Q.6a) Effective Nuclear Charge (Z)

The effective nuclear charge is the net positive charge experienced by an electron (valence electron) in a polyelectronic atom.

Due to shielding effect of inner electrons on outer electrons, valence electrons experience less attractive pull or force from the nucleus. The decrease in the attractive force decreases the nuclear charge. This decreased nuclear charge is called effective nuclear charge, shown by Z^*

$$Z^* = Z - \sigma$$

Z = atomic no. of element

σ = screening constant

Thus effective nuclear charge Z^* is actual nuclear charge minus the screening effect caused by electrons present between the nucleus and outer electrons. More the number of electrons between nucleus and outer electrons, more will be the magnitude of σ, and hence the magnitude of effective nuclear charge Z^* will decrease.

Variation of effective nuclear charge in Periodic table :-

In periods from left to right

It increases from left to right in a period, in periodic table.

Elements of 2nd period.

Li	Be	B	C	N	O	F	Ne
1·30	1·95	2·60	3·25	3·90	4·55	5·20	5·85

→ periods.

from left to right in periods, the atomic number is increased by one at each next element, and the next

element has one more valence electron with its effective repulsion equal to 0.35 and therefore effective nuclear charge increases by 1 − 0.35 = 0.65 from member to member. Thus effective nuclear charge of each next atom is greater by 0.65 than previous atom.

In groups form from top to Bottom:—

In groups the effective nuclear charge remain constant /almost same

example → group IA

Li → 1.30

Na → 2.20

K → 2.20

Rb → 2.20

Cs → 2.20

Fr → 2.20

Atomic Radii

Radius of an atom or ion is defined as the distance from the centre of the nucleus to the outermost shell of atom or ion.

In periods from left to right :—

The atomic radius decreases from left to right in period.

Li	Be	B	C	N	O	F
152	111	88	77	70	66	64

→

Radius decreases because of 2 effects

i) Electrons get pulled in, due to increasing value of nuclear charge (Z), as we move from left to right in periods, greater the value of 'Z' greater is the contraction in size.

ii) As we move from left to right, due to increase in number of electron, the atom expand because of mutual repulsion and increased screening from the nuclear charge due to intervening electrons.

Both effect act in opposite direction, by experiment we came to know that size decreases from Li to F, it shows that effect (i) predominates over (ii)

	Li	Be	B	C	N	O	F
Atomic radii (pm)	152	111	88	77	70	66	64
Effective nuclear (Z) charge	1·3	1·85	2·60	3·25	3·90	4·55	5·20
electronic conf.	$1s^2 2s^1$	$1s^2 2s^2$	$1s^2 2s^2 2p^1$	$1s^2 2s^2 2p^2$	$1s^2 2s^2 2p^3$	$1s^2 2s^2 2p^4$	$1s^2 2s^2 2p^5$

In group from top to bottom :—

The size of elements increases in group, it is because due to the addition of new shell of electron at each step, while the effective nuclear charge almost remain constant, This increase in size is not regular as we go down the group, but become irregular once the filling of d, f series of electron begins. This expansion in size become gentle after third row.

	Atomic Radi (pm)	Nuc Effective nuclear charge	electronic conf.
Li	152	1.3	$1s^2 2s^1$
Na	186	2.2	$1s^2 2s^2 2p^6 3s^1$
K	231	2.2	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Rb	244	2.2	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$
Cs	267	2.2	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$

Ionic Radii

When neutral atom gain or lose electrons, they are converted into ions and radii are changed.

When atom looses electron positive ion (cation) is formed, size of cation is always smaller then neutral atom, it is because when atom loose electron then electron number decreases and magnitude of nuclear charge remain the same, so nuclear charge act on fewer number of electrons, so attract them more tightly and hence electron cloud shrink in size.

When neutral atom gain electron, a negative ion (anion) is formed, size of anion is always larger then its neutral atom, because same nuclear charge act over greater number of electrons, so electron cloud is now less tightly held which cause an expansion in the size.

In periods :—

for isoelectronic series (i.e ions which have same number of electrons), ionic radius decreases as nuclear charge increases. The increased nuclear charge is acting on same number of electrons.

~~Radii~~	C^{4-}	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}
Radii	260	171	140	133	95	65	50	40
Nuclear charge	+6	+7	+8	+9	+11	+12	+13	+14

In groups :—

In groups ionic radius increases, as atomic no. increases down in group & effective nuclear charge remain constant.

Electron Affinity

The amount of energy released when an electron is added to neutral gaseous atom.

$$X(g) + \bar{e} \longrightarrow X^{-}(g) + \text{Energy}$$

example = electron affinity of a 'H' atom is $-72.8\ kJ\ mol^{-1}$, i.e $72.8\ kJ$ energy is released. when 1 mole of H atoms combine with 1 mole of electrons to give 1 mole of H^- ions.

The greater the electron affinity, the more negative is the ΔE value and greater is the energy released.

In Periods :—

In periods from left to right, size of atom decreases and their nuclear charge increases ; and both these factors favour increases in electron affinity.

Group 17 elements have highest value of electron affinity due to their tendency to acquire an additional electron to form stable octet.

The elements on right side of periodic table always have tendency to acquire more electrons to complete their octet, & so they have high electron affinities.

In F & Cl

Electron affinity in Cl is greater due to strong inter electronic repulsion in relatively small & compact 2p subshell on addition of another electron.

In 'F' electron is added in bigger sized 3p orbital which

can easily accomodate additional electron.

In groups :—

from top to bottom, in groups atoms size increases, which lead to a decrease in their electron affinity values.

electron affinities of some Gaseous Atom

H						
-72.8						
Li	Be	B	C	N	O	F
-52.1	-	-28.9	-109.0	-19.3	-142.8	-328
Na	Mg	Al	Si	P	S	Cl
-71.4	-	-38.6	-183.3	-77.2	-199.7	-349
						Br
						-325

Second electron affinity :—

It is positive i.e energy is required instead of being released, it is because of electrostatic repulsion of the second electron by the negative charge on the ion.

$$O^- + e^- \longrightarrow O^{2-}$$

Electronegativity

The measure of the ability of an atom in a molecule to attract the shared electron pair toward in itself

In periods :—

from left to right in periods electronegativity increases.

In groups :—

from top to bottom, electronegativity decreases.

The ability of an atom to attract electron depend on the environment of that atom, 2 main factor which determine the attraction of atoms for electrons are.

i) Charge on atom :— An atom with positive charge will attract electrons more readily than a neutral atom, A negatively charged atom attracts less readily than a neutral atom.

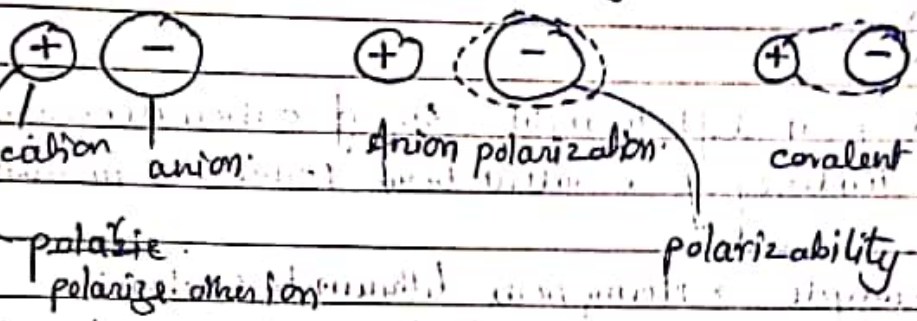
ii) Hybridization of atom :—

Electronegativity of atom varies with hybridization. ~~orbitals~~ Note cubes with more s-character are more electronegative. methane with sp^3 hybridization (having 25% s character) is unreactive. In ethylene carbon atom is sp^2 hybridised (33% s character) is more reactive, showing increased electronegativity of carbon.

In acetylene carbon is sp hybridized, thus 50% s character is most electronegative.

Polarizing Power & Polarizability

The power of an ion to distort the other ion is called its polarizing power and the tendency of the ion to distortion is known as its polarizability



Fajan's Rule

for detection of non polar character between two ions.

i) High charge of cation or anion
ii) Small size of positive ion
iii) large size of negative ion.

i) High charge of cation or anion. :— highly charged cation will exert more polarization on electron density of anion and increase more covalence character in compound. And highely charged anion get more easily polarized. Thus polarizing power of cation & polarizability of anion increase with increase in charge of ions.

ii) Small size of cation.

Small sized cation, will have high charge density and so it will be able to distort the electron cloud of anion more effectively.

iii) Large size of anion :— polarizability of anion increases with increase in its size because, its electron cloud is not

firmly held by its own nuclear charge and thus can be readily polarized by incoming cations.

In periods :—

In periods from left to right size of cation decreases and so tendency of covalent bond formation increases in these compounds.

example → Moving from lithium to carbon through beryllium & boron in second period. size of cation decreases and tendency of covalent bond formation increases.

In groups

from top to Bottom size of cation increases, so tendency of covalent bond formation decreases.

example Li^+ is more polarizing than other members of group, therefore compounds of lithium are covalent in nature, while similar compounds of sodium and potassium are ionic. Thus LiCl is covalent in nature while NaCl or KCl are ionic.

In groups, size of anions increases, there polarizability increases & their compound become more covalent.

Oxidation States :—

Oxidation states of an element can be readily predicted from the electronic configuration of atom.

Oxidation states of atom different elements is due to gain or loss of electron by their atoms so that they acquire a closed shell configuration of eight electrons ($ns^2 np^6$)

In group 1, 2 & 13 where the elements acquire noble gas configuration by losing electrons and thus show a single positive oxidation state equal to their group number.

On the other hand, elements on the right side of periodic table show negative oxidation states varying from -3 to -1, In 14th gp. tendency is to form covalent compound instead of gaining or losing electrons.

In periods eg. in 3rd period positive oxidation state increases and reaches a maximum value at aluminium.