

Topic on Chemistry

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ROPERTIES OF ELEMENTS IN RELATION TO THEIR ELECTRONIC STRUCTURE

Introduction—The electronic configuration of elements is intimately related with properties of elements. The recurrence of similar properties of elements after certain regular intervals, when they are arranged in the order of increasing atomic numbers, is only on account of recurrence of similar type of electronic configuration in the outermost or valency shell of the elements. Thus all elements belonging to a particular family (group) have similar outer electronic configuration.

The cause of periodicity in properties of elements lies, therefore, in the recurrence of similar outer electronic configurations of their atoms at a certain regular intervals. Thus there is no denying the fact that the properties of elements totally depend upon their electronic configuration. In order to understand the nature of chemical bond, it is necessary to have adequate knowledge of certain atomic properties.

Following are some important atomic properties of elements which have their bearing with electronic configuration.

Ionization Energy

It is the energy required to pull an electron from an isolated gaseous atom.



To measure the ionization potential, energy can be added to the neutral atom to raise the outermost electron to higher energy levels. When the electron falls back, it emits energy, which can be viewed as spectral lines. A whole series of lines will be obtained corresponding to re-emission of energy from various excited states. The energy emitted converge on a series of limit corresponding to return of an electron from the farthest removed orbit to the K shell. The series limit is equal to the ionization potential. It gives a direct measure of the energy required to remove the electron from L shell to farthest removed orbit that is completely away from the atom. The ionization energy is measured in kJ mol^{-1} or in electron volts.

The factors affecting the ionization energy

- (i) The size of atom
- (ii) Effective nuclear charge
- (iii) Extent of penetration of valency shell into inner shells
- (iv) Electronic configuration.

(i) **Atomic Size**—With the increase in atomic size of the atom, the ionization energy decreases because as the size of atom increases the outermost shell lies away from the nucleus and the electrons from this shell can be pulled off easily or with less input of energy. Smaller the size of an atom, greater will be its ionization energy.

(ii) **Effective Nuclear Charge**—In a multielectron atom, the whole of the nuclear charge is not effective on outermost electrons. The electrons of inner lying energy states exercise repulsive effect on outermost electrons. Therefore, the electrons present in the energy states between nucleus and outermost shell act as a screen or a

shield for nuclear attraction on outermost electrons. This is known as **screening or shielding effect**.

The magnitude of the screening effect depends upon the number of inner electrons *i.e.*, the greater the number of inner electrons, greater shall be the value of screening effect. The screening effect constant is represented by the symbol σ . The magnitude of ' σ ' is determined by the following empirical rules known as Slater's rules—

(i) The various orbitals are grouped as follows starting from the side of the nucleus.

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

(ii) For an electron in a group of *s*, *p* electrons the value of screening constant is determined as follows :

(a) No contribution from any electron present in groups of orbitals lying on the right hand side of the group in which the electron is present.

(b) A contribution of 0.35 for each electron present in *ns* and *np* orbitals. A contribution of 0.30 from the other electron in 1s orbital if the electron for which the shielding constant is to be calculated belongs to 1s orbital.

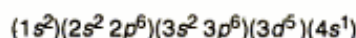
(c) A contribution of 0.85 per electron from all electrons present in $(n-1)^{\text{th}}$ shell.

(d) A contribution of 1.0 per electron from all electrons present in $(n-2)^{\text{th}}$ and the next inner shell.

(iii) For an electron in a group of *d* or *f* electrons, the rules (ii) a and (ii) b apply as such. However the rules (ii) c and (ii) d are replaced by the rule that the contribution per electron from all electrons in the inner shells is 1.0.

Example—To determine the effective nuclear charge felt by a 3d electron of chromium atom ($Z = 24$).

According to Slater's rules the grouping of orbitals will be



There will be no contribution from 4s electron.

$\therefore Z_{\text{eff}}$ felt by a 3d electron of Cr atom

$$= 24 - (0.35 \times 4 + 18 \times 1.0)$$

$$= 4.60$$

Remember

- With the increase in effective nuclear charge, the value of ionization potential increases.
Ionization potential $\propto Z_{\text{eff}}$.
- With the increase in screening effect, the nuclear attraction for outermost electron decreases, hence, ionization potential also decreases.

$$\text{Ionization potential} \propto \frac{1}{\text{Screening effect}}$$

On moving from left to right in a period, the effective nuclear charge (Z_{eff}) constantly increases, therefore, the value of ionization potential also increases.

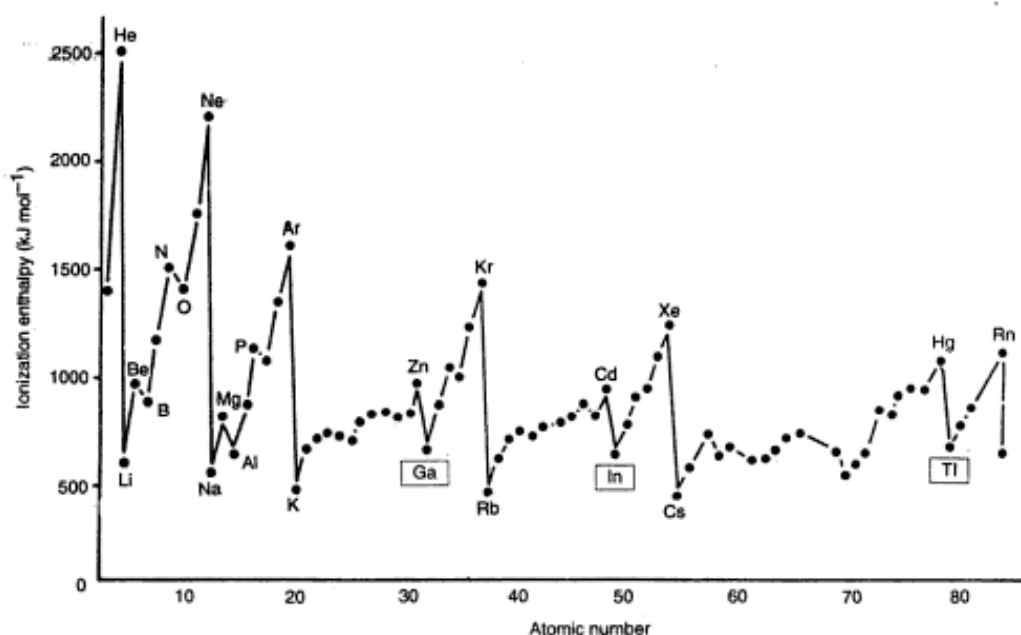
On going down the group nuclear charge (Z) gradually increases and atomic size also increases. There is increase in the number of inner electrons which shields the valency electrons from the nucleus. The overall effect of increase in atomic size and the screening or shielding

effect is much more than, the overall effect of increase in nuclear charge (Z). Consequently, outermost electron is less and less tightly bound to the nucleus, as one moves down the group. Hence, ionization energy decreases as one goes down from top to bottom in any group.

First Ionization Energies of the Elements (kJ mol⁻¹)

Group ↓ Period →	1	2	Group										13	14	15	16	17	18						
1	H ● 1311																		He ● 2372					
2	Li ● 520	Be ● 899																	B ● 801	C ● 1086	N ● 1403	O ● 1410	F ● 1681	Ne ● 2080
3	Na ● 496	Mg ● 737																	Al ● 577	Si ● 786	P ● 1012	S ● 999	Cl ● 1255	Ar ● 1521
4	K ● 419	Ca ● 590	Sc ● 631	Ti ● 656	V ● 650	Cr ● 652	Mn ● 717	Fe ● 762	Co ● 758	Ni ● 736	Cu ● 745	Zn ● 906							Ga ● 579	Ge ● 760	As ● 947	Se ● 941	Br ● 1142	Kr ● 1351
5	Rb ● 403	Sr ● 549	Y ● 616	Zr ● 674	Nb ● 664	Mo ● 685	Tc ● 703	Ru ● 711	Rh ● 720	Pd ● 804	Ag ● 731	Cd ● 876							In ● 558	Sn ● 708	Sb ● 834	Te ● 869	I ● 1191	Xe ● 1170
6	Cs ● 376	Ba ● 503	La ● 541	Hf ● 760	Ta ● 760	W ● 770	Re ● 759	Os ● 840	Ir ● 900	Pt ● 870	Au ● 889	Hg ● 1007							Tl ● 589	Pb ● 715	Bi ● 703	Po ● 813	At ● 912	Rn ● 1037
7	Fr	Ra	Ac																					

(Large circles indicate high values and small circles low values)



First Ionization Energies of the Elements

(iii) **Extent of penetration of valency shell into inner shells**—The ionization energy of elements depends

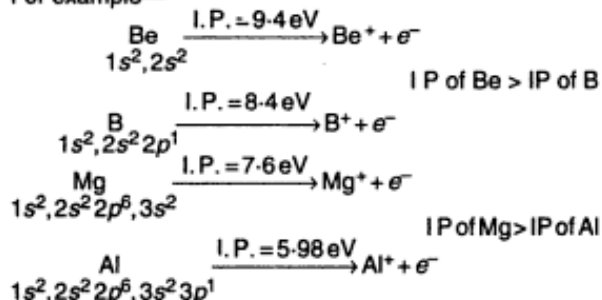
upon the nature of subshells (*s, p, d, f*) in which electron is present. The ionization energy for pulling out

an electron from s -subshell is maximum and is minimum for f -electrons of the same principal shell. Thus ionization energy for a given energy level decreases in the order,

$$s > p > d > f$$

This is on account of the fact that s -orbit penetrates more into inner shell than p -orbit which in turn penetrates more than d -orbit and so on.

For example—



The variation in the first ionization energies of the elements are shown in the figure. The graph shows three features—

1. The noble gases He, Ne, Ar, Kr, Xe and Rn have the highest ionization energies in their respective periods.

Li	Be	>	B	C	N	>	O	F	Ne
5-4	9.32		8.29	11.26	14.58		13.61	17.42	24.58
Na	Mg	>	Al	Si	P	>	S	Cl	Ar
5-14	7.64		5.98	8.15	10.48		10.36	13.01	21.56
K	Ca	>	Ga	Ge	As	>	Se	Br	Kr
4-34	6.11		6.00	7.88	9.81		9.75	10.84	13.99
Rb	Sr	~	In	Sn	Sb		Te	I	Xe
4-17	5.69		5.78	7.34	8.64		9.01	10.45	12.13
Cs	Ba	>	Tl	Pb	Bi		Po	At	Rn
3-89	5.21		5.10	7.41	7.28		8.43	8.40	10.75

2. The group 1 metals Li, Na, K and Rb have the lowest ionization energies in their respective periods.
3. There is a general upward trend in ionization energy within a horizontal period. For example from Li to Ne or from Na to Ar.

The values for Ne and Ar are the highest in their periods because a great deal of energy is required to remove an electron from a stable filled shell of electrons.

The graph does not increase smoothly. The values for Be and Mg are high, and this is attributed to the stability of a filled s level. The values for N and P are also high, and this indicates that a half-filled p level is also particularly stable. The values for B and Al are lower because removal of one electron leaves a stable filled s shell and similarly with O and S a stable half filled p shell is left.

Departure from expected trend occurs in group III, where expected decrease occurs between B and Al, but the values for remaining elements, Ga, In, Tl do not continue the trend and are irregular. The reason for the change at Ga is that it is preceded by ten elements of 1st

transition series, where $3d$ shell is being filled. Due to delayed contraction effect, the atomic size of Ga is small than it would otherwise be. A similar effect is observed with the second and third transition series in the groups IV and V elements.

The ionization energies of transition elements are slightly irregular, but the third row elements starting at Hf have lower values than would be expected due to the interpolation of 14 lanthanide elements between La and Hf.

(iv) **Electronic Configuration**—Certain electronic configurations are more stable than others. For example, if an atom has fully filled or half filled orbits, its ionization energy is higher than expected normally from its position in periodic table.

For example Be and N in second period and Mg and P in the third period have slightly higher ionization potentials than expected. It is due to extra stability of the fully filled s -orbitals in Be and Mg and half-filled p -orbitals in N and P.

Ionization potentials of some elements are given below in electron volts—

Exceptions

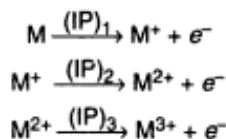
- I. P. of N > I. P. of O
- I. P. of Be > I. P. of B
- I. P. of P > I. P. of S
- I. P. of Mg > I. P. of Al.

Measurement of Ionization Energy

Ionization energy is generally measured by the spectroscopic techniques. Another method is to get the vapours of the element in a discharge tube and connect it to the source of current. The voltage applied is gradually increased. At a certain voltage there will be sudden rise in the current flowing through the tube. The energy corresponding to this voltage is known as the **first ionization potential**. The sudden rise in current is due to liberation of an electron from each neutral atom, producing cation.

If the applied voltage is increased further, there may again be a sudden rise in current passing through the tube. This is due to the elimination of another electron from each positively charged ion (M^+) produced earlier.

The energy corresponding to this change is known as **second ionization potential**. These point to sudden rise in current correspond to the loss of three or more electrons and give third or higher ionization potentials of the elements.



Remember

- **Ionization energy** is measured in electron volts (eV)
- Electron Volt (eV) is the energy acquired by an electron having charge of 1.602×10^{-19} coulomb, moving under the fall of potential of 1 volt.
- $1 \text{ eV} = 1.602 \times 10^{-19} \text{ Joule}$.
- 1 million electron volt, MeV = $1.602 \times 10^{-13} \text{ Joule}$.
- $1 \text{ eV} = 1.602 \times 10^{-19} \text{ Joule}$ or $1.602 \times 10^{-22} \text{ k Joule}$.
- The values in electron volt give ionization energy per atom of element and those represented in k joule are energies of per mole of element that is per Avogadro number of atoms of the element.
- The ionization energy of hydrogen is 13.60 eV per atom and $13.60 \times 1.602 \times 10^{-22} \times 6.023 \times 10^{23} = 1312.00 \text{ kJ per mole of hydrogen}$.
- $(IP)_1 < (IP)_2 < (IP)_3 \dots\dots\dots$
- Ionization potential \propto Effective nuclear charge.
- Ionization potential $\propto \frac{1}{\text{Size of atom}}$
- In the respective periods, the ionization potential of alkali metals is minimum and that of inert gases is maximum.
- Aluminium and Gallium are the elements of same group (III), they have same value of ionization energy.
 $IP \text{ of } {}_{13}\text{Al} = IP \text{ of } {}_{31}\text{Ga}$
 This is due to the presence of filled 3d orbit in ${}_{31}\text{Ga}$, which causes the contraction in the volume of ${}_{31}\text{Ga}$ atom.
- Ionization potential of ${}_{79}\text{Au}$ is higher than ${}_{47}\text{Ag}$, though they are the elements of same group (IB). This is on account of delayed effect of Lanthanide contraction on the Au, whereby the atomic size of Au decrease and hence has high I. P. value than Ag which is beyond the expected trend.

Excitation energy—The energy required to take away an electron from ground energy state to n th state is called excitation energy.

The energy required to send hydrogen electron from $n = 1$ to $n = 2$ energy state is called first excitation energy.

$$\text{First excitation energy} = E_2 - E_1$$

$$E_1 = -13.6 \text{ eV}$$

$$E_2 = -13.6 \times \frac{Z^2}{n^2} = -13.6 \times \frac{(1)^2}{2^2}$$

$$= -13.6 \times \frac{1}{4} = -3.4 \text{ eV}$$

$$\text{Hence, first excitation energy}$$

$$= E_2 - E_1 = -3.4 - (-13.6)$$

$$= 10.2 \text{ eV}$$

The energy required to remove an electron from any excited state of an atom is called **separation energy**.

Applications of ionization energy

$$\text{Relative reactivity of metals} \propto \frac{1}{\text{ionization potential}}$$

$$\text{Metallic character of elements} \propto \frac{1}{\text{ionization potential}}$$

$$\text{Reducing power of elements} \propto \frac{1}{\text{ionization potential}}$$

$$\text{Alkaline nature of metallic hydroxides} \propto \frac{1}{IP \text{ of metal}}$$

Determining the stability of oxidation state of elements.

If the difference between two consecutive ionization potentials of an element is about 10 to 15 eV or less than this value, then higher oxidation state will be more stable.

If this difference is 16.0 eV or more than this value, then lower oxidation state will be stable.

Illustration

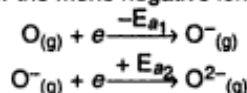
The difference of first and second ionization potential of Mg is 7.4 eV. Hence, Mg^{2+} will be more stable than Mg^+ . Similarly the difference between first and second I. P. for Na is 42 eV. Hence, Na^+ state is more stable than Na^{++} .

Electron Affinity

Electron affinity is the amount of energy released when an electron is added to a neutral atom to form an anion.



The greater the energy released, higher will be the electron affinity. The first electron affinity is always negative, the second electron affinity of the same element will be positive. This is so because second electron has to be forced to enter the mono negative ion.



It follows that the energy required to form the ion must come from some other source, such as lattice energy when the ions are packed together in regular arrays to form a crystalline solid or from solvation energy in solution.

It is always dangerous to consider one energy term in isolation, and a complete energy cycle should be considered whenever possible. The electron affinity cannot be determined directly, but is obtained indirectly from the **Born-Haber cycle**.

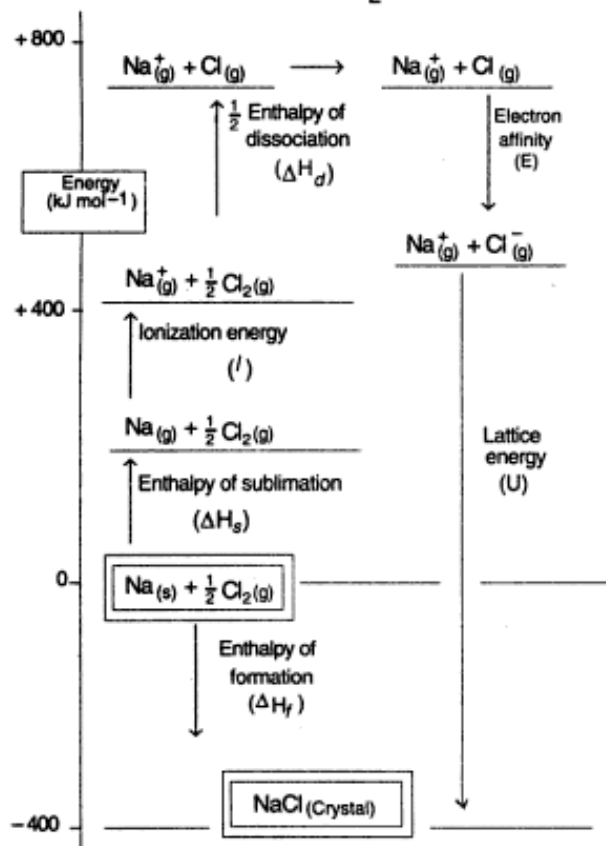
Born-Haber Cycle

This cycle was formulated by Born-Haber in 1919. It relates the lattice energy of a crystal to other thermochemical values. The energy terms involved in forming a crystal lattice such as NaCl may be considered in various steps. The elements in their standard state are first converted to gaseous atoms and then to ions, and finally packed into a crystal lattice.

The enthalpies of sublimation and dissociation and the ionization energy are positive, since energy is supplied to the system. The enthalpy of formation, electron affinity and lattice energy are negative as energy is released in these steps. According to Hess's law of summation of energy, the overall energy change in a

process depends only on the energy of the initial and final states and not on the route adopted. As can be seen from the following figure, the enthalpy of formation (ΔH_f) is the algebraic sum of the terms going round the cycle.

$$\Delta H_f = \Delta H_s + I + \frac{1}{2} \Delta H_d + E + U$$



Born-Haber cycle for the formation of NaCl

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

$$\Delta H_f = +\Delta H_s + I + \frac{1}{2} \Delta H_d + E + U$$

For NaCl

$$-381.2 = +108.4 + 495.4 + 120.9 + E - 757.3$$

Hence, $E = -348.6 \text{ kJ mol}^{-1}$

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

Factors affecting electron affinity

(1) **Atomic size**—Electron affinity $\propto \frac{1}{\text{Size of atom}}$

Smaller the size of an atom, greater is its electron affinity. As the size of atom increases, the effective nuclear charge decreases or the nuclear attraction for adding electron decreases. Consequently, atom will have less tendency to attract additional electron towards itself. Therefore,

Electron affinity \propto Effective nuclear charge.

In general, electron affinity decreases in going down the group and increases in going from left to right across the period. On moving down the group atomic size increases and on going from left to right in a period atomic size decreases.

(2) **Shielding or Screening Effect**—

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

Electronic energy states, lying between nucleus and outermost state hinder the nuclear attraction for incoming electron. Therefore, greater the number of inner lying states, less will be the electron affinity.

(3) **Electronic Configuration**—The electronic configurations of elements influence their electron affinities to a considerable extent.

Electron affinities of inert gases are zero. This is because their atoms have stable $ns^2 np^6$ configuration in their valency shell and there is no possibility for addition of an extra electron.

Electron affinity of beryllium, magnesium and calcium is practically zero. This is attributed to extra stability of the fully completed *s*-orbitals in them. Thus, if an atom has fully filled or half filled orbits, its electron affinity will be low.

Electron Affinities of Main Group Elements

Values without brackets are in kJ mol^{-1} while those within brackets are in electron-volts

Periods	Group I ↓	Group II ↓	Group III ↓	Group IV ↓	Group V ↓	Group VI ↓	Group VII ↓	Group Zero ↓
II Period →	Li 59.8 (0.63)	Be = 0	B 27.0 (0.3)	C 122.3 (1.29)	N 0.2	O 140.9 (1.48)	F 332.6 (3.49)	Ne 0
III Period →	Na 53.1 (0.56)	Mg = 0	Al 45 (0.53)	Si 133.6 (1.40)	P 74.3 (0.77)	S 200.7 (2.10)	Cl 348.5 (3.66)	Ar 0
IV Period →	K 48.4 (0.50)	Ca = 0	Ga 35.7 (0.37)	Ge 120.0 (1.26)	As 77.2 (0.81)	Se 195.0 (2.04)	Br 324.7 (3.40)	Kr 0
V Period →	Rb 46.9 (0.49)	Sr = 0	In 29.0 (0.30)	Sn 120.9 (1.27)	Sb 101.0 (1.06)	Te 190.1 (1.99)	I 295.5 (3.10)	Xe 0
VI Period →	Cs 45.5 (0.48)	Ba = 0	Tl 30.0 (0.31)	Pb 110.0 (1.15)	Bi 110.0 (1.15)	Po 180.0 (1.89)	At 270.0 (2.83)	Rn 0

Exceptional values of electron affinity

The atomic size of fluorine is smaller than that of chlorine even then the electron affinity of fluorine is lower than that of chlorine. This fact can be explained by a simple mechanism. It is due to small size of fluorine atom. The addition of an extra electron produces a high electron density in relatively compact $2p$ sub-shell and, therefore, a strong electron-electron repulsion. The repulsive forces between electrons cause low electron affinity.

$$E_a \text{ of F} < E_a \text{ of Cl}$$

Electron affinity of N is less than that of C and electron affinity of P is less than that of Si. It is on account of half filled p -sub-shell in N and P. Due to extra stability of half filled p -orbit in N and P they have less tendency for accepting electrons.

In general atomic size of atoms of second period elements is smaller than that of elements of third period. Elements of second period have high electron density due to small size of atoms, therefore, additional electrons feels electron-electron repulsion. This is the reason that the electron affinity of third period elements is higher than that of second period elements.

$$E_a \text{ of Cl} > E_a \text{ of F}$$

$$E_a \text{ of S} > E_a \text{ of O}$$

$$E_a \text{ of Si} > E_a \text{ of C}$$

$$E_a \text{ of P} > E_a \text{ of N}$$

Remember

- Electron affinity $\propto \frac{1}{\text{Atomic volume}}$
- Electron affinity $\propto \frac{1}{\text{Screening effect}}$
- Electron affinity \propto Effective nuclear charge
- Electron affinity $\propto \frac{1}{\text{Stable electronic configuration}}$
- Element having highest electron affinity is chlorine.
- In the second period sequence of electron affinity deviates at nitrogen, while in third period it deviates at phosphorus.
- In the VII group the sequence of electron affinity deviates at chlorine.
- The sequence of electron affinity in second period is—
$$\text{Be} < \text{N} < \text{B} < \text{C} < \text{O} < \text{F}$$
- The sequence of electron affinity of VII group elements is—
$$\text{At} < \text{I} < \text{Br} < \text{F} < \text{Cl}$$
- Reactivity of non-metal \propto Electron affinity.
- Oxidising power of element \propto Electron affinity.
- When the difference between I. P. and E_a of two bonding atoms A and B respectively is very less, then the possibility of electrovalent compound formation is there, as the energy is compensated by lattice energy.
- When I. P. and E_a difference is very high then formation of covalent bond is favoured, as such a high energy cannot be compensated by lattice energy.

Electronegativity

In 1931, Pauling defined the electronegativity of an atom as the tendency of the atom to attract bonded pairs of electrons towards itself, when combined in the formation of molecule. If the bonding electrons spend more time round one atom, that atom will have δ^- charge, and consequently other atom will have δ^+ charge. Pauling and others have attempted to relate the electronegativity difference between two atoms to the amount of ionic character in the bond between them.

The term electronegativity has been defined differently by different scientists and each of them has suggested a method of his own to calculate electronegativities of different elements. Some methods are given below.

1. Pauling's Method

Pauling calculated electronegativities of different elements from bond energies. Consider a bond A—B between two dissimilar atoms A and B of a molecule AB. Let the bond energies of A—A, B—B and A—B bonds be represented as E_{A-A} , E_{B-B} and E_{A-B} respectively. It may be seen that the bond dissociation energy of A—B is almost always higher than the mean of the bond dissociation energies of A—A and B—B bonds *i.e.*,

$$E_{A-B} > \sqrt{E_{A-A} \times E_{B-B}}$$

Their difference (Δ) is related to the difference in the electronegativities of A and B according to the following equation:

$$\begin{aligned} \Delta &= E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}} \\ &= (X_A - X_B)^2 \end{aligned}$$

Here, X_A and X_B are the electronegativities of A and B respectively.

$$\text{or, } 0.208\sqrt{\Delta} = X_A - X_B$$

The factor 0.208 arises from the conversion of kcal to electron volt.

Considering arbitrarily the electronegativity of hydrogen to be 2.1, Pauling calculated electronegativities of other elements with the help of this equation.

Example

Calculation of electronegativity of chlorine from following data—

$$E_{H-H} = 104 \text{ k cal mol}^{-1}$$

$$E_{Cl-Cl} = 36 \text{ k cal mol}^{-1}$$

$$E_{H-Cl} = 134 \text{ k cal mol}^{-1}$$

According to Pauling's equation—

$$\Delta = E_{HCl} - \sqrt{E_{H-H} \times E_{Cl-Cl}}$$

$$\Delta = 134 - \sqrt{104 \times 36}$$

$$= 134 - 61.18$$

$$= 72.82$$

$$x_{Cl} - x_H = 0.208\sqrt{\Delta}$$

$$= 0.208\sqrt{72.82}$$

$$= 1.77$$

$$\begin{aligned} \text{Since } x_H &= 2.1 \\ \therefore x_{Cl} - 2.1 &= 1.77 \\ \text{or, } x_{Cl} &= 1.77 + 2.1 \\ &= 3.87 \end{aligned}$$

2. Mulliken's Method

In 1934, Mulliken suggested an alternative approach to electronegativity based on ionization energy and electron affinity of an atom. According to this method electronegativity could be regarded as the average of the ionization energy and electron affinity of an atom.

$$\text{Electronegativity} = \frac{I_e + E_a}{2}$$

Mulliken used I_e and E_a values measured in electron volts and the values were found to be 2.8 times higher than Pauling values.

The values of I_e and E_a are measured in kJ mol^{-1} and 1 eV per molecule = $96.48 \text{ kJ mol}^{-1}$. Therefore, the commonly accepted Pauling values are more nearly obtained by performing this calculation

$$\frac{I_e + E_a}{2 \times 2.8 \times 96.48} \text{ or } \frac{I_e + E_a}{540}$$

This method has an ordinary theoretical basis and also has advantage that different values can be obtained for different oxidation states of the same element.

3. Allred and Rochow Method

In 1958, Allred and Rochow worked out the electronegativities of 69 elements. They defined electronegativity as the attractive force between a nucleus and an electron at a distance equal to the covalent radius. This force of attraction (F) is given by—

$$F = \frac{Z_{\text{eff}} \times e^2}{r^2} \left\{ \begin{array}{l} e = \text{Charge on electron} \\ r = \text{Covalent radius} \\ Z_{\text{eff}} = \text{Effective nuclear charge} \end{array} \right.$$

F values may be converted to electronegativity values on the Pauling's scale using an empirical equation.

$$x = 0.744 + \frac{0.359 Z_{\text{eff}}}{r^2}$$

Example

Calculation of electronegativity of carbon—

Atomic radius of carbon = 0.77 \AA

Z_{eff} at the outermost orbit of C atom

$$= Z - S$$

Where Z = Atomic number

S = Screening constant

For carbon, $Z = 6$

$$\begin{aligned} S &= 1s^2, 2s^2, 2p^2 \\ &= (4 \times 0.35 + 2 \times 0.85) \\ &= 3.1 \end{aligned}$$

$$\begin{aligned} \therefore Z_{\text{eff}} &= Z - S \\ &= 6 - 3.1 \\ &= 2.9 \end{aligned}$$

$$\begin{aligned} \therefore x_C &= \frac{0.359 \times 2.9}{(0.77)^2} + 0.744 \\ &= 2.5 \end{aligned}$$

Factors Affecting Electronegativity

(1) **Charge on the atom**—The cation will be more electronegative than parent atom which in turn will be more electronegative than its anion. Higher the positive oxidation state of any atom in a compound, the greater will be its electronegativity.

Example

The oxidation state of Cl in HClO is +1 and in HClO₃ it is +5. Hence, the chlorine atom in HClO₃ is more electronegative than in HClO. On account of this reason, the release of H⁺ will be easier in HClO₃ as compared to HClO or HClO₃ is a stronger acid than HClO.

(2) **Effect of substitution**—Electronegativity of an atom depends upon the nature of the substituents attached to that atom. For example—carbon atom in CF₃I acquires a greater positive charge than in CH₃I. Hence, the carbon atom in CF₃I is more electronegative than in CH₃I.

The difference in electronegativity of an atom caused by substituents results in different chemical behaviour of that atom.



(3) **Ionization energy and electron affinity**—Mulliken propounded that electronegativity is related to the ionization energy and electron affinity of an atom. Evidently, higher the ionization energy and electron affinity, greater would be the electronegativity of the atom.

(4) **Effective nuclear charge**—As proposed by Allred and Rochow that the electron attracting power of an atom in a molecule is proportional to the effective nuclear charge, Z_{eff} . Thus any factor which increases Z_{eff} , will also increase the electronegativity of the atom. For example Z_{eff} decreases as one goes down a group in the periodic table. This is because with increase in atomic number within a group, the atomic size increases. Hence, electronegativity decreases as one moves down the group.

$$F(4.0) > Cl(3.0) > Br(2.8) > I(2.5)$$

Electronegativity goes on increasing with increase in atomic number as one moves along the period from left to right, as the size of the atom decreases in the same order.

$$\begin{aligned} \text{Li}(1.0) < \text{Be}(1.5) < \text{B}(2.0) < \text{C}(2.5) < \text{N}(3.0) < \text{O}(3.5) \\ < \text{F}(4.0) \end{aligned}$$

(5) **Hybridised state**— s -electrons are more penetrating than p -electrons. So, if an atom has hybrid orbitals with greater s -character the electronic charge in such orbitals will remain more closer to the nucleus of that atom. Thus electronegativity of such atom will be higher.

For example—

CH ₄	sp^3	25% s -character
C ₂ H ₄	sp^2	33% s -character
C ₂ H ₂	sp	50% s -character

The electronegativity of carbon atom increases as we move from CH₄ to C₂H₂. Due to greater electronegativity of carbon atom in C₂H₂, the electron pair of C—H bond is

pulled towards carbon atom thereby facilitating the release of H^+ ion. Thus H atom in CH_4 is neutral, the H atom in C_2H_4 is slightly acidic while that in C_2H_2 is considerably acidic.

Similarly, the basicity of amines also changes with the kind of hybridisation of nitrogen atom. Higher the s-character in hybrid orbitals, greater will be electronegativity and lower will be electron donating capacity of N atoms and hence lower will be basicity of the amine.

$R-C \equiv N$	sp	50% s-character
C_6H_5N	sp^2	33% s-character
$C_6H_5NH_2$	sp^3	25% s-character

Thus order of basicity is—



Applications of Electronegativity

(i) **Calculation of partial ionic character in a covalent bond**—Greater the difference between electronegativities of bonded atoms, greater will be the ionic character. **Pauling** suggested following correlation between the electronegativity difference ($x_A - x_B$) and the per cent ionic character in a covalent bond.

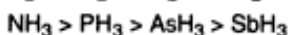
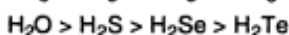
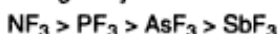
$$\text{Per cent ionic character} = [1 - e^{-0.25(x_A - x_B)}] \times 100.$$

He also suggested an alternative empirical formula for calculating per cent ionic character.

$$\text{Per cent ionic character} = 18(x_A - x_B)^{1.4}$$

(ii) **Explanation of bond angles**—Lesser the electronegativity of the central atom in a polyatomic molecule, lesser will be the bond angle. Central atom with low electronegativity will not be able to hold the bond pairs towards itself. Therefore, the bonding electron pairs will more shift towards other atoms attached to central atom. This will result in a decrease in the bond pair—bond pair repulsion and a decrease in bond angle.

Decreasing trend of bond angles with decrease in electronegativity of central atom is—



(iii) **Calculation of Bond-Length**—If a covalent bond is formed between two atoms A and B having different electronegativities, the bond acquires the polarity. Greater the polarity, shorter will be the bond length. **Shoemaker** and **Stevenson** proposed following empirical relation to calculate the bond length in such molecules.

$$d_{A-B} = r_A + r_B - 0.09(x_A - x_B)$$

$$d_{A-B} = \text{Bond distance between A and B}$$

$$r_A \text{ and } r_B = \text{Covalent radii of A and B}$$

$$x_A - x_B = \text{Electronegativity difference between A and B.}$$

The shortening of the bond between A and B due to electronegativity difference is equal to $0.09(x_A - x_B)$. Due to this shortening of bond, the bond becomes more strong and stable.

Size of Atoms and Ions

The size of atoms and ions is generally represented in the magnitudes of their respective radii. The radius of an atom or an ion may be taken in the ordinary sense as the distance between the centre of the nucleus and outermost shell of electrons.

Remember

- Fluorine is the element in whole of periodic table having highest electronegativity.
- If the difference of electronegativity between two bonded atoms exceeds 2.5, the bond will be electrovalent.
- If the difference in electronegativity between bonded atoms is less than 2.5, but otherwise quite appreciable, the bond formed would be polar covalent.
- Enthalpies of formation of compounds can be calculated with the help of the formula.

$$\Delta H_f = 23 \sum (x_A - x_B)^2 - 55.4 n_N - 26.0 n_O$$
 n_N and n_O are number of N and O atoms in the molecule

$$\Sigma = \text{No. of bonds in the molecule}$$

$$x_A - x_B = \text{Electronegativity difference}$$
- Per cent ionic character in a covalent bond between A and B can be determined as—

$$\text{Per cent ionic character} = [1 - e^{-0.25(x_A - x_B)}] \times 100.$$
- Atom of same element may have different values of electronegativity in different compounds, but electron affinity does not change.

There are three operational concepts of these radii—

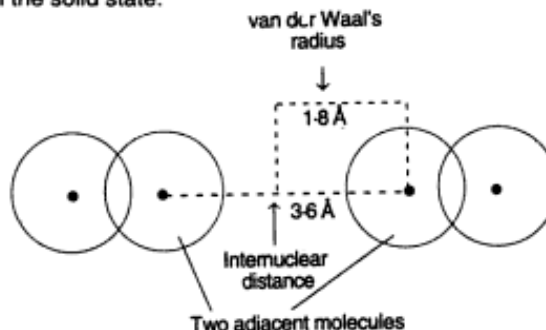
(i) Covalent radius, (ii) van der Waal's radius, (iii) ionic radius.

(i) **Covalent radius**—One-half of the distance between nuclei of two covalently bonded atoms of same element in the molecule, is taken as covalent radius of atom of that element.

For example, we know from spectroscopic data that the distance between the nuclei of two hydrogen atoms in a H_2 molecule is 0.74 Å. Half of this distance *i.e.*, 0.37 Å gives the covalent radius of hydrogen atom.

The covalent radii decrease in moving from left to right in any period and increase in moving down the group.

(ii) **van der Waal's radius**—It is defined as one half of the distance between the nuclei of two adjacent identical atoms belonging to two neighbouring molecules in the solid state.



It is actually the distance between two non-bonded atoms of two adjacent molecules.

(iii) **Ionic radius**—Ionic radius corresponds to the radius of an ion in an ionic crystal. The distance from the nucleus of an ion upto which it has influence on its electron charge cloud.

The inter nuclear distance in any ionic compound is determined from X-ray measurements. This distance is taken as the sum of radii of two ions involved.

Variation of ionic radii in isoelectronic ions

Isoelectronic ions have the same number of electrons but they differ in nuclear charge. As the nuclear charge

increases, the electrons are held more tightly with the result that the ionic radius decreases. Some examples are given below—

Ions	N ³⁻	O ²⁻	F ⁻	Na ⁺	Mg ²⁺	Al ³⁺
No. of electrons	10	10	10	10	10	10
Charge on nucleus	+7	+8	+9	+11	+12	+13
Radius Å	1.71	1.40	1.36	0.95	0.60	0.45

The radius of cation is invariably smaller than that of corresponding atom, while the radius of an anion is invariably larger than that of corresponding atom.

Periodic trend in ionic radii—The ionic radii increase in moving from top to bottom in a group and decrease in moving along a period from left to right.

Remember

- The bond length of the bond between unlike atoms *i.e.*, atoms differing in their electronegativities, is shorter than the sum of their covalent radii.
- According to **Shoemaker and Stevenson**, the actual bond length between atoms A and B is given by the relation—

$$d_{A-B} = r_A + r_B - 0.09(x_A - x_B)$$
- The covalent radius of an element determined from double or a triple bond is shorter than the normal covalent radius of the same element determined from a single bond.
The covalent radius of carbon in ethane is 0.77 Å, in ethylene 0.67 Å and in acetylene it is 0.60 Å.
- Covalent radius is always smaller than van der Waal's radius.
- In the crystals of noble gases, no chemical forces are operating between the atoms. The van der Waal's forces are the only attractive forces in these cases. Hence, the atomic radii of noble gases are only van der Waal's radii.
- Covalent radius can be calculated as—

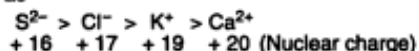
$$d_{A-A} = r_A + r_A$$

(when single covalent bond is
between identical atoms)

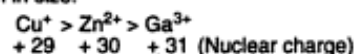
$$\therefore 2r_A = d_{A-A}$$

$$r_A = \frac{d_{A-A}}{2}$$

- Sequence of ionic size for isoelectronic species having 18 electrons is as



Isoelectronic ions having 28 electrons show the following gradation in size.



- Though it is possible to measure internuclear distance in a crystal very accurately by X-ray diffraction, but there is no universally accepted formula for apportioning this to the two ions.
- Historically several different sets of ionic radii have been calculated. The main ones are by **Goldschmidt, Pauling and Ahrens**. The most recent values of ionic radii are the most accurate and they are worked out by **Shannon (1976)**.
- The ionic radii are not absolute constants, and are best seen as a working approximations.
- d* and *f* orbitals do not shield the nuclear charge very effectively. Thus there is significant reduction in size of ions just after 10 *d* or 14 *f* electrons have been filled in. In the case of lanthanides it is called **Lanthanide Contraction** and results in the size of the second and third row transition elements being almost same.
- Atomic volumes of metal atoms can be determined from metallic phases by dividing their atomic masses by their respective densities. The radii calculated from atomic volumes are called **metallic radii**.
- The size of free atom and its size determined from a single non-polar covalent bond are almost same. Therefore, the terms covalent radius and atomic radius are synonymous.