# Periodic Table(Long Form) Atomic Numbers and Atomic masses(nearest whole numbers) of Elements

# Left portion

**Right portion** 

Н																	He
1																	2
1																	4
11	Be	1										B	C	N	0	F	Ne
3	4											5	6	7	8	9	10
7	-											11	12	14	16	19	20
																-	-
Na	Mg											AI	Si	Р	S	CI	Ar
11	12				Mie	ddle p	oortio	n				13	14	15	16	17	18
23	24											27	28	31	32	35.5	40
κ	Са	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
39	40	45	48	51	52	55	56	59	59	63.5	65	70	72.5	75	79	80	84
Rb	Sr	Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те		Xe
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
85.5	88	89	91	93	96	98	101	103	106	108	112	115	119	122	128	127	131
Cs	Ва	La*	Ht	Ta	w	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
55	56	57	/2	/3	74	75	76	11	/8	79	80	81	82	83	84	85	86
133	137	139	178	181	184	186	190	192	195	197	201	204	207	209	209	210	222
Fr	Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	FI	Uup	Lv	Uus	Uuo
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116		118
223	226	227															

	Boltom portion												
*Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
58	59	60	61	62	63	64	65	66	67	68	69	70	71
140	141	144	147	150	152	157	159	162	165	167	169	173	175
**Th	Ра	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
90	91	92	93	94	95	96	97	98	99	100	101	102	103
232	231	238											

#### Bottom portion

# Periodic Table(Long Form)



# PERIODIC CLASSIFICATION

Although the world is varied and complex, everything in it, namely air, water, rocks, living tissue and almost infinite number of other objects and materials around us is actually made up of only a limited number of chemical elements. There are only 92 elements that exist naturally on earth from which every thing has been created by nature. Man has prepared many new elements in the laboratory from the old elements and the total number of elements including both natural and artificial is nearly 117. Until the middle part of nineteenth century nearly 60 elements were discovered and scientists went on studying the physical and chemical properties of these elements. It was revealed to them that many elements had similar properties. Necessity therefore arose at that time to make the study of the elements more systematic and for this reason a table consisting of all the elements discovered till that time was prepared. The elements were arranged in that table in a regular and orderly manner so that similar elements were kept in one vertical column. This was called the periodic table. Russian scientist Mendeleef(1834-1907) was the first scientist to put forth a highly meaningful and systematic table of elements. Before Mendeleef, although scientists like Dobereiner, Newland did make some ordering of the elements, their work lost all importance after the preparation of periodic table by Mendeleef. Another contemporary scientist Lother Meyer also arranged the elements in the form of a curve analogous to Mendeleef's table, but his classification also did not gain much popularity. Major credit for the work of periodic classification of elements had gone to Mendeleef for the simplicity of his table. At his time (mid nineteenth century), the fundamental particles such as electron, proton and neutron present in an atom were not discovered. Dalton's theory of atom was held supreme at that time which said that atom is the smallest unit of matter which cannot be divided further. Only atomic mass of the elements were known at that time. It was therefore believed at that time that the difference of properties among elements is due to the difference in atomic masses. Mendeleef had recorded the properties of all the elements known at that time in individual cards. When he arranged these cards in the order of increasing atomic masses of the elements he surprisingly found that elements having similar properties occurred repeatedly at regular intervals or *periodically*. For example, 8 elements after the element lithium(Li), the 9th element sodium was found to be similar to lithium. Again after 8 elements from sodium, the new element potassium had similar properties as lithium and sodium. He used this observation to construct the periodic table. He placed the elements in horizontal rows with increasing atomic masses with the lightest element in the beginning(left) of each row and heaviest element at the last(right) of each row. He constructed several rows one below the other in such a manner that all elements with similar properties fell in one vertical column. Much of Mendeleef's success was due to his placing elements with similar properties in the same vertical column called group. This mode of arrangement, however, left many occasional gaps in the table. He argued that the elements which belonged to these gaps had not been discovered yet. The locations of the gaps enabled Mendeleef to predict with remarkable accuracy the properties of yet-to-be found elements. Subsequently when new elements were discovered, they exactly fitted into the gaps and properties matched with those predicted. He believed that the physical and chemical properties of elements varied in a periodic way with their atomic masses(old periodic law) and placed the elements one after the other with increasing atomic mass. Occasionally he was forced to change the order of the elements so as to make the table systematic. For that he had to place elements having greater atomic mass before those having lower atomic masses. Argon was placed before potassium although potassium has a lower atomic mass(39) than argon(40). It was simply because, potassium is an alkali metal and is similar to lithium, sodium and not with argon which is an inert gas. Argon is similar to He and Ne, the inert gases. Similar elements should be kept in one vertical column(group), that was the main consideration for making periodic table. Similarly, tellurium(127.6) was placed before iodine(127) only because iodine had to fall in the same vertical column as other halogens, fluorine, chlorine etc. and tellurium had to fall in the same vertical column which contained oxygen, sulphur etc. Likewise cobalt(58.9) was placed before nickel(58.7). These were major defects in the Mendeleef's periodic table. He was unable to explain why the ordering of elements according to atomic masses did not work at some places as explained before. Until the early part of

twentieth century this ambiguity persisted. Only after the discovery of fundamental particles like electron, proton, neutron and the structure of atom in the beginning of twentieth century, this defect was rectified. After the discovery of electron and proton, Moseley discovered another property of elements called atomic number, which is equal to the number of protons present in the nucleus of an element. It was then found that the properties of elements change with atomic numbers(not atomic masses as thought by Mendeleef). The periodic law was modified as follows.

# **Periodic Law:**

The physical and chemical properties of elements are periodic functions of their atomic numbers. In other words the properties vary in a periodic manner with their atomic numbers. It was then known that Mendeleef had not done anything wrong by placing argon before potassium, tellurium before iodine and cobalt before nickel. Argon has lower atomic number(18) than potassium(19); tellurium(52) has lower atomic number than iodine(53) and so also cobalt(27) has a lower atomic number than nickel(28).

Mendeleef's Periodic table also had many defects besides the one we discussed before. Since Mendeleef's original table is not in use today, we are not giving that table in this book. However we discuss below the primary defect of the Mendeleef's table.

# Primary Defect of Mendeleef's Periodic Table:

There were two columns in each group as each group was divided into two subgroups (A) and (B). For example group I has two columns, the (A) column containing Li, Na, K..(alkali metals) while the (B) column containing Cu, Ag and Au(called the coinage metals). Alkali metals are largely different from coinage metals in their properties. The objection was how can dissimilar elements be put in one group?

Mendeleef's table was subsequently modified to remove the above defects. This is called the LONG FORM of the Periodic table. Long form of the periodic table is now the most popular and widely used periodic table. Table-1 gives the long form with the atomic numbers and atomic masses(nearest whole number or 0.5 decimal values) of elements. We shall discuss the important features of this table below.

# FEATURES OF LONG FORM OF PERIODIC TABLE:

[Reader is advised to see the periodic table-2 while going through the following paragraphs]

1. There are 7 horizontal rows called *periods* and 18 vertical columns called *groups*. According to old system, the eighteen columns consist of 16 groups written in roman numerical, I, II, III .... and according to new system, there are 18 groups for the 18 columns numbered in arabic numerical 1, 2, 3.... serially up to 18. The groups in the old and new systems have been written at the top of each group in table-2.

- 2. The whole periodic table is divided into the following four portions.
- (a) *Left Portion:* This portion consists of two groups: IA and IIA(1 and 2)
  - *IA(1)*: These are called **alkali metals**(except H): Li, Na, K, Rb, Cs, Fr.
  - *IIA(2)*: These are called **alkaline earth metals**: Be, Mg, Ca, Sr, Ba and Ra.

(b) *Right Portion*: This portion consists of six groups IIIA, IVA, VA, VIA, VIIA and zero.

- *IIIA(13)*: This is called **Boron Family** and consist of B, Al, Ga, In, Tl and Uut.
- *IVA(14)*: This is called the **Carbon Family** and consist of C, Si, Ge, Sn, Pb and Uuq
- *VA(15)*: This is called the **Nitrogen Family** and consists of N, P, As, Sb, Bi and Uup.
- These are commonly called *pnicogens (Greek : pnicogen-* choking. Compounds of P, As, Sb and Bi are called pnictides)
  - *VIA(16)*: This is called the **Oxygen Family** and consists of O, S, Se, Te, Po and Uuh
    - These are commonly called *chalcogens*.(Greek: *chalcogen* ore former)
  - *VIIA(17)*: This are called **Halogens** and consist of F, Cl, Br, I and At.(Greek: halogen sea salt

former)

*Zero(18)*: This group consist of **noble or inert gases** He, Ne, Ar, Kr, Xe, Rn and Uuo The elements of left and right portions are commonly called **normal or representative elements**.

(c) *Middle Portion*: This consists of eight groups according to old system. From left to right these groups are IIIB, IVB, VB, VIB, VIIB, VIII, IB and IB. Note that group VIII has not been given any subgroup but consists of three columns, the Fe, Co and Ni groups which are commonly called group VIII elements. In the new system there are ten groups in the middle portion and the groups starts from group-3 and ends at group-12. Group IIIB in old system is called the group 3 in new system, group IVB is group 4 and so on, up to group IIB which is group 12 according to the new system. All the elements belonging to the middle portions are commonly called **transition elements**. The transition elements are also studied in terms of periods. There are four series of transition elements. Each series consists of ten elements.

Ist transion series (from left to right): Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn(from atomic number 21 to 30)

2nd Transition series: (from left to right): Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd

3rd Transition series: (from left to right) : La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg

4th Transition series: (from left to right) : Ac, Rf, Db, Sg, Bh, Hs, Mt, Ds, Rg, Uub

(d) **Bottom Portion**: This consists of two rows of elements each containing 14 elements. These are commonly called *inner transition elements*. The first  $row(_{58}Ce_{71}Lu)$  elements are commonly called **Lanthanoids or Lanthanons** (previously called lanthanides). They are so called because they follow just after the element lanthanum(La) of group 3 (III-B).Lanthanum(La-57) and the 14 lanthanoid elements(Ce-Lu) belong to group 3(IIIB) and 6th period(3rd transition series) and similar properties properties. According to current IUPAC terminology lanthanoid series consists of 15 elements starting from La(57) and ending at Lu(71). So the element lanthanum(57) belongs to the lanthanoid series. These 15 elements along with Sc and Y in group IIIB are commnly called **rare earth metals** as they occur together in the minerals called 'rare earths'. This name is a misonomer as these elements have high relative abundance but their mining and extraction are difficult. The second row(90-103) of elements are called **Actinoids or actinons** (previsously called actinides), as they follow the element actinium(89). According to current IUPAC terminology the actinoid series also consists of 15 elements at Lu(103) which have similar properties.

# **DUAL POSITION OF HYDROGEN:**

Usually the element hydrgen(H) is kept in group 1 (I-A) alongwith alkali metals. Hydrogen can also be placed in group 17 (VII-A) alongwith halogens. Hence it has two positions in the table. Hydrogen has some similarities with alkali metals, such as (i) it has one electron in the valence shell (ns<sup>1</sup>) and it shows oxidation number of +1 like alkali metals and forms  $H^+(H_3O^+)$  ion like Na<sup>+</sup>, K<sup>+</sup>. (ii)Hydrogen gas can be obtained at the cathode during electrolysis of acidulated water like alkali metals from molten alkali metal halides etc. It has also some similarities with halogens such as (i) it is a diatomic gas like few halogens and it has one electron short of the noble gas configuration(He) like all halogens; (ii) it is a nonmetal like halogens and form H<sup>-</sup>(hydride) ion(ON=-1) like F<sup>-</sup>, Cl<sup>-</sup> and form H<sub>2</sub> at anode when moltan metal hydride is electrolysed.

# STUDY OF THE PERIODIC TABLE ON THE BASIS OF PERIODS:

There are seven periods.

*Ist Period*: This consists of **two** elements H and He with atomic numbers 1 and 2 respectively. *2nd period*: This consists of **eight** elements from atomic number 3 to 10. The elements from left to right are Li, Be, B, C, N, O, F and Ne. These are commonly called **bridge elements** because they have some similarity with their diagonal elements in the third period. For example Li has some similarity with its diagonal element Mg, Similarly Be has similarity with Al and so on.

*3rd Period*: This consists of **eight** elements from atomic number 11 to 18. The elements are Na, Mg, Al, Si, P, Cl and Ar. These are commonly called **typical elements**.

*4th Period:* This consists of **eighteen elements**(19-36), out of which two(K, Ca) belong to left portion, ten belong to middle portion(1st series of transition elements from Sc to Zn) and remaining six(Ga, Ge, As, Se, Br and Kr belong to right portion.

*5th Period*: This also consists of **eighteen elements**(37-54), out of which two(Rb, Sr) belong to left portion, ten belong to middle portion(2nd series of transition elements from Y to Cd) and the remaining six(In, Sn, Sb, Te, I and Xe) belong to the right portion.

*6th period*: This consists of **thirty two** elements(55-86), out of which two(Cs, Ba) belong to left portion, fourteen elements( $_{58}$ Ce- $_{71}$ Lu)belong to the bottom portion, ten elements( $_{57}$ La,  $_{72}$ Hf- $_{80}$ Hg)belong to the middle portion and six elements(Tl, Pb, Bi, Po, At, Rn) belong to the right portion.

**7th Period**: This period consists of 32 elements, out of which two(Fr, Ra) are in left portion, fourteen elements( $_{90}$ Th- $_{103}$ Lr) belong to the bottom portion, ten elements( $_{89}$ Ac,  $_{104}$ Rf -  $_{112}$ Uub) in the middle portion and the remaining 6 elements in the right portion(Uut - Uuo). Uub(ununbium-112), Uut(ununtrium-113), Uuq(ununquadium-114), Uup(ununpentium-115), Uuh(ununhexium-116), Uus(ununseptium) and Uuo(ununoctium-118) names have been given on the basis of the latin names for the atomic numbers of these elements on temporary basis as controversies still exist in giving proper names to these elements.[In latin, nil(n)=0, un(u) =1, bi(b) =2, tri(t) =3, quad(q)=4, pent(p)=5, hex(h)=6, sept(s)=7, oct(o)=8, enn(e)=9. The suffix *ium* is added at the end.

SAQ 1: Give the latin name for the following atomic numbers and name those elements which have been assigned unambiguously.

(a) 103	(b) 107	(c) 111	(d) 118	
Answer : (a) unniltrium		(b) unnilseptium	(c) unununium	(d) ununoctium

# **PHYSICAL STATE:**

# Gaseous Elements:

There are 11 elements which exist in gaseous state at room temperature. These are inert or noble gases(zero group or group 18) which exist as monoatomic gases in nature(He, Ne, Ar, Kr, Xe and Rn). Other gaseous elements(H, N, O, F, Cl) remain as diatomic molecules( $H_2$ ,  $N_2$ ,  $O_2$ ,  $F_2$  and  $Cl_2$ ).

# Liquid Element:

There are two elements which exist in the liquid state at room temperature. These are mercury(Hg) which is a metal and bromine(Br) which is a nonmetal. Br exists as diatomic molecule( $Br_2$ ). Note that there are four more

solid elements which have low melting points close to room temperature and some times considered as liquid elements. These are Rb, Cs, Fr(GroupIA) and Ga(group IIIA).

# Solid Elements:

All other elements which are not gases and liquids at room temperature exist in the solid state. Few solid elements like P and S remain in molecular form while the rest remain in atomic form in a net-work arrangement(details to be learnt in chemical bonding chapter). Phosphorous usually exists as tetra-atomic molecule( $P_4$ ) while sulphur remains as octa-atomic molecule( $S_8$ ) in the solid state.

# Radioactive elements:

All the elements above atomic number 83(Bi) i.e **from polonium(Po) onwards are spontaneously radioactive** and emit rays like alpha, beta and gamma(refer the chapter *radioactivity*). Note that there are two elements below atomic number 83 which are also radioactive. These are Technetium(Tc) among the transition elements(middle portion) and promethium(Pm) existing in the bottom portion(lanthanoid).

# Natural and man-made elements:

All the elements up to atomic number 92(Uranium) are natural and are available in different forms on earth. Beyond uranium i.e from atomic number 93(Neptunium) and onwards all the elements are man-made and are artificially prepared from natural elements. These are solids at room temperature. These are commonly called **transuranic elements**. Note that all these are radioactive elements. Note also that the elements Tc(43) and Pm(61) which are radioactive as mentioned before are also man-made. Six elements which are present in trace quantities in earth crust are believed to be absent for all practicall purposes. These are Tc(43), Pm(61), At(85), Fr(87), and the two transuranic elements Np(93) and Pu(94). It is believed that these six elements were available in nature long time ago. But now they are found in trace quantities on earth and are artificially prepared. So strictly speaking there are 94 natural elements including Np and Pu. But for all practical purposes there are now 88 natural elements (94 - 6).

# **METALS, NONMETALS AND METALLOIDS:**

See the *staircase line* starting just below boron(5) in PT running down on the right side of Al, Ge and Sb. This is the dividing line between metals and nonmetals. Metals lie to the left side of this staircase while nonmetals lie to the right side. The elements which lie in the immediate vicinity of the staircase(except Al), such as B, Si, Ge,As, Sb, Te, Po and At are neither true metals nor true nonmetals and they have some metallic properties and some nonmetallic properties and are called **semi-metals or metalloids**. Here we discuss some of the important properties of metals, nonmetals and their differences.

# **METALS Versus NONMETALS:**

1. *Melting Points*: Metals have high melting points whereas the nonmetals have low melting points. That is why all metals are solids at room temperature except mercury(Hg) which is a liquid. Nonmetals are usually gases, liquid(bromine) or low melting solids( $P_4$ ,  $S_8$ ,  $I_2$  etc). Excepting alkali metals(Li, Na, K, Rb, Cs, Fr) whose melting points are low, metals have fairly high melting points usually above 500°C. Nonmetals however have very low melting points. Take for example,  $O_2$  gas which has melting point of -183°C and phosphorous(solid) has a melting of 44°C. The reason for these observations will be discussed later

2. **The difference between melting point and boiling point of metals is very high** while that for nonmetals is very low. Take for example aluminum(Al) metal whose melting point is 660°C and boiling point is 2467°C. This means that Al remains as a liquid over a wide range of temperature i.e 2467-660=1807°C. But in case of nitrogen gas, the melting point is -210°C and boiling point is -196°C and the difference is only 14°C. Every nonmetal behaves in the same way i.e they remain in liquid state for a narrow range of temperature. The reason is like this. While we melt a metal the strong metallic bond(discussed in Chemical Bond) is weakened and when when we boil a liquid metal the metallic bond is completed broken for which a large heat is required. But when we melt a nonmetallic solid the weak Van der Waals forces are weakend and when the liquid nonmetal is boiled these weak forces are further weakend. For this a small heat is required.

3. *Electrical Conductivity*: Metals are good conductors of electricity in solid as well as in liquid states while nonmetals are poor conductors. This is because metals possess free electrons while the nonmetals do not. The only exception of a nonmetal being a good conductor of electricity is **graphite**(one allotrope of carbon). This is because of presence of free electrons in graphite(refer the chapter *carbon*).

4. **Thermal Conductivity**: Metals are good conductors of heat while nonmetals are not. If you heat one end of a metal(say iron), the other end is heated soon. But when you do the same thing to iodine solid, the other end is not heated soon. This is because iodine is a nonmetal and is a poor conductor of heat.

5. *Metallic lustre*: Metals when freshly cut show a shining surface, i.e it has its lustre. For example, when silver is polished and the impurities on the surface are removed, it shines. So also it is true for all metals. But nonmetals do not have a shining surface. This is again due to free electrons present in the metals which scatter light when falls on them.

6. **Tensile Strength**: Metals have high mechanical strength (tensile strength) while nonmetals have low strength. When you take a piece of iron metal and stretch it on two sides, can you pull it? No, because metals have high strength. But if you do the same thing with a nonmetal solid (say phosphorous), you can pull the solid apart by applying force. This is because the metallic bond which bind the atoms in a metal crystal is strong while the weak vander waals forces which bind the nonmetal atoms/molecules are weak.

7. *Malleability and Ductility*: Metals are malleable and ductile while nonmetals are not. Rather the nonmetals are brittle. Malleable means the metals can be hammered or pounded to make thin sheets. Do you remember the Rutherford's gold foil experiment? Gold was hammered to a thin sheet of 0.00004cm thickness. All metals are malleable to different extents. On the other hand if you hammer iodine solid, it will crumble into pieces because it is brittle. The strong metallic bond present in the metals is responsible for these properties.

8. *Nature of Ions Produced*: Metals produce positive ions easily while nonmetals produce negative ions easily. Na will give Na<sup>+</sup> ions(not Na<sup>-</sup> ions) while Cl gives Cl<sup>-</sup> ion(not Cl<sup>+</sup>) easily.

# **METALLOIDS OR SEMIMETALS**

The elements which lie in the immediate vicinity(except Al) of the *staircase* mentioned before are called metalloids. They have some resemblance with metals and some other resemblance with nonmetals. They are all **solids** at room temperature (metallic property) but are **not good conductors (nonmetallic** property). Their boiling points and melting points are high and have a wide difference between them (metallic property). Metalloids have very important applications as semiconductors in electronics industries the details of which are not discussed here.

**SAQ 2** :

- (i) Indicate, to which group of elements do the following belong? Refer table-2 for this.
   (a)alkali metals (b)alkaline earth metals (c)Halogen family (d)Oxygen familiy
   (e)coinage metals (f)Nitrogen family (g)Noble gases
- (ii) How many liquid and gaseous elements(at room temperature) are present and name them.
- (iii) Identify which are metals, which nonmetals and which metalloids. Cu, As, N, S, Fe, Bi, B, Te, Na, P, O, Mg, Si, Ne

(iv) What do you call to the 1st row of elements from Cerium(Ce) to Lutetium(Lu) belonging the bottom portion of the periodic table?

- (v) Identify which is a representative element and which is a transition element. K,  $Cl_2$ , Fe,  $P_4$ , Ca, Ni, Mn, Ar,  $S_8$ ,  $I_2$
- (vi) Po, At and Rn have atomic numbers 84, 85 and 86 respectively. What is the common aspect in them.
- (vii) All man-made elements are also spontaneously radioactive. Is it true?

#### Answer:

(i)	(a)IA(1)	(b)IIA(2)	(c)VIIA(17)	(d)VIA(16)
	(e)IB(11)	(f)VA(15)	(g)zero $(18)$	

(ii) **Liquid:** 2: Hg and Br. Some authors consider Cs, Fr and Ga as the other three liquid elements because they have low melting point(close to 30°C). In the cold seasons, they remain as

solids.

Gaseous: 11: H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, F<sub>2</sub>, Cl<sub>2</sub>, He, Ne, Ar, Kr, Xe and Rn

- (iii) Metals:Cu, Fe, Bi, Na,Mg Nonmetals: N, S, P, O, Ne Metalloids:As, B, Te, Si
- (iv) Lanthanides or the rare earths.
- (v) Representative Elements: K, Cl<sub>2</sub>, P<sub>4</sub>, Ca, Ar, S<sub>8</sub>, I<sub>2</sub> Transition Elements: Fe, Ni, Mn
- (vi) All are naturally radioactive elements.
- (vii) Yes, these are called transuranium elements(above U) and are all radioactive.

# MAGIC NUMBERS FOR FINDING ATOMIC NUMBERS OF ELEMENTS:

# (DRAWING PERIODIC TABLE)

The student is advised to practise drawing a simple periodic table in a piece of paper as suggested below. Refer table-3 given later for the purpose. First draw seven rows and then eighteen columns. The first two columns belong to left portion and the last six columns belong to right portion. First fill elements group-wise in the left and right portions. Fill group IA(1) with H, Li, Na, K, Rb, Cs, Fr from top to bottom. Remember the proper sequence of these alkali metals. Then fill group IIA(2) with alkaline earth metals Be, Mg, Ca, Sr, Ba and Ra. Note that Be is placed beside Li(not H) and other elements are placed from top to bottom. After filling the left portion, jump to the right portion. Start filling elements of boron family i.e group IIIA(13): B, Al, Ga, In, Tl and Uut. Remember the sequence of elements in each group. Then fill carbon family, i.e IVA(14): C, Si, Ge, Sn, Pb and Uuq followed by nitrogen family i.e groupV(A)(15): N, P, As, Sb, Bi and Uup; oxygen family, i.e group VIA(16): O, S, Se, Te, Po and Uuh; then halogens i.e group VIIA(17): F, Cl, Br, I and At and finally the inert gases i.e group zero(18): He, Ne, Ar, Kr, Xe, Rn and Uuo. Note that group zero elements start from the 1st period. Helium is placed at the top right corner in the first period horizontal with H and all other elements follow in sequence written above. After filling group-wise to the left portion and right portion, let us

look to 4th period. Fill row-wise all the ten elements of the 1st transition series in between calcium and gallium. The elements in sequence are Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn. Note that elements belonging to 1st transition series are very common and widely available. Then fill the transition elements groups-wise starting from group IIIB(3) to IIB(12). <u>Sc-group:</u> Sc, Y, La, Ac; <u>Ti group</u>: Ti, Zr, Hf, Rf; <u>V group</u>: V, Nb, Ta, Db; <u>Cr group</u>: Cr, Mo, W, Sg; <u>Mn group</u>: Mn, Tc, Re, Bh; <u>Fe group</u>: Fe, Ru, Os, Hs; <u>Co group</u>: Co, Rh, Ir, Mt; <u>Ni group</u>: Ni, Pd, Pt, Ds(Durmstadtium); <u>Cu group(coinage metals)</u>: Cu, Ag, Au, Rg(Roentgenium); <u>Zn group</u>:Zn, Cd, Hg, Cn(Copernicium).

#### Atomic numbers of the elements are obtained by following the magic numbers. *MAGIC NUMBERS FOR THE LEFT PORTION*: 8, 8, 18, 18 and 32.

Before applying magic numbers, first give the atomic numbers of the elements of second period i.e from 3 to 10(from Li to Ne). Then start applying magic numbers to elements group wise. That means you add the first magic number(8) to the atomic number of the first element Li(3) to get the atomic number of the second element, sodium(3+8=11). Then add the second magic number(8) to the atomic number of second element, sodium(11) to get the atomic number of third element and so on(+8+8+18+18+32) successively starting from lithium to get the atomic numbers of all the elements. So the atomic numbers of Na, K, Rb, Cs and Rb will be respectively 11, 19, 37, 55 and 87. Note that H is not to be considered while applying magic numbers. You have to start applying the rules from the element of second period. For groupIIA(2) elements either you add 1 to each of group 1 atomic number to get the atomic number of the corresponding element of group IIA in the same period, or you can apply magic numbers to group IIA starting from Be (+8+8+18+18+32) to get the atomic numbers of all the elements. The atomic number of group 2 elements respectively are 4, 12, 20, 38, 56 and 88 for Be, Mg, Ca, Sr, Ba and Ra respectively.

#### *Magic Numbers for the right portion*: 8+18+18+32 + 32

Here one 8 is missing in the beginning which is compensated by 32 at the end. The atomic numbers of successive elements can be known while starting from the first element of 2nd period(B, C, N, O, F and Ne) and adding +8+18+18+32+32 in sequence. Let us take group III A(13). The atomic number of Al=5 +8=13, followed by Ga= 13+18=31, then In = 31+18=49, Tl=49+32=81 and finally Uut = 81+32=113. The atomic numbers of all other elements of the groups of the right portion can be known by two ways. The easiest way is by successively adding one to the elements in a given period till the last element(noble gas) is reached. Look to the elements after Al in the same period(3rd). Si is 13+1=14, P=14+1=15, S=16, Cl=17 and finally Ar=18. Similarly you find the atomic numbers to the right of Ga(31) in the 4th period, In(49) in the 5th period and Tl(81) in the 6th period. The other method is to apply magic numbers to the individual groups elements starting from the first element(of 2nd period) as indicated before. Thus we have got the atomic numbers of all the elements of the left and right portion. The atomic numbers of H and He are already known(1 and 2 respectively).

*Ist transition series*: The atomic numbers of the 1st row transition series from Sc to Zn can be obtained by successively adding one to the atomic numbers of elements starting from Ca(20). Sc = 21, Ti = 22, V=23, Cr=24, Mn=25, Fe=26, Co=27, Ni=28, Cu=29, Zn=30. After Zn, the next element is Ga(31) belonging to the right portion.

The student is advised to practise drawing this simple format of periodic table as explained before a few times so that the same table can be drawn within two minutes in a photocopied format of blank PT. Then it is possible to locate the position of any element in the table. Look to the following example.

Example:	Locate the element present in the	
	(i)third period and group VIA(16) and	<i>(ii)6th period and IIA(2)?</i>
Solution:	Refer the periodic table that you prepared of you	ir own.
(i	)The element present in the third period and group VIA	(oxygen family) is sulphur(S).

(ii)The element in the 6th period and groupII(A) is barium(Ba).

# **SAQ 3**:

(i) Name the elements of group VA(15) and find their atomic numbers by using the magic numbers if the atomic number of the first element is 7.

(ii) Identify the element present in the (a)3rd period and group VA(15), (b)5th period and group VIIA(17).

(iii) Name the elements of group IIA and find the atomic numbers of these elements by using the magic numbers(the atomic number of the first element is 4).

(iv) To which group halogens belong? Name them. Find the atomic numbers of all halogens if the atomic number of the first halogen is 9.

(v) An element has the atomic number 13. Identify it and indicate to which period and group does it belong.

(vi) The atomic numbers of a few elements are 12, 6, 38, 53, 36. Identify the elements and give their period and group numbers.

# Answer:

(i) N, P, As, Sb and Bi: 7, (7+8=)15, (15+18=) 33, (33+18=)51, (51+32=) 83

(ii) (a)P (b)I

(iii) Be,Mg, Ca, Sr, Ba, Ra: 4, (4+8=) 12, (12+8=)20, (20+18=) 38, (38+18=)56, (56+32=)88

- (iv) VIIA(17). F, Cl, Br, I and At. 9, (9+8=) 17, (17+18=)35, (35+18=)53, (53+32=)85
- (v) Al. It belongs to 3rd period and group IIIA(13).
- (vi) 12=Mg(3rd period and group IIAor 2);
   38=Sr(5th period and group IIAor 2);
   36=Kr(4th period and group zero or 18)

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6=C(2nd period and group IVA or 14)
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53=I(5th period and group VIIA or 17)

# *ELECTRONIC BASIS OF PERIODIC CLASSIFICATION AND VALENCY(OXIDATION STATES) OF ELEMENTS*:

Group IA:	$H(1): 1s^{1},$	Li(3): 1s <sup>2</sup> , <b>2s</b> <sup>1</sup> ,	Na(11): 1s <sup>2</sup> , 2s <sup>2</sup> , 2p <sup>6</sup> , <b>3s</b> <sup>1</sup> ,
	K(19): 1s <sup>2</sup> , 2s <sup>2</sup> ,	2p <sup>6</sup> , <b>3s<sup>2</sup></b> , 3p <sup>6</sup> , <b>4s<sup>1</sup></b>	and so on.
	-		

We find that each element of group IA has the valence shell(last shell) configuration  $ns^{1}$  (where n = 1-7). Each contain one unpaired electron in the valence shell. So the valency of the element is **one** (oxidation number = +1)

*Group IIA*: Be(4):  $1s^2$ ,  $2s^2$  Mg(12):  $1s^2$ ,  $2s^2$ ,  $2p^6$ ,  $3s^2$  Ca(20):  $1s^2$ ,  $2s^2$ ,  $2p^6$ ,  $3s^2$ ,  $3p^6$ ,  $4s^2$  and so on.

Each element of group IIA has valence shell configuration  $ns^2$  (n = 2 - 7). Each contains two electrons(called a lone pair) in the valence shell. So the valency of the elements is 2(oxidation number = +2)

*Group IIIA(13)*: B(5): 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>1</sup>, Al(13): 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>1</sup>:

Ga(31): 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>6</sup>, 4s<sup>2</sup>, 3d<sup>10</sup>, 4p<sup>1</sup> and so on

Here we find that each element of group IIIA has the valence shell configuration  $ns^2 np^1$  (n = 2 - 7) and each contains three electron in its valence shell. So the valency shown by this elements is 3(ON = +3).

*Group IVA*: C(6): 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>2</sup> Si(14): 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>2</sup>,

Ge(32):  $1s^2$ ,  $2s^2$ ,  $2p^6$ ,  $3s^2$ ,  $3p^6$ ,  $4s^2$ ,  $3d^{10}$ ,  $4p^2$  and so on.

each element of group IIIA has the valence shell configuration  $ns^2 np^2$  (n = 2 - 7)), so the valency of the element is 4. Maximum ON is +4 (eg. CO<sub>2</sub>, SiO<sub>2</sub>) and minimum ON = -4 (eg. Al<sub>4</sub>C<sub>3</sub>).

(N.B: Note that upto group IIIA, the max ON is the group number while the minimum ON is zero.But for groups IVA, VA, VIA and VIIIA, the maximum ON is equal to the group number but the minimum ON is equal to - (8 - group number). This is because by losing/or sharing all the valence electrons the atom will acquire a maximum ON equal to group number while by gaining (8-group number) of electrons it will acquire the configuration of the nearest noble gas and the minimum ON.)

*Group VA*: N(7):  $1s^2$ ,  $2s^2$ ,  $2p^3$ , P(15):  $1s^2$ ,  $2s^2$ ,  $2p^6$ ,  $3s^2$ ,  $3p^3$ As(33):  $1s^2$ ,  $2s^2$ ,  $2p^6$ ,  $3s^2$ ,  $3p^6$ ,  $4s^2$ ,  $3d^{10}$ ,  $4p^3$  and so on.

The valence shell of all these elements contain five electrons( $ns^2 np^3$ ). Hence maximum ON of the elements is +5 (N<sub>2</sub>O<sub>5</sub>, H<sub>3</sub>PO<sub>4</sub> etc.) while the minimum oxidation number is -3 (eg. NH<sub>3</sub>, AlN, Mg<sub>3</sub>P<sub>2</sub>).

*Group VIA*: O(8): 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>4</sup> S(16): 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>4</sup>

Se(34):  $1s^2$ ,  $2s^2$ ,  $2p^6$ ,  $3s^2$ ,  $3p^6$ ,  $4s^2$ ,  $3d^{10}$ ,  $4p^4$  and so on.

The valence shell of all these elements contain six electrons( $ns^2 np^4$ ). The maximum ON is +6( $H_2SO_4$ , SeO<sub>3</sub> etc) while the minimum ON is -2(eg. H<sub>2</sub>O, H<sub>2</sub>S etc).

*Group VIIA*: F(9): 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>5</sup> Cl(17): 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>5</sup>

Br(35): 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>6</sup>, 4s<sup>2</sup>, 3d<sup>10</sup>, 4p<sup>5</sup> and so on.

The valence shell in each element contains seven( $ns^2 np^5$ ) electrons. The maximum ON is +7 (HClO<sub>4</sub>, I<sub>2</sub>O<sub>7</sub>) and minimum ON is -1 (NaCl, KBr etc.).

**Zero group**: He(2): 1s<sup>2</sup>

Ar(18):  $1s^2$ ,  $2s^2$ ,  $2p^6$ ,  $3s^2$ ,  $3p^5$ 

Ne(10): 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup> Kr(36): 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>6</sup>, 4s<sup>2</sup>, 3d<sup>10</sup>, 4p<sup>6</sup>

The valence shell of all these elements contain eight electrons( $ns^2 np^6$ - octet) except for He which has got 1s<sup>2</sup> (duplet)configuration. Noble gases usually show a zero oxidation state as they have stable octet/duplet configuration. However the inert gases too show nonzero ON in majority of compounds particularly that of Xe(XeF<sub>2</sub>, XeF<sub>4</sub>, XeF<sub>6</sub> etc.). This will be discussed elsewhere.

From all these what did we find? Elements belonging to a particular group have same number of electrons in their valence shell. For example, alkali metals(group IA) have one electron in their valence shell, alkaline earth metals have two electrons in their valence shell and so on. So the similarity in properties in respect of the elements of a particular group is definitely due to their identical valence shell configuration. Conversely, the difference in properties between elements of different groups is due to the difference in valence shell configurations.

Note that each group of the middle portion of the periodic table consisting of B groups(group IIIB, IVB, VB, VIB, VIIB, VIII, IB and IIB) also have same number of valence electrons. We shall discuss their period-wise electronic configurations now instead of group wise.

SAQ 4: Explain why

(a)NCl<sub>5</sub> does not exist while PCl<sub>5</sub> exists.

(b)O can show a maximum ON of +2 in  $OF_2$  while other members of the family can show a maximum ON of +6.

(c) F can show only one nonzero ON of -1 while all others in the family can show a maximum ON of +7.

#### Answer:

(a)N does not have vacant d-orbitals as it belongs to 2nd period and cannot expand its valence shell configuration while other elements P, As etc. have vacant d-orbitals and can expand their valence shell configuration. By expansion of valence shell we mean the lone pair of electron present in these elements will be unpaired. One electron from the lone pair will be excited to a vacant orbital in these cases and make a total of 5 unpaired electrons showing pentavalency. More about this will be discussed in chemical bond chapter.

(b) O does not have vacant d-orbitals like N and hence cannot expand its valence shell. While all others have vacant d orbitals and the two lone pairs can be unpaired by two excitation processes to produce 6 unpaired electrons for showing maximum ON of +6. This will be discussed in detail in chemical bond chapter.

(c) F does not have vacant d-orbital like N and F. Hence cannot expand its valence shell. The other elments have vacant d orbitals and the three lone pairs can be unpaired by excitation processes to produce 7 unpaired electrons for showing the maximm ON of +7. Since F is the most electronegative element, it does not show any +ve ON.

#### **DIVISION OF PERIODIC TABLE INTO BLOCKS:**

Based on the valence shell configuration, the periodic table is divided into four blocks.

(a) **S-BLOCK** : Group 1 and 2 elements consitute the s-block. So the left portion of the PT is called the sblock elements. The last electron(differentiating electron) is present in a s-subshell. Group 1 and 2 have their valence shell configurations  $ns^1$  and  $ns^2$  respectively where n varies from 2 to 7 ( H is not considered).

(b) **P-BLOCK** : Group 13 to 18 elements consitute the p-block. So the right portion of PT is called the p-block elements. In these groups the last electron(differentiating electron) is present in the p-subshell. The valence configurations of different groups are as follows.

	Group 13(Boron	family) : $ns^2np^1$ ;	Group 14(Carbon	familiy) : ns <sup>2</sup> np <sup>2</sup>
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Group 15(Nitrogen family) :  $ns^2np^3$ ; Group 16(Oxygen family) :  $ns^2np^4$ 

Group 17(Halogen familty) : ns<sup>2</sup>np<sup>5</sup>; Group

Group 18(Noble gases) :  $ns^2np^6$ 

(where n varies from 2-7, He is not considered which has 1s<sup>2</sup> configuration)

(c) **D-BLOCK** : Group 3 to 12 elements consitute the d-block. The middle portion of the PT is called the d-block elements. In these elements the last electron enters into a d-subshell. The d-subshell configuration of these groups are as follows.

Group 3(Scandium family) :  $ns^2 (n-1)d^1$ .....Group 12(Zinc family):  $ns^2 (n-1)d^{10}$ .

(d) **F-BLOCK** : The bottom portion of PT consisting of Lanthanoids and Actinoids are called f-block elements as the last electron in these elements enter into a f-subshell.

#### **PERIOD-WISE ELECTRONIC CONFIGURATIONOF ELEMENTS:**

**1st Period**:  $H(1) : 1s^1$   $He(2) ; 1s^2$ 

2nd Period: The 2nd period starts with the filling of 2nd shell.

Li(3) : [He]  $2s^1$ ;Be(4): [He]  $2s^2$ ;B(5): [He]  $2s^2 2p^2$ ;C(6): [He]  $2s^2 2p^2$ N(7) : [He]  $2s^2 2p^{3}$ ;O(8): [He]  $2s^2 2p^4$ F(9): [He]  $2s^2 2p^{5}$ ;Ne(10): [He]  $2s^2 2p^6$ 

Note that while we begin a new period, we write first the configuration of the previous noble gas by writing its symbol within square bracket and the rest of the configuration for the elements belonging to that period. By this we save a lot of time and space.

**3rd Period**: The 3rd period starts with the filling of 3rd shell(Refer arrow filling diagram. After completing 2p, the arrow goes to 3s)

Na(11): [Ne] 3s <sup>1</sup> ;	Mg(12): [Ne] 3s <sup>2</sup> ;	Al(13): [Ne] 3s <sup>2</sup> 3p <sup>1</sup> ;	Si(14): [Ne] 3s <sup>2</sup> 3p <sup>2</sup> ;	
$P(15)$ : [Ne] $3s^2 3p^3$ ;	$S(16)$ : [Ne] $3s^2 3p^4$ ;	Cl(17): [Ne] 3s <sup>2</sup> 3p <sup>5</sup> ;	Ar(18): [Ne] 3s <sup>2</sup> 3p <sup>6</sup> ;	
• 1 171 4/1 • 1 /		1 11/D C (1 C1)	1. 1	1

**4th Period**: The 4th period starts with the filling of 4th shell(Refer the arrow filling diagram. After completing 3p, the arrow goes to 4s, not 3d).

s-block elements:

K(19): [Ar] 4s<sup>1</sup>; Ca(20): [Ar] 4s<sup>2</sup> First transition series: Sc(21): [Ar]  $4s^2 3d^1$ ; Ti(22): [Ar] 4s<sup>2</sup> 3d<sup>2</sup>; V(23): [Ar]  $4s^2 3d^3$ ; Cr(24): [Ar] 4s<sup>1</sup> 3d<sup>5</sup>; Mn(25): [Ar]  $4s^2 3d^5$ ; Fe(26): [Ar] 4s<sup>2</sup> 3d<sup>6</sup>; Co(27): [Ar]  $4s^2 3d^7$ ; Ni(29): [Ar] 4s<sup>2</sup> 3d<sup>8</sup>; **Cu(29):** [Ar]  $4s^1 3d^{10}$ ; Zn(30): [Ar]  $4s^2 3d^{10}$ ; p-block elements: Ga(31):  $[Ar] 4s^2 3d^{10} 4p^1;$ Ge(32):  $[Ar] 4s^2 3d^{10} 4p^2$ ; As(33):  $[Ar] 4s^2 3d^{10} 4p^3$ ; Se(34):  $[Ar] 4s^2 3d^{10}4p^4; Br(35): [Ar] 4s^2 3d^{10}4p^5; Kr(36): [Ar] 4s^2 3d^{10}4p^6;$ 

Note that the EC of Cr and Cu are exceptional due to stable half filled and full filled d-subshell configurations respectively.

**5th Period**: The 5th period starts with the filling of 5th shell(In the arrow filling diagram, you shall find that after completing 4p, the arrow goes to 5s, not 4d)

Ag(47): [Kr]5s <sup>1</sup> 4d <sup>10</sup> ;	Cd(48): [Kr]5s <sup>2</sup> 4d <sup>10</sup> ;		
Tc(43): [Kr]5s <sup>1</sup> 4d <sup>6</sup> ;	Ru(44): [Kr]5s <sup>1</sup> 4d <sup>7</sup> ;	Rh(45): [Kr]5s <sup>1</sup> 4d <sup>8</sup> ;	Pd(46): [Kr]5s <sup>0</sup> 4d <sup>10</sup> ;
Y(39): [Kr]5s <sup>2</sup> 4d <sup>1</sup> ;	Zr(40): [Kr]5s <sup>2</sup> 4d <sup>2</sup> ;	Nb(41): [Kr]5s <sup>1</sup> 4d <sup>4</sup> ;	Mo(42): [Kr]5s <sup>1</sup> 4d <sup>5</sup> ;
Second transition series	<u>s</u> :		
$Rb(37)$ : [Kr] $5s^{1}$ ;	Sr(38): [Kr] 5s <sup>2</sup> ;		
s-block elements:			

p-block elements:
In(49): [Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>1</sup> ;
Te(52): $[Kr]5s^2 4d^{10}5p^4$ :

Sn(50): [Kr]5s<sup>2</sup> 4d<sup>10</sup> 5p<sup>2</sup>; I(53): [Kr]5s<sup>2</sup> 4d<sup>10</sup> 5p<sup>5</sup>; Sb(51): [Kr]5s<sup>2</sup> 4d<sup>10</sup> 5p<sup>3</sup>; Xe(54): [Kr]5s<sup>2</sup> 4d<sup>10</sup> 5p<sup>6</sup>;

Note that besides Mo(42) and Ag(47) having half filled and full filled d-subshell configurations respectively, elements such as Nb, Tc, Ru, Rh, Pd have anomalous EC. Excepting Pd, in all others, one electron is transferred from 5s to 4d. In Pd, two electrons from 5s have been transferred to 4d. Hence it is diamagnetic. Note that ns and (n-1)d subshells have small gap in energy between them, so exchange of electron often takes place. Why it takes place in the 2nd transition series more often and not in the 1st and 3rd transition series is not clearly known. However these ECs have been corroborated from the magnetic moment measurements(number of unpaired electrons).

**6th Period**: The 6the period starts with the filling of 6th shell. In the arrow filling diagram after completing 5p subshell, the arrow goes to 6s, not 5d or 4f.

<u>s-block elements</u> :		
$Cs(55)$ : [Xe] $6s^1$ ; Ba(56): [Xe] $6s^2$	s <sup>2</sup> ;	
Third transition series:		
La(57): $[Xe]6s^2 5d^1;$		
Lathanoids: Ce(58): [Xe] 6s <sup>2</sup> , 4f <sup>2</sup> ;	$Pr(59)$ : [Xe] $6s^2$ , $4f^3$ ; Nd(60)	): [Xe] $6s^2$ , $4f^4$ ;
Pm(61): [Xe] 6s <sup>2</sup> , 4f <sup>5</sup> ;	Sm(62): [Xe] $6s^2$ , $4f^6$ ; Eu(63)	): [Xe] $6s^2$ , $4f^7$ ;
Gd(64): [Xe] 6s <sup>2</sup> , 5d <sup>1</sup> , 4f <sup>7</sup> ;	Tb(65): [Xe] $6s^2$ , $4f^9$ ; Dy(66	): [Xe] $6s^2$ , $4f^{10}$ ;
Ho(67): [Xe] $6s^2$ , $4f^{11}$ ;	Er(68): [Xe] 6s <sup>2</sup> , 4f <sup>12</sup> ; Tm(69)	P): [Xe] 6s <sup>2</sup> , 4f <sup>13</sup> ;
Yb(70): [Xe] $6s^2$ , $4f^{14}$ ;	Lu(71): [Xe] 6s <sup>2</sup> , 5d <sup>1</sup> , 4f <sup>14</sup> ;	
Third transition series(contd.)		
Hf(72): [Xe] $6s^2$ , $4f^{14}$ , $5d^2$ ;	Ta(73): [Xe] $6s^2$ , $4f^{14}$ , $5d^3$ ;	W(74): [Xe] 6s <sup>2</sup> , 4f <sup>14</sup> , 5d <sup>4</sup> ;
$Re(75)$ : [Xe] $6s^2$ , $4f^{14}$ , $5d^5$ ;	$Os(76)$ : [Xe] $6s^2$ , $4f^{14}$ , $5d^6$ ;	Ir(77): [Xe] 6s <sup>2</sup> , 4f <sup>14</sup> , 5d <sup>7</sup> ;
Pt(78): [Xe] 6s <sup>1</sup> , 4f <sup>14</sup> , 5d <sup>9</sup> ;	Au(79): [Xe] 6s <sup>1</sup> , 4f <sup>14</sup> , 5d <sup>10</sup> ;	Hg(80): [Xe] $6s^2$ , $4f^{14}$ , $5d^{10}$ ;
p-block elements:		
Tl(81): [Xe] $6s^2$ , $4f^{14}$ , $5d^{10}$ , $6p^1$ ;	Pb(82): [Xe] 6s <sup>2</sup> , 4f <sup>14</sup> , 5d <sup>10</sup> , 6p <sup>2</sup> ;	
Bi(83): [Xe] $6s^2$ , $4f^{14}$ , $5d^{10}$ , $6p^3$ ;	Po(84): [Xe] 6s <sup>2</sup> , 4f <sup>14</sup> , 5d <sup>10</sup> , 6p <sup>4</sup> ;	
At(85): [Xe] $6s^2$ , $4f^{14}$ , $5d^{10}$ , $6p^5$ ;	Rn(86): [Xe] $6s^2$ , $4f^{14}$ , $5d^{10}$ , $6p^6$	•

\* Note that in the lanthanoids, lanthanum has  $6s^2$ ,  $5d^1$  configuration which is a violation to the arrow filling diagram as 4f comes after 6s. But after lanthanum, the electrons in the other lanthanoids enter in 4f subshell and excepting Gd and Lu, the electrons in the rest of the lanthanoids do not enter in the 5d subshell. All of the them remain in the 4f subshell. Only in case of Gd(half filled f subshell), and Lu(full filled f subshell), one electron enters in the 5d subshell like lanthanum.

\* In the 3rd transition series, the anomalous EC is that for Pt and Au. In Au, one electron transfer from 6s to 5d is due to full filled stability of d subshell. But in Pt, one electron transfer is also there, whose acutal cause is not known).

**7th Period**: The 7th period starts with the filling of the 7th shell as in the arrow filling diagram 7s comes after 6p, not 6d or 5f.

	s-block elements:						
	Fr(87): [Rn] 7s <sup>1</sup> ; Ra(88)	): $[Rn] 7s^2;$					
	Fourth transition series:						
	Ac(89): $[Rn]$ 7s <sup>2</sup> , 6d <sup>1</sup> ;						
	Actinoids: Th(90): [Rn] 7s <sup>2</sup> , 6d	2;	Pa(91): [Rn] 7s	$^{2}, 6d^{1}, 5f^{2}$	; U(9	$92$ ): [Rn] $7s^2$ ,	6d <sup>1</sup> ,
5f <sup>3</sup> ;							
	Np(93): [Rn] 7s <sup>2</sup> , 5f <sup>5</sup> ;	P	$u(94):[Rn] 7s^2, 5f^6;$		Am(95): [R	n] 7s <sup>2</sup> , 5f <sup>7</sup> ;	
	Cm(96):[Rn] 7s <sup>2</sup> , 6d <sup>1</sup> , 1	5f <sup>7</sup> ; B	k(97): [Rn] 7s <sup>2</sup> , 6d <sup>1</sup> , 5	f <sup>8</sup> ;	Cf(98): [Rn	$7s^2$ , $5f^{10}$ ;	
	Es(99): [Rn] 7s <sup>2</sup> , 5f <sup>11</sup> ;	F	m(100): [Rn] 7s <sup>2</sup> , 5f <sup>12</sup> ;		Md(101): []	$[n] 7s^2, 5f^{13};$	
	No(102): [Rn] 7s <sup>2</sup> , 5f <sup>14</sup>	; L	r(103): 7s <sup>2</sup> , 6d <sup>1</sup> , 5f <sup>14</sup> ;				
	Fourth transition series(contd):						
	Rf(104): $7s^2$ , $5f^{14}$ , $6d^2$ ;	Db(105):	$7s^2$ , $5f^{14}$ , $6d^3$ ;	Sg(106):	$7s^2$ , $5f^{14}$ , $6c^{14}$	d <sup>4</sup> :	

 $Lv(116): 7s^2, 5f^{14}, 6d^{10}, 7p^4; \qquad Uus(117) 7s^2, 5f^{14}, 6d^{10}, 7p^5; \qquad Uuo(118): 7s^2, 5f^{14}, 6d^{10}, 7p^6;$ 

# (114(ununquadium) : Fl - Flerovium, 116(ununhexium) : Lv - Livermorium)

8th Period: 8th period will start by filling the 8th shell as in the arrow filling diagram, 8s comes after 7p.

s-block: Uue(119-ununennium): It is not yet discovered. It will be like an alkali metal having configuration [Uuo] 8s<sup>1</sup>.

Ubn(120-unbinilium): It is not yet discovered. It will be like an alkaline earth metal having configuration [Uuo]8s<sup>2</sup>.

#### **SAQ 5**:

(i) How many electrons are there in the valence shell of the following groups of elements?

(a)Group VIA (b)Group Zero (c)Group IIIA (d)Group IA

(e)Group IVA (f)Group IIA (g)Group VA

(ii) An element has the valence shell configuration  $3s^23p^3$ . What is the element? To which group and period does it belong? What are its maximum and minimum oxidation states. Give one compound of each, exhibiting the maximum and minimum oxidation number.

(iii) Flourine is the first member of the halogen group. What is its valence shell configuration?

How many unpaired electrons it has? What oxidation number does it exhibit? Give an example.

(iv) A certain element has valence shell configuration  $3s^1$  and certain other element has the valence shell configuration  $2s^22p^4$ . What are the elements. What are the common oxidation states each exhibits? Give the formula of a compound between them.

(v) How many electrons are present in the valence shell of sulphur? What is its maximum and mimum oxidation numbers? Give an example of each.

Answer: (i) (a)six (b)eight (c)three (d)one (e)four (f)two (g)five Note that excepting group zero(inert gases) which has 8 valence electrons, all other elements have valence electrons equal to their group number.

- (ii) The element is in the third period and group V(five valence electrons): P(group VA or 15) Maximum oxidation state=+5(eg:  $P_2O_5$ ) and minimum  $ON = -(8-5) = -3(eg: PH_3)$
- (iii)  $2s^22p^5$ . One unpaired electron in the p-subshell. It shows only two ON:  $0(F_2)$  and -1(HF).
- (iv)  $3s^1$ : Na(0 and +1),  $2s^22p^4$ : O(0, -1, -2 and +2). Their compound: Na<sub>2</sub>O
- (v) S(16): It belongs to group VIA, So it has six valence electrons. Maximum ON=+6 and minimum ON=-(8-6)=-2. Examples: H<sub>2</sub>SO<sub>4</sub>(S=+6) and H<sub>2</sub>S(S=-2)

**SAQ 6**: Write the electronic configuration of the following elements from its location in the PT in the manner given above. Do not use the arrow filling diagram for answering this question as atomic numbers will not be given in these cases.

(a) As (b) Ba (c) Co (d) Pb (e) Pd (f) Hf (g) Au Answer:

(a) [Ar]  $4s^2 3d^{10} 4p^3$ ; First write the noble gas which appears before the element in the previous period. Then begin with the shell equal to the period in which the elment is present. Then see the position of the element and accordingly first fill ns then (n-1)d then np orbitals. Arsenic lies in the p-block, so we have to first go through s-block by writing  $4s^2$ , then d-block by writing  $3d^{10}$  and while enter in the p-block, count from the start when the element appears. Accordingly write electrons in the np orbital. In this case As appears at the 3rd position after Zn, so it is  $4p^3$ .

(b)  $[Xe] 6s^2$ ; (c)  $[Ar] 4s^2$ ,  $3d^7$ ; (d)  $[Xe] 6s^2 4f^{14} 5d^{10} 6p^2$ ;

Note that After La(57) when we come to Hf(72) the 4f orbitals are completely filled(4f<sup>14</sup>).

- (e) [Kr]  $5s^0 4d^{10}$ (refer the anomaly for Pd) (f) [Xe]  $6s^2 4f^{14} 5d^2$ ;
- (g) [Xe]  $6s^1 4f^{14} 5d^{10}$  (refer the anomaly for Au)

#### **PERIODIC PROPERTIES**

If we move from one element to the other in a period, we shall find that both physical and chemical properties of the elements gradually change from most metallic to most nonmetallic. For example, if you move from left to right in a period the size of the atom gradually decreases. Say for instance in the second period, size of Li atom is the greatest and the atomic size gradually decreases as we move from Li to B-C -N -O to Ne. In a group although the elments have similar chemical properties, their physical properties vary in a regular manner. For example if you move down a group, the size of the atom gradually goes on increasing. Take for instance group VA, nitrogen atom has the smallest size in that group and size go on increasing as we move down from nitrogen to phosphorous, then to arsenic, antimony and finally bismuth. Bismuth has the largest size in that group. Like size of atoms there many other physical properties which vary gradually across periods and groups. These are called *periodic properties* which change gradually and periodically. We shall discuss 10 periodic properties below.

(i)Atomic size or the Atomic Radius:
(iii)Electron Affinity/Affinity Energy:
(v)Ionic Size
(vii)Density
(ix)Valency(OS)

(ii)Ionisation Energy or Ionization Potential(iv)Electronegativity(vi)Melting and Boiling Points(viii)Atomic volume(x)Nature of oxides

# **ATOMIC SIZE**

Size of an individual atom of an element can known from its radius. The exact radius of an atom cannot be determined precisely like a macroscopic(big) particle due to its extremely small size and the non-existence of any sharp boundary of the electron cloud(Heisenburg uncertainty concept). However their approximate values can be determined experimentally by measuring the distance between two neighbouring atoms in their bonded state which is the distance of the closest approach between them with the help x-ray and electron diffraction methods. Because in the bonded state atoms approach to the closest extent by the overlap of electron clouds. Half of this length gives the atomic radius.

#### **Types of Atomic Radius:**

(a) Covalent Radius (b) Metallic radius

**Covalent Radius**: This type of radii are determined for atoms which can covalently bond with itself and form single bond. The nonmetals fall into this category. One half of the internucluear distance between two covalently bonded identical atoms (single bond length) is called covalent radius.

(C.R) (V.R) For example the single bond length between oxygen atoms (O-O) is 1.46 Å, hence the covalent radius of O atom is 0.73 Å.



#### Metallic Radius(Crystal Radius):

This type of radius is determined for metals in which the atoms are bonded with each other by metallic bonding(refer 'chemical bond' chapter for details). One half the distance between two adjacent atoms in the solid state of the metal is called metallic radius. This is analgous to covalent bonding for nonmetals.

N.B: Covalent radius and metallic radius are commonly called atomic radius. The atomic radius data table below gives these two types of radii only for the purpose of comparison.

#### Van der Waals Radius:

Van der Walls radius was available in the olden literature which is now obsolete in recent times. This was used primarily for noble gases which were believed not to form covalent bond with itself. Van der Waals radii of other nonmetals were also available.

Definition: It is one half of the internuclear distance between two neighbouring nonbonded atoms in the solid state of the element.



Note that in the solid state of nonmetals including the noble gases which remain in the monoatomic state there is no strong bond (like covalent or metallic bond) that exists between the atoms. In stead, the atoms or molecules are held together by weak Van der Walls forces. So the approach between two neighbouring nonbonded atoms towards each other in the solid state of the element is not as close as found in actual bonding(covalent/metallic) state. Therefore Van der Waals radii of elements are always greater than their respective atomic radii(covalent/metallic) and Van der Waals radii therefore cannot give a correct idea on the size of an atom. When the covalent radii data for the noble gases were determined, then the Van der Waals radii have very littel use. In this book, we shall not use Van der Waals radius anywhere.]

Refer the atomic radius table given below.

н																	He 0.32
0.37																	
Li 1.34	Be 0.9											B 0.82	C 0.77	N 0.75	0 0.73	F 0.71	Ne 0.69
Na 1.54	Mg 1.3											AI 1.18	Si 1.11	P 1.06	S 1.02	CI 0.99	Ar 0.97
К 1.96	Ca 1.74	Sc 1.44	Ti 1.36	V 1.25	Cr 1.27	Mn 1.39	Fe 1.25	Co 1.26	Ni 1.21	Cu 1.28	Zn 1.34	Ga 1.26	Ge 1.22	As 1.19	Se 1.16	Br 1.14	Kr 1.1
Rb 2.11	Sr 1.92	Y 1.62	Zr <u>1.48</u>	Nb <u>1.37</u>	Mo 1.45	Тс 1.56	Ru 1.26	Rh 1.35	Pd <u>1.31</u>	Ag 1.44	Cd <u>1.51</u>	In 1.44	Sn 1.41	Sb 1.38	Te 1.35	l 1.33	Xe 1.3
Cs 2.25	Ba 1.98	La* 1.69	Hf 1.5	Та 1.38	W 1.46	Re 1.59	Os 1.28	lr 1.37	Pt 1.28	Au 1.44	Hg 1.51	TI 1.48	Pb 1.47	Bi 1.46	Po -	At -	Rn 1.45
Fr -	Ra -	Ac** -	Rf	На	Sg	Ns	Hs	Mt									

Atomic Size in Å (COVALENT RADIUS)

#### Variation across a period:

In any given period, the atomic size is expected to decrease gradually. For example if you look to 3rd period, you will find that the atomic radius of Na is 1.54 Å and as we move to Mg, the atomic radius becomes 1.38 Å, then to Al (1.25Å) and the radius continues to decrease till end of the period. Note that this is not true for transition metal series about which we shall discuss later. Explanation:

(i) In a period, successive electrons enter the same shell(Na= $3s^1$ , Mg= $3s^2$ , Al= $3s^23p^1$ , Si= $3s^23p^2$  and so on). But since the number of protons also increases as we move from element to element, the nuclear pull (attraction) to the electron cloud increases and therefore the atomic size decreases.

# (ii)SCREENING OR SHIELDING EFFECT AND EFFECTIVE NUCLEAR CHARGE(ENC):

The outermost electron actually determines the size. The electrons in the inner shells act as mechanical shield or screen to reduce the interaction between the nucleus and the valence electrons. In other words the valence electrons do not experience the full force of the nucleus due to intervention of inner shell electrons. In stead the nuclear pull is reduced due this. This is called screening effect. Just like a student who is sitting in the last bench of a class does not experience the full force of the teacher as the students sitting in front benches produce a mechanical obstacle or barrier to reduce his interaction with the teacher. In the similar way in an atom, some of the nuclear charge is wasted due to screening effect of inner shell electrons onto the valence electrons and hence valence electrons experience less nuclear charge than the actual charge present in the nucleus. The net nuclear charge that the valence electron experiences is called effective nuclear charge(ENC). We can understand more clearly about ENC from its following most general expression.

Effective Nucler Charge(Z\*)

= Atomic Number or actual charge (Z) - number of screening electrons

In a period the effective nuclear charge increases from left to right for which there is an increase in the nuclear pull to the valence electrons and hence atomic size decreases. Note that in a period, the number of screening electrons i.e the inner shell electrons remains constant for all the elements as the successive electrons enter the valence shell. Therefore ENC increases. For example, for 3rd period, the number of screening electrons is 8 ( $1s^2 2s^2 2p^6$ ) for all elements from Na to Ar. Therefore ENC increases from Na (11-8=3) to Ar (18-8=10).

#### SLATER'S THEORY ON EFFECTIVE NUCLEAR CHARGE :

Although the above method of determining the ENC is most general and simplified for understanding purpose, it does not represent the true picture on the screening effect and ENC. Slater put forth a modified concept of determining ENC. According to his theory, both the inner shell electrons as well as the electrons present in the valence shell produce screening effect onto the outermost electron which would determine the size. For that purpose, we shall have to consider any one electron of the outermost subshell of the valence shell as outermost electron and other electrons in the same shell producing screening effect onto the outermost electron the outermost electron the outermost electron that the electrons present in the same valence shell will produce less screening effect on the outermost electron than the electrons present in the inner shells. Slater used a term **Screening Constant(\sigma)** to make quantitave expression of the screening effect. The screening constant is calculated with the help of the following data table used by Slater.

<u>Orbital</u>	<u>σ <b>per e</b></u>		
	n	(n-1)	(n-2),(n-3)
s or p	0.35	0.85	1.0
d or f	0.35	1.0	1.0

For valence shell(nth shell), the screening constant is 0.35 per electron for all types of orbitals(s, p, d and f). For the penultimante shell i.e (n-1) th shell, the screening constant is 0.85 per electron for s and p orbitals and 1 for d and f orbitals. From (n-2)th shell downwards the screening constant per electron is 1 for all types of orbitals.

$$ENC(Z^*) = Nuclear Charge(Z) - \sigma$$

Exampe: Find the ENC of all elements for 3rd period.

Let us first find the screening constants for these elements.

Na: $\sigma = 0 + 8 \ge 0.85 + 2 \ge 1 = 8.8$ ;	Mg : $\sigma = 0.35 \text{ X } 1 + 8 \text{ X } 0.85 + 2\text{X1} = 9.15;$
A1 $\cdot \sigma = 0.35 X2 + 8 X 0.85 + 2X1 = 9.5$	Si $\cdot \sigma = 0.35 \times 3 + 8 \times 0.85 + 2 \times 1 = 9.85$ and so on

(note that one electron has been excluded from the valence shell for calculation of  $\sigma$  as that is considered to be the ourtermost electron)

Now we can find their ENC values( $Z^*$ ).

Na :  $Z^* = 11 - 8.8 = 2.2$ ; Mg:  $Z^* = 12 - 9.15 = 2.85$ ; Al:  $Z^* = 13 - 9.5 = 3.5$  and so on. From all these data, what do we find ? In period, the screening constant(screening effect) increases as well as ENC increases. This appears to be contradictory since increase in screening effect should bring about decrease in ENC. But the fact is while the screening constant increases by 0.35 with each successive element, the atomic number(Z) increases by 1 unit. Therefore, ENC(Z\*) increases across a period. We can use the following equation to correlate between atomic radius and ENC of a multi-electron element.

$$r_n = 0.529 \text{ X} (n^2/Z^*) \text{ Å}$$

(n = the principal quantum number of outermost electron) (For H atom Z is used in stead of Z\* as there is no screening effect in one electron species) For a period n is constant and so the atomic radius is inversely proportional to ENC.

#### Variation along a group:

In any given group the atomic radius is expected to increase. In other words the atom becomes more and more bulky. While this is true for groups belonging to normal elements but not true for groups in the d-block. So let us first take up the discussion on groups of normal elements. Take for example group IIA(alkaline earth metals) - the size of the Be is 1.06 Å and that of Mg is 1.38 Å and as we go down the group the size further increases.

Explanation:

(i) The valence electrons occupy the successive higher shells as we go down a group. For example, the valence shell configuration of Be is  $2s^2$ , while that for Mg is  $3s^2$  and for Ca  $4s^2$  and so on. Since the valence electrons are present in successive higher shells as we move down a group, the distance between the nucleus and the valence electrons increases substantially and therefore nuclear pull to the valence electrons decreases. So the size goes on increasing down the group.

(ii) In a group, the screening constant( $\sigma$ ) increases as the number of screening electrons increases. Nuclear charge(Z) also increases proportionately so that ENC(Z\*) remains nearly constant. Since nuclear pull depends both on ENC and the principal quantum number of the outermost electron(n), atomic size increases as n increases down the group. This can be understood from the following equation.

$$r_n = 0.529 \text{ X } n^2/\text{Z*}\text{\AA}$$

As n increases down the group atomic radius increases although Z\* remains nearly constant.

**SAQ 7:** Find out the Z\* values of all elements of group 1 following Slater's theory.

# Variation of Screening Effect among Orbitals

#### s > p > d > f

s-orbitals produces the maximum screening effect to the valence electron while f orbital produces the least. This is the same order in which the penetration effect among the orbitals vary(Refer the chapter 'Atomic Structure).

#### Variation of Atomic Size Across Transition Series:

The variation in size is far less pronounced in a transition series than that is observed in a period among normal elements. Although there is a slight contraction at the beginning of the series, the atoms are all much the same size.

#### Explanation:

The size is determined by the valence electrons i.e ns electrons . In a transition series, the successive electrons are added in the penultimate shell[(n-1)d] while the valence shell(ns) configuration remains nearly the same. For example in the 1st transition series(Sc-Zn), the valence shell is 4s, but the successive electrons enter in the 3d subshell. The nucler pull of the increasing number of protons in the nucleus to the valence electron(ns) is more or less offset by the extra screening due to the increasing number of 3d electrons. Note that increasing the number of protons in the nucleus tries to increase the pull while increase in the number of inner shell electrons(n-1) tries to increase the screening effect which tends to reduce the nuclear pull. This two oppsing effects nearly cancel each other and size remains more or less the same.

Different literature sources give slightly different data on atomic size or in fact any physical property of elements. This is because of the difference in experimental techniques and precision adopted for their measurements. A closer look to the data table for atomic radius given in this book reveals that the atomic radius decreases upto certain element in the series and thereafter remains more or less same. But towards the end the size increases again. For example in 1st transition series, the size decreases from Sc to V and thereafter remains nearly same up to Ni and again increses sligtly at Cu and Zn. Although the actual cause is not easy to predict, the most possible explanation could be like this. Upto a few elements when the number of (n-1) d electrons is small, the screening effect is not pronounced and the nuclear pull increases due to increase in the number of protons in the nucleus. However when the number of (n-1)d electrons increases, the screening effect becomes pronounced and almost balances the effect of the increase in the number of protons in the nucleus. Thus the nuclear pull remains more or less same and so also the size. Towards the end(sav Cu, Zn) the (n-1)d orbitals are completely filled  $[(n-1)d^{10}]$ . At this state, the screening effect dominates over the increase in the number of protons in the nucleus and so the nuclear pull decreases. Thus size increases again. The unexpected increase in the screening effect when the d orbitals are completely filled could be due to attainment of spherical symmetry when the orbitals are completely filled. Just like a s-orbital, the completely filled d-subshell looks like a sphere and like s-orbital it acquires greater screening effect than incompletely filled d-subshell.

#### **SAQ 8**: *Why size of Zn is greater than Cu.*

**Answer**: The metallic radius is found out in the solid state where there is metallic bonding. Although Cu has d<sup>10</sup> configuration like Zn, some d electrons of Cu take part in metallic bonding and hence do not screen. This is not case with Zn. Hence the nuclear pull is relatively more in Cu than Zn and so the size of Cu is less. The presence of stronger metallic bonding in Cu is corroborated by its greater bp/mp/density compared to Zn.But why some d electrons of Cu participate in metallic bonding and not of Zn, it is not clearly known.

#### EFFECT OF D-BLOCK CONTRACTION ON ATOMIC SIZE

In group 13, Ga has nearly same atomic radius as Al. While the size increases drastically as we move from B to Al but it does not increase much while moving from Al to Ga. This is due to **d-block or scandide contraction**. In Ga the valence shell configuration is  $4s^2$ ,  $4p^1$  while the inner 3d is completely filled. Since d-orbitals produce lesser screening effects than s and p oribitals, the nuclear pull becomes suddenly greater for which size becomes less than expected from the addition of a new shell. The same effect explains why other elements in the 4th period after Ga namely Ge, As, Se, Br and Kr have not much greater atomic radius than their preceding elements in 3rd period which are respectly Si, P, S, Cl and Ar.

#### VARIRATION OF ATOMIC SIZE ALONG TRANSITION GROUPS

In Sc group(Group 3) the size increases from Sc to La. However in all other groups, the size increases from the 1st to 2nd element and then remains nearly constant in the 3rd element of any particular group.

Group 4(Ti Group): Ti  $\leq$  Zr  $\approx$  Hf; Group 5(V group): V  $\leq$  Nb  $\approx$  Ta

and so on ........... Group 11(Cu group):  $Cu < Ag \approx Au$ ; Group 12(Zn group):  $Zn < Zn \approx Hg$ This trend is due to Lanthanide or f-block contranction.

#### **F-BLOCK OR LANTHANIDE CONTRACTION:**

While moving from La(57) to Hf(72), 14 other lanthanoid elements come in between in which electrons are filled in 4f orbitals. So from Hf(72) onwards the 4f orbitals is completely filled. Since f-orbitals produce the poorest screening effect, the nuclear pull is suddenly increased and a contraction in size occurs. Therefore the size of elements from Hf to Hg remains nearly same as their preceding elements in the 2nd transition series although a new shell has been added when we move from any element in the 2nd transition series belonging to a particular group.

# Effect of Lanthanoid contraction on post transition series elements:

The atomic size of Thallium(Tl) which comes after Hg is nearly same as its preceding element Indium(In) in group 13. This is due to lanthanoid contraction effect. The atomic sizes of other elements in the same period i.e Pb, Bi also are not much greater from their preceding elements in their respective groups. **SAO 9**:

- (i) Between F and Cl atom which has a bigger size and why?
- (ii) Between B and C which has a smaller atomic radius and why?
- (iii) Arrange the following in the order of increasing atomic size
  (a) Mg, Ca, Be, Sr, Ba
  (b)Al, P, Cl, Si, S
  (c)Mg, Na, K, Al, Si
  (d)Al, B, C, N, O
  (e)F, Cl, Br, I
  (f)O, S, Se
  (g)Cu, Ag, Au
- (iv) Indicate in which region of the periodic table i.e north east(upper right), south east(lower right), north west(upper left) or south west(lower left) are the following present.
   (a)Bulky elements(large sized) (b)Thin elements(small size)
- (v) Indicate whether the metal atoms, in general, are bulkier than the nonmetal atoms or vice versa? Arrange the following in order of decreasing size K, Ca, Rb, Br, Cl, F.
- (vi) The difference in atomic sizes between Sc and Zn in the 1st transition series is merely 0.07 Å while this difference between Na and Cl in 3rd period 0.55 Å. Explain.
- (vii) The difference in atomic sizes between N an P is 0.31Å while the same difference between P and As is 0.13 Å. Explain.
- Answer: (i) Cl: Because they belong to the same group(VIIA). In a group, the size increases as we go down.
- (ii) C: Because they belong to the same period(2nd) and in a period, the atomic radius decreases as we move from left to right.
- (iii) (a)Be<Mg<Ca<Sr<Ba(same group) (b)Cl<S<P<Si<Al(same period) (c)Si<Al<Mg<Na<K(The first four belong to the same period and K is in a higher period below Na) (d)O<N<B<Al(The first three belong to the same period and Al in the higher group) (e)F<Cl<Br<l(same group) (f)O<S<Se(same group)</li>
- (iv) (a)Bulky elements: south west(lower left) (b)North east(upper right).
- (v) Metals atoms, in general, are bulkier than nonmetal atoms.Rb>K>Ca>Br>Cl>F

Rb is in 5th period(group IA), K is in 4th period(group IA), Ca, Br are in the same period as K. Cl and F belong to the same group as Br but present above Br.

(vi) Between Sc to Zn, the electrons are added in the penultimate shell which produce screening effect on the valence shell. So the effect of increasing nuclear charge is nearly nullified by the increase in screening effect. So the size does not change much in the transition series. But between Na to Cl in the 3rd period, the electrons are added in the same shell and the effective nuclear charge increases steadily for which the size decreases significantly.

(vii) While moving from N to P, 3s and 3p subshell are filled which produce stronger screening effect. So the nulcear pull is reduced considerably. But while moving from P to As, 3d subshell is filled up before 4p. Due to d-block or scandide contraction effect, the increase in size becomes small.

# **IONISATION ENERGY/IONISATION ENTHALPY(IONISATION POTENTIAL):**

When one electron is removed from a neutral atom, it is converted to a positive ion carrying +1 charge. This electron is removed from the valence shell(the last shell) as the electrons are loosely bound to the nucleus in it and can be easily removed. For example, in sodium atom, we can remove the only electron present in its valence shell (3s<sup>1</sup>). For removing an electron from the hold of the nucleus (nuclear attraction) i.e to bring about ionization, we need to supply some energy. In other words, the atom has to absorb some energy so as to lose one electron. This amount of energy absorbed by an atom is called *ionization energy/enthalpy* and was formerly called *ionization potential*.

**Definition**: The amount of energy required(absorbed by the atom) to remove one loosely bound valence electron from an isolated gaseous atom is called ionization energy or ionisation enthalpy. Note that the atom has to exist in the gaseous state as well as in atomic state before measuring the ionization energy. This ionization energy is strictly called **Ist ionization energy(IE**) as this amount of energy is spent to remove the 1st electron from an atom. If a second electron is removed from the first formed positive ion i.e to convert X<sup>+</sup> to X<sup>2+</sup>, we have to supply still more energy. This is called the **2nd ionization energy(IE**). For the removal of the third electron, we need to supply still more energy called the **3rd ionization energy(IE**) and so on.

$$\begin{split} X(g) + IE_1 &\to X^+(g) + e \\ X^+(g) + IE_2 &\to X^{++}(g) + e \\ X^{++}(g) + IE_3 &\to X^{+++}(g) + e \text{ and so on} \end{split}$$

H 1311																	He 2372
Li 520	Be 899											В 801	C 1086	N 1403	O 1314	F 1681	Ne 2080
Na 496	Mg 737											AI 577	Si 786	P 1012	S 999	CI 1251	Ar 1521
К 419	Ca 590	Sc 633	Ti 659	V 651	Cr 653	Mn 717	Fe 762	Co 760	Ni 737	Cu 745	Zn 906	Ga 579	Ge 762	As 947	Se 941	Br 1140	Kr 1351
Rb 403	Sr 549	Y 600	Zr 640	Nb 652	Mo 684	Тс 702	Ru 710	Rh 720	Pd 804	Ag 731	Cd 868	In 558	Sn 709	Sb 834	Те 869	I 1008	Xe 1170
Cs 376	Ba 503	La* 538	Hf 658	Та 761	W 770	Re 760	Os 840	lr 880	Pt 870	Au 890	Hg 1007	TI 589	Pb 716	Bi 703	Po 812	At 920	Rn 1037
Fr	Ra	Ac**	Rf	На	Sg	Ns	Hs	Mt									

# $IE_1 < IE_2 < IE_3 < ....$ IONISATION ENERGY(Kjoule/mole)

The successive higher orders of IE values go on increasing. This is because, once a +ve charge is formed or the magnitude of +ve charge is increased, it becomes still more difficult to remove the subsequent electron. The nuclear pull becomes greater due to increase in effective nuclear charge as electrons are successively removed while proton number remaining unchanged.

#### Note that merely saying IE means it is first ionisation energy(IE<sub>1</sub>).

#### Determination of the Group or Valency of an Element from the IE Values:

When electrons are successively removed from the valence shell, the increase in ionisation energy between two successive steps is small but when the electron is removed from the penultimate or inner shell while breaking the stable octet or duplet configuration, the increase in ionisation energy is remarkably large. A big jump in the IE values is noticed while moving from valence shell to the penultimate shell. Hence it is possible to predict the valency of the atom by looking to the IE values of the element. Look to the following example.

Example: IE values of an unknown element is given below. From the data predict the number of its valence electrons(valency) and hence its group number in the peridic table.

IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>	$IE_5$ (in KJ/mole)
737	1450	7740	10500	13600
	$\uparrow$			

big jump in IE values

Here we find that IE<sub>2</sub> is nearly 2 times greater than IE<sub>1</sub> while IE<sub>3</sub> is more than 5 times greater than IE<sub>2</sub>. But IE<sub>4</sub> is 1.35 times greater than IE<sub>3</sub> and IE<sub>5</sub> is 1.3 times greater than IE<sub>4</sub>. So big jump in the IE values occur after removing 2 electrons. Therefore we conclude that there are two electrons present in its valence

shell(valency = 2) and the element belongs to group 2. In fact the above IE data are given form magnesium. Note that it is therefore easier to remove the valence electrons rather than inner electrons. The metal atoms of Group 1, 2 and 3 have lower IE values and lose all of their valence electrons and attain stable octet/duplet configuration and easily form their respective positive ions such as Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup> etc. However the nonmentals have high IE values and to remove even the 1st valence electron is difficult. That is why nonmentals atoms do not form +ve ions easily. Refer the data table on IE for the comparative study given

# below.

# Variation of Ionisation Energy across a Period:

The ionization energy is expected to increase across any period.

Explanation: In period, as we know, the ENC increases and hence the nuclear pull increases. So it becomes more and more diffucult to remove the valence electron and hence IE increases. The IE is minimium for the alkali metal(group1) and maximum for the noble gas(group 18) in any period.

Although the variation of IE is more or less regular accorss periods among normal elements, it is highly irregular among elements belonging to transition series.

# ANOMALY AMONG NORMAL ELEMENTS:

In periods 2, 3 and 4 among the normal elements we notice two humps at Group 2 and 15. In the 2nd period, Be has greater IE both than its preceding element Li and also its succeeding element B. Similarly, N has greater IE than both C as well as O. Hence Be(group 2) and N(group 15) sit on two humps in the increasing IE hill slope. Similarly in 3rd period Mg(group 2) and P(group 15) sit on humps while in 4th period Ca and As sit on humps. Note that 5th and 6th periods do not show this trend. Look to the IE data table given before for 2nd period elements and tally with the graph of IE vs. atomic number given here. Same trend is noticed for the elements in 3rd and 4th periods.

2nd period: Li < B < Be < C < O < N < F < Ne

3rd period: Na < Al < Mg < Si < S < P < Cl < Ar

4th period: K < Ga < Ca < Ge < Se < As < Br < Kr



Trend for 4<sup>th</sup> period is similar to 2<sup>nd</sup> and 3<sup>rd</sup> periods.

#### **Explanation**:

Let us analyse for the 2nd period elements. Be has greater IE than Li due to increase in the nuclear pull. The effect of increase in nuclear charge far outweighs the effect of electron-electron repulsion that exists in the s-electron pair. Note that e-e repulsion and screening effect tend to decrease the nuclear pull while increase in nuclear charge tends to increase the nuclear pull. The net effect of these two opposinng effects is what really observed. So in this case the net effect is increase in nuclear pull and hence IE. However B has lower IE than Be. This is because of the following reasons.

(i) The electron removed belongs to p-orbital which has greater energy than s-orbital

(ii) The p-electron is screened both by 1s and 2s electrons which prouduce stronger

screening effect.

These two effects combinedly outweigh the effect of increase in nuclear charge and the net result is decrease in nuclear pull and so IE of B becomes less than Be.

(Note that some authors believe that due to full filled  $s^2$  configuration, Be has an unexpectedly higher IE so much so that its succeeding element goes below it. But it does seem to be a convincing explanation. The actual cause lies with B but not with Be)

Similarly O has lower IE than N which sits on another hump. This is because, in the case of O the electron is removed from a pair in the p-orbital while in case of N an unpaired electron is removed. Due to e-e repulsion, less energy is required for O. Repusion effect outweighs the effect of increase in the nuclear charge in this case

(Some authors believe that since N has stable half filled p-subshell configuration for which its IE is so high and for which its successor O possesses less IE than it. This, however, does not appear to be correct)

The same explanation holds good for the similar anomaly found in 3rd and 4th period. But why the same anomaly is not found in the 5th and 6th period is not clearly known. In these periods the IE increases from left to right among normal elements without encountering with any deviation like previous periods. This may be due the dominance of increase in nuclear charge over the screening and e-e repulsion effects when the valence shell remains farther away from the nucleus.

**SAQ 11**: Explain why while moving from a noble gas(group 18) to the next alkali metal(group1), there is a sudden fall the IE value.

**Answer**: In any given period the nuclear pull increase and becomes maximum in the noble gas for which its IE is maximum. But when we move to the next alkali metal, a new shell is added to the electronic configuration and the nuclear pull is suddenly decreased. Hence there is a suden fall in the IE value.

**SAQ 12**: Arrange the following in the order of inceasing 2nd IE and explain. (a) C, N, O, F (b) Li, Be, B, C **Answer**: (a) C < N < F < O. This is because in case of F, the second electron is removed from an electron pair(s<sup>2</sup>p<sup>4</sup>) which requires less energy than for O, in which an upaired electron is removed(s<sup>2</sup>p<sup>3</sup>).

(b) Be < C < B < Li. This is because in case of Li, the 2nd electron is removed from stable duplet(s<sup>2</sup>) i.e He configuration, so the energy required is the highest. This value is even higher than the 1st IE of He due to greater nuclear charge in Li. In case of C, the 2nd electron goes from the p-orbital(s<sup>2</sup>p<sup>1</sup>) while for B it is from the s-orbital. Since p-orbital has higher energy and experiences greater screening effect, the nuclear pull in C is less than for B.

**SAQ 13**: Why Hg is a liquid(low mp/bp) although it has the greatest IE among TM and has high density(13. g/cc)?

**Answer**: The 6s electrons of Hg is inert and does not take much part in metallic bonding. In fact diatomic Hg is not formed in the gaseous state like other TMs. Its metallic bond is very weak. That is why its bp/mp are low and its conductivity is also less than all other TMs. The inertness of 6s pair is due to a phenomenon called 'relativisitic contraction'. The s electrons are able to come very close to the nucleus. They swing around very massive nucleus at speeds comparable to that of light. When objects move at such high speeds, relativistic effects occur. The s electrons behave as though they were more massive than electrons moving at slower speeds. The increased mass causes them to spend more time close to the nucleus. This *relativistic contraction* of the 6s orbital lowers its energy and makes its electrons much less likely to participate in metallic bonding. In other words the s-electrons are buried deep in the atomic core.

But why its IE is very high and in fact the highest among TM? That is again to deal with isolated gaseous atom where screening effects on 6s electron comes into force. Both f-block and d-block contractions effects makes the nuclear pull very high and thus explains why Hg has a very high IE. But again its density is quite high(13.6g/cc) not in agreement with its mp/bp. This is due to the heaviness of the individual particle (mass/v is greater) and not due to the effect of metallic bonding in the bulk.

# Variation of Ionisation Energy along a Group:

Along a group, the ionization energy is expected to decrease down the group. Explanation:

In a group the valence electron goes farther away from the nucleus due to addition of newer shells and the nuclear pull decreases. Hence the valence electron becomes more and more loosely bound to the nucleus and lesser amount of energy is required to remove it. In s- block this trend is strictly observed while in p-block and d-blocks there are many anomalies.

# ANOMALOUS BEHAVIOUR IN GROUPS:

#### Transition elements:

(i) In Sc group(group 3) the IE decreases like any other normal group.

(ii) In V, Cr and Ni groups the IE increases from 1st to 3rd elements.

(iii) In all other groups of d-block, the IE decreases from 1st to 2nd element and then increases in the 3rd element. For example, in Fe group the IE values are: Fe = 762 KJ/mole, Ru = 710 KJ/mole, Os = 840 KJ/mole

(iv) The 3rd element in each group(expect Sc group) usually has the greatest IE. This is due to

**Lanthanide or f-block contraction** which is noticed from Hf(72) onwards. Due to large increase in nucler pull, the IEs of all the elements from Hf-Hg in the 3rd transition series are very high and often the highest in their respective groups.

# *p-block elements:*

(i) In group 13, Tl has greater IE than In, Ga and Al because of lanthanide contraction. Again Ga has a greater IE than Al due to d-block contraction.

Order of IE in group 13: B > TI > Ga > AI > In

(ii)In group 14, Pb has greater IE than Sn due to lanthanide contraction.

Order of IE in group 14: C > Si > Ge > Pb > Sn

(iii) The IE of Pb is greater than Bi in the 6th period also due to lanthanide contraction.

# VARIATION OF IE IE TRANSITION SERIES:

The variation of IE among each transition series is irregular and so there is no specific trend like atomic radius. No reason could be given for this. However one common thing is noticed in all the series is that the last element of each series namely Zn, Cd and Hg are the highest values in the respective periods. Hg has the highest IE among the TMs.

SAQ 14: Why Zn has greater IE than Cu, although its size is greater? Is it not contradictory?

**Answer**: It appears contradictory in terms of size-IE correlation. But this contradiction can be explained in this way. In measuring IE, isolated gaseous atoms are taken, not solid state where metallic bonding comes into force. In the absence of metallic bonding, d<sup>10</sup> electrons screen equally for Cu and Zn. But in Zn the extra proton in the nucleus brings about greater nuclear pull and overweighs the effect of e-e repulsion. Note that the effect of increasing nuclear charge is more dominating over e-e repulsion for s-orbital whose penetrating power is greater.

**SAQ 15**: Why there is a sudden fall of IE as we move from the last element in a transition series to the next element in p-block. For example: Zn to Ga, Cd to In and Hg to Tl.

**Answer**: For TM, the electron is removed from ns orbital, but for the next p-block element, the electron lost from np orbital which has a greater energy than ns. So less energy is required.

**SAQ 16**: Contrary to the trend in IE in the above question, the atomic size slightly decreases while we move from the last TM to the next p-block element in a given period. Explain.

**Answer**: Again for metallic radius measurement, we expect metallic bonding to come in force. The ns and np electrons taking part in bonding reduces the screening effect, and effect of increasing nuclear charge brings about decrease in size. This effect is not observed in the gaseous isolated atoms for measuring the IE. The p-electron to be lost is clearly from a higher energy level requiring less energy.

# SAQ 17 :

- (i) Between Na and Mg which has a higher Ionization Energy and why?
- (ii) Between Be and B which has greater IE and why?
- (iii) Explain why N has a greater IE than O although the IE generally increases across a period.
- (iv) Arrange the following in the increasing order of IE.
  - (a)Be, Mg, Ca, Sr and Ba (b)Li, Be, B, C, N,O, F, Ne

(v) Among all the elements in the periodic table which element has the highest IE and which has the lowest? Do not consider the naturally occurring radioactive elements in the comparison.

(vi) Na has an ionization energy of 496 Kjoules/mole while Mg has an ionization energy of 737 Kjoule per mole. Which metal is easily ionized? Which is a stronger metal among the two.

(vii) Although Be belongs to group IIA and is an alkaline earth metal like Mg, Ca, Sr and Ba, Be does not form Be<sup>++</sup>. Why?

- (viii) Li, Na, K, Rb and Cs(alkali metals) have the following IE : 520, 496, 419, 403 and 376 kjoules/mole respectively. Indicate which is ionized most easily and which least easily.
- (ix) Why do metals form positive ions easily, not the nonmetals?

still

Answer: (i) Mg has higher IE as it comes after Na in the same period.

- (ii) Be has greater IE as it has completely filled(hence more stable)  $2s^2$  configuration.
- (iii) N has a more stable half filled configuration of  $2s^2$ ,  $2p^3$ .
- (iv) (a)Ba<Sr<Ca<Mg<Be(same group) (b)Li<B<**Be**<C<O<**N**<F<Ne(Be and N have higher IE because of their full filled and half filled electronic configurations respectively).
- (v) He has the highest IE and Cs has the lowest IE(Refer table-5).
- (vi) Na is easily ionised as it has lower IE. Thus Na is a stronger metal
- (vii) Be has a very high IE for which it is difficult to undergo ionisation.
- (viii) Cs is ionised most easily and Li least easily.
- (ix) Metals have lower IE than nonmetals.

# ELECTRON AFFINITY(EA)/AFFINITY ENERGY(AE)/ELECTRON GAIN ENTHALPY:

When an atom accepts one electron from an outside source it is converted to a negative ion. You know that atoms form their respective positive ions by losing electron(s). Here we shall find that atoms can form their negative ions by accepting electron(s).

#### X(g) + e ----> X(g) + Electron Affinity(EA)

In case of many elements particulary nonmetals some amount of energy is evolved or released during the process of accepting an electron. This is an exothermic process.

**Definition:** The amount of energy released when an isolated gaseous atom accepts an electron to form a negative ion is called electron affinity. In fact this is the first electron affinity.

More the electron affinity of an element, more is the tendency or ease of forming negative ion. The electron affinity is a measure of the attraction between the incoming electron and the nucleus - the stronger the attraction, the more energy is released. The factors which influence IE also affect EA.

(Note that some elements do not have a spontaneous tendency to accept electron. Their atoms can accept electron only when energy is supplied to them i.e by absorbing energy. In that case the process would be endothermic. The above definition excludes such elements which accept electron by abosorbing energy. In the given table for EA, the numerical values of the energy released have been given for those elements which accept electron exothermically. However for other elements which accept electron endothermically, EA values are given as zero. In the true sense they have their numerical EA values which are not given in the table for the sake of simplicity and for avoiding confusion during the analysis of the trend of their variation along groups and periods. Acutally in the thermodynamic sense, exothermic processes are associated with -ve sign with their enthalpy values while endothermic processes are associated with +ve signs. The actual EA table consisting of +ve and -ve values of EA of all the elements is also given for sake of reference. However since no particular trend could emerge from this table and shall create more confusion than give meaningful concepts to the young learners, such a table has not been considered for analysis. Elements having full filled s<sup>2</sup>, half filled p<sup>3</sup> and octet/duplet configuration have positive EA or lower -ve EA. In first EA table only the numerical values of exothermic EAs have been given for analysis. In the following text, we shall only consider the elements which accept electron exothermically only.)

# The EA for the nonmetals are greater than those of metals which means that nonmetals have a stronger tendency to form negative ions than metals.

SAQ: What is 2nd and higher orders of EAs. Explain with example.

**Answer**: The addition of 2nd electron to the mononegative ion to form dinegative ion requires always absorption of energy. For example, for O atom two EAs are involved i.e  $EA_1$  which is evolved and  $EA_2$  which is absorbed. This is because the 2nd electron will face severe replsion from the -ve charge of a small size O and will be added to it forcefully by absorbing energy. In fact all higher orders of EAs are endothermic processes, while the 1st EA could be both exothermic or endothermic.

$$O(g) + e -----> O^{-}(g) + EA_1$$
 (EA<sub>1</sub> = -142 KJ/mole)  
 $O^{-}(g) + e + EA_2 ----> O^{2}(g)$  (EA<sub>2</sub> = + 844 KJ/mole)

Н 73																	He 0
Li 60	Be 0											В 27	C 122	N 0	0 141	F 328	Ne 0
Na 53	Mg 0											AI 43	Si 134	Р 72	S 200	CI 349	Ar 0
K 48	Ca 0	Sc 18	Ti 8	V 51	Cr 64	Mn 0	Fe 16	Co 64	Ni 111	Cu 118	Zn 0	Ga 30	Ge 120	As 78	Se 195	Br 325	Kr 0
Rb 47	Sr 0	Y 30	Zr 41	Nb 82	Мо 72	Тс 53	Ru 101	Rh 110	Pd 54	Ag 126	Cd 0	In 30	Sn 120	Sb 103	Те 190	l 295	Xe 0
Cs 45	Ba 0	La* 50	Hf 0	Та 31	W 79	Re 14	Os 110	lr 151	Pt 205	Au 223	Hg 0	TI 20	Pb 35	Ві 91	Ро 180	At 270	Rn 0
Fr -	Ra	Ac**	Rf	На	Sg	Ns	Hs	Mt									

# ELECTRON AFFINITY OF ELEMENTS (Kjoules/mole)

Note that the sum total of the two EAs for O is +ve(endothermic) because numerical value of energy absorbed in the 2nd step is more than the numerical value of energy released in the first step. Then question arises how the a metallic oxide like MgO, CaO etc. is formed spontaneously. This is because the *lattice energy* is hugely negative which compensates for all positve energy terms. Discussion on *lattice energy* will be made in *Chemical Bond* chapter. The tables for EA gives only the first EAs of elements)

N.B: Note that EA values are important for nonmetals while they carry little significance for metals.

# Variation of EA across a period:

Electron affinity is expected to increase from left to right in a period. This means that the elements acquire greater tendency to form their negative ions while moving from left to right. This is due to increase in the nuclear pull across a period for which the incoming electron is accepted more efficiently by releasing more amount of energy. Note that elements for which Electron Affinity(EA) is written as zero are not considered for analysing this trend. In 2nd period, the EA of B, C, O and F are 15, 121, 141 and 333 Kjoule/mole respectively. So the tendency to form negative ion(anion) is maximum for F and minimum for B.

SAQ 18: Explain why the EA of B is less than that of Li.

**Answer**: For Li, the gain of one electron converts its configuration from  $s^1$  to  $s^2$  which is stable. The added electron experiences very little screening effect as it enters the same orbital, so the nuclear pull is more. But for B, the extra electron enters into a different p-orbital(Hund's rule) and hence experiences greater screening effect from both full filled 1s orbital and one p-orbital. Therefor the nuclear pull is less than Li.

SAQ 19: Why halogens have the highest EA in their respective periods?

**Answer**: At the halogen in each period, the nuclear pull is very high. So the added electron is most efficiently accepted. We can also say that by gaining one electron, each halogen attains the stable noble gas configuration for which it releases maximum energy in their repective periods.

SAQ 20: Why carbon has an unexpectedly greater EA than B?

Answer : The nuclear pull becomes greater compared to the screening effet of one additional electron in the same subshell.

Similary in the 3rd, 4th and 5th periods, excepting P, As, Sb of group 15, the trend is same(increasing) as in the 2nd period. Note that elements(normal elements only) belonging to groups 2, 15, 18 in respect of these periods as well as the three transition series of elements are excluded while analysing the trend in periods.

# Variation of EA along Groups:

The EA is expected to decrease along a group. Since nuclear pull decreases down the group due to addition of newer shells, the incoming electron is accepted by the atom with less and less ease down the group.

Although this trend is noticed in group 1 of the s-block, there are a few anomalies in the groups of the p-block. The most important anomaly noticed in the p-block is given below.

#### Anomaly in groups of the p-block:

The 2nd element in each group of the p-block has a greater EA than their respective 1st element.

Al > B, Si > C, P > N, S > O, Cl > F

This anomaly is explained like this. The atoms of the first elements of all these groups namely C, N, O, F belonging to the 2nd period have very small size. The electronic charge density(charge/volume) is quite high and the incoming electron suffers from considerable e-e repulsion. This repulsion lessens the attraction that the incoming electron experiences and so electron affinity is lowered. In other words, a part of energy evolved is used up to overcome the e-e repulsion for which the net quantity of energy evolved becomes less. That is why the 2nd element in each group overtakes the 1st element in the EA value.

Decreasing order in p-block:

B family: Al > Ga = In > B > Tl; C family: Si > C > Ge = Sn > Pb

N family: Sb > Bi > As > P (N is not included as it has 0 EA value as per our definition, but actually ve)

+ve)

Halogens: Cl > F > Br > I > At

to

#### Variation among Transition Elements:

O family: S > Se > Te > Po > O

The variation of EA in the TM among groups and periods is highly irregular. Moreovere it is not important to consider about the EA values of metals.

N.B: The highest EA among all elments in the periodic table is of Cl and the lowest value is of Cs(since there is no EA data for Fr)

SAQ 21 :Look to EA data table and answer the following questions.

- (i) Between Cl and F which has got the greater tendency to form negative ion Cl<sup>-</sup> and F<sup>-</sup> respectively and why?
- (ii) Arrange O, S, Se and Te in the order of decreasing tendency of forming negative ions.

# (iii) Explain why C has a great tendency to form negative ion while B has very low tendency form its negative ion.

- (iv) Nitrogen has no tendency to form a negative ion although it is a strong non-metal. Explain.
- (v) Alkaline earth metals have no tendency form their negative ions. Explain.
- (vi) Arrange the halogens in the order of increasing EA.

**Answer**: (i) Cl has a greater tendency to form negative ion as its EA is greater.

- (ii) S>Se>Te>O. This is because their EA decreases in the same order.Refer table-6.
- (iii) C has much higher EA(121Kj/mole) while B has a much lower EA(15 Kj/mole).
- (iv) N has zero EA.
- (v) All of them have zero EA.
- (vi)  $I \leq Br \leq F \leq Cl$

# ELECTRONEGATIVITY

To know which element is more metallic and which is less metallic or more nonmetallic on a relative basis, a scale has been introduced. This is called *electronegativity* (EN).

It is defined as the relative tendency of an atom to attract a bonding pair of electrons towards itself. More the tendency of an atom to attract an electron pair, more is its electronegativity. Again more the electronegativity more is its nonmetallic character. For example oxygen atom has greater tendency to attract electron and so its electronegativity value is small. Note that all metals have less tendency to attract electrons and have low electronegativity values, while all nonmetals have greater tendency to attract electrons and have higher electronegativity values. You know that nonmetals are found in the upper right region of the periodic table and have small atomic sizes. This is because, the nuclear pull to the valence electronegativity. EN values are used among elements on a relative basis for the purpose of comparison They do not give the absolute values of the force of attraction of an atom on bonding electron pair. The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is assigned an EN value of 4.0, and values range down to caesium and francium which are the least electronegative EN value of 0.7.

\* In a period the EN increases as a result the metallic character decreases and the nonmetallic character increases. The increase in EN is due to increase in the nuclear pull for which the bonding pair of electron is dragged closer to the atom.

\* In a group the EN decreases and as a result the nonmetallic character decreases while metallic character increases. This is due to decrease in nuclear pull as newer shells are added down the group for which the bonding pair gets less attracted to the atom.

\* Nonmetals have high EN values( 2 and above) while metals have low EN values( less than 2).

\* O has the 2nd highest EN of 3.5 and Cl and N have the 3rd highest EN of nearly 3.

Br = 2.8, C = 2.5, H = 2.2

\* When the EN difference between two elements is high (> 1.7) the bond between them is predominantly ionic or electrovalent like NaCl, CaO etc.. If this difference is small( < 1.7), the bond is predominantly covalent like HCl,  $H_2O$ ,  $NH_3$  etc.

\* When EN difference is zero the covalent bond becomes pure and non-polar. This is the case with bond between identical atoms like  $H_2$ ,  $Cl_2$ ,  $N_2$  etc. While the EN difference is non-zero but less than 1.7 the bond is polar covalent (i.e covalent bond with some ionic character) like HCl,  $H_2O$ ,  $NH_3$  etc. More the electronegativity difference in covalent bond, more is the polarity of the bond. This will be discussed in details in the chapter *chemical bonding*.

\* The variation of EN across transion series and groups have no regular trend. There are some anomalies among groups in the p-block whose cause is not clearly known.

# ELECTRONEGATIVITY SCALES

# 1. PAULING SCALE:

Pauling observed that the covalent bond between two different atoms (A–B) is stronger than would be expected by taking the average of the strengths of the A–A and B–B bonds. This "additional stabilization" of the heteronuclear bond(bond between two different atoms) is due to the contribution of ionic charcter to the covalent bond. The additioal stabilisation called the extra bond energy( $\Delta_{H_x}$ ) in the equation given below.

$$\chi_{\rm X}^{-}$$
  $\chi_{\rm H}^{-} = 0.208 \sqrt{\Delta_{\rm H-X}}$ 

where  $\chi$  = electronegavity;  $\Delta_{H-X}$  = extra bond energy

Bond energy in Kcals/mol

$$\Delta_{\text{H-X}} = E_{\text{H-X}} \sqrt{E_{\text{X-X}} E_{\text{H-H}}}$$

The EN of H has been arbitrarily taken as be 2.2. The EN of any other element, X can be found out from the bond energy data of the X-H bond  $(E_{H-X})$ , the bond energy data of H-H bond  $(E_{H-H})$  and X-X bond  $(E_{X-X})$ . The difference  $\Delta_{H-X}$  calculated as per the given equation is called the extra bond energy which is used in the first equation to calculate the EN of the unknwon element, X.

#### 2. MULLIKEN SCALE:

First Mulliken proposed that EN to be the average of the IE and EA of an element [EN = (IE + EA)/2]. But the EN values thus calculated were found to be 2.8 times greater than the EN obtained from Mulliken scale. So for attaining a close match between the two scales, the Mulliken scale was modifed as given below.

$$EN = 0.187 (IE + EA) + 0.17$$

$$OR$$

$$EN = \frac{IE + EA}{2 \times 2.8}$$
(IE and EA values taken in eV unit)
$$EN = 1.97 \times 10^{-3} (IE + EA) + 0.19$$

$$OR$$

$$EN = \frac{IE + EA}{540}$$
(IE and EA in kJ/mole unit)

Н																	He
2.2																	
Li	Be	]										В	С	Ν	0	F	Ne
0.98	1.57											2.0	2.5	3	3.5	3.98	
Na	Mg											AI	Si	Р	S	CI	Ar
0.93	1.3											1.6	1.9	2.19	2.6	3.2	
	_											_	_	_	_	-	
κ	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.82	1.0	1.4	1.5	1.6	1.6	1.5	1.8	1.8	1.9	1.9	1.6	1.8	2	2.18	2.5	2.96	3
	_													_			
Rb	Sr	Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Aq	Cd	In	Sn	Sb	Те	I	Xe
0.82	0.95	1.2	1.3	1.6	2.2	1.9	2.2	2.3	2.2	1.9	1.7	1.78	1.9	2	2.1	2.66	2.6
														_			
Cs	Ва	La*	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Ро	At	Rn
0.8	0.9	1.1	1.3	1.5	2.3	1.9	2.2	2.2	2.3	2.5	2	1.6	2.3	2.0	2.0	2.2	
													_	_			
Fr	Ra	Ac**	Rf	На	Sq	Ns	Hs	Mt							l l		1
0.7	0.9	1.1															

# **ELECTRONEGATIVITY OF ELEMENTS**

#### 3. ALLRED AND ROCHOW SCALE

$$\chi = 0.359 \frac{Z^*}{r_{\rm cov}^2} + 0.744.$$

Where  $r = covalent radius of the atom and Z^*$  is the effective nuclear charge of the atom.

#### Difference between electronegativity and Electron Affinity:

Electron affinity is the tendency of an element to accept or gain an electron and form negative ion, but electronegativity is the tendency of an element to attract a bonding pair of electrons towards itself(not accept). Electron affinity is an energy term and corresponds to an absolute value while electronegativity is a relative value used for making comparison among elements and so EN values are not absolute. Although elements which have high electron affinity values have also high electronegativity values the reverse is not always true. Some elements have high electronegativity values but have lower electron affinity values. For example, F is the most electronegative element(EN=4) while Cl has the highest EA value.

N.B: Note that some noble gases have almost no tendency to attract electrons as they do not form covalent bonds easily and EN data are not available. The EN data for Kr and Xe are available as they form covalent bonds relatively easily.

# SAQ 22:

- (i) The elements with their electronegativity values are given below. Indicate which are metals(M) and which nonmetals (NM).
  - A(0.9), B(2.5), D(1.5), E(2.1), F(0.9), G(3.5)
- (ii) Between Mg and Ca which has greater EN and which is more metallic among the two?
- (iii) Between B and C which has less EN and which is more nonmetallic?
- (iv) Arrange the following in decreasing order of EN.Na, Mg, Al, P, S and Cl. Also arrange these elements with increasing nonmetallic properties.
- (v) Arrange the following with decreasing EN.
- F, Cl, Br and I. Arrange these elements with decreasing non-metallic character.
- (vi) Why Ga has a greater EN than Al.

#### Answer:

- (i) A:M; B:NM; D:M; E:NM; F:M;
- (ii) Mg has greater EN and hence Ca is more metallic.
- (iii) B has lesser EN. C is therefore more nonmetallic.
- (iv) EN: Cl>S>P>Al>Mg>Na. They belong to the same period. No-metallic character: Na<Mg<Al<P<S<Cl
- (v) EN: F>Cl>Br>I; Nonmetallic character: F>Cl>Br>I
- (vi) Due to d-block contraction, Ga has greater IE and EN.

# **IONIC SIZE**

# Cationic Size:

The cationic size is always less than the corresponding atomic size. For example, the size of  $Na^+$  ion is less than Na atom, the size of  $Mg^{2+}$  is smaller than Mg atom and so on. This is because as the electron is removed from a neutral atom, the nuclear pull further increases due to increase in the ENC for which contraction in size occurs. We know that metals form their cations easily as their ionisation energies are low. Refer the table giving the sizes of some common ions(both cations and anions).

G:NM

If we compare the sizes between the cations having different charges(ON), for example  $Fe^{2+}$  and  $Fe^{3+}$  we shall find that the cationic size decreases with the increase in the magnitude of charge of the cation. For example,  $Fe^{3+}$  has smaller size than  $Fe^{2+}$ ;  $Mg^{2+}$  has smaller size than  $Mg^+$  and so on. This is due to further increase in ENC as additional electron is removed from the ion and hence nuclear pull further increases.

Na<sup>+</sup> (1.02 Å) < Na (1.54 Å) ; 
$$Fe^{3+} < Fe^{2+} < Fe$$

#### Anionic Size:

The anionic size is always greater than the corresponding atomic size. For example, the size of  $Cl^{-}$  is greater than Cl atom, the size of  $O^{2-}$  ion is greater than O atom and so on. This is because as one electron is added to the neutral atom, electron-electron repulsion comes into force for which ENC decreases. So expansion in size occurs.

# Sizes of some common Cations and Anions in Angstrom unit

-																	
H 0.012																	He
Li <sup>⁺</sup> 0.76	Be <sup>2+</sup> 0.31											B <sup>3+</sup> 0.23	с	N <sup>3+</sup> 0.13	0 <sup>2-</sup> 1.40	F <sup>-</sup> 1.36	Ne
Na <sup>⁺</sup> 1.02	Mg <sup>2+</sup> 0.72											Al <sup>3+</sup> 0.53	Si	P <sup>3+</sup> 0.38	S <sup>2.</sup> 1.84	CI <sup>-</sup> 1.81	Ar
K⁺ 1.38	Ca <sup>2+</sup> 0.99	Sc³⁺ 0.81	Ті	v	Cr	Mn	Fe	Co	Ni	Cu⁺ 0.96	Zn <sup>2+</sup> 0.74	Ga³⁺ 0.62	Ge⁴⁺ 0.53	As³⁺ 0.58	Se <sup>2-</sup> 1.98	Br <sup>-</sup> 1.95	Kr
Rb <sup>+</sup> 1.48	Sr <sup>2+</sup> 1.13	Y <sup>3+</sup> 0.93	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag <sup>⁺</sup> 1.26	Cd <sup>2+</sup> 0.97	In <sup>3+</sup> 0.81	Sn⁴⁺ 0.71	Sb <sup>3+</sup> 0.76	Te <sup>2-</sup> 2.21	ľ 2.16	Xe
Cs <sup>⁺</sup> 1.69	Ba <sup>2+</sup> 1.35	La* <sup>3+</sup> 1.15	Hf	Та	w	Re	Os	Ir	Pt	Au <sup>+</sup> 1.37	Hg <sup>2+</sup> 1.10	TI <sup>3+</sup> 0.95	Pb <sup>4+</sup> 0.84	Bi <sup>3+</sup> 1.03	Po <sup>2-</sup>	At <sup>-</sup>	Rn
Fr⁺	Ra <sup>2+</sup>	Ac**	Rf	На	Sg	Ns	Hs	Mt									

The anionic size increases further if the magnitude of the anionic charge increases. For example, the size  $O^{2-}$  is greater than that of  $O^{-}$ . This is because the addition of extra electron on a negative ion brings about further decrease in ENC.

 $Cl^{-}(1.81\text{ Å}) > Cl(0.99 \text{ Å});$   $O^{2-} > O^{-} > O$ Isoelectronic Species:

Species(cations, anions or neutral atoms) having same number of electrons are called isoelectronic species. In such species more the nuclear charge, less is the size. This is because greater the nuclear charge greater is the ENC as screening effect remains constant. Hence size decreases.

Example: (i)  $O^{2-}$ , F<sup>-</sup>, Ne, Na<sup>+</sup>, Mg<sup>2+</sup> : all have ten electrons and are isoelectronic. The size of Mg<sup>2+</sup> is the least as its nuclear charge is maximum(12) and the size of  $O^{2-}$  is maximum as its nuclear charge is minimum (8).  $O^{2-}>F >Ne>Na^+>Mg^{2+}$ 

(i) Between Ca and  $Ca^{2+}$  which has a smaller size and why?

- (ii) Between Br and Br which has a larger size and why?
- (iii) Arrange according to decreasing size among the following isoelectronic species K<sup>+</sup>, Ca<sup>2+</sup>, Ar, Cl<sup>-</sup>, S<sup>2-</sup>
- (iv) Between  $Cu^{2+}$  and  $Cu^{+}$  which has a lesser size and why?

# Answer:

- (i) Ca<sup>2+</sup> has a smaller size. Cationic size is always less than the atomic size due to greater nuclear pull in case of the cation.
- (ii) Br has a larger size. Anionic size is always greater than the atomic size due to less nuclear pull.
- (iii)  $S^2 > Cl > Ar > K^+ > Ca^{2+}$ . Since S has the minimum nuclear charge(16) and Ca has the maximum nuclear charge(20).

(iv) Cu<sup>2+</sup> has less size than Cu<sup>+</sup> because the size decreases as the magnitude of cationic charge increases.

# DENSITY

Hydrogen is the lightest element having density is 0.000089gm/cc while Os an Ir are the heaviest element having densities nearing 22.6 g/cc. Li the lightest metal while Sc is the lightest d-block metal. Besides gaseous elements(which are nonmetals), three other metals namely Li, Na and K are lighter than water. In general transition elements are heavier than normal elements. Refer the density table given for elements at standard conditions(25°C and 1 atmosphere).

#### Variation of Densities across a Period:

Rn: 0.0097

The variation of density across a period is not systematic. However we can observe that the density across a period increases upto certain element in the period and thereafter it decreases. Take for example the 2nd period. The density of Li is 0.53, then Be is 1.8, followed by B (2.3) and C (3.5) and thereafter the density suddenly decreases to 0.0012gm/cc as nitrogen is a gaseous element. Thereafter the densities vary very little among gaseous elements. Look to 4th period, the density increases regularly through the transition series up to Cu(8.96) and thereafter the density decreases regularly. This is because in a period, the metallic bond strength increases upto certain element as more number of valence electrons are available for the bonding(Refer metallic bonding in the chapter *chemical bond*). Therefore the packing of atoms in their solid state becomes more efficient for which density increases. Beyond that the metallic bond starts to become gradually weaker and finally the metallic bond is replaced by weak Van der Waals forces in nonmetals. That is why the packing of atoms and molecules in the standard state becomes loose and less efficient for which density decreases.

н																	He
*																	*
Li 0.53	Be 1.8											В 2.3	C 3.5	N *	0 *	F *	Ne *
Na 0.97	Mg 1.7	-										Al 2.7	Si 2.3	P 1.8	S 2.0	CI *	Ar *
K 0.86	Ca 1.5	Sc 3.0	Ti 4.5	V 6.1	Cr 7.2	Mn 7.4	Fe 7.9	Co 8.9	Ni 8.9	Cu 8.96	Zn 7.1	Ga 5.9	Ge 5.3	As 5.8	Se 4.8	Br 3.1	Kr *
Rb 1.53	Sr 2.5	Y 4.5	Zr 6.5	Nb 8.6	Mo 10.2	Тс 11.5	Ru 12.37	Rh 12.4	Pd 12.0	Ag 10.5	Cd 8.6	In 7.3	Sn 7.3	Sb 6.7	Те 6.2	l 4.9	Xe *
Cs 1.87	Ba 3.6	La* 6.1	Hf 13.3	Та 16.6	W 19.3	Re 21.0	Os 22.59	lr 22.56	Pt 21.4	Au 19.3	Hg 13.6	TI 11.8	Pb 11.3	Bi 9.7	Po 9.3	At	Rn *
Fr	Ra 5.0	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub						
Gases	: Н <sub>2</sub> : Но	0.000	089,	<u> </u>	N <sub>2</sub> : (	0.0012	25, C	D <sub>2</sub> : 0.00	14	F <sub>2</sub> :	0.001	1 7, 7	Cl <sub>2</sub> : (	0.003	2	<u> </u>	L

# Densities of Elements (gm/cm<sup>3</sup>)

# Variation of density along a group:

<u>Group 1</u>: Increases down the group (exception: K < Na). The increase is due to a greater increase of mass relative to increase in volume down the group. Density also depends on how atoms pack in the solid state in the crystal. So the anomalies cannot be easily explained.

<u>Group 2</u>: Irregular- decreases upto Ca and thereafter increases. The crystal structure changes down the group. So it is not possible to give any reason for this anomaly.

<u>Transition groups</u>: In transition group, the density increases. In this case the increase in mass is greater than the increase in volume for which density increases.

<u>p-block groups</u>: Density usually increases down the group as the metallic character increases and nonmetallic character increases, the weak Van der Waals forces are gradually replaced by stronger metallic bond. Therefore the packing of the particles become more efficient down the group.

SAQ 23 : Look to density table and answer the following .

- (i) Between Na and K which is lighter?
- (ii) Between Cu and Ag which is heavier?
- (iii) Arrange the following in order of decreasing density:  $F_2$ ,  $Cl_2$ ,  $Br_2$ ,  $I_2$
- (iv) Arrange the following in the order of increasing density: Fe, Co, Ni, Cu, Zn
- (v) Which element is the heaviest and which lightest in the periodic table?
- (vi) Which elements are lighter than water?
- (vii) Arrange in the order of decreasing densities: Pt, Au, Os, Fe

**Answer:** i) K is lighter (ii)Ag is heavier (iii) $I_2 > Br_2 > Cl_2 > F_2$ 

(iv) Zn<Fe<Co=Ni<Cu (v)Os,Ir are heaviest while H, is the lightest.

- (vi) All gaseous elements, Li, Na and K are lighter than water.
- (vii) Os > Pt > Au > Fe

# **MELTING AND BOILING POINTS**

Metals have greater melting points(mp) and boiling points(bp) than nonmetals because there is metallic bonding in metals which are stronger while there is weak Van der Waals forces in nonmetals. Like density, transition elements have greater mp/bp than normal elements due to greater metallic bond strength in case of the former. Of course, the highest melting and boiling element is exceptionally a nonmetal- diamond(carbon) having mp of  $3547^{\circ}$ C. This is due to its network structure(Refer the chapter Carbon Family). Note that graphite another allotrope of carbon melts at a lower temperature than diamond. The highest melting/boiling metal is W( $3407^{\circ}$ C) and lowest melting/boiling element is He( $-272^{\circ}$ C).

				-		3			• • • • • • •								
Н																	He
-259																	Ξ.
-253																	<u>272</u>
																	267
																	201
Li	Be											В	C*	N	0	F	Ne
181	1278											2300	3547	-210	-	-	-
1347	2970											3658	4827	-196	218	220	249
															-	-	-
															183	188	246
Na	Ma											Δι	Si	Р	S	CI	Δr
98	649											660	1410	44	113	-	-
883	1090											2467	2355	280	445	101	189
																-34	-
																	186
к	Ca	Sc	Ті	v	Cr	Mn	F٩	Co	Ni	Сп	7n	Ga	Ge	Δs	Se	Br	Kr
64	839	1541	1660	1887	1857	1244	1535	1495	1453	1083	420	30	938	817**	217	-7	-
774	1484	2831	3287	3377	2672	1962	2750	2870	2732	2567	907	2403	2830	616	685	59	156
																	-
DI	0	V	7.	NIL.		<b>T</b> .	<b>.</b>	DI	D.I		0.1	1	0	01	Ŧ	<u> </u>	152
20 80	5r 760	Y 1522	2r 1952	ND 2469	1VIO	10	RU 2210	1066	P0	Ag	221	156	5n 222	5D 621	10	114	xe
688	1384	3338	4377	4742	4612	4877	3900	3727	3140	2212	765	2080	232	1635	990	184	- 112
								•••=•	•••••								-
																	107
Cs	Ba	La*	Hf	Та	W	Re	Os	lr	Pt	Au	Hg	TI	Pb	Bi	Ро	At	Rn
29	727	921	2227	2996	3407	3180	3054	2410	1772	1065	-39	304	328	271	254	302	-71
0/9	1097	3457	4002	9429	3057	3027	5027	4130	3021	2007	357	1457	1740	1360	302	331	-02
Fr	Ra	Ac**	Rf	На	Sq	Ns	Hs	Mt								<u> </u>	
27	700	-		-	- 5	-	_	-									
677	1140																

# Melting and Boiling Points of Elements\*

\* The lower value in each is the melting point and the higher value the boiling point \*As boils only at high pressure of 28atm. At normal pressure it is vaporized at 616⁰C

# Variation along groups:

Group 1: decreases due to decrease in metallic bond strength as size increases.

<u>Group 2</u>: Irregular. Group 2 metals have much greater mp/bp than group 1 metals due to stronger metallic bond in the former. Since the crystal structures are widely different for group 2 metals the reason of irregular trend cannot be understood.

<u>Transition groups</u>: Increases like density except in group 11 and 12. In group 12, the mp/bp decreases from Zn to Hg(Zn > Cd > Hg) while in group 11, Cu has the highest mp/bp while Ag has the lowest(Cu > Au > Ag). p-block groups: Irregular

# Variation across periods: Irregular

Howerver in Transiton series, the mp/bp increases upto certain element and thereafter decreases analgous to density. Same explanation can be given for this as has been given for the density variation. Note that the decrease in mp/bp does not take place upto the same element as observed for density.

**SAQ 24:** Explain why the difference between mp and bp in case of any metal is quite large while this difference is very small in case of a nonmetal.

**Answer**: While melting a metal the metallic bond is weakended. But when we boil the metallic liquid to its vapour, the metallic bond is completely broken for which a large energy is required. So the gap between mp and bp is large. On the other hand when we melt a nonmetal, the Van der Waals forces are weakened and when we boil the liquid this forces are further weakened. This process does involve large increase in energy. So the gap between mp and bp is small.

SAO 25: Look to the mp/bp table and answer the following.

- Give the trend of melting points among alkali metals. Is there any specific trend in its (i) variation?
- (ii) Which is the highest melting metal and which is the highest melting nonmetal? Among all the elements which has the greatest melting and boiling point?
- Between Cu and Al both of which are used in electrical wiring, which has a greater (iii) melting point? Which is better conductor of electricity between them?
- (iv) Between Hg and Br both of which are liquids which exhibits a greater difference between the melting and boiling points and why?

#### Answer:

- There is a smooth decrease in melting point from Li to Fr. (i)
- (ii) W is the highest melting metal (3407°C) and Hg is the lowest melting metal(-39°C).

Among all elements diamond(an allotrope of carbon) has the highest melting point(3547°C) and He has the lowest melting point(-272.05°C).

- Cu has a much greater melting point than Al(see table-10). Cu is better conductor of (iii) electricity also.
- Mercury exhibits a greater difference between the m.p and b.p as it is a metal(refer text) (iv)

# **OXIDATION STATE/VALENCY**

The maximum OS or valency of elements is the total number of electrons present in the valence shell which would be used in making ionic or covalent bond. From carbon family onwards there is a minimum OS which is equal to (8- group number as per the old name) with a -ve sign. This is because by gaining that many number of electrons it can form negative ions.

Normal Groups:

Group 1(I): Max OS = +1, Group 2(II) : Max OS = +2, Group 13(III) : Max OS = +3 Group 14(IV) : Max. OS = +4, Min. OS = -4 [-(8-4)] Group 15(V): Max OS = +5, Min OS = -3 Group 16(VI): Max. OS = +6, Min. OS = -2; Group 17(VII): Max OS = +7, Min OS = -1Group 18(zero): Max OS = +8; Min OS = 0

# **Transition Groups:**

The maximum OS goes on increasing from Sc group(+3) to Mn group (+7) and thereafter the maximum OS goes on decreasing to +2 in the Zn group. In a transition series both ns and (n-1)d electrons constitute valence electrons due to their small energy difference. Upto Mn group, the electrons remain unpaired in the d-orbitals(Hund's rule) and take part in bonding and OS goes upto +7 [ns<sup>2</sup>, (n-1)d<sup>5</sup>]. From Fe group onwards pairing of electron starts and these electron pairs do not take part in bonding and therefore the maximum OS decreases again. More on this point will be discussed the chapter Transition Elements.

# **INERT PAIR EFFECT:**

As we go down a group in the p-block, the stability of the highest +ve OS decreases and that of lowest +ve OS increases. If there are 'x' number of valence electrons( $ns^2 np^y$ ), then x (=2+y) is the maximum +ve OS while y is the minimum +ve OS. For example in carbon family the highest OS is +4 and lowest is +2. The stability of +4 state decreases and +2 state increases as we move from C to Pb. This explains why PbCl, does not exist at room temperature because +4 state of Pb is unstable while PbCl, stable. Similarly for nitrogen family the +5 state becomes unstable and +3 state become stable as we move down the group. BiCl<sub>s</sub> does not exist at room temperature due to the same reason. For oxygen and halogen families +6 and +7 states respectivley becomes unstable while going down the group. Its reason is like this. As we go down a group size increases and hence bond energy with any other element decreases. The excitation of one ns electron to np orbitals is required to show the higher OS. This requires some energy which is provided by the bond energy. Since bond energy goes on decreasing down the group, this cannot adequately compensate for the excitation of electron and hence the s-electron pair becomes inert and does not like to take part in bonding. More on excitation of electron, you shall get in the chapter chemical bond.

# **ATOMIC VOLUME:**

The volume occupied by one mole of an element in the solid state is called atomic volume.

Atomic Volume = (Atomic mass/density)

Note that the density of the element in its solid state has to be used. Some authors define atomic volume as the volume of one mole of an element in its condensed state(solid and liquid states). For gaseous element, the density in its liquid state is used.

Example: Calculate the atomic volume of Fe if its density is 7.86 g/cc.

 $V_{M}$ (atomic volume) = 56/7.86 = 7.12 cc/mole. In other words, one mole(avogadro's number) of Fe atoms in the solid state will occupy 7.12 cc.

Note that there is no similarity in the trends of atomic radius and atomic volume. This is because atomic radius is known from the distance between adjacent atoms in the bonded state. But atomic volume is the volume of the entire bulk of the sample in its condensed state. Since the crystal structure changes as we move across a period and also in groups particularly in the p-block, so no fixed trend of atomic volume are found in periods and many groups. The molar volume depends upon density, phase, allotrope, and temperature. Hence it is based on a bulk effect of many atoms and has to do with how well the atoms pack together.

# **NATURE OF OXIDES**

Generally the oxides of metals are basic while that of nonmetals acidic. Basic oxides produce their hydroxide and acidic oxides produce their acids by reacting with water. Some oxides are amphoteric which have both acidic and basic property. They react with acids as well as strong bases.

\* In a period the basic nature of oxides decrease and acidic nature increases. For example in the 3rd period, the variation acidic/basic property is as follows.

In fact the first two are distinctly basic while the 3rd(Al<sub>2</sub>O<sub>3</sub>) is amphoteric and the remaining are acidic.

\* In group the basic nature increases and acidic nature decreases. For example in group 1, the increasing basic nature is :

$$Li_2O < Na_2O < K_2O < Rb_2O < Cs_2O$$

Although all are basic as they are metallic oxides, the  $Cs_2O$  is most basic and  $Li_2O$  is least basic. Same is the case with group 2.

In nitrogen family the basic nature increases in the order :

 $N_2O_3 < P_2O_3 < As_2O_3 < Sb_2O_3 < Bi_2O_3$ 

The acidic nature of these oxides decreases in the same order. While the first three oxides are acidic,  $Sb_2O_3$  is amphoteric and  $Bi_2O_3$  is basic. This is because N, P, As are nonmetals, Sb is a metalloid while Bi is a metal. Note that As although is considered as metalloid but it has more nonmetallic character than metallic.

In boron family, oxide of B is acidic, that of Al is amphoteric and the oxides of the rest(Ga, In and Tl) are basic.

Note that every  $oxide(M_2O_x)$  by reacting with water produce  $M(OH)_x$  where x the valency of the element M. But whether the latter will behave as an acid or a base depends on the relative polarites of M-O and O-H bond. If M-O bond is more polar than O-H bond then M-O bond breaks and OH- ions are produced to make the nature basic. On the other hand if O-H bond is more polar than the M-O bond then former breaks to form H<sup>+</sup>(H<sub>3</sub>O<sup>+</sup>) and the nature is acidic. For example, P(OH)<sub>3</sub> the O-H bond is more polar and hence it is an acid(H<sub>3</sub>PO<sub>3</sub>/phosphorous acid) while in Bi(OH)<sub>3</sub>, Bi-O bond is more polar so it is basic.

# **HYDRATION ENERY:**

Hydroation energy is the amount of energy evolved when one mole of a gaseous ion is completely dissolved to form hydrated ion.

 $M^{n\pm} + aq. \longrightarrow M^{n\pm}(aq.) + Hydration energy$ 

In the aqueous solution, each ion is surrounded by water molecules due to attraction between the ion and the -ve poles(O) of water molecules. The ion is jailed inside a cage of water and due to the attaction some energy is released(hydration energy). Hydration energy depends on the following two factors.

(a) Charge of the ion: Greater the charge greater is the hydration energy as the attraction between the ion and H<sub>2</sub>O molecules increases. For example, the hydration energy is in the order

Na 
$$^+ < Mg^{2+} < Al^{3+}$$

(ii) Size: As size decreases the hydration energy increases. This is because the +ve charge density increases with decrease in size(hence volume). This results greater attraction between the ion and water molecules.

 $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ 

#### **Consequences of Hydration Energy:**

2.

(a) Greater the hydration energy greater is the size of the hydrated ion. For example,  $Li^+(aq)$  has greatest size and  $Cs^+(aq.)$  has the least size although in the unhydrated state, the order of size is the opposite. This is because, more number of water molecules surround when the +ve charge density is more and hydrodynamic radius(radius including the surrounding water molecules) of the ion increases.

(b) The ionic mobility and hence the electrical conductivity of the hydrated ion decreases if the hydration energy increases. For example, in aqueous solution,  $Li^+(aq.)$  conducts least while  $Cs^+(aq)$  conducts the most as the former's hydrodynamic radius is highest and the latter's the smallest.

# **PROBLEMS FOR PRACTICE**

1. Arrage the following in decreasing order of the property as indicated.

(i) $Br^+$ , $Br$ , $Br^-$ (size)	(ii)Mg, Al, Si and Na ( $IE_1$ )	(iii) C, N, O, F (IE <sub>1</sub> )
(iv) F, Cl, Br, I (EA)	(v) Ca, P, Al, Cl (size)	(vi) Cu, Ag, Au (IE <sub>1</sub> )
(vi) Mg <sup>2+</sup> , F <sup>-</sup> , Ne, O <sup>2-</sup> (size)	(vii) O, S, Se(EA)	(viii) Zn, Cd, Hg (mp)
(ix) Li, Na, K, Rb(density)	(x) Al, Ga, In, $Tl(IE_1)$	(xi), O, S, S <sup>2-</sup> (Size)
(xii) Sc, Y, La(size)	(xiii)Si, Ge, Sn, Pb(IE <sub>1</sub> )	$(xiv) C, N, O \le F(IE_2)$
(xv) Ni, Pd, Pt(size)	(xvi)Pb, Pb <sup>2+</sup> , Pb <sup>4+</sup> (size)(xvii)	Li, Be, B $(IE_1)$
(xviii)SiO <sub>2</sub> , P <sub>2</sub> O <sub>5</sub> , SO <sub>3</sub> , Cl <sub>2</sub> O <sub>7</sub> (ad	cidic nature)	(xix) As, S, Cl(EN)
(xx)Na, Al, Fe, Pb(density)	(xxi) MgO, SrO, Rb <sub>2</sub> O, NiO, C	Cs <sub>2</sub> O(basic nature)
(xxii) Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup> (ior	nic radii in water)	(xxiii)Li, Na, K, Rb, Cs(mp)
$(xxiv) O^{2-}, O_2^{-2-}, O, O^+ (EA)$	$(xxv) Cl^{-}, K^{+}, Ca^{2+}, Ar(IE_{1})$	
$(xxvi)CO_2$ , $N_2O_5$ , $SiO_2$ , $SO_3$ (action)	idic nature) $(xxvii)Be^{2+}$ , M	Ig <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup> (hydration energy)
(xxviii)Cl, Br, F, I (EA	.)	
$(xxix)N, O, F(IE_1)$	(xxx) S, O, Se, F(size)	(xxxi) B, Be, Li, Na(size)
$(xxxii) Al_2O_3, MgO, SiO_2, P_4O_3$	<sub>10</sub> (acidic nature)	$(xxxiii) O^+, O, O^-(IE_1)$
(xxxiv) Na <sup>+</sup> , Cl <sup>-</sup> , O <sup>2-</sup> Ne(size)	(xxxv)Ni, Cu, Zn(size)	(xxxvi)Cr, Mn, Fe(size)
(xxxvii) Li <sup>2+</sup> , Be <sup>3+</sup> , He <sup>+</sup> (size)	$(xxxviii)$ Na,Mg $(IE_2)$	(xxxix) Be, N(IE <sub>3</sub> )
(xxxx) Ga, Ge(IE <sub>4</sub> )	$(\mathbf{x}\mathbf{x}\mathbf{x}\mathbf{x}\mathbf{i}) \mathbf{S} \mathbf{C} \mathbf{I} \mathbf{A} \mathbf{r} \mathbf{K}(\mathbf{I}\mathbf{F})$	(vvvii) Cl Se S(IE)
	$(\mathbf{X},\mathbf{X},\mathbf{X})$ 5, C1, $\mathbf{X}$ , $\mathbf{K}(\mathbf{IL}_1)$	$(XXXXII)$ CI, SC, $S(IL_1)$
(xxxxiii) Ge, $As(IE_5)$	$(XXXX)$ 5, $C_1$ , $M_1$ , $R(\Pi L_1)$	$(XXXXII) CI, SC, S(IE_1)$
(xxxxiii) Ge, As(IE <sub>5</sub> ) Explain why:	$(\mathbf{X},\mathbf{X},\mathbf{X})$ 5, CI, $\mathbf{X}$ , $\mathbf{X}(\mathbf{IL}_1)$	$(XXXII)$ CI, SC, $S(IL_1)$
(xxxxiii) Ge, As(IE <sub>5</sub> ) Explain why: (a)Ga has nearly equal atomic r	radius as Al.	$(XXXII)$ CI, SC, $S(IL_1)$
<ul> <li>(xxxxiii) Ge, As(IE<sub>5</sub>)</li> <li>Explain why:</li> <li>(a)Ga has nearly equal atomic in</li> <li>(b)EA of S is greater than O.</li> </ul>	radius as Al.	(XXXII) CI, 5C, 5(IL <sub>1</sub> )
<ul> <li>(xxxxiii) Ge, As(IE<sub>5</sub>)</li> <li>Explain why:</li> <li>(a)Ga has nearly equal atomic to (b)EA of S is greater than O.</li> <li>(c)The IE<sub>1</sub> of C is greater than</li> </ul>	radius as Al. B, but the reverse is true for $IE_2$ .	(XXXII) CI, 5C, 5(IE <sub>1</sub> )
(xxxxiii) Ge, As(IE <sub>5</sub> ) Explain why: (a)Ga has nearly equal atomic 1 (b)EA of S is greater than O. (c)The IE <sub>1</sub> of C is greater than (d) IE <sub>1</sub> of K is less than that of	radius as Al. B, but the reverse is true for $IE_2$ . Cu, but the reverse is true for $IE_2$ .	2 <sup>2</sup>

	(f)Pb has greater IE than Sn.
	(g)Hf has nearly same size as Zr
	(h) Au has a greater IE than Ag.
	(i) O has greater $IE_2$ than F.
	(j)Covalent radii from Cr to Cu in the 1st transition series remain nearly constant.
	(k)IE <sub>1</sub> of Be is greater than that of B, but the reverse is true for IE <sub>2</sub> .
	(l)Al has a lower IE than Mg.
	(m)Ca has greater $IE_1$ than K but the reverse is true for $IE_2$ .
	(n) EA of Cu is -ve(exothermic) while that of Zn is +ve(endothermic).
3.	Name the following by referring the PT.
	(a) a halogen element in th 3rd period
	(b) a low melting element similar in properties to Al
	(c) the most reactive metal in the 5th period
	(d) an element having atomic number smaller than 30 and similar to Strontium.
4.	Elements A, B, C, D and E have the following EC. Which of these will belong to the same group in
PT.	
	A: $1s^2$ , $2s^2 2p^2$ B: $1s^2$ , $2s^2 2p^6$ , $3s^2 3p^6 3d^5$ , $4s^2$ C: $1s^2$
	D: $1s^2$ , $2s^2 2p^6$ , $3s^2 3p^6 3d^{10}$ , $4s^2 4p^6 4d^5$ , $5s^2$ E: $1s^2$ , $2s^2 2p^2$ , $3s^2 3p^6$
5.	Locate the element and indicate its group and period in the PT.
-	(a) $[Ar]4s^2 3d^5 4p^3$ (b) $[Xe] 6s^2$ (c) $[Kr] 5s^1, 4d^5$ (d) $[Xe]6s^2, 4t^{14}, 5d^1$
6.	Without referring the electron filling diagram(aufbau rule), write the EC of the following only by
looking	to the PT.
7	(a) Se (b) Pd (c) Kb (d) Pt (e)Ag (f)Gd
1.	Identify the element from the following data.
	(a) An element having $+3$ charge and having 6 electrons in the 3d- subshell.
	(b) An element having -2 charge and having 8 electrons in the 3rd shell.
ah all	(c) An element having $\pm 1$ charge and having 32 electrons in the 4th shell and 18 electrons in the 5th
snen.	Identify the element belong to the following period and group
0.	(a) 4th paried and group 16 (b) 5th paried and group 8 (c) 6th paried and group 2
0	(a) 4 in period and group 10 (b) 5 in period and group 8 (c) our period and group 2 Match the block to which the element belong with their atomic numbers
9.	Z Block
	$56  fmtext{f}$
	AA s
	67 n
	53 d
10.	Identify the group and period to which the following element belong from their valence shell ECs. (a) $4s^2 3d^{10} 4p^5$ (b) $5s^1 4d^8$ (c) $6s^1 4f^{14} 5d^{10}$ (d) $7s^1$
11.	Explain why there is recurrence of properties after certain fixed interval (say 2, 8, 8, 18, 18, 32 for s-
block).	
12.	Explain why ?
	(a) $PbO_2$ is an excellent oxidising agent while $GeO_2$ is not. In stead $GeCl_2$ is a better reducing agent.
13.	Using Slater's theory calculate the atomic radius of Na. (Use the formula $r = 0.529 \times n^2/Z^*Å$ .)
14.	Three atoms have the following EC, arrange them in the decreasing order of IE.
	(i) $1s^2$ , $2s^2 2p^6$ , $3s^2 3p1$ (ii) $1s^2$ , $2s^2 2p^6$ , $3s^2 3p^5$ (iii) $1s^2$ , $2s^2 2p^6$ , $3s^2 3p^6$ , $4s^1$
15. Wh	ich has greater IE in each pair ?
	(a) N or $O^+$ (b) $Be^+$ or $B^+$ (c) $Na^+$ or $Ne$
16. The	first four IE values of an element in kJ/mle are approximately 738, 1450, 7.7 X 10 <sup>3</sup> and 1.1 X 10 <sup>4</sup> . To
which g	group does it belong and what is its maximum OS.
17. The	IE1 and IE2 in kJ/mole of a few elements are given in the following table.

	Element	IE <sub>1</sub>	IE <sub>2</sub>	
	Р	2080	3952	
	Q	520	7298	
	R	899	1757	
	S	1681	3374	
Which	h of the above element	is expected to be a		
	(a) noble gas	(b) reactive nonmetl	(c) reactive metal	(d) metal having valency 2
18.	Which has greater EA in each pair?			
	(a) F or Cl <sup>-</sup>	(b) $F$ or $Cl$ (c) $O$	or $O^-$ (d) Ne <sup>+</sup> or F	(e) F or F
19.	If IE of Na is 496 kJ/mole what is the EA of Na <sup>+</sup> ?			