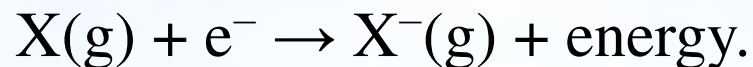# *Periodic Properties

Part - II

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ELECTRON AFFINITY

The electron affinity (E_A) of an atom is defined as the amount of energy *released* when an electron is added to a neutral atom in the gaseous state to form a negative ion.

$$X(g) + e^- \rightarrow X^-(g) + energy.$$

In other words, this enthalpy change and the electron affinity differ by a negative sign.

The magnitude of electron affinity measures the ability of an atom to hold an additional electron.

If an atom has more tendency to accept electron, larger will be Electron Affinity and the vice versa.

EA can be positive also. The EA is expressed in terms of kJmol^{-1} .

Factors on which electron affinity depends

1.Nuclear Charge
The electron affinity increases as the nuclear charge increases. This is because the incoming electron experiences greater attraction if nuclear charge is more.

2.Size of atom
With increase in size of the atom, the distance between the nucleus and incoming electron increases and this results in lesser attraction. Consequently the EA decreases.

3. Electronic Configuration

The element having stable electronic configuration of half and completely filled valence subshells show very small tendency to accept additional electron and thus electron affinity are low or almost zero in certain cases.

Trends in electron affinities

- Decrease down a group and increase across a period in general but there are not clear cut trends as with atomic size and I.E.

Variation down a group

- On moving down the group the atomic size and nuclear charge increases.
- But the effect of increase in atomic size is much more pronounced than that of nuclear charge
- Thus the additional electron feels less attraction by large atom.
- Consequently electron affinity decreases.

Variation along a period

- On moving across a period the size of atom decreases and nuclear charge increases.
- Both these factors result into greater attraction for incoming electrons, therefore the EA increases from left to right in a period.

However certain irregularities are observed in general trend due to stable electronic configuration.

Electron Affinities (kJ/mol)

1A							8A
H −73	**2A**	**3A**	**4A**	**5A**	**6A**	**7A**	**He** >0
Li −60	**Be** >0	**B** −27	**C** −122	**N** >0	**O** −141	**F** −328	**Ne** >0
Na −53	**Mg** >0	**Al** −43	**Si** −134	**P** −72	**S** −200	**Cl** −349	**Ar** >0
K −48	**Ca** −2	**Ga** −30	**Ge** −119	**As** −78	**Se** −195	**Br** −325	**Kr** >0
Rb −47	**Sr** −5	**In** −30	**Sn** −107	**Sb** −103	**Te** −190	**I** −295	**Xe** >0

i) Halogens have the highest electron affinities

EA of halogens are highest (ns^2, np^5). It requires only one electron to attain noble gas configuration (ns^2, np^6). Thus have strong tendency to accept an additional electron and attain noble gas configuration. Thus their EA are high.

ii) Electron Affinity of noble gases is zero

The electronic configuration of noble gas is ns^2, np^6. They have no tendency to gain or accept additional electron. The incoming electron does not feel any attraction for the nucleus. Thus no energy is released. So, their EA values are zero.

iii) Be, Mg, N and P EA values are nearly Zero

Be and Mg have extra stability due to fully filled 2s orbital in

Be ($2s^2$) and 3s orbital in Mg ($3s^2$). N and P half filled 2p and 3p orbital respectively. Half filled and fully filled orbitals have little tendency to accept electrons due to stability. So, their EA values are nearly zero.

iv) Electron affinity of Fluorine is less than chlorine

F atom has very small size of the atom . Due to small size, there are strong inter-electronic repulsion in the relatively compact subshell of fluorine. Thus the incoming electron does not feel much attraction. As the result EA is low.
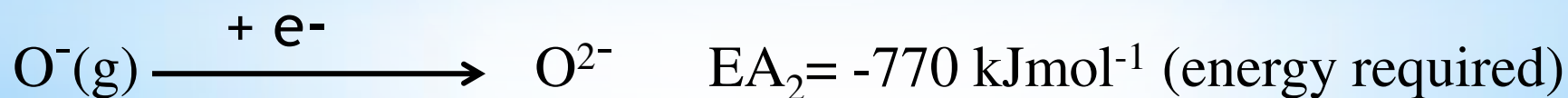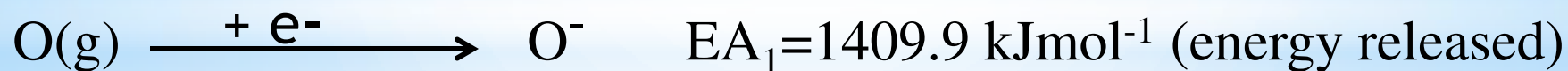
On the other hand the EA of Cl atom is larger because the electron is being added to relatively large 3-p orbital which can easily accommodate the additional electron.
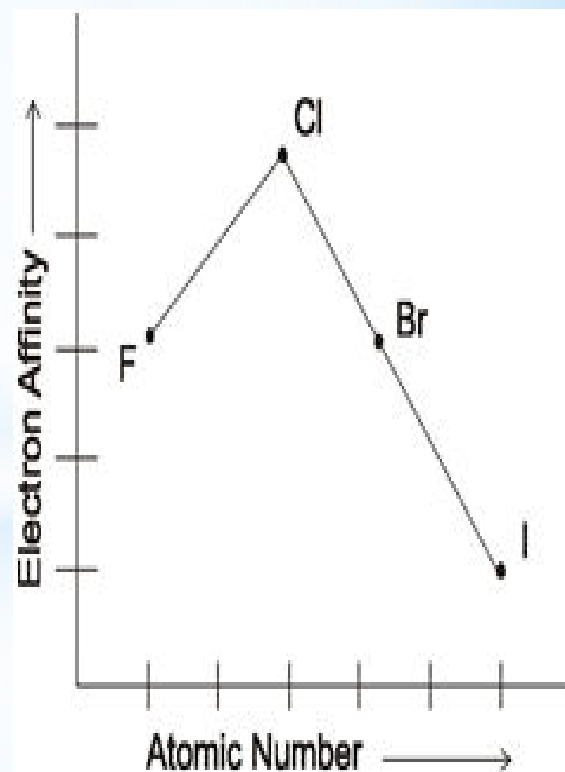
The EA for some third period elements (e.g. P, S, Cl) are greater than the corresponding second period members (e.g. N, O, F).

This is due to the smaller size of atoms of the second period element (N,O,F) which would produce large electron-electron repulsions for the additional electron.

Successive Electron Affinity: Similar to IE the second Electron affinity are also possible. As in the second electron affinity second electron is added to a negatively charged ion, the addition is opposed by coulomb repulsions. The energy has to be supplied to force the second electron to attach itself.

$$O(g) \xrightarrow{+ \ e^-} O^- \qquad EA_1 = 1409.9 \ kJmol^{-1} \ (\text{energy released})$$

$$O^-(g) \xrightarrow{+ \ e^-} O^{2-} \qquad EA_2 = -770 \ kJmol^{-1} \ (\text{energy required})$$

In other words second (and higher) electron affinity would have negative value (since the first electron affinity in which energy is released is taken as + ve).

For Example first and second electron affinity of O and S

Element	EA_1	EA_2
O	1409.9kJ	-770kJ
S	200.7kJ	-333kJ

In other words, this enthalpy change and the electron affinity differ by a negative sign.
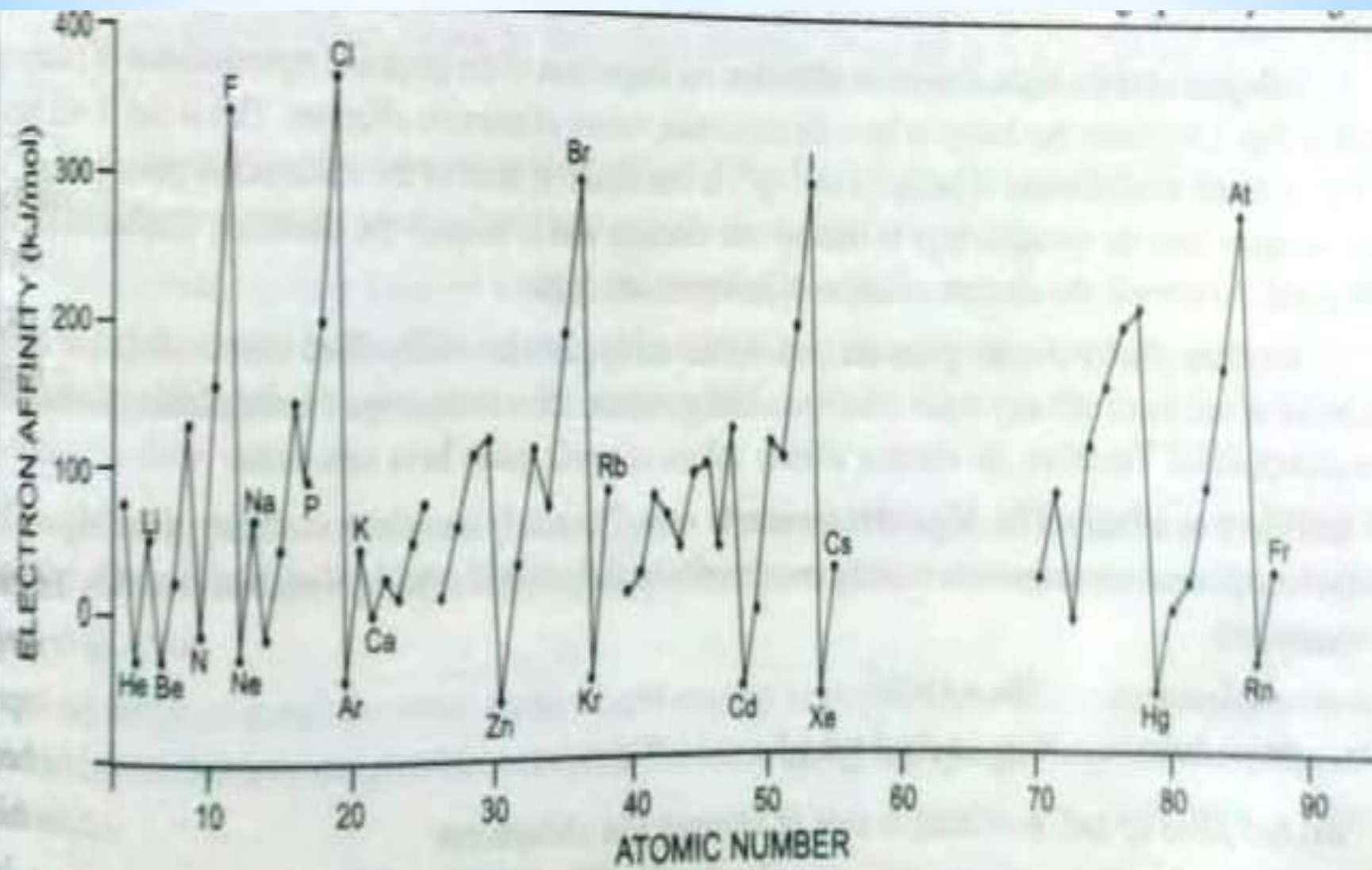
FIGURE 2.8.

Graphical representation of electron affinities.

ELECTRONEGATIVITY

- In homonuclear diatomic molecules the shared pair of electrons lie exactly midway between the nuclei of the two atoms because both the atom have same attraction for these electron.

- In heteronuclear diatomic molecule (HCl) the covalent bond is between dissimilar atoms. So, the electron pair may be closer to one atom than the other.

- The tendency of an atom to attract the shared pair of electron towards itself is called **electronegativity.**

- Different atoms have different tendencies to attract the bonding pair of electrons towards themselves.

- Greater the ability of an atom to attract electrons in a bond towards itself, greater is its electronegativity.

- Unlike IE and EA which are related to the individual gaseous atom, the electronegativity is related to atoms in their bonded state.

METHODS FOR DETERMINATION OF ELECTRONEGATIVITY

1. Pauling scale of electronegativity

- Proposed scale based on the **bond energies** in hetero-nuclear bonds.

- He suggested that if two atoms had same electronegativity values, the bond energy of A-B bond would be equal to the geometrical mean of the bond energies of A-A and B-B bonds

$$E_{AB} = (E_{A-A} \times E_{B-B})^{1/2}$$

- Based upon the assumption of pure covalent bonds in A_2 and B_2 and A-B molecules, he observed that for most of the A-B bonds, the **actual bond energy is more** than the geometrical mean of bond energy of E_{A-A} and E_{B-B}.

- This means that two participating atoms have **different tendencies to attract the shared pair of electrons.**

- Hence both the combining atoms have **different electronegativity's.**

- In other words the **A-B bond** will be **no longer purely covalent bond.**

- It means there is **contribution of ionic structure A^+B^-** (assuming B is more electronegative) in addition to pure covalent A-B structure

- The difference between the actual bond energy of A-B bond **(E_{AB})** and geometrical mean energy **$[(E_{A-A} \times E_{B-B})^{1/2}]$** is a measure of the different electronegativities of the two atoms.

Thus,

$$\Delta E = [(E_{A-B}) - (E_{A-A} \times E_{B-B})^{1/2}]$$

ΔE is the **extra bond energy** and measures the polarity of the bond A – B which depends on electronegativities of atoms A and B.

Excess bond energy (ΔE) arises due to **resonance** between the structure **AB (covalent) and A⁺B⁻ (ionic)** and is also known as **ionic resonance energy.**

$$\text{AB (covalent)} \leftrightarrow A^+B^- \text{ (ionic)}$$

Pauling calculated the ΔE for different bonds and gave an empirical relationship to correlate ΔE with the electronegativities (X_A **and** X_B) of the two atoms.

$$X_A - X_B = 0.18 \, (\Delta E)^{\frac{1}{2}} \; \text{kcal /mol.}$$

If ΔE is expressed in **eV**, then the above expression becomes

$$X_A - X_B = 0.208 \, (\Delta E)^{\frac{1}{2}} \, \text{eV}$$

In **S.I units**, the above relation becomes

$$X_A - X_B = 0.088 \, (\Delta E)^{\frac{1}{2}}$$

▶ **Example.** *Calculate the electronegativity of carbon in C—H bond if bond energies of E_{C-H}, E_{H-H} and E_{C-C} are 98·8, 104 and 83 kcal/mole respectively.*

Solution. According to Pauling's electronegativity scale

$$X_C - X_H = 0·18 \sqrt{\Delta E}$$

where ΔE = resonance energy in kcal/mol.

If the C—H bond is 100% covalent, then

$$E_{C-H} = \sqrt{E_{H-H} \times E_{C-C}}$$

$$= \sqrt{104 \times 83} = 92·91 \text{ kcal/mol}$$

Given bond energy $E_{C-H} = 98·8$.

$$\Delta E = (\text{Actual bond energy of C—H bond}) - (\text{Energy for 100\% covalent bond})$$

$$= 98·80 - 92·91 = 5·89 \text{ kcal/mol}$$

Now $X_C - X_H = 0·18 (5·89)^{1/2} = 0·44$

Electronegativity of hydrogen = 2·1

∴ Electronegativity of carbon = 0·44 + 2·10 = 2·54.

2. Mulliken Scale of electronegativity (1934)

Mulliken scale is based on the ionization energy and the electron affinity of an atom.

Mulliken defined the electronegativity of an atom as the arithmetic mean of its ionisation energy and electron affinity.

$$X_A = \frac{1}{2}(I.P. + E.A.)$$

The values of I.P. and E.A. were taken in electron volts (eV).

The values of electronegativities found by this method were seen to be **2.8 times** more than Pauling's value

$$X \text{ (Pauling)} = \frac{X(Mulliken)}{2.8}$$

But it is much more convenient if the values of I.P. and E.A. are taken in kJ / mol.

$$1eV = 1.602 \times 10^{-19} \times 6.023 \times 10^{23} \text{ J/mol} = 96.48 \text{ kJ / mol}$$

So, in order to correlate Mulliken's values with Pauling's values

$$\text{Electronegativity} = \frac{I.E. + E.A.}{2 \times 2.8 \times 96.48}$$

$$X \text{ (Pauling)} = \frac{X(Mulliken)}{2.8 \times 96.48} = \frac{IE + EA}{540}$$

Disadvantages of Mulliken Scale of Electronegativity

1. Electron affinity values of only few elements are known.
2. The IE and EA values changes with valence state of the element.

3. **Allred and Rochow Electronegativity Scale (1958)**

This is based on the electrostatic force of attraction between an valence electron and its nucleus. The force of attraction is taken as the measure of its electronegativity.

$$F = \frac{(Z^* \, e)(e)}{r^2}$$

e = charge on electron
r = mean distance from the nucleus
Z* = effective nuclear charge

The electronegativity can thus be measured as

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

covalent radius (Å)

elements with higher χ values have higher Z_{eff} and smaller r values

Disadvantages of Allred and Rochow's Scale

1. The covalent radii of elements are not available.
2. The slater rules for calculating effective nuclear charge are empirical.

However this scale has gained importance because it does not

contain quantities such as electron affinities, bond dissociation energies which are known for comparatively lesser number of elements.

▶ **Example.** *Find the electronegativity of nitrogen, given r = 74 pm.*

Solution. According to Allred and Rochow, the electronegativity is given by

$$\chi = 0.359 \, \frac{Z_{eff}}{r^2} + 0.744$$

and

$$Z_{eff} = Z - S = 7 - [2 \times 0.85 + 4 \times 0.35]$$

$$= 7 - [3.10] = 3.9$$

Thus

$$\chi = 0.359 \times \frac{3.9}{(0.74)^2} + 0.744 = 3.30$$

4. Sanderson scale of electronegativity

Sanderson proposed a scale of electronegativities based on the compactness of the electron cloud around the nucleus or average electron density of an atom.

The average Density of an atom is given as

$$D = \frac{3Z}{4\pi r^2}$$

Acc. to him electronegativity is expressed as stability ratio for an atom

$$SR = \frac{D}{D_i}$$

D= electron density of the atom
D_i = ideal electron density of the hypothetical noble gas having same number of electrons.

The stability ratio of an atom is a measure of the electronegativity.

The SR values are similar to electronegativity values obtained by Pauling.

These are adjusted to Pauling electronegativity (X) by

$$X^{1/2} = 0.21 \text{ SR} + 0.77$$

5. <u>Mulliken and Jaffe scale</u>

Mulliken and Jaffe proposed a new scale which takes into account the role of hybridization while calculating the electronegativities based on ionization energy and electron affinity.

Factors Affecting the Electronegativity

1. **Oxidation State:**
-   The electronegativity **increases** as the **positive oxidation state** of atom **increases.**
-   For **anions** however the electronegativity **decreases** with the **increasing negative charge on the anion**.

2. **Type of hybridization**:
-   The **type of hybridization** also affects the electronegativity of an atom.
-   s, p, d, f-orbitals **can penetrate** to different extent.
-   Due to their **greater penetration effect s orbitals** are near to nucleus than p, d, f-orbitals.
-   In brief **the electronegativity increases with increasing s character.**

Hydrocarbon	Types of hybridization	s-character	Electronegativity
CH_4 , C_2H_6	sp^3	25	2.48
C_2H_4	sp^2	33	2.75
C_2H_2	sp	50	3.29

3. Nature of substituents

- The electronegativities of group varies with the nature of the substituents.
- This is due to inductive effect of the substituent present in the molecule

Molecule	Substituent	Electronegativity
CH_3	3 H	2.30
CCl_3	3 Cl	3.30
CF_3	3 F	3.35

- The electronegativities of these groups will be electronegativity of carbon as it is adjusted by the presence of substituents (3H,3Cl and 3F atoms).

- These values are based on dipole moment, atomic radii, electronegativity and kinetic data.

Periodic Variation of electronegativity:

- The electronegativity increases on moving across a period from left to right.

- This is mainly due to decrease in atomic size and increase in effective nuclear charge. As the effective nuclear charge increases the attraction for the electrons increases.

Electronegativity generally decreases from top to bottom as atomic size increases and the bonding electrons moves away from the nucleus.
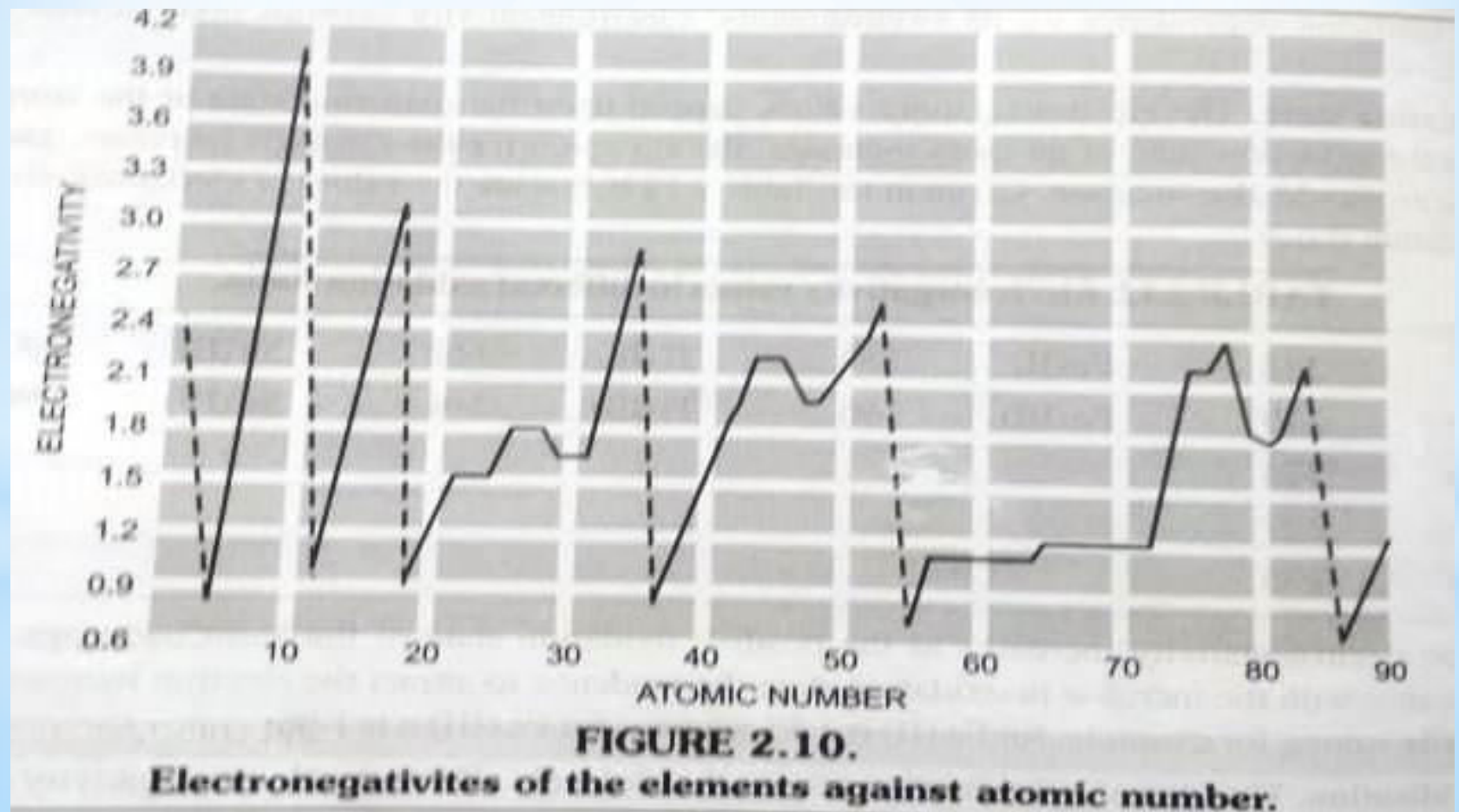
FIGURE 2.10.
Electronegativites of the elements against atomic number.

Periodicity of chemical properties can be summed in three ways :

i.   Comparison of properties of elements going down the group
ii. Comparison of properties of elements going across a period
iii. Comparison of properties of elements that are diagonal to each other.

CHANGE IN PROPERTIES DOWN A GROUP

METALLIC CHARACTER

* The chemical reactivity of main group metals and non metals increases down the group.

- On moving down the group, the size of the elements goes on increasing due to greater shielding effect.

- So, the ionisation energy goes on decreasing down the group.

- Elements at the bottom of the group can easily lose one or more of their outermost electrons.

- **Metallic Character increases down the group.**

CHANGE IN PROPERTIES ACROSS A PERIOD

METALLIC CHARACTER

 On moving across a period, the size of elements goes on decreasing.

- In a period, the electrons are being added to the same shell and nuclear charge increases.

- The nucleus exerts a strong attractive force on the outer electrons.

- So, the effective nuclear charge, ionisation energies and electron affinity value increases.

- The atoms lose electrons with difficulty rather the atoms prefer to gain electrons.

- In chemical reactions , **metals tend to lose electrons whereas non metals tend to gain electrons.**

- **In moving left to right in a period metallic character reduces**

IONIC CHARACTER

- It depends on the **elecronegativity difference** between the bonded atoms.

- Greater the difference in the electronegativities of the bonded atoms, **larger will be the ionic character** of the bond.

- For e.g. in hydrogen halides, the ionic character increases in the order

$$HF \; > \; HCl \; > \; HBr \; > \; HI$$

Ionic Character: 45%   17%   11%   5%

Because electronegativity of halogen atoms decrease down the group.

- As a result of ionic and covalent character, their properties also change.

- For example: AlF_3 is essentially ionic in nature, $AlCl_3$ has an intermediate character whereas $AlBr_3$ and AlI_3 exist as covalent dimers.

- Melting point of these halides decrease from AlF_3 to AlI_3 .

- AlF_3 and $AlCl_3$ are conductors in fused state (ionic character) whereas $AlBr_3$ and AlI_3 are non conductors (covalent character)

- The covalent or ionic character influences chemical behaviour of compounds.

- Most of the main group elements form halides which vary from

ionic halides to covalent halides. This arises due to difference in electronegativity character.

- The halides of alkali metals are ionic in nature as we move across the period covalent character of halide increases

	AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
M. Pt	1563	465	370	464
Conductivity	conductor	Intermediate conductor	Non conductor	Non conductor
Structure	Semi-ionic	Intermediate layer lattice	Molecular lattice	Molecular lattice

- The properties of halides show a gradual change from ionic to covalent character due to electronegativity values.

- The halides of alkali metals are ionic in nature.

- On moving left to right in a period, the covalent character increases

Ionic/covalent character of Chlorides of second and third period

Second Period						
Element	Li	Be	B	C	N	O	F
Chloride	LiCl	$BeCl_2$	BCl_3	CCl_4	NCl_3	OCl_2	ClF
Nature	Ionic	Covalent	Covalent	Covalent	Covalent	Covalent	Covalent

Third Period						
Element	Na	Mg	Al	Si	P	S	Cl
Chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	SCl_2	Cl_2
Nature	Ionic	Partially Covalent	Covalent	Covalent	Covalent	Covalent	Covalent

OXIDISING AND REDUCING CHARACTER

- Oxidation is a process in which electrons are lost and reduction is a process in which electrons are gained.

- Thus oxidising agent is a substance which gains electrons while reducing agent is a substance which loses electron.

- Tendency to loose electron depends upon Ionization energy.

- Since IE increases along a period, the element on the left have low IE energy and therefore have good tendency to loose electron.

- Consequently they act as strong reducing agents.

- IE values decreases on moving down a group, so reducing character increasing on moving down a group.

- **Thus the oxidizing and reducing character of elements depends upon their ionization energies.**

- As we move along a period the IE increases and consequently reducing character decreases while the oxidizing character increases.

$$M^+ + e^- \leftrightarrow M$$

- Standard electrode potential value measures the tendency for reduction to occur.
- If the value is large or less negative the substance will be easily reduced and will act as strong oxidising agent.

- For e.g. [$E^o(1/2\ Br_2 / Br^-) = 1.06V$] is better oxidising agent than [$E^o(1/2\ I^2 / I^- = 0.53\ V$].

Table 19. Standard electrode potentials of some elements of main groups.

1 (IA)	2 (IIA)	13 (IIIA)	14 (IVA)	15 (VA)	16 (VIA)	17 (VIIA)
$H^+\mid H$ 0						
$Li^+\mid Li$ −3.04	$Be^{2+}\mid Be$ −1.85	$B^{3+}\mid B$ −0.87			$O_2\mid OH^-$ +0.44	$½F_2\mid F^-$ +2.85
$Na^+\mid Na$ −2.71	$Mg^{2+}\mid Mg$ −2.37	$Al^{3+}\mid Al$ −1.68			$S\mid S^{2-}$ 0.49	$½I_2/I^-$ +1.36
$K^+\mid K$ −2.92	$Ca^{2+}\mid Ca$ −2.87	$Ga^{3+}\mid Ga$ −0.52		$As^{3+}\mid As$ +0.25		$½Br_2\mid Br-$ +1.06
$Rb^+\mid Rb$ −2.99	$Sr^{2+}\mid Sr$ −2.89	$In^{3+}\mid In$ −0.34	$Sn^{2+}\mid Sn$ −0.14	$Sb^{3+}\mid Sb$ +0.21		$½I_2\mid I^-$ +0.53
$Cs^+\mid Cs$ −3.02	$Ba^{2+}\mid Ba$ −2.90	$Tl^+\mid Tl$ −0.34	$Pb^{2+}\mid Pb$ −0.13	$Bi^{3+}\mid Bi$ +0.23		

- On the other hand if the substance has high negative electrode potential value it will not be easily reduced .

- It will be oxidised and act as reducing agent.

- Li is the strongest reducing agent and fluorine is the strongest oxidizing agent.

OXIDATION STATES

- Like periodic properties, oxidation state is closely related to number of electron in outermost orbit/valence shell.

- Different oxidation state can be easily explained by the electronic configuration.

- Oxidation state of different elements corresponds to the number of electrons gained or lost by their atoms to acquire a complete shell of eight electrons.

- Elements of group 1, 2 and 13 gain noble gas configuration by loosing 1, 2 and 3 electrons respectively.

- Thus they show oxidation states equal to their group numbers.

- On the other hand elements belonging to group 15,16 and 17 have tendency to gain electron to acquire stable gas configuration.

- These elements exhibit oxidation state -3, -2 and -1 respectively.

Variation of oxidation state in period:

- As we across the period the positive oxidation state increases and the negative oxidation state decreases.

- For e.g. in the second period the oxidation state increases from Li to C (+1 to +4) and decreases from nitrogen to fluorine (-3 to -1).

Second Period							
Element	Li	Be	B	C	N	O	F
Elec. Con	$2s^1$	$2s^2$	$2s^22p^1$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2s^22p^5$
Ox. State	+1	+2	+3	+4,-4	-3	-2	-1
Third Period							
Element	Na	Mg	Al	Si	P	S	Cl
Elec. Con	$3s^1$	$3s^2$	$3s^23p^1$	$3s^23p^2$	$3s^23p^3$	$3s^23p^4$	$3s^23p^5$
Ox. State	+1	+2	+3	+4,-4	+5, -3	+6, -2	+7,-1

Variation in the group:

- Oxidation state shown by p-block element is equal to sum of p and s electrons which is same as the group number.

- In addition to the usual oxidation state, some elements also show another oxidation state which differs from group oxidation state by step of two.

- For e.g., the atoms of group 13 have three valence electrons. All these elements show maximum of +3 oxidation state.

- However , except Boron all other elements also exhibit +1 oxidation state.

- It has been seen that +1 oxidation state becomes more stable as we moves down the group.

- The last two elements In and Tl show +1 and +3 two oxidation states but +1 oxidation state is more predominant in Tl.

- The greater stability of lower oxidation state than the group number oxidation state of heavier p-block element can be explained in terms of inert pair effect.

Group III A		Group IVA	
B	+3	C	+4
Al	+1, +3	Si	+2, +4
Ga	+1, +3	Ge	+2, +4
In	+1, +3	Sn	+2, +4
Tl	+1, +3	Pb	+2, +4

Stability of lower Oxidation State increases
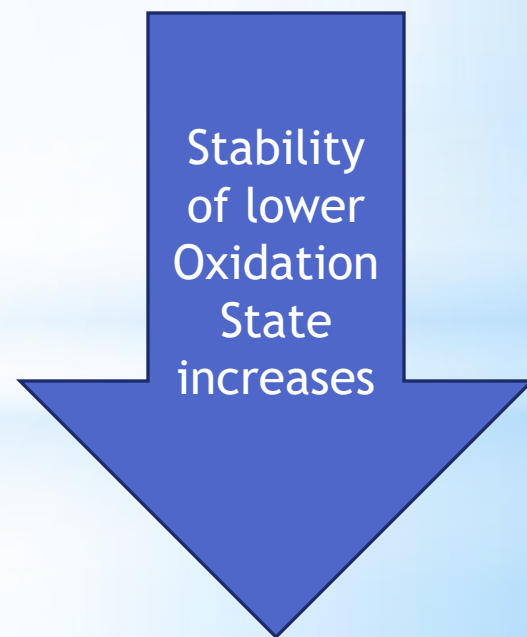
The formation of lower oxidation state involves the removal of p electrons only. The remaining s – electrons act or behave as inert pair i.e.do not participate in bonding.

1. s-orbitals have greater penetration power and therefore they penetrate the preceding 18 electron shell to greater extent.

2. As a result the pair of ns^2 electron is nearer to the nucleus and strongly held.

3. Consequently more energy is required to ionize these s-electrons and the energy required cannot be compensated by the energy released during the formation of two additional bond.

4. In case of heavier elements the size of the atom is large and therefore the electrons are spread over a large volume.

5. As a result they cannot have effective overlap of atomic orbitals.

6. Consequently small amount of energy released in case of heavier elements is not sufficient to compensate the energy needed for ionization of s-electrons.

7. Basically the inert pair is mainly due to decrease in strength of the covalent bonds in higher oxidation states as we move down the group.

The variation in oxidation states of different elements in periodic table may be summarised as:

1. For representative elements (s and p-block) the maximum possible oxidation equal to the represented group number (from I to IV) because of involvement of all s and p electrons in bonding.

2. The s-block element show only one oxidation state.

3. Most of p-block elements show more than one oxidation state.

4. Halogens other than Fluorine have either oxidation state of -1 or they have positive oxidation states when combined with more electronegative elements.

5. Transition and inner transition elements (d and f-block) also show variable oxidation state which differ by one (unlike p block)

ACIDIC AND BASIC CHARACTER OF HYDROXIDES

The acidic or basic character of hydroxide and oxide depends upon the position of the elements in periodic table.

Acidic or basic character of hydroxide having formula

$$\text{E} \underset{a}{—} \text{O} \underset{b}{—} \text{H}$$
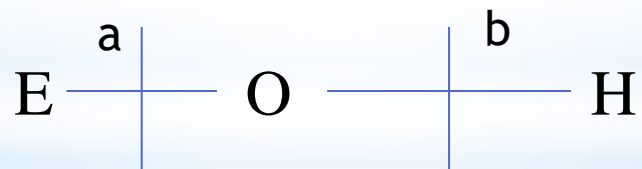
❖ If the electronegativity of E is low, as the case of metals like

Na, K, Mg and Ca , the electrons of E-O bonds are drawn more closely to the oxygen atom.

This is because oxygen is a highly electronegative element. As a result the bonds breaks at 'a' giving OH^-.

$$E - O - H \longrightarrow E^+ + OH^- \quad \text{(basic nature)}$$

❖ If the electronegativity of E is high as in case of F, Cl, N etc., the electrons of E-O bond are shared more equally between non-metal and oxygen atom.

As a result the oxygen-hydrogen bond becomes weaker and cleavage occurs at b forming proton

$$E-O-H \longrightarrow EO^- + H^+ \quad \text{(acidic nature)}$$

- Electronegativity increases as we move left to right in a period.

- The basic character of hydroxide decreases and acidic character increases from left to right.

- However in the middle , the atoms have intermediate electronegativity, so their hydroxide are amphoteric.

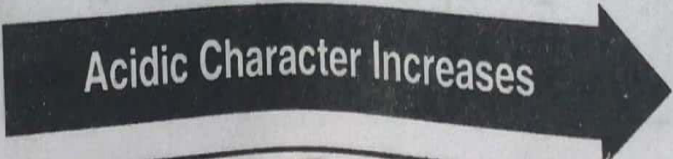**Table 21. Behaviour of hydroxides of second and third period elements**

Second Period

Element	Li	Be	B	C	N	O	F
Hydroxide	LiOH	$Be(OH)_2$	$B(OH)_3$	$O = C\overset{OH}{\underset{OH}{<}}$	O_2NOH	HO–OH	Not stable
			or H_3BO_3	or H_2CO_3	or HNO_2	or H_2O_2	
Behaviour	Basic	Amphoteric	Acidic	Acidic	Acidic	Acidic	–

Third Period

Element	Na	Mg	Al	Si	P	S	Cl
Hydroxide	NaOH	$Mg(OH)_2$	$Al(OH)_3$	$O = Si\overset{OH}{\underset{OH}{<}}$	$\overset{H}{\underset{O}{>}}P\overset{OH}{\underset{OH}{<}}$	$\overset{O}{\underset{O}{>}}Si\overset{OH}{\underset{OH}{<}}$	Cl–OH
				or H_2SiO_3	or H_3PO_3	or H_2SO_4	or HClO
Behaviour	Strongly basic	Basic	Amphoteric	Acidic	Acidic	Acidic	Acidic

Basic character decreases and acidic character increases →

ACIDIC AND BASIC CHARACTER OF OXIDES

- On moving across a period the basic character of oxides decreases while acidic character increases.

- For example while moving across the third period, it is seen Na_2O is basic, MgO is less basic, Al_2O_3 is amphoteric, SiO_2 is weakly acidic, P_2O_5 is acidic, SO_3 is strongly acidic and Cl_2O_7 is very strongly acidic

Element	Na	Mg	Al	Si	P	S	Cl
Oxide Behaviour	Na_2O Strongly basic	MgO Basic	Al_2O_3 Amphoteric	SiO_2 Weakly acidic	P_2O_5 Acidic	SO_3 Strongly acidic	Cl_2O_7 Very strongly acidic

Acidic Character Increases →

- As we go down the group the basic character of oxide increases or the acidic character decreases.

- The increase in basic character of the oxide is due to decrease in electronegativity of the element.

	I A	II A	III A
	Li_2O basic	BeO amphoteric	B_2O_3 acidic
	Na_2O basic	MgO basic	Al_2O_3 amphoteric
	K_2O basic	CaO basic	Ga_2O_3 amphoteric
			In_2O_3 basic

Increasing basic character of oxides

or decreasing acidic character of oxides

Increasing basic character of oxides or decreasing acidic character of oxides

- The acidic, basic and amphoteric character of oxides can be also explained on the basis of size of cation.

- If cation is small, its electronegativity will be high and therefore, the electronegativity difference between the cation and oxygen will be small.

- Consequently they will be ionic and behave as acidic.

The following generalization has been obtained for the acidic, basic or amphoteric behaviour of oxide and corresponding size of the cation.

Size of the cation	Nature of its oxide
Less than 0.5 Å	Acidic
Between 0.5 Å to 0.9 Å	Amphoteric
Greater than 0.9 Å	Basic

REACTIVITY OF ALKALI AND ALKALINE EARTH METALS

- The IE decreases down the group from Li to Cs therefore, the reactivity of alkali metal increases from Li to Cs.

- All elements are highly electropositive giving +1 ions.

- The second IE is very high, so the compound never exceeds +1 state.

- On the other hand alkaline earth metals in general less reactive than alkali metals.

- This is because of their relatively high ionization energy, high heat of atomisation in comparison in alkali metals. The chemistry of this group is mainly dominated by +2 oxidation state.

Some important trends are discussed below:

(i). The anomalous properties of element in first short period (from Li to fluorine) are explained due to peculiar atomic properties such as small size, high ionization energy and high electronegativity.

(ii) Diagonal relationship between elements of different groups (such as Li-Mg, Be-Al, B-Si) are due to their similar atomic properties (ionisation energies, electronegativities etc.)

(iii). Trends in bond type with position of the element in the periodic table and with oxidation state for a given element.

(iv).Variable oxidation states of transition elements.

(v). The stability of compounds and their trends.

(vi). Trends in the stability of coordination compounds and electron donor power of various types of ligands.