left[\begin{array}{c}\text{Energy for 100\%}\\ \text{covalent bond}\\ \text{(C – H)}\end{array}\right] \quad ...(i)$$

$$E_{100\% \text{ covalent bond C–H}} = \sqrt{E_{H-H}\, E_{C-C}} = \sqrt{104 \times 83} = 92.9 \text{ kcal mole}^{-} \quad ...(ii)$$

Substituting values in Eq. (*i*) from (*ii*), we get, Resonance energy = 98.8 – 92.9 = 5.9 kcal mol^- ...(*iii*)

(*b*) To find electronegativity difference of C – H bond.

Electronegativity difference between C and H atoms

$$= 0.18\sqrt{\text{Resonance energy in kcal mol}^-} = 0.18\sqrt{5.9} = 0.44 \quad ...(iv)$$

(*c*) To find electronegativity of C atom

Taking electronegativity of H = 2.05 as origin of scale, the electronegativity of carbon.

$$= 2.05 + \text{Electronegativity difference of C – H bond} \quad ...(v)$$

Substituting the values from Eq. (*iv*) in (*v*), we get the electronegativity of carbon = 2.05 + 0.44 = **2.49.**

3. **Sanderson's Scale.** Sanderson suggested electro-negativity scale which was based upon *stability ratio (S.R.).*

The stability ratio of an atom is defined as :

"the ratio of average electron density (E.D.) around the nucleus and its ideal electron density (E.D$_i$) calculated for an inert atom having the same number of electrons."

Mathematically, $SR = \dfrac{ED}{ED_i}$

According to Sanderson :

Stability ratio of an atom is a measure of electronegativity. He related electronegativity (X_A) of an atom, A with stability ratio (SR) by the following equation called *Sanderson equation*

$$(X_A)\ \text{Sanderson} = \frac{ED}{ED_i}$$

where (*i*) E.D. is a measure of comparative compactness of the atom. Since electrons are not evenly spaced around the nucleus, electron density differs from point to point. Thus, average electron density is used. It is given by the following relation.

$$ED = \frac{3Z}{4\pi r^3} = \frac{Z}{4.19\, r^3}$$

where r = Covalent radius of atom in Å

Z = nuclear charge

(*ii*) ED_i is the ideal electron density. For a particular atomic number, it is found from interpolation obtained when electron density of inert gas atoms is plotted against atomic numbers.

Relation between Pauling's values and Sanderson's values. In order to make Sanderson's electronegativity values approximately equal to Pauling's values, following relation is used.

$$\sqrt{\chi_{\text{Pauling}}} = 0.21\,\chi_{\text{Sanderson}} + 0.77$$

Example

EXAMPLE 20. Calculate the electronegativity of nitrogen from the data given below. Bond energies of N – F bond, N – N bond and F – F bonds are 56, 32 and 37.8 k cal mol^-. Electronegativity of F-atom = 4.0.

SOLUTION. In NF, electronegativity of F is more than that of N. We know that :

EN of less electronegative atom, N = EN of more electronegative atom, F – 0.208 $(\Delta)^{1/2}$ ...(1)

where Δ = (B.E. of N–F)–[(B.E. of N–N) (B.E. of F–F)]$^{1/2}$

∴ $\Delta = 56 - [32 \times 37.8]^{1/2} = 56 - 34.8 = 21.2\ k$ cal mol^- ...(2)

Substituting the value of Δ from relation (2) in relation, (1) we get

EN of less electronegative atom, N = 4 – 0.208 $(21.2)^{1/2}$ }= 4 – (0.208 × 4.6) = 4 – 0.95 = **3.05**