Periodic Table & Periodicity

Section (A) : Development of Periodic Table & Modern Periodic Table

Need to classify Elements:

- At present 118 elements are known. Of them the recently discovered elements are man-made.
- With such a large no. of elements it is very difficult to study individually the chemistry of all these elements and their innumerable compounds individually.
- To ease out this problem, scientists searched for a systematic way to organize their knowledge by classifying the elements.
- It would rationalize known chemical facts about elements, but even predict new ones for undertaking further study.

Development of Modern Periodic Table:

(a) Dobereiner's Triads: He arranged similar elements in the groups of three elements called as triads, in which the atomic mass of the central element was merely the arithmetic mean of atomic masses of other two elements or all the three elements possessed nearly the same atomic masses.

Li	Na	K	
7	23	39	$\frac{7+39}{2} = 23$
Fe	Co	Ni	
55.85	58.93	58.71	nearly same atomic masses

It was restricted to few elements, therefore discarded.

(b) Newland's Law of Octave: He was the first to correlate the chemical properties of the elements with their atomic masses.

According to him if the elements are arranged in the order of their increasing atomic masses the eighth element starting from given one is similar in properties to the first one.

This arrangement of elements is called as Newland's Octave.

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca					

This classification worked quite well for the lighter elements but it failed in case of heavier elements and therefore, discarded

(c) Lother Meyer's Classification: He determined the atomic volumes by dividing atomic masses with their densities in solid states.

He plotted a graph between atomic masses against their respective atomic volumes for a number of elements. He found the following observations.

- Elements with similar properties occupied similar positions on the curve.
- Alkali metals having larger atomic volumes occupied the crests.
- Transitions elements occupied the troughs.
- The halogens occupied the ascending portions of the curve before the inert gases.
- Alkaline earth metals occupied the positions at about the mid points of the descending portions of the curve.

On the basis of these observations he concluded that the atomic volumes (a physical property) of the elements are the periodic functions of their atomic masses.

It was discarded as it lacks practical utility.

(d) Mendeleev's Periodic Table:

Mendeleev's Periodic's Law

According to him the physical and chemical properties of the elements are the periodic functions of their atomic masses.

He arranged then known elements in order of their increasing atomic masses considering the facts that elements with similar properties should fall in the same vertical columns and leaving out blank spaces where necessary.

This table was divided into nine vertical columns called groups and seven horizontal rows called periods.

The groups were numbered as I, II, III, IV, V, VI, VII, VIII and Zero group

Merits of Mendeleev Periodic table:

- It has simplified and systematised the study of elements and their compounds.
- It has helped in predicting the discovery of new elements on the basis of the blank spaces given in its periodic table.

Mendeleev predicted the properties of those missing elements from the known properties of the other elements in the same group. Eka-aluminium and Eka-silicon names were given for gallium and germanium (not discovered at the time of Mendeleev). Later on it was found that properties predicted by Mendeleev for these elements and those found experimentally were almost similar.

Table-1

Proeprty	eka-aluminium (predicted)	Gallium (found)	eka-silicon (predicted)	Germanium (found)
Atomic Mass	68	70	72	72.6
Density / (g/cm^3)	5.9	5.94	5.5	5.36
Melting point (K)	Low	30.2	High	1231
Formula of oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
Formula of chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$

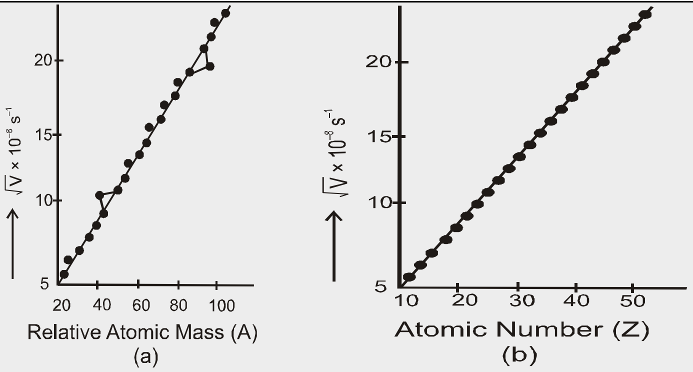
- Atomic weights of elements were corrected. Atomic weight of Be was calculated to be 3 × 4.5 = 13.5 by considering its valency 3, was correctly calculated considering its valency 2 (2 × 4.5 = 9)

Demerits in Mendeleev's Periodic Table :

- Position of hydrogen is uncertain. It has been placed in IA and VIIA groups because of its resemblance with both the groups.
- No separate positions were given to isotopes.
- Anomalous positions of lanthanides and actinides in periodic table.
- Order of increasing atomic weights is not strictly followed in the arrangement of elements in the periodic table. For example Ar(39.94) is placed before K(39.08) and Te (127.6) is placed before I (126.9).
- Similar elements were placed in different groups e.g. Cu in IB and Hg in IIB and similarly the elements with different properties were placed in same groups e.g. alkali metals in IA and coinage metals in IB.
- It didn't explained the cause of periodicity.

(e) Long form of the Periodic Table or Moseley's Periodic Table or Modern Periodic Table :

S.No.	Introduction	DISCRIPTION
1.	**Proposed by**	**Moseley**
2.	**Contribution**	(i) In the long form of periodic table there is contribution of Ramsey, Werner, Bohr and Bury. (ii)This table is also referred to as Bohr's table since it follows Bohr's scheme of the arrangements of elements into four types based on electronic configuration of elements The modern periodic table consits of horizontal rows (periods) and vertical column (groups).
3.	**Based on**	Atomic number
4.	**Experiment**	(i) Moseley did an experiment in which he bombarded high speed electrons on different Metal surfaces and obtained X-rays(electromagnetic rays). He observed regularities in the characteristic X-ray spectra of the elements and found that plot $\sqrt{\nu}$ *vs.* Z (atomic number) is straight line while $\sqrt{\nu}$ *vs. A* (atomic weight) is not, and $\sqrt{\nu} = a(Z - b)$, where *a* and *b* are constants that are same for all elements and ν is frequency of X-rays. Thus he concluded that atomic number is more fundamental property than atomic weight.

		 (ii) Moseley concluded that the physical and chemical properties of the elements are periodic function of their atomic number.
5.	**Modern Periodic Law**	The physical and chemical properties of elements are periodic function of their **atomic number**. So the elements are arranged in order of increasing atomic number, the elements with similar properties comes after regular intervals.
6.	**Periodicity**	The repetition of the properties of elements after regular intervals when the elements are arranged in the order of increasing atomic number is called periodicity. (a) In a period, the ultimate orbit remain same, but the number of electrons gradually increases. (b) In a group, the number of electrons in the ultimate orbit remains same, but the values of n increases.
7.	**Cause of Periodicty**	The periodic repetition of the properties of the elements is due to the recurrence of similar valence shell electronic configuration after certain regular intervals. For example, alkail metals have same electronic configuration ns^1, therefore, have similar properties. In the periodic table, elements with similar properties occur at intervals of 2, 8, 8, 18, 18 and 32. These numbers are called as magic numbers.

The modern periodic table consists of horizontal rows (periods) and vertical column (groups).

Periods :

There are seven periods numbered as 1, 2, 3, 4, 5, 6 and 7.

- Each period consists of a series of elements having same valence shell.
- Each period corresponds to a particular principal quantum number of the valence shell present in it.
- Each period starts with an alkali metal having outermost electronic configuration as ns^1.
- Each period ends with a noble gas with outermost electronic configuration ns^2np^6 except helium having outermost electronic configuration as $1s^2$.
- Each period starts with the filling of new shell.
- The number of elements in each period is twice the number of atomic orbitals available in shell that is being filled. For illustration–
    - Ist period shortest period having only two elements. Filling of electrons takes place in the first shell, for which, n = 1, ℓ = 0 (s-subshell) and m = 0.

      Only one orbital (1s) is available and thus it contains only two elements.
    - 3rd period (short period) having only eight elements. Filling of electrons takes place in the third shell. For which,

      n = 3, ℓ = 0, 1, 2 and number of orbitals 1 3 5
      (3s) (3p) (3d)

      Total number of orbitals 9

      But the energy of 3d orbitals are higher than 4s orbitals. Therefore, four orbitals (one 3s and three 3p orbitals) corresponding to n = 3 are filled before filling in 4s orbital (next energy level). Hence 3rd period contains eight elements not eighteen elements.

Groups :

There are eighteen groups numbered as 1, 2, 3, 4, 5, ... 13, 14, 15, 16, 17, 18.

Group consists of a series of elements having similar valence shell electronic configuration.

Table-2

Periods	Number of elements	Called as
$(1)^{st}$ n = 1	2	Very short period
$(2)^{nd}$ n = 2	8	Short period
$(3)^{rd}$ n = 3	8	Short period
$(4)^{th}$ n = 4	18	Long period
$(5)^{th}$ n = 5	18	Long period
$(6)^{th}$ n = 6	32	Very long period
$(7)^{th}$ n = 7	32	Very long period

S–Block	**Elements**													**p–Block Elements**			
1 IA																	18 VIII A
1 H 1.007	2 II A					**d –Block Elements**						13 III A	14 IV A	15 V A	16 VI A	17 VII A	2 He 4.002
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.006	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.98	12 Mg 24.30	3 III B	4 IV B	5 V B	6 VI B	7 VII B	8 VIII	9 VIII	10 VIII	11 I B	12 II B	13 Al 26.981	14 Si 28.085	15 P 30.973	16 S 32.006	17 Cl 35.452	18 Ar 39.948
19 K 39.08	20 Ca 40.078	21 Sc 44.959	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.938	26 Fe 55.84	27 Co 55.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.921	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.46	38 Sr 87.62	39 Y 88.905	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc 98	44 Ru 101.07	45 Rh 102.905	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.904	54 Xe 132.29
55 Cs 132.90	56 Ba 137.27	57 La* 138.905	72 Hf 178.49	73 Ta 180.947	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.666	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 207.980	84 Po 209	85 At 210	86 Rn 222
87 Fr 223	88 Ra 226	89 Ac** 227	104 Rf 261.11	105 Ha 262.114	106 Sg 263.118	107 Bh 262.12	108 Hs 265	109 Mt 266	110 Ds 269	111 Rg 272	112 Cn 285	113 Uut 284	114 Fl 289	115 Uup 288	116 Lv 292	117 Uus	118 Uuo 294
									Inner - Transition Metals (f-Block elements)								
			***Lanthanides**	58 Ce 140.115	59 Pr 140.907	60 Nd 144.24	61 Pm 145	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
			****Actinides**	90 Th 232.038	91 Pa 231	92 U 238.028	93 Np 237	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260

Classification of the Elements :

It is based on the type of orbitals which receives the differentiating electron (i.e., last electron).

(a) s-block elements

When shells upto (n – 1) are completely filled and the last electron enters the s-orbital of the outermost (n^{th}) shell, the elements of this class are called s-block elements.

- Group 1 & 2 elements constitute the s-block.
- General electronic configuration is [inert gas] ns^{1-2}
- s-block elements lie on the extreme left of the periodic table.
- This block includes metals.

(b) p-block elements

When shells upto (n – 1) are completely filled and differentiating electron enters the p-orbital of the n^th^ orbit, elements of this class are called p-block elements.

- Group 13 to 18 elements constitute the p-block.
- General electronic configuration is [inert gas] $ns^2\ np^{1-6}$
- p-block elements lie on the extreme right of the periodic table.
- This block includes some metals, all nonmetals and metalloids.

(c) d-Block elements

When outermost (n^{th}) and penultimate shells $(n-1)^{th}$ shells are incompletely filled and differentiating electron enters the (n – 1) d orbitals (i.e., d-orbital of penultimate shell) then elements of this class are called d-block elements.

- Group 3 to 12 elements constitute the d-block.
- General electronic configuration is [inert gas] $(n-1)d^{1-10}ns^{1-2}$ (except, palladium which has valence shell electron configuration $4d^{10}5s^0$).
- All the transition elements are metals and most of them form coloured complexes or ions.
- d-block elements are classified into four series as given below.

(1) I^st^ transition series i.e. 3d series contains 10 elements and starts from $_{21}$Sc–$_{30}$Zn. Filling of electrons takes place in 3d sub-shell.

(2) II^nd^ transition series i.e. 4d series contains 10 elements and starts from $_{39}$Y–$_{48}$Cd. Filling of electrons takes place in 4d sub-shell.

(3) III^rd^ transition series i.e. 5d series contains 10 elements and starts from $_{57}$La, $_{72}$Hf–$_{80}$Hg. Filling of electrons takes place in 5d sub-shell.

(4) IV^th^ transition series i.e. 6d series contains 10 elements and starts from $_{89}$Ac, $_{104}$Rf–$_{112}$Uub. Filling of electrons takes place in 6d sub-shell (incomplete series).

- Those elements which have partially filled d-orbitals in neutral state or in any stable oxidation state are called transition elements. (Zn, Cd, Hg, Uub are not transition elements)

(d) f-Block elements

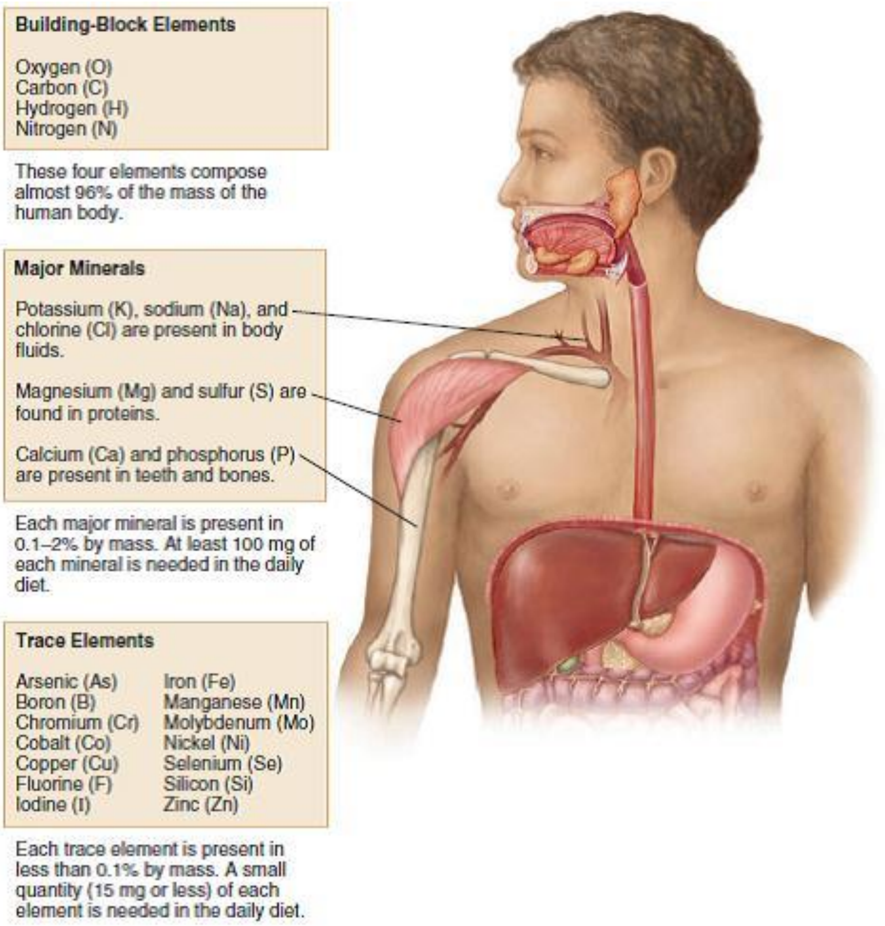
When n, (n – 1) and (n – 2) shells are incompletely filled and last electron enters into f-orbital of antepenultimate i.e., $(n-2)^{th}$ shell, elements of this class are called f-block elements. General electronic configuration is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

- All f-block elements belong to 3rd group.
- They are metals
- Within each series, the properties of the elements are quite similar.
- The elements coming after uranium are called transuranium elements.
- They are also called as inner-transition elements as they contain three outer most shell incomplete and were also referred to as rare earth elements since their oxides were rare in earlier days.

The elements of f-blocks have been classified into two series.

1. I^st^ inner transition or 4 f-series, contains 14 elements $_{58}$Ce to $_{71}$Lu. Filling of electrons takes place in 4f subshell.
2. IInd inner transition or 5 f-series, contains 14 elements $_{90}$Th to $_{103}$Lr. Filling of electrons takes place in 5f subshell.

- The actinides and lanthanides have been placed at the bottom of the periodic table to avoid the undue expansion of the periodic table.



Building-Block Elements

Oxygen (O)
Carbon (C)
Hydrogen (H)
Nitrogen (N)

These four elements compose almost 96% of the mass of the human body.

Major Minerals

Potassium (K), sodium (Na), and chlorine (Cl) are present in body fluids.

Magnesium (Mg) and sulfur (S) are found in proteins.

Calcium (Ca) and phosphorus (P) are present in teeth and bones.

Each major mineral is present in 0.1–2% by mass. At least 100 mg of each mineral is needed in the daily diet.

Trace Elements

Arsenic (As)
Boron (B)
Chromium (Cr)
Cobalt (Co)
Copper (Cu)
Fluorine (F)
Iodine (I)
Iron (Fe)
Manganese (Mn)
Molybdenum (Mo)
Nickel (Ni)
Selenium (Se)
Silicon (Si)
Zinc (Zn)

Each trace element is present in less than 0.1% by mass. A small quantity (15 mg or less) of each element is needed in the daily diet.

Solved Examples

Ex-1 Elements A, B, C, D and E have the following electronic configurations :

A : $1s^2\ 2s^2\ 2p^1$ B : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$ C : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
D : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ E : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

Which among these will belong to the same group in the periodic table ?

Sol. Out of these, elements A and B will belong to the same group of the periodic table because they have same outer electronic configuration, $ns^2\ np^1$.

Prediction of period, group and block:

- Period of an element corresponds to the principal quantum number of the valence shell.
- The block of an element corresponds to the type of subshell which receives the last electron.
- The group is predicted from the number of electrons in the valence shell or/and penultimate shell as follows.

(a) For s-block elements, Group number = the number of valence electrons
(b) For p-block elements, Group number = 10 + number of valence electrons
(c) For d-block elements, Group number = number of electrons in (n – 1) d sub shell + number of electrons in valence shell.
(d) For f block element – $\left.\begin{matrix}(58\text{-}71) & 4f \\ (92\text{-}103) & 5f\end{matrix}\right]$ - All f block elements are belongs to group number 3.

Two exceptions to this categorization:

Strictly, helium belongs to the s-block but its positioning in the p-block along with other group 18 elements in justified because it has a completely filled valence shell ($1s^2$) and as a result, exhibits properties & characteristics of other noble gases.

Hydrogen has only one s-electron and hence can be placed in group 1 (alkali metals). It can also gain an electron to achieve a noble gas arrangement and hence it can behave similar to a group 17 (halogen family) elements. Because it is a special case, we shell place hydrogen separately at the top of the periodic table.

Isotopes in modern periodic table:

As isotopes of a elements have same atomic number and in modern periodic table the elements have been allotted places based on their atomic number. All the isotopes an elements have been assigned the same position in the modern periodic table.

Solved Examples

Ex-2 An element X with Z = 112 has been recently discovered. What is the electronic configuration of the element ? To which group and period will it belong ?

Sol. (a) The electronic configuration of element X is $[Rn]^{86}\ 5f^{14}\ 6d^{10}7s^2$

(b) It belongs to d-block as last electron enters in d subshell.

(c) As number of electrons in (n – 1)d subshell and valence shell is equal to twelve i.e. 10 + 2. So it belongs to group 12.

(d) It belongs to period 7 of the periodic table as principal quantum number of valence shell is 7 (i.e., $7s^2$).

Metals and nonmetals :

- The metals are characterised by their nature of readily giving up the electron(s) and from shining lustre. Metals comprises more than 78% of all known elements and appear on the left hand side of the periodic table. Metals are usually solids at room temperature (except mercury, gallium). They have high melting and boiling points and are good conductors of heat and electricity. Oxides of metals are generally basic in nature (some metals in their higher oxidation state form acid oxides e.g. CrO_3).
- Nonmetals do not lose electrons but take up electrons to form corresponding anions. Nonmetals are located at the top right hand side of the periodic table. Nonmetals are usually solids, liquids or gases at room temperature with low melting and boiling points. They are poor conductors of heat and electricity. Oxides of nonmetals are generally acidic in nature.

Metalloids (Semi metals) :

- It can be understood from the periodic table that nonmetallic character increases as we move from left to right across a row. It has been found that some elements which lie at the border of metallic and nonmetallic behavior, possess the properties that are characteristic of both metals and nonmetals. These elements are called semi metals or metalloids.
- The metalloids comprise of the elements Si, Ge, As, Sb, Se and Te.
- Oxides of metalloids are generally amphoteric in nature.

Diagonal relationship :

Some elements of certain groups of 2nd period resemble much in properties with the elements of third period of next group i.e. elements of second and third period are diagonally related in properties. This phenomenon is known as diagonal relationship. For example, the similarity between lithium (the first member of group 1) and magnesium (the second element in group 2) is called a diagonal relationship. Diagonal relationship also exist between other pairs of elements Be and Al, B and Si as shown in figure;

$$\begin{tikzcd} 2^{nd}\text{ period} & \text{Li} \arrow[dr] & \text{Be} \arrow[dr] & \text{B} \arrow[dr] & \text{C} \\ 3^{rd}\text{ period} & \text{Na} & \text{Mg} & \text{Al} & \text{Si} \end{tikzcd}$$

Diagonal relationship arises because of ;

(i) on descending a group, the atoms and ions increase in size. On moving from left to right in the periodic table, the size decreases. Thus on moving diagonally, the size remains nearly the same. (Li = 1.23 Å & Mg = 1.36 Å; Li^+ = 0.76 Å & Mg^{2+} = 0.72 Å)

(ii) it is sometimes suggested that the diagonal relationship arises because of diagonal similarity in electronegativity values. (Li = 1.0 & Mg = 1.2; Be = 1.5 & Al = 1.5; B = 2.0 & Si = 1.8)

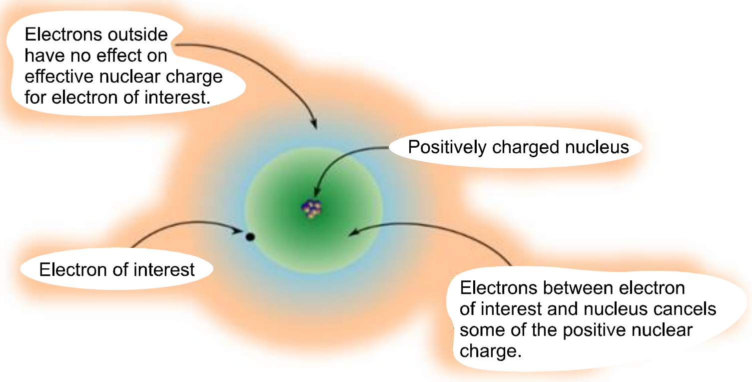
(iii) Be and Al also show a diagonal relationship. In this case sizes are not so close (Be^{2+} = 0.45 Å and Al^{3+} = 0.535 Å) but the charge / ionic radius ratio is nearly similar because the charges are 2+ and 3+ respectively.

$$\text{Charge /Ionic radius ratio} = \frac{(\text{Ionic charge})}{(\text{Ionic radius})}$$

Section (B) : Shielding Effect and Z_{eff}

The periodicity of atomic properties :

(1) Effective nuclear charge (Z_{eff}):



The outer electron experiences two opposing force : -
(i) Force of attraction from nucleus.
(ii) Force of repulsion from inner electrons.
Suppose inner electrons are not present there then force of attraction experience by test electron must be greater than it actually experienced because electronic repulsion weakens the force of attraction. **This reduced nuclear charge or nuclear actually experienced by an electron is termed as effective nuclear charge.**

$Z_{eff} = Z - \sigma$
Z_{eff} = Effective nuclear charge
Z = Atomic number
σ = Screening constant or shielding constant or slater constant

Effective nuclear charge is not same for all the electrons present in an atom and it varies with distance between electron and nucleus.

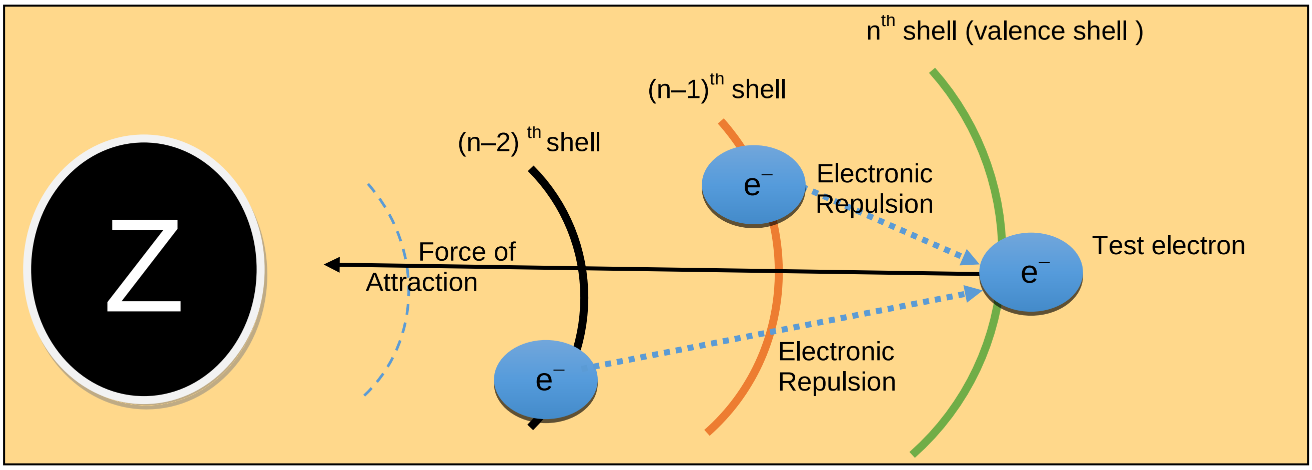
This effect in which inner electrons shield valence electron from the attraction due to nucleus is called shielding effect.

It is also known as screening effect as inner electron create a protective screen between nucleus and valence electrons.

Due to shielding effect valence electron experiences less attraction from the side of nucleus as if inner electrons are absent.

s-orbitals have the largest screening effect for a given n value since s electrons are closer to the nucleus.

Screening effect decreases as s-orbital > p-orbital > d-orbital > f-orbital.



Section (C) : Oxidation states & Inert pair effect

(2) **Oxidation States:**

Definition: The oxidation states (O.S) of an atom in a molecule or in an ion is the (imaginary) charge the atom would have if the electron in each bond were located on the more electronegative atom.

Rule for determining the oxidation state

Fundamental Rule: Sum of oxidation no. of all the atoms of a species is equal to the charge on that species.

e.g. For SO_4^{2-} ion ; (O.N. of S atom) + (O.N. of O atom) × 4 = –2
For C_{60} molecule ; (O.N. of C atom) × 60 = 0
For NO_2^+ ion ; (O.N. of N atom) + (O.N. of O atom) × 2 = +1

Corollary 1: All atoms have oxidation state zero in their elemental state
Eg. Phosphorus atoms in P_4, C atoms in graphite or diamond or fullerenes, O atoms in nascent oxygen [O], diatomic O_2.

Remember: Oxidation state of uncombined element is zero.

Corollary 2: Charge on any monoatomic ion is equal to its oxidation state.

Note : Oxidation state is often imagined as charge on the atom. In an ionic species this idea work very well. In a covalent molecule, the electrons involved in bonding are considered to belong entirely to the more electronegative species (i.e. it is assumed to be entirely ionic).

Caution: This is just an imagination, not the real picture.

Other Rules: In species when the following are combined with dissimilar atom(s) their O.No. is

(i) F atom: –1 ; alkali metals : +1 ; alkaline earth metals : +2; Al, Ga : +3 No exception.

(ii) H is mostly: +1, Exception: Hydrides of metals mentioned in (i) Where it's O.N is –1.

(iii) O is mostly: –2, exceptions, (a) in peroxides (b) when in conflict with rules (i) and (ii) e.g. in peroxides like BaO_2 , Ba is fixed as + 2. If we assume O as –2, Ba will have to assume a charge of +4 which is not permissible [Since Rule (i) has more weightage than rule (ii) or (iii)]. Hence, Ba must have a charge of +2. Accordingly, we must adjust oxygen. Naturally we have O_2^{2-}, this is immediately identified as our familiar peroxide ion. Naturally oxidation number of each atom is –1 in this case. Similarly O atom is +1 or +2 with fluorine in O_2F_2 and OF_2.

(iv) N is mostly: –3 e.g. in ammonia or ammonium ion e.g. in CN^-, we can simply assume N as –3 and move a head. Accordingly, C will be +2 (Check it for yourself by fundamental rule). Exceptions : When in conflict with rule (i) (iii) eq. N +3 in NF_3 (since F must be –1) and +5 in NO_3^- (since O must be –2).

(v) Cl, Br and I are usually –1 e.g. in halides.

Exceptions: When is conflict with rules (i)-(iv). Amongst halogens, the reactivity order is Cl > Br > I e.g. in ICl, Cl is regarded as –1. Naturally, I must adjust itself as +1. $BrCl_3$ Br is + 3 since Cl must be –1. However, is Cl_2O, Cl must adjust to +1 state. Since O should preferably be –2.

Interestingly, in a case like $POCl_3$, both O and Cl can have their desirable state of –2 and –1 respectively. In this case, P must adjust as per the convenience of O and Cl atoms (which have higher priority i.e. higher electonegativity).

(vi) S is –2 in sulphides. If however, can have higher oxidation state, highest being equal to the group no. (i.e. 6)

(vii) Metal usually do not exhibit negative oxidation states. **Exceptions:** Gold is sometimes found in –1.

Remember: Non-stoichiometric compounds always have metal cation in at least two different oxidation state.

Average oxidation number: A given element may be present in more than one oxidation states within a given molecule if more than one atoms of the element are present.

e.g. NH_4NO_2 contain N atom in NH_4^+ ion as well as NO_2^- ion. Try finding their oxidation state separately. In NH_4^+ ion, N is present in –3 oxidation state and in NO_2^- ion N is present in +3 oxidation state. Else, even if you consider the average state of N atom in the compound, it comes out to be [{(+3) + (–3)}/2] that is 0.

(3) Inert Pair Effect :

The outer shell ‘s’ electrons (ns^2) penetrate to (n–1)d electrons and thus become closer to nucleus and are more effectively pulled towards the nucleus. This results in less availability of ns^2 electron pair for bonding or ns^2 electron pair becomes inert. This is called Inert Pair Effect. The inert pair effect begins after $n \geq 4$ and increases with increasing value of n. This can be thought as a reason for two different oxidation states, normal and (normal – 2), among elements of Boron, Carbon and Nitrogen family.

In these families, the stability of higher oxidation state decreases while that of lower oxidation state increases on moving down the group.

Eg. $Ga^{3+} > In^{3+} > Tl^{3+}$; $Ga^+ < In^+ < Tl^+$
$Ge^{4+} > Sn^{4+} > Pb^{4+}$; $Ge^{2+} < Sn^{2+} < Pb^{2+}$
$As^{5+} > Sb^{5+} > Bi^{5+}$; $As^{3+} < Sb^{3+} < Bi^{3+}$

Thats why, Pb^{4+} and Bi^{5+} compounds are strong oxidising agents. However the last elements of the group do form compounds in oxidation state, but only with highly electronegative higher elements like F and O.

So compounds like TlF_3, Tl_2O_3, PbF_4, $PbCl_4$, BiF_5, $NaBiO_3$ exist in nature while compounds like PbI_4, $PbBr_4$, BiI_5, $BiBr_5$, $BiCl_5$ etc do not exist. TlI_3 exists exceptionally as $Tl^+(I_3)^-$.

Table-3

List of common oxidation sate of an element in Periodic Table

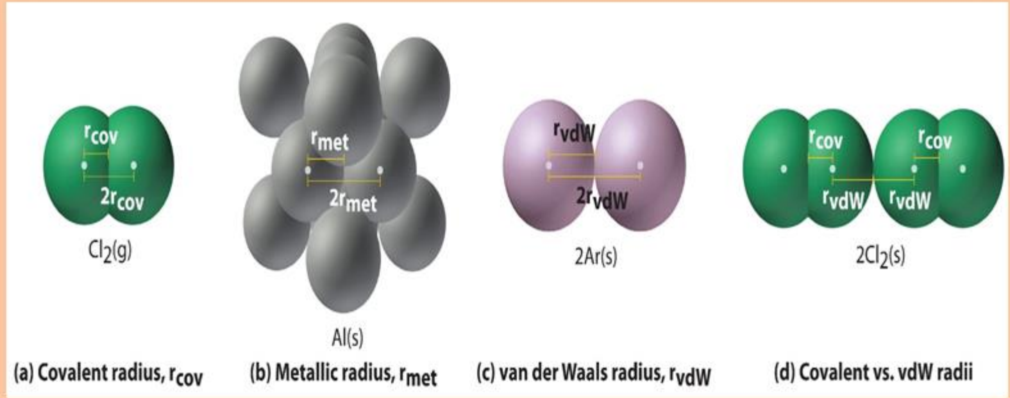
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H **+1** –1																	2 **He**
3 Li +1	3 Be +2											5 **B** **+3** –3	6 **C** **+4** +2 –4 etc.	7 **N** +5 +4 +3 +1 –3 **0** etc.	8 **O** +2 – 1/2 –1 **–2**	9 **F** **–1**	10 **Ne**
11 Na +1	12 Mg +2											13 **Al** +3	14 **Si** **+4** –4	15 **P** **+5** +3 +1 –3	16 **S** **+6** +4 +2 –2	17 **Cl** +7 +5 +3 +1 0 **–1**	18 **Ar** **0**
19 **K** +1	20 **Ca** +2	21 **Sc** +2 **+3**	22 **Ti** +2 **+3** **+4**	23 **V** +2 **+3** +4 +5	24 **Cr** +2 **+3** +4 +5 +6	25 **Mn** **+2** +3 **+4** +5 +6 +7	26 **Fe** **+2** +3 +4 +5 +6	27 **Co** **+2** +3 +4 +5	28 **Ni** **+2** +3 +4	29 **Cu** **+1** +2	30 **Zn** **+2**	31 **Ga** +3	32 **Ge** **+4** –4	33 **As** **+5** **+3** –3	34 **Se** **+6** +4 –2	35 **Br** +7 +5 +3 +1 **–1**	36 **Kr** +4 +2 **0**
37 **Rb** +1	38 **Sr** +2											49 **In** **+3** +1	50 **Sn** **+4** +2	51 **Sb** **+5** **+3** –3	52 **Te** **+6** +4 –2	53 **I** +7 +5 +3 +1 **0** **–1**	54 **Xe** +8 +6 +4 +2 **0**
55 **Cs** +1	56 **Ba** +2											81 **Tl** +3 **+1**	82 **Pb** +4 **+2**	83 **Bi** +5 **+3**	84 **Po**	85 **At**	86 **Rn**

* **Bold mark oxidation number are general stable oxidation number of an element in compound state.**

Section (D) : Atomic and Ionic radius

(4) Atomic radius :

It is distance between outermost electron and nucleus.

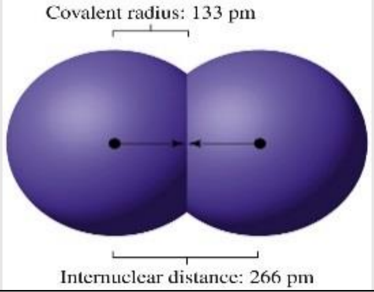


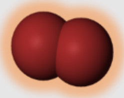
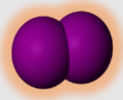
(a) Covalent radius, r_{cov} (b) Metallic radius, r_{met} (c) van der Waals radius, r_{vdW} (d) Covalent vs. vdW radii

X-ray diffraction, electron diffraction method and nuclear magnetic resonance (NMR) spectrum methods are used to determine internuclear distance or bond length.

Atomic radius depends on the type of chemical bond between atoms in a molecule. These are :

1. Covalent radius 2. Ionic radius 3. Metallic radius 4. Vander waal's radius

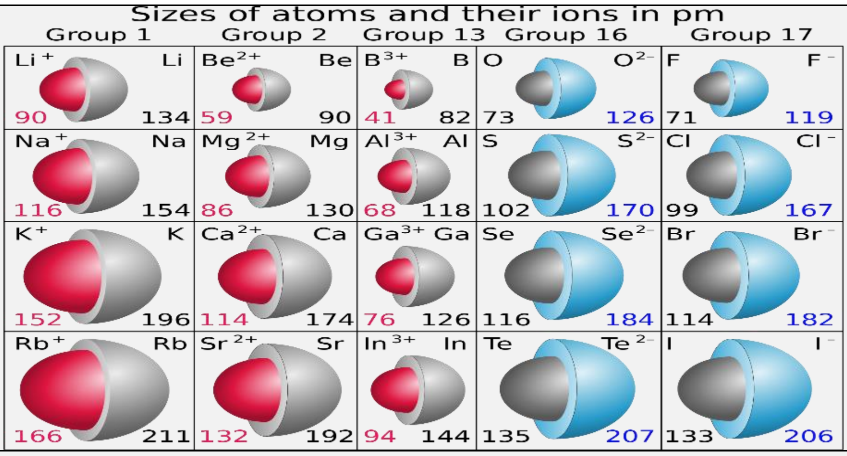
S.No.	Type of radius	DISCRIPTION
1.	**Covalent radius** SBCR(Single Bonded Covalent Radius)	 Covalent radius is calculated in covalent compounds. Covalent compound's form covalent bonds. Covalent bonds are formed by overlapping of atomic orbitals. Type of Covalent radius.

Halogen	Molecule	Structure	Model	*d*(X−X) / pm (gas phase)	*d*(X−X) / pm (solid phase)
Fluorine	F_2	F — F ⟷ 143pm		143	149
Chlorine	Cl_2	Cl — Cl ⟷ 199pm		199	198
Bromine	Br_2	Br — Br ⟷ 228pm		228	227
Iodine	I_2	I — I ⟷ 266pm		266	272

	(i) In Homo	Covalent radius is the one-half of the internuclear distance between two singly

<table>
<tr><td></td><td>atomic Molecules</td><td>bonded two nuclei (of like atoms).</td></tr>
<tr><td></td><td></td><td>Internuclear distance of A–A(A_2) molecule is (d_{A-A}) and covalent radius is r_A then
$d_{A-A} = r_A + r_A \Rightarrow d_{A-A} = 2r_A$
$\boxed{r_A = \frac{d_{A-A}}{2}}$</td></tr>
<tr><td></td><td></td><td>e.g. – In Cl_2 molecule, internuclear distance is 1.98 Å so $r_{Cl} = \frac{1.98}{2} = 0.99$ Å</td></tr>
<tr><td></td><td></td><td>SBCR of O, N and C etc. elements can be determined by taking H_2O_2, N_2H_4, C_2H_6 respectively.</td></tr>
<tr><td></td><td>(ii) Hetero atomic molecule</td><td>(a) For Hetero atomic molecule with not E.N. difference.
$\boxed{d_{A-B} = r_A + r_B}$</td></tr>
<tr><td></td><td></td><td>Example : For A–B molecule Electronegativities of A and B are approximately equal e.g. C–I E.N. of C and I are approx equal (2.5) internuclear distance of C–I is 2.13Å and r_C is 0.77Å.
Solution : $d_{C-I} = r_C + r_I \therefore r_I = 2.13 - 0.77 = 1.36$Å</td></tr>
<tr><td></td><td></td><td>(b) Heteroatomic molecule with Δ E.N. difference more</td></tr>
<tr><td></td><td></td><td>If in a diatomic molecule electronegativities of A–B have more difference. Then actual bond length will be reduced.</td></tr>
<tr><td>2.</td><td>Ionic Radius</td><td></td></tr>
<tr><td></td><td>(i) Cationic radius</td><td>When an neutral gaseous atom loses electron it converts into cation.
Radius = Atomic radius > Cationic radius</td></tr>
<tr><td></td><td></td><td>Reason: After loosing electron number of electron reduces, but number of protons remains same, due to this Z_{eff} increases, hence electrons pulls towards nucleus and atomic radius decreases, moreover after losing all the electrons from the outer most shell, penultimate shell becomes ultimate shell which is nearer to nucleus so size decreases.</td></tr>
<tr><td></td><td></td><td>$\boxed{\text{Size of cation} \propto \frac{1}{\text{Magnitude of +ve charge or } Z_{eff}}}$</td></tr>
<tr><td></td><td></td><td>Example
Size of cation = Fe > Fe^{+2} > Fe^{+3}
Size of cation = Pb^{+2} > Pb^{+4}
Size of cation = Mn > Mn^{+2} > Mn^{+3} > Mn^{+4} > Mn^{+5} > Mn^{+6} > Mn^{+7}</td></tr>
<tr><td></td><td>(ii) Anionic radius</td><td>When neutral gaseous atom gains electron it converts into anion.
Radius = Anionic radius > Atomic radius</td></tr>
<tr><td></td><td></td><td>Reason: In an anion electron are more than protons so effective nuclear charge reduces, and inter electronic repulsion increases, which also increases screening effect. So distance between electron and nucleus increases and size of anion also increases.</td></tr>
<tr><td></td><td></td><td>$\boxed{\text{Size of anion} \propto \text{Magnitude of} - \text{ve charge}}$</td></tr>
<tr><td></td><td></td><td>Example : Size of F^- > F why ?
Sol.
<table>
<tr><th></th><th>F</th><th>F^-</th></tr>
<tr><td>Proton</td><td>9</td><td>9</td></tr>
<tr><td>electron</td><td>9</td><td>10</td></tr>
<tr><td>$\frac{Z}{e^{\ominus}}$</td><td>$\frac{9}{9} = 1$</td><td>$\frac{9}{10} = 0.9$</td></tr>
</table>
As Z_{eff} of F^- is less than F so size of F^- > F</td></tr>
</table>

(iii) Size of iso electronic species



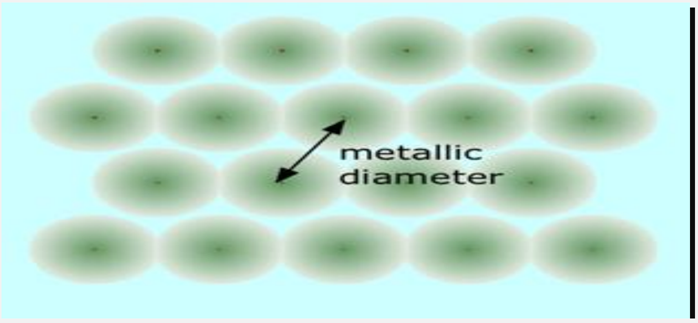
					H^-	He
Li^+	Be^{+2}		N^{3-}	O^{2-}	F^-	Ne
Na^+	Mg^{+2}	Al^{+3}		S^{2-}	Cl^-	Ar
K^+	Ca^{+2}	Sc^{+3}		Se^{2-}	Br^-	Kr
Rb^+	Sr^{+2}	Y^{+3}		Te^{2-}	I^-	Xe
Cs^+	Ba^{+2}	La^{+3}				

Those species having same number of electron but different nuclear charge forms isoelectronic series.
For isoelectronic species the atomic radius increases with decrease in nuclear charge.

Ions	**K^+**	**Ca^{2+}**	**S^{2-}**	**Cl^-**
Atomic number	19	20	16	17
electron	18	18	18	18

Example
Order of radius = $S^{2-} > Cl^- > K^+ > Ca^{2+}$
Order of radius = $P^{3-} > S^{2-} > Cl^-$
Order of radius = $N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$
Order of radius = $Au^+ > Hg^{2+} > Tl^{3+} > Pb^{4+}$

3. **Metallic radius**



It is one-half of the nuclear distance between two adjacent metallic atoms in crystalline lattice structure.
so metallic radius > Covalent radius.

$$\text{Metallic radius} \propto \frac{1}{\text{Metallic bond strength}}$$

More metallic radius → loose crystal packing → less bond strength (body centered packing)

Less metallic radius → tight crystal packing FCC → High bond strength
(Hexagonal close packing)

4. **Van der Waal's**

Those atoms (like noble gases) which are not bonded with each other, experiences a weak attractive force to come nearer.

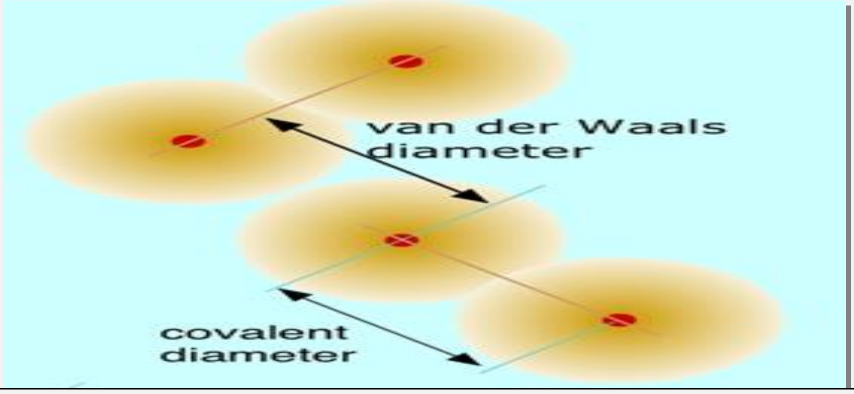
	radius	The half of the distance between the nuclei of adjacently placed atoms in solid state of a noble gas is Vander Waal's radius.
		Vander Waal radius > Covalent radius.
		Inert gas have only Vander Waal radius
		In molecules of nonmetals both covalent and Vander Waal radius exists. 
		Radius = Vander Waal radius > Metallic Radius > Covalent Radius
		Van der waal force of attraction $\propto$ Molecular weight OR atomic weight (in inert gases)
		In a period from left to right Vander Waal radius decreses. In a group from top to bottom its values increases.
5.	**Factors affecting atomic size**	
	(i) Effective nuclear charge	Atomic radius $\propto \frac{1}{\text{Effective nuclear charge}}$ **Example** Li > Be > B > C > N > O > F
	(ii) Number of shells	Atomic radius $\propto$ No. of shells **Example** Li < Na < K < Rb < Cs
	(iii) screening effect	Atomic radius $\propto$ Screening effect
	(iv) Magnitude of +ve charge	Atomic radius $\propto \frac{1}{\text{Magnitude of + ve charge}}$ **Example** Mn > Mn^{+2} > Mn^{+3} > Mn^{+4}
	(v) Magnitude of -ve charge	Atomic radius $\propto$ Magnitude of – ve charge **Example** O < O^{-} < O^{-2}
	(vi) Bond order	Atomic radius $\propto \frac{1}{\text{Bond order}}$ **Example** N–N > N=N > N≡N

Table-4

Variation in a Period (left to right) :	**Variation in a Group (top to bottom) :**
Nuclear charge (Z) increases by one unit	Nuclear charge (Z) increases by more than one unit
Effective nuclear charge (Z_{eff}) also increases	Effective nuclear charge (Z_{eff}) almost remains constant because of increased screening effect of inner shells electrons.
But number of orbitals (n) remains constant	But number of orbitals (n) increases.
As a result, the electrons are pulled closer to the nucleus by the increased Z_{eff}. $r_n \propto \frac{1}{Z*}$ Hence atomic radii decrease with increase in atomic number in a period from left to right.	The effect of increased number of atomic shells overweighs the effect of increased nuclear charge. As a result of this the size of atom increases from top to bottom in a given group.

Irregularties

- In the transition series (e.g. in first transition series), the covalent radii of the elements decrease from left to right across a row until near the end when the size increases slightly. On passing from left to right, extra protons are placed in the nucleus and the extra electrons are added. The orbital electrons shield the nuclear charge incompletely. Thus the nuclear charge attracts all the electrons more strongly, hence a contraction in size occurs. The radii of the elements from Cr to Cu, are very close to one another because the successive addition of d-electrons screen the outer electrons (4s) from the inward pull of the nucleus. As a result of this, the size of the atom does not change much in moving from Cr to Cu.

Table-5

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radius (pm)	144	132	122	117	117	117	116	115	117	125

- The elements of group 3 belonging to d-block show the expected increase in size as that found in case of s-block and p-block elements. However, in the subsequent groups that is 4th onwards (upto 12th group), there is increase in size between the first and second member, but hardly any increase between the second and third elements of the given group. There are 14 lanthanide elements between lanthanum and hafnium, in which the antepenultimate 4f shell of electrons (exert very poor shielding effect) is filled. There is a gradual decrease in size of the 14 lanthanide elements from cerium to lutetium. This is called lanthanide contraction. This lanthanide contraction cancels out the normal size increase on descending a group in case of transition elements.

Solved Examples

Ex-3 Atomic radius of Li is 1.23 Å and ionic radius of Li^+ is 0.76 Å. Calculate the percentage of volume occupied by single valence electron in Li.

Sol. Volume of Li = $\frac{4}{3} \times 3.14 \times (1.23)^3 = 7.79$ Å^3 ($-Li = 1s^2 2s^1$)

Volume of Li^+ = $\frac{4}{3} \times 3.14 \times (0.76)^3 = 1.84$ Å^3 ($-Li^+ = 1s^2$)

$\therefore$ Volume occupied by 2s subshell = 7.79 – 1.84 = 5.95 Å^3.

$\therefore$ % Volume occupied by single valence electron i.e., 2s electron = $\frac{5.95}{7.79} \times 100 = 76.4\%$

Ex-4 Select from each group the species which has the smallest radius stating appropriate reason.
(a) O, O^-, O^{2-} (b) P^{3+}, P^{4+}, P^{5+}

Sol. (a) O is having smallest radius. Anion is larger than its parent atom. Also the anion of the same atom with higher negative charge is bigger in size as compared to anion with smaller negative charge as proton to electron ratio decreases thus attraction between valence shell electrons and nucleus decreases. Hence electron cloud expands.

(b) The ionic radius decreases as more electrons are ionized off that is as the valency increases. So the correct order is $P^{5+} < P^{4+} < P^{3+}$.

Ex-5 Mg^{2+} is smaller than O^{2-} in size, though both have same electronic configuration. Explain ?

Sol. Mg^{2+} and O^{2-} both are isoelectronic i.e., have same number of electrons. But Mg^{2+} having 12 protons in its nucleus exerts higher effective nuclear charge than O^{2-} having 8 protons and thus valence shell as well as inner shells electrons are more strongly attracted by the nucleus in Mg^{2+} resulting smaller size than O^{2-}.

Section (E) : Ionisation energy

(5) Ionisation Energy :

Ionisation energy (IE) is defined as the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom to form a cation.

$$M(g) \xrightarrow{(IE_1)} M^+(g) + e^- \quad ; \qquad M^+(g) + IE_2 \longrightarrow M^{2+}(g) + e^-$$

$$M^{2+}(g) + IE_3 \longrightarrow M^{+3}(g) + e^-$$

IE_1, IE_2 & IE_3 are the I^{st}, II^{nd} & III^{rd} ionization energies to remove electron from a neutral atom, monovalent and divalent cations respectively.

In general, $(IE)_1 < (IE)_2 < (IE)_3 <$ .... because, as the number of electrons decreases, the attraction between the nucleus and the remaining electrons increases considerably and hence subsequent ionization energies increase.

♦ Ionization energies are determined from spectra and are measured in kJ mol^{-1}, k Cal mol^{-1}, eV (electron volt).

♦ **Factors Influencing Ionisation energy**

Variation in ionization energies in a period and group may or not be regular and can be influenced by the following factors.

(A) Size of the Atom : Ionisation energy decreases with increase in atomic size.

As the distance between the outer most electrons and the nucleus increases, the force of attraction between the valence shell electrons and the nucleus decreases. As a result, outer most electrons are held less firmly and lesser amount of energy is required to knock them out.

For example, ionisation energy decreases continuously in a group from top to bottom with increase in atomic size. But in 13th & 14th group the ionisation energy does not decrease continuously and order is as follows:

For 13th group: B > Tl > Ga > Al > In

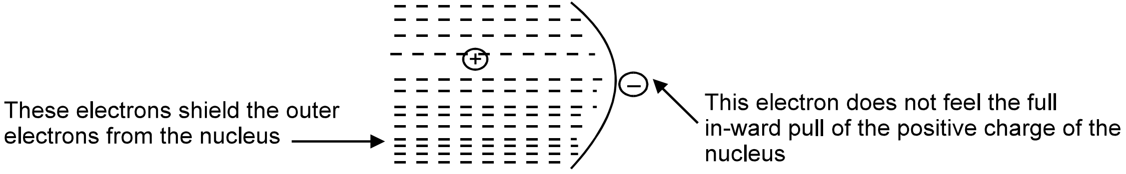
For 14th group: C > Si > Ge > Pb > Sn

(B) Nuclear Charge : The ionisation energy increases with increase in the nuclear charge.

This is due to the fact that with increase in the nuclear charge, the electrons of the outer most shell are more firmly held by the nucleus and thus greater amount of energy is required to pull out an electron from the atom.

For example, ionisation energy increases as we move from left to right along a period due to increase in nuclear charge.

(C) Shielding or screening effect : The electrons in the inner shells act as a screen or shield between the nucleus and the electrons in the outer most shell. This is called shielding effect. The larger the number of electrons in the inner shells, greater is the screening effect and smaller the force of attraction and thus ionization energy (IE) decreases.



(D) Penetration effect of the electron : The ionization energy also depends on the type of electron which is removed. s, p, d and f electrons have orbitals with different shapes. An s electron penetrates closer to the nucleus, and is therefore more tightly held than a p electron. Similarly p-orbital electron is more tightly held than a d-orbital electron and a d-orbital electron is more tightly held than an f-orbital electron. If other factors being equal, ionisation energies are in the order s > p > d > f.

For example, ionisation energy of aluminium is comparatively less than magnesium because outer most electron is to be removed from 3p-orbital (having lesser penetration effect) in aluminium where as in magnesium it will be removed from 3s-orbital (having larger penetration effect) of same energy level.

(E) Electronic Configuration:

If an atom has exactly half-filled or completely filled orbitals, then such an arrangement has extra stability.

The removal of an electron from such an atom requires more energy then expected. For example, first ionisation energy of beryllium is greater than boron because beryllium has extra stable outer most completely filled outer most 2s orbital while boron has partially filled less stable outer most 2p-orbital.

Be (Z = 4) $1s^2, 2s^2$ B (Z = 5) $1s^2, 2s^2, 2p^1$

Similarly noble gases have completely filled electronic configurations and hence they have highest ionisation energies in their respective periods.

- Metallic or electropositive character of elements increases as the value of ionisation energy decreases.
- The relative reactivity of the metals in gaseous phase increases with the decrease in ionisation energy.
- The reducing power of elements in gaseous phase increases as the value of ionisation energy decreases. Amongst alkali metals, the lithium is strongest reducing agent in aqueous solution.

Solved Examples

Ex-6 From each set, choose the atom which has the largest ionization enthalpy and explain your answer with suitable reasons. (a) F, O, N (b) Mg, P, Ar

Sol. (a) Fluorine (F) has the largest ionization enthalpy because in moving from left to right in a period, atomic size decreases and electrons are held more tightly. Since F has the smallest size and maximum nuclear charge. It has the largest ionization enthalpy among these elements.

(b) Argon (Ar) has the largest ionization enthalpy as argon has extra stable fully filled configuration.

Ex-7 First and second ionisation energies of magnesium are 7.646 eV and 15.035 eV respectively. The amount of energy in kJ needed to convert all the atoms of magnesium into Mg^{2+} ions present in 12 mg of magnesium vapour will be ? [Given 1 eV = 96.5 kJ ml^{-1}].

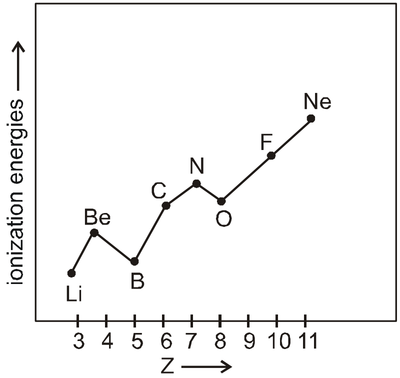
Sol. Total energy needed to convert one Mg atom into Mg^{2+} gas ion,

$= IE_I + IE_{II} = 22.681$ eV = 2188.6 kJ mol^{-1}.

$\Rightarrow$ 12 mg of Mg = 0.5×10^{-3} mole.

$\therefore$ Total energy = $0.5 \times 10^{-3} \times 2188.6 = 1.0943$ kJ **Ans.**

Ex-8 Following graph shows variation of ionization energies with atomic number in second period (Li–Ne). Value of ionization energies of Na(11) will be :



(A) above Ne (B) below Ne but above O.
(C) below Li (D) between N and O.

Sol. Na is 3rd period element and is bigger than Li. The distance between the nucleus and outer most electron is more as compared to Li. Thus the outer most electron is loosely bound with nucleus and removal of electron is easier. So option (C) is correct.

Ex-9 $M(g) \longrightarrow M^+(g) + e^-$; $\Delta H = 100$ eV.
$M(g) \longrightarrow M^{2+}(g) + 2e^-$; $\Delta H = 250$ eV.
Which is/are correct statement(s) ?
(A) IE_1 of M(g) is 100 eV (B) IE_1 of M^+ (g) is 150 eV.
(C) IE_2 of M(g) is 250 eV. (D) IE_2 of M(g) is 150 eV.

Sol. $M(g) \longrightarrow M^+(g) + e^-$ IE_1 of M
$M^+ \longrightarrow M^{2+} + e^-$ IE_2 of M but IE_1 of M^+
$M \longrightarrow M^{2+} + 2e^-$ $(IE_1 + IE_2)$. **Ans.** (A,B,D)

Section (F) : Electron gain enthalpy

(6) Electron Affinity:

Electron affinity is conventionally defined as the energy released when an electron is added to the valence shell of an isolated gaseous atom.

$$F + e^- \longrightarrow F^- \quad E_a = 328 \text{ kJ mol}^{-1}$$

A positive electron affinity indicates that the ion X^- has a lower, more negative energy than the neutral atom X. The second electron gain enthalpy, the enthalpy change for the addition of a second electron to an initially neutral atom, invariably positive because the electron repulsion out weighs the nuclear attraction.

$$O(g) + e–(g) \xrightarrow{\text{Exothermic}} O^-(g) \; ; \qquad E_a = 140.9 \text{ kJ mol}^{-1} \; ; \Delta_{eg}H^{\ominus} = – 140.9 \text{ kJ mol}^{-1}$$

$$O–(g) + e–(g) \xrightarrow{\text{Endothermic}} O^{2-}(g) \; ; \qquad E_a = – 744 \text{ kJ mol}^{-1} \; ; \Delta_{eg}H^{\ominus} = 744 \text{ kJ mol}^{-1}$$

An element has a high electron affinity if the additional electron can enter a shell where it experiences a strong effective nuclear charge.

The electron gain enthalpy $\Delta_{eg}H^{\ominus}$, is the change in standard molar enthalpy when a neutral gaseous atom gains an electron to form an anion.

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

Now a days both electron affinity and electron gain enthalpy terms are used.

Both are same in magnitude but opposite in sign.

E.A. = +ve (Exothermic):– $\Delta_{eg}H^{\ominus} < 0$.

E.A. = –ve (Endothermic):– $\Delta_{eg}H^{\ominus} > 0$.

The units of EA and Electron gain enthalpy are ev/atom or Kcal / mole or KJ / Mole.

Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion. Electron gain may be either exothermic or endothermic depending on the elements.

When an electron is added to the atom and the energy is released, the electron gain enthalpy is negative and when energy is needed to add an electron to the atom, the electron gain enthalpy is positive.

Although the electron gain enthalpy is the thermodynamically appropriate term, much of inorganic chemistry is discussed in terms of a closely related property, the electron affinity, E_a of an element which is the difference in energy between the gaseous atoms and the gaseous ions.

$$E_a = E(X, g) – E(X^-, g)$$

- Group 17 elements (halogens) have very high negative electron gain enthalpies (i.e. high electron affinity) because they can attain stable noble gas electronic configuration by picking up an electron.
- Across a period, with increase in atomic number, electron gain enthalpy becomes more negative because left to right across a period effective nuclear charge increases and consequently it will be easier to add an electron to a small atom.
- As we move in a group from top to bottom, electron gain enthalpy becomes less negative because the size of the atom increases and the added electron would be at larger distance from the nucleus.

In general the electron gain enthalpies for some third period element (e.g. P, S, Cl) are more negative than the corresponding second period members (e.g. N, O, F). This is due to the smaller size of the atoms of the second period elements which would produced larger electron-electron repulsions for the additional electron.

Group 1	**$\Delta_{e.g.}$ H**	**Group 16**	**$\Delta_{e.g.}$ H**	**Group 17**	**$\Delta_{e.g.}$ H**	**Group 0**	**$\Delta_{e.g.}$ H**
H	–73					He	+48
Li	–60	O	–141	F	–328	Ne	+116
Na	–53	S	–200	Cl	–349	Ar	+96
K	–48	Se	–195	Br	–325	Kr	+96
Rb	–47	Te	–190	I	–295	Xe	+77
Cs	–46	Po	–174	At	–270	Rn	+68

- Noble gases have large positive electron gain enthalpies because the electron has to enter the next higher energy level leading to a very unstable electronic configuration.
- Negative electron gain enthalpy of O or F is less than S or Cl. This is due to the fact that when an electron is added to O or F, the added electron goes to the smaller n = 2 energy level and experiences

significant repulsion from the other electrons present in this level. In S or Cl, the electron goes to the larger n = 3 energy level and consequently occupies a larger region of space leading to much less electron-electron repulsion.

- ❍ Electron gain enthalpies of alkaline earth metals are very less or positive because the extra electron is to be added to completely filled s-orbitals in their valence shells.
- ❍ Nitrogen has very low electron affinity because there is high electron repulsion when the incoming electron enters an orbital that is already half filled.
- ❍ (i) Electron affinity $\propto \frac{1}{\text{Atomic size}}$

  (ii) Electron affinity $\propto$ Effective nuclear charge (z_{eff})

  (iii) Electron affinity $\propto \frac{1}{\text{Screening effect}}$

  (iv) Stability of half filled and completely filled orbitals of a subshell is comparatively more and the addition of an extra electron to such an system is difficult and hence the electron affinity value decreases.

Solved Examples

Ex-10 Consider the elements N, P, O and S and arrange them in order of increasing negative electron gain enthalpy.

Sol. Order of increasing negative electron gain enthalpy is N < P < O < S. For detail refer text.

Ex-11 Why do halogens have high electron gain enthalpies (i.e. $-\Delta_{eg}H^{\ominus}$) ?

Sol. The valence shell electronic configuration of halogens is ns^2np^5 and thus they require one electron to acquire the stable noble gas configuration ns^2np^6. Because of this they have strong tendency to accept an additional electron and hence have high electron gain enthalpies.

Ex-12 Which will have the maximum value of electron affinity O^x ,O^y, O^z [x, y and z respectively are 0, –1 and –2] ?

(A) O^x (B) O^y (C) O^z (D) All have equal.

Sol. Being neutral atom oxygen will have higher electron affinity as there is electrostatic repulsion between additional electron and negative ion in case of O^- and O^{2-}. So option (A) is correct.

Ex-13 The amount of energy when million atoms of iodine are completely converted into I^- ions in the vapour state according to the equation, $I(g) + e^-(g) \rightarrow I^-(g)$ is 5.0×10^{-13} J.

Calculate the electron gain enthalpy of iodine in terms of kJ mol^{-1} and eV per atom.

Sol. The electron gain enthalpy of iodine is equal to the energy released when 1 mole of iodine atoms in vapour state are converted into I^- ions.

$$= -\frac{5.0\times10^{-13}\times6.023\times10^{23}}{10^6} = -30.1 \times 10^4 \text{ J} = -301 \text{ kJ}.$$

Electron gain enthalpy of iodine in eV per atom = $\frac{-301}{96.5} = -3.12$.

Ex-14 Account for the large decrease in electron affinity between Li and Be despite the increase in nuclear charge.

Sol. The electron configurations of Li and Be are $[He]2s^1$ and $[He]2s^2$, respectively. The additional electron enters the 2s orbital of Li but the 2p orbital of Be and hence is much less tightly bound. In fact, the nuclear charge is so well shielded in Be that electron gain is endothermic.

Section (G) : Electronegativity

(7) Electronegativity:

Electronegativity is a measure of the tendency of an element to attract shared electrons towards itself in a covalently bonded molecules.

The magnitude of electronegativity of an element depends upon its ionisation potential & electron affinity. Higher ionisation potential & electron affinity values indicate higher electronegativity value.

- With increase in atomic size the distance between nucleus and valence shell electrons increases, therefore, the force of attraction between the nucleus and the valence shell electrons decreases and hence the electronegativity values also decrease.
- With increase in nuclear charge force of attraction between nucleus and the valence shell electrons increases and, therefore, electronegativity value increases
- In higher oxidation state, the element has higher magnitude of positive charge.
  Thus, due to more positive charge on element, it has higher polarising power.
  Hence with increase in the oxidation state of element, its electronegativity also increases.
  Charge on cation α electronegativity of the atom.
- The electronegativity also increases as the s-character in the hybrid orbitals increases.

Hybrid orbital	sp^3	sp^2	sp
s-character	25%	33%	50%

⟶

Electronegativity increases

Electronegativity of some elements according to pauling scale.

Elements	H	Li	Be	B	C	N	O	F	Ne	P	S	Cl	Br	I
Electronegativity	2.1	1.0	1.5	2.0	2.5	3.0	3.5	4.0	0.9	2.1	2.5	3.0	2.8	2.5

Table-6

Variation of electronegativity in a group	Variation of electronegativity in a period
On moving down the groups, Z increases but Z_{eff} almost remains constant, number of shells (n) increases, r_n (atomic radius) increases. Therefore, electronegativity decreases moving down the groups.	While moving across a period left to right, Z, Z_{eff} increases & r_n decreases. Therefore, electronegativity increases along a period.

There is no direct method to measure the value of electronegativity, however, there are some scales to measure its value.

(a) **Pauling's scale :** Linus Pauling developed a method for calculating relative electronegativities of most elements. According to Pauling

$$\Delta = X_A - X_B = 0.208\sqrt{E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}}\ ^{*}$$

E_{A-B} = Bond enthalpy/ Bond energy of A – B bond.

E_{A-A} = Bond energy of A – A bond

E_{B-B} = Bond energy of B – B bond

(All bond energies are in kcal / mol)

$$\Delta = X_A - X_B = 0.1017\sqrt{E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}}\ ^{*}$$ All bond energies are in kJ / mol.

(b) **Mulliken's scale :** Electronegativity χ (chi) can be regarded as the average of the ionisation energy (IE) and the electron affinity (EA) of an atom (both expressed in electron volts).

$$\chi_M = \frac{IE + EA}{2}$$

[Paulings's electronegativity χ_P is related to Mulliken's electronegativity χ_M as given below.

$$\chi_P = 1.35\,(\chi_M)^{1/2} - 1.37$$

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

* Only for reference, student need not memorize it.

APPLICATION OF ELECTRONEGATIVITY :

(a) **Nomenclature :**

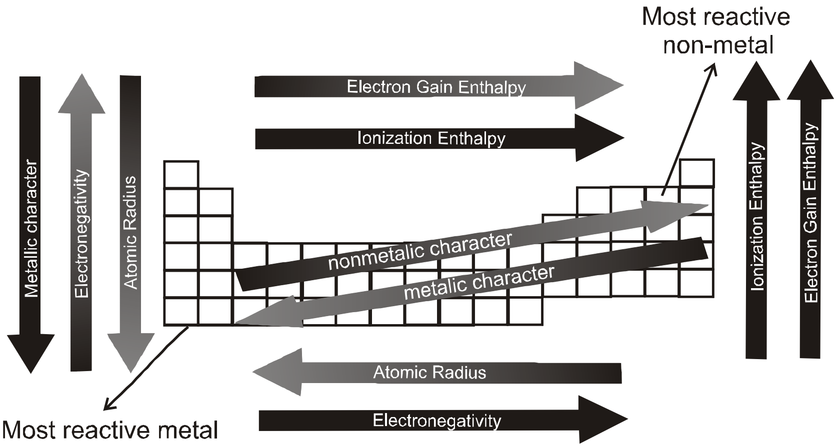
Compounds formed from two nonmetals are called binary compounds. Name of more electronegative element is written at the end and 'ide' is suffixed to it. The name of less electronegative element is written before the name of more electronegative element of the formula. For example -

Correct formula	Name
(a) $I^+ Cl^-$	Iodine chloride
(b) $Cl^+ F^-$	Chlorine fluoride
(c) $Br^+ Cl^-$	Bromine chloride
(d) IBr	Iodine bromide
(e) OF_2	Oxygen difluoride
(f) Cl_2O	Dichlorine oxide

(b) **Effect on bond length:** When the Δ EN increases between two atoms in a molecule then bond length between that atoms decreases.

Order of Δ EN:– HF > HCl > HBr > HI

Order of bond length:– HF < HCl < HBr < HI



MISCELLANEOUS SOLVED PROBLEMS

1. A M^{2+} ion derived from a metal in the first transition metal series has four electrons in 3d subshell. What element might M be ?

Ans. Chromium

Sol. Electron configuration of M^{2+} is : $[Ar]^{18}\,4s^0\,3d^4$

$\therefore$ Electron configuration of M is : $[Ar]^{18}\,4s^1\,3d^5$ (and not $4s^2\,3d^4$)

So total number of electrons = 24.

Hence, metal M is chromium (Cr).

2. Following are the valence shell electronic configurations of some elements.

(i) $3s^2\,3p^5$ (ii) $3d^{10}\,4s^2$ (iii) $2s^2\,3p^6\,4s^1$ (iv) $1s^2\,2s^2$

Find out the blocks to which they belong in the periodic table ?

Ans. (i) p-block (ii) d-block (iii) s-block (iv) s-block

Sol. The block of the elements depend on the type of sub-shell which receive the last electron. In case of (i) it enters in 3p-subshell, (ii) it enters 3d-subshell, (iii) it enters 4s-subshell and (iv) it enters 2s-subshell.

3. Find out the group of the element having the electronic configuration, $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,4s^2$.

Ans. As last electron enters in d-subshell, therefore this belongs to d-block. For d-block element the group number is equal to the number of valence shell electrons + number of electrons in (n-1) d-subshell. So, group number = 6 + 2 = 8.

4. Arrange the following ions in the increasing order of their size : Be^{2+}, Cl^-, S^{2-}, Na^+, Mg^{2+}, Br^- ?

Ans. $Be^{2+} < Mg^{2+} < Na^+ < Cl^- < S^{2-} < Br^-$

Sol. Be^{2+} is smaller than Mg^{2+} as Be^{2+} has one shell where as Mg^{2+} has two shells.

Mg^{2+} and Na^+ are isoelectronic species : Ionic radius $\propto$ 1/nuclear charge.

Cl^- and S^{2-} are isoelectronic species : Ionic radius $\propto$ 1/nuclear charge.

Cl^- is smaller than Br^- as Cl^- has three shells where as Br^- has four shells.

5. The (IE_1) and the (IE_2) in kJ mol^{-1} of a few elements designated by Roman numerals are shown below:

	I	II	III
IE_1	403	549	1142
IE_2	2640	1060	2080

Which of the above elements is likely to be a

(a) non-metal (b) alkali metal (c) alkaline earth metal ?

Ans. (a) non-metal(III) – Due to highest ionisation energy, (IE_1) and (IE_2).

(b) alkali metal(I) – Due to lowest ionisation energy, (IE_1) and there is quite high jump in (IE_2) due to inert gas configuration.

(c) alkaline earth metal (II) – There is little difference in (IE_1) and (IE_2) and the value of (IE_1) is slightly greater than(I) due to stable configuration(ns^2).

6. Ionisation energy and electron affinity of fluorine are respectively 17.42 and 3.45 eV. Calculate electronegativity of fluorine atom.

Sol. According to Mulliken's electronegativity (χ_M) = $\dfrac{\text{Ionisation energy} + \text{Electron affinity}}{2}$

$$= \frac{17.42 + 3.45}{2} = 10.435$$

Therefore, electronegativity on Pauling's scale (χ_P) = $\dfrac{10.435}{2.8}$ = 3.726

Ans. $\chi_P = 3.726$

7. Why the electron gain enthalpy values of alkaline earth metals are lower (i.e. less negative) or positive?

Sol. The general valence shell electron configuration of alkaline earth metals is ns^2 (stable configuration). The extra electron must enter np subshell, which is effectively shielding by the two ns electrons and the inner electrons. Consequently, the alkaline earth metals have little or no tendency to pick up an extra electron.

8. In Column-I, there are given electronic configurations of some elements. Match these with the correct metals given in Column-II :

Column-I		**Column-II**	
(A)	ns^2, np^5	(p)	Chromium
(B)	$(n-1)\,d^{10}, ns^1$	(q)	Copper
(C)	$(n-1)\,d^5, ns^1$	(r)	Krypton
(D)	$(n-1)\,d^{10}, ns^2, np^6$	(s)	Bromine

Ans. (A) → (s) ; (B) → (q) ; (C) → (p) ; (D) → (r).

Sol. (A) ns^2np^5 is general valence shell electron configuration of halogens. So this configuration belongs to bromine.

(B) $(n-1)\,d^{1-10}\,ns^{1-2}$; This is electron configuration of d-block elements. As it contains $(n-1)\,d^{10}ns^1$ configuration it belongs to copper.

(C) $(n-1)\,d^{1-10}\,ns^{1-2}$; This is electron configuration of d-block elements. As it contains $(n-1)\,d^5ns^1$ configuration it belongs to chromium.

(D) Noble gases has valence shell electron configuration $ns^2\,np^6$, so it belongs to krypton.

9. Match the metals given in Column-II with their type given in Column-I :

Column-I		**Column-II**	
(A)	Metalloid	(p)	Sulphur
(B)	Radioactive	(q)	Gold
(C)	Transition metal	(r)	Arsenic
(D)	Chalcogen	(s)	Uranium

Ans. (A) → (r) ; (B) → (s) ; (C) → (q) ; (D) → (p)

Sol. (A) Arsenic is a metalloid because it behaves as metal (forming cation, As^{3+} -$AsCl_3$) as well as nonmetal (forming anion, As^{3-} -AsH_3).

(B) Uranium is a radioactive element.

(C) Those elements which in their neutral atoms or in most common oxidation state have partially filled d-orbitals are called as transition elements. Gold in its +3 oxidation state has electron configuration $[Xe]^{54}$, $5d^86s^0$.

(D) 16th group elements like oxygen and sulphur are ore forming elements and therefore are called as chalcogens.

10. Match the metals given in Column-II with their type given in Column-I :

Column-I		**Column-II**	
(A)	Representative element	(p)	Cerium
(B)	Lanthanide	(q)	Aluminum
(C)	Coinage metal	(r)	Thorium
(D)	Actinide	(s)	Gold

Ans. (A) → (q) ; (B) → (p) ; (C) → (s) ; (D) → (r)

Sol. (A) s-block and p-block elements are collectively called as representative elements. As in aluminium last electron enters in p-subshell ($[Ne]^{10}3s^23p^1$).

(B) Lanthanide series follows lanthanum (atomic number 57) and starts from cerium (atomic number 58) to lutetium (atomic number 71), fourteen 4f- series elements.

(C) Group 11- transition elements copper, silver & gold are known as coinage metals (used for making the coins).

(D) Actinides series follows actinium (atomic number 89) and starts from thorium (atomic number 90) to lawrencium (atomic number 103), fourteen 5f- series elements.

11. Match the particulars given in Column-I with the process / metal / species given in Column-II.

Column-I		**Column-II**	
(A)	Isoelectronic species	(p)	$A^+(g) + \text{energy} \rightarrow A^{++}(g) + e^-(g)$
(B)	Half filled orbital	(q)	Ar, K^+, Ca^{++}
(C)	Second ionisation energy	(r)	Lutetium
(D)	Inner transition element	(s)	Antimony

Ans. (A) → (q) ; (B) → (s) ; (C) → (p) ; (D) → (r)

Sol. (A) Species having same number of electrons but different nuclear charge are called isoelectronic species. Ar, K^+ & Ca^{++} have same number of electrons i.e. 18 but 18, 19 & 20 number of protons respectively.

(B) np^3, $(n–1)\ d^5$ and $(n–2)\ f^7$ represent half filled orbitals. Antimony has ($[Kr]^{36}\ 4d^{10}5s^25p^3$).

(C) The energy required to remove an electron from an univalent cation(g) is called second ionisation energy.

(D) 4f and 5f- series elements are called inner transition elements because they have three outer most shells incomplete.

12. Match the type of elements / characteristic of the elements listed in Column-I with the correct element listed in Column-II.

Column-I		**Column-II**	
(A)	Highest 1st ionisation energy	(p)	Technitium
(B)	Highest electronegativity	(q)	Lithium
(C)	Synthetic element	(r)	Helium
(D)	Strongest reducing agent	(s)	Fluorine

Ans. (A) → (r) ; (B) → (s) ; (C) → (p) ; (D) → (q).

Sol. (A) Helium has highest 1st ionisation energy amongst all the elements of periodic table because of ns^2 valence electron configuration and its small size of atom.

(B) Fluorine has highest electronegativity i.e. 4.0 on Pauling scale on account of its small size.

(C) Technitium is a man made element.

(D) Lithium is a strongest reducing agent because of its highest negative value of E^o due to its higher hydration energy on account of its small size of atom.

13. The Column-I has certain details about the elements of s-, p- and d-block elements. Match those with the group number of the elements listed in Column-II.

Column-I		**Column-II**	
(element / elements)		**(group number)**	
(A)	An element whose fourth shell contains two p-electrons	(p)	8th group
(B)	An element whose valence shell contains one unpaired p-electron	(q)	12th group
(C)	An element which receives last electron in (n – 1) d-subshell	(r)	14th group
(D)	An element with the ground-state electron configuration $[Ar]4s^23d^{10}$	(s)	17th group

Ans. (A) → (r) ; (B) → (s) ; (C) → (p, q) ; (D) → (q).

Sol. (A) $[Ar]3d^{10}4s^24p^2$: Fourth shell contains two electron in 4p-sub shell i.e., $4p^2$. Therefore, group number = 10 + 4 = 14.

(B) Halogens (i.e. group number 17) have valence shell electronic configuration ns^2np^5 and there is one unpaired electron in p-subshell i.e., $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$

(C) The element in which last electron enters in d-subshell belongs to d-block. For d-block elements the group number = number of electrons in valence shell + number of electrons in (n – 1) d-subshell.

Group number 8. Valence shell electronic configuration is $ns^2(n – 1)d^6$. Therefore, group number = 2 + 6 = 8.

Like wise, group 12 is $ns^2(n – 1)d^{10}$. Therefore, group number = 2 + 10 = 12.

So in group 8 and 12 last electron enters in d-subshell.

(D) For electronic configuration. $[Ar]\ 4s^23d^{10}$ the group number = 2 + 10 = 12.