Chap - 2
# Periodic Table & Periodic Properties

Periodic Table :-
→ Tabular arrangements of elements is called periodic table

* first Classification by Lavosier into metals and non-metals.

→ Difference b/w metals and non-metals.

| Metals	Non-metals
1. They are sonorous	No such property
2. They are hard but not brittle	They are soft and brittle
3. They are good conductor of heat and electricity.	In general, they are not good conductor of heat and electricity Exception - graphite - electricity - diamand - heat
4. They are Lustrous.	Non-lustrous

* Electron Sea Model

$$M \longrightarrow M^{+n} + ne^-$$

$$\downarrow$$
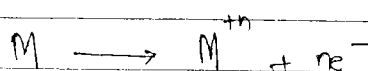
Kernel

ne^- — valence $e^{\ominus}$

* Purity of diamond is measured by its thermal conductor.
* Conductor → means only electrical conductor not thermal conductor.

Electron Sea Model
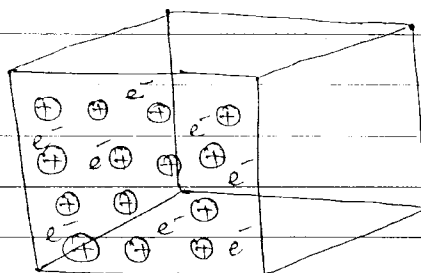
→ To explain electrical conductivity of metals.
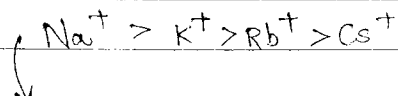
→ The two +ively charged species are supposed to repel each other but they become stabilised due to the presence of electronic flirs present between them and this mobile electron is nothing but cause for electrical conductity.

→ The attraction b/w the two species depends upon the following factors.

1. Charge :- Higher the charge of kernel, higher will be the attraction.
   $Al^{3+} > Mg^{2+} > Na^+$

   $Na → Na^+ + e^-$
   $Mg → Mg^{2+} + 2e^-$
   $Al → Al^{3+} + 3e^-$
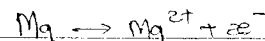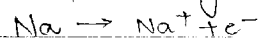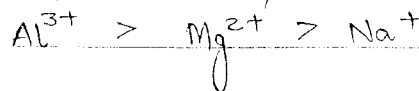
2. Smaller the size of kernel, higher will be the attraction.

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

$$\text{Charge density} (\phi) = \frac{Charge}{size}$$

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⭐⭐ Transition Triad :- Fe, Co, Ni

Dobereiner Triad Rule.

(i) He made groups of three elements having chemical properties called triads.

(ii) In Dobereiner triad, atomic weight of middle element is equal to the average at. weight of the first and 3rd element.

Ex -

Cl	Br	I		Li	Na	K
35.5	80	127		7	23	39

Limitations:-

It worked only for a few elements

Newland Octave Rule

He arranged the elements in the increasing order of their atomic mass and observed that properties of every 8th element was similar to 1st one like in the case of musical vowels notation.

Sa	Re	Ga	Ma	Pa	Dha	Ni	Sa
1	2	3	4	5	6	7	8

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

At that time, inert gases were not known.

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The properties of li are similar to 8th element Na
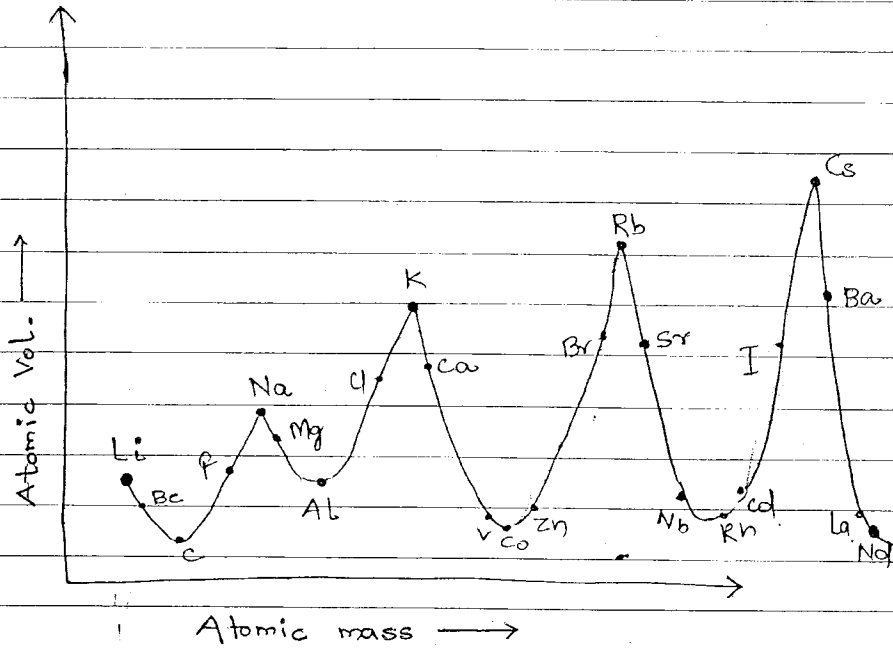
Limitations :-

1) This rule is valid only upto Ca bcz after Ca due to presence of d-block element there is difference of 18 elements instead of 8 element.

2) After discovery of inert gases, this law had to be dropped out.

c) He failed in the case heavier metals as Fe has been placed with O and S.

Lother Meyer's Curve

(i) He plotted a curve b/w atomic weight and atomic volume of different elements.

(ii) Elements having similar properties occupy similar position in the curve.

(a) Most electropositive elements i.e. alkali metals occupy the peak positions.

(b) less electropositive elements i.e alkaline earth metals (Be, Mg, Ca, Sr, Ba) occupy descending position

(c) Metalloids and transition elements occupy bottom part of curve.

(iv) Most electronegative (halogens) occupy ascending position on the curve.

Atomic Vol. →

Atomic mass →

Li, Be, F, Na, Mg, Al, C, Cl, Ca, K, V, Co, Zn, Br, Sr, Rb, Nb, Rh, Cd, I, Ba, Cs, La, Na

Periodic Table (hand-drawn)

s-block

Period	1 IA	2 IIA
1	H 1	Be
2	Li 3	Mg
3	Na 11	Ca
4	K 19	Sr
5	Rb 37	Ba
6	Cs 55	Ra ★
7	Fr ★ 87	

d-block

3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIII	10	11 IB	12 IIB
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc ★	Ru	Rh	Pd	Ag	Cd
La ★	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac ★★	Unq								

p-block

13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 O
B	C	N	O	F	He 2
Al	Si	P	S	Cl	Ne 10
Ga	Ge	As	Se	Br	Ar 18
In	Sn	Sb	Te	I	Kr 36
Tl	Pb	Bi	Po ★	At ★	Xe 54
					Rn 86

f-block

Lanthanide :- Ce 58

Ce	Pr	Nd	Pm ★	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu 71

Actinide :- Th 90

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr 103

Radioactive Elements

(i)   s-block — Fr, Ra
(ii) p-block — Po, At
(iii) d-block — Tc, La, Ac
(iv) f-block — $\underset{90}{Th} \rightarrow \underset{103}{Lr}$ and Pm

Drawbacks of Dobereiner Triad.

This rule is not followed by the examples :-

(a) H   Li   Na $\frac{23+1}{2} = 12$
     1   7   23

(b) O   S   Se $\frac{79+16}{2} = 47.5$
     16   32   79

(c) N   P   As $\frac{75+14}{2} = 44.5$
     14   31   75

Other Examples of Dobereiner Triad

1. Cl, Br, I   6. Li, Na, K   **11. H,F,Cl
2. S, Se, Te   7. Na, K, Rb, Cs
3. P, As, Sb   8. Be, Mg, Ca
4. Si, Ge, Sn   9. Ca, Sr, Ba
5. Al, Ga, In   **10. Sc, Y, La

Imp. observation
→ Elements of triad should be in same group for same chemical properties
→ There should difference of 8 or 18 in atomic no:- for following weight Rule.

Mendeleev's Periodic Table

Periodic Law :- The physical and chemical properties of elements are the periodic function of their atomic weight

It is based on atomic wt.

63 elements were known, noble gases were not discovered.

He was the first scientist to classify elements in a systematic manner i.e. in horizontal rows (series) and vertical columns (groups)

Horizontal rows called series were later called periods. There were 12 series (7 period) in Mendeleev's Periodic Table.

Vertical columns are called groups and there were 8 groups in Mendeleev's Periodic Table.

Each group upto VII is divided into subgroup A and B subgroups. 'A' subgroups elements are called normal elements or 'B' subgroups elements are called transition elements.

The VIII group was consists of 9 elements in 3 rows.

Fe   Co   Ni
Ru   Rh   Pd
Os   Ir   Pt

Elements belonging to same group exhibit similar properties.

Advantages of Mendeleev's Periodic Table

(a) Study of elements - first time all known elements were classified in groups according to their similar properties. So, study of the properties of elements become easier.

(b) Prediction of new elements - He encouraged discovery of new elements as left some gaps for unknown elements.

Sc - Eka Boron
Ga - Eka Aluminium
Ge - Eka silicon
Tc - Eka Manganese

Sc, Ga, Ge, Tc were the elements for which position were left unoccupied and properties were predicted by Mendeleev before their discovery

(c) Correction of atomic weight - Correction were made in at. weight of some elements.

Initially, it was found eq. wt of Be was 4.5 and it was trivalent, so its at. weight was 13.5 but there was no space for this element in mendleev table so after correction, it was found that Be is divalent.

There was space b/w Li and B., Be was placed

Correction in At. wt. $\rightarrow$ U, Be, In, Au, Pt

(d) Noble gases when discovered could be placed without disturbing.

Demerits

(i) Position of hydrogen is not certain in periodic table bcz it resemble both alkali metal and halogens. Thus, its position remains undecided

(ii) Position of isotopes - at. weight of isotopes differ, so they should be placed at different position in mendeleev periodic table but no such place were given in his table

(iii) Analogous pair of elements - There were some pairs of elements which do not follow order of atomic weight

** (Ar, K) ; (Co, Ni) (Te, I) (Te, Ra)
39.9 39.1   58.9 58.6   127.5 127   232 23

like elements were placed in different group
ex - Pt & Au

More reactive metals were placed with coinage metals.

$$I$$

$$IA \longleftarrow \qquad \longrightarrow IB$$

alkali Metal $\begin{cases} Na \\ K \\ Rb \\ Cs \end{cases}$ $\left.\begin{matrix} \\ Cu \\ Ag \\ Cu \end{matrix}\right\}$ Coinage Metal
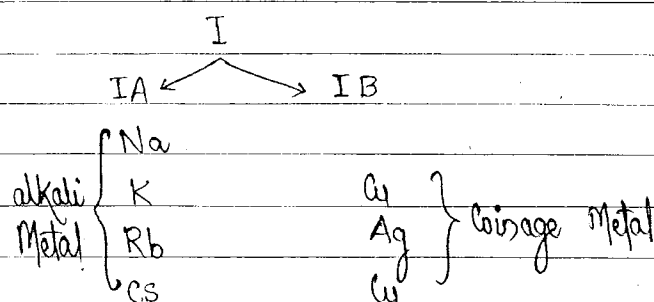
Modern Periodic Table

Modern Periodic Law - Physical and Chemical properties of elements are periodic function of their atomic No:-

It is based on Moseley's experiment.

Modern periodic -table is based on atomic no:-

He bombarded high speed electron on different metal surface and obtained X rays

$\sqrt{\nu} \times 10^{-8}$
H_z

Atomic No:-

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The graph has vertical axis labelled $\sqrt{\nu}$ and horizontal axis labelled "Atomic wt."
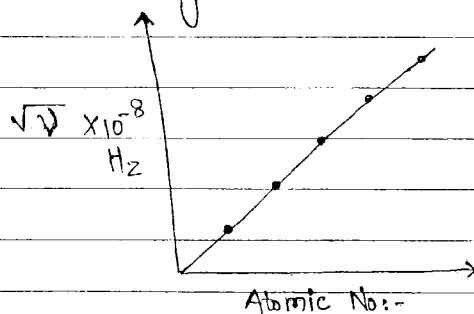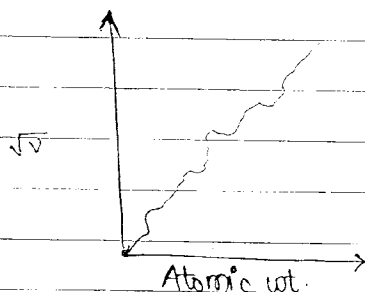
He found that $\sqrt{\nu} \propto Z$ where, ν is the frequency of X-rays

From this experiment, he concluded that physical and chemical properties of elements are periodic function of their atomic no:-

It means that when elements are arranged in order of their increasing atomic no:- element having similar properties get repeated after a certain regular interval. This is also known as modern periodic law.

Modern / Long -form of periodic Table.

It is bohr- bury electronic configuration concept and atomic no:-

It was proposed by Rang and Werner

It consists seven horizontal periods and 18 vertical columns (groups.

Correlation b/w group is long form of periodic table are given below.

I A	-1	I B	-11
II A	-2	II B	-12
III B	-3	III A	-13
IV B	-4	IV A	-14
V B	-5	V A	-15
VI B	-6	VI A	-16
VII B	-7	VII A	-17
VIII	-8, 9, 10	Zero	-18

Elements belonging to same group have same no. of valence electrons. So, their properties are similar

Period

			no. of elements	
1	Shortest period	S	2	H - He
2	short	sp	8	Li - Ne
3	short	sp	8	Na - Ar
4	long	sdp	18	K - Kr
5	long	sd p	18	Rb - Xe
6	longest	sf dp	32	Cs - Rn
7	incomp.	sfd	incomp.	fr -

s	2
sp	8
sp	8
sdp	18
sdp	18
sfdp	32
sfdp	32
sgfdp	50
sgfdp	50
shgfdp	72
shgfdp	72

We have only 2 group in s-block bcz s
orbital can accomodate only 2 $e^\ominus$

✱✱ s-block → ns^{1-2}

$$IA - ns^1 \quad \text{alkali metals}$$
$$IIA - ns^2 \quad \text{alkaline earth metals}$$

★★Note :- Be - not alkaline
earth metal.

→ NCERT
Group 1 is called alkali metal bcz they form hydroxides
on reax^n with water which are strongly
alkaline in nature.

→ NCERT
Group 2 elements are called alkaline earth metal bcz
their oxide and hydroxide are alkaline in nature and
these metal oxides are found in the earth's crust

✱✱ p-block $ns^2 np^{1-6}$

$ns^2 np^1$ = 13	Boron family	★★ Note :- He = $1s^2$	
$ns^2 np^2$ = 14	Carbon family		
$ns^2 np^3$ = 15	Picogens	He group = 18	
$ns^2 np^4$ = 16	Chalogens	decided by properties	
$ns^2 np^5$ = 17	halogens		
$ns^2 np^6$ = 18	Noble gases.	He = s-block	
		decided by configuration	

✱✱ d-block $(n-1) d^{1-10} ns^{0-2}$ → zero only in case of palladium

d-block elements are transition elements except
zinc, cadmium, mercury

All d block elements are transition elements false
All transition elements are d-block elements True

$$_{11}Na = 1s^2 2s^2 2p^6 \underline{3s^1}$$
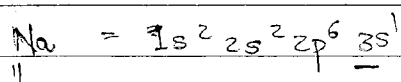
s - block

period = 3

group = 1 or IA
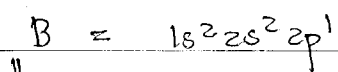
$$_{11}B = 1s^2 2s^2 2p^1 \qquad\qquad group = ns^2 np^{1-6} + 10$$

Block = p

period = 2

group = 10 + 3 = 13
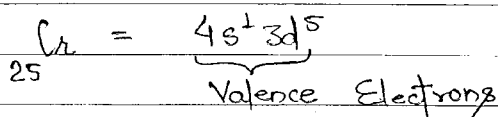
$$_{25}Cr = \underline{4s^1 3d^5} \qquad\qquad group = no:- of (n-1) de^{\ominus} +$$
$$\underbrace{}_{Valence\ Electrons} \qquad\qquad\qquad\qquad\qquad no:- of\ nse^{\ominus}$$

Block = d - block

period = 4

group = 6 or VI B

Transition Elements

d- block elements in which d-orbitals is partially filled in ground state or stable oxidation state

Note:- $Zn = 3d^{10} 4s^2 \qquad Zn^{2+} = 3d^{10} 4s^0$ not transition elements
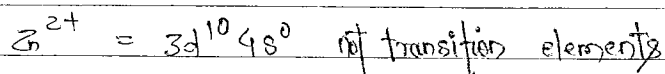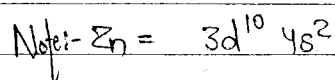
4 period / 3d series Sc — — — — — Zn	$3d^{10} 4s^2$	- 1st Transition Series
5 period / 4d series Y — — — — — Cd	$4d^{10} 5s^2$	- 2nd ,, ,,
6 period / 5d series La — — — — — Hg	$5d^{10} 6s^2$	- 3rd ,, ,,
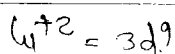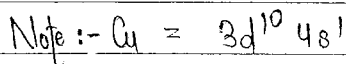
Note :- $Cu = 3d^{10} 4s^1 \qquad Cu^{+2} = 3d^9 \qquad$ yes transition elements
$Cu^+ = 3d^{10}$
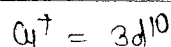
f - block $\qquad$ $(n-2) f^{0-14}$ $(n-1) d^{0-2}$ ns^2

(i) last electron entered in f subshell

$\underset{58 \quad 71}{Ce - Lu}$ 4f series - Lanthanide Series - 6th period
$\underset{90 \quad 103}{Th - Lr}$ 5f series - Actinide Series - 7th period

(ii) All f-block element have same group III B.

(iii) They are also called inner Transition elements.

IUPAC Nomenclature

0	= nil			
1	= un	101	Unnilunium	= Unu
2	= bi	102	Unnilbium	= Unb
3	= tri	103	Unniltrium	= Unt
4	= quad	104	Unnilquadium	= Unq
5	= pent	105	Unnilpentium	= Unp
6	= hex	106	Unnilhexium	= Unh
7	= ~~oct~~ sept	107	Unnilseptium	= Uns
8	= oct	108	Unniloctium	= Uno
9	= enn	109	Unnilennium	= Une
		110	Ununnilium	= Uun

Diagonal Relationship
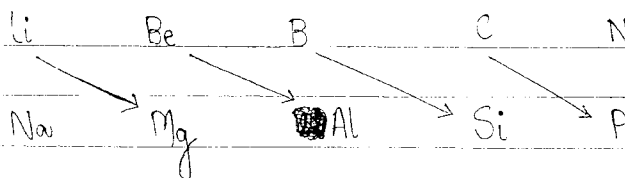
Cause:- It is due to similarity in ionic sizes or charge/radius ratio of elements.

Li   Be   B   C   N
Na   Mg   Al   Si   P

$$\phi = \text{charge density} = \frac{\text{charge}}{\text{size}}$$

H.W. Representative, Bridged, typical, why? s, p, d, f properties. Race #5, 112 nomenclature

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Typical elements

Second and third period elements are called typical elements

* Properties of s-block elements

Properties of p-block Elements

Electronic Configuration :- They ns^2np^{1-6} configuration. The s-orbital is completely filled and if p orbital is half-filled (group 15), they show extra stability and if p-orbital is fully filled, they show very low or no reactivity, are called noble gases.

Atomic Radii - It increases down the group. Consider increase from 2nd to 3rd period.

Electron gain enthalpy

- The two groups of halogen and chalcogens have very high electron gain enthalpy and readily add one or more electrons to attain the stable noble gas configuration

Metallic and Non-metallic Character.

The non-metallic character increases as we move from left to right across a period and -metallic character increases as we go down the group.

Properties of d-block Elements

They are all metals.

They mostly form coloured ions, exhibit variable valence (oxidation states), paramagnetism and oftenly used as catalysts.

Zn, Cd, Hg

Periodic Properties

Atomic Radii

1. It is the distance between the electron in the outermost shell and the nucleus of an atom

2. Atomic size of an isolated atom can't be determined experimentally because atom does not have well defined boundary.

3. It is bcz position of an electron can only be expressed as a probability. So, boundary can't be defined even at large distance. So, for estimating its size, internuclear distance of associated species is used to calculate the radius

Q. x has higher covalent radius than y, then atomic radius of x and y

(i) x > y   (iii) x = y
(ii) y > x   (iv) can't be predicted

Note :-

(a) Covalent Radii

1. It is defined for atoms which forms covalent bond with themseles (non-metals)

(a) Homodiatomic species :- molecules formed by atoms of the same element.

$$d_{A-A} = \text{internuclear distance / Bond length}$$

· Internuclear distance is the distance between nuclei of two atoms.

**Note :- Atomic Radii > Covalent Radii

Q. If bond length of Cl_2 molecule is 198 pm. find radius of Cl.

Ans . Radius of $Cl = \dfrac{198}{2} = 99$ pm.

2. Covalent radii is always less than atomic radii However, difference is negligible. So, covalent radii is used to compare the atomic size

3. Experimentally bond length can be found by following methods :-

(i) NMR (Nuclear Magnetic Resonance)
(ii) Electron diffraction
(iii) X - Ray.

b) Heteronuclear diatomic molecule :-

$$\overset{\text{\Large $\star\star\star$}}{\overset{\delta^+}{H} - \overset{\delta^-}{F}}$$

attraction
reduces the bond length
from $r_A + r_B$.
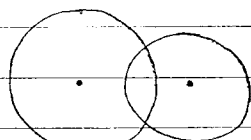
Shomaker and Stevensen

$$d_{A-B} = r_A + r_B - 0.09 (\Delta x) \quad , \text{ in } A°$$

$$r_A + r_B - 9 (\Delta x) \quad , \text{ in pm}$$

$$\Delta x = \text{E.N. difference}$$

$$r_A = \text{covalent radius of A in } A° \text{ or pm}$$
$$r_B = \text{covalent radius of B in } A° \text{ or pm}$$

Q. If $r_H = 0.74 A°$ $\qquad d_{Cl-Cl} = 198 \, pm$

then $d_{H-Cl} = ?$

$$d_{H-Cl} = 0.74 + 0.99 - 0.09 \times 0.9$$
$$= 1.649$$

$$\begin{array}{r} 171 \\ \end{array} \quad \begin{array}{r} 1.730 \\ \cdot 081 \\ \hline 1.649 \end{array}$$

Note :- (i) $d_{A-B} < r_A + r_B$
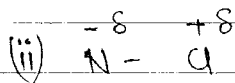
(ii) $\overset{-\delta}{N} - \overset{+\delta}{Cl}$ Due to small size, N
has higher Z_{eff}

(iii) B.O = no of bonds b/w two atoms in a molecule.

B.O ↑   B.L ↓   B.S ↑

Covalent radii :-

ex - (a) $\rangle C - C \langle$ > $\rangle C = C \langle$ > $- C \equiv C -$

S.B.C.R   D.B.C.R   T.B.C.R

(b) N - N > N = N > N ≡ N

(c) O - O > O = O

(d) H - H   O = O
     $\underbrace{\qquad\qquad}_{\text{can't be compared}}$
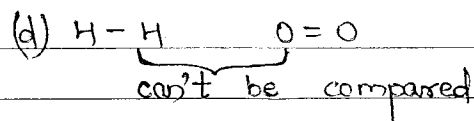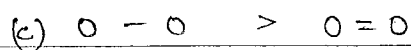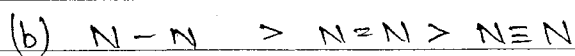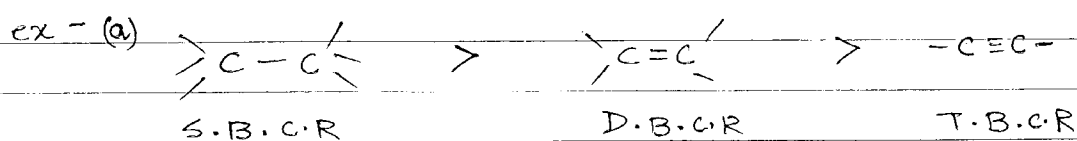
Metallic Radii
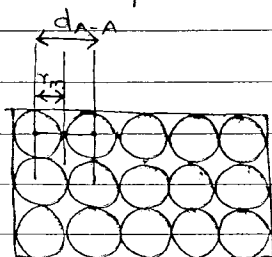
$$d_{A-A} = r_m + r_m \Rightarrow 2r_m = d_{A-A}$$
$$\Rightarrow r_m = \frac{d_{A-A}}{2}$$

Note   M.R > C.R

M.R ≈ A.R

Vander waal's   Radii :- It is defined   for noble gases
                                  and   gaseous   molecules.
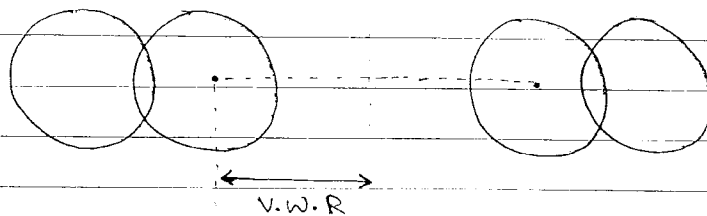
Note. $V.W.R > A.R \approx M.R > C.R$

$N_2 \cdots N_2$ Vanderwaal   radii
$N \cdots N$ covalent   radii
$He \cdots He$ vanderwaal   radii

Ionic   Radii

ions $\searrow$ cation - cationic radii
              anion - anionic   radii

Cationic   Radii $A > A^+ > A^{+2} > A^{+3}$

$$\frac{e}{p} = \frac{10}{10} \quad \frac{9}{10} \quad \frac{8}{10} \quad \frac{7}{10}$$

+ive   charge $\uparrow$, then   size $\downarrow$

fewer $e^{\ominus}$ and
same $p^{\oplus}$ results
in $Z_{eff} \uparrow$

$Na >>> Na^+ > Na^{+2}$
$2s^2 2p^6 3s^1$ $2s^2 2p^6$ $2s^2 2p^5$

due to change in shell no:-

$Mg > Mg^+ >>> Mg^{+2}$
$2s^2 2p^6 3s^2$ $2s^2 2p^6 3s^1$ $2s^2 2p^6$

Due to change in shell no:-

Anionic Radii

$$X < X^- < X^{-2}$$

$$\frac{e}{P} = \frac{10}{10} \qquad \frac{11}{10} \qquad \frac{12}{10}$$
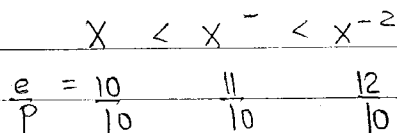
Repulsion b/w $e^\ominus$ results in decrease in Z_{eff}.

−ive charge ↑ size ↑

ex − (a) $O < O^- < O^{-2}$

− (b) $N < N^- < N^{-2} < N^{-3}$

Isoelectronic Series

(i) $N^{-3} > O^{-2} > F^- > Na^+ > Mg^{+2} > Al^{+3}$

$$\frac{e}{P} = \frac{10}{7} \qquad \frac{10}{8} \qquad \frac{10}{9} \qquad \frac{10}{11} \qquad \frac{10}{12} \qquad \frac{10}{13}$$

(ii) $N^{-3} \quad O^{-2} \quad F^- \quad Ne \quad Na^+ \quad Mg^{+2} \quad Al^{+3}$

(Ne) $> N^{-3} > O^{-2} > F^- > Na^+ > Mg^{+2} > Al^{+3}$

→ due to vanderwaal radii
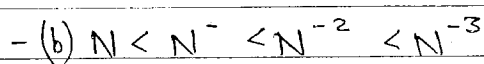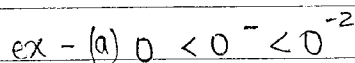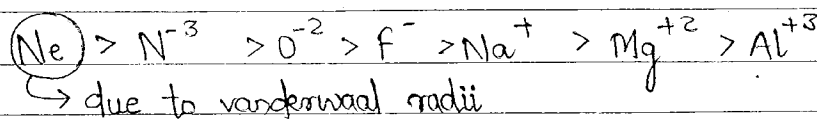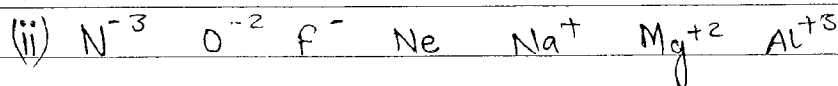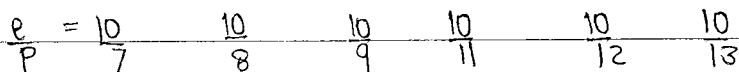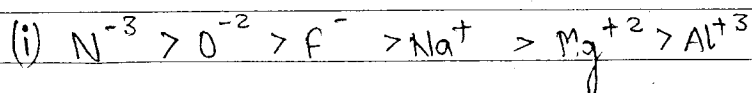
★★
✓ Q. find order of radii

$$Li^+ \quad Mg^{+2} \quad K^+ \quad Al^{+3}$$
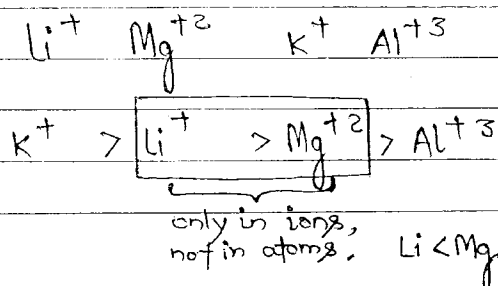
Use
(i) charge ↑ size ↓
(ii) shell comparison
when same charge

$$K^+ > \boxed{Li^+ > Mg^{+2}} > Al^{+3}$$

only in ions, not in atoms. $Li < Mg$

Atomic Radii   B=88
                Al=143
                Ga=135
                In=167
                Tl=170

Q. K^+ Li^+ Mg^{+2} Be^{+2}

$K^+ > Li^+ > Mg^{+2} > Be^{+2}$

** Q. $Be^{+2} < Al^{+3}$ (violates our statement)
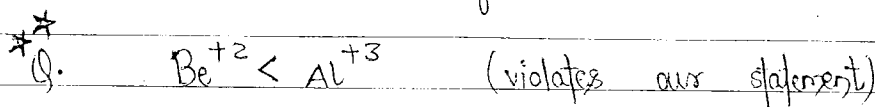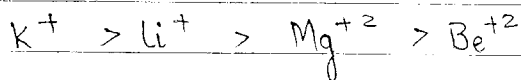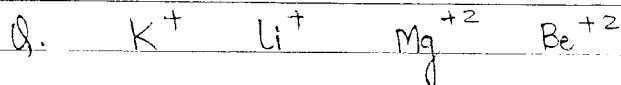
$\phi = 6.4$ 6

$$\phi = \frac{charge}{size}$$

$6.4 = \dfrac{+2}{size}$ $6 = 3/size$

$size = 0.4$ $size = 0.5$

Q. K^+, S^{2-}, Ca^{+2} Cl^-

$S^{2-} > Cl^- > K^+ > Ca^{+2}$
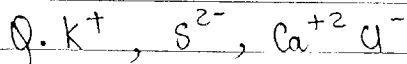
factor affecting size

1. $Z_{eff} \uparrow$,   radius $\downarrow$

2. $n \uparrow$,   radius $\uparrow$

3. Bond order $\uparrow$,   radius $\downarrow$

4. $S \uparrow$,   radius $\uparrow$

★★☆ Imp

Note:-   1. Smallest   cation = H^+
         2. Smallest   anion = F^- $H^- \approx Br$
         3. Largest   Cation = Cs^+
         4. Largest   anion = I^-
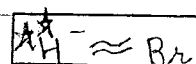
Li^+	Na^+	K^+	NH_4^+	Cs^+	$[N(CH_3)_4]^+$
0.068	0.095	0.133	0.148	0.169	0.347

Be^{+2}	Mg^{+2}	Fe^{+2}	Ca^{+2}	Ba^{+2}
0.07	0.065	0.076	0.099	0.135

Al^{+3}	Fe^{+3}	La^{+3}
0.05	0.064	0.104

F^-	OH^-	Cl^-	Br^-	I^-	NO_3^-
0.136	0.176	0.181	0.195	0.216	0.264

radii   along   the   period

Li   Be   B   C   N   O   F
———————→ $Z_{eff} \uparrow$ $r \downarrow$

vanderwaal radii
Ne >>>   Li > Be > B > C > N > O > F

Noble gases have highest sizes is their
respective periods.

निकल	पैलेडियम	प्लैटिनम
Ni	Pd	Pt

कोबाल्ट	रोडियम	इरीडियम
Co	Rh	Ir

लोहा	रुथेनियम	ओसमियम
Fe	Ru	Os

क्रोमियम	मोलिब्डेनम	...
Cr	Mo	W

वैनेडियम	नायोबियम	टैंटलम	...	तांबा	चांदी	सोना
V	Nb	Ta	Ha	Cu	Ag	Au

टाइटेनियम	जिरकोनियम	हैफ्नियम	...
Ti	Zr	Hf	Ku/Rf

स्कैंडियम	इट्रियम	लैंथेनम	ऐक्टिनियम
Sc	Y	La	Ac

radii down the group $n \uparrow$ size $\uparrow$

exception - in III A group $B < Al \approx Ga < In < Tl$

Penetration effect $s > p > d > f$
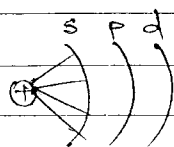
Cause :- Due to lower shielding effect of 3d subshell, increase in shell is compensated and size remains almost same. This is called scandide contraction / d-block contraction

D - block

along the period

$3d^1 4s^2 \quad 3d^2 4s^2 \quad 3d^3 4s^2 \quad 3d^5 4s^2 \quad 3d^5 4s^2 \quad 3d^6 4s^2 \quad 3d^7 4s^2 \quad 3d^8 4s^2 \quad 3d^{10} 4s^1 \quad 3d^{10} 4s^2$

$Sc > Ti > V > Cr > Mn \qquad Fe \approx Co \approx Ni \qquad Cu < Zn$

$Z_{eff} \uparrow \qquad$ size $\downarrow$

→ In d- block, along the period size decreases till middle of the block, remains almost constant till Ni, then size increases

→ At the beginning, size decreases because $Z_{eff} \uparrow$,

then size remains same as nuclear charges gets cancelled by increased screening effect.

→ In the middle, Z_{eff} and σ balance each other because of $e^- - e^-$ repulsion due to pairing of be electron.

→ At the end of the period, $e^- - e^-$ increases very significantly and increasement in σ is more than Z_{eff}, so size ↑.

along the group

$$\underset{21}{Sc} \quad \underset{22}{Ti} \quad V \quad \text{------------------} \quad Zn$$
$$\quad \wedge \quad\quad \wedge \quad\quad \wedge$$
$$\underset{39}{Y} \quad \underset{40}{Zr} \quad Nb \quad \text{------------------} \quad Cd$$
$$\quad \wedge \quad\quad \approx \quad\quad \approx$$
$$\underset{57}{La} \quad \underset{72}{Hf} \quad Ta \quad \text{------------------} \quad Hg$$
$$\quad \wedge$$
$$\underset{89}{Ac} \quad \underset{104}{Ku/Rf}$$

(i) $S < Y < La < Ac$

(ii) $Ti < Zr \approx Hf$

(iii) $V < Nb \approx Ta$

In case of d-block on moving down from 3d to 4d, size increases but from 4d to 5f size remains almost same due

to lanthanide contraction / 4f contraction.

On moving from 4d to 5d series after lanthanum along lanthanide series nuclear charge increases by 1 unit at each successive element but a new electron is added to f subshell. Due to poor shielding effect of f-subshell, increasement in σ is very less, so it is unable to counterbalance increased nuclear charge, so Zeff increase significantly. This nullifies the effect of increament of atomic no:- due to increase in shell no:-. This results in contraction of atomic size. This is known as lanthanide contraction.

Contraction due to 5f subshell in actinoids is called actinide contraction. It is stronger than lanthanide and scandide contraction because 5f is large /more - diffused as compared to 4f.

Note:-   Actinide > Lanthanide > Scandide.

Ionisation Energy ①

→ Amount of required energy to remove one electron from isolated gaseous atom.

$$Na_{(s)} \xrightarrow{-e} Na^{+}_{(s)} \longrightarrow not \ I.e$$

$$Na_{(g)} \xrightarrow{-e} Na^{+}_{(g)} \quad I.E/I.P$$

Unit :- $1ev/atom = 96.4 \ KJ/mole$

$1ev/atom = 23.1 \ Kcal/mole.$

$$A \xrightarrow[I.E_1]{-e} A^{+} \xrightarrow[I.E_2]{-e} A^{+2} \xrightarrow[I.E_3]{-e} A^{+3}$$

$$\frac{e}{p} \quad \frac{10}{10} \qquad\qquad \frac{9}{10} \qquad\qquad \frac{8}{10}$$

Note:- $I.E_3 > I.E_2 > I.E_1$ always

$$Na \xrightarrow[I.E_1]{-e} Na^{+} \xrightarrow[I.E_2]{-e} Na^{+2} \xrightarrow[I.E_3]{-e} Na^{+3}$$
$$2s^2 2p^6 3s^1 \qquad 2s^2 2p^6 \qquad 2s^2 2p^5$$
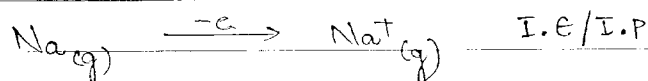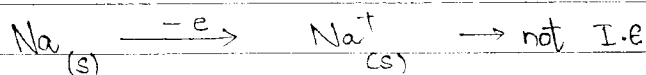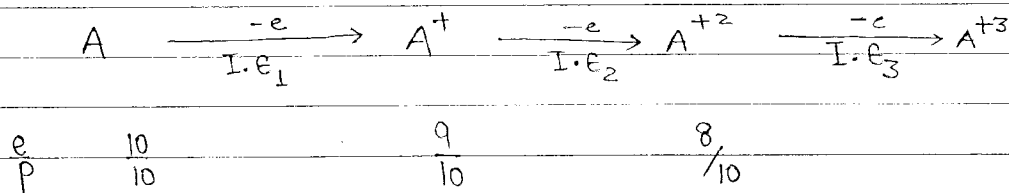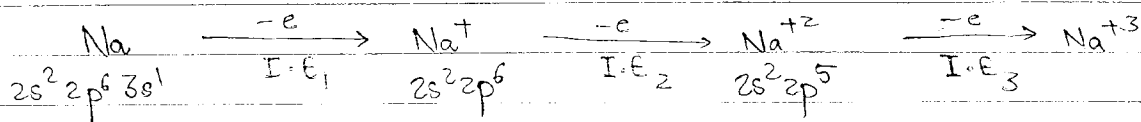
$$I.E_3 > I.E_2 > I.E_1$$

factors affecting I.E

1. $Z \uparrow \ I.E \uparrow$
2. $Z_{eff} \uparrow \ I.E \uparrow$
3. $\sigma \uparrow \ I.E \downarrow$
4. $n \uparrow \ I.E \downarrow$

5. half-filled / fully-filled - extra stable configuration

$$N > O$$
$$2s^2 2p^3 \quad 2s^2 2p^4$$

$$P > S$$

$$3p^3 \quad 3p^4$$

$$As > Se$$
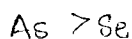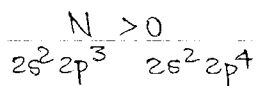
6. Penetration effect $\quad s > p > d > f \longrightarrow$ closeness towards nucleus

$$Be > B$$
$$1s^2 2s^2 \quad 1s^2 2s^2 2p^1$$

$$Mg > Al$$

$$Ca > Ga$$
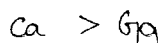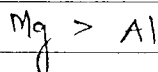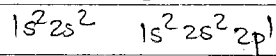
Trends along the period

$\underbrace{\text{penetration effect}}$ $\quad \underbrace{\text{half-filled config.}}$

Li $< B <$ Be $< C < O < N < F <$ Ne

Na $< Al < Mg < Si < S < P < Cl < Ar$

K $< Ga < Ca < Ge < Se < As < Br < Kr$
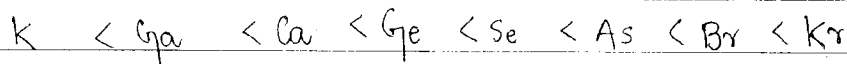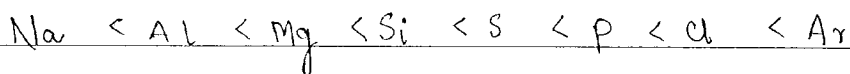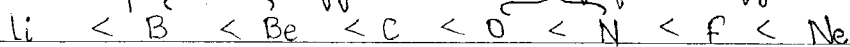
After this, trend is regular,

Rb $< Sr < In < Sn < Sb < Te < I < Xe$

Cs $< Ba < Tl < Pb < Bi < Po < At < Rn$
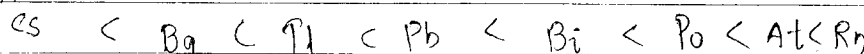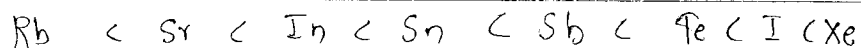
Noble gases have highest ionization energy along the periods

Trends along the group

Ⓘ A

B   ** Al < Ga
Al   (due to poor shielding effect of 3d-orbital)
Ga
In   ** In < Tl
Tl   (due to poor shielding effect of 4f subshell)
113

Experimental value
:- B > Tl > Ga > Al > In

Ⓥ A

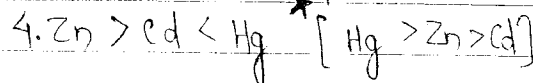C   → due to poor s.E of
Si   4f subshell
Ge   C > Si > Ge > ┌──────────┐
Sn   │ Pb > Sn │
Pb   └──────────┘ → no such effect in
114   size

Ⓥ A

N
P
As   N > P > As > Sb > Bi
Sb
Bi
115

(VI)

O

S $\qquad$ O > S > Se > Te

Se

Te

Po

116

(VII)

F

Cl

Br $\qquad$ F > Cl > Br > I

I

At

117

O or 18

He

Ne

Ar $\qquad$ He > Ne > Ar > Kr > Xe

Kr

Xe

Rn

★★★
Note :- (i) He has highest ionization energy in the periodic table.

(ii) Cs has lowest ionization energy in the periodic table

Trends in s-block

Li	Be
Na	Mg
K	Ca
Rb	Sr
Cs	Ba
Fr	Ra

$Li > Na > K > Rb > \boxed{Cs < Fr^{*}}$

$Li > Na > K > Rb > Fr > Cs$

} due to poor SE of 4f subshell

$Be > Mg > Ca > Sr > \boxed{Ba < Ra}$

$Be > Mg > Ca > Sr > Ra > Ba$
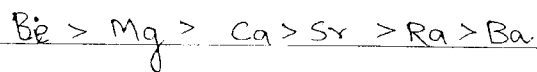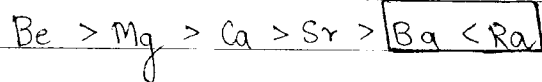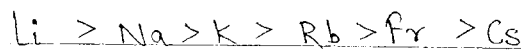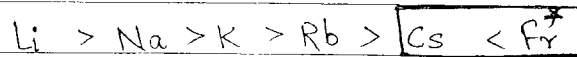
Trends in d-block

3d series	Sc	Ti	V	. . . . .	Zn
4d series	Y	Zr	Nb	. . . .	Cd
5d series	La	Hf	Ta	. . . .	Hg
	Ac	Ku/Rf	Ha	. . . .	

$3d$ series $> 4d$ series $< 5d$ series

↓
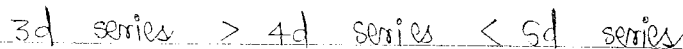
due to poor S.E. of 4f subshell (Lanthanide Contraction)

1. $Sc > Y > La > Ac$ 3. $Cu > Ag < Au$ $[Au > Cu > Ag]$

2. $Ti > Zr < Hf$ 4. $Zn > Cd < Hg$ $[Hg > Zn > Cd]$
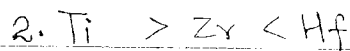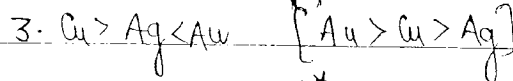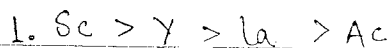
Q. Compare I.E of N and O^+

$$1s^2 2s^2 2p^3$$

$N < O^+ \rightarrow$ same no of $e^\ominus$ but o has larger no of $p^\oplus$

Q. I.E of C N O F

$$\underbrace{C < O < N < F}_{e^\ominus \text{ config.}}$$

$\xrightarrow{\hspace{4cm}}$

$Z_{eff} \uparrow$, $I.E \uparrow$

Imp
Q. find order of $I.E_1$ and $I.E_2$ for above elements.

	P^1	P^3	P^2	P^4
	C^+	O^+	N^+ F^+	

order of $I.E_2$ $C^{\bullet+} < \ominus N^+ < \underbrace{F^+ < O^+}_{\text{half filled config.}}$

	P^0	P^2	P^1	P^3

order of $I.E_3$ $\underbrace{N^{2+} < C^{2+}}_{\text{penetration effect}} < O^{2+} < F^{2+}$ ✕

Imp
Q. find order of $I.E_1$ of Li Be B

Order of $I.E_1$ $\underset{1s^2 2s^1}{Li} < \underset{1s^2 2s^2 2p^1}{B} < \underset{1s^2 2s^2}{Be}$

order of $I.E_2$ $Be^+ < B^+ < Li^+$

Q. $(I.E_1) A$ $= 10$

$(I.E_2) A$ $= 20$ $A^{3+} \rightarrow$ stable ion

$(I.E_3) A$ $= 30$ Belongs to 13th group

$(I.E_4) A$ $= 160$ valence $e^{\ominus} - 3$, stable oxidation state
$= +3$

Q. Which of the following configuration large.
I.E jump b/w I.E$_1$ and I.E$_2$

Q.   (1) $1s^2 \, 2s^2 \, 2p^2$ (3) $1s^2 \, 2s^2 \, 2p^4$

(2) $1s^2 \, 2s^2 \, 2p^3$ (4) $1s^2 \, 2s^2 \, 2p^6 \, 3s^1$

Q. $Na \xrightarrow{a} Na^+ \xrightarrow{b} Na^{+2} \xrightarrow{e} Na^{+3}$

$Mg \xrightarrow{c} Mg^+ \xrightarrow{d} Mg^{+2} \xrightarrow{f} Mg^{+3}$

$c > a$ $b > a$ $d > c > a$

$f > e > b > d > c > a$ $\overset{**}{e > b}$

$\hookrightarrow Z_{eff} \uparrow$ dominates over

$a < b$ $e^{\ominus}$ configuration

$a < c$

$b > d$ $\overset{**}{f > e}$

$c < d$ due to stable $e^{\ominus}$ config.

Q. find order of $I.E_2$ of Cr Mn Fe Co

Cr	Mn	Fe	Co
$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$

$Mn^+ < Fe^+ < Co^+ < Cr^+ < Co^+$

Imp$\overset{**}{}$ $Mn^+ < Fe^+ < Cr^+ < Co^+$

Properties affected by ionisation energy

1. I.E ↓   Ionic bond formation tendency ↑

{alkali

2. I.E ↓   electropositive character ↑

down the group, I.E ↓ electropositive character ↑

3. Reducing power

* I.E ↓ , reducing power ↑ ✭✭✭ (but other factor also decides it. e.g. H.E., I.E., ΔH_{ab})

$$M \longrightarrow M^{\oplus} + e^{\ominus}$$
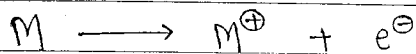
Reducing agent

4. (i) If difference b/w two successive I.E is 16 ev or greater, then lower O.S. is more stable but element does not variable. O.S.

ex - Iron Fe^{+2}, Fe^{+3} → not applicable for it.

(ii) If difference b/w two successive I.E is 11ev or less than 11ev, then higher O.S. is more stable

(iii) If difference b/w two succesive I.E is b/w 11ev and 16 ev, then both O.S will exist.

5. Metallic character

~~Generally~~
I.E ↓ , Metallic character ↑

~~Always~~
along the period , I.E ↑ , so metallic character ↓
down the group, I.E ↓ , so metallic character ↑

Electron Affinity

H = heat content

ΔH = change in enthalpy

$$\Delta H = P - R$$

A + B ⟶ C + D   ΔH = -ive Exothermic (energy released

A + B ⟶ C + D   ΔH = +ive Endothermic (energy absorbed
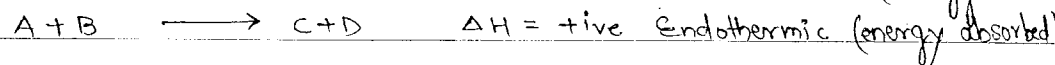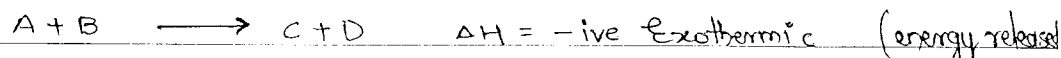
Defn:- Amount of released energy when one electron is added in an isolated gaseous atom is called electron affinity.

$$X_{(g)} + e^{\ominus} \longrightarrow X^{-}_{(g)} \qquad \Delta H = -ive$$
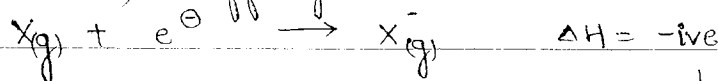
Note:(i) Ionisation energy is always endothermic → true for elements only
(generally)

(ii) first electron gain enthalpy is -ive, but second electron gain enthalpy is +ive ~~but~~ bcz energy is required for addition of another electron against $e^{\ominus}$ and $e^{\ominus}$ repulsion.

$$\star^{\star\star} \boxed{E \cdot A = -\Delta H_{eg}}$$

Explanation :—
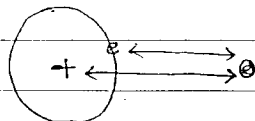
→ Coming electron experiences two forces:-

(i) Attraction from nucleus
(ii) Repulsion from electron

→ But, in most of cases, attraction is dominant ; so energy is released. Hence, first electron gain enthalpy is generally -ive.

→ Second electron gain enthalpy bcz coming electron faces more repulsion from already present electron.

Note :—   (i) $|\Delta H_{eg_2}| > |\Delta H_{eg_1}|$ (always)

(ii) $\Delta H_{eg_1} + \Delta H_{eg_2} > 0$

factors affecting electron affinity

1. $Z\uparrow$,   neg. $\Delta H_{eg} \uparrow$

2. $Z_{eff}\uparrow$,   neg. $\Delta H_{eg} \uparrow$

3. $n\uparrow$,   neg $\Delta H_{eg} \downarrow$

4. $6\uparrow$,   neg $\Delta H_{eg} \downarrow$

Note:- (i) N   for these,
       (ii) II A $\Delta H_{eg} = $ +ive
       (iii) Noble gas - extra stable config. $E.A \leq 0$

★★★ N > II A > Noble gas.

Q.   B , C , N, O

       N < B < C < O

Q.   Al , Si, P, S

       Al < P < Si < S

★★★ Note:-   N = $2s^2 2p^3$

       $\begin{matrix} N \\ P \end{matrix}$ = no vacant d orbital $\Delta H_{eg} = $ +ive.

       $\left.\begin{matrix} A s \\ Sb \\ Bi \end{matrix}\right\}$ vacant d orbital is present
                                $\Delta H_{eg} = $ -ive

Q. Which of the following ion is least stable?

       (i) B^- (ii) Li^- (iii) Be^- (iv) C^-

→ Highest electron gain enthalpy in the periodic
table is of chlorine.

       (I)   B   C   N   O :F:
              ∧   ∧   ∧   ∧ ∧   F < Cl
       (II)   Al   Si   P   S :Cl:

              2nd period < 3rd period

73

Reason~

Because of small size of 2p subshell and absence of d-subshell, electron density is significantly high and hence, coming electron feels repulsion, so amount of energy released is less than expected value due to attraction

Facts :-

→ Highest -ive electron gain enthalpy = Chlorine

→ Highest electron gain enthalpy = Chlorine

→ **Highest +ive electron gain enthalpy = Neon.
   ↳ in noble gases
   ↳ Due to extra stable config (octet completion)

Data :-

H = -73	Be≤0 (+18)	4 B = -27	He = +48
Li = -60	Mg ≤0 (+232)	1 Al = -43	*Ne = +116
Na = -53	Ca =186	2 Ga = -29	Ar = +96
K = -48	Sr = 146	3 In = -29	Kr = +96
Rb = -47	Ba = +46	5 Pl = -19	Xe = +77
Cs = -46			Rn = +68
Fr			

C = -122	N = +8	5O = -141	2F = -328
Si = -134	P = -72	1S = -200	LCl = -348
Ge = -116	As = -78	2 Se = -195	3 Br = -325
Sn = -116	Sb = -103	3 Te = -190	4 I = -295
		4 Po = -174	5 At = -270

Q. In 16th group, which of the following ⊕ has highest and lowest -ive electron gain enthalpy?

highest = Sulphur
lowest = Oxygen

Q.

$$O + e^{\ominus} = O^{\ominus} \qquad -ive$$
$$O^{\ominus} + e^{\ominus} = O^{-2} \qquad +ive$$

$$O + 2e^- = O^{-2} \qquad \Delta H_{eg} = +ive$$
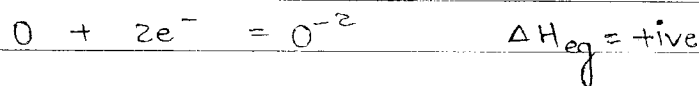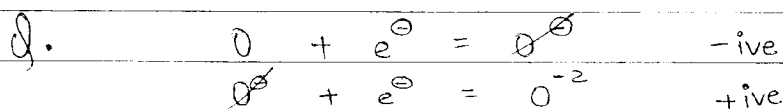
Q. Which of the following order is correct of ΔH_{eg}?

(i) $O < S > Se$ (i) $F < Cl > Br$
(ii) $S > Se > O$ (ii) $Cl > F > Br$
(iii) $Se > S > O$ (iii) $Cl > Br > F$
(iv) $S > O > Se$ (iv) $Br > F > Cl$

Data Based

Q. Which of the following involve max ΔH

1. $Li(g) + Cl(g) \longrightarrow Li^+(g) + Cl^-(g)$

2. $Na(g) + Cl(g) \longrightarrow Na^+(g) + Cl^-(g)$

3. $Li(g) + Br(g) \longrightarrow Li^+ + Br^-$

4. $Na + Br \longrightarrow Na^+ + Br^-$
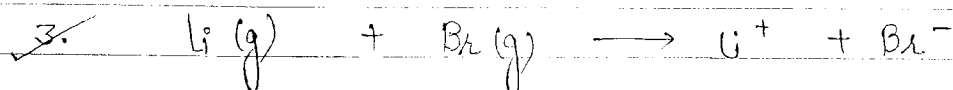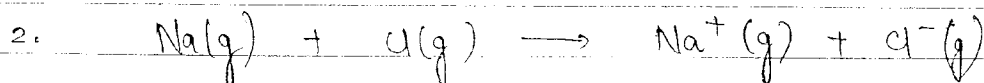
$Li = 520 \text{ KJ/mole}$
$Na = 496 \text{ KJ/mole}$

Q. Endothermic

$$N + e^{\ominus} \longrightarrow N^- \qquad \Delta H = +ive$$
$$N^{\ominus} \longrightarrow N + e^{\ominus} \qquad \Delta H = -ive$$

(1) $N \longrightarrow N^+$

(2) $N^- \longrightarrow N$

(3) $Li \longrightarrow Li^+$

(4) $O^- \longrightarrow O^{2-}$

$$A \longrightarrow A^- \qquad |\Delta H_{eg}\, A|$$
$$A^- \longrightarrow A \qquad |IE \text{ of } A^-|$$
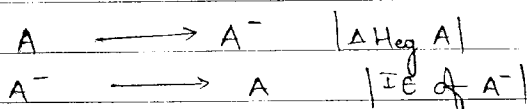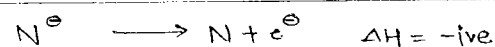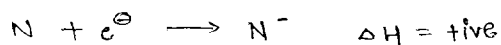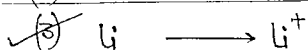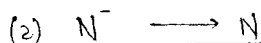
$$|\Delta H_{eg}\, A| = |I.E \text{ of } A^-|$$

Very Very Imp

Order of I.E of F^- f Cl Cl^-

$$F > Cl > Cl^- > F^-$$

$$\left.\begin{array}{l} F > F^- \\ Cl > Cl^- \\ F > Cl \end{array}\right\} \Rightarrow F > Cl > Cl^-$$
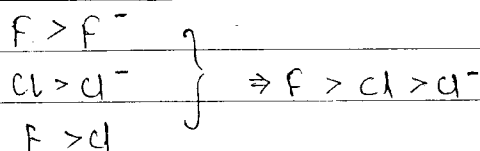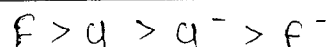
position of F^-

$$F \xrightarrow{+e} F \qquad \Delta H_{eg}\, of\, F$$
$$F^- \longrightarrow F \qquad I.E \text{ of } F^-$$
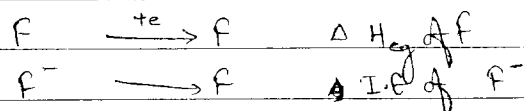
$$|\Delta H_{eg}\, of\, F| = |I.E \text{ of } F^-|$$

Similarly, $\quad |\Delta H_{eg}\, of\, Cl| = |I.E \text{ of } Cl^-|$

Properties $\times$ Affected by $\times$ Electron Affinity

1. Non - metallic character

~~Generally~~ ~~When~~ -ive electron gain enthalpy $\uparrow$, non - metallic character $\uparrow$.

~~Always~~ ~~On~~ moving left to right, non - metallic character $\uparrow$.

2. Type of Bond.

for ionic bond formation, metal should have low I.E and non - metal should have high electron gain enthalpy

3. Oxidising power

$\rightarrow$ When -ive ΔH_{eg} $\uparrow$, ~~non~~ oxidising power $\uparrow$

★★★
$\rightarrow$ However, overall oxidising power determined by 3 factors :-

(i) Dissociation Energy
(ii) ΔH_{eg}
(iii) Hydration Energy

{ In case of d - block element, on moving from left to right -ive electron gain enthalpy increases and down the group, $-\Delta H_{eg}$ increases.

Electronegativity

It is defined as the tendency of atom to attract shared pair electron in **single covalent** bond.

Different × scales for × calculation × of electronegativity

→ Pauling Scale

$$X_A \ (E.N \ of \ A) - X_B \ (E.N \ of \ B) \propto \sqrt{\Delta}$$

, where Δ = ionic resonance energy

$$\Delta = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$$

E_{A-B} is bond energy of A-B bond.

E_{A-A} is bond energy of A-A ''

E_{B-B} '' '' '' '' A-B ''

→ Ionic resonance energy is equal to difference of actual bond energy of A-B and theoretical bond energy of A-B bond.

→ Theoretical bond energy of A-B bond is equal to geometrical mean of E_{A-A} and E_{B-B} using **100 %** covalent bond.

★ Δ is measure of partial ionic character of Bond.

$$\Delta = (\text{Actual Bond Energy}) - (\text{Theoretical Bond Energy})$$

→ Pauling Scale is based on Bond energy of molecules.

→ When a bond is formed, energy is released which is called bond energy. The energy required for breaking a bond is Bond dissociation energy.

★★ → Higher the E.N difference, higher will be the value of partial ionic character and higher will be the value of Δ.

→ Bond energy is given in Kcal/mol.

$$1 ev = 23.1 \text{ Kcal/mol} = 96.4 \text{ KJ/mol}$$

$X_A - X_B = 0.208\sqrt{\Delta}$	in Kcal/mole
$X_A - X_B = 0.102\sqrt{\Delta}$	in KJ/mole

★ → Actual Bond energy is more than theoretical Bond energy bcz of Δ partial ionic character which results in more attraction, and hence more actual Bond Energy.

Mullikan Scale
Jeffe

$$E.N = \frac{I.E + E.A}{2} \quad ev \quad , \quad I.E \text{ and } E.A \text{ in ev}$$

$$E.N = \frac{I.E + E.A}{2 \times 96.4} \quad ev \quad , \quad I.E \text{ and } E.A \text{ in } kJ$$

$$E.N = \frac{I.E + E.A}{2 \times 23.1} \quad ev \quad , \quad I.E \text{ and } E.A \text{ in } Kcal$$

He considered the tendency to attract shared pair $e^{\ominus}$ should be average of following :-

1. Tendency to lose $e^{\ominus}$
2. Tendency to gain $e^{\ominus}$

$$X_P = \frac{X_m}{2.8}$$

Allred Roctow Scale

$$\rightarrow \quad F = \frac{Z_{eff} \, e^2}{r^2_{cov}} \quad , \quad r_{cov} = \text{radius (in } A^\circ)$$
$$Z_{eff} = \text{effective nuclear charge on periphery.}$$
$$e = \text{charge (in c)}$$

$$\rightarrow \quad X_{AR} = \frac{0.359 \, Z_{eff}}{r^2_{cov.}}$$

$$\rightarrow \quad X_P = X_{A-R} + 0.744$$

✱✱✱ In this scale all electron contributes towards σ

X_{A-R} $\tan\theta = 0.359$

X_p $\tan\theta = 0.359$ $\}\, 0.744$
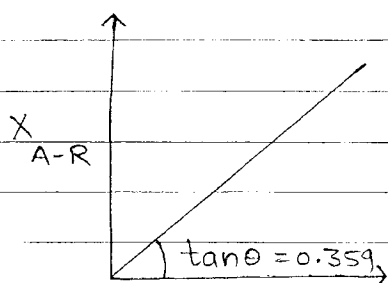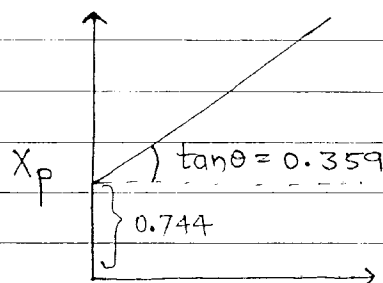
$\dfrac{Z_{eff}}{r^2_{cov}}$ $\dfrac{Z_{eff}}{r^2_{cov.}}$

factors Affecting electronegativity

1. $Z\uparrow$, $E.N\uparrow$

2. $Z_{eff}\uparrow$, $E.N\uparrow$

3. $\sigma\uparrow$, $E.N\downarrow$

4. $n\uparrow$, $E.N\downarrow$

5. E.N of hybrid orbital

$$sp > sp^2 > sp^3$$

$$\overset{\diagup}{\underset{\diagdown}{C}} - \overset{\diagup}{\underset{\diagdown}{C}} \quad < \quad \overset{\diagup}{}C = C\overset{\diagdown}{} \quad < \quad -C\equiv C-$$
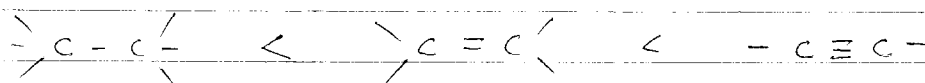
6. Oxidation state

$$A < A^+ < A^{+2} < A^{+3}$$

$$\dfrac{e}{p} = \dfrac{10}{10} \quad \dfrac{9}{10} \quad \dfrac{8}{10} \quad \dfrac{7}{10}$$

$$F < Fe^{+2} < Fe^{+3} \quad , \quad Al < Al^+ < Al^{+3}$$

7. Electronegativity also depends upon surrounding atom.

Eg.- (i)

c in CF_4 acquires more +tive charge than c in CCl_4.

(ii)
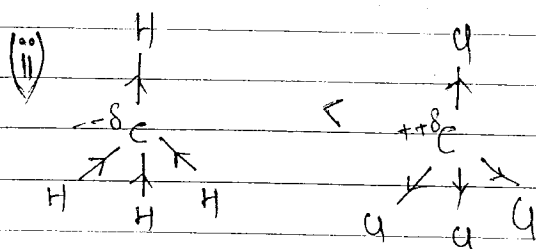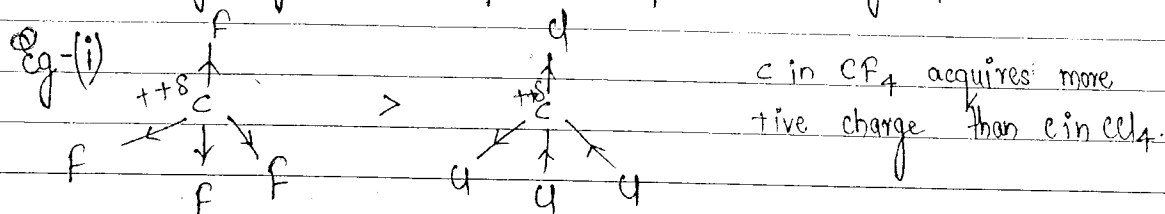
Trends along the periods and groups

→ Left to Right $Z_{eff}\uparrow$, size $\downarrow$ and E.N $\uparrow$ except Noble gases.

⚡ E.N of Noble gases = 0 (According to Pauling Scale)

→ On going down the group, EN $\downarrow$ except aluminium family.

→

H						
2.1						
Li	Be	B	C	N	O	F
1	1.5	2.0	2.5	3.0	3.5	4
						Cl
						3

A Properties affected by Electronegativity

1. More electronegativity difference, more partial charges, more ionic character and polarity.

Henry Smith,

$$\boxed{\% \text{ ionic character} = 16\,\Delta + 3.5\,\Delta^2} \quad , \quad \Delta = \text{E.N diff.}$$

$$\underset{1.9}{} \qquad \underset{0.9}{} \qquad \underset{0.7}{} \qquad \underset{0.1}{}$$

$$\underset{2.1 \quad 4}{H-F} \;>\; \underset{2.1 \quad 3}{H-Cl} \;>\; \underset{2.1 \quad 2.8}{H-Br} \;>\; \underset{2.1 \quad 2.2}{H-I}$$
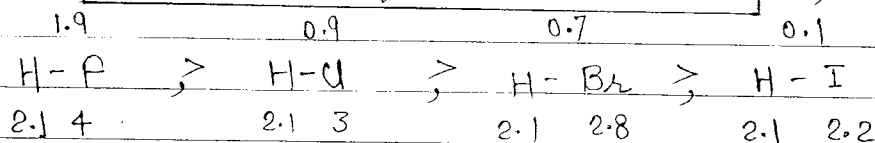
Q. find ionic character of HCl

Sol: $16(0.9) + 3.5(0.9)^2 = 14.4 + 2.835$
$$= 17.235 \%$$

★★★
✓Imp. (i) $\overset{-\delta}{N} - \overset{+\delta}{Cl}$ Bond
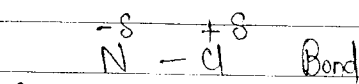
Effective nuclear charge due to small size of N.

$$\overset{-\delta}{P} - \overset{+\delta}{H}$$
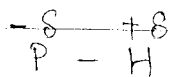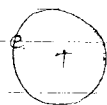
(ii) Due to slight variation in their value.

$$\underset{}{} \quad \underset{0.9}{} \qquad \underset{0}{} \qquad \underset{0.1}{} \qquad \underset{0.2}{}$$
$$\overset{★★}{} N-H \quad , \quad P-H, \quad As-H, \quad Sb-H$$

$$N-H > Sb-H > As-H > \cancel{P}-H$$
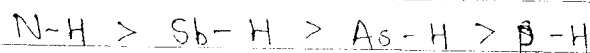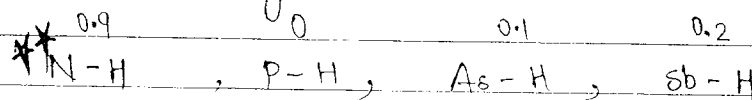
(least polar, not non-polar)

Q. Identify D.S of P in H_3PO_3 in following structure.

$$O^{-2}$$
$$\Uparrow$$
$$P \;\; ^{+2+1+1-1=3}$$
$$OH \;\; \downarrow \;\; H$$
$$OH$$

2. Comparison of Bond length and Bond strength

If electronegativity $\uparrow$, then bond length $\downarrow$ and bond strength $\uparrow$ (keeping other parameters constant like size-similar and hybridisation -same)

→ strength. H-F > H-O > H-N

→ Bond length H-F < H-O < H-N

→ ★★★ But we can't compare H-H and H-Cl on the basis of this factor size of Cl too much greater than that of hydrogen.

3. Case of dissolution of Bond in Polar solvent.

Dielectric property - property of solvent by which electrostatic interaction decreases in polar molecules is called dielectric property. It is expressed by a constant which is called electric constant.

for water - its value is 80.

$$F_{air} = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{r^2} \qquad\qquad F_{water} = \frac{1}{80(4\pi\varepsilon_0)} \times \frac{q_1 q_2}{r^2}$$

$$H \quad H \quad H$$
$$\text{diagram of } Na^+ \text{ hydration}$$

$$\longrightarrow \text{Hydration Energy}$$

$$\text{diagram of } Cl^- \text{ hydration}$$
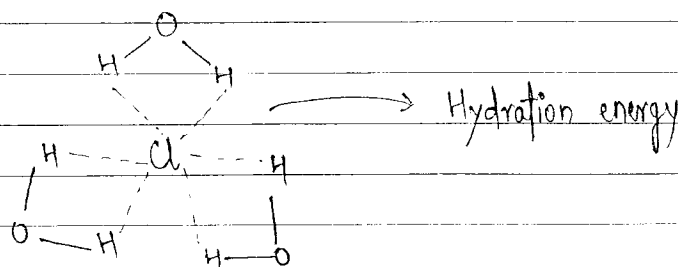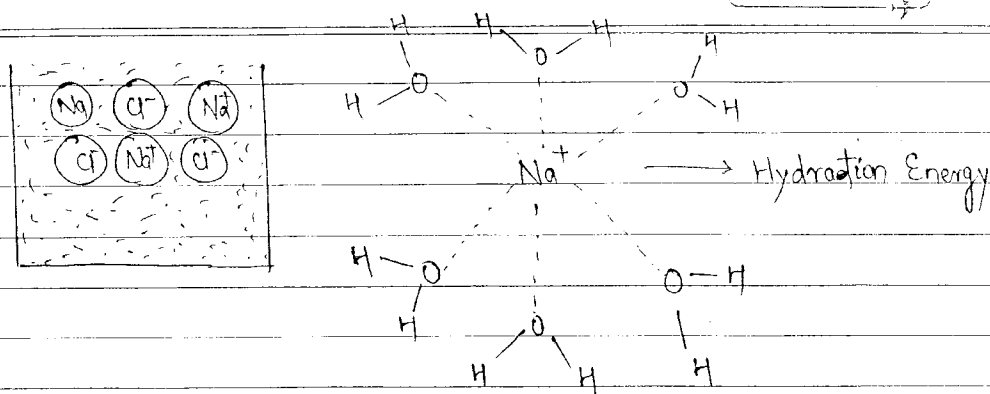
$$\longrightarrow \text{Hydration energy}$$

If Hydration Energy $>$ Lattice Energy $\Rightarrow$ Soluble.

Note:- Dielectric constant is higher in polar solvent as compared to non-polar solvent. When compounds are dissolved in a polar solvent like water, ammonia, they reduce electrostatic force of attraction present in the ions of the compound. For water, dielectric constant $= 80$. Relative value of ε of water is higher than other, so it acts as universal solvent because in water ionic forces of attraction are reduced to $\frac{1}{80}^{th}$ parts.

In case of polar solvent only, electrostatic force of attraction is reduced and therefore, there is no effect on covalent attraction. So, in case of polar

solvent, it is easier to break bonds with high E.N difference.

In case of gaseous/non-polar solvent CCl_4, CS_2, benzene, there is no reduction of electrostatic force of attraction. Hence, it is easier to break a bond having less E.N difference.

A-B bond will break easily in polar solvent However C-D bond will break easily in non-polar solvent if E.N difference in A-B is greater than that of C-D.

4. To decide whether X-O-H molecule will exhibit acidic or basic character in water.

$$X \underset{1}{\overset{2.5}{}} O \underset{2.1}{\overset{1.4}{}} H$$

X   2.5   O   1.4   H
1   3.5   2.1
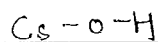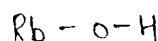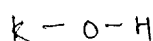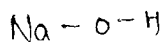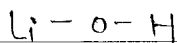
Li — O — H	
Na — O — H	
K — O — H	↓ down the group basic character ↑
Rb — O — H	because E.N difference of X-O ↑.
Cs — O — H	

Q. find the no. of compound which are basic/acid.

$Ba(OH)_2$, $B(OH)_3$, $Si(OH)_4$, $Te(OH)_6$, $NaOH$, $O_2S(OH)_2$, $OP(OH)_3$

basic = $Ba(OH)_2$, $NaOH$
acidic = $B(OH)_3$, $Si(OH)_4$, $Te(OH)_6$, $O_2S(OH)_2$, $OP(OH)_3$

Basicity

$$LiOH \quad > \quad Be(OH)_2$$
$$\wedge \qquad\qquad \wedge$$
$$NaOH \quad > \quad Mg(OH)_2$$
$$\wedge \qquad\qquad \wedge$$

most basic = CsOH

$$KOH \quad > \quad Ca(OH)_2$$
$$\wedge \qquad\qquad \wedge$$

least basic = Be(OH)$_2$

$$RbOH \quad > \quad Sr(OH)_2$$
$$\wedge \qquad\qquad \wedge$$
$$CsOH \quad > \quad Ba(OH)_2$$
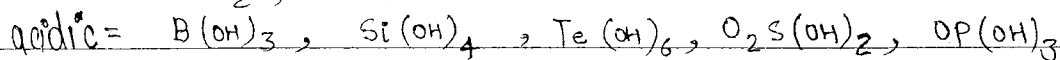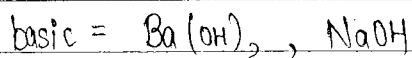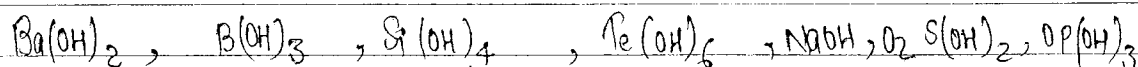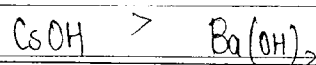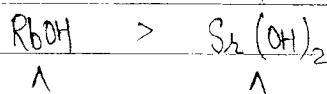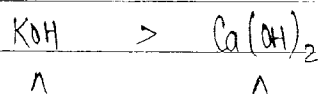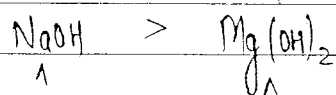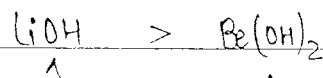
पं	जा	बे	अली	गा	सुना	कर	में
→Pb	Zn	Be	Al	Ga	Sn	Cr^{+3}	

Ampoteric oxide and hydroxide

→ As$_2$O$_3$, V$_2$O$_5$ are also amphoteric

→ Only for Oxyacid — atleast one H , one oxygen.
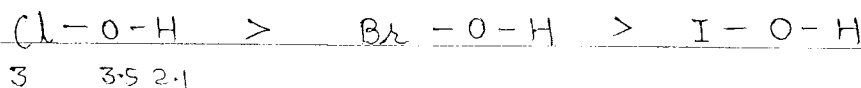
$$Cl - O - H \quad > \quad Br - O - H \quad > \quad I - O - H$$
$$3 \qquad 3.5 \; 2.1$$
$$0.5 \quad 1.4$$

★★

Hydra Acids — In case of these acids, the above method is not applicable.

Ex — HF < HCl < HBr < HI
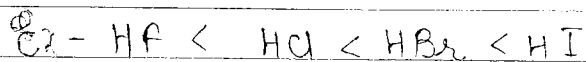
Reason:-size ↑ , bond strength ↓ , acidity ↑
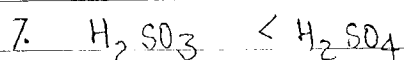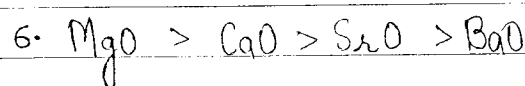
Metallic oxides are basic while non-metallic are Acidic.

Nature of Oxides

Na_2O < MgO < Al_2O_3 < SiO_2 < P_2O_5 < SO_3 < Cl_2O_7

most basic   Basic   Amphoteric   light Acid   acidic   strong acid   strongest acid

↓   ↓   ↓   ↓   ↓   ↓   ↓

$NaOH$ $Mg(OH)_2$ $Al(OH)_3$ H_4SiO_4 H_3PO_4 H_2SO_4 $HClO_4$

P ⟨ $+3$ H_3PO_3 phosphorous acid, orthophosphorous acid, phosphonic acid

$+5$ H_3PO_4 phosphoric acid, ortho phosphoric acid

S ⟨ $+4$ H_2SO_3 Sulphurous acid

$+6$ H_2SO_4 Sulphuric acid

$Si \longrightarrow H_4SiO_4$ Silicic acid

N ⟨ $+3$ HNO_2 nitrous acid

$+5$ HNO_3 nitric acid

$HClO$ $HClO_2$ $HClO_3$ $HClO_4$

hypochlorous acid   Chlorous acid   Chloric acid   perchloric

---

H_3BO_3 (Boric Acid)

Note :- 1. CO, NO, N_2O → neutral oxide

2. N_2O $(+1)$ < NO $(+2)$ < N_2O_3 $(+3)$ < N_2O_4 $(+4)$ < N_2O_5 $(+5)$ Oxidation state↑ acidity ↑

↓   ↓   ↓   ↓   ↓

X   X HNO_2 HNO_2 HNO_3

+

HNO_3

(Mixed Oxide)

3. $\overset{+2}{CO} < \overset{+4}{CO_2}$

4. $CO_2 > SiO_2$

5. $Li_2O > Na_2O > K_2O > Rb_2O > CS_2O$

6. $MgO > CaO > SrO > BaO$

7. $H_2SO_3 < H_2SO_4$

8. $HClO < HClO_2 < HClO_3 < HClO_4$

Exception

$H_3PO_2 > H_3PO_3 > H_3PO_4$

9.

| MnO | Mn_3O_4 | Mn_2O_3 | MnO_2 | Mn_2O_7 |
| Basic | | Amphoteric | | (green colour oil acidic) |

$\uparrow HMnO_4$

10.
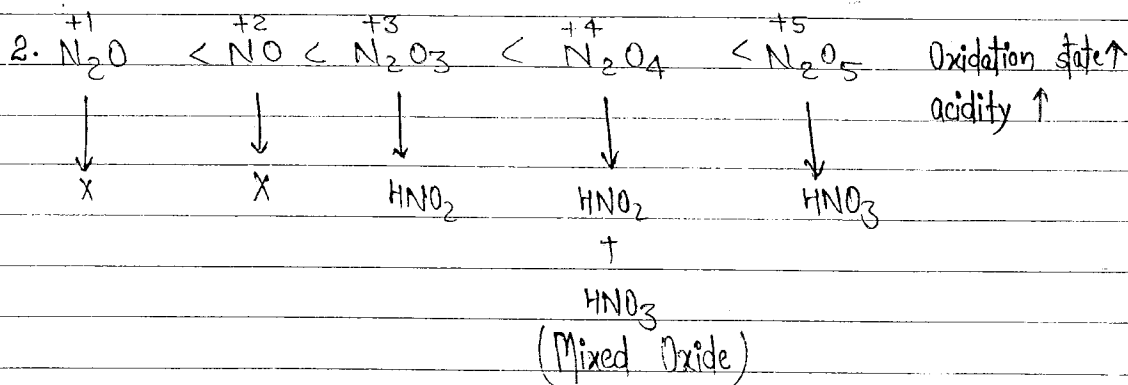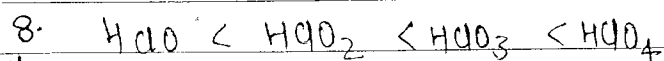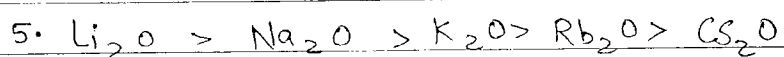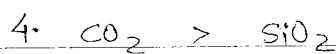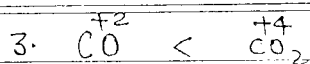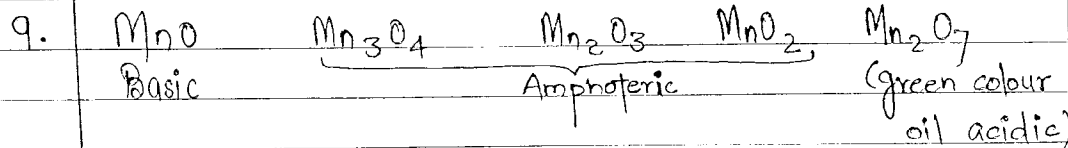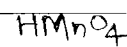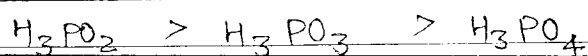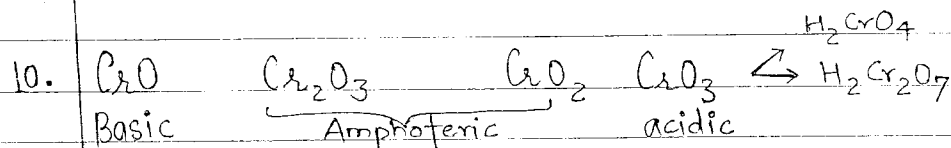
| CrO | Cr_2O_3 | CrO_2 | $CrO_3 \rightleftharpoons H_2Cr_2O_7$ |
| Basic | Amphoteric | | acidic |

H_2CrO_4

** **lattice Energy** — Amount of Released energy when one mole of gases cation and anion form 1 mole of ionic solid.

It is also defined as amount of required energy to break 1 mole of ionic solid compound into its constituent gaseous cation and anion.

(U) $L.E = \dfrac{-kq_1q_2}{r^2}$, $r =$ radius of Cation + radius of anion

$q_1 q_2 = $charge

$r \uparrow$ L.E $\downarrow$ charge $\uparrow$ L.E $\uparrow$

1. $LiCl > NaCl > KCl > RbCl > CsCl$

2. $KF > KCl > KBr > KI$

3. $CaF_2 > CaCl_2 > CaBr_2 > CaI_2$

Same group, see radii

4. $LiF^{-1} < Li_2O^{-2} < Li_3N^{-3}$
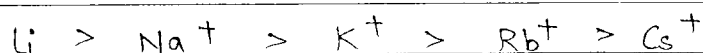
5. $MgO^{-2} < Mg_3N_2^{-3}$

Same period, see charge

** Hydration Energy — It is the amount of released energy when one mole of ionic compound completely dissolves in a polar solvent, then it is called solvation energy. If water is taken as polar solvent, then it is called hydration energy.

$\longrightarrow$ hydration energy
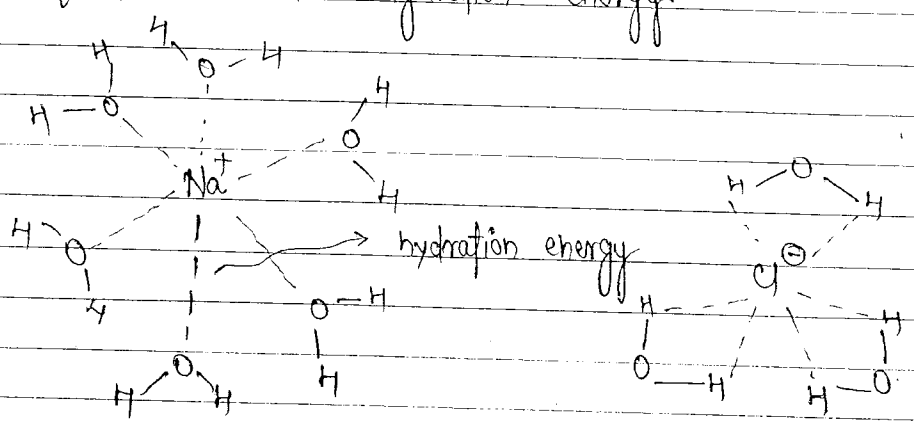
Ion-dipole interaction

$\rightarrow$ Charge density $= \dfrac{Charge}{size}$ $=$ Represented by ϕ

$\rightarrow$ Charge density (ϕ),

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

$\rightarrow$ Hydrated size,

$\rightarrow$ Hydrated size

$$Li^+_{(aq)} > Na^+_{(aq)} > K^+_{(aq)} > Rb^+_{(aq)} > Cs^+_{(aq)}$$

$\rightarrow$ Ionic mobility,

$$Li^+_{(aq)} < Na^+_{(aq)} < K^+_{(aq)} < Rb^+_{(aq)} < Cs^+_{(aq)}$$

Note: Charge density $\uparrow$, hydrated size $\uparrow$, ionic mobility $\downarrow$

Imp $Be^{+2} > Al^{+3}$ charge density

$\phi = 6.4 \qquad 6$

$Be^{+2}_{(aq)} > Al^{+3}_{(aq)}$ aqueous radius

$Be^{+2}(aq) < Al^{+3}_{(aq)}$ Conductivity
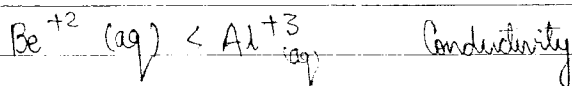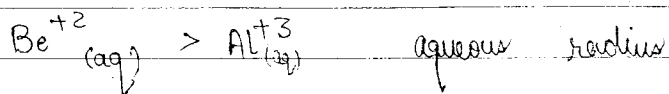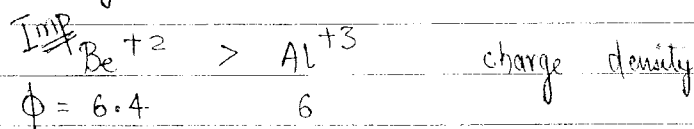
After water molecules are attracted by ions, the new radius of species is called hydrated radius.

** Oxygen ion does not exist in water because it is very strong base, so gets converted into OH^- ion, therefore its hydrated radius can't be measured.

Ionic mobility / Electrical conductance / molar conductance
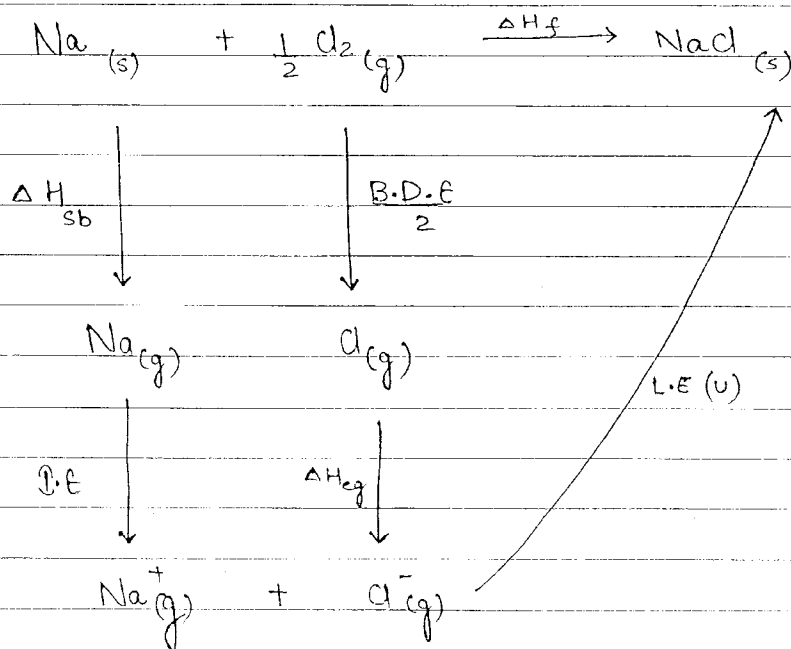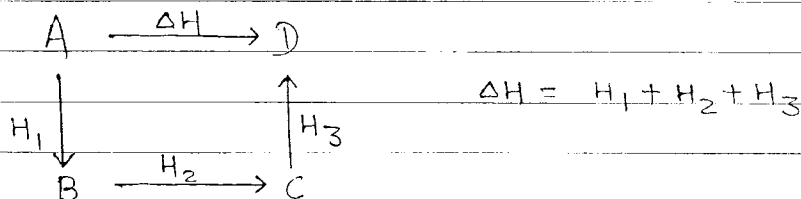- It is the ability by which an ion can move in the solution.

$$Na_2O \longrightarrow 2Na^+ + O^{-2}$$

$$H_2O \longrightarrow H^+ + OH^-$$

$$Na_2O + H_2O \longrightarrow NaOH + OH^-$$
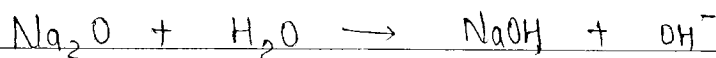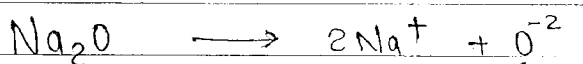
Born Haber Cycle

It is a cycle which co-relates the thermodynamical data with the enthalpy of different physical and chemical routes.

Hess Rule :-

Energy Associated with particular Reaction is always constant at a particular temp. and is independent of path.

$$A \xrightarrow{\Delta H} D$$

$H_1 \downarrow \qquad \uparrow H_3 \qquad \qquad \Delta H = H_1 + H_2 + H_3$

$$B \xrightarrow{H_2} C$$

$$Na_{(s)} + \frac{1}{2} Cl_{2(g)} \xrightarrow{\Delta H_f} NaCl_{(s)}$$

$\Delta H_{sb} \downarrow \qquad \qquad \frac{B.D.E}{2} \downarrow$

$$Na_{(g)} \qquad \qquad Cl_{(g)}$$

$I.E \downarrow \qquad \qquad \Delta H_{eg} \downarrow \qquad \qquad L.E \ (U)$

$$Na^+_{(g)} + Cl^-_{(g)}$$

Q.
$$-411.2 = 108.4 + 495.6 + 121 - 348.6 + x$$
$$= \overset{725}{\cancel{846}} - 348.6 + x$$
$$x = 34 \times 8.6 - 616 - 411.2$$

→ Heat of Sublimation — It is the energy required to evaporate one mole of solid compound to vapour directly.

→ Heat of fusion — It is the energy required to convert one mole of solid compound to liquid

→ Heat of vaporisation — It is the energy required to convert one mole of liquid to one mole of gas.

→ | Heat of Sublimation = Heat of fusion + Heat of evaporation |

108.4
495.0
121.0
736.0
411.2

1027.2
348.6
676.6

788.

PAGE NO.:
DATE: / /

→ Heat of formation — It is the energy associated with formation of one mole of compound from it constituent element in their standard state.
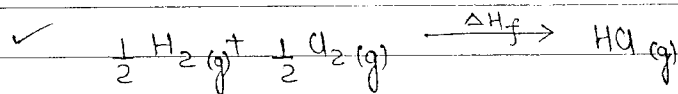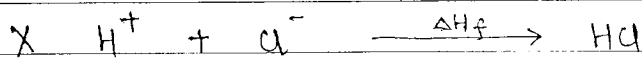
✦✦ Standard state :- 1. F_2, Cl_2 → gas

2. Br_2 → liquid

3. I_2 → solid.

4. Phosphorous — P_4 (solid)

5. Sulphur — S_8 (solid)

✗ $H^+ + Cl^- \xrightarrow{\Delta H_f} HCl$
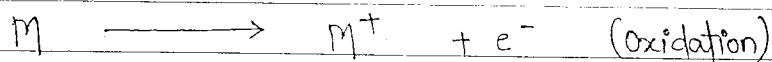
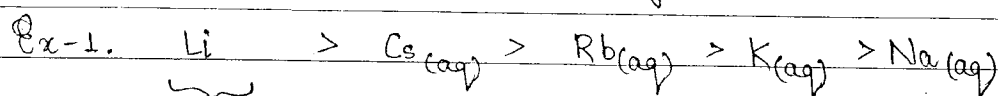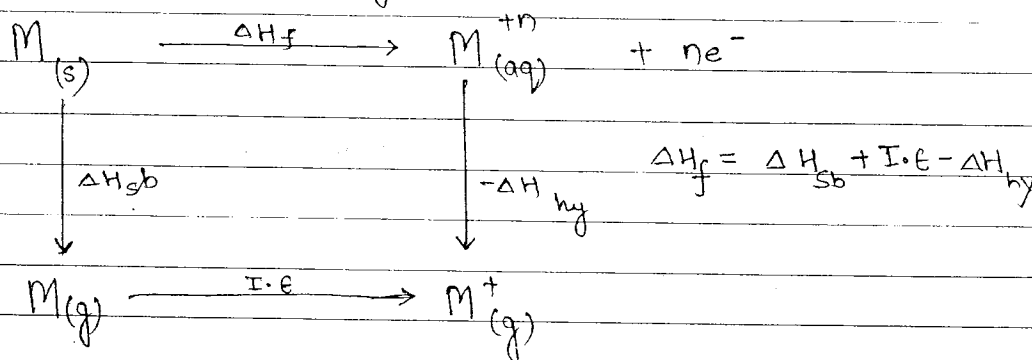✓ $\frac{1}{2} H_2 (g) + \frac{1}{2} Cl_2 (g) \xrightarrow{\Delta H_f} HCl (g)$

→ Heat of Solvation — It is the energy associated with the solvation of one mole of a substance in a particular solvent.

→ Bond Dissociation Energy — It is the energy required to break the bond present in one mole of substance, but molecule should be covalent bonded.
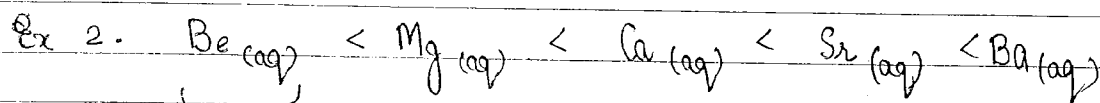
Oxidation and Reduction

$$M \longrightarrow M^+ + e^- \quad \text{(oxidation)}$$

$$M^+ + e^- \longrightarrow M \quad \text{(Reduction)}$$

Order of Reducing power

$$M_{(s)} \xrightarrow{\Delta H_f} M^{+n}_{(aq)} + ne^-$$

$$\downarrow \Delta H_{sb} \qquad \downarrow -\Delta H_{hy} \qquad \Delta H_f = \Delta H_{sb} + I.E - \Delta H_{hy}$$

$$M_{(g)} \xrightarrow{I.E} M^+_{(g)}$$

Ex-1. $\quad Li \quad > \quad Cs_{(aq)} > Rb_{(aq)} > K_{(aq)} > Na_{(aq)}$
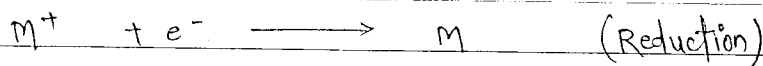
** Due to high hydration energy i.e. $\Delta H_{hy} \propto \phi$ and there is large diff in size b/w 2nd and 3rd period elements

*** Note:- $\therefore$ Li - It is the strongest reducing agent.

Ex 2. $\quad Be_{(aq)} < Mg_{(aq)} < Ca_{(aq)} < Sr_{(aq)} < Ba_{(aq)}$
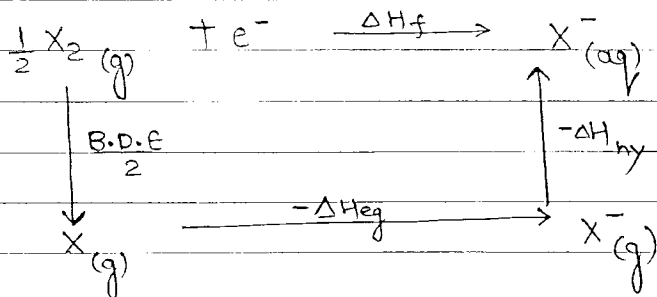
** I.E is very high which overcomes high hydration energy.

** Note:- Be is the weakest reducing agent in S block.

⇒ Fluorine and oxygen – both are strong oxidising ← agent because of small size and high
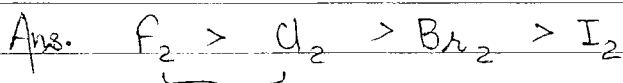electron affinity

$F\ell > 0$

Order of Reducing Oxidising power.

$$\frac{1}{2} X_{2\,(g)} + e^- \xrightarrow{\Delta H_f} X^-_{(aq)}$$

$$\downarrow \frac{B.D.E}{2} \qquad \uparrow -\Delta H_{hy}$$

$$X_{(g)} \xrightarrow{-\Delta H_{eg}} X^-_{(g)}$$

$$\therefore \quad \Delta H_f = \frac{B.D.E}{2} - \Delta H_{eg} - \Delta H_{hy}$$

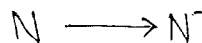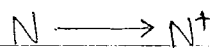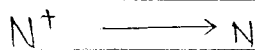Ex – Q. find order of oxidising power F_2, Cl_2, Br_2, I_2

Ans. $F_2 > Cl_2 > Br_2 > I_2$

Due to high $-\Delta H_{hy}$

Q. Which of the following Reax^n is possible?

(i) $F_2 \longrightarrow F^-$ F_2 is strongest oxidising agent

(ii) $F^- \longrightarrow F_2$

Q. Which of following is endothermic or exothermic?

$N^+ \longrightarrow N$
$N^- \longrightarrow N$ } exothermic

$N \longrightarrow N^+$
$N \longrightarrow N^-$ } endothermic