

PERIODIC CLASSIFICATION & PERIODIC PROPERTIES

INTRODUCTION:

It is the arrangement of element in a particular pattern in such a way that element having similar properties comes together.

DEVELOPEMENT OF PERIODIC TABLE

1. PROUT'S HYPOTHESIS :

He simply assumed that all the elements are made up of hydrogen, so we can say that

Atomic weight of element = $n \times$ (Atomic weight of one hydrogen atom)

Atomic weight of H = 1 where n = number of hydrogen atom = 1, 2, 3,....

Drawback or Limitation :

- (i) Every element can not be formed by Hydrogen.
- (ii) The atomic weights of all elements were not found as the whole numbers.

Ex. Chlorine (atomic weight 35.5) and strontium (atomic weight 87.5)

2. DOBEREINER TRIAD RULE [1817] :

- (i) He made groups of three elements having similar chemical properties called TRIAD.
- (ii) In Dobereiner triad, atomic weight of middle element is nearly equal to the average atomic weight of first and third element. **Ex.**

$\begin{array}{ccc} \text{Cl} & \text{Br} & \text{I} \\ 35.5 & 80.0 & 127 \\ x = \frac{35.5 + 127}{2} = 81.25 \end{array}$	$\begin{array}{ccc} \text{Ca} & \text{Sr} & \text{Ba} \\ 40 & 87.5 & 137 \\ x = \frac{40 + 137}{2} = 88.5 \end{array}$	$\begin{array}{ccc} \text{Li} & \text{Na} & \text{K} \\ 7 & 23 & 39 \\ x = \frac{7 + 39}{2} = 23 \end{array}$
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Where x = average atomic weight

- (iii) Other examples – (K, Rb, Cs), (P, As, Sb), (S, Se, Te), (H, F, Cl), (Sc, Y, La)

Illustration 1

Is Fe, Co, Ni are dobereiner triad ?

Solution.

No

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3. NEWLAND'S RULE OF OCTAVE

- As in music, the eighth note is same as the first note. If the elements are arranged in the increasing order of atomic weights, on starting with an element, the first element will exhibit similarities with the eighth element e.g.

Symbol of element	Li	Be	B	C	N	O	F
	7	9	11	12	14	16	19
Symbol of element	Na	Mg	Al	Si	P	S	Cl
	23	24	27	28	31	32	35.5

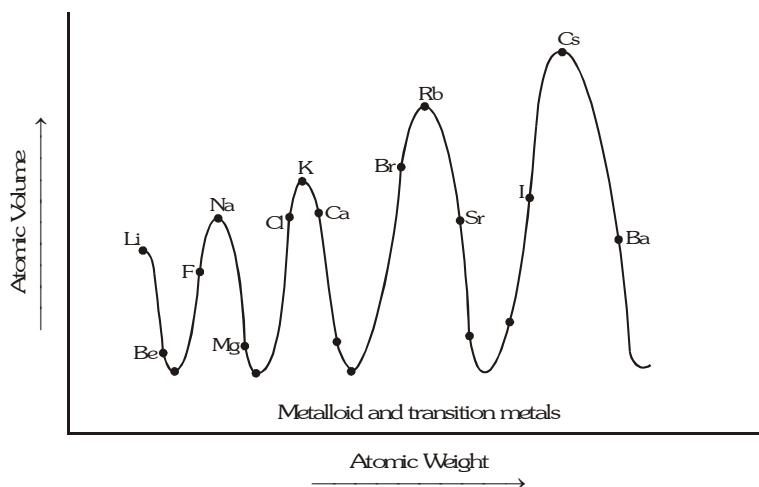
- It is clear from the above table that sodium is the eighth element from lithium, whose properties resemble that of lithium.
- Noble gases were not discovered till then.
- This type of classification was limited up to only 20 elements.

4. LOTHER MEYER'S CURVE

- He plotted a curve between atomic weight and atomic volume of different elements.
- The following observation can be made from the curve –
 - Most electropositive elements i.e. alkali metals (Li, Na, K, Rb, Cs etc.) occupy the peak positions on the curve.
 - Less electropositive i.e. alkali earth metal (Be, Mg, Ca, Sr, Ba) occupy the descending position on the curve.
 - Metalloids (B, Si, As, Te, At etc.) and transition metals occupy bottom part of the curve.
 - Most electronegative i.e. halogens (F, Cl, Br, I) occupy the ascending position on the curve.

Note : Elements having similar properties occupy similar position on the curve.

Conclusion : On the basis of this curve Lotther Meyer proposed that the physical properties of the elements are periodic function of their atomic wt. and this become the base of Mendeleef's periodic table.



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5. MENDELEEV'S PERIODIC LAW

- According to Mendeleev's periodic law, the physical and chemical properties of elements are periodic functions of their atomic weights.

5.1 Mendeleev's Periodic Table

- Periodic table is based on atomic weight.
- In the periodic table, the horizontal lines are called periods and the vertical lines are called groups.
- The periodic table consists of seven periods and nine groups (The earlier periodic table had only 8 groups). The noble gases were added later in the zero group because these were not discovered when Mendeleev put forward his periodic table.
- All the groups (except VIII and Zero groups) are divided into subgroups A and B.
- 2, 8, 18 and 32 are called magic numbers.

5.2 Merits of Mendeleev's Periodic Table

- Classification of elements then known, was done for the first time and the elements having similar properties were kept in the same group.
- It encouraged research and led to discovery of newer elements.
- Mendeleev had even predicted the properties of many elements not discovered at that time. This helped in the discovery of these elements. For example, Mendeleev predicted the properties of the following elements.
 - (a) Eka-boron- This was later called scandium (Sc)
 - (b) Eka-aluminium - This was later called gallium (Ga)
 - (c) Eka-silicon - This was later called germanium (Ge)

5.3 Defects of Mendeleev's Periodic Table

- (1) **Position of Hydrogen** – Hydrogen resembles alkali metals and halogens in its properties. Hence its position was not sure.
- (2) **Position of Isotopes** – The isotopes have different atomic weights and the periodic table is based on atomic weights. Therefore, isotopes should get different places in the periodic table on the basis of atomic weights.
- (3) The periodic table is not fully based on increasing order of atomic weights.
- (4) It is not proper to place together the elements having differing properties, such as coinage metals (Cu, Ag and Au) with alkali metals; Zn, Cd and Hg with alkaline earth metals and metal like Mn with halogens. Similarly, Pt and Au having similar properties have been placed in different groups.
- (5) There is no indication whether lanthanides and actinides are associated with group IIIA or group IIIB.
- (6) Position of Isobars – These elements have different groups when mass remains same.
- (7) Lot of stress was given to valency of elements.

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6 MODERN PERIODIC LAW AND MODERN PERIODIC TABLE

- **Mosley** proved that the square root of frequency (ν) of the rays, which are obtained from a metal on showering high velocity electrons is proportional to the nuclear charge of the atom. This can be represented by the following expression.

$$\sqrt{\nu} = a(Z-b) \text{ where } Z \text{ is nuclear charge on the atom and } a \text{ and } b \text{ are constants.}$$

- The nuclear charge on an atom is equal to the atomic number.
- According to modern periodic law. "The properties of elements are the periodic functions of their atomic numbers"

6.1 Modern Periodic Table

- On the basis of the modern periodic law, **Bohr** proposed a long form of periodic table that was prepared by Rang and Warner.
- In the periodic table the horizontal lines are periods and the vertical lines are groups.
- The periodic table has a total of seven periods and 18 groups. But according to CAS system, the number of groups is 16, because the eighth group has been divided into three groups.
- There are 2 elements in the first period 8 elements in each of the second and third periods, 18 elements in each of the fourth and fifth period 32 elements in the sixth period and only 19 elements till now in the seventh period. Total 105 elements have been discovered so far.
- The first period is very short period, second and third are short periods fourth and fifth are long periods sixth is very long period, while the seventh is incomplete period.
- The lanthanides (Elements from atomic numbers 58 to 71) and actinides (elements from atomic numbers 90 to 103) are included in the sixth and seventh periods through these have been kept outside the periodic table.

The Periodic Table HD

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	H Hydrogen 1.00784	He Helium 4.002602																	
2	Li Lithium 6.941	Be Beryllium 9.012182																	
3	Na Sodium 22.98976928	Mg Magnesium 24.3040																	
4	K Potassium 39.0983	Ca Calcium 40.078	Sc Scandium 44.955912	Ti Titanium 47.867	V Vanadium 50.9415	Cr Chromium 51.9961	Mn Manganese 54.938045	Fe Iron 55.845	Co Cobalt 58.933195	Ni Nickel 58.6934	Cu Copper 63.546	Zn Zinc 65.38	Ga Gallium 69.723	Ge Germanium 72.64	As Arsenic 74.92160	Se Selenium 78.96	Br Bromine 79.904	Kr Krypton 83.798	
5	Rb Rubidium 85.4678	Sr Strontium 87.62	Y Yttrium 88.90585	Zr Zirconium 91.224	Nb Niobium 92.90638	Mo Molybdenum 95.96	Tc Technetium (97.9072)	Ru Ruthenium 101.07	Rh Rhodium 102.90550	Pd Palladium 106.42	Ag Silver 107.8682	Cd Cadmium 112.411	In Indium 114.818	Sn Tin 118.710	Sb Antimony 121.760	Te Tellurium 127.60	I Iodine 126.90447	Xe Xenon 131.293	
6	Cs Cesium 132.9054519	Ba Barium 137.327	Lanthanoids		Hf Hafnium 178.49	Ta Tantalum 180.94788	W Tungsten 183.84	Re Rhenium 186.207	Os Osmium 190.23	Ir Iridium 192.222	Pt Platinum 195.084	Au Gold 196.966569	Hg Mercury 200.59	Pb Lead 207.2	Bi Bismuth 208.98040	Po Polonium 209	At Astatine 209	Rn Radon 222	
7	Fr Francium 223	Ra Radium 226	Actinoids		Rf Rutherfordium 261	Db Dubnium 262	Sg Seaborgium 266	Bh Bohrium 264	Hs Hassium 277	Mt Meitnerium 268	Ds Darmstadtium 271	Rg Roentgenium 272	Cn Copernicium 285	Uut Ununtrium 284	Uuq Ununquadium 289	Uup Ununpentium 288	Uuh Ununhexium 292	Uus Ununseptium 286	Uuo Ununoctium 294

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

Au
Gold
196.966569

79

Noble gases

Alkali metals

Alkaline earth metals

Transition metals

Lanthanoids

Actinoids

Metalloids

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6.2 Merits of long form of Periodic Table over Mendeleev's Periodic Table

- **Positions of Isotopes and Isobars** - Isotopes have same atomic number and the periodic table is based on atomic numbers. Therefore, various isotopes of the same elements have to be provided the same position in the periodic table. Isobars gave same atomic weights but different atomic numbers and therefore they have to be placed at different positions.
- The positions of actinides and lanthanides is more clear now because these have been placed in IIIB groups and due to paucity of space, these are written at the bottom of the periodic table.
- The general electronic configurations of the elements remains same in group.

6.3 Defects of Long Form of Periodic Table

- The position of hydrogen is still disputable as it was there in Mendeleef periodic table in group I A as well as VIIA.
- Helium is an inert gas but its configuration is different from that of the other inert gas elements
- Lanthanide and actinide series could not be adjusted in the main periodic table and therefore they had to be provided with a place separately below the table.

7. IUPAC NOMENCLATURE FOR ELEMENTS WITH $Z > 100$

Nomenclature of elements CNIC (commission on nomenclature of inorganic chemistry) appointed by IUPAC in 1994, approved a nomenclature scheme as well as also gave official names for elements after $Z > 100$ (upto atomic number 104 to 109 discovered by that time). This nomenclature is to be followed for naming the elements until their names are officially recognised. The names are derived by using roots for the three digits in the atomic number of the element and adding the ending ium. The roots for the numbers are.

Digit	Latin Word	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

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Table. Name and Symbols in current Use (or proposed) for**Trans-fermium Elements (Z=101-112)**

Atomic numbers	Systematic 1977	IUPAC 1997
101	Unnilunium (Unu)	Mendelevium(Md)
102	Unnilbium(Unb)	Nobelium (No)
103	Unniltrium(Unt)	Lawrencium (Lr)
104	Unnilquadium(Unq)	Rutherfordium(Rf)
105	Unnipentium(Unp)	Dubnium (Db)
106	Unnilhexium(Uns)	Seaborgium(Sg)
107	Unnilseptium(Uns)	Bohrium (Bh)
108	Unniloctium(Uno)	Hassium (Hs)
109	Unnilennium(Une)	Meitnerium (Mt)
110	Ununnilium(Uun)	Darmstadtium(Ds)
111	Unununium(Uuu)	Rontgenium(Rt)
112	Ununbium(Uub)	-----
113	Ununtrium(Uub)	-----
114	Ununquadium(Uuq)	-----
115	Ununpentium(Uup)	-----
116	Ununhexium(Uuh)	-----
117	Ununseptium(Uus)	-----
118	Ununoctium(Uuo)	-----

Example :

The element with atomic number 120 has not been discovered. What would be the IUPAC name and symbol of this element? Also predict the electronic configuration ,group number and period of this element.

Solution :

The IUPAC name for the element with atomic number 120 would be Unbinilium and its symbol would be Ubn. The electronic configuration of this element would be $(Uuo)8s^2$. The element would belong to group 2 and period-8.

8. CLASSIFICATION OF ELEMENTS**8.1 Classification based on Electronic Configuration**

Elements are classified in to four blocks on the basis of differentiating electron enters in to which subshell of the main shell.

(a) s-Block Elements

(b) p-Block Elements

(c) d-Block Elements

(d) f-Block Elements

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• - **සමස්ත ඛණිතය :**

Differentiating electrons enter into s-subshell.

S-sublevel can accommodate 2-electrons, hence S-block elements are arranged in two groups, IA, IIA.

General electronic configuration is ns^{1-2} .

H, Li, Na, K, Rb, Cs, Fr elements (alkali metals) have 1 electron in their outer shell with “ ns^1 ” general outer shell configuration, they belongs to IA.

Be, Mg, Ca, Sr, Ba and Ra (Alkaline Earth elements) have 2-electrons in their outer shell, with “ ns^2 ” general outer shell configuration, they belongs to IIA.

Most of these are active metals.so they are \Rightarrow never found pure in nature.

Most of these compounds are ionic. \Rightarrow These are powerful reducing agents.

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Differentiating electrons enter into p-subshell.

The general outer shell configuration of P-block elements. $ns^{1-2}np^{1-6}$

p-block elements are arranged in 6-groups they are from IIIA to VII A and zero group.

(a) B,Al,Ga,In and Tl are called IIIA group (boron family) these elements have 3-electrons in outershell, with “ ns^2np^1 ” general outer shell configuration.

(b) C,Si,Ge,Sn and Pb are called IVA group (Carbon Family) these elements have 4-electrons in outer shell,with “ ns^2np^2 ” general outer shell configuration.

(c) N,P,As,Sb and Bi are called VA group(Nitrogen Family) (Pnicogens).

These elements have 5-electrons in outer shell, with “ ns^2np^3 ” general outer shell configuration.

(d) O, S, Se, Te, and Po are called VIA group (Chalcogens)

these elements have 6-electrons in outer shell, with “ ns^2np^4 ”, general outer shell configuration.

(e) F, Cl, Br, I and At are called VIIA group(Halogens)

these elements have 7-electrons in outer shell, with “ ns^2np^5 ”, general outer shell configuration.

(f) He, Ne, Ar, Kr, Xe and Rn - Inert gases (O-group), Except He ($1s^2$), remaining inert gases have 8-electrons in outer shell with “ ns^2np^6 ” general outer shell configuration.

(g) p-block contains some metals,all non-metals and all metalloids.

(e) Most of the p-block element compounds are covalent.

(f) Most of these are oxidising agents

Remember:

Infact Helium belongs to s-block, but keeping its chemical inertness, Helium is placed along with other inert gases in zero-group.

The first p-block element is Boron [(He) $2s^2 2p^1$]

The only group with all gaseous elements is “zero-group”.

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If differentiating electrons enter into the 'd' subshell of (n-1) shell (i.e, d-orbitals of penultimate shell), the elements of this class are called "**d-block elements**".

The general electronic configuration of d-block elements is $(n-1)d^{1-10} ns^{1 \text{ or } 2}$ (n = outer shell).

d-Block elements are placed between s-block and p-block and they are also called transition elements.

d-Block elements are further classified into following transition series on the basis of which (n-1)d is being filled.

- (1) 1st Transition series (3d series) electronic configuration. $3d^{1-10} 4s^{1-2}$ [Sc (Z=21) to Zn (Z=30)]
- (2) 2nd Transition series (4d - series) electronic configuration. $4d^{1-10} 5s^{1-2}$ [Y(Z=39) to Cd (Z=48)].
- (3) 3rd Transition series (5d - series) electronic configuration. $5d^{1-10} 6s^{1-2}$. [La (Z=57), Hf (Z=72) to Hg (Z=80)]
- (4) 4th Transition series (6d - series) is an incomplete series.
- (5) Most of them are less active metals.
- (6) Most of their compounds are ionic and co-ordinate covalent.

Remember :

After completion of 6s, the differentiating electron suppose to enter into 4f, but in the case of Lanthanum the differentiating electron is entering into 5d, instead of 4f (**La - $6s^2 4f^0 5d^1$**). Therefore "La" belongs to d-block.

Similarly in case of Actinium, the differentiating electron is entering into 6d, instead of 5f

(**Ac- $7s^2 5f^0 6d^1$**). Therefore Ac also belongs to d-block.

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If differentiating electrons enter into f-subshell of Anti penultimate i.e., (n-2) shell, the elements of this class are called **f-block** elements.

- The general electronic configuration $(n-2)f^{1-14} (n-1)d^{0 \text{ or } 1} ns^2$ (n = outer shell).
- These f-block elements are placed at the bottom of the periodic table in two rows, they are 4f series and 5f series. The properties of 4f-series elements are similar to Lanthanum they are known as Lanthanides (or) Lanthanons or rare earths.
- 4f-series - Lanthanide series - configuration **$4f^{1-14} 5d^{0-1} 6s^2$ from Ce(58) to Lu (71)**
- 4f- series elements belongs to 6th period and IIIB Group.
- 5f - series elements - Actinide series - configuration **$5f^{1-14} 6d^{0-1} 7s^2$ from Th (90) to Lr (103).**
- 5f - series elements belongs to 7th period and III B group.
- Among Lanthanides, only promethium (${}_{61}\text{Pm}$) is radioactive.
- All actinides are radioactive in nature
- Elements coming after 92 atomic number are known as "Trans Uranic Elements" or "Synthetic Elements" and they are "Radioactive".

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Illustration 1:

Which alphabet is not used in nomenclature of elements.

- (1) K (2) W (3) V (4) J & Q

Solution (4) :

K is potassium (Kalium), W is Tungsten (Wolfram) and V is vanadium. There is no element associated with the letters J and Q.

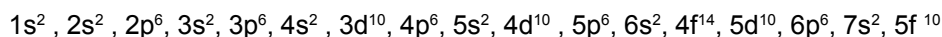
Illustration 2:

Which of the following is the period number of the element whose atomic number is 98

- (1) 4 (2) 7 (3) 5 (4) 6

Solution (2):

The electronic configuration of the element with atomic number 98 is as follow



The last electron enters in f orbital, so it belongs to f block in the period.

Illustration 3:

The nuclei of elements X, Y and Z have same number of protons, but different numbers of neutrons. According to Mendeleef periodic table, the elements X, Y and Z

- (1) belong to same group and same period
- (2) belong to different groups and different periods
- (3) belong to same group and different periods
- (4) are isotopes, which do not have different positions

Solution (4):

Isotopes have same number of protons (i.e. same atomic number). So they occupy same position in the periodic table. However, due to different numbers of neutrons their atomic weights are different.

Illustration 4:

Which of the following is the artificial element in the periodic table

- (1) Tc (2) Te (3) Ru (4) Os

Solution (1) :

Tc⁴³ is the first artificial element.

Illustration 5:

Which of the following is not a transition element

- (1) Co (2) Ni (3) Mn (4) Zn

Solution (4):

There is only one incomplete orbit in Zn⁺² and its stable oxidation state is (+2) does not have incomplete d orbital. Therefore it is not a transition element.

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8.2 Classification based on chemical properties.

All the elements are divided into four types on the basis of their chemical properties and electronic configuration.

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- He, Ne, Ar, Kr, Xe and Rn belongs to "0" group in the periodic table are called **Inert Gas Elements**.
- Except He ($1s^2$), all the other elements have ns^2np^6 outer electronic configuration.
- All are chemically inert due to the presence of stable ns^2np^6 (octet) configuration in their outer most shell.

He is inactive due to its completely filled 'K' shell. ($1s^2$)

- It is known that heavier elements (Kr, Xe) forms compounds under special controlled conditions with Oxygen, Fluorine, $XeOF_2$, and $XeOF_4$. So they are now called **Noble gases**.
- All are monoatomic gases.
- They are also known as Rare gases (or) Aerogens.

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- These are the elements whose outer shells are not completely filled.
- Excluding "0" group, remaining s and p block elements (IA, IIA, IIIA, IVA, VA, VIA, VIIA) are called representative elements.
- Most of these elements are abundant and active.
- Their general outer electronic configurations $ns^{1-2}np^{1-5}$.
- Metals, nonmetals and metalloids are present in representative elements.
- Atoms of these elements enter chemical combination by losing, gaining or sharing of electrons to attain stable nearest inert gas configuration.
- In case of representative elements, electrons of outer ns and np orbitals will take part in bonding.

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- These are the elements whose outer most and penultimate shells are incompletely filled.
- Elements which have incompletely filled or partly filled d-orbitals either in elementary state or in any possible oxidation state are called as transition elements.
- Their properties are intermediate to s - and p - block elements.
- The general electronic configuration is $(n-1)d^{1-10} ns^{1-2}$.
- II B group elements Zn ($3d^{10} 4s^2$), Cd ($4d^{10} 5s^2$) Hg ($5d^{10} 6s^2$) are not transition elements (due to the absence of partly filled d-orbitals both in atomic and in ionic states) (Zn, Cd, Hg - are referred as Non-typical Transition Elements) or volatile metals .
- In the case of Transition elements both $(n-1)d$ and ns electrons participate in bonding.

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- The characteristic properties of transition elements are
 1. They are hard and heavy metals
 2. Variable Oxidation states
 3. Formation of coloured ions due to d-d- transition
 4. Formation of metal complexes
 5. Paramagnetism
 6. Catalytic activity.
 7. High M.P., B.P and densities.
 8. Good conductors of heat and electricity
 9. Alloy formation.
- These characteristic properties are due to
 - a. Small size
 - b. High nuclear charge
 - c. Unpaired electrons in d-orbitals.

Note : Ni used as a catalyst in Hydrogenation of oils.

Fe used as a catalyst in Haber's process

Mo used as a promoter in Haber's process.

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- These elements have three outermost shells incomplete i.e., n, (n-1) and (n-2)
- The f-block elements are called inner transition elements.
- General configuration $(n-2)f^{1-14} (n-1)d^{0 \text{ or } 1} ns^2$.
- Since the last two shells have similar configuration these elements have similar physical and chemical properties (eg - these elements shows common oxidation state of +3).
- There are two series of inner transition elements.

4f-series - Lanthanide series - $4f^{1-14} 5d^{0 \text{ or } 1} 6s^2$.

5f - series - Actinide series - $5f^{1-14} 6d^{0 \text{ or } 1} 7s^2$.

In periodic table, lanthanides are present between $_{57}\text{La}$ & $_{72}\text{Hf}$ and Actinides are present between $_{89}\text{Ac}$ & $_{104}\text{Rf}$.
- Lanthanides are rare earths, and all most all Actinides are radioactive.

8.3 ~~Periodicity~~ Periodic Properties

- When elements are arranged in increasing order of atomic number, elements with similar properties reoccur (due to similar outer electronic configuration) at regular intervals in the periodic table.
- Elements coming at intervals of 2, 8, 8, 18, 18, 32 will have similar properties and thus grouped in one particular group.

Ex : Elements with atomic number 1, 3, 11, 19, 37, 55 & 87. Elements with atomic number 4, 12, 20, 38, 56 & 88 will have similar properties.

Note : Two successive elements in a group generally differ by atomic number 2, 8, 8, 18, 18, 32.

DAILY PRACTICE PROBLEM-1

- Which of the following is/ are Doeberiners triad-
(i) P, As, Sb (ii) Cu, Ag, Au (iii) Fe, Co, Ni (iv) S, Se, Te
Correct answer is -
(1) (i) and (ii) (2) (ii) and (iii) (3) (i) and (iv) (4) All
- Which of the following set of elements obeys Newland's octave rule -
(1) Na, K, Rb (2) F, Cl, Br (3) Be, Mg, Ca (4) B, Al, Ga
- Which is not an anomalous pair of elements in the Mendeleev's periodic table -
(1) Ar and K (2) Co and Ni (3) Te and I (4) Al and Si
- Elements which occupied position in the Lothar Meyer curve, on the peaks, were -
(1) Alkali metals (2) Highly electro positive elements
(3) Elements having large atomic volume (4) All
- Modern periodic table is based on atomic no. experiments which proved importance of atomic no. was -
(1) Bragg's work on X-ray diffraction
(2) Moseley's work on X-ray spectrum
(3) Millikan's oil drop experiment
(4) Lothar Meyer curve plotted between atomic vol. & atomic wt.
- Mendeleev's periodic law is based on -
(1) Atomic number (2) Atomic weight (3) Number of neutrons (4) None of the above
- Which of the following is the atomic number of metal ?
(1) 32 (2) 34 (3) 36 (4) 38
- The places that were left empty by Mendeleev were, for -
(1) Aluminium & Silicon (2) Gallium and germanium
(3) Arsenic and antimony (4) Molybdenum and tungsten
- The electronic configuration of an element is $1s^2 2s^2 2p^6 3s^2 3p^3$. What is the atomic number of the element, which is just below the above element in the periodic table ?
(1) 33 (2) 34 (3) 36 (4) 49
- An atom has electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$, you will place it in which group ?
(1) Fifth (2) Fifteenth (3) Second (4) Third

BY RAJESH SHAH

9. EFFECTIVE NUCLEAR CHARGE (Z_{eff})

Outer shell electrons gets repelled by inner- shell electrons are placed away from the nucleus and are thus held less tightly. Part of the attraction of the nucleus for an outer electron is thereby cancelled and the outer electrons are shielded from the nucleus by the inner electrons. The net nuclear charge actually felt by an electron is called the effective nuclear charge, it can be presented in the following figure :

The effective atomic number (Z_{eff}) can be calculated by two methods :

$$(1) Z_{\text{eff}} = Z - S \text{ (or) } Z_{\text{eff}} = Z - \sigma$$

Where, Z = Nuclear charge

S = Shielding or Screening constant (σ)

J.C. Slater has given following rules to calculate the shielding or Screening constant for an np or ns- orbital

- (i) Write out the electronic configuration of the element in the following order and groupings : (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 4p), etc.
- (ii) Electrons in any group to the right of the (ns, np) group contribute nothing to the shielding constant
- (iii) All of the other electrons in the (ns, np) group, shield the valence electron to an extent of 0.35 each
- (iv) All electrons in the (n-1) shell shield to an extent of 0.85 each
- (v) All electrons (n - 2) or lower shield completely, i.e. its contribution is 1.00 each.
- (vi) When the electron being shielded is in an nd or nf group, rules (ii) and (iii) are the same
All electrons in groups lying in the left of the nd or nf group contribute 1.00 each.
- (vii) If electron facing repulsion is present in (1s) group, then another electron in 1s contribute 0.30 instead of 0.35.

Examples : (i) Let us consider the valence electron in the nitrogen (${}_{7}\text{N}$) atom = $1s^2 2s^2 2p^3$. Grouping of the orbitals gives $(1s^2)(2s^2 2p^3)$

$$\sigma = (2 \times 0.85) + (4 \times 0.35) = 3.10$$

$$Z_{\text{eff}} = Z - \sigma = 7.0 - 3.1 = 3.9$$

(ii) We can also calculate the value of 'S' for valence (4s) electron in the zinc atom (${}_{30}\text{Zn}$)

The grouped electron configuration is $(1s)^2 (2s2p)^8 (3s3p)^8 (3d)^{10} (4s)^2$

$$\sigma = (10 \times 1.00) + (18 \times 0.85) + (1 \times 0.35) = 25.65$$

$$Z_{\text{eff}} = Z - \sigma = 30 - 25.65 = 4.35$$

$$(2) Z_{\text{eff}} = \sqrt{\frac{(E)(n^2)}{1312 \text{KJ/mol}}}$$

Where, E = The energy necessary to remove an electron from an atom

n = The principal quantum number of the electron

BY RAJESH SHAH

10. ATOMIC RADIUS

- In atoms, the electron cloud around the nucleus extends to infinity.
- The distance between the centre of the nucleus and the electron cloud of outer most energy level is called atomic radius.
- Atomic radius cannot be determined directly, but measured from the inter nuclear distance of combined atoms, using X-ray diffraction techniques.
- Atomic radius depends on
 - (a) Nature of bonding
 - (b) Number of bonds (multiplicity of bonding)
 - (c) Oxidation states etc.
- Three types of atomic radii are considered based on the nature of bonding they are
 - (a) Crystal radius (b) Vander waals radius (c) Covalent radius
- Atomic radii expressed in angstrom, nanometers, picometer units. $1\text{\AA} = 10^{-10}\text{m}$; $1\text{\AA} = 10^2\text{ pm}$

10.1 Crystal Radius

Half of the internuclear distance between the adjacent atoms of a solid metallic crystal is called crystal radius or metallic radius.

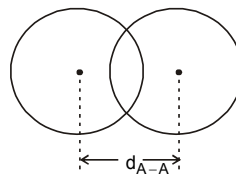
Ex : Distance between two sodium atoms is 3.72\AA , crystal radius of Na = $3.72 / 2 = 1.86\text{\AA}$.

The distance of the outermost orbit from the centre of the nucleus of an atom is called atomic radius.

10.2 Single Bond Covalent Radius, SBCR

(a) For Homoatomic molecules

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



(b) For heteroatomic molecules in which electronegativity remains approximately same.

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

- For heteronuclear diatomic molecule, A – B, while difference between the electronegativity values of atom A and atom B is relatively larger,

$$d_{A-B} = r_A + r_B - 0.09 (X_A - X_B)$$

where X_A and X_B are electronegativity values of high electronegative element A and less electronegative element B, respectively. This formula is given by **Stevenson & Schomaker**.

Note : Covalent radius is slightly smaller than actual radius.

BY RAJESH SHAH

Illustration 1:

Calculate the bond length of C–X bond, if C–C bond length is 1.54 Å, X–X bond length is 1.00 Å and electronegativity values of C and X are 2.0 and 3.0 respectively

Solution:

(1) C–C bond length = 1.54 Å

$$r_c = \frac{1.54}{2} = 0.77 \text{ Å}$$

$$r_x = \frac{1.00}{2} = 0.50 \text{ Å}$$

(2) C–X bond length

$$d_{C-X} = r_c + r_x - 0.09 (X_x - X_c)$$

$$= 0.77 + 0.50 - 0.09 (3-2)$$

$$= 0.77 + 0.50 - 0.09 \times 1$$

$$= 1.27 - 0.09 = 1.18 \text{ Å}$$

Thus C–X bond length is 1.18 Å

Illustration 1:

If bond length of $F_2 = 1.44 \text{ Å}$, Bond length of $H_2 = 0.74 \text{ Å}$. Find out the bond length of H–F? (EN of F is 4.0, EN of H is 2.1)

Solution:

$$d_{H-F} = r_F + r_H - 0.09 (X_F - X_H)$$

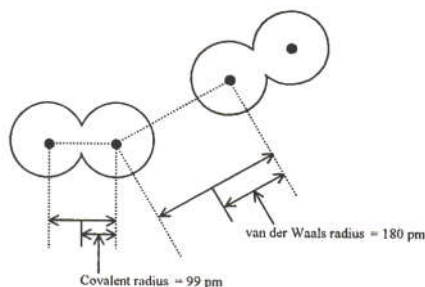
$$\therefore d_{F-F} = 1.44 / 2 = 0.72 \text{ Å}, d_{H-H} = 0.74 / 2 = 0.37 \text{ Å}$$

$$\therefore d_{H-F} = 0.72 + 0.37 - 0.09 (4.0 - 2.1)$$

$$= 1.09 - (0.09 \times 1.9) = 1.09 - 0.171 = 0.919 \text{ Å}$$

10.3 VANDER WAALS RADIUS

- Half of the distance between the nuclei of two non bonded atoms belonging to two different molecules closest to one another is called van der waals radius.
- The values of atomic radii in noble gases are always determined as van der Waals radii. Therefore, the value of van der waals radius of a noble gas is always greater than that of the halogen coming before it in the same period.



van der Waals radius > Metallic radius > Covalent radius

Note : vander Waals radius is slightly larger than the actual radius.

BY RAJESH SHAH

10.4 .Periodicity in Atomic Radius

□ **The atomic radius depends on the following factors.**

- (a) **Effective Nuclear Charge** - The effect of increase in the number of protons increases the effective nuclear charge. This results in decrease in the value of atomic radius because protons attract the electronic orbits with greater force .
- (b) **Number of orbits** - The effect of increase in the number of orbit in an atom increases the atomic size.
- (c) **Shielding effect/screening effect** - The electrons of inner shell repel the electrons of valence shell from coming closer to the nucleus. Due to this the atomic radius increasing . This is called as shielding. When an atom has more number of shells, the shielding provided will also be greater.

Within a shell the shielding provided by different types of orbitals follows the order $s > p > d > f$. (As 's' orbitals experience greater penetration towards the nucleus, they provide greater shielding to the electrons of p, d and f orbitals).

In the elements of 'd' and 'f' blocks where number of shells remain the same in a particular series along with shielding provided, the nuclear charge is also compared. ($r \propto \sigma$)

උපදිගු කාලයේ සහ වාමන දිශාවට පිටුපසට ගිය විට පරමාණුක අරය:

- In a period from left to right, atomic radius decreases as the effective nuclear charge increases.

Example : Variation of atomic radius in second period $\text{Li} > \text{Be} > \text{B} > \text{C} > \text{N} > \text{O} > \text{F}$

in third period $\text{Na} > \text{Mg} > \text{Al} > \text{Si} > \text{P} > \text{S} > \text{Cl}$

- On moving from left to right across a particular period, the atomic radius decreases upto Halogens and increases to Inert gases.
- In a given *period*, alkali metal is the largest and halogen is the smallest in size.
- **Note :** For atoms of Inert gases, only vander waal radius is applicable because these are mono atomic gases.
- In *groups* from top to bottom, the atomic radius increases gradually due to the increase in the number of orbits and it over weighs the effect of increased nuclear charge.

Variation of atomic radius in IA group is



In halogens $\text{F} < \text{Cl} < \text{Br} < \text{I} < \text{At}$

උපදිගු කාලයේ සහ වාමන දිශාවට පිටුපසට ගිය විට පරමාණුක අරය:

- (a) In case of transition elements the decrease in size in a period across a particular transition series is less than in case of representative elements, this is due to screening effect of (n-1)d-electrons.
- (b) During filling of electrons in (n-1)d subshell, there is increase in force of repulsion after filling of some electrons. Hence atomic size decreases from Sc to Cr, remains nearly constant from Mn to Ni, and increases upto Zn.

BY RAJESH SHAH

රිථඩියමය ශ්‍රේණි සහ ලන්තනයිඩ් ශ්‍රේණි පිළිබඳව ප්‍රධාන ලක්ෂණ සහ සාමාන්‍ය ගුණ සලකා බැලීම:

- The elements in Lanthanide series are La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb & Lu
- In Lanthanides (Ce-Lu) the atomic and ionic radii decreases steadily. This steady decrease in atomic and ionic radii is known as “Lanthanide Contraction”
- The contraction is due to the fact that f-orbitals are not capable of providing effective shielding for the valence electrons from nuclear attraction.

ලන්තනයිඩ් ශ්‍රේණි සහ ප-බ්ලොක් මූලද්‍රව්‍යවල ප්‍රතිසමානතාවය :

- Atomic sizes of 4d and 5d transition elements become almost equal, due to which their properties are very close.
- Zr and Hf : Nb and Ta : Mo and W resemble very closely.
- The crystal structure and other properties of lanthanides are very similar.
- Separation of lanthanides is not easy from their mixture.
- Super heavy metals of P- block exhibit inert pair effect.

Eg : Tl, Pb, Bi

රිථඩියමය ශ්‍රේණි සහ ඇක්ටිනයිඩ් ශ්‍රේණි පිළිබඳව ප්‍රධාන ලක්ෂණ සහ සාමාන්‍ය ගුණ සලකා බැලීම:

- The elements in actinide series are Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No and Lr
- The size of the trivalent ions of these elements decreases as we move from left right this is because of poor shielding effect of f-electrons
- Effect of actinide contraction is higher in comparison to Lanthanide contraction.

Illustration 3:

The increasing order of atomic size of Li, Be, B and Ne is

Solution:

$B < Be < Li < Ne$

Inert gas is biggest in a period

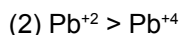
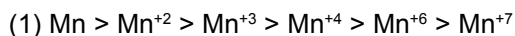
10.5 Ionic Radius

- When a neutral atom loses one or more electrons it forms a **cation** having one or more number of positive charge. Similarly when a neutral atom acquires one or more electrons it forms an **anion** having one or more number of negative charge.
- **Ionic radius** is the distance between the nucleus and the limit of the electron cloud scattered around the nucleus in an ion.

10.5.1 Cationic Radius

- An atom forms a cation on loss of electron/s. The cationic radius can be defined as the distance between the nucleus and the limit of the electron cloud scattered around the nucleus.
- The size of a cation is smaller in comparison to the size of its corresponding atom. Usually a cation has one shell less than the neutral atom hence it has smaller size than the atom. This is because of the fact that an atom on losing electrons/s form a cation, which has lesser number of electrons/s than the number of proton/s. This results in increase in the effective nuclear charge.

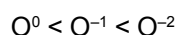
Examples -



Note : Radius of Al is greater than Ga (due to poor screening effect of 3d electrons of Ga), but radius of Al^{+3} is lower than Ga^{+3} .

10.5.2 Anionic Radius

- When a neutral atom gains electron/s it becomes a negatively charged ion called an anion. The distance between the nucleus of an anion and the limit of the electron cloud scattered around the nucleus, is called its **anionic radius**.
- The size of an anion is greater than the size of its corresponding atom, because the number of electrons present in the anion gets larger than the number of protons due to gain of electron/s. This results in decrease in the effective nuclear charge.



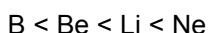
10.6 Size of Isoelectronic Species

- The species, which have same number of electrons but different nuclear charges, constitute an isoelectronic series. In the isoelectronic species with the increase in effective nuclear charge, the size of ion goes on decreasing.

Illustration 1:

The increasing order of atomic size of Li, Be, B and Ne is

Solution.



Inert gas is biggest in a period

Illustration 2:

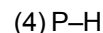
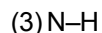
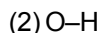
The increasing order of atomic size As, Bi, Sn, Pb and Sb is

Solution.



Illustration 3:

Which of the following should be the longest bond ?



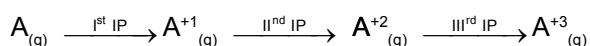
Solution (4)

The atomic radius of P is largest out of O, S, N, and P therefore, P–H bond will be the longest one .

BY RAJESH SHAH

11. IONISATION POTENTIAL

- The energy required to remove the most loosely bound electron from the outermost orbit of one mole of isolated gaseous atoms of an element, is called **ionisation potential (IP)**. This ionisation is an endoergic or energy-absorbing process.
- An electron cannot be removed directly from an atom in solid state. For this purpose, the solid state is converted to gaseous state and the energy required for this is called **sublimation energy**.
- The energy required to remove one electron from a neutral gaseous atom to convert it to monovalent cation, is called first ionisation potential (Ist IP). The energy required to convert a monovalent cation to a divalent cation is called second ionisation potential (IInd IP)



- Ist IP < IInd IP < IIIrd IP because as the electrons go out of the atom, the effective nuclear charge increases & the ionic size goes on decreasing. Thus the forces of attraction on valence shell electrons increases and hence the order.

11.1 Factors Affecting Ionisation Potential

- (i) **Number of shells** : With the increase in number of shells the atomic radius increases i.e. the distance of outer most shell electron from the nucleus increases and hence the ionisation potential decreases.
- (ii) **Effective Nuclear Charge** : Atomic size decreases with increase in effective nuclear charge because, higher the effective nuclear charge stronger will be the attraction of the nucleus towards the electron of the outermost orbit and higher will be the ionisation potential
- (iii) **Shielding Effect** : The electrons of internal orbits repel the electron of the outermost orbit due to which the attraction of the nucleus towards the electron of the outermost orbit decreases and thus atomic size increases and the value of ionisation potential decreases.
- (iv) **Stability of half filled and fully filled orbitals** : The atoms whose orbitals are half-filled (p^3 , d^5 , f^7) or fully-filled (s^2 , p^6 , d^{10} , f^{14}) have greater stability than the others. Therefore, they require greater energy for removing an electron. However stability of fully filled orbitals is greater than that of the half filled orbitals
- (v) **Penetration power** : In any atom the s orbital is nearer to the nucleus in comparison to p , d and f orbitals. Therefore, greater energy is required to remove an electron from s orbital than from p , d and f orbitals. Thus the decreasing order of ionisation potential of s , p , d and f orbitals is as follows

$$s > p > d > f$$

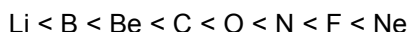
11.2 Periodic Trends in Ionisation Potential

- (a) **In a Period :-** The value of Ionisation potential normally increase on going from left to right in a period, because effective nuclear charge increases and atomic size decreases.

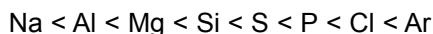
11.2.1 Exceptions

- In second period ionisation potential of Be is greater than that of B, and in the third period ionisation potential of Mg is greater than that of Al due to high stability of fully filled orbitals.
- In second period ionisation potential of N is greater than O and in the third period ionisation potential of P is greater than that of S, due to stability of half filled orbitals.

- The increasing order of the values of ionisation potential of the second period elements is



The increasing order of the values of ionisation potential of the third period elements is



11.2.2 Ionisation Potential of Transition Elements

- In transition elements, the value of ionisation potential has very little increase on going from left to right in a period because the outermost orbit remains the same but electrons get filled up in the (n-1)d orbitals resulting in very little increase in the values of ionisation potential.
- In transition element series the first ionisation potential normally increases with increase in atomic number on going from left to right, but this periodicity is not uniform. The value of ionisation potential of transition elements depends on the following two important factors.

(a) The value of ionisation potential increases with increase in effective nuclear charge.

(b) The value of ionisation potential decreases with increase in shielding effect when the number of electrons increases in (n - 1)d orbitals

- In the first transition element series the first ionisation potential normally increases on going from left to right from Sc to Cr because shielding effect is much weaker in comparison to effective nuclear charge. The value of first ionisation potential of Fe, Co and Ni remains constant, because shielding effect and effective nuclear charge balance one another. The value of ionisation potential shows slight increase from Cu to Zn because they have fully filled s and d orbitals. The value of first ionisation potential of Mn is maximum because it has maximum stability due to fully filled s and half filled orbitals.

11.2.3 Inner Transition Elements

The size of inner transition elements is greater than that of d block elements. Therefore the value of ionisation potential of f block elements is smaller than that of d block elements and due to almost constant atomic size of f block elements in a period the value of their ionisation potential remains more constant than that of d block elements.

11.2.4 In a Group

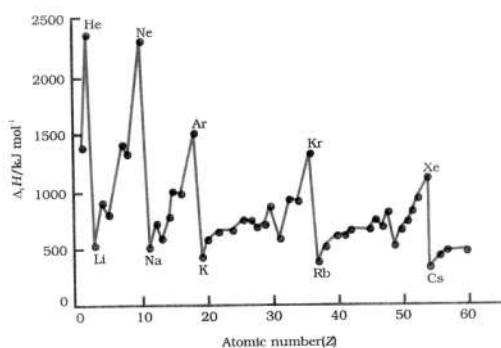
- The value of ionisation potential normally decreases on going from top to bottom in a group because both atomic size and shielding effect increase.

Exception :

- The value of ionisation potential remains almost constant from Al to Ga in the III A group.
(B > Tl > Ga > Al > In)
- In IVB group i.e. Ti, Zr and Hf the I.P. of Hf is higher than that of Zr due to Lanthanide contraction. Thus the I.P. of IVB group varies as Ti > Zr < Hf.
- In the periodic table the element having highest value of ionisation potential is He.
- The values of ionisation potential of noble gases are extremely high, because the orbitals of outermost orbit are fully-filled (ns^2 , np^6) and provide great stability.
- In a period, the element having least value of ionisation potential is an alkali metal (group I A) and that having highest value is inert gas (Group 0)

11.3 Applications of Ionisation Potential

- The elements having high values of ionisation potential have low reactivity, e.g. inert gases.
- The value of ionisation potential decreases more on going from top to bottom in a group in comparison to a period. Therefore, reactivity increases and the atom forms a cation by loss of electron.
- The elements having low value of ionisation potential readily lose electron and thus behave as strong reducing agents.
- The elements having low value of ionization potential readily lose electron and thus exhibit greater metallic property.
- The elements having low value of ionisation potential readily lose electron and thus oxide and hydroxides of these elements have basic property.



In the curve the maxima of curve occupied by noble gases.

The minima of the curve occupied by alkali metals.

BY RAJESH SHAH

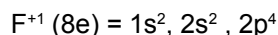
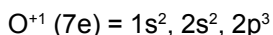
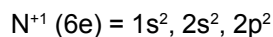
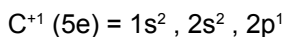
Illustration 1:

Which of the following should be the order of increasing values of second ionisation potential of C, N, O and F

- (1) $C > N > F > O$ (2) $C < F < N < O$ (3) $C < F < N < O$ (4) $C < N < F < O$

Solution (4):

The second ionisation potential means removal of electron from a cation

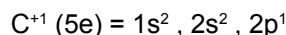
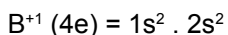
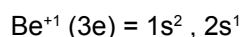
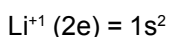


Therefore $C < N < F < O$

Illustration 2:

Which of the following should be the correct order of the second ionisation potential of Li, Be B and C

- (1) $Li < Be > B < C$ (2) $Be < B < C < Li$ (3) $Be < C < B < Li$ (4) $Li < C < B < Be$

Solution (3):

Therefore $Be < C < B < Li$

Here, Li^{+1} has inert configuration and B^{+1} has fully filled s orbital. Hence these will have high value of second ionisation potential.

Illustration 3:

Which of the following should have least value of ionisation potential

- (1) Be^{+3} (2) H (3) Li^{+2} (4) He^{+1}

Solution (2):

All the above four species have one electron each, H has least number of proton. Therefore, H will have least value of ionisation potential.

Illustration 4:

Compare the size of Cl, Cl^- , and Fe^{++} ion

Solution :

$$\frac{Z}{e} \text{ ratio for Cl} = \frac{17}{17} = 1.00 \Rightarrow Cl^- = \frac{17}{18} = 0.944 \Rightarrow Fe^{++} = \frac{26}{24} = 1.08 \Rightarrow Cl^- > Cl > Fe^{++}$$

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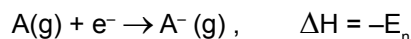
DAILY PRACTICE PROBLEM-2

- The screening effect of d - electrons is -
 - equal to the p - electrons
 - much more than p - electron
 - same as f - electron
 - less than p - electron
- The correct order of ionization energies is
 - Zn < Cd < Hg
 - Hg < Cd < Zn
 - Ar > Ne > He
 - Cs < Rb < Na
- In which of the following compounds manganese shows maximum radius -
 - MnO₂
 - KMnO₄
 - MnO
 - K₃[Mn(CN)₆]
- Which of the following order of radii is correct -
 - Li < Be < Mg
 - H⁺ < Li⁺ < H⁻
 - O < F < Ne
 - Na⁺ > F⁻ > O⁻²
- Atomic radii of fluorine and Neon in Angstrom units are given by -
 - 0.72, 1.60
 - 1.60, 1.60
 - 0.72, 0.72
 - None of these
- In the isoelectronic species the ionic radii (1) of N³⁻, O²⁻ and F⁻ are respectively given by -
 - 1.36, 1.40, 1.71
 - 1.36, 1.71, 1.40
 - 1.71, 1.40, 1.36
 - 1.71, 1.36, 1.40
- In correct orders of 1st I.P. are -
 - Li < B < Be < C
 - O < N < F
 - Be < N < Ne
 - Be < N < O
- The ionisation potential order for which set is correct ?
 - Cs < Li < K
 - Cs > Li > B
 - Li > K > Cs
 - B > Li > K
- In which of the following pairs, the ionisation energy of the first species is less than that of the second -
 - O⁻, O²⁻
 - S, P
 - N, P
 - Be⁺, Be
- 2nd IP of which of the element is maximum -
 - Lithium
 - oxygen
 - nitrogen
 - fluorine

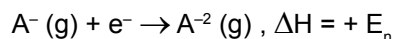
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12. ELECTRON AFFINITY

- The energy released on adding up one mole of electron to one mole of neutral atom (A) in its gaseous state to form an anion (A^-) is called **electron affinity** of that atom. Since the electron adds up in the outermost orbit, energy is given out. Therefore, **electron affinity** is associated with an exothermic process.



- When one electron adds up to a neutral atom, it gets converted to a uninegative ion and energy is released. On adding one more electron to the mononegative anion, there is a repulsion between the negatively charged electron and anion. In order to counteract the repulsive forces, energy has to be provided to the system. Therefore, the value of the second electron affinity is positive.



12.1 Factors Affecting Electron Affinity

- **Atomic Size or Atomic Radius**

When the size or radius of an atom increases, the electron entering the outermost orbit is more weakly attracted by the nucleus and the value of electron affinity is lower.

- **Effective Nuclear charge**

When effective nuclear charge is more then, the atomic size less. Then the atom can easily gain an electron and higher electron affinity.

- **Stability of Fully-Filled and Half-Filled Orbitals**

The stability of the configuration having fully-filled orbitals (p^6, d^{10}, f^{14}) and half-filled orbital (p^3, d^5, f^7) is relatively higher than that of other configurations. Hence such type of atoms have less tendency to gain an electron, therefore their electron affinity values will be very low or zero.

12.2 Trends in Electron Affinity

12.2.1 In a period

Atomic size decreases with increase in effective nuclear charge and hence increase in electron affinity.

Exception :

- On going from C_6 to N_7 in the second period, the values of electron affinity decreases instead of increasing. This is because there are half-filled ($2p^3$) orbitals in the outermost orbit of N, which are more stable. On the other hand, the outermost orbit in C has $2p^2$ configuration.
- In the third period, the value of electron affinity of Si is greater than that of P. This is because electronic configuration of the outermost orbit in P atom is $3p^3$, which being half-filled, is relatively more stable.
- The values of electron affinity of inert gases are zero, because their outermost orbit has fully-filled p orbitals.
- In a period, the value of electron affinity goes on decreasing on going from group IA to group IIA. The value of electron affinity of the elements of group IIA is zero because ns orbitals are fully-filled and such orbitals have no tendency to accept electrons.

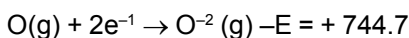
12.2.2 In a Group

- The values of electron affinity normally decrease on going from top to bottom in a group because the atomic size increases which decreases the actual force of attraction by the nucleus.

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Exceptions

- The value of electron affinity of F is lower than that of Cl, because the size of F is very small and compact and the charge density is high on the surface. Therefore, the incoming electron experiences more repulsion in comparison to Cl. That is why the value of electron affinity of Cl is highest in the periodic table.
- The values of electron affinity of inert gases and alkaline earth metals can be regarded as zero, because they do not have tendency to form anions by accepting electron.

Illustration 1:

The reason for the positive value of E is

- | | |
|--------------------------|--------------------------------|
| (1) endothermic reaction | (2) exothermic reaction |
| (3) both 1 and 2 | (4) All of the above are wrong |

Solution (1):

When electron is brought near O^{-1} there will be repulsion between them, and therefore the energy will be positive i.e there will be absorption of energy during the process.

Illustration 2:

The increasing order of electron affinity of N, P and As is

- | | | | |
|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| (1) $\text{N} < \text{P} < \text{As}$ | (2) $\text{As} < \text{P} < \text{N}$ | (3) $\text{As} < \text{N} < \text{P}$ | (4) $\text{As} < \text{N} > \text{P}$ |
|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|

Solution (3):

Phosphorus have vacant 'd' orbitals due to which it has higher electron affinity than Nitrogen.

Illustration 3:

Why electron gain enthalpy of chlorine is more negative than Fluorine ?

Solution (3):

Fluorine have small size and hence-electronic repulsion is higher in fluorine, so addition of an electron to fluorine is difficult than large sized chlorine.

Some electron affinity values (kJ mol^{-1})

$\text{H} \rightarrow \text{H}^{-}$ -72	$\text{Na} \rightarrow \text{Na}^{-}$ -21
$\text{He} \rightarrow \text{He}^{-}$ 54	$\text{Mg} \rightarrow \text{Mg}^{-}$ 67
$\text{Li} \rightarrow \text{Li}^{-}$ -57	$\text{Al} \rightarrow \text{Al}^{-}$ -26
$\text{Be} \rightarrow \text{Be}^{-}$ 66	$\text{Si} \rightarrow \text{Si}^{-}$ -135
$\text{B} \rightarrow \text{B}^{-}$ -15	$\text{P} \rightarrow \text{P}^{-}$ -60
$\text{C} \rightarrow \text{C}^{-}$ -121	$\text{S} \rightarrow \text{S}^{-}$ -200
$\text{N} \rightarrow \text{N}^{-}$ 31	$\text{S} \rightarrow \text{S}^{-2}$ 332
$\text{O} \rightarrow \text{O}^{-}$ -142	$\text{Cl} \rightarrow \text{Cl}^{-}$ -348
$\text{O} \rightarrow \text{O}^{-2}$ 702	$\text{Br} \rightarrow \text{Br}^{-}$ -324
$\text{F} \rightarrow \text{F}^{-}$ -333	$\text{I} \rightarrow \text{I}^{-}$ -295
$\text{Ne} \rightarrow \text{Ne}^{-}$ 99	

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13. ELECTRONEGATIVITY

- The measure of the capacity or tendency of an atom to attract the shared pair of electrons of the covalent bond towards itself is called **electronegativity** of that atom.
- Electronegativity is a relative value that indicates the tendency of an atom to attract shared electrons more than the other atom bonded to it. Therefore it does not have any unit. Pauling was the first scientist to put forward the concept of electronegativity. On Pauling's scale the electronegativity is expressed in Paulings.
- The numerical value of electronegativity of an atom depends on its ionisation potential and electron affinity values.

13.1 Factors Affecting Electronegativity

- **Atomic size** – Electronegativity of a bonded atom decreases with increase in size with increase in size the forces of attractions on valence shell electrons decrease and hence electron negativity decreases.
- When effective nuclear charge is high the nucleus will attract the shared electrons with greater strength and the electronegativity will be high.
- This effect increases the atomic size which decreases the electronegativity value.
- **Hybridisation state of atom** – Electronegativity increases with increases in the s character of the hybrid orbital. This is because the s orbital is nearer to the nucleus and thus suffers greater attraction resulting in increase in electronegativity.
- The number of covalent bonds present between two bonded atoms is known as bond order. With increases in the bond order, the bond distance decreases, effective nuclear charge increases and thus electronegativity increases. Increasing order of electronegativity is as follows : $C-C < C=C < C\equiv C$
- **Oxidation number** – The electronegativity value increases with increase in oxidation number because radius decreases with increase in oxidation number.
The increasing order of electronegativity is as follows : $Fe < Fe^{+2} < Fe^{+3}$
- Electronegativity does not depend on stability of fully-filled or half-filled orbitals because it is simply the capacity of nucleus to attract bonded pair of electrons.

13.2 Trends in Electronegativity

Atomic size decreases on going from left to right in a period thus electronegativity increases. Atomic size increases on going from top to bottom in a group thus electronegativity decreases.

- **Inert Gases** - The electronegativity value of inert gases is zero, because they do not form covalent bonds
- In a period, the electronegativity value of halogen is maximum, while the electronegativity value of alkali metal is minimum.
- F has maximum electronegativity value in the periodic table, while Cs has minimum electronegativity.
- According to Pauling scale, the electronegativity value of F is 4.0, O is 3.5 N is 3.0 and Cl is 3.1.
- In Pauling's scale, elements having almost same electronegativity are

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$$C = S = I = 2.5$$

$$N = Cl = 3.0$$

$$P = H = 2.1$$

$$Cs = Fr = 0.7$$

$$Be = Al = 1.5$$

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- The elements of group II B i.e. Zn, Cd and Hg show increase in electronegativity value on going from top to bottom in the group.
- The elements of group III A, i.e. Al to Ga show increase in electronegativity value on going from top to bottom in the group.
- The elements of group IV A, show no change in electronegativity value on going from top to bottom in the group from Si on words.

14. MEASUREMENT OF ELECTRONEGATIVITY

14.1 Pauling Scale

If two atoms, A and B, having different electronegativity values, get bonded to form a molecule, AB, then the bond between A and B in A – B will have both covalent and ionic properties.

$$\Delta_{A-B} = \text{Observed bond energy} - \text{Energy of 100\% covalent} \text{ or } \Delta_{A-B} = D - E_{A-B}$$

where D = Observed bond energy

$$E_{A-B} = \text{Bond energy of pure covalent bond of } A - B = \sqrt{E_{A-A} \times E_{B-B}}$$

$$X_A - X_B = 0.208 \sqrt{\Delta_{A-B}} \text{ where } X_A > X_B \text{ or } 0.043 \times \Delta_{A-B} = (X_A - X_B)^2$$

14.2 Mulliken Scale

Mulliken suggested that the value of electronegativity of an element as an average of the values of ionisation potential and electron affinity of the element.

$$X_M = \frac{I.P. + E.A.}{2} \text{ (in eV),} \quad X_M = \frac{I.P. + E.A.}{540} \text{ kJ/mol}$$

where X_M = Electronegativity value as given by Mulliken

$$X_p = \frac{X_M}{2.8} = \frac{I.P. + E.A.}{5.6}$$

where X_p = Electronegativity value as given by Pauling or $X_p = 0.336 (X_M - 0.615)$

14.3 Allred Roschov's scale :

As per Roschov, electronegativity is the force by which nucleus of an atom attracts electron which are on the covalent radius.

$$(X_{AR}) \text{ Electronegativity} = \frac{Z_{eff} \times e^2}{r^2}$$

or

$$X_p = 0.359 X_{AR} + 0.744$$

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15. APPLICATIONS OF ELECTRONEGATIVITY

(i) ~~बिनामूलक यौगिक~~

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

Illustration 1:

Write the correct formula and name of the following

- (a) ICl or ICl₂ (b) FCl or ClF (c) BrCl or ClBr (d) BrI or IBr
 (e) OF₂ or F₂O (f) Cl₂O or OCl₂

Solution:

Correct formula	Name
(a) I ⁺ Cl ⁻	Iodine chloride
(b) Cl ⁺ F ⁻	Chlorine fluoride
(c) Br ⁺ Cl ⁻	Bromine chloride
(d) IBr	Iodine bromide
(e) OF ₂	Oxygen difluoride
(f) Cl ₂ O	Dichlorine oxide

(ii) ~~बिनामूलक यौगिक में बंध~~

If difference of electronegativities of the two elements is 1.7 or more, then ionic bond is formed between them whereas if it is less than 1.7, then covalent bond is formed. (HF is exception in which bond is covalent although difference of electronegativity is 1.9).

- (a) According to Hanny & Smith formula

$$\text{Ionic \%} = 16 (X_A - X_B) + 3.5 (X_A - X_B)^2$$

$$\text{Here } X_A = \text{Electronegativity of A}$$

$$X_B = \text{Electronegativity of B}$$

$$\text{If } X_A - X_B \geq 2.1 \quad \text{Ionic \%} > 50\% \text{ i.e. Ionic bond}$$

$$\text{If } X_A - X_B \leq 2.1 \quad \text{Ionic \%} < 50\% \text{ i.e. covalent bond}$$

- (b) According to Gallis

$$X_A - X_B \geq 1.7 \quad \text{Ionic}$$

$$X_A - X_B \leq 1.7 \quad \text{Covalent}$$

$$\text{If } X_A = X_B; \text{ then A - B will be non polar.} \quad \text{Ex. H-H, F-F}$$

$$\text{If } X_A > X_B \text{ and difference of electronegativities is small then}$$

$$A^{\delta-} \text{ --- } B^{\delta+} \text{ bond will be polar covalent}$$

(iii) ~~बिनामूलक यौगिक में बिनामूलक यौगिक~~

Generally values of electronegativity of metallic elements are low, whereas electronegativity values of nonmetals are high.

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Illustration 2:

Explain the relation between % s-character of C and its electronegativity.

Solution:

Electronegativity $\Rightarrow C(sp) > C(sp^2) > C(sp^3)$ because Z_{eff} increases due to increases in % s-character.

15.1 Partial Ionic Character in Covalent bonds

Partial ionic characters are generated in covalent compounds by the difference of electronegativities. **Hanny and smith** calculated percentage of ionic character from the difference of electronegativity.

$$\begin{aligned} \text{Percentage of ionic character} &= 16(X_A - X_B) + 3.5(X_A - X_B)^2 \\ &= 16\Delta + 3.5\Delta^2 = (0.16\Delta + 0.035\Delta^2) \times 100 \\ &\quad (\text{Here } X_A, X_B) \end{aligned}$$

X_A is electronegativity of element A

X_B is electronegativity of element B

$$\Delta = X_A - X_B$$

15.2 Bond Length

When difference of electronegativities of atoms present in a molecule is increased, then bond length decreases. Shoemaker and stephensen determined.

$$\text{Bond length } d_{A-B} = r_A + r_B - 0.09(X_A - X_B)$$

$$\text{or } d_{A-B} = \frac{1}{2}(D_{A-A} + D_{B-B}) - 0.09(X_A - X_B)$$

Here $X_A > X_B$

15.3 Bond Strength & Stability

Bond strength and stability of A-B increases on increase in difference of electronegativities of atoms A and B bonded A-B. Therefore $H-F > H-Cl > H-Br > H-I$

16. NATURE OF OXIDES

If difference of the two electronegativities ($X_O - X_A$) is 2.3 or more than 2.3 then the oxide will be basic in nature. Similarly if value of $X_O - X_A$ is lower than 2.3 then the compound will be first amphoteric then acidic in nature.

Oxide	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl ₂ O ₇
($X_O - X_A$)	2.6	2.3	2.1	1.8	1.5	1.1	0.5
Nature	Strong basic	Basic	Amphoteric	weak acidic	Acidic	Strong acidic	Strongest acidic

17. NATURE OF HYDROXIDES

According to Gallis if electronegativity of A in a hydroxide (AOH) is more than 1.7 then it will be acidic in nature whereas it will be basic in nature if electronegativity is less than 1.7

For example	<u>NaOH</u> and	<u>ClOH</u>
Electronegativity (X_A)	0.9	3.00
Nature	Basic	Acidic

If the value is more than $X_O - X_H$, then that hydroxide will be basic otherwise it will be acidic.

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Illustration 1:

Increasing order of electronegativities of F, Cl, Br and I is

- (1) $F < Cl < Br < I$ (2) $I < Br < Cl < F$ (3) $Br < I > Cl > F$ (4) $I < Br > Cl < F$

Solution (2):

Electronegativity decreases in a group on going from top to bottom. Therefore increasing electronegativity order is $I < Br < Cl < F$.

Illustration 2:

Which of the following is the most polar bond

- (1) N-H (2) Cl-H (3) O-H (4) Br-H

Solution (3):

Difference of electronegativities of O and H is very high.

Illustration 3:

Which of the following formula is incorrectly written

- (1) OF_2 (2) Cl_2O (3) $BrCl$ (4) None of these

Solution (4):

In all the formulae less electronegative element (cation) could be indicated followed by the more electronegative element (anion)

Illustration 4:

OF_2 is called oxygen difluoride, whereas Cl_2O is called dichlorine monoxide. Why ?

Solution :

Electronegativity of O in OF_2 is less than F. Therefore, there will be positive charge on oxygen and negative charge on fluorine. Whereas in Cl_2O , electronegativity of Cl is less than that of O therefore there will be positive charge on Cl and negative charge on O. Positive charge is written first followed by negative charge.

Illustration 5:

Arrange the following compounds in the order of their decreasing stability if the electronegative values of elements are as follows

H = 2.1 F = 4, Cl = 3.0, Br = 2.8

I = 2.3, N = 3.0

HF, NCl_3 , HBr, HI, HCl

Solution :

Electronegativity difference for

HF = $4.0 - 2.1 = 1.9$ $NCl_3 = 3.0 - 3.0 = 0.0$ HBr = $2.8 - 2.1 = 0.7$

HI = $2.3 - 2.1 = 0.2$ HCl = $3.0 - 2.1 = 0.9$

So their order of their decreasing stability

HF > HCl > HBr > HI > NCl_3

1.9 0.9 0.7 0.4 0.0

उदाहरण 5 :

Negative N is written first in NH_3 because it became very common from the very beginning. There is no scientific basis for that. Otherwise according to rule it should have been written as H_3N in the form of trihydrogen nitride.

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17.1 Acidic and Basic Nature of Hydroxides of Elements

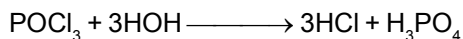
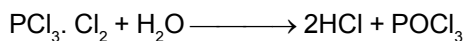
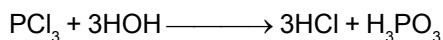
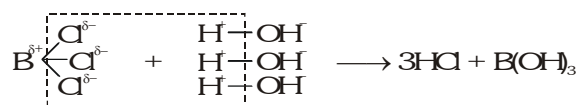
Acidic and basic nature of hydroxide of an element AOH depends on ionisation potential of A. If ionisation potential of A is low then it will give its electron to oxygen easily thus AOH will be basic.

(I) Hydrolysis of AX :

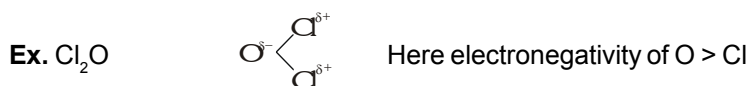
Where A = Other element and X = Halogen

- (a) If electronegativity of X > Electronegativity of A then on hydrolysis product will be HX.

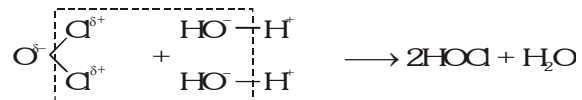
Ex. (BCl₃), Electronegativity of Cl > Electronegativity of B



- (b) If electronegativity of X < electronegativity of A then on hydrolysis product will be HOX (hypohalous acid)

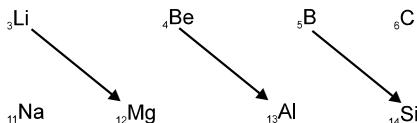


So On hydrolysis –



18. DIAGONAL RELATIONSHIP

- Some elements of second period Li, Be, B shows dissimilarities with other elements of this group but shows similarities with elements of third group like Mg, Al, Si situated diagonally to them. It is called diagonal relationship.



- Similarities between properties of Li and Mg are as follows.
- Li and Mg both react directly with nitrogen to form lithium nitride (Li_3N) and magnesium nitride (Mg_3N_2) whereas other alkali metals of IA group do not form nitride.
 - Fluoride carbonate and phosphate of Li and Mg are insoluble in water whereas these compounds of other alkali metals are soluble.
 - Li and Mg both are hard metals, whereas other metals of IA group are soft.
 - LiOH and Mg(OH)_2 both are weak bases, whereas hydroxides of other elements of IA group are strong bases.
 - Metallic bond in Li and Mg both are strong compared to other alkali metals.
 - Their melting and boiling points are high.
 - By thermal disintegration of LiNO_3 and $\text{Mg(NO}_3)_2$, Li_2O and MgO are obtained respectively.
 - Thermal stability of Li_2CO_3 and MgCO_3 is very less compared to other alkali metals and they liberate CO_2 gas easily.
- Similarly Be shows similarity to Al of IIIA group compared to other elements of IIA group which are as follows.
- These both elements do not provide colour to Bunsen burner.
 - They both are comparatively stable in air.
 - Both are insoluble in NH_3 therefore do not form blue coloured solution.
 - There is no tendency of making peroxide and superoxide in them.
 - Reducing power is very less due to low value of standard electrode potential in the form of oxidation potential.
 - Be and Al both form halogen bridge halides.

DAILY PRACTICE PROBLEM-3

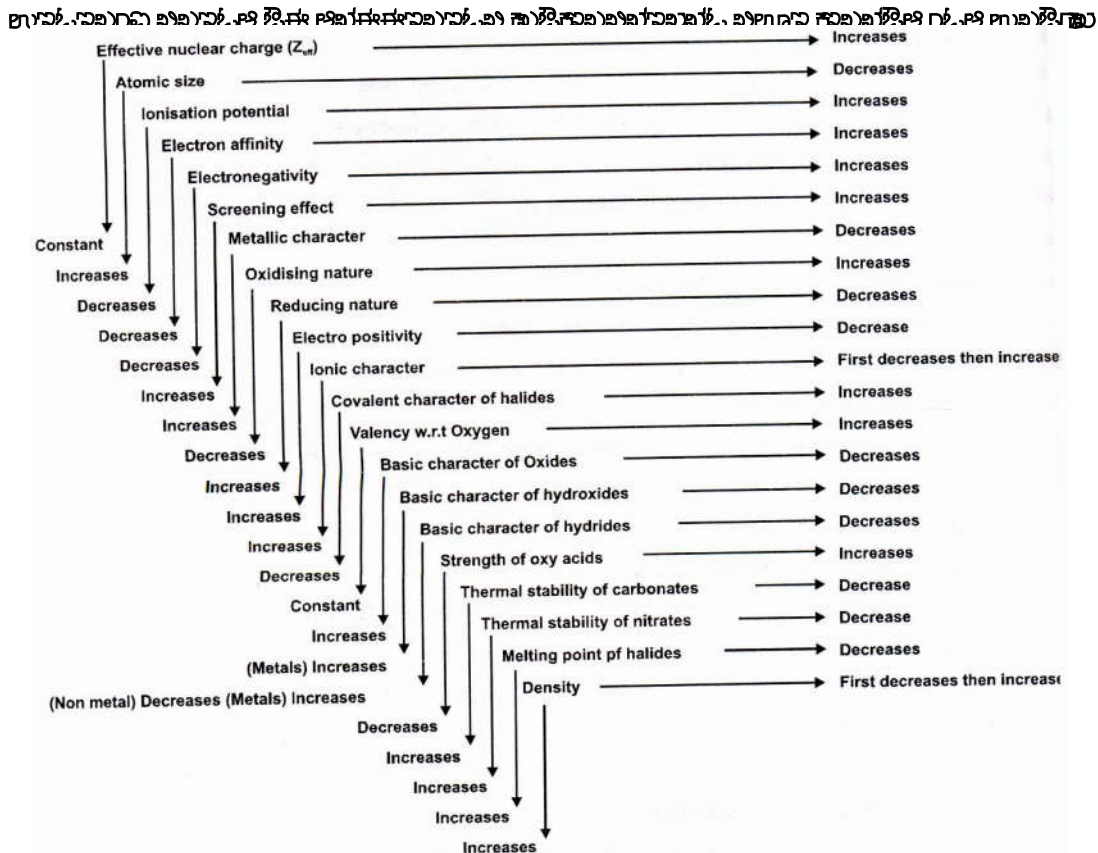
- The correct order of electron affinity is -
 - Be < B < C < N
 - Be < N < B < C
 - N < Be < C < B
 - N < C < B < Be
- The electron affinity values for the halogens shows the following trend -
 - Cl > F > Br > I
 - F < Cl < Br < I
 - F > Cl > Br > I
 - F < Cl > Br < I
- Be and Mg have zero value of electron affinities, because -
 - Be and Mg have (He)2s² and (Ne)3s² configuration respectively
 - 2s and 3s orbitals are filled to their capacity
 - Be and Mg are unable to accept electron
 - all the above are correct
- Which of the following acid is strongest :-
 - HF
 - HCl
 - HBr
 - HI
- In the formation of a chloride ion, from an isolated gaseous chlorine atom, 3.8 eV energy is released, which would be equal to -
 - Electron affinity of Cl⁻
 - Ionisation potential of Cl
 - Electronegativity of Cl
 - Ionisation potential of Cl⁻
- Second electron affinity of an element is -
 - Always exothermic
 - Endothermic for few elements
 - Exothermic for few elements
 - Always endothermic
- Which one of the following arrangements does not truly represent the property indicated against it?
 - Br₂ < Cl₂ < F₂ Oxidising power
 - Br₂ < Cl₂ < F₂ Electronegativity
 - Br₂ < F₂ < Cl₂ Electron affinity
 - Br₂ < Cl₂ < F₂ Bond energy
- The electronegativities of F and H are 4.0 and 2.1 respectively. The percent ionic character in H and F bond is
 - 43
 - 34
 - 94
 - 39
- Give the correct order of electronegativity of central in following compounds –

CH ₃ – CH ₃ ,	CH ₂ = CH ₂ ,	CH ≡ CH
(a)	(b)	(c)

The correct order is –

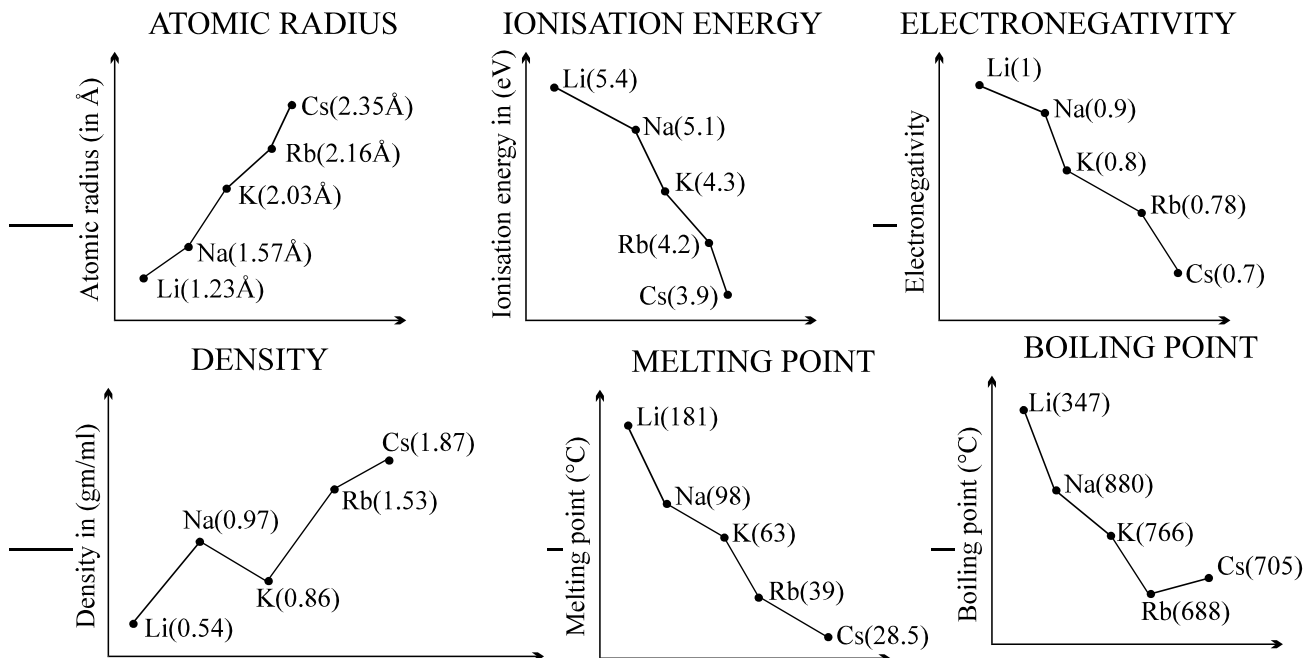
 - a > b > c
 - c > a > b
 - c > b > a
 - b > c > a
- The X–X bond length is 1.00 Å and C – C bond length is 1.54 Å. If electronegativities of 'X' and 'C' are 3.0 and 2.0 respectively, the C – X bond length is likely to be -
 - 1.27 Å
 - 1.18 Å
 - 1.08 Å
 - 1.28 Å

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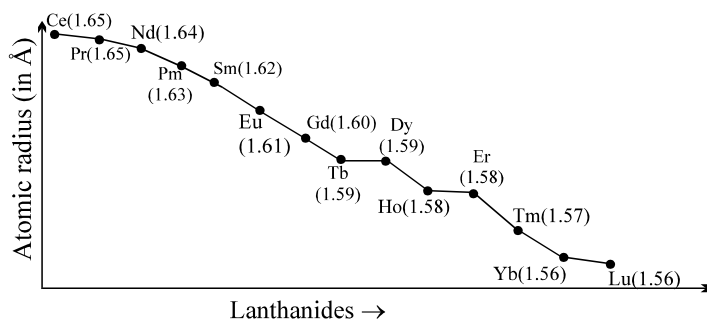
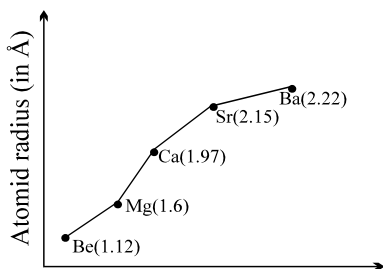
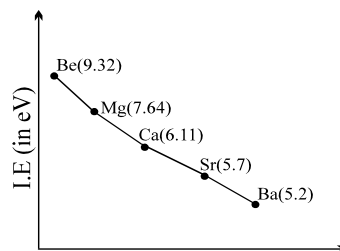
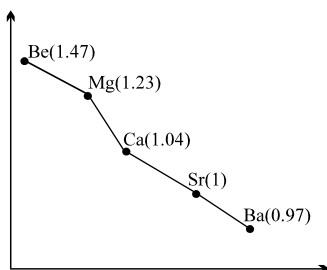
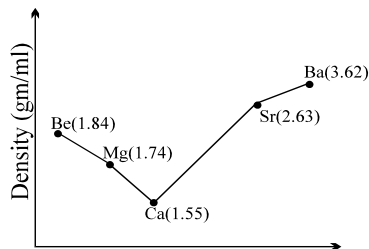
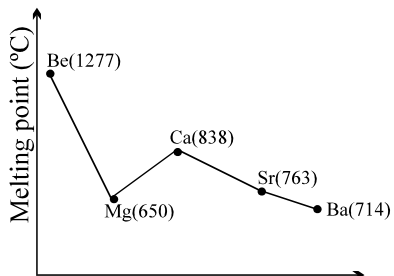
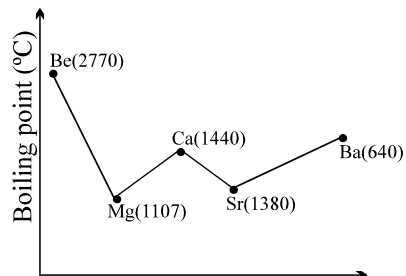


19. GRAPHS OF PERIODIC PROPERTIES

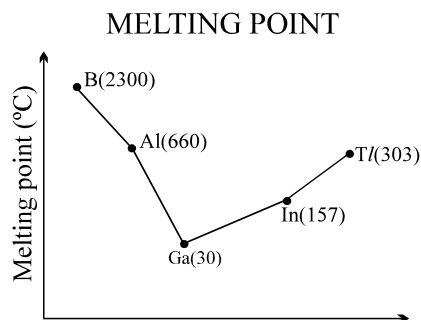
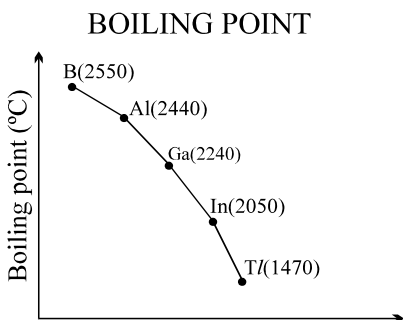
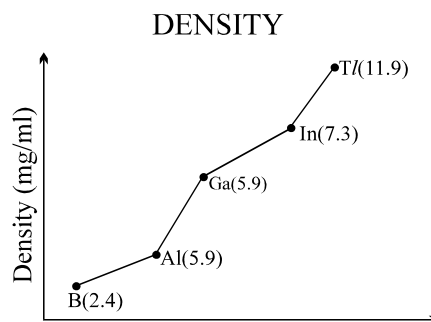
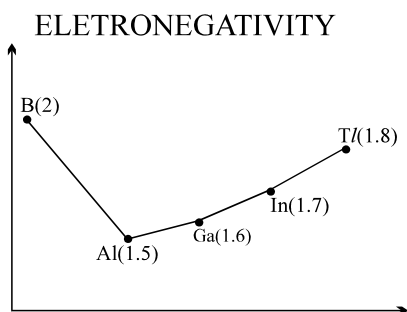
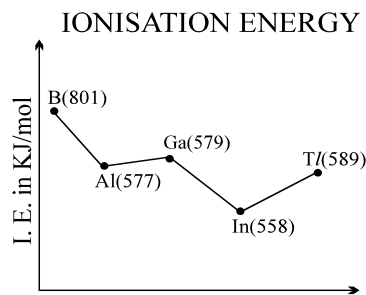
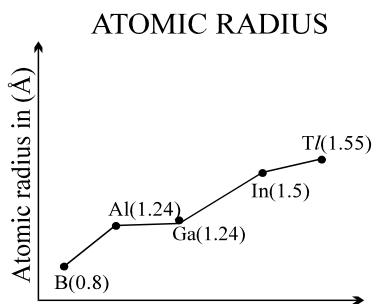
ALKALI METALS



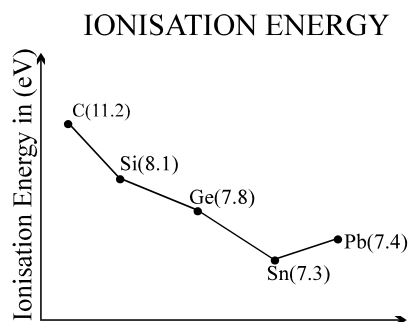
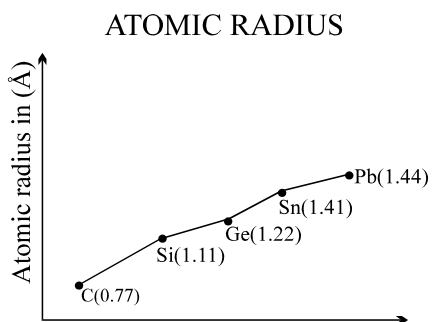
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LANTHANIDES**ATOMIC RADIUS (LANTHANIDE CONTRACTION)****ALKALINE EARTH METALS****ATOMIC RADIUS****IONISATION ENERGY****ELECTRONEGATIVITY****DENSITY****MELTING POINT****BOILING POINT****BY RAJESH SHAH**

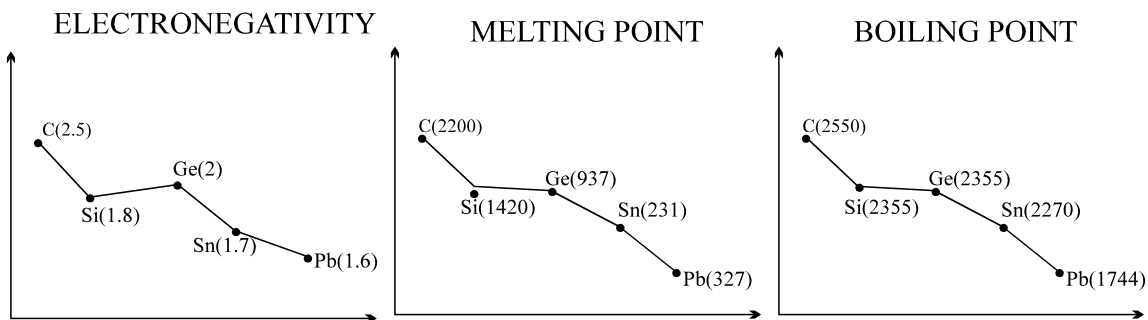
ELEMENT OF GROUP IIIA



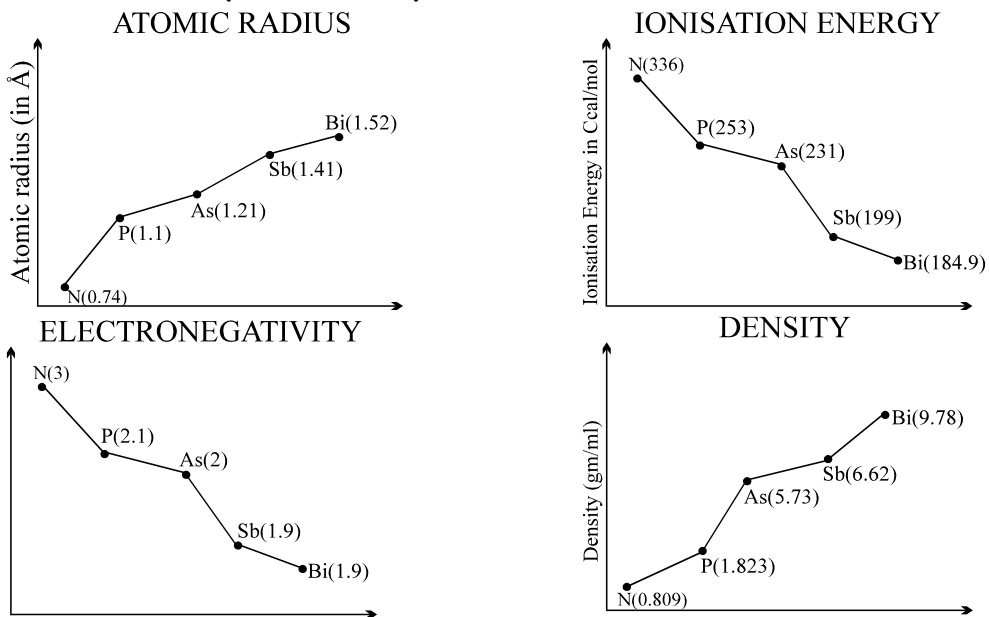
CARBON FAMILY



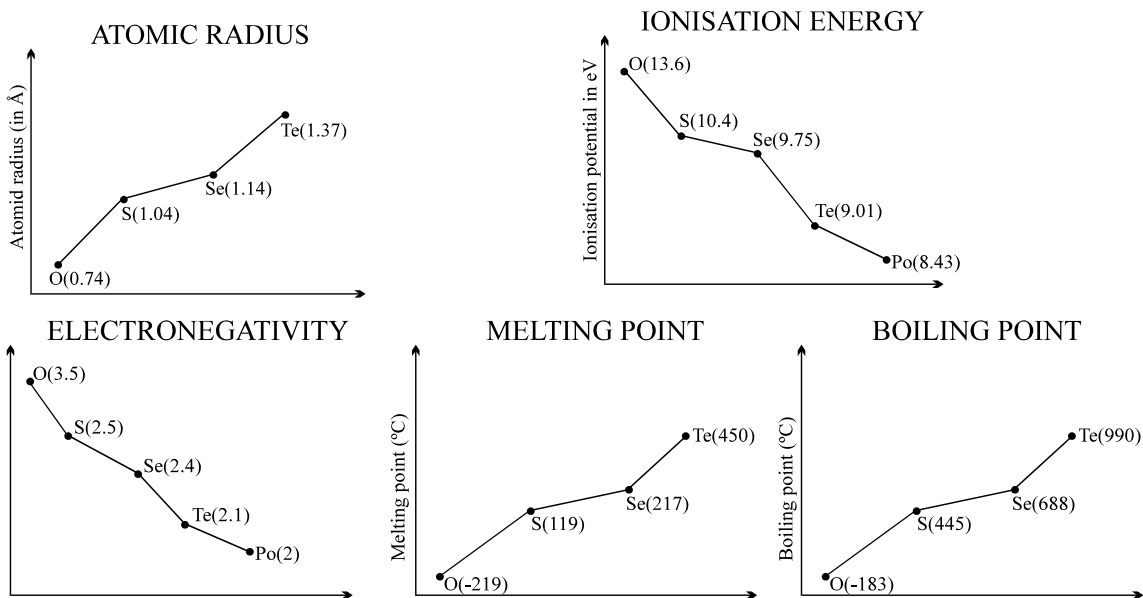
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NITROGEN FAMILY (PNICOGENS)

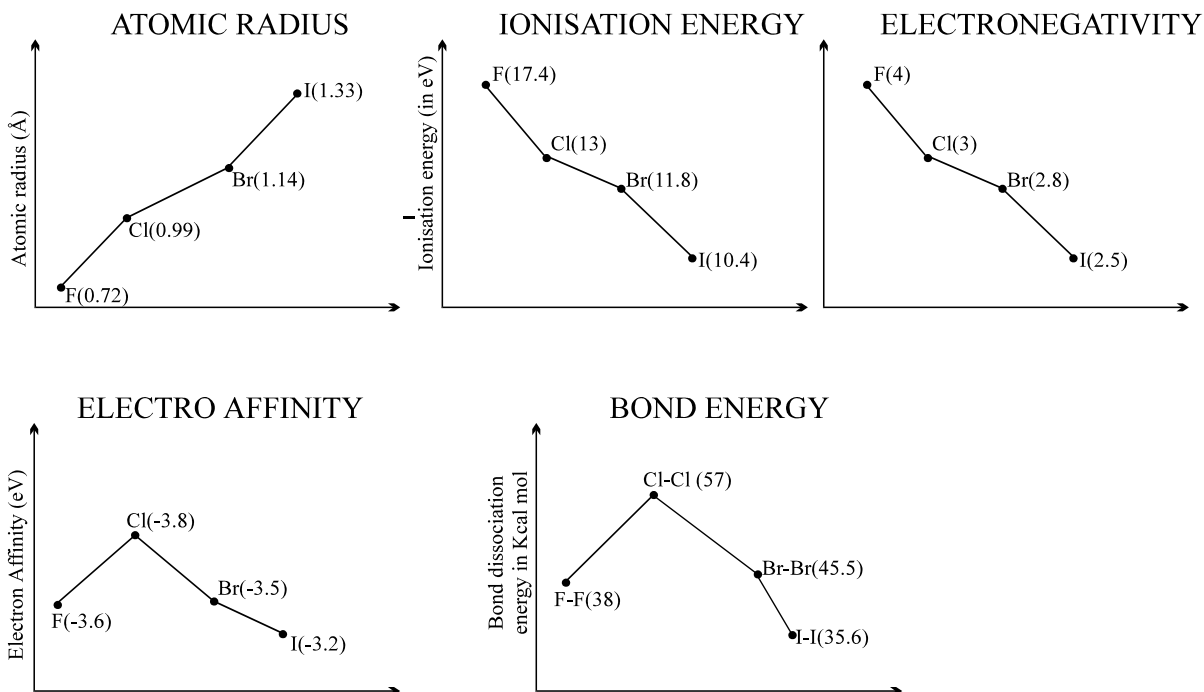


CHALCOGENS

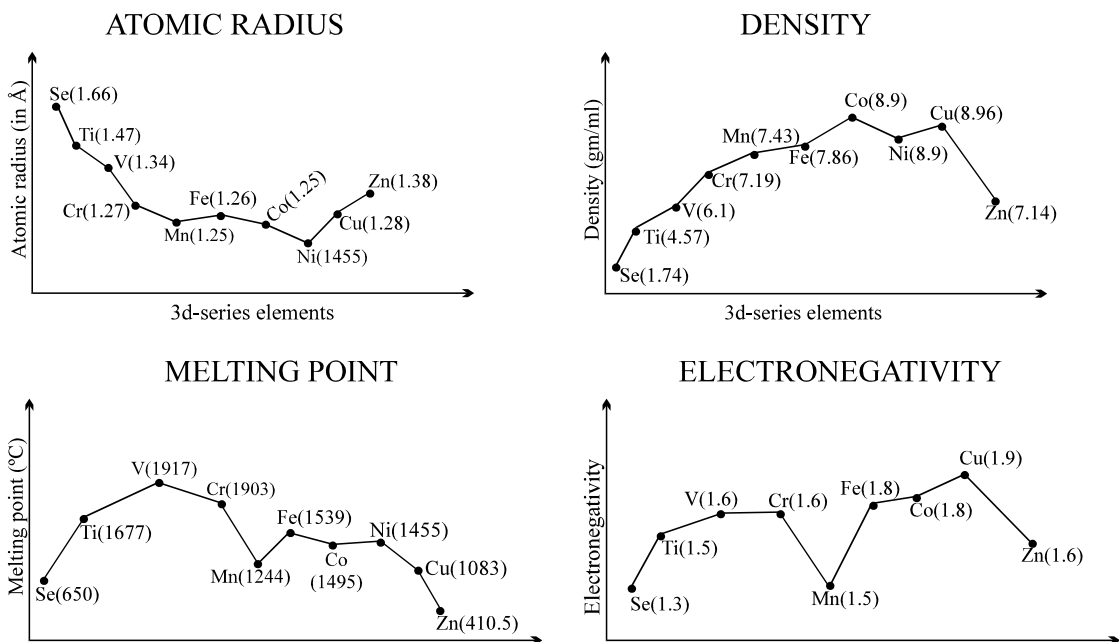


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HALOGENS



3-d SERIES



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