INDEX

Note:- $\underset{\text{W·B}}{NH_3} + H_2O \rightarrow \underset{\text{W·B}}{NH_4OH}$

Type of chemical Rex^n:—

1) Direct elemental combination:—
When reactants are in their elementary form:-
metal + nonmetal → Ionic
non-metal + non-metal → Co-valent

2) Acid and Base reaction:—
- Cation from base and
- Anion from acid.

Acid + Base → salt

Anion = Acid
Cation = Base

Acidic characte
- → having H^+
- → Acidic salt ; eg $NaHSO_4$ etc.
- → Non-metal oxide
- → Aqueous solution of salt (S.A + W.B)
  eg NH_4Cl

Basic characte
- → having OH^-
- → Basic salt, eg $Ca(OH)Cl$ etc.
- → metalic oxide
- → Aq sol^n of salt (W.A + S.B)
  eg Na_2CO_3 etc.

Examples—

$CaO + H_2SO_4 \longrightarrow CaSO_4 + H_2O$ ✓

$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$

$CaO + CO_2 \longrightarrow CaCO_3$
(H_2CO_3)

$CaO + SO_3 \longrightarrow CaSO_4$
(H_2SO_4)

$CaO + P_4O_{10} \longrightarrow Ca_3(PO_4)_2$ ✓
(H_3PO_4)

$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2 \uparrow$
(S.B + W.A) $\quad H_2CO_3$

(3) Redox reactions :-

O.A + R.A ⟶ Products

↳ Atleast one of the reagents must be good.

(4) Ionic displacement by precipitation :-

$$AB_{(aq)} + CD_{(aq)} \longrightarrow AD_{(aq)} + CB_{(aq)}$$

$$\cancel{A^+} + \cancel{B^-} + \cancel{C^+} + \cancel{D^-} \longrightarrow \cancel{A^+} + \cancel{D^-} + \cancel{C^+} + \cancel{B^-}$$

} Rexn not possible :-

for,

one of the product must have low K_{sp}.

$$AB_{(aq)} + CD_{(aq)} \longrightarrow AD_{(s)} + CB_{(aq)}$$

$$A^+ + \cancel{B^-} + \cancel{C^+} + D^- \longrightarrow AD_{(s)} + \cancel{C^+} + \cancel{B^-}$$

$$\boxed{A^+_{(aq)} + D^-_{(aq)} \longrightarrow AD_{(s)}}$$

(5) Displacement due to volatility difference :-

(6) Hydrolysis reaction :-

(7) Lewis acid and lewis base rexn :-

modern periodic table
or
Bohr's periodic table
or
long form of periodic table.

(1) After moseley x-ray experiments atomic no. becomes the most important properties to characterize an element.

(2) modern periodic table was proposed by Bohr, Bents, Runge, werner etc.

(3) modern periodic table consist of 18 groups and 7 periods.

(4)

New	1	2	3	4	5	6	7	8	9	10	11	12
old	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIB	VIIIB	VIIIB	IB	IIB

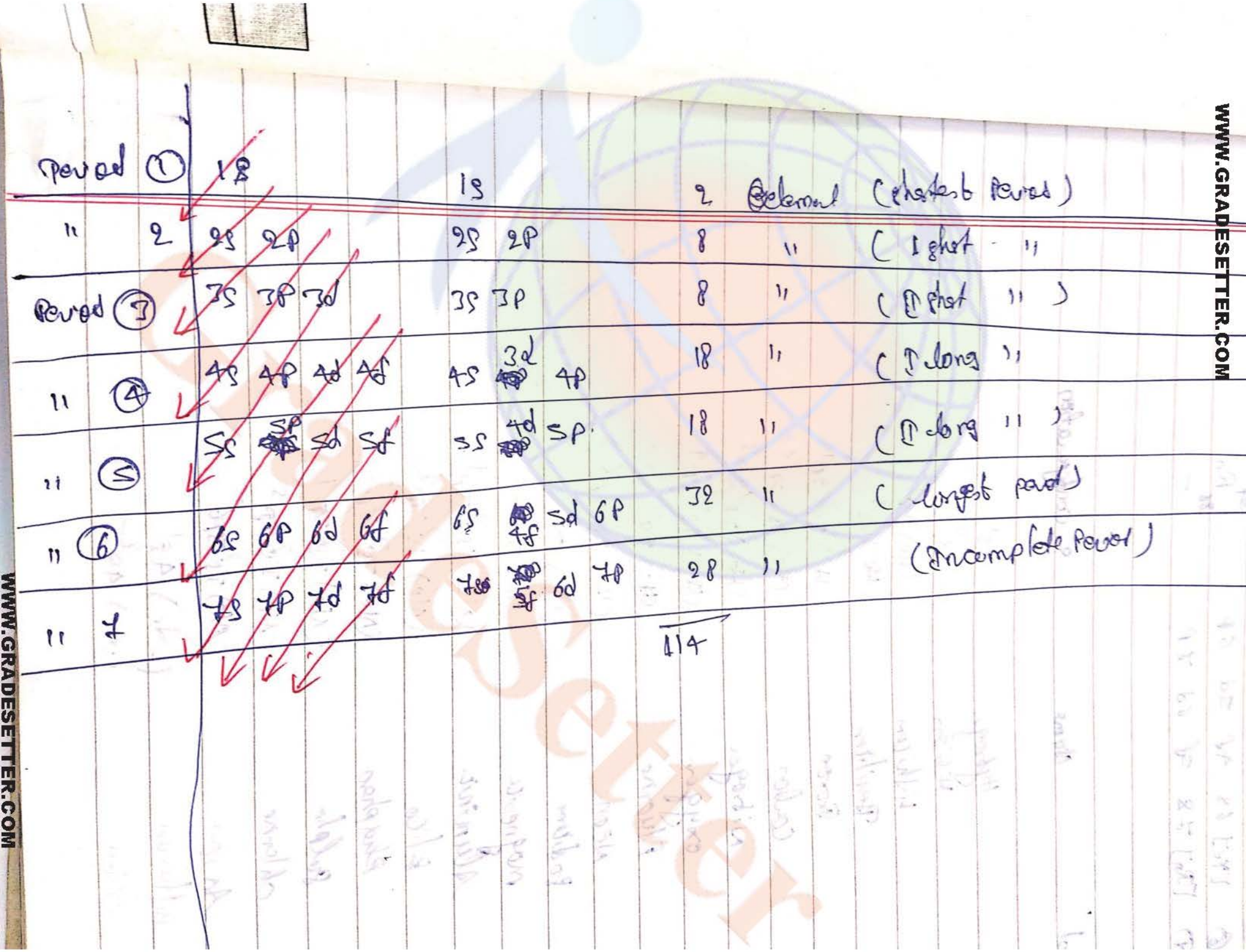
13	14	15	16	17	18
IIIA	IVA	VA	VIA	VIIA	0

(5) Period number of an element represents total no. of shell and outermost shell (valence shell).

(6) Each period starts with s-subshells of a new shell and ends with p-subshell of that shell.

(7) From 3rd period period elements almost all elements have vacant d-subshell.

) In outermost shell of any element only two subshells are present "s" and "p". Hence in outermost shell maximum 8e⁻'s are possible.



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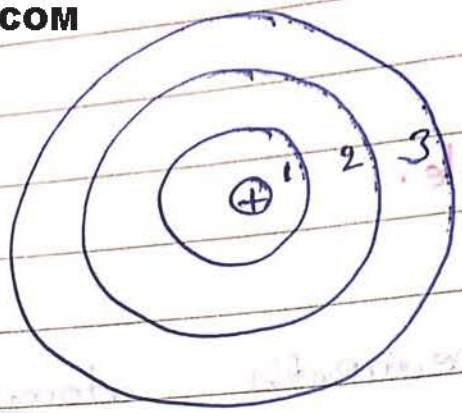
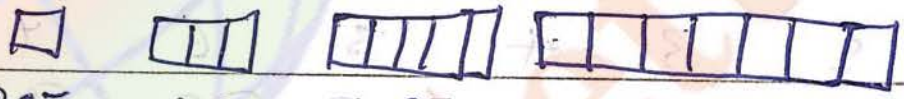


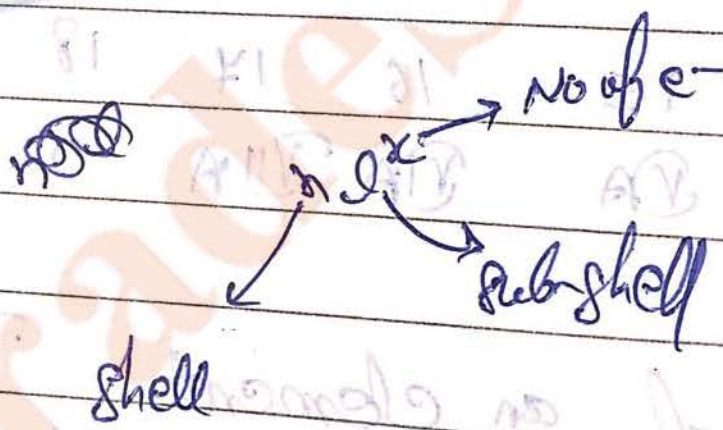
shell : 1, 2, 3, 4, ---

K L M N

sub-shell : s p d f

orbitals - 1 3 5 7





Noble gas

$_{2}He$
$_{10}Ne$
$_{18}Ar$
$_{36}Kr$
$_{54}Xe$
$_{86}Rn$

Atomic no.	Symbol	Name	e⁻ configuration
1	H	Hydrogen	$1s^1$
2	He	Helium	$1s^2$
3	Li	Lithium	(He) $2s^1$
4	Be	Beryllium	(He) $2s^2$
5	B	Boron	(He) $2s^2\ 2p^1$
6	C	Carbon	(He) $2s^2\ 2p^2$
7	N	Nitrogen	(He) $2s^2 2p^3$
8	O	oxygen	(He) $2s^2\ 2p^4$
9	F	Fluorine	(He) $2s^2\ 2p^5$
10	Ne	Neon	(He) $2s^2\ 2p^6$
11	Na	Sodium	(Ne) $3s^1$
12	Mg	magnesium	(Ne) $3s^2$
13	Al	Aluminium	(Ne) $3s^2\ 3p^1$
14	Si	Silica	(Ne) $3s^2\ 3p^2$
15	P	Phosphorus	(Ne) $3s^2\ 3p^3$
16	S	Sulphur	(Ne) $3s^2\ 3p^4$
17	Cl	chlorine	(Ne) $3s^2\ 3p^5$
18	Ar	Argon	(Ne) $3s^2\ 3p^6$
19	K	Potassium	(Ar) $4s^1$
20	Ca	calcium	(Ar) $4s^2$

Period ① [He] 1,2
Period ② [Ne] 2s 2p
Period ③ [Ar] 3s 3p
Period ④ [Kr] 3s 3d 4p
Period ⑤ [Xe] 4s 4d 5p
Period ⑥ [Rn] 5s 4f 5d 6p
Period ⑦ [Rn] 7s 5f 6d 7p

CAREER POINT

Target Course for NITs (JEE Main)-2014

DAILY PRACTICE PROBLEM SHEET

CHEMISTRY

Periodic Table - 1

Question based on atomic radii

Q.1 Arrange the following ions in the order of increasing size :
Be^{2+}, Cl^-, S^{2-}, Na^+, Mg^{2+}, Br^-

Q.2 Which of the following species will have the largest and the smallest size ?
Mg, Mg^{2+}, Al, Al^{3+}

Q.3 The radii of Cl, Cl^-, S and S^{2-} are in the order
(1) $S^{2-} > S > Cl^- > Cl$ (2) $S^{2-} > Cl^- > S > Cl$
(3) $Cl > Cl^- > S > S^{2-}$ (4) $Cl^- > S^{2-} > Cl > S$

Q.4 Which of the following trends of atomic sizes is(are) correct ?
(1) F > O > N > C (2) Rb > K > Na > Li
(3) Be > B > C > N (4) Ne > He > Ar > Kr

Q.5 The correct order of increasing radius of the elements Si, Al, Na and P is :
(1) Si < Al < P < Na (2) P < Si < Al < Na
(3) Al < Si < P < Na (4) Al < P < Si < Na

Q.6 The radii of F, F^-, O and O^{2-} are in the order :
(1) $O^{2-} > F^- > O > F$ (2) $O^{2-} > F^- > F > O$
(3) $F^- > O^{2-} > F > O$ (4) $O^{2-} > O > F^- > F$

Question based on period, Block & group

Q.7 **Statement-1 :** The 4f- and 5f- inner transition series of elements are placed separately at the bottom of the periodic table.
Statement-2 : (i) This prevents the undue expansion of the periodic table i.e., maintains its structure.

Question based on atomic radii

Q.1 निम्न आयनों को आकार के बढ़ते क्रम में व्यवस्थित कीजिए–
Be^{2+}, Cl^-, S^{2-}, Na^+, Mg^{2+}, Br^-

Q.2 निम्न में से कौनसी स्पीशीज अधिकतम व न्यूनतम आकार रखती है ?
Mg, Mg^{2+}, Al, Al^{3+}

Q.3 Cl, Cl^-, S व S^{2-} की त्रिज्या निम्न क्रम में है–
(1) $S^{2-} > S > Cl^- > Cl$ (2) $S^{2-} > Cl^- > S > Cl$
(3) $Cl > Cl^- > S > S^{2-}$ (4) $Cl^- > S^{2-} > Cl > S$

Q.4 निम्न में से परमाणु आकार का कौनसा क्रम सही है ?
(1) F > O > N > C (2) Rb > K > Na > Li
(3) Be > B > C > N (4) Ne > He > Ar > Kr

Q.5 Si, Al, Na व P तत्वों की बढ़ती हुई त्रिज्या का सही क्रम है–
(1) Si < Al < P < Na (2) P < Si < Al < Na
(3) Al < Si < P < Na (4) Al < P < Si < Na

Q.6 F, F^-, O व O^{2-} की त्रिज्याF, F^-, O व O^{2-} की त्रिज्याऐं निम्न क्रम में हैं :
(1) $O^{2-} > F^- > O > F$ (2) $O^{2-} > F^- > F > O$
(3) $F^- > O^{2-} > F > O$ (4) $O^{2-} > O > F^- > F$

Question based on period, Block & group

Q.7 **कथन-1 :** तत्वों की 4f- व 5f- अंतः संक्रमण श्रेणियां, आवर्त सारणी के पैंदे पर अलग से स्थित होती है।
कथन-2 : (i) यह आवर्त सारणी के अत्यधिक प्रसार को रोककर इसकी संरचना को व्यवस्थित रखता है।

(1) If both statement-I and statement-II are true but statement-II is not the correct explanation of statement-I
(2) If both statement-I and statement-II are true, and statement-II is the correct explanation of statement-I.
(3) If statement-I is true but statement-II is false.
(4) If statement-I is false but statement-II is true

Q.8 Which one of the following statements related to the modern periodic table is incorrect ?
(1) The p-block has 6 columns, because a maximum of 6 electrons can occupy all the orbitals in a p-subshell
(2) The d-block has 8 columns, because a maximum of 8 electrons can occupy all the orbitals in a d-subshell
(3) Each block contains a number of columns equal to the number of electrons that can occupy that subshell
(4) s-block include group 1 & 2 with general configuration ns^1 and ns^2 respectively

Question based on Ionization energy

Q.9 Which of the following is the correct order of ionization energy ?
(1) $O^{2-} < F^- < Na^+ < Mg^{2+}$
(2) $F^- < O^{2-} < Na^+ < Mg^{2+}$
(3) $O^{2-} < Na^+ < F^- < Mg^{2+}$
(4) $Mg^{2+} < Na^+ < F^- < O^{2-}$

Q.10 Which of the following statements is incorrect in relation to ionization enthalpy ?
(1) Ionization enthalpy increases for each successive electron
(2) The greatest increase in ionization enthalpy is experienced on removal of electrons from core noble gas configuration
(3) End of valence electrons is marked by a big jump in ionization enthalpy
(4) Removal of electron from orbitals bearing lower n value is easier than from orbital having higher n value.

(1) कथन-I और कथन-II दोनों सही है तथा कथन- II, कथन- I का सही स्पष्टीकरण नहीं है
(2) कथन- I और कथन- II दोनों सही है तथा कथन- II, कथन- I का सही स्पष्टीकरण है
(3) कथन- I सही है तथा कथन- II गलत है
(4) कथन- I गलत है तथा कथन- II सही है

Q.11 निम्न में से आधुनिक आवर्त सारणी से संबंधित कौनसा एक कथन गलत है ?
(1) p-ब्लॉक 6 स्तम्भ रखता है क्योंकि p-उपकोश में सभी कक्षक अधिकतम 6 इलेक्ट्रॉनों से भरें होते है।
(2) d-ब्लॉक 8 स्तम्भ रखता है क्योंकि d-उपकोश में सभी कक्षक अधिकतम 8 इलेक्ट्रॉनों से भरें होते है।
(3) प्रत्येक ब्लॉक में उपस्थित स्तम्भों की संख्या इलेक्ट्रॉनों की संख्या के बराबर होती है जिसमें उपकोश भरें हो सकते है।
(4) s-ब्लॉक में सामान्य विन्यास क्रमशः ns^1 व ns^2 युक्त वर्ग 1 व 2 सम्मिलित होते है

Question based on Ionization energy

Q.9 निम्न में से आयनन ऊर्जा का सही क्रम कौनसा है ?
(1) $O^{2-} < F^- < Na^+ < Mg^{2+}$
(2) $F^- < O^{2-} < Na^+ < Mg^{2+}$
(3) $O^{2-} < Na^+ < F^- < Mg^{2+}$
(4) $Mg^{2+} < Na^+ < F^- < O^{2-}$

Q.10 निम्न में से आयनन एन्थैल्पी के संबंध में कौनसा कथन गलत है?
(1) प्रत्येक क्रमागत इलेक्ट्रॉन के लिए आयनन एन्थैल्पी बढ़ती है।
(2) बाह्य उत्कृष्ट गैस विन्यास से इलेक्ट्रॉनों के हटाने पर आयनन एन्थैल्पी में अधिकतम वृद्धि अनुभव होती है।
(3) संयोजी इलेक्ट्रॉनों का अंत, आयनन एन्थैल्पी में वृहद् मात्रा के द्वारा चिन्हित होता है।
(4) इलेक्ट्रॉन का हटना निम्न n मान रखने वाले कक्षकों से, उच्च n मान रखने वाले कक्षकों की तुलना में आसान होता है।

Q.11 Which of the following order is not correct ?
(1) IE(I) of Be > IE(I) of B but IE(II) of Be < IE(II) of B
(2) IE(I) of Be < IE(I) of B but IE(II) of Be < IE(II) of B
(3) IE(II) of O > IE(II) of N
(4) IE(I) of Mg > IE(I) of Al

Q.12 A large difference between the fourth and fifth ionization energies indicates the presence of :
(1) 5 valence electrons in an atom
(2) 6 valence electrons in an atom
(3) 4 valence electrons in an atom
(4) 8 valence electrons in an atom

Q.13 Among the element A, B, C and D having atomic numbers 9, 10, 11 and 12 respectively the correct order of ionization energies is :
(1) A > B > C > D (2) B > A > D > C
(3) B > A > C > D (4) D > C > B > A

Q.14 Which of the following species has the highest ionization potential ?
(1) Li^+ (2) Mg^+
(3) Al^+ (4) Ne

Q.15 The lowest first ionization energy would be associated with which of the following structures ?
(1) $1s^2\ 2s^2\ 2p^6\ 3s^1$ (2) $1s^2\ 2s^2\ 2p^5$
(3) $1s^2\ 2s^2\ 2p^6$ (4) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

Q.11 निम्न में से कौनसा क्रम सही नहीं है ?
(1) Be का IE(I) > B का IE(I) परन्तु Be का IE(II) < B का IE(II)
(2) Be का IE(I) < B का IE(I) परन्तु Be का IE(II) < B का IE(II)
(3) O का IE(II) > N का IE(II)
(4) Mg का IE(I) > Al का IE(I)

Q.12 चौथी व पांचवी आयनन ऊर्जाओं के मध्य उच्च अंतर निम्न की उपस्थिति दर्शाता हैं।
(1) एक परमाणु में 5 संयोजी इलेक्ट्रॉन
(2) एक परमाणु में 6 संयोजी इलेक्ट्रॉन
(3) एक परमाणु में 4 संयोजी इलेक्ट्रॉन
(4) एक परमाणु में 8 संयोजी इलेक्ट्रॉन

Q.13 A, B, C व D तत्व क्रमशः 9, 10, 11 व 12 परमाणु क्रमांक रखते हैं। आयनन ऊर्जा का सही क्रम है–
(1) A > B > C > D (2) B > A > D > C
(3) B > A > C > D (4) D > C > B > A

Q.14 निम्न में से कौनसी स्पीशीज उच्चतम आयनन विभव रखती है ?
(1) Li^+ (2) Mg^+
(3) Al^+ (4) Ne.

Q.15 निम्नतम प्रथम आयनन ऊर्जा, निम्न में से किस संरचना के साथ संबंधित है ?
(1) $1s^2\ 2s^2\ 2p^6\ 3s^1$ (2) $1s^2\ 2s^2\ 2p^5$
(3) $1s^2\ 2s^2\ 2p^6$ (4) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

Periodic Table - 2

Question based on Ionization energy

Q.1 Which of the following statements is incorrect ?

(1) The second ionization energy of sulphur is greater than that of chlorine

(2) IE of $T\ell > Al$

(3) The first ionization energy of aluminium is greater than gallium

(4) The second ionization energy of boron is greater than that of carbon

Q.2 Correct order of ionisation potential is -

(1) B > Al > Ga (2) B > In > Al

(3) B > Tl > Ga (4) Ga > In > Tl

Q.3 The first ionization energies in eV/atom of magnesium and aluminium are respectively given by -

(1) 7.64, 5.98 (2) 7.64, 7.64

(3) 5.98, 7.64 (4) 5.98, 5.98

Question based on electron affinity

Q.4 Select equation having exothermic step :

(1) $S^-(g) \rightarrow S^{2-}(g)$

(2) $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

(3) $N(g) \rightarrow N^-(g)$

(4) $Al^{2+}(g) \rightarrow Al^{3+}(g)$

Question based on Ionization energy

Q.1 निम्न में से कौनसा कथन गलत है ?

(1) सल्फर की द्वितीय आयनन ऊर्जा, क्लोरीन की अपेक्षा अधिक होती है।

(2) $T\ell > Al$ का IE

(3) एल्युमिनियम की प्रथम आयनन ऊर्जा, गैलियम से अधिक होती है।

(4) बोरोन की द्वितीय आयनन ऊर्जा, कार्बन की अपेक्षा अधिक होती है।

Q.2 आंयनन विभव का सही क्रम है–

(1) B > Al > Ga (2) B > In > Al

(3) B > Tl > Ga (4) Ga > In > Tl

Q.3 मैग्निशियम व एल्युमिनियम की इलेक्ट्रॉन वोल्ट प्रति परमाणु (eV/atom) में प्रथम आयनन ऊर्जाऐं क्रमशः निम्न द्वारा दी जाती है -

(1) 7.64, 5.98 (2) 7.64, 7.64

(3) 5.98, 7.64 (4) 5.98, 5.98

Question based on electron affinity

Q.4 ऊष्माक्षेपी पद युक्त समीकरण चुनिए–

(1) $S^-(g) \rightarrow S^{2-}(g)$

(2) $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

(3) $N(g) \rightarrow N^-(g)$

(4) $Al^{2+}(g) \rightarrow Al^{3+}(g)$

Assertion & Reason type questions (Q. No. 5 to 6) :

(1) If both statement-I and statement-II are true but statement-II is not the correct explanation of statement-I

(2) If both statement-I and statement-II are true, and statement-II is the correct explanation of statement-I.

(3) If statement-I is true but statement-II is false.

(4) If statement-I is false but statement-II is true

Q.5 **Assertion :** Formation of Cl^- ion is exothermic whereas O^{2-} ion formation is endothermic.

Reason : EA_2 of oxygen is endothermic and greater than its exothermic EA_1 value of oxygen.

Q.6 **Assertion :** The electron gain enthalpy of N is +ve while that of P is –Ve.

Reason : Smaller atomic size of N in which there is a considerable electron-electron repulsion and hence the additional electron is not accepted easily.

Q.7 Match the column

Column-I	Column-II
(A) Increasing order of I.E.	(P) $F < O < S < Se$
(B) Increasing order of electron affinity	(Q) $O < N < F < Ne$
(C) Increasing order of atomic size	(R) $Na < Mg < Al < Si$
	(S) $O^{2-} < O^- < O < O^+$

Q.8 The first order of electron affinities is :

(1) $Cl > O > C > B > N$

(2) $O > Cl > C > B > N$

(3) $N > O > Cl > B > C$

(4) $Cl > N > O > B > C$

Assertion & Reason

(1) कथन-I और कथन- II सही है तथा कथन- II, कथन- I का सही स्पष्टीकरण है

(2) कथन- I और कथन- II दोनों सही है तथा कथन- II, कथन- I का सही स्पष्टीकरण है

(3) कथन- I सही है तथा कथन- II गलत है

(4) कथन- I गलत है तथा कथन- II सही है

Q.5 कथन : क्लोराइड आयन का निर्माण ऊष्माक्षेपी है जबकि ऑक्साइड आयन का निर्माण ऊष्माशोषी होता है।

कारण : ऑक्सीजन की EA_2 ऊष्माशोषी होती है तथा ऑक्सीजन की ऊष्माक्षेपी EA_1 के मान से अधिक होती है।

Q.6 कथन : नाइट्रोजन की इलेक्ट्रॉन ग्रहण एन्थेल्पी धनात्मक जबकि फास्फोरस की ऋणात्मक होती है।

कारण : नाइट्रोजन का छोटा परमाणु आकार जिसके यहाँ इलेक्टॉन–इलेक्टॉन प्रतिकर्षण सम्मिलित किया जाता है तथा यह योगात्मक इलेक्ट्रॉन को आसानी से ग्रहण नहीं करता है।

Q.7 स्तम्भ सुमेलित कीजिए–

स्तम्भ-I	स्तम्भ -II
(A) I.E. का बढ़ता क्रम	(P) $F < O < S < Se$
(B) इलेक्ट्रॉन बंधुता का बढ़ता क्रम	(Q) $O < N < F < Ne$
(C) परमाणु आकार का बढ़ता क्रम	(R) $Na < Mg < Al < Si$
	(S) $O^{2-} < O^- < O < O^+$

Q.8 इलेक्ट्रॉन बंधुता का प्रथम क्रम है–

(1) $Cl > O > C > B > N$

(2) $O > Cl > C > B > N$

(3) $N > O > Cl > B > C$

(4) $Cl > N > O > B > C$

Q.9 The correct order of electron affinities is
(1) Cl > Si > Na > Ar (2) Si > Cl > Na > Ar
(3) Cl > Na > Si > Ar (4) Cl > Si > Ar > Na

Q.10 The correct order of electron affinities of Si, P and Cl is
(1) P > Si > Cl (2) Cl > P > Si
(3) Cl > Si > P (4) Si > P > Cl

Question based on Electro negativity

Q.11 Electronegativity is given by
(1) Average of first and second ionization energies
(2) Average of first and second electron affinities
(3) Average of ionization energy and electron affinity
(4) None of these

Q.12 Oxidising action increases in the following order
(1) Cl < Br < I < F (2) Cl < I < Br < F
(3) I < F < Cl < Br (4) I < Br < Cl < F

Q.13 Considering the elements F, Cl, O and N, the correct order of their electron affinity is :
(1) F > Cl > O > N (2) F > O > Cl > N
(3) Cl > F > O > N (4) O > F > N > Cl

Q.14 Aqueous solutions of two compounds M_1–O–H and M_2 – O – H are prepared in two different beakers. If, the electronegativity of M_1 = 3.4, M_2 = 1.2, O = 3.5 and H = 2.1, then the nature of two solutions will be respectively :
(1) acidic, basic (2) acidic, acidic
(3) basic, acidic (4) basic, basic

Q.9 इलेक्ट्रॉन बंधुता का सही क्रम है–
(1) Cl > Si > Na > Ar (2) Si > Cl > Na > Ar
(3) Cl > Na > Si > Ar (4) Cl > Si > Ar > Na

Q.10 Si, P व Cl की इलेक्ट्रॉन बंधुता का सही क्रम है–
(1) P > Si > Cl (2) Cl > P > Si
(3) Cl > Si > P (4) Si > P > Cl

Question based on Electro negativity

Q.11 विद्युतऋणता निम्न द्वारा दी जाती है–
(1) प्रथम व द्वितीय आयनन ऊर्जाओं के योग
(2) प्रथम व द्वितीय इलेक्ट्रॉन बंधुता के योग
(3) आयनन ऊर्जा व इलेक्ट्रॉन बंधुता के योग
(4) इनमें से कोई नहीं

Q.12 निम्न क्रम में ऑक्सीकारक क्रिया बढ़ती है–
(1) Cl < Br < I < F (2) Cl < I < Br < F
(3) I < F < Cl < Br (4) I < Br < Cl < F

Q.13 F, Cl, O व N तत्वों की इलेक्ट्रॉन बंधुता का सही क्रम है–
(1) F > Cl > O > N (2) F > O > Cl > N
(3) Cl > F > O > N (4) O > F > N > Cl

Q.14 दो यौगिकों M_1–O–H तथा M_2–O–H के जलीय विलयनों को दो अलग पात्रों में बनाया गया है। यदि M_1 = 3.4, M_2 = 1.2, O = 3.5 तथा H = 2.1, की विद्युत ऋणताऐं है, तो दोनों विलयनों की प्रकृति क्रमशः होगी –
(1) अम्लीय, क्षारीय (2) अम्लीय, अम्लीय
(3) क्षारीय, अम्लीय (4) क्षारीय, क्षारीय

1.[3] IE :B > Tl > Ga > Al > In

2.[3] Refer hint to Q.1

3.[1] Refer hint to Q.1

4.[2] $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$. in this process energy is released in form of lattice energy. Nitrogen is already stable due to half filled configuration thus addition of electron to nitrogen require absorption of energy. (endothermic process.)

5.[1] Statement I and II both are correct and statement II is correct explanation of statement I. Addition of 2^{nd} e^- is always endothermic.

6.[1] Statement I and II both are correct and statement II is correct explanation of statement I.

7.[A→Q, B→S, C→P]

8.[1] N has +ive value of EA_1.

9.[1] Noble gases have least EA.

10.[3] Cl has max EA in Periodic Table.

11.[3] $\boxed{EN = \frac{IE + EA}{2}}$

12.[4] F is strongest oxidizing halogen due to high hydration energy.

13.[3] N has least EA due to stable configuration

14.[1] More will be value of ΔEN in hydroxides, more will be polarity of bond and hence it is easily broken.

$M_1 - O - H \rightarrow MO^- + H^+$

$3.4 \leftrightarrow 3.5 \leftrightarrow 2.1$

$0.1 \quad 1.4$

$M_2 - O - H \rightarrow M^+ + OH^-$

$1.2 \leftrightarrow 3.5 \leftrightarrow 2.1$

$2.3 \quad 1.4$

21	Sc	Scandium	$(Ar)\ 4s^2\ 3d^1$
22	Ti	Titanium	$(Ar)\ 4s^2\ 3d^2$
23	V	Vanadium	$(Ar)\ 4s^2\ 3d^3$
24	Cr	Chromium	$[Ar]\ 4s^1\ 3d^5$
25	Mn	Manganese	$(Ar)\ 4s^2\ 3d^5$
26	Fe	Iron	$(Ar)\ 4s^2\ 3d^6$
27	Co	Cobalt	$(Ar)\ 4s^2\ 3d^7$
28	Ni	Nickel	$(Ar)\ 4s^2\ 3d^8$
29	Cu	Copper	$[Ar]\ 4s^1\ 4d^{10}$
30	Zn	Zinc	$(Ar)\ 4s^2\ 3d^{10}$
31	Ga	Gallium	$(Ar)\ 4s^2\ 3d^{10}\ 4p^1$
32	Ge	Germanium	$(Ar)\ 4s^2\ 3d^{10}\ 4p^2$
33	As	Arsenic	$(Ar)\ 4s^2\ 3d^{10}\ 4p^3$
34	Se	Selenium	$(Ar)\ 4s^2\ 3d^{10}\ 4p^4$
35	Br	Bromine	$(Ar)\ 4s^2\ 3d^{10}\ 4p^5$
36	Kr	Krypton	$(Ar)\ 4s^2\ 3d^{10}\ 4p^6$

Note

(8) Group (1) and (2) → s-block
(Their last e⁻ present in s-subshell)

(9) Group (13) to (18) → p-block
(Their last e⁻ present in p-subshell)
[(except ⇒ He = $1s^2$ (Noble gas)]

(10) Group (1), (2), (13) to (18) → Representative / Normal / main group elements.
↳ In representative elements outermost shell is incomplete.

eg. Mg (Z=12) = [Ne] $3s^2$ (Incomplete outermost shell)

eg. Br (Z=35) = [Ar] $4s^2$ $3d^{10}$ $4p^5$ (Incomplete outermost shell)

(11) Group (3) to (12) → d-block / transition elements

↳ In transition elements ionizing inner d-subshell is partially filled

Note:-
a) last e⁻ is decided by e⁻ configuration
b) In d-block elements last e⁻ is present inner shell

Fe (Z=26) = [Ar] $4s^2$ $3d^6$
(Inner d-subshell is partially fil

Zn (Z=30) = Ar [$4s^2$ $3d^{10}$] (fully filled)

} Zn, Cd, Hg are no transition elements

Cu = [Ar] $4s^1$ $3d^{10}$ (fully filled)

Cu^{+2} = [Ar] $4s^0$ $3d^9$ (Partially filled)

} transition elements

CAREER POINT

Target Course for NITs (JEE Main)-2014

DAILY PRACTICE PROBLEM SHEET

CHEMISTRY

Periodic Table - 3

Question based on periodic propeerties (IE, EA, EN)

Q.1 The correct order for the electronegativities of N, O, F and P is

(1) F > N > P > O (2) F > O > P > N

(3) F > O > N > P (4) N > O > F > P

Q.2 Which of the following statements is true about electronegativity ?

(1) Electronegativity of an element depends upon its effective nuclear charge

(2) Electronegativity of a cation is proportional to charge on the cation

(3) Electronegativity increases as the *s*-character in hybrid orbital increases

(4) Electronegativity of a anion is proportional to charge on the anion

Q.3 The ground state electronic configurations of some elements, P, Q, R, S and T (these symbols represent the some of the known elements given in the periodic table) are as follows.

P : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

Q : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

R : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

S : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

T : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$.

Match the electronic configurations of the elements with the properties given below and select the correct sequence by choosing the correct codes given.

(1) Element forms a cation which is isoelectronic with P^{3-}.

(2) Element which in its compounds can show a maximum oxidation state of +6.

(3) Element has largest atomic radius and highest first ionisation energy in the respective period.

(4) Element which has intermediate value of electronegativity and its oxide forms salts with strong acids and bases.

(1) QRTP (2) QSTR

(3) QRST (4) PQRS

Question based on periodic propeerties (IE, EA, EN)

Q.1 N, O, F व P का विद्युत ऋणता के लिए सही क्रम है–

(1) F > N > P > O (2) F > O > P > N

(3) F > O > N > P (4) N > O > F > P

Q.2 निम्न में से विद्युत ऋणता के बारे में कौनसे कथन सही है ?

(1) तत्व की विद्युत ऋणता, इसके प्रभावी नाभिकीय आवेश पर निर्भर करती है।

(2) धनायन की विद्युत ऋणता, धनायन पर उपस्थित आवेश के समानुपाती होती है।

(3) संकर कक्षक में *s*-लक्षण बढ़ने पर विद्युत ऋणता बढ़ती है।

(4) ऋणायन की विद्युत ऋणता, ऋणायन पर उपस्थित आवेश के समानुपाती होती है।

Q.3 P, Q, R, S व T कुछ तत्वों का आद्य अवस्था इलेक्ट्रॉनिक विन्यास (यह संकेत आवर्त सारणी में दिए गए कुछ ज्ञात तत्वों को प्रदर्शित करते हैं) निम्न प्रकार है–

P : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

Q : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

R : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

S : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

T : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$.

नीचे दिए गए लक्षणों के साथ तत्वों के इलेक्ट्रॉनिक विन्यास का मिलान करिए तथा दिए गए सही कोडों को चुनकर सही क्रम बताइए–

(1) तत्व एक धनायन निर्मित करता है जो P^{3-} के साथ समइलेक्ट्रॉननिक है।

(2) तत्व जिसमें इसके यौगिक अधिकतम +6 ऑक्सीकरण अवस्था दर्शा सकते है।

(3) तत्व अधिकतम परमाण्विय त्रिज्या तथा सापेक्ष आवर्त में उच्चतम प्रथम आयनन ऊर्जा रखता हैं।

(4) तत्व जो विद्युत ऋणता का मध्यवर्ती मान रखता है तथा इसके ऑक्साइड प्रबल अम्लों व क्षारों के साथ लवणों का निर्माण करते हैं।

(1) QRTP (2) QSTR

(3) QRST (4) PQRS

Q.4 The properties which are common to both groups 1 and 17 elements in the periodic table are :
(1) metallic character increases down the groups.
(2) reactivity decreases from top to bottom in groups.
(3) atomic radii increases as the atomic number increases.
(4) electronegativity decreases on moving down a group.

Q.5 Which of the following statement is incorrect ?
(1) Oxide of aluminium (Al_2O_3), and arsenic (As_2O_3) are amphoteric
(2) Oxide of chlorine (Cl_2O_7) is less acidic than oxide of nitrogen (N_2O_5)
(3) Oxide of carbon (CO_2) is more acidic than oxide of silica (SiO_2)
(4) The correct increasing order of basic character of various oxides is $H_2O < CuO < MgO < CaO$

Q.6 The ground state electronic configurations of the elements, *U, V, W, X* and *Y* (these symbols do not have any chemical significance) are as follows :

U $1s^2\,2s^2\,2p^3$
V $1s^2\,2s^2\,2p^6\,3s^1$
W $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$
X $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^2$
Y $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6$

Determine which sequence of elements satisfy the following statements :
(i) Element forms a carbonate which is not decomposed by heating
(ii) Element is most likely to form coloured ionic compounds
(iii) Element has largest atomic radius
(iv) Element forms only acidic oxide

(1) *VWYU* (2) *VXYW*
(3) *VWYX* (4) *VXWU*

Q.4 वह गुण जो आवर्त सारणी में ... तत्वों में समान है।
(1) समूह में नीचे जाने पर धात्विक लक्षण बढ़ते है।
(2) समूह में ऊपर से नीचे जाने पर क्रियाशीलता ... होती है।
(3) परमाणु क्रमांक बढ़ने पर परमणु त्रिज्या ... बढ़ती है।
(4) समूह में नीचे जाने पर विद्युत ऋणता ... होती है।

Q.5 निम्न में से कौनसा कथन गलत है ?
(1) एल्यूमिनियम तथा आर्सेनिक के ऑक्साइड उभयधर्मी होते है
(2) क्लोरीन का ऑक्साइड, नाइट्रोजन के ऑक्साइड से कम अम्लीय होता है।
(3) कार्बन के ऑक्साइड, सिलिका के ऑक्साइड से अधिक अम्लीय होता है।
(4) ऑक्साइडो के क्षारीय लक्षण का बढ़ता हुआ सही क्रम $H_2O < CuO < MgO < CaO$ है।

Q.6 *U, V, W, X* व *Y* तत्वों का आद्य अवस्था में इलेक्टॉनिक विन्यास (ये संकेत कोई रासानिक महत्व नहीं रखते हैं) निम्न प्रकार है–

U $1s^2\,2s^2\,2p^3$
V $1s^2\,2s^2\,2p^6\,3s^1$
W $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$
X $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^2$
Y $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6$

निम्न कथनों में से जो तत्वों का क्रम संतुष्ट करता है ज्ञात कीजिए–
(i) तत्व कार्बोनेट निर्मित करते है जो ऊष्मा द्वारा विघटित नहीं होते है।
(ii) तत्व समान रूप से अधिक रंगीन आयनिक यौगिकों को निर्मित करते है।
(iii) तत्व अधिकतम परमाण्विय त्रिज्या रखते है।
(iv) तत्व केवल अम्लीय ऑक्साइड बनाते है।

(1) *VWYU* (2) *VXYW*
(3) *VWYX* (4) *VXWU*

Q.7 (1) (2 (3 (

Q.8 (

Q.9

C

Q.7 Which of the following statement is wrong ?
(1) Vanderwall radii of iodine is more than its covalent radii
(2) IE_1 of N is higher than that of O while IE_2 of O is higher than that of N
(3) All isoelectronic species belong to same period of periodic table
(4) The electron affinity of N is less than that of P

Q.8 Which of the following statement are correct -
(1) the elements like F,Cl, Br, O etc having high values of electron affinity act as strong oxidising agent
(2) the element having low value of ionization energies act as strong reducing
(3) Formation of $S^{2-}_{(g)}$ is an endothermic process
(4) All of these

Q.9 Which of the following order is incorrect -
(1) $HF < HCl < HBr < HI$: order of acidic character
(2) $O < O^- < O^{2-}$: order of EN
(3) $HF < HCl < HBr < HI$: order of covalent character
(4) $Ca^{2+} < K^+ < S^{2-}$: order of size

Q.10 Select the correct statements -
(1) The first I.E. of Na is less than first IE of Mg
(2) the third I.E. of Mg is greater than the third I.E. of Al
(3) The $I.E_1$ of Al is less than $I.E_1$ of Mg
(4) The $I.E_2$ of Mg is greater than $I.E_2$ of Na
(1) Only (1) (2) (1) and (3)
(3) (1), (2) and (3) (4) (1), (2) and (4)

Q.7 निम्न में से कौनसा कथन गलत है ?
(1) आयोडिन की वाण्डरवाल त्रिज्या, इसकी सहसंयोजक त्रिज्या से अधिक होती है
(2) N की IE_1, O से उच्च जबकि O की IE_2, N से उच्च होती है
(3) सभी समइलेक्ट्रॉनी प्रजाति, आवर्त सारणी के समान आवर्त से सम्बन्धित होते है
(4) N की इलेक्ट्रॉन बंधुता P से कम होती है

Q.8 निम्न में से कौनसा कथन सही है -
(1) उच्च इलेक्ट्रॉन बंधुता के मान युक्त F,Cl, Br, O तत्व प्रबल ऑक्सीकारी की तरह कार्य करते है
(2) न्यून आयनन ऊर्जाओं युक्त तत्व प्रबल अपचायक की तरह कार्य करते है
(3) $S^{2-}_{(g)}$ का निर्माण, एक ऊष्माशोषी प्रक्रम होता है
(4) उपर्युक्त सभी

Q.9 निम्न में से कौनसा क्रम गलत है -
(1) $HF < HCl < HBr < HI$: अम्लीय प्रकृति का क्रम
(2) $O < O^- < O^{2-}$: विद्युतऋणता का क्रम
(3) $HF < HCl < HBr < HI$: सहसंयोजक लक्षणों का क्रम
(4) $Ca^{2+} < K^+ < S^{2-}$: आकार का क्रम

Q.10 सही कथन चुनिए -
(1) Na का प्रथम I.E., Mg के प्रथम I.E. से कम है
(2) Mg का तृतीय I.E., Al के तृतीय I.E. से अधिक है
(3) Al की $I.E_1$, Mg के $I.E_1$ से कम है
(4) Mg की $I.E_2$, Na की $I.E_2$ से अधिक है
(1) (1) केवल (2) (1) व (3)
(3) (1), (2) व (3) (4) (1), (2) व (4)

1.[3] F, O, N are most EN elements with EN 4, 3.5 and 3 respectively.

2.[1,2,3] EN decreases with increase in –ve charge

3.[2] "Q" $4s^1$ will form $Q^+ = [_{18}Ar]$ & this will be isoelectronic with $_{15}P^{3-}$ $(Q = _{19}K)$

> "S" $3d^5, 4s^1$ can loose $6e^-$ $(S = _{24}Cr)$

> "T" $4p^6$ has largest radius (r_{van}) & highest IE_1

> "R" $3p^1$ is A1 and its oxide is amphoteric

4.[1,3,4] Reactivity increase down the group due to decrease in I.E.

5.[2] Acidic character of oxide increases towards right in periodic table.

6.[2] V^{3s^1} is Na & Na_2CO_3 is thermally stable

> $X^{3d^5,4s^2}$ is Mn. Transition elements are expected to form coloured compounds.

> Y^{4p^6} is noble gas and r_{van} is determined for it.

> W^{3p^2} = Si. SiO_2 is acidic

7.[3] Na^+ belong to 3^{rd} period & F^- belong to 2^{nd} period.

8.[4] EA_2 is endothermic

9.[2] EN increases with increase in +ive charge.

10.[3] Na^+ has configuration of Ne & Mg^+ has configuration of Na

(12) All elements after $_{82}Pb$ are radioactive.

(13) All elements after $_{92}U$ are transurane. These are man-made or synthetic

(13) & $_{43}Tc$ and $_{61}Pm$ are also man-made

(14) Lanthanoids (58-71) (Rare earth metal) and Actinoids (90-103) Radioactive } f-block / Inner transition elements.

→ In inner transition elements inner f-subshell is partially filled.

(15) $_{57}La$ and $_{89}Ac$ are member of d-block but they have properties similar to f-block.

☆ Prediction of period, block and group of an elements —

Period :→

Atomic number	Period No.
1 - 2	I
3 - 10	II
11 - 18	III
19 - 36	IV
37 - 54	V
55 - 86	VI
87 onwards	VII

Block → Name of subshell in which last electron present → called as block of element

eg. Z = 31, IV period ; [Ar] $4s^2 3d^{10} 4p^1$; p-block

~~Z = 40, V period~~ ;

Z = 40, V period ; [Kr] $5s^2, 4d^2$, d-block

* $\left.\begin{matrix} 58 - 71 \\ \text{and} \\ 90 - 103 \end{matrix}\right\}$ f-block elements

* Group :-

(a) s-block :-

Group No. = No of $ns e^-$ (n = outermost shell)

eg. Z = 20 IV period ; [Ar] $4s^2$, s-block , Group 2

(b) p-block elements :-

Group no → $(ns + np) e^- + 10$

eg Z = 16, III period [Ne] $3s^2 4p^4$, p-block; Group 16

(c) d-block :-

Group No. = [No of $(n-1)d$] e^-

eg → Z = 24, IV period, [Ar] $4s^2 3d^4$, d-block, Group 6

$ns (n-1)d$

Date
Page

d) f-block

Group no = I / II B

Note:- Group I have maximum elements (32)

Q4.) Predict period, block and group of following elements:

Z = 14 ⇒ [Ne] $3s^2 3p^2$, p-block , III period, group = 14

Z = +1 ⇒ [Kr] $5s^2 4d^1$, V period,

Z > 102 ⇒ f-block elements, VII period, Groups I

☆ Quantum no for last e^- of an element :—

n = 4 , l = 2 , m = +1 , s = $+\frac{1}{2}$

Predict period and block of element :—

Ans :-

4d

↳ d block

Period - V

l = 0 ⇒ s
l = 1 ⇒ p
l = 2 ⇒ d
l = 3 ⇒ f

Q5.) Period no of $_{92}U^{238}$ is III B predict Period no. of new element which is formed after removal of α-particle.—

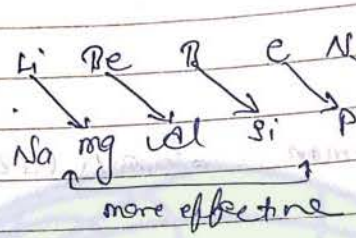
Ans → $_{92}U^{238} \longrightarrow {}_{90}M^{234} + {}_{2}He^{4}$

Actinoid

III B

α-particle

(1) ✡ Diagonal Relationship



(2) classification of elements into blocks :-

s-blocks :-

There general outermost shell e- configuration is ns^{1-2} ↳ outermost shell/ Valence shell

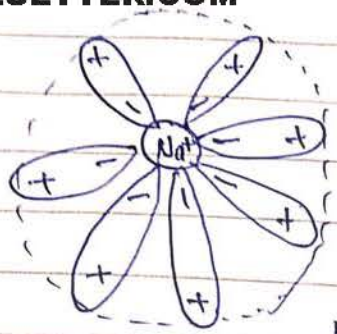
Group (1)			Group (2)		
हाइड्रोजन को छोड़कर सभी क्षार धातु हैं	$_1H \rightarrow +1/-1$	$1s^1$	बेरा मैग्नेशियम कार्बन स्ट्रोंटियम बेरियम रेडियम	$_4Be$	$2s^2$
	$_3Li$	$2s^1$		$_{12}Mg$	$3s^2$
	$_{11}Na$	$3s^1$		$_{20}Ca$	$4s^2$
	$_{19}K$	$4s^1$		$_{38}Sr$	$5s^2$
	$_{37}Rb$	$5s^1$		$_{56}Ba$	$6s^2$
	$_{55}Cs$	$6s^1$		$_{88}Ra$	$7s^2$
	$_{87}Fr$	$7s^1$			
	(+1) alkali metal		(+2) alkaline earth metal		

✡ Hydration :-

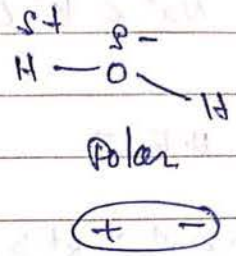
(I) Formation of bond b/w ion and water molecule is called as Hydration.

(II) During this process some energy is released called as Hydration energy (H.E)

$$Na^+(g) + H_2O \xrightarrow{\text{Hydration}} Na^+(aq) + H.E$$

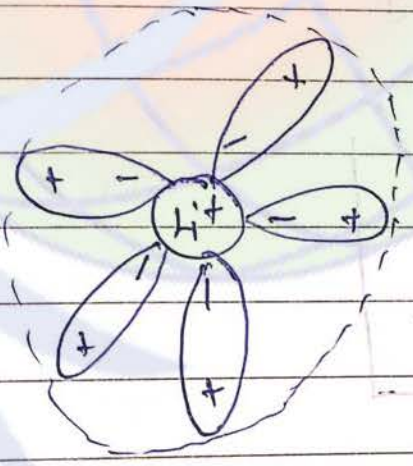


Hydrated ion
or
$Na^+(aq)$



$\Rightarrow$ Hydration of Anion is also possible

$H.E \propto \frac{1}{\text{size of anion}} \propto$ Hydrated radius



size of ion ↓

H.E ↑

Hydrated radius ↑

(i) order of radius :-

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

(ii) order of H.E →

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

(iii) order of Hydrated radius

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

Q) which ion has highest H.E ?

(a) F^- (b) Cl^- (c) Br^- (d) I^-

(iv) Drop

Ionic conductivity or Ionic mobility $\propto \frac{1}{\text{size of ion.}}$

☆ size depends on medium →

order of Ionic conductivity :-

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

Q) Arrange in order of ionic conductivity -

$LiCl_{(aq)} < NaCl_{(aq)} < KCl_{(aq)}$

02) Which ion has highest conductivity in aqueous medium?

(a) Ba^{+2}
(b) Mg^{+2}
(c) Ca^{+2}
(d) Be^{+2}

★ P-block elements →

Their general outermost shell e⁻ configuration is $ns^2 np^{1-6}$

Group 13	Group 14	Group 15
B-family	C-family	N-family
$ns^2 np^1$	$ns^2 np^2$	$ns^2 np^3$
(valency = 3)	(valency = 4)	(valency = 5)
बोरॉन B	कार्बन C	नाइट्रोजन N
आल्म Al	सिलिकन Si	फास्फोरस P
गैलियम Ga	जर्मेनियम Ge	आर्सेनिक As
इन In	टिन Sn	एन्टीमनी Sb
थैलियम Tl	पर्मेनियम Pb	बिस्मथ Bi

Group 16	Group 17	Group 18
O-family	Halogen family	Noble gas family
$ns^2 np^4$	$ns^2 np^5$	$ns^2 np^6$
valency = 6	(valency = 7)	valency = 8
ऑक्सीजन O	F	He
सल्फर S	Cl	Ne
सेलेनियम Se	Br	Ar
टेलीरियम Te	I	Kr
पोलोनियम Po	At (Astatine	Xe
		Rn

✡ Inert pair effect →

(I) It explains stability of the O.S in p-block

(II) Negligence of nse⁻ to participate in bonding is called as Inert pair effect

(III) There are two the O.S in p-block —

+N and +(N-2)

[N = valence e⁻]

← Anomalous behaviour of p-block ★

B-family →	+3,	+1
C-family →	+4,	+2
N-family →	+5,	+3

↓ To achieve Noble gas configuration

→ To show Inert pair effect

(IV) As we move down the group after removal of npe⁻ removal of nse⁻ become more difficult Hence stability of higher oxidation state decrease and stability of lower O.S Increase

(chance of Inert Pair effect Increases)

Eg →

$Ga^{+3} > In^{+3} > Tl^{+3}$

$Ge^{+4} > Sn^{+4} > Pb^{+4}$

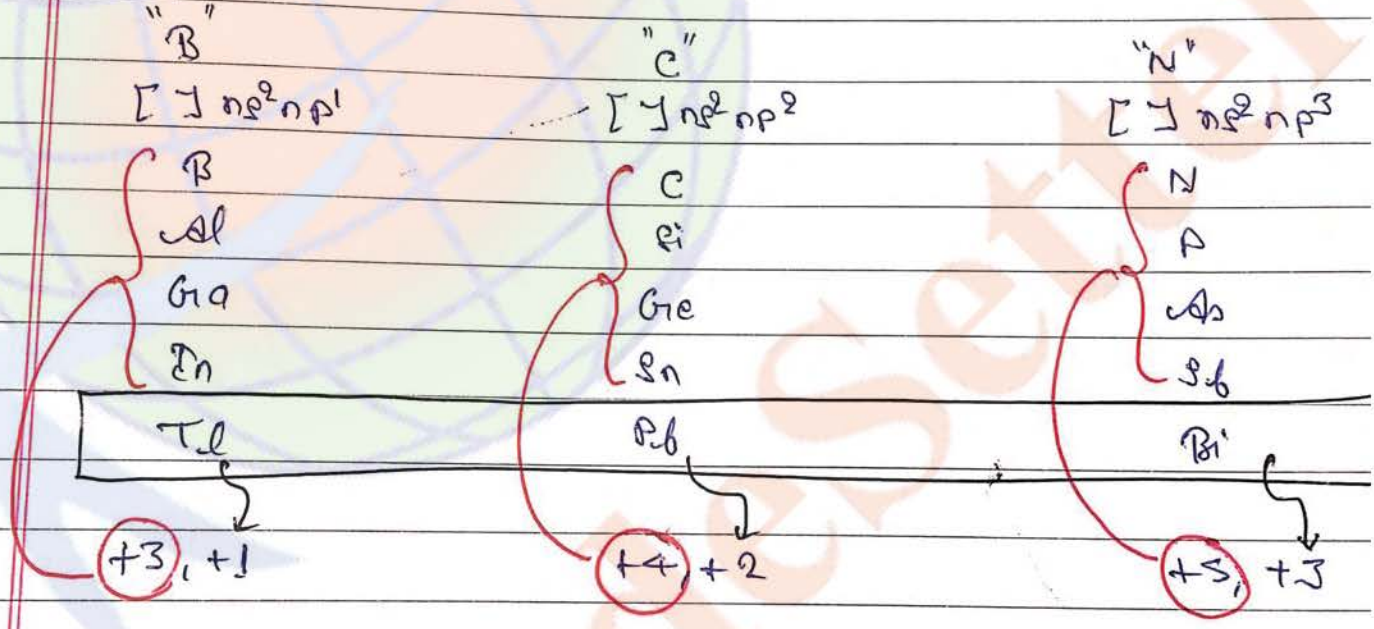
$Ga^{+} < In^{+} < Tl^{+}$

$Ge^{+2} < Sn^{+2} < Pb^{+2}$

(v) Inert pair effect is mainly applicable for last element of group

$Tl^{+} > Tl^{+3}$
$Pb^{+2} > Pb^{+4}$
$Bi^{+3} > Bi^{+5}$
} Inert pair effect

$Si^{+2} < Si^{+4}$
$Sn^{+4} > Sn^{+2}$
$As^{+3} < As^{+5}$
$Al^{+2} < Al^{+1} < Al^{+3}$



Q.] ~~Bi(5)~~ Bi(5) is stable while Bi(3) is unstable why?

Sol] Due to Inert pair effect.

Q.] Tl^{+3} is good O.A why?

Sol] Ti^{+3} $\xrightarrow{\text{Reduction}}$ Ti^{+1}
[O.A]

(3) Pb^{+4} ei good O.A why?

So/n Pb^{+4} $\xrightarrow{\text{Reduction}}$ Pb^{+2}

[O.A]

(4) Sn^{+2} ei good R.A why?

So/n Sn^{+2} $\xrightarrow{\text{oxidation}}$ Sn^{+4}

(R.A)

Q5.)

$TlI_3 \rightarrow Tl^{+3} + I^-$

$TlI_3 \rightarrow Tl^{+1} + I_3^-$ ⇌

1) These elements are mainly classified in d-block series

2) Their General outermost shell e⁻ configuration is $ns^{1-2}(n-1)^{1-10}$

3) 3d - series / 1st transition series →
(21-30)

21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$4s^2$ $3d^1$	$3d^2$	$3d^3$	$3d^5$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^{10}$	$3d^{10}$

[Ar] $4s^1 3d^5$ [Ar] $4s^1 3d^{10}$

4) 4d series / IInd transition series —
(39-48)

आरी जरा निमा मौत तक सकावट राह में पड़े तो आगा में बढ़ जा

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
↓		↓			↓	↓			
Yttrium		Niobium			Ruthenium	Rhodium			

5) 5d-series / IIIrd transition series —
(57, 72-80)

ला हफ्ता वरना है खट खट पिटाई और होगी

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
		↓		↓					
		Tantalum		Renium					

Pd = [Kr] $5s^0 4d^{10}$ (diamagnetic)

Diamagnetic → when all e⁻ are paired

Paramagnetic → when any e⁻ is unpaired

magnetic moment (μ or μ_s) = $\sqrt{n(n+2)}$ B.M

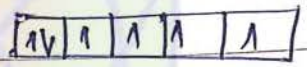
spin only

$n = 1$, $\mu_s = \sqrt{3} \approx 1.73$

$n = 2$, $\mu_s = \sqrt{8} \approx 2\sqrt{2} = 2.83$

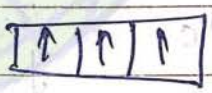
$n = 3$, $\mu_s = \sqrt{15} \approx 3.9$

Fe (Z = 26) = [Ar] $4s^2 3d^6$



$n = 4$, $\mu_s \approx 4.9$

N (n = 7) = [He] $2s^2 2p^3$



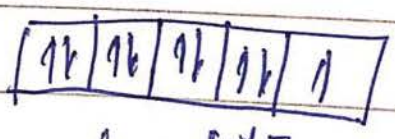
$n = 3$, $\mu_s = 3.9$

Fe^{+3} (Z = 26) = [Ar] $4s^0 3d^5$

$n = 5$, $\mu_s = 5.9$

$CuSO_4$

$Cu^{+2} \rightarrow [Ar] 4s^0 3d^9$



$n = 1$, $\mu_s = 1.73$

Q1) which of the following ions has highest magnetic moment

a) Cr^{+3}, b) Fe^{+3} c) Mn^{+3} d) V^{+3}

Sol/n (a) Cr^{+3} $3d^2$ (3)

(b) Fe^{+3} $3d^5$ (5)

(c) $3d^4$ (4)

(d) $3d^2$ (2)

Q2) which comp. is diamagnetic?

(a) $CuSO_4 \cdot 5H_2O$

(b) $MnSO_4 \cdot 5H_2O$

(c) $FeSO_4 \cdot 5H_2O$

(d) $ZnSO_4 \cdot 5H_2O \rightarrow 3d^{10}$

Q3) which comp of Vanadium has magnetic moment 1.7 J

a) VO

b) VCl

c) VCl_2

d) VO_2

Sol/n $\mu_s = 1.7$ J

$n = 1$

$V(Z=23) = [Ar]\ 4s^2\ 3d^3$

$V^{+4} = [Ar]\ 4s^0\ 3d^1$

(a) $V^{+2}O$

(b) V^{+4}

(c) $V^{+3}d_2$

(d) $V^{+4}O_2$

Q4) An unknown ion M^{+x} ($Z=26$) has magnetic moment $2\sqrt{6}$ calculate No of unpaired e^-'s and possible value of "x".

a) 4, 1, (b) 1, 4, (c) (4, 2), (d) 2, 4

Sol/n

Sol $_{46}$Pd $= [Kr]\, 4d^{10}$

$n = 4$

$n(Z=26) = [Ar]\, 4s^2\, 3d^6$

$n+2 = [Ar]\, 4s^0\, 3d^{10}$

✡ f-Block elements →

$_{57}La = [Xe]\, 6s^2\, 5d^1$

$\therefore$ Lanthanoids ($_{58}$-$_{71}$) $= [Xe]\, 4f^{0-14}\, 6s^2\, 5d^{0-1}$

(4f-series)

$_{89}Ac = \otimes [Rn]\, 7s^2\, 6d^1$

$\therefore$ Actinoids (90-103) $= [Rn]\, 7s^2\, 6d^{0-1}\, 5f^{1-14}$

(5f series)

Their general outermost shell e⁻ configuration is

$$\boxed{ns^2(n-1)d^{0-1}(n-2)f^{1-14}}$$

Lanthanoids ($_{58}$-$_{71}$)

सीरे	Ce	Cerium
पर	Pr	Praseodymium
नरियाँ	Nd	Neodymium
प्रेम की	Pm	Promethium
समाहि	Sm	Samarium
यूँ ही	Eu	Europium
गद गद	Gd	Gadolinium

बब	Tb	Tebium
सिल	Dy	Dysprosium
हुया	Ho	Holium
अौट	Er	Erbium
ढुम	Tm	Thullium
अब	Yb	Ytterbium
लैटे	Lu	Lutetium

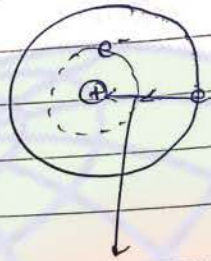
Actinoids (90-103)

थोरै	Th	Thorium
पापड़	Pb	Protactinium
यूँ	U	Uranium
नापो	Np	Neptunium
पुराने	Pu	Plutonium
आम	Am	Americium
कम	Cm	Curium
बिकेंगे	Bk	Berkelium
कैफे में	Cf	Californium
ऐसे	Es	Einsteinium
फरमा ओ	Fm	Fermium
मैंडम	Md	Mendelevium
नाश्ता	No	Nobelium
लाओ	Lr	Lawrencium

Cause of Reversal ↓

1) Screening effect / shielding effect →

1) The Repulsion produced by all inner e⁻ on outermost e⁻.



→ (Repulsion produced by inner e⁻'s (Screening effect)

Attraction from nucleus.

2) Order of screening produced by various e⁻.

s > p > d > f

0 > ∞ > ∮ > ⋯

2) Effective nuclear charge :-

It is the net attraction produced by nucleus on outermost e⁻,

$Z_{eff} = Z - \sigma$

σ → Screening coefficient

Z → Nuclear charge or No of Proton or Atomic no.

Z_{eff}

$I.E \propto Z_{eff}$

Calculation of σ (Slater's rule) →

1) for outermost $e^- \rightarrow 0$
2) for outer ns and np $e^- \rightarrow 0.35$
3) for (n-1)s and (n-1)p $e^- \rightarrow 0.85$
4) for other $e^- \rightarrow 1$

1) Li $(Z=3) \Rightarrow \underbrace{1s^2}_{(n-1)s} \underbrace{2s^1}_{ns}$

$\sigma = 0 + 2\times0.85 = 1.70$

$Z_{eff} = 3 - 1.70 = 1.30$

2) $B (Z=5) = \underbrace{1s^2}_{(n-1)s} \underbrace{2s^2\ 2p^1}_{ns \text{ and } np}$

$\sigma = 0 + 2\times0.35 + 2\times0.85$

$= 2.40$

3) $O (Z=8) = \underbrace{1s^2}_{(n-1)s} \underbrace{2s^2\ 2p^4}_{ns \text{ and } np}$

$\sigma = 0 + 5\times0.35 + 2\times0.85$

$= 3.45$

$Z_{eff} = 8 - 3.45 = 4.55$

Note:- As we move from left to right in a period Z_{eff} is the main cause of periodicity along the period.

(4) $Na\ (Z=11) = 1s^2\ 2s^2\ 2p^6\ 3s^1$

(other) (n-1)s (n-1)p ns

$= 0 + 8 \times 0.85 + 2 \times 1 = 8.80$

$Z_{eff} = 11 - 8.80 = 2.20$

(5) $K\ (Z=19) = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

other (n-1)s (n-1)p n

$= 0 + 8\ (0.85) + 10 \times 1$

$= 6.80 + 10$

$= 16.80$

$Z_{eff} = 19 - 16.80$

$= 2.20$

1) Elements in a group generally have simila Zeff. Hence along the group main cause of periodicity is increasment in no. of shell.

3) Atomic Radius

Atomic radius of an element can not be determined because atom never exist in free state

Atomic radius is always determined in bonded state.

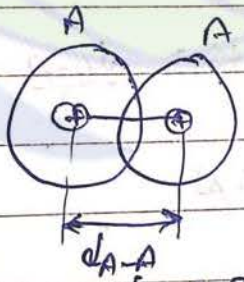
Type of radius —

1) Co-valent radius (r_c)

(a) such type of radius is determined when an atom form single co-valent bond with "similar atom"

eg) N_2, F_2, Cl_2, Br_2, I_2, N_2O_2, N_2H_4 etc

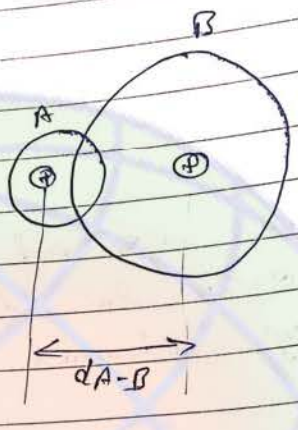
$N-O-O-N$, H_2N-NH_2



d_{A-A} → Internuclear distance or Bond length

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

(b) Bond length of covalent bond is present b/w two different atoms.



$d_{A-B} = r_A + r_B - 0.09 (\Delta E.N)$: A°

(Bond length) (Schomaker - Stevenson formula)

r_A = covalent radius of A = $\frac{d_{A-A}}{2}$

r_B = covalent radius of B = $\frac{d_{B-B}}{2}$

$\Delta E.N$ = difference in E.N

Q.) Calculate bond length of HCl, Bond length of H_2 and Cl_2 are 4A° and 20A° respectively

$\Delta E.N = 0.9$

Ans $d_{H-Cl} = r_H + r_{Cl} - 0.09 (\Delta EN)$

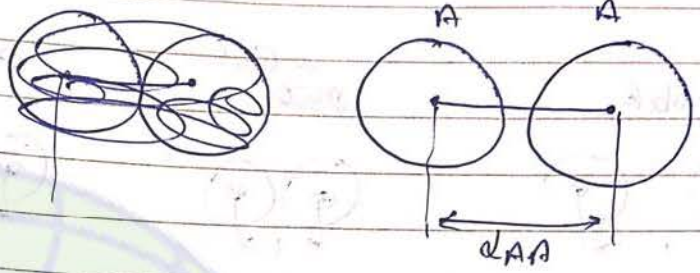
$= 2 + 10 - 0.09(0.9)$

$= 12 - 0.081$

$= 11.919$ A°

2) metallic radius (r_m) :-

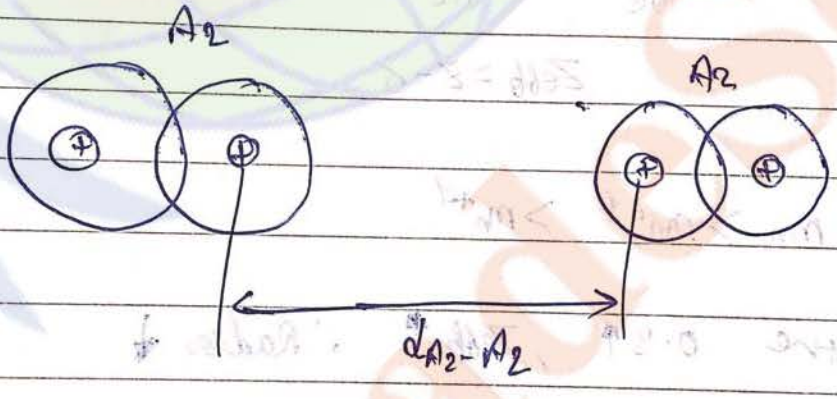
It is calculated when atoms are bonded with metallic bond.



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

3) vandercoalls radius (r_v)

When molecule are bonded with vande. walls force of attacts.

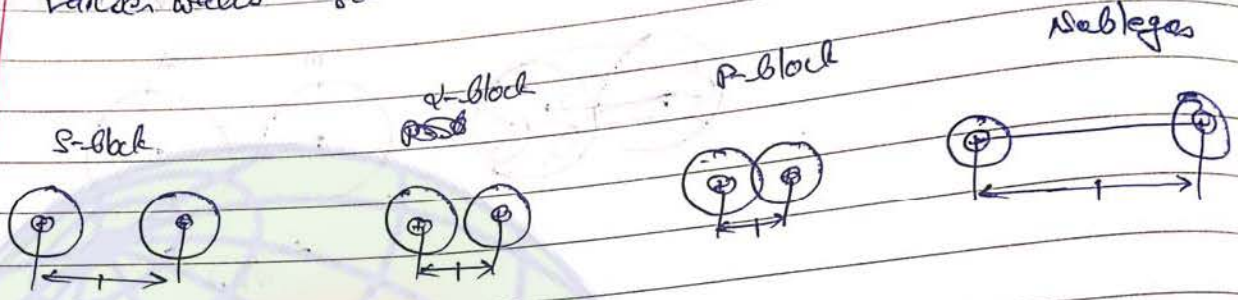


$$r_v = \frac{d_{A_2-A_2}}{2}$$

$$r_v > r_m > r_c$$

Note

1) Noble gas are monoatomic molecule, bonded with vander wells force of attraction hence for noble gas vander wells radius is calculated.



(4) Ionic Radius →

(a) Cation is always smaller than parent atom because cation has greater Zeff than parent atom.

(Zeff ↑) $Na^{\oplus}$ < Na

11p 11p

10e⁻ 11e⁻

$Z_{eff} = Z - \sigma$

$Mn > Mn^{+4} > Mn^{+7}$

more O.S ↑, Zeff ↑, Radius ↓

$K_2Cr_2O_7$ < $CrCl_3$

(b) Anion is always larger than parent atom because anion has lower Zeff than parent atom.

Cl < Cl^- (Zeff ↓)

17p 17p

17e⁻ 18e⁻

$Z_{eff} = Z - \sigma$

$O < O^- < O^{-2}$

-ve OS ↑ , Zeff ↓ , Radius ↑

H_2O_2 < H_2O^{-2}

$O^+ < O < O^- < O^{-2}$

$I^- > I > I^+$

Isoelectronic species

1) Atoms, molecules or Ions having similar no of electrons.

eg Si , N_2, CO , CN^- , NO^+

14e 14e⁻ 14e⁻ 14e⁻ 14e⁻

eg) Ne NH_3 H_3O^+ CH_3^-

10e⁻ 10e⁻ 10e⁻ 10e⁻

2) Order of radius in monoatomic Isoelectronic species—

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

7p 8p 9p 10p 11p 12p 13p

10e⁻ 10e⁻ 10e⁻ 10e⁻ 10e⁻ 10e⁻ 10e⁻

Z ↑, σ → constant, Zeff ↑, Radius ↓

$P^{-3} > S^{-2} > Cl^- > Ar > K^+ > Ca^{+2}$

Periodicity in atomic radius :-

(a) ↓ : No of shell ↑ , Radius ↑

(नीचे जाने पर)

$Li < Na < K < Rb < Cs$

(b) exception :- due to lanthanoid contraction (in d-block)

(c) exception :- $Al > Ga$ ($Al \approx Ga$)

Due to poor screening of 3d electron's "Ga" has greater Z_{eff} than Al

$_{13}Al = [Ne]\ 3s^2 3p^1$

↓ IP ↓ IE⁻

$_{31}Ga = [Ne]\ 3s^2 3p^6 4s^2 3d^{10} 4p$

↓ 18 P ↓ 18e⁻ 2e⁻ 8 + 6e P + 2e⁻ 8

(Poor screening effect)

b) In periods :-

(a) ⟶ , Zeff ↑ , Radius ↓

(except noble gas)

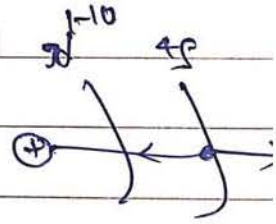
Li > Be > B > C > N > O > F < < Ne

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

(b) Code of Radius in 3d-series

Sc > Ti > V > Cr > Mn > Fe ≃ Co ≃ Ni < Cu < Zn

1.64 Å 1.70 Å



Exception →

As we move from Sc to Zn one proton is successively added to nucleus Hence Nuclear charge is increases and one e⁻ is successively added to same 3d subshell Hence screening effect also increase.

In starting element nuclear charge is dominating while in last elements screening effect is dominating

Radius of Ions

If all Ions have similar charge then their order of radius is similar as their parent atoms.

eg $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

$F^- < Cl^- < Br^- < I^-$

$Na^+ > Mg^+ > Al^+$

Q) Arrange the following in order of radius

a) Na^+, Mg^+, Al^{+3}

$10e$, $10e^-$, $10e^-$

$Na^+ > Al^{+3}$

$Na^+ > Mg^+$

b) N^{-3}, O^-, F^-

$10e^-$, $9e^-$, $10e^-$

$N^{-3} > F^-$

$O^- > F^-$

c) K^+, Be^{+2}, Ca^{+2}, Mg^{+2}, Rb^+

Be^{+2}

Mg^{+2}

K^+ Ca^{+2}

Rb^+

$K^+ > Ca^{+2}$

$Be^{+2} < Mg^{+2} < Ca^{+2}$

$K^+ < Rb^+$

Q) Which order of radius is correct?

(A) C < O < F < Cl < Br

(B) F < C < O < Cl < Br

(C) F < O < C < Cl < Br

(D) F < O < C < Br < Cl

C O F
Cl
Br

F < Cl < Br
C > O > F

Note (1) Smallest element is "H" / (on No 2 → F)
(2) Except noble gas, largest element is Fr (on N 2 → Cs)
(3) Smallest cation is H^+
(4) Largest cation is Cs^+
(5) Smallest anion is H^-
(6) Largest anion is I^-

Lanthanoid Contraction (लैंथेनाइड संकुचन)

(1) In Lanthanoid series as atomic no increases radius decreases it is called as Lanthanoid Contraction,

$$_{57}La > (_{58}Ce > Pr > Nd > \cdots > {}_{71}Lu)$$

$$_{57}La^{+3} > (Ce^{+3} > Pr^{+3} > Nd^{+3} > \cdots > {}_{71}Lu^{+3})$$

2) Cause →
As we move from Ce to Lu one (1) proton is successively added to Nucleus. Hence nuclear charge increase

and one e^- is successively added to inner 4f subshell.

f-e$^-$'s produce negligible screening Hence "σ" remains almost constant and Z_{eff} increases. (due to poor screening by 4f e$^-$s)

$$Z_{eff} = Z - \sigma$$
$$\uparrow \quad \uparrow \quad \leftrightarrow$$

(3) Effect of Lanthanoid contraction is also present from $_{72}Hf$ to $_{82}Pb$

Due to this effect these elements have greater Z_{eff} than expected ~~effect~~ it is due to poor screening by 14 e$^-$s in 4f subshell.

	3	4		13	14
1					
2				B	C
3				Al	Si
4	Sc	Ti	3d	Ga	Ge
5	Y	Zr	4d	In	Sn
6	La	Hf ($_{72}$)	5d	Tl	Pb ($_{82}$)
7					

$$_{71}Lu = [Xe]\,6s^2\,5d^1\,4f^{14}$$

$Z_{eff} > Z - \sigma$

↑ more than expected ; ↑ as expected ; ← less than expected.

Date
Page

Size of radius along the group:-

d-block :-

4d series ≈ 5d-series (Zeff high)

Y < La (No lanthanoid contraction)

P-block :-

In ≈ Tl

Sn ≈ Pb

☆ Ionization energy (I.E.) / Ionization potential (I.P.) / Ionization enthalpy.

(i) It is the energy required to remove an e⁻ from outermost shell of an isolated (free gaseous atom.

(ii) This process is endothermic ($\Delta H = +ve$)

* Endothermic → Energy/heat is required or absorbed.

$$A + x \longrightarrow B + C \; ; \; \Delta H = +x$$

* Exothermic :→ Energy/heat is released.

$$A \longrightarrow B + C + y \; ; \; \Delta H = -y$$

Now

$M(g) + I.E \longrightarrow M^+(g) + e^-$, $\Delta H = +I.E$

[$Na^+(g) + x \longrightarrow Na^+(g) + e^-$, $\Delta H = +x$]

I.E of $Na = x$

[I.E of $Mg^+ = y$

$Mg^+(g) + y \longrightarrow Mg^{+2}(g) + e^-$: $\Delta H = +y$

Factors affecting I.E :-

1) Zeff :

I.E $\propto$ Zeff

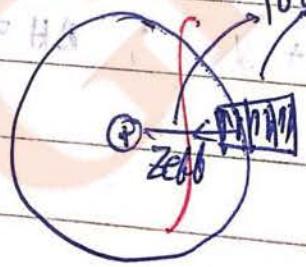
2) At size : (No. of shell)

I.E $\propto \frac{\text{No. of shell}}{\text{At. size}}$

** (3) "e⁻" configuration of outermost subshell -

(a) If outermost subshell is fullfilled or half filled then elements has greate I.E than expected

(b) Such elements have greate I.E than adjecent elements in a period.



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* ① ns^1 ② ns^2 ⑬ np^1 ⑭ np^2 ⑮ np^3 ⑯ np^4 ⑰ np^5 ⑱ np^6

② ns^2 ↓ fullfilled

⑮ np^3 ↓ half filled

⑱ np^6 ↑ fullfilled

① < ② < ⑬ < ⑭ < ⑮ > ⑯ < ⑰ < ⑱

① < ⑬ < ② < ⑭ < ⑯ < ⑮ < ⑰ < ⑱

Li < B < Be < C < O < N < F < Cl

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

Q1) Arrange the following in order of IE →

(a) O^{-2}, O, O^-, O^+

Sol^n $O^{2-} < O^- < O < O^+$

(b) Mn < Mn^{+4} < Mn^{+7}

(c) $N^{-3} < O^{-2} < F^-$ (Iso-electronic)

Q2) Which of the following has highest IE?

(a) [Ne] $3s^1$ Na

(b) [Ne] $3s^2$ Mg

(c) [Ne] $3s^2 3p^2$ Si

(d) [Ne] $3s^2 3p^1$ Al

Na < Al < Mg < Si

Periodicity in I.E

(i) In groups
(ii) In periods

(a) ↓ at. size ↑ : I.E ↓

F > Cl > Br > I

(b) exception : Al < Ga
(high Zeff)

(c) exception :- Due to lanthanoid contraction

d-block :

4d series < 5d series
(high Zeff)

Ag < Au

Y > La (No . L.C)

P-block :-

In < Tl

Sn < Pb

Note

(i) element having highest I.E is "He"
(ii) element having least I.E is "Ce"

c) Successive I.E always "↑" because due to successive removal of e^- Z_{eff} ↑ or size ↓

$M(g) + I.E_1 \longrightarrow M^+(g) + e^-$; $\Delta H = +I.E_1$

$M(g) + I.E_2 \longrightarrow M^{+2}(g) + e^-$; $\Delta H = +I.E_2$

$M^{+2}(g) + I.E_3 \longrightarrow M^{+3}(g) + e^-$; $\Delta H = +I.E_3$

$I.E_1 < I.E_2 < I.E_3$

* सभी Ionisation energy Positive होगा ||

Energy required to remove n^{th} e^- = $I.E_n$

" " " " $n e^-$ = $(I.E_1 + I.E_2 + \dots + I.E_n)$

d) For an element

$I.E_1 = 10eV$, $I.E_2 = 20eV$, $I.E_3 = 35eV$ determine

(a) Energy required to 2nd e^-

Ans 20.0 V ($I.E_2$)

(b) Energy required to remove 3 e^-

Ans 65eV ($I.E_1 + I.E_2 + I.E_3$)

) $I.E_2$ of $M = I.E_1$ of M^+

$I.E_3$ of $M = I.E_2$ of $M^+ = I.E_1$ of M^{+2} /

Q.) $M(g) \longrightarrow M^{+}(g) + e^-$ $\therefore \Delta H > x$ ev

$M(g) \longrightarrow M^{+2}(g) + 2e^-$; $\Delta H > 2x$ ev

Determine:

(a) I.E$_2$ of $M = 15$ ev

(b) I.E$_1$ of $M^{+} = 15$ ev

Sol.) Successive I.E always "↑" but during removal of successive e^-, if e^- configuration becomes stable then rate of increment becomes more than expected.

$Na \xrightarrow{I.E_1} Na^{+} \xrightarrow{I.E_2} Na^{+2} \xrightarrow{I.E_3} Na^{+3}$

$1s^2, 2s^2, 2p^6, 3s^1$ $\quad 1s^2, 2s^2 2p^6$ $\quad 1s^2, 2s^2 2p^5$

$I.E_1 << I.E_2 < I.E_3$

* $Mg = [Ne]\,3s^2$

$I.E_1 < I.E_2 < I.E_3$

* $Al = [Ne]\,3s^2\,3p^1$

$I.E_1 << I.E_2 << I.E_3 << I.E_4$

If no. of valence e^- is "n" then difference b/w two successive I.E, $I.E_n$ and $I.E_{n+1}$ is very high.

$I.E_n << I.E_{n+1}$

Q.) For which element diff b/w $I.E_2$, $I.E_3$ is very high

(a) $[Ne]\,3s^1$

(b) $[Ne]\,3s^2\,3p^2$

(c) $[Ne]\,3s^2\,3p^1$

~~(d)~~ $[Ne]\,3s^2$

Soln $\underset{(n)}{I.E_2} << \underset{n+1}{I.E_3}$

$(n=2)$ (Valence e^-)

Q:) For an element, successive I.E value are given 1.2 eV, 2.6 eV, 31.9 eV, 38.6 eV,
Predict that element
(a) Na (b) Mg (c) Si (d) Al

$\underset{(n)}{I.E_2} << I.E_{n+1}$

$(n=2)$ (valence e)

Note * Along the group order of high I.E is similar as I.E,
* In a particular period alkali metal has highest I.E$_2$

Note

1) Along the group order of Ligho. I.E is similar as $I.E_1$
2) In a particula period alkali metal has highest $I.E_2$.
3) In a particula period alkaline earth metal has highest $I.E_2$.

order of IE in period (2) :-

Li^+ (Be^+ B^+ C^+ N^+ O^+ F^+ Ne^+)

$1s^2$ $2s^1$ $2s^2$ $2p^1$ $2p^2$ $2p^3$ $2p^4$ $2p^5$ $2p^6$

full filled — full filled — half filled

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

alkali metal.

Note order of $I.E_2$ in period - (I)

order of $I.E_2$ in period (II)

Q8) Arrange in order of I.E.
K, Ca, Ba

K^+, Ca^+ Ca > Ba
K > Ca
Ba^+
K > Ca > Ba

★ Application of I.E.

1) metallic and Non-metallic properties

metallic properties $\propto \frac{1}{I.E.}$

Non metallic properties $\propto$ I.E.

2) Stability of oxidation state

(a) If difference b/w two successive I.E. value is very high (more than 16 eV) then lower oxidation state is more stable

(b) If difference b/w two successive I.E. is very low (less than 11.2 eV) than higher oxidation state is more stable

Q) Na = [Ne] $3s^1$

I.E. $_1$ << I.E. $_2$
+1 +2
(✓) (X)

* $Mg = [Ne]\ 3s^2$

$I.E_1 < I.E_2 < < I.E_3$
$+1 \quad +2 \quad +3$
(X) (✓) (X)

T_1 * $Al = [Ne]\ 3s^2 3p^1$

$I.E_1 << I.E_2 < I.E_3 <<< I.E_4$
$+1 \quad +2 \quad +3 \quad +4$
✓ (X) ⇒ (X)

(c) If Diffence b/co two I.E value is moderate then both oxidation state exist.
(Cause of variable oxidation state in d and f-block)

3.) Strength of R.A and O.A →

St. of R.A (metals) $\propto \frac{1}{I.E}$

Strength of O.A (non-metals) $\propto I.E$

→ Best O.A is F_2
→ Best R.A is H^-
→ measurement of strength of O.A and R.A takes place in aqueous medium
→ strength of R.A

$$M(s) \xrightarrow[+S.E]{\text{Sublimation}} M(g) \xrightarrow[+I.E]{-e^{\ominus}} M^+ \xrightarrow[-H.E]{+H_2O} M^+(aq)$$

→ Strength of R.A ∝

$\frac{1}{2}X_2(g) \xrightarrow{+\frac{1}{2}B.E} X(g)$

→ Total required energy = $\underbrace{S.E + E.E - H.E}_{\text{minimum}}$

→ order of strength of R.A in alkali metals

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

→ Li is best R.A because Li^+ has exceptionally high H.E

⇒ Strength of O.A

$\frac{1}{2}X_2(g) \xrightarrow{+\frac{1}{2}B.E} X(g) \xrightarrow[-E.A]{+E} X^-(g) \xrightarrow[-H.E]{+H_2O} X^-(aq)$

→ Total required energy = $\frac{1}{2}B.E - E.A - H.E$

→ order of O.A in halogen

$F_2 > Cl_2 > Br_2 > I_2$

→ F_2 is best O.A because F^- has exceptionally high H.E

$X_{(g)} + e^- \longrightarrow X^-_{(g)} + E.A$

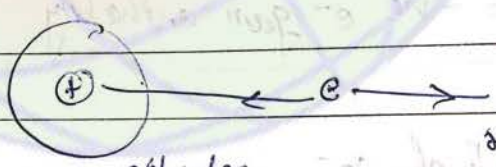
(Net attraction)

Net-attraction ∝ Stability of anion ∝ E.A

1) Elements having fullfilled or half filled outermost subshell do not add another e⁻. Hence their E.A is almost zero.

2) If we still add e⁻ to such elements then formed anion is unstable and process becomes endothermic.

(II)



$Y_{(g)} + e^- \longrightarrow Y^-_{(g)}$; E.A = +ve ; ΔH = +ve

group → 2, 13, 18 (unstable)

Q:) which anion is least stable?

(a) Li^- (b) Be^- (c) B^- (d) C^-

generally exothermic while other higher E.A process are always endothermic. because anion do not add energy

$X_{(g)} + e^- \longrightarrow X^-_{(g)} + E.A$; $\Delta H = -EA_1$

$X^-_{(g)} + e^- \longrightarrow X^{-2}_{(g)} + -EA_2$; $\Delta H = +EA_2$

$X^{-2}_{(g)} + e^- \longrightarrow X^{-3}_{(g)} - EA_3$; $\Delta H = +EA_3$

पहला E.A के अलावा बाकी वाला सभी Positive होगा ||

$O_{(g)} + e^- \longrightarrow O^-_{(g)}$; $\Delta H_1 = -x$ /

$O^-_{(g)} + e^- \longrightarrow O^{-2}_{(g)}$; $\Delta H_2 = +y$ /

ΔH_2 is true why

O^- resists addition of another e^-. /

Periodicity in E.A →

D In period:

⟶ E.A ↑

(except fulfilled or half filled)

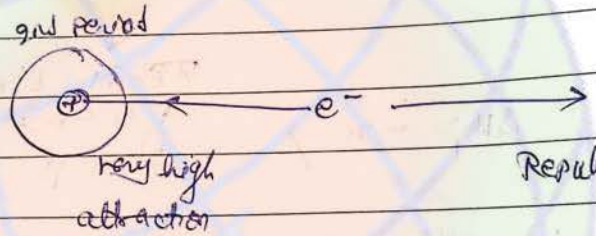
(18) < (2) < (15) < (1) < (13) < (14) < (16) < (17)

Ne < Be < N < H < B < C < O < F

(1) In group -

↓ ; E.A ↓

(2) In p-block, 2nd period elements have exceptionally low E.A because they have exceptionally small size. Hence, incoming e⁻ feels more repulsion than expected.



Net attraction becomes less than expected.

* order of E.A ⇒

Cl > F > Br > I

S > Se > Te > O

Note → element having highest E.A is called Proton acceptor

Q) which process is (are) endothermic

(a) $O^-(g) + e^- \rightarrow O^{-2}(g)$; $E.A_2$ of O

(b) $Ne(g) + e^- \rightarrow Ne^-(g)$; $E.A_1$ of Ne

(c) $Na(g) + Na^{+}(g) + e^-$; I.E$_1$ of Na

~~(d) $Na(s) + N$.~~

(d) $Mg^{+}(g) \longrightarrow Mg^{+2}(g) + e$; I.E$_2$ of Mg.

Q2) In which process minimum energy is released

(a) $Cl \longrightarrow Cl^-$ E.A$_1$ of Cl

(b) $H \longrightarrow H^-$ E.A$_1$ of H

(c) $C \longrightarrow C^-$ E.A$_1$ of C

(d) $N \longrightarrow N^-$ E.A$_1$ of N

Q3) In which process minimum energy is released

(a) $Cl^-(g) + e^- \longrightarrow Cl^{-2}(g)$ E.A$_2$ of Cl (requires)

(b) $Ar(g) + e^- \longrightarrow Ar^-(g)$ E.A$_1$ of Ar (requires)

(c) $O(g) + e^- \longrightarrow O^-(g)$ E.A of O

(d) $S(g) + e^- \longrightarrow S^-(g)$ E.A$_1$ of S (max. released)

L-2 : 2/10 Lec 6

Note : Electro Positivity (E·P) is opposite of ~~electropositivity~~ electronegativity

Electronegativity (E·N)

↓ Tendency of an atom to attract bonded e⁻ pair towards itself in a bond is called as its electronegativity

↓ Noble gas do not form Diatomic bond. Hence their electronegativity is assumed as zero

$A^{\delta+} : B^{\delta-}$

less E·N — more E·N

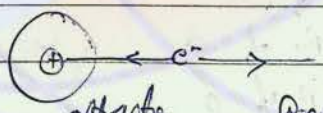
(Polar bond)

A · · A

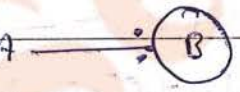
(Non-polar bond)

E·A

E·N



E·A ∝ Net attraction



E·N ∝ attraction

Factors affecting E·N :→

1. Zeff

   E·N ∝ Zeff

2. At. Size

   $E \cdot N \propto \frac{1}{\text{At. Size}}$

(3) oxidation state :-

(a) +ve o.s ↑ ; E.N ↑

$Mn < Mn^{+4} < Mn^{+7}$

$\overset{+7}{KMnO_4} > \overset{+4}{MnO_2}$

(b) −ve o.s ↑ ; EN ↓

$O > O^{-} > O^{-2}$

$\underset{-1}{H_2O_2} > \underset{-2}{H_2O}$

4) % s character

% s ch ↑ ; E.N ↑

$sp > sp^2 > sp^3$

50% 33.3% 25%

$H-C\equiv C-H > H-\overset{H}{\underset{|}{C}}=\overset{H}{\underset{|}{C}}-H > H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H$

sp sp^2 sp^3

☆ Periodicity in E.N →

(1) In period →

⟶ Zeff ↑ , E.N ↑

(except noble gas)

→ Li < Be < B < C < N < O < F

2) In Period:

(a) ↓ ; atomic size ↑ ; EN ↓

F > Cl > Br > I

(b) Exceptions due to L.C

d-block:→

4d-series < 5-d series
(Z-eff high)

Zr < Hf

Ag < Au

Y > La (No L.C)

P-block:→

In < Tl

Sn < Pb

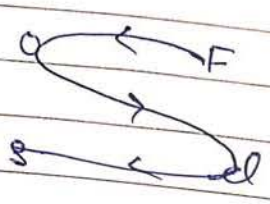
(c) exception: Al < Ga
(high Zeff)

Note

(1) most EN element is F.

(2) least EN element is Cs

Group (16) Group (17)



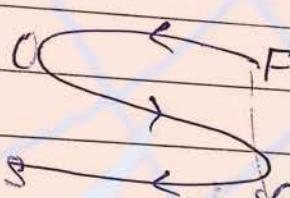
Period (II)

Period III

F > O > Cl > S

(except noble gas)

Ex. F) → Group (16) Group (17)



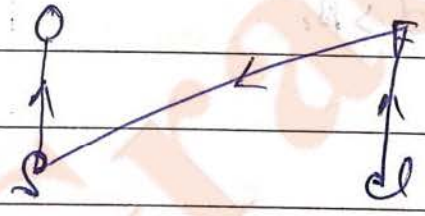
Period (II)

(Period III)

F > O > Cl > S

(except full-filled and half-filled)

Ex. A) → Group (16) Group (17)

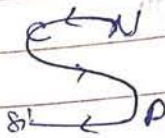


Cl > F > S > O

(except full-filled and half-filled)

Q.) Arrange in order of E.N →

C, Si, N, P



N > C > P > Si

* E.N of some Important elements -

$H_{2.1}$

$B_{2.0}$ $C_{2.5}$ $N_{3.0}$ $O_{3.5}$ $F_{4.0}$

$P_{2.1}$ $S_{2.5}$ $Cl_{3.0}$

$Br_{2.8}$

$I_{2.5}$

F > O > N ≈ Cl > Br

* Measurement of E.N →

(i) Mulliken Scale -

$$X_m = \frac{I.E + E.A}{2}$$

(ii) Pauling scale

A — B

$$DE\cdot N = |x_A - x_B| = 0.208 \sqrt{E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}}$$

Diff in E·N of A and B

Bond energy in Kcal/mol

(iii) Allred-Rochow scale

$$x = \frac{0.359\, Z_{eff}}{r^2} + 0.744$$

☆ Applications of E·N

(1) Greater E·N → more tendency to form anion
Lower E·N → more tendency to form cation

(2) metallic and non-metallic properties.

met. properties $\propto \frac{1}{E\cdot N}$

Non-metallic prop $\propto$ E·N

E.N ↑ ; N.m ↑ , M ↓

E.N ↓
N.M ↓
M ↑

metalloids :-
Elements which can both gain and loose e⁻ →

B C N O F
Si P S Cl
Ge As Se Br
Sb Te I
Po At → metalloids

metal

Non-metals

① Reactivity of metals $\propto \frac{1}{E.N}$

Reactivity of non-metals $\propto$ E.N

(4) Bond length (B.L), Bond energy (B.E) and Bond polarity -

Bond energy :-

Bond dissociation :-

$$A-B + B.E \longrightarrow A + B \quad ; \Delta H = +ve$$

Bond formation :-

$$A + B \longrightarrow A-B + B.E \quad ; \Delta H = -ve$$

☆ **ΔEN**

- $\delta+$ $\delta-$ (more)
  $A - B$
  10 30 — 20
- $\delta+$ $\delta-$ (more (with))
  $A - C$
  10 20 — 10

$\Delta EN \propto$ Bond polarity

$$\propto \frac{1}{B.L}$$

$$\propto B.E$$

Q1) Which bond is most polar?

(a) C-Cl
(b) C-O
(c) C-N
(d) C-F

Q2) Change in order of B.L ?

H-F < H-Cl < H-Br < H-I

(5) Nature of Bond -

Nature of Interatomic bond depends on $\Delta E \cdot N$

$\Rightarrow$ % Ionic character $= 16(\Delta E \cdot N) + 3.5(\Delta E \cdot N)^2$

$\Delta E \cdot N$	Nature of bond	
0	Pure covalent	Covalent
0.1 - 0.8	Co-valent	
0.9 - 2.1	Polar covalent	
2.2 or more	Ionic	

* metal + Non-metal = Ionic
Non-metal + Non-metal = Co-valent
metal + metal = metallic

(6) Nature of Hydride

Hydrides - Binary compound having one element "H".

Eg:- CH_4, NH_3, H_2O, HF, H_2S etc ~~$[N_2, H_2Se]$~~

C	N	O	F	(i) Size of central atom ↑
Si	P	S	Cl	(ii) B.L ↑
Ge	As	Se	Br	(iii) chance of H^+ removal ↑
Sn	Sb	Te	I	(iv) Acidic st. ↑

(i) E.N of central atom, $\Delta E.N$ ↑
(ii) Bond polarity ↑
(iii) chance of H^+ removal in H_2O ↑
(iv) Acidic strength ↑

* Order of Acidic Strength →

$H_2O < H_2S < H_2Se < H_2Te$

$CH_4 < NH_3 < H_2O < HF$

$CH_4 < H_2S < HI$

Nature of oxide and Hydroxides:-

(a) Nature of oxide and Hydroxide of an element is similar (oxide form hydroxide in water)

$$Na_2O + H_2O \longrightarrow 2NaOH$$

A–O–H

Case 1st:→

If $|x_A - x_O| > |x_O - x_A|$

$$A-O-H \xrightarrow{H_2O} A^+ + OH^-$$

(base)

A must be less E.N

Case 2nd:↓

If $|x_A - x_O| < |x_O - x_H|$

$$A-O-H \xrightarrow{H_2O} A_O^- + H^+$$

(Acid)

A must be high E.N.

(b) Acidic strength of oxides and hydroxide ∝ E.N of central atom.

★ Order of Acidic Strength →

$CaO > SrO > BaO$

$ClOH > BrOH > IOH$

$Na_2O < MgO < Al_2O_3 < SiO_2 < P_4O_{10} < SO_3 < Cl_2O_7$

$K_2O < ZnO_2 < NO_2$

$MnO < MnO_2 < Mn_2O_7$

$FeO < Fe_2O_3$

$CO < CO_2$

$SO_3 > SO_2$

(C) metallic oxides are generally basic in nature (some metallic oxides are amphoteric)

Amphoteric :- which can react with both acid and base.

s-block ⇒ BeO

d-block → TiO_2, VO_2, V_2O, CrO_2, Cr_2O_3, MnO_2, Mn_3O_4, Fe_2O_3, ZnO etc

p-block → Al_2O_3, Ga_2O_3, SnO, SnO_2, PbO, PbO_2 etc

(d) Non-metallic oxides are generally acidic in nature. (Some non-metallic oxides are neutral)

* Neutral oxides: which can't react with both acid and base.

CO, NO, N_2O, H_2O

Note →

(1) oxyacids are hydroxide of non-metals

(2) Non-metallic oxides form oxyacids in water in which there is no change in O.S of central atom.

(3) Non-metallic oxides are anhydride of oxy-acids.

oxyacids: Acids in which H-atom is attached with O-atom.

eg: H_2SO_4, HNO_3, $HClO_4$ etc.

$(OH)_2SO_2$ $(OH)NO_2$ $(OH)ClO_3$

$$\overset{+6}{SO_3} + H_2O \longrightarrow \overset{+6}{H_2SO_4}$$

acidic sulphonic anhydride — sulphuric acid

$SO_3 + H_2O \longrightarrow H_2SO_4$ (+4 → +6)

$N_2O_5 + H_2O \longrightarrow HNO_3$ (+5 → +5)

$Cl_2O_7 + H_2O \longrightarrow HClO_4$ (+7 → +7)

(Perchloric acid)

☆ Some Important Periodic Properties →

(1) Atomic density:

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

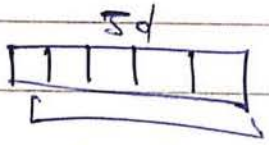
(a) In groups →

Both mass and volume "↑" but Increasement in mass is much more than volume Hence, atomic density "↑"

exception: Density of Na > K

" " Mg > Ca

$Na = 1s^2\ 2s^2\ 2p^6\ 3s^1$

$K = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ 

Due to vacant 3d-subshell its volume drastically Increase.

(2) In period:

s-block < d-block > P-block

○○○ ○○○ (light metal)

(Heavy metal)

○ ○ ○ ○ ○ ○

(2) m.p and b.p in periods :-

(a) In periods :-

⟶ s-Block < d-Block > p-Block

Note :- In d-Block, In a particular series, as no. of unpaired electron's Increases strength of metallic bond Increases. Hence m.p also Increases (strength of metallic bond depends on no. of unpaired electron's)

Order of m.p / strength of metallic bond in 3d-series :-

Sc < Ti < V < Cr > Fe > Co > Ni > Cu > Zn

(Mn ka chakkar hai isliye)

(b) In groups :-

Group (1) and (2)	Group (3) to (12)	Group (13) to (14)	Group (15) to (18)
[decreases]	[Increases]	[decreases]	[Increase]

⇒ Di Di

Note :-

(1) lightest element is "H"

(2) lightest metal is Lithium (Li)

(3) lightest element in d-block is "Sc"

(4) Heaviest element in d-block is Iridium (Ir) or No. 2 (Osmium)

(5) Metal having highest melting point Tungestant (W), or No 2 Ta (tantalum)

(6) Non-metal having high melting point is "C" (Diamond)
↳ allotrope

(7) most abundant compound on earth is SiO_2 (silica), or No 2 Al_2O_3 (alumina)

* most abundant element on earth is oxygen (O)
* most abundant metal on earth is Al (aluminium)

(8) most abundant gas in atmosphere is N_2 (O_2, CO_2, Argon) etc.

(9) most abundant element in universe is Hydrogen (H)

(10) liquid Non-metal is Br_2 (Bromine)

(11) liquid metals are Cs, Fr, Hg, Ga

(Ga is used in High temp. thermometer)

CAREER POINT

Target Course for NITs (JEE Main)-2014

DAILY PRACTICE PROBLEM SHEET

CHEMISTRY

d & f - block elements-1

Sub topic : General properties of d-block elements

Q.1 Which of the following is/are colourless ?
(I) $ScCl_3$ (II) $TiCl_4$
(III) Cu_2Cl_2 (IV) $ZnCl_2$
(1) I and II (2) I, II and III
(3) II, III and IV (4) all of these

Q.2 Which of the following is responsible for complex formation by the elements of d-block ?
(1) Vacant d-orbitals (2) High nuclear charge
(3) Small size (4) all of these

Q.3 Magnetic moments of $Cr^{+}(Z = 24)$, $Mn^{+2}(Z = 25)$ and $Fe^{+3}(Z = 26)$ are x, y and z respectively. The correct relation is shown is -
(1) $x > y > z$ (2) $z > y > x$
(3) $x = y = z$ (4) $x + y > z$

Q.4 In +2 oxidation state, the electronic configuration of a transition metal is [Ar] $3d^3$. Its atomic number is -
(1) 23 (2) 24
(3) 25 (4) 26

Q.5 Which of the following statements is incorrect -
(1) Sc has lowest density among d-block elements
(2) In 3d-series highest melting point is shown by Mn
(3) Zn does not show variable oxidation state
(4) Metal having highest melting point is W.

Q.6 Among the following series of transition metal ions the one where all metal ions have $3d^2$ electronic configuration is
(1) $Ti^{+3}, V^{+2}, Cr^{+3}, Mn^{+4}$
(2) $Ti^{+}, V^{+4}, Cr^{+6}, Mn^{+7}$
(3) $Ti^{+4}, V^{+4}, Cr^{+2}, Mn^{+3}$
(4) $Ti^{+2}, V^{+3}, Cr^{+4}, Mn^{+5}$

Q.1 निम्न में से कौनसे यौगिक रंगहीन है ?
(I) $ScCl_3$ (II) $TiCl_4$
(III) Cu_2Cl_2 (IV) $ZnCl_2$
(1) I तथा II (2) I, II तथा III
(3) II, III तथा IV (4) उपरोक्त सभी

Q.2 निम्न में से कौनसा d-ब्लॉक के तत्वों द्वारा संकुल निर्माण के लिए उत्तरदायी है ?
(1) रिक्त d-कक्षक (2) उच्च नाभिकीय आवेश
(3) छोटा आकार (4) उपरोक्त सभी

Q.3 $Cr^{+}(Z = 24)$, $Mn^{+2}(Z = 25)$ तथा $Fe^{+3}(Z = 26)$ के चुम्बकीय आघूर्ण क्रमशः x, y तथा z है। सही सम्बंध दर्शाया गया है -
(1) $x > y > z$ (2) $z > y > x$
(3) $x = y = z$ (4) $x + y > z$

Q.4 +2 ऑक्सीकरण अवस्था में संक्रमण धातु का इलेक्ट्रॉनिक विन्यास [Ar] $3d^3$ है इसका परमाणु क्रमांक है -
(1) 23 (2) 24
(3) 25 (4) 26

Q.5 निम्न में से कौनसा कथन असत्य है -
(1) Sc, d-ब्लॉक तत्वों में सबसे कम घनत्व रखता है।
(2) 3d-श्रेणी में Mn द्वारा अधिकतम गलनांक दर्शाया जाता है
(3) Zn परिवर्तनशील ऑक्सीकरण अवस्था नहीं दर्शाता है
(4) धातु में W आधिकतम गलनांक रखता है

Q.6 संक्रमण धातु आयनों की श्रेणियों में से एक जिसमें सभी धातु आयन $3d^2$ इलेक्ट्रॉनिक विन्यास रखते है -
(1) $Ti^{+3}, V^{+2}, Cr^{+3}, Mn^{+4}$
(2) $Ti^{+}, V^{+4}, Cr^{+6}, Mn^{+7}$
(3) $Ti^{+4}, V^{+4}, Cr^{+2}, Mn^{+3}$
(4) $Ti^{+2}, V^{+3}, Cr^{+4}, Mn^{+5}$

Q.7 A compound of a metal ion M^{x+} (Z = 24) has a spin only magnetic moment of $\sqrt{15}$ BM. The number of unpaired electrons in the compound are -

(1) 2 (2) 4
(3) 5 (4) 3

Q.8 The highest oxidation state is exhibited by the transition metal with electronic configuration -

(1) $(n-1)d^5\,ns^1$ (2) $(n-1)d^5\,ns^2$
(3) $(n-1)d^8\,ns^2$ (4) $(n-1)d^6\,ns^2$

Q.9 Which of the following is not correct about transition metals ?

(1) Their melting and boiling points are high
(2) Their compounds are generally coloured
(3) They can form ionic or covalent compounds
(4) They do not exhibit variable oxidation state

Q.10 Which of the following statements is incorrect ?

(1) ZnO is an amphoteric oxide
(2) d-block elements show variable oxidation state due to partially filled d-subshell
(3) Cause of colour in $K_2Cr_2O_7$ is charge transfer from Cr to O.
(4) d-block elements and compounds show catalytic properties because d-block elements can show variable oxidation satate

Q.7 धातु आयन M^{x+} (Z = 24) का एक यौगिक विस्थापन चक्रण केवल $\sqrt{15}$ BM का चुम्बकीय आघूर्ण रखता है। यौगिक में अयुग्मित इलेक्ट्रॉनों की संख्या है -

(1) 2 (2) 4
(3) 5 (4) 3

Q.8 कौनसे इलेक्ट्रॉनिक विन्यास युक्त संक्रमण धातु देंगे अधिकतम ऑक्सीकरण अवस्था दर्शाई जाती है -

(1) $(n-1)d^5\,ns^1$ (2) $(n-1)d^5\,ns^2$
(3) $(n-1)d^8\,ns^2$ (4) $(n-1)d^6\,ns^2$

Q.9 निम्न में से कौनसा संक्रमण धातुओं के बारे में सही नहीं है ?

(1) इनका गलनांक तथा क्वथनांक उच्च होता है
(2) इनके यौगिक प्रायः रंगीन होते हे
(3) ये आयनिक या सहसंयोजी यौगिक बना सकते है
(4) ये परिवर्तनशील ऑक्सीकरण अवस्था नहीं दर्शाते है

Q.10 निम्न में से कौनसा कथन असत्य है ?

(1) ZnO एक उभयधर्मी ऑक्साइड है
(2) d-ब्लॉक तत्व, आंशिक भरे d-उपकोशो के कारण परिवर्तन शील ऑक्सीकरण अवस्था दर्शाते है
(3) $K_2Cr_2O_7$ में रंग का कारण Cr से O में आवेश स्थानांतरण है
(4) d-ब्लॉक तत्व तथा यौगिक उत्प्रेरकीय गुण दर्शाते है। क्योंकि d-ब्लॉक तत्व परिवर्तनशील अवस्था दर्शा सकते है

HINTS & SOLUTION

1.[4] In Sr^{+3}, Ti^{+4}, Cu^{+} and Zn^{+2} all electrons are paired.

2.[4]

3.[3] Cr^{+}, Mn^{+2} and Fe^{+3} all have 5 unpaired electrons

4.[1] $M^{+2} = [Ar]3d^3$
$M = [Ar]4s^2\,3d^3$ (At. No. = 23)

5.[2] In 3d-series highest melting points is shown by Cr.

6.[4]

7.[4] Magnetic moment $= \sqrt{n(n+2)}$
$= \sqrt{15} = \sqrt{n(n+2)}$
$n = 3$

8.[4] highest oxidation state is shown by Os.

9.[4] Transition metals show variable oxidation state

10.[3] Cause of colour in $K_2Cr_2O_7$ is charge transfer from O to Cr.

Dand f- Block elements

classmate
Date
Page

Part - 1st

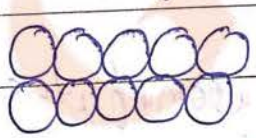
(1)* Properties of d-block elements →

1) Transition elements - except (Zn, Cd, Hg)
2) Electronic configuration →
3) Series - 3d-series
4d →
5d -
4) Magnetic Properties → $\mu = \sqrt{n(n+2)}$
5) Size of radius in 3d-series →
Fe, Co, Ni
Same
6) L.C → S-d
7) Nature of oxides -
8) Size of melting point →
No. of unpaired e⁻

Ans

(1) d-block elements are also called as heavy metals. because they have high density melting point and boiling point due to strong metallic bond.

→ These elements are found in F.C.C and B.C.C and H.C.P arrangement



d-block elements have high enthalpy or heat of atomization
Cause → due to strong metallic bond.

→ Heat of atomization is the heat required to convert any element into gaseous atoms.

(3) These elements and their compounds show magnetic properties (General statement)
Due to unpaired electrons.

(4) → d-block elements can form co-ordination or complex compounds
eg: $K_4[Fe(CN)_6]$, $[Ni(CO)_4]$ etc

→ Conditions required to form coordination compounds:
(a) metal ion must have small size or high charge density

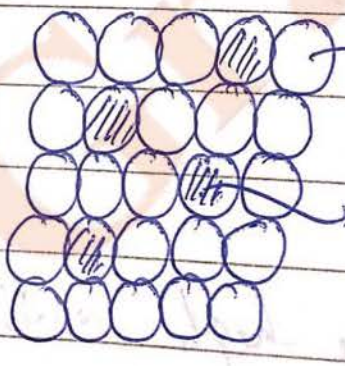
$$\text{charge density} = \frac{\text{charge}}{\text{size}}$$

(b) metal ion must have vacant d-orbital.

(5) (a) d-block elements can form alloys and interstitial compounds

(b) Homogeneous mixture of elements is called as alloy.

(c) d-block elements form alloys because they have almost similar atomic size.



(alloy)

CAREER POINT

Target Course for NITs (JEE Main)-2014

DAILY PRACTICE PROBLEM SHEET

CHEMISTRY

d & f - block elements-2

Sub topic : General properties of f-block elements

Q.1 Which lanthanoid had electronic configuration $[Xe]\ 4f^7\ 6s^2$?

(1) Sm (Z = 62) (2) Eu (Z = 63)

(3) Gd (Z = 64) (4) Tb (Z = 65)

Q.2 Which of the following is correct order of size of M^{+3} ions of La(57), Sm(62), Dy(66) and Lu(71) ?

(1) La > Sm > Dy > Lu

(2) Lu > Dy > Sm > La

(3) La > Dy > Sm > Lu

(4) La > Dy = Sm > Lu

Q.3 Which elements of d-block are not considered transition elements ?

(1) Sc, Y, La and Ac (2) Fe, Co and Ni

(3) Cu, Au and Ag (4) Zn, Cd and Hg

Q.4 $La(OH)_3$ is more basic than $Lu(OH)_3$ because -

(1) La is more electronegative than Lu

(2) La^{+3} is larger in size than Lu^{+3}

(3) ionic character of bond in $Lu(OH)_3$ is high

(4) all of the above

Q.5 Which of the following can act as oxidizing agent ?

(1) Ce^{+4} (2) Sm^{+2}

(3) Gd^{+3} (4) Lu^{+3}

Q.6 Which of the following ions has tendency to form co-ordination compounds ?

(1) Eu^{+3} (2) Ce^{+3}

(3) Nd^{+3} (4) Pr^{+3}

Q.1 कौनसे लैन्थेनॉइड का इलेक्ट्रॉनिक विन्यास $[Xe]\ 4f^7\ 6s^2$ होता है ?

(1) Sm (Z = 62) (2) Eu (Z = 63)

(3) Gd (Z = 64) (4) Tb (Z = 65)

Q.2 निम्न में से कौनसा La(57), Sm(62), Dy(66) तथा Lu(71) के M^{+3} आयनों का सही क्रम है ?

(1) La > Sm > Dy > Lu

(2) Lu > Dy > Sm > La

(3) La > Dy > Sm > Lu

(4) La > Dy = Sm > Lu

Q.3 d-ब्लॉक के कौनसे तत्व, सक्रमण तत्व नहीं है ?

(1) Sc, Y, La तथा Ac (2) Fe, Co तथा Ni

(3) Cu, Au तथा Ag (4) Zn, Cd तथा Hg

Q.4 $La(OH)_3$, $Lu(OH)_3$ से अधिक क्षारीय है, क्योंकि -

(1) La, Lu से अधिक विद्युतऋणी है

(2) La^{+3}, Lu^{+3} से आकार में बडा है

(3) $Lu(OH)_3$ में बंध के आयनिक लक्षण उच्च होते है

(4) उपरोक्त सभी

Q.5 निम्न में से कौनसा ऑक्सीकारक के रूप में कार्य कर सकता है ?

(1) Ce^{+4} (2) Sm^{+2}

(3) Gd^{+3} (4) Lu^{+3}

Q.6 निम्न आयनों में से कौनसा उपसहसंयोजी यौगिक बनाने की उच्चतम प्रवृत्ति रखता है?

(1) Eu^{+3} (2) Ce^{+3}

(3) Nd^{+3} (4) Pr^{+3}

Q.7 Chromite ore (X) $\xrightarrow[\text{fuse}]{NaOH/air}$ (Y) X and Y are -

(1) Cr_2O_3 and $Na_2Cr_2O_7$
(2) FeO. Cr_2O_3 and $Na_2Cr_2O_7$
(3) FeO. Cr_2O_3 and Na_2CrO_4
(4) Cr_2O and Na_2CrO_4

Q.8 Ice cold $K_2Cr_2O_7$ reacts with H_2O_2 to produce blue colour of -

(1) CrO_3 (2) CrO_5
(3) Cr_2O_3 (4) $Cr_2O_7^{-2}$

Q.9 $K_2Cr_2O_7 \xrightarrow{\Delta} K_2CrO_4 + O_2 + ?$

(1) CrO_3 (2) Cr_2O_3
(3) CrO_5 (4) CrO_2

Q.10 A mixture of $KCl_{(s)}$, $K_2Cr_2O_{7(s)}$ and Conc. H_2SO_4 is heated. The orange-red fumes are -

(1) CrO_3 (2) Cr_2O_3
(3) CrO_2 (4) CrO_2Cl_2

Q.7 क्रमाइट अयस्क (X) $\xrightarrow[\text{fuse}]{NaOH/air}$ (Y) X तथा Y है -

(1) Cr_2O_3 तथा $Na_2Cr_2O_7$
(2) FeO. Cr_2O_3 तथा $Na_2Cr_2O_7$
(3) FeO. Cr_2O_3 तथा Na_2CrO_4
(4) Cr_2O तथा Na_2CrO_4

Q.8 ठण्डा $K_2Cr_2O_7$, H_2O_2 के साथ क्रिया कर नीले रंग का कौनसा योगिक बनाता है -

(1) CrO_3 (2) CrO_5
(3) Cr_2O_3 (4) $Cr_2O_7^{-2}$

Q.9 $K_2Cr_2O_7 \xrightarrow{\Delta} K_2CrO_4 + O_2 + ?$

(1) CrO_3 (2) Cr_2O_3
(3) CrO_5 (4) CrO_2

Q.10 $KCl_{(s)}$, $K_2Cr_2O_{7(s)}$ तथा सान्द्र H_2SO_4 के मिश्रण को गर्म किया जाता है तो नारंगी-लाल गैस निम्न के बनने के कारण निकलती है -

(1) CrO_3 (2) Cr_2O_3
(3) CrO_2 (4) CrO_2Cl_2

HINTS & SOLUTION

1.[2] $Eu = [Xe]\ 4f^7 6s^2$

2.[1] As atomic no increases ionic radius decreases in lanthanoids.

3.[4] In Zn, Cd and Hg all electrons are paired

4.[2]

5.[1] $Ce^{+4} \xrightarrow{\text{Reduction}} Ce^{+3}$

6.[1] Ions having small size have greater tendency to form co-ordination compounds.

7.[3]

8.[2]

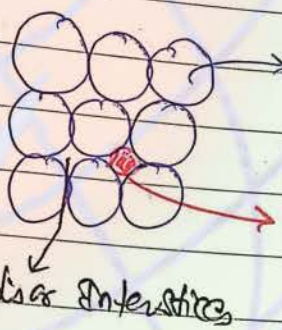
9.[2]

10.[4]

(d) Some Important alloys:-

Brass → Cu + Zn
Bronze → Cu + Sn
Steel → Fe + Ni
Stainless steel → Fe + Ni + Cr

(e) If a small size atoms are present in voids of d-block element then resultant comp. is called as Interstitial compound.
eg. Steel is an Interstitial comp in which carbon atoms are present in voids of iron.



(6) Due to unstable core or partially filled d-subshell, d-block elements show variable oxidation state.

$Na = \underbrace{[Ne]}_{\text{core stable}} \underbrace{3s^1}_{x}$ (+1) fixed 0.5

$Fe = \underbrace{[Ar]}_{\text{core unstable}} \underbrace{4s^2 3d^6}_{x}$ (+2) variable 0.5

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	(+2)	(+2)	(+2)	(+2)	(+2)	(+2)
(+3)	+3	+3	(+3)	+3	(+3)	+3	+3	+3	
	(+4)	+4	+4	(+4)	+4	+4	+4		
		(+5)	+5	+5	+5	+5			
			(+6)	+6	+6				
				(+7)					

○ → most common o.s

◌ → Next Common o.s

(b) In 3d-series Cr shows fixed o.s +3

(c) In 3d-series Mn shows highest o.s +7

(d) In d-block Os, Ru, show highest o.s +8

(e) Comparision of stability of similar o.s in different elements:-

A^{+n}	B^{+n}
$(I.E_1 + I.E_2 + \cdots + I.E_n) = x$	$(I.E_1 + I.E_2 + \cdots + I.E_n) = y$

$x > y$

+n o.s is more stable for "A"

(a)

Ni	Pt
$I.E_1 = 10eV$	11eV
$I.E_2 = 20eV$	22eV
$I.E_3 = 30eV$	26eV
$I.E_4 = 40eV$	28eV

d & f - block elements-3

Sub topic : $KMnO_4$ & $K_2Cr_2O_7$

Q.1 $Cr_2O_7^{-2} \underset{pH=y}{\overset{pH=x}{\rightleftharpoons}} CrO_4^{-2}$

x and y are respectively -

(1) 2 and 10 (2) 8, 4

(3) 4, 8 (4) 8 , 10

Q.2 In the structure of dichromate ion, the number of Cr–O bonds equal in length are -

(1) 2 and 6 (2) 3 and 5

(3) 2 and 4 (4) 3 and 3

Q.3 $KMnO_4$ is heated with HCl, the greenish yellow gas evolved is -

(1) MnO_2

(2) $MnSO_4$

(3) Cl_2

(4) $HClO_4$

Q.4 To an acid solution of an anion a few drops of $KMnO_4$ solution are added. Which of the following, if present will not decolourise the $KMnO_4$ solution

(1) CO_3^{-2} (2) NO_2^-

(3) S^{-2} (4) Cl^-

Q.5 CrO_3 dissolves in aqueous NaOH to give -

(1) CrO_4^{-2}

(2) $Cr(OH)_3$

(3) $Cr_2O_7^{-2}$

(4) $Cr(OH)_2$

Q.1 $Cr_2O_7^{-2} \underset{pH=y}{\overset{pH=x}{\rightleftharpoons}} CrO_4^{-2}$

x व y क्रमश: है -

(1) 2 व 10 (2) 8, 4

(3) 4, 8 (4) 8 , 10

Q.2 डाइक्रोमेट आयन की संरचना में लम्बाई में समान Cr–O बंधो की संख्या है -

(1) 2 व 6 (2) 3 व 5

(3) 2 व 4 (4) 3 व 3

Q.3 $KMnO_4$, HCl के साथ गर्म करने पर हरी-पीली गैस मुक्त करता है -

(1) MnO_2

(2) $MnSO_4$

(3) Cl_2

(4) $HClO_4$

Q.4 ऋणायन के अम्लीय विलयन में कुछ बूदें $KMnO_4$ विलयन की मिलाते है तो वह $KMnO_4$ विलयन को रंगहीन नहीं करता है, तो वह ऋणायन कौनसा होगा-

(1) CO_3^{-2} (2) NO_2^-

(3) S^{-2} (4) Cl^-

Q.5 CrO_3, जलीय NaOH में विलेय होने पर देता है-

(1) CrO_4^{-2}

(2) $Cr(OH)_3$

(3) $Cr_2O_7^{-2}$

(4) $Cr(OH)_2$

Q.6 In which of the following compounds cause of colour is charge transfer -
(1) K_2CrO_4 (2) $KMnO_4$
(3) $K_2Cr_2O_7$ (4) all of these

Q.7 $MnO_2 \xrightarrow[\Delta]{KOH/air} X \text{ (green mass)} \xrightarrow{Cl_2} KMnO_4$

X is -
(1) K_3MnO_4 (2) K_2MnO_4
(3) Mn_3O_4 (4) None of these

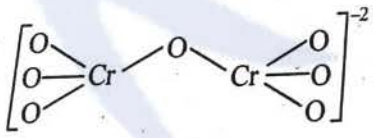
Q.6 निम्न यौगिको में से कौनसा आवेश स्थानांतरण कारण रंगीन होता है -
(1) K_2CrO_4 (2) $KMnO_4$
(3) $K_2Cr_2O_7$ (4) सभी

Q.7 $MnO_2 \xrightarrow[\Delta]{KOH/air} X \text{ (green mass)} \xrightarrow{Cl_2} KMnO_4$

X है -
(1) K_3MnO_4 (2) K_2MnO_4
(3) Mn_3O_4 (4) इनमें से काई नहीं

HINTS & SOLUTION

1.[2] $Cr_2O_7^{-2} \underset{\text{acidic}}{\overset{\text{basic}}{\rightleftharpoons}} CrO_4^{-2}$

2.[1] 

3.[3] $KMnO_4 + HCl \rightarrow MnCl_2 + KCl + H_2O + Cl_2$

4.[1] CO_3^{-2} is not a reducing agent

5.[1] $CrO_3 + NaOH \rightarrow Na_2CrO_4$

6.[4]

7.[2]

element +2 O.S is more stable?

ans → Ni

(-6) For which element +4 O.S is more stable?

ans → Pt

(5)(F) Comparision of stability of O.S for an element-

$$M_{(s)} \xrightarrow{+S.E} M_{(g)} \xrightarrow[+(IE_1 + IE_2 + \cdots + IE_n)]{-ne^-} M^{n+}_{(g)} \xrightarrow[-H.E]{+H_2O} M^{n+}_{(aq)}$$

Total required energy = $S.E + (IE_1 + IE_2 + \cdots + IE_n) + H.E$

"n" O.S is most stable if total required energy is minimum.

> d-block elements can form non-stoichiometric compounds because they can show variable O.S

eg:-

$Fe_{0.93}O$, $Ni_{0.98}O$ etc.

Stoichiometric compound :→ In which element are in simple whole no. ratio

eg → NaCl, FeO, Fe_2O_3 etc

FeO

$Fe_{100}O_{100}$

$Fe_{0.93}O$ -

$Fe_{93}O_{100}$

+186 −200

↓+14

+200

$Fe^{+2} \longrightarrow Fe^{+3}$

all except 2 a)

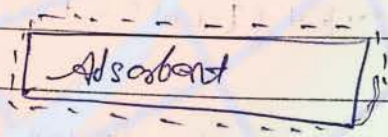
L-2 → 1, +2, 3, 6, 8 to 13,
L-3 → 2, 3, 4, 8, 14, 15, 16, 18, 19, 20, 22, 23, P,
4A → 1, 3, 4 to 8, 11, 17, 18,
4B → 4, 5

Q8) d-block elements and their compounds show catalytic properties because they can show variable o.s and they are good adsorbent.

$$SO_2 + V_2O_5 \xrightarrow{} SO_3$$

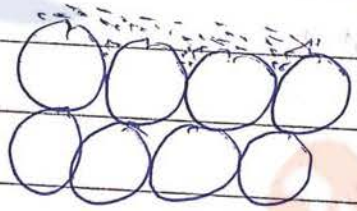
I: $SO_2 + V_2O_5 \longrightarrow SO_2 + V_2O_4$ (+4)

II) $V_2O_4 + \frac{1}{2}O_2 \longrightarrow V_2O_5$



Adsorption

Adsorption

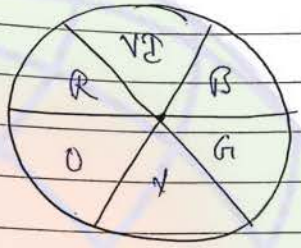


Imp All "s-Block" and Colourless.

(1) d-block elements can form coloured compounds :-

d-d transition | charge trans. for spectra

[V + I + B + G + Y + O + R = white]



Complementary colour cycle

a) d^0 or d^{10} → colourless (white)

eg:- CuCl (aq) (colourless)

$Cu^+ = [Ar]\ 4s^0\ 3d^{10}$

b) d^1 to d^9 → coloured

eg

$CuSO_4(aq)$

$Cu^{+2} = [Ar]\ 4s^0\ 3d^9$ (coloured)

c. Compounds of Zinc are colourless (white)

$\underset{d^0}{\overset{+7}{KMnO_4}}$, $\underset{d^0}{\overset{+6}{K_2Cr_2O_7}}$, $\underset{d^0}{\overset{+6}{K_2CrO_4}}$

$\underset{d^0}{\overset{+6}{CrO_3}}$, Compounds of $\underset{d^{10}}{Cd^{+2}}$

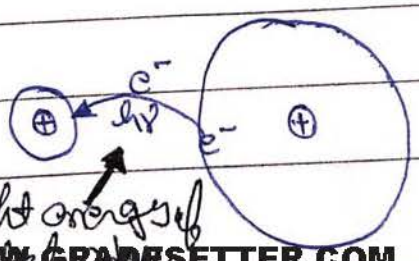
and $\underset{d^{10}}{Hg^{+2}}$ etc

Note All s-block cation are colourless

$KMnO_4$

K^+ (colourless) MnO_4^- (coloured)

Mn^{+7} O^{-2}



light energy of a particular

$_{57}La = [Xe]\ 6s^2\ 5d^1$; $Ln(58-71) = [Xe]\ 6s^2\ 5d^{0-1}\ 4f^{1-14}$

$_{89}Ac = [Rn]\ 7s^2\ 6d^1$; $An(90-103) = [Rn]\ 7s^2\ 6d^{0-1}\ 5f^{1-14}$

$Gd = [Xe]\ 6s^2\ 5d^1\ 4f^7$

$Gd^{+3} = [Xe]\ 6s^0\ 5d^0\ 4f^7$

$Lu = [Xe]\ 6s^2\ 5d^1\ 4f^{14}$

$Lu^{+3} = [Xe]\ 6s^0\ 5d^0\ 4f^{14}$

$La^{+3} = [Xe]\ 6s^0\ 5d^0$

Due to partially filled "f" subshell, these elements show oxidation state, their main oxidation state is "+3"

Other possible O.S :-

Ln :- → +2 and +4

An :- → +2, +4, +5, & +6 and +4

Q1) Ce^{+4} is good O.A why?

Sol) $Ce^{+4} \xrightarrow{\text{Reduction}} Ce^{+3}$

(O.A)

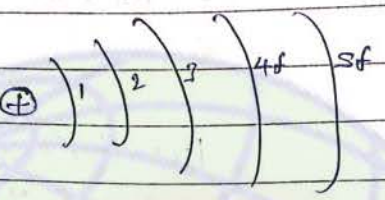
Q2) Sm^{+2} is good R.A why

$Sm^{+2} \xrightarrow{\text{oxidation}} Sm^{+3}$

(R.A)

Q.2 Actinoids show more no. of oxidation state than Lanthanoids.

Sol 1) Because Removal of e⁻ from 5f-subshell is easier than 4f-subshell



2) Due to partially filled f-subshell these elements can form colored compounds. (f-f transition)

3) Due to partially filled f-subshell these elements and their compounds show magnetic properties.

4) Their oxides and hydroxides are basic.

(5) Application of Lanthanoid contraction →

(a) order of basic strength of hydroxides –

$La(OH)_3 > Ce(OH)_3 > \cdots\cdots > Lu(OH)_3$

size of central atom ↑ ; B.L ↑

chance of removal of OH^- ↑ ; basic strength ↑

tendency to form complex/ co-ordination comp.

$La^{+3} < Ce^{+3} < ---- < Lu^{+3}$

(6) These elements have high electro positivity, high reactivity and tendency to form ionic bond. Due to Low IE, comparable to alkaline earth metals.

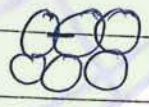
General order of I.E :→

s-block < f-block < d-block < P-block

Note

① Volatile metals :- Zn, Cd, Hg (Gr 12)

(Zero unpaired e^-)



> Coinage metals :- Cu, Ag, Au (Group 11)

(high ductility and malleability)

> Blue vitriol → $CuSO_4 \cdot 5H_2O$, ~~white vitriol~~ $ZnSO_4 \cdot 7H_2O$, ~~green vitriol~~, ~~$FeSO_4$~~

White vitriol :→ $ZnSO_4 \cdot 7H_2O$

Green vitriol :→ $FeSO_4 \cdot 7H_2O$

mischmetal : an alloy of lanthanoids,

are :-

+

Fe ($\approx$ 5%)

+

S + C + Si + G + Al (small amount)

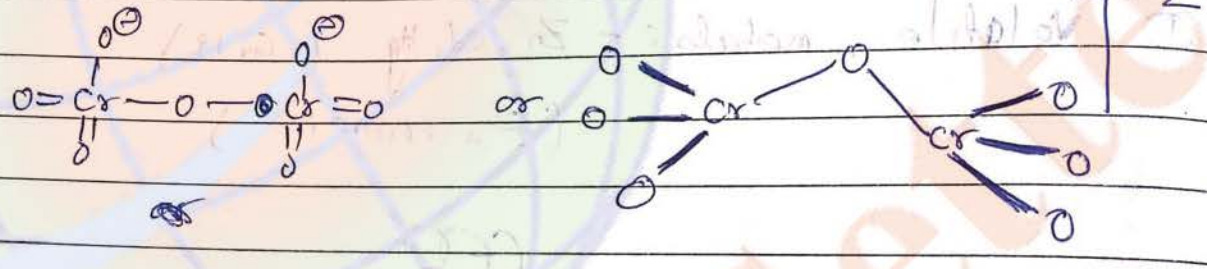
✱ Compound of d-block

① Potassium di-chromate ($K_2Cr_2O_7$) →

Bonding -

$2K^+$ $Cr_2O_7^{-2}$

Di-chromate ion



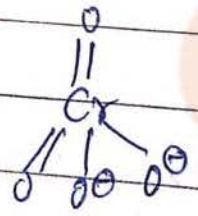
— , single bond

═ , Partial double bond

2 Cr–O bonds are similar

6 Cr═O bonds are simila

✱ Chromate ion, CrO_4^{-2}



Tetrahedral.

[H_2CrO_4 → Chromic Acid]

$K_2Cr_2O_7$ is Prepared a chromate ore ($\overset{+2}{Fe}\overset{+3}{Cr_2}O_4$ or $\overset{+2}{FeO}\cdot\overset{+3}{Cr_2O_3}$)

Basic (+3 → +6)

step 1st :-

$\overset{+3}{Fe}\overset{+3}{Cr_2}O_4 + NaOH + O_2 \longrightarrow \overset{+6}{Na_2CrO_4} + Fe_2O_3 + H_2O$

NaOH: base; O_2: air; Na_2CrO_4: Sodium chromate

step 2nd :-

$Na_2CrO_4 + H_2SO_4 \text{ (dil)} \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

step 3rd :-

$Na_2Cr_2O_7 + KCl \longrightarrow K_2Cr_2O_7 + NaCl$

* Properties :-

(1) $K_2Cr_2O_7$ is orange-red crystalline compound (due to charge transfer)

(2) $\overset{+6}{CrO_4}^{-2} \underset{\text{base (pH > 7)}}{\overset{\text{acid (pH < 7)}}{\rightleftharpoons}} \overset{+6}{Cr_2O_7}^{-2}$

chromate (yellow) ⇌ dichromate (orange red)

→ It is not a redox rex?

[$\overset{+6}{CrO_3} + NaOH \longrightarrow Na_2CrO_4$]

(yellow)

> Upon Heating

$\overset{+6}{K_2Cr_2O_7} \xrightarrow{\Delta} K_2CrO_4 + Cr_2O_3 + O_2\uparrow$

O.A

Note → order of oxidising agent →

$KMnO_4 + Cl_2 + K_2Cr_2O_7 > Br_2 > I_2$

Rule -

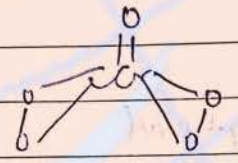
(*) If anion of an oxy-salt is good O.A then upon heating salt will liberate O_2 gas.

(4) Reaction with H_2O_2 :→

$Cr_2O_7^{-2} + H^+ + H_2O_2 \longrightarrow CrO_5 + H_2O$
(orange-red) (or $CrO(O_2)_2$) (deep blue)

O^{-2} → oxide
O_2^{-2} → Peroxide
O_2^{-1} → Superoxide

Note → Note some time products of this reaction are Cr^{+3} (green) in place of CrO_5. //



(chromic peroxide) //

(5) chromyl chloride test :-

$NaCl + K_2Cr_2O_7 + H_2SO_4 \longrightarrow KHSO_4 + NaHSO_4 + H_2O + \overset{+6}{CrO_2Cl_2}\uparrow$
(cl) (Chromyl chloride) (orange-red)

Note → $Cr_2O_7^{-2} + H^+ + \underset{\text{or } Br^-}{I^-} \longrightarrow Cr^{+3} + \underset{\text{or } Br_2}{I_2} + H_2O$

$\overset{+6}{CrO_2Cl_2} + NaOH \longrightarrow \underset{\text{(yellow)}}{Na_2CrO_4} + NaCl + H_2O$

(6) $K_2Cr_2O_7$ acts as O.A in Acidic medium Acidic medium means presence of strong acid like HCl, HBr, HI, H_2SO_4 etc.

Halogen -1 to $+7$

"O"-family -2 to $+6$

"N"-family -3 to $+5$

"C"-family -4 to $+4$

"B"-family 0 to $+3$

$K_2\overset{+6}{Cr_2}O_7 + H_2SO_4 + AA \longrightarrow \overset{+3}{Cr_2}(SO_4)_3 + \text{oxidised} + H_2O + K_2SO_4$

O.A Acid green product

$K_2Cr_2O_7 + H_2SO_4 + KI^- \longrightarrow Cr_2(SO_4)_3 + I_2^0 + H_2O + K_2SO_4$

R.A

$K_2Cr_2O_7 + H_2SO_4 + H_2S^{-2} \longrightarrow Cr_2(SO_4)_3 + S^0 + H_2O + K_2SO_4$

(R.A)

$K_2Cr_2O_7 + H_2SO_4 + \overset{+2}{FeSO_4} \longrightarrow Cr_2(SO_4)_3 + \overset{+3}{Fe_2}(SO_4)_3 + H_2O + K_2SO_4$

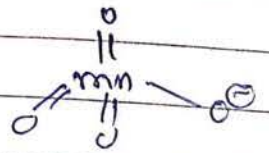
$K_2\overset{+6}{Cr_2}O_7 + HI^- \longrightarrow \overset{+3}{CrI_3} + I_2^0 + H_2O + KI$

O.A Acid/R.A

Potassium permanganate, $KMnO_4$

Bonding K^+ MnO_4^-

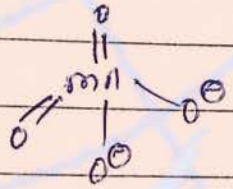
Permanganate ion



Tetrahedral

$HMnO_4$, Permanganic acid

manganate ion, MnO_4^{-2}



Tetrahedral

H_2MnO_4, manganic acid

Preparation –

$KMnO_4$ is prepared from pyrolusite ore (MnO_2)

Step 1st –

$$\underset{\text{black}}{MnO_2} + \underset{\text{lime}}{KOH} + \underset{\text{air}}{O_2} \longrightarrow \underset{\text{pot. manganate (green)}}{K_2MnO_4} + H_2O$$

(+4 → +6)

$HMnO_4$, ~~Potmanganic acid~~,

Step 2nd –

$$\underset{\text{R.A}}{K_2MnO_4} + \underset{\text{any O.A}}{Cl_2} \longrightarrow KMnO_4 + KCl$$

(+6 → +7, 0)

CHEMICAL BONDING - 1

Q.1 Choose the **incorrect** option -
(1) N_2H_4 is pyramidal about each N-atom
(2) In trisilyl amine $(SiH_3)_3N$, the Si–N bond length is lesser than expected value
(3) The bond angle in OF_2 is lesser than OCl_2
(4) The Be atom in dimer of $BeCl_2$ is sp^3 hybridised

Q.2 Identify the **correct** option(s)
(1) $NH_4^+ > NH_3 > NH_2^-$ order of bond angle
(2) $(CH_3)_3B$ is a trigonal planar molecule (not considering the H-atoms on 'C')
(3) In NH_4Cl 'N' atom is in sp^3d hybridization
(4) Bond Angle : $HgCl_2 < SnCl_2$

Q.3 Which of the following is a **wrong** order with respect to the property mentioned against each ?
(1) $O_2^{2-} > O_2 > O_2^+$ [magnetic moment]
(2) Bond Angle : $H_2O > H_2S > H_2Se$
(3) $H_2 > H_2^+ > He_2^+$ [bond energy]
(4) $NO_2^+ > NO_2 > NO_2^-$ [bond angle]

Q.4 Which of the following statements is incorrect ?
(1) Among O_2^+, O_2 and O_2^- the stability decreases as $O_2^+ > O_2 > O_2^-$
(2) He_2 molecule does not exist as the effect of bonding and anti-bonding orbitals cancel each other
(3) C_2, O_2^{2-} and Li_2 are diamagnetic
(4) In F_2 molecule, the energy of σ_{2p_z} is more than π_{2p_x} and π_{2p_y}

Q.5 Arrange the following in order of decreasing N–O bond length : NO_2^+, NO_2^-, NO_3^-
(1) $NO_3^- > NO_2^+ > NO_2^-$
(2) $NO_3^- > NO_2^- > NO_2^+$
(3) $NO_2^+ > NO_3^- > NO_2^-$
(4) $NO_2^- > NO_3^- > NO_2^+$

Q.1 गलत विकल्प चुनिए -
(1) N_2H_4 की आकृति पिरामिडिय है दोनों नाइट्रोजन परमाणुओं के सापेक्ष।
(2) ट्राइसिलिल एमीन $(SiH_3)_3N$ में, Si–N बंध लम्बाई, आपेक्षित मान से कम होती है
(3) OF_2 में बंध कोण OCl_2 से कम होता है
(4) $BeCl_2$ के द्विलक में Be परमाणु sp^3 संकरित होता है

Q.2 सही विकल्पों को पहचानिए -
(1) बंधकोण का क्रम $NH_4^+ > NH_3 > NH_2^-$
(2) $(CH_3)_3B$ एक त्रिकोण समतलीय अणु है। (C पर H-परमाणुओं का ध्यान ना करते हुए)
(3) NH_4Cl में 'N' परमाणु sp^3d संकरण में होता है
(4) बन्ध कोण : $HgCl_2 < SnCl_2$

Q.3 निम्न में से प्रत्येक के विरूद्ध उल्लेखित गुणों के सापेक्ष कौनसा क्रम गलत है ?
(1) $O_2^{2-} > O_2 > O_2^+$ [चुम्बकीय आघूर्ण]
(2) बंध कोण : $H_2O > H_2S > H_2Se$
(3) $H_2 > H_2^+ > He_2^+$ [बंध ऊर्जा]
(4) $NO_2^+ > NO_2 > NO_2^-$ [बंध कोण]

Q.4 निम्न में से कौनसा कथन असत्य है ?
(1) $O_2^+ > O_2 > O_2^-$ के रूप में O_2^+, O_2 व O_2^- के स्थायित्व में कमी होती है
(2) He_2 अणु का अस्तित्व नहीं है क्योंकि बंधित व प्रतिबंधित कक्षक एक–दूसरे के प्रभाव को निरस्त कर देते हैं
(3) C_2, O_2^{2-} व Li_2 प्रतिचुम्बकीय होते है
(4) F_2 अणु में σ_{2p_z} की ऊर्जा, π_{2p_x} व π_{2p_y} से अधिक होती है

Q.5 निम्न को N–O बंध लम्बाई के घटते क्रम में व्यवस्थित कीजिए : NO_2^+, NO_2^-, NO_3^-
(1) $NO_3^- > NO_2^+ > NO_2^-$
(2) $NO_3^- > NO_2^- > NO_2^+$
(3) $NO_2^+ > NO_3^- > NO_2^-$
(4) $NO_2^- > NO_3^- > NO_2^+$

Q.6 Which among the following molecules have sp^3d hybridisation with one lone pair of electrons on the central atom ?
(i) SF_4 (ii) $[PCl_4]^+$ (iii) XeO_2F_2 (iv) $ClOF_3$
(1) (i), (ii) and (iii) only (2) (i), (iii) and (iv) only
(3) (i) and (iii) only (4) (iii) and (iv) only

Q.7 Match the species/molecules listed in column-I with their characteristics listed in column-II.

Column-I	Column-II
(A) ClF_5, BrF_4^+, IF_6^-	(P) All molecules / ions are polar in nature
(B) ClF_3, BrF_2^+, ICl_4^-	(Q) All molecules / ions have same number of lone pair(s) and same shape
(C) XeF_2, ICl_2^-, I_3^-	(R) All molecules / ions have same oxidation state of central atoms
(D) $ClOF_3$, ClF_4^+, $IO_2F_2^-$	(S) All molecules / ions have same hybridisation of central atoms

(1) $A \to P$; $B \to Q$; $C \to P$; $D \to S$
(2) $A \to P,S$; $B \to Q,R$; $C \to Q,S$; $D \to R$
(3) $A \to Q$; $B \to R$; $C \to S$; $D \to P$
(4) $A \to P,R$; $B \to R$; $C \to Q,S$; $D \to P,Q,R,S$

Q.8 Least melting point is shown by the compound
(1) $PbCl_2$ (2) $SnCl_4$ (3) NaCl (4) $AlCl_3$

Q.9 For BF_3 molecule which of the following is true
(1) B-atom is sp^2 hybridised
(2) There is a $p\pi$-$p\pi$ back bonding in this molecule
(3) Observed B–F bond length is found to be less than the expected bond length
(4) All of these

Q.6 निम्न से कौनसे अणुओं में केन्द्रीय परमाणु पर एकल युग्म के साथ sp^3d संकरण पाया जाता है
(i) SF_4 (ii) $[PCl_4]^+$ (iii) XeO_2F_2 (iv)
(1) केवल (i), (ii) व (iii) (2) केवल (i),
(3) केवल (i) व (iii) (4) केवल (iii) व

Q.7 स्तम्भ-I में उपस्थित स्पीशीज / अणुओं की सूची में इनके लक्षणों की सूची के साथ सुमेलित कीजि

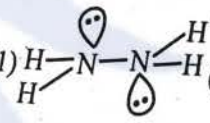
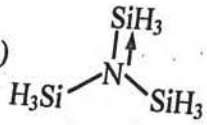
स्तम्भ-I	स्तम्भ-II
(A) ClF_5, BrF_4^+, IF_6^-	(P) सभी अणु / आयन में ध्रुवीय होते है
(B) ClF_3, BrF_2^+, ICl_4^-	(Q) सभी अणु / आयन युग्म की समान संख्या समान आकृति रखते
(C) XeF_2, ICl_2^-, I_3^-	(R) सभी अणु / आयन परमाणुओं की ऑक्सीकरण अवस्था है
(D) $ClOF_3$, ClF_4^+, $IO_2F_2^-$	(S) सभी अणु / आयन परमाणुओं के संकरण रखते है

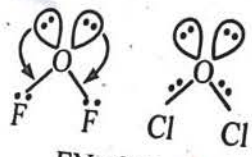
(1) $A \to P$; $B \to Q$; $C \to P$; $D \to S$
(2) $A \to P,S$; $B \to Q,R$; $C \to Q,S$; $D \to$
(3) $A \to Q$; $B \to R$; $C \to S$; $D \to P$
(4) $A \to P,R$; $B \to R$; $C \to Q,S$; $D \to P,Q$

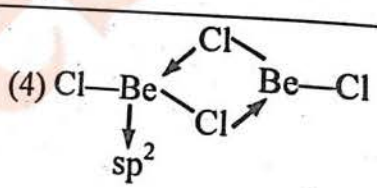
Q.8 निम्न में किसके गलनांक का मान न्युनतम होगा
(1) $PbCl_2$ (2) $SnCl_4$ (3) NaCl (4) $AlCl_3$

Q.9 BF_3 अणु के लिए निम्न में से कौनसा कथन सत्य
(1) बॉरोन परमाणु sp^2 संकरित होता है
(2) BF_3 में $p\pi$-$p\pi$ पश्यबंधन होता है
(3) BF_3 में B–F बंध लम्बाई अपेक्षा से कम आती
(4) सभी

HINTS & SOLUTION

1. [4] (1)  (2) 

(3) 
EN of F > Cl

(4) 

2.[1,2] N does not have d orbital.
Bond angle $HgCl_2 > SnCl_2$

3.[1] O_2 have two unpaired electron, O_2^+ have o unpaired electron, O_2^{2-} have zero unpair electron. As number of unpaired electro increases paramagnetic character increases.

K_2CrO_4 does not acts as oxidising agent.

element :-

alkali metals -
(Li, Na, K, Rb, Cs)

Alkaline earth metal
(Be, mg, Ca, Sr, Ba)

Sc

Zn

Cl

F

O (−2 to +2)

Cl (−1 to +7)

N (−1 to +4)

0, 2

+1

+2

+3

+2

+3

−1

finest

−2

−1

+1

mostly finest

4.[4] In the absence of inter electronic repulsion, the energy of σ_{2p_z} is less than π_{2p_x} and π_{2p_y}

5.[2] Bond length $\propto \frac{1}{\text{Bond order}}$

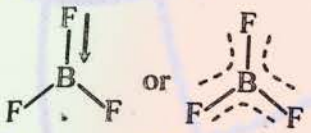
NO_3^-	NO_2^-	NO_2^+	
1.33	1.5	2.0	(bond order)

6.[2] PCl_4^+ has sp^3 hybridised P

7.[4]

	Compound	Hybridisation	Shape
1.	ClF_5	sp^3d^2	Square pyramidal
2.	BrF_4^+	sp^3d	Sea-saw
3.	IF_6^-	sp^3d^3	Distorted octahedral
4.	ClF_3	sp^3d	T-shape
5.	ICl_4^-	sp^3d	square planar
6.	$IO_2F_2^-$	sp^3d	Sea-saw
7.	BrF_2^+	sp^3	V-shape
8.	ICl_2^-	sp^3d	Linear

8.[2] $SnCl_4$ possess highest covalent character and thus has lowest melting point.

9.[4] 

Chemical bonding

1) Type of bond :-

(1) Intra atomic (b/w atoms) → Ionic, Co-valent, Co-ordinate, Metallic

(2) Inter molecular (b/w molecules) → H-bond, vander walls force of attraction

(1) Ionic or electrovalent bond →

(1) In this bond stability comes through transfer of e⁻

(2) Ionic bond is actually electrostatic force of attraction b/w cation and anion.

(3) Condition to form Ionic bond :→

<A> Low I.E + High E.A

<B> ΔE.N must be high (2.2 or more)

[metal + Non-metal]

<4> In an Ionic Compound cations and anions are arranged in a regular 3-dimensional arrangement called as lattice.

* During formation of any chemical bond, total P.E of system decreases.

(5) Due to presence of lattice Ionic Comp. exist in solid state and they have very high density, melting point and boiling point.

(6) During formation of lattice some energy is released called as lattice energy.

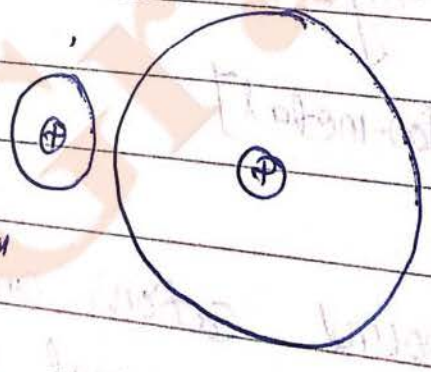
$M^+ X^-$ $M^+ X^-$
$X^- M^+$ $X^- M^+$
$M^+ X^-$ $M^+ X^-$
lattice

$$M^+_{(g)} + X^-_{(g)} \longrightarrow MX_{(s)} + \underset{\text{energy}}{\text{Lattice}} \quad ; \quad \Delta H = -U$$
$$(U)$$

$$U \propto \frac{q_1 q_2}{r}$$

lattice energy

q_1 and q_2 are charge of cation and anion.



$r = r^+ + r^-$

CAREER POINT

Target Course for NITs (JEE Main)-2014

DAILY PRACTICE PROBLEM SHEET

CHEMISTRY

CHEMICAL BONDING - 2

Q.1 Which of the following process involves the breaking of covalent bond ?
(1) Evaporation of water
(2) Sublimation of iodine
(3) Formation of atomic hydrogen
(4) Melting of sodium metal

Q.2 Which of the following pair contains iso-structural species -
(1) CH_3^- and CH_3^+ (2) NH_4^+ and NH_3
(3) SO_4^{2-} and BF_4^- (4) NH_2^- and BeF_2

Q.3 Which is not true about the N–N bond length among the following species ?
(I) $H_2N–NH_2$ (II) N_2 (III) N_2O
(1) N–N bond length is shortest in II
(2) N–N bond length in I is shorter than that of in III
(3) N–N bond length in III is shorter than that of in I
(4) N–N bond length is less than N–O in (III)

Q.4 Which is correct statement ?
As the s-character of a hybrid orbital decreases
(I) The bond angle decreases
(II) The bond strength increases
(III) The bond length increases
(IV) Size of orbitals increases
(1) (I), (III) and (IV) (2) (II), (III) and (IV)
(3) (I) and (II) (4) All are correct

Q.1 निम्न में से कौनसा प्रक्रम सहसंयोजक बंधों के विदलन को प्रदर्शित करता है ?
(1) जल का वाष्पन
(2) आयोडीन का उर्ध्वपातन
(3) परमाण्विय हाइड्रोजन का निर्माण
(4) सोडियम धातु का गलन

Q.2 निम्न में से कौनसा युग्म समसंरचनात्मक रखता है -
(1) CH_3^- तथा CH_3^+ (2) NH_4^+ तथा NH_3
(3) SO_4^{2-} तथा BF_4^- (4) NH_2^- तथा BeF_2

Q.3 निम्न स्पीशीज में से N–N बंध लम्बाई के बारे में कौन सही नहीं है ?
(I) $H_2N–NH_2$ (II) N_2 (III) N_2O
(1) II में N–N बंध लम्बाई सबसे कम हैं
(2) I में N–N बंध लम्बाई, III से कम हैं
(3) III में N–N बंध लम्बाई, I से कम हैं
(4) III में N–N बंध लम्बाई, N–O बंध लम्बाई से कम हैं

Q.4 कौनसा कथन सही है ?
संकर कक्षक के s-लक्षण कम होते हैं
(I) बंध कोण कम होता है
(II) बंध सामर्थ्य बढ़ती है
(III) बंध लम्बाई बढ़ती है
(IV) कक्षकों का आकार बढ़ता हैं
(1) (I), (III) तथा (IV) (2) (II), (III) तथा (IV)
(3) (I) तथा (II) (4) सभी सही हैं

Q.5 Select the incorrect statement about N_2F_4 and N_2H_4 :
(I) In N_2F_4, d-orbitals are contracted by electronegative fluorine atoms, but d-orbital contraction is not possible by H-atom in N_2H_4
(II) The N–N bond energy in N_2F_4 is more than N–N bond energy in N_2H_4
(III) The N–N bond length in N_2F_4 is more than that of in N_2H_4
(IV) The N–N bond length in N_2F_4 is less than that of in N_2H_4
Choose the correct code -
(1) I, II and III (2) I and III
(3) II and IV (4) II and III

Q.6 The hybridization of the central atom will change when -
(1) NH_3 combines with H^+
(2) H_3BO_3 combines with OH^-
(3) NH_3 forms NH_2^-
(4) H_2O combines with H^+

Q.7 In which of the following compounds B–F length is shortest ?
(1) BF_4^-
(2) $BF_3 \leftarrow NH_3$
(3) BF_3
(4) $BF_3 \leftarrow N(CH_3)_3$

Q.8 How many S–S bonds, S–O–S bonds, σ-bonds, π-bonds are present in trimer of sulphur trioxide
(1) 0, 3, 16, 2
(2) 0, 3, 12, 6
(3) 0, 6, 12, 16
(4) 0, 4, 12, 6

Q.5 N_2F_4 व N_2H_4 के बारे में गलत कथन चुनिए
(I) N_2F_4 में, d-कक्षक विद्युतऋणी फ्लोरीन से जुड़े होते है लेकिन d कक्षक संयोजन में H परमाणु द्वारा सम्भव नहीं है
(II) N_2F_4 में N–N बंध ऊर्जा, N_2H_4 में N–N ऊर्जा से अधिक होती हैं।
(III) N_2F_4 में N–N बंध लम्बाई, N_2H_4 से होती है
(IV) N_2F_4 में N–N बंध लम्बाई, N_2H_4 से कम
सही कोड चुनिए -
(1) I, II तथा III (2) I तथा III
(3) II तथा IV (4) II तथा III

Q.6 केन्द्रीय परमाणु का संकरण परिवर्तित होगा, जब,
(1) H^+ के साथ NH_3 जुड़ा हो
(2) OH^- के साथ H_3BO_3 जुड़ा हो
(3) NH_3 , NH_2^- बनाता हो
(4) H^+ के साथ H_2O जुड़ा हो

Q.7 निम्न में से किस यौगिक में B–F लम्बाई न्यूनतम होती है ?
(1) BF_4^-
(2) $BF_3 \leftarrow NH_3$
(3) BF_3
(4) $BF_3 \leftarrow N(CH_3)_3$

Q.8 कितने S–S बंध, S–O–S बंध, σ-बंध, π-बंध सल्फर ट्राई ऑक्साइड के त्रिलक में उपस्थित होते है?
(1) 0, 3, 16, 2
(2) 0, 3, 12, 6
(3) 0, 6, 12, 16
(4) 0, 4, 12, 6

Q.9 The correct order of strength of H-bond in the following compound -

(1) $H_2O > H_2O_2 > HF > H_2S$

(2) $HF > H_2O_2 > H_2O > H_2S$

(3) $HF > H_2O > H_2S > H_2O_2$

(4) $HF > H_2O > H_2O_2 > H_2S$

Q.10 Which of the following is arranged order of increasing boiling point ?

(1) $H_2O < CCl_4 < CS_2 < CO_2$

(2) $CO_2 < CS_2 < CCl_4 < H_2O$

(3) $CS_2 < H_2O < CO_2 < CCl_4$

(4) $CCl_4 < H_2O < CO_2 < CS_2$

Q.9 निम्न यौगिकों में से H-बंध की सामर्थ्य का सही क्रम है -

(1) $H_2O > H_2O_2 > HF > H_2S$

(2) $HF > H_2O_2 > H_2O > H_2S$

(3) $HF > H_2O > H_2S > H_2O_2$

(4) $HF > H_2O > H_2O_2 > H_2S$

Q.10 निम्न में से कौन क्वथनांक बिंदू के बढ़ते क्रम में व्यवस्थित है ?

(1) $H_2O < CCl_4 < CS_2 < CO_2$

(2) $CO_2 < CS_2 < CCl_4 < H_2O$

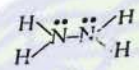
(3) $CS_2 < H_2O < CO_2 < CCl_4$

(4) $CCl_4 < H_2O < CO_2 < CS_2$

1.[3] $H\text{–}H \longrightarrow \underset{\text{Covalent bond}}{\uparrow} 2H(g)$

2.[3] Both SO_4^{2-} and BF_4^- are tetrahedral.

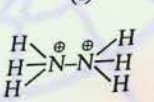
3.[2]



(I)

$N \equiv N$

(II)



(III)

$\overset{\oplus}{N}=\overset{\oplus}{N}=O \leftrightarrow N\equiv\overset{\oplus}{N}-\overset{\ominus}{O}$

(IV)

> Due to triple bond (N≡N), N–N bond length is shorted in (II)

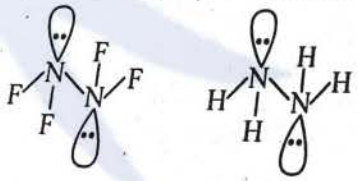
> Lone pair occupies more s-character, hence N–N bond length in (III) is shorter than that of in (I)

> Due to resonance in N_2O, N–N bond length is intermediate between I and II.

4.[1]

	sp	sp^2	sp^3
%s	50%	33%	25%
angle	180°	120°	109°

5.[2] N does not have d-orbitals



> In N_2F_4, N–N bond has more s-character hence bond length decreases.

> While in N_2H_4, N–N bond has less s-character (i.e., more p-character), hence bond lengths is more.

6.[2]

> $\underset{sp^3}{\ddot{N}H_3} + H^+ \longrightarrow \underset{sp^3}{NH_4^+}$

> $\underset{sp^3}{2NH_3} \rightleftharpoons \underset{sp^3}{NH_2^-} + \underset{sp^3}{NH_4^+}$

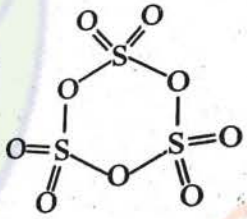
> $\underset{sp^2}{H_3BO_3} + OH^- \longrightarrow [\underset{sp^3}{B(OH)_4}]^-$

> $\underset{sp^3}{H_2O} + H^+ \rightleftharpoons \underset{sp^3}{H_3O^+}$

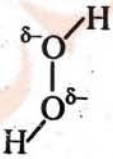
7.[3] Only in BF_3 pπ-pπ back bonding is possible due to which B–F bond length is shortest. In other compounds, p-orbital at boron is vacant hence, pπ-pπ back bonding is not possible.

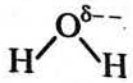
> Water molecules are hexagonally closed packed in ice with the help of H-bonding hence due to existence of voids/interstitial spaces it has cage like structure with less density than water.

8.[2]



9.[4] Strength of H-bonding is higher in H_2O, than H_2O_2 because the amount of formal negative charge on oxygen atom in case of water is more than that of H_2O_2.





10.[2] BP of H_2O is increased by about 200° due to H bonding.

(c) Arrange in order of lattice energy:

$$U \propto \frac{1}{r_c}$$

(a) $LiF > LiCl > LiBr > LiI$

(b) $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3$

Note: अगर ___ दोनों अलग-अलग (दोगा) तो lattice energy change से find करें ___

(d) Ionic bond is non-directional Hence Ionic comp do not show stereo isomerism.

(e) In solid state due to absence of free ion's Ionic compounds are bad conductor of heat and electricity.

In aqueous medium or In molten or fused state Ionic compounds become good conductor./

NaCl(s) bad conductor
NaCl(aq) Conductor
NaCl(molten/fused) conductor
Fe(s) Conductor./

(9) Ionic comp. are soluble in polar solvent like water, ether as dielectric material

(10) Ionic compounds produce free ions in water or any other polar solvent.

These free ions are main cause of their chemical rexn.

$$KCl(aq) + AgNO_3(aq) \longrightarrow AgCl(s) + KNO_3(aq)$$

(11) Those comp. dissolve in that polar solvent in which their solvation energy is greater than or equals to lattice energy.

If solvent is water then solvation means hydration

$$MX_{(s)} + U \longrightarrow M^+_{(g)} + X^-_{(g)}$$

$$M^+_{(g)} + \text{solvent} \xrightarrow{\text{solvation}} M^+(\text{solvated}) + \text{solvation energy}$$

$$X^-_{(g)} + \text{Solvent} \xrightarrow{\text{solvation}} X^-(\text{solvated}) + S.E_2$$

For solubility;

$$S.E_1 + S.E_2 \geq U$$

CAREER POINT

Target Course for NITs (JEE Main)-2014

DAILY PRACTICE PROBLEM SHEET

CHEMISTRY

CHEMICAL BONDING - 3

Q.1 Match the column

Column-I (Pair of species)	Column-II (Identical property in pairs of species)
(1) PCl_3F_2, PCl_2F_3	(P) Hybridisation of central atom
(2) BF_3 and BCl_3	(Q) Shape of molecule/ion
(3) CO_2 and CN_2^{-2} (Cyanamide ion)	(R) μ (dipole moment)
(4) C_6H_6 and $B_3N_3H_6$	(S) Total number of electrons

Q.2 Which of the following statement is incorrect
(1) O_2 is paramagnetic, O_3 is also paramagnetic
(2) O_2 is paramagnetic, O_3 is diamagnetic
(3) B_2 is paramagnetic, C_2 is also paramagnetic
(4) Different observation is found in their bond length when $NO \rightarrow NO^+$ and $CO \rightarrow CO^+$

Q.3 Which is not the geometry of covalent molecules ?
(1) Pentagonal bipyramidal
(2) Octahedral
(3) Hexagonal
(4) Tetrahedral

Q.4 The correct order of bond angles is -
(1) $NO_2^- > NO_2^+ > NO_2$
(2) $NO_2^+ > NO_2^- > NO_2$
(3) $NO_2 > NO_2^+ > NO_2^-$
(4) $NO_2^+ > NO_2 > NO_2^-$

Q.1 स्तम्भ सुमेलित कीजिए

स्तम्भ-I (स्पीशीज का युग्म)	स्तम्भ-II (स्पीशीज का युग्मों में सामान्य गुण)
(1) PCl_3F_2, PCl_2F_3	(P) केन्द्रीय परमाणु का संकरण
(2) BF_3 तथा BCl_3	(Q) अणु/आयन की आकृति
(3) CO_2 तथा CN_2^{-2}	(R) μ (द्विध्रुव आघूर्ण)
(4) C_6H_6 तथा $B_3N_3H_6$	(S) इलेक्ट्रॉनों की कुल संख्या

Q.2 निम्न में से कौनसा कथन ग़लत है ?
(1) O_2 अनुचुम्बकीय है, O_3 भी अनुचुम्बकीय है
(2) O_2 अनुचुम्बकीय है, O_3 प्रतिचुम्बकीय है
(3) B_2 अनुचुम्बकीय है, C_2 भी अनुचुम्बकीय है
(4) $NO \rightarrow NO^+$ व $CO \rightarrow CO^+$ की बंध लम्बाई में भिन्न प्रेक्षण पाए जाते हैं

Q.3 सहसंयोजक अणुओं की ज्यामिति कौनसी नहीं है ?
(1) पंचकोणीय द्विपिरामिडीय
(2) अष्टफलकीय
(3) षटकोणीय
(4) चतुष्फलकीय

Q.4 बंध कोणों का सही क्रम है -
(1) $NO_2^- > NO_2^+ > NO_2$
(2) $NO_2^+ > NO_2^- > NO_2$
(3) $NO_2 > NO_2^+ > NO_2^-$
(4) $NO_2^+ > NO_2 > NO_2^-$

1.[1 → P, Q ; 2 → P,Q,R ; 3 → P,Q,R,S ; 4 → PQ,R,S]

> PCl_3F_2 and PCl_2F_3 has sp^3d hybrid P.

> BF_3 and BCl_3 are trigonal planar

> C_6H_6 and $B_3N_3H_6$ are isosters

2.[1,3,4]> O_2 = Paramagnetic molecule with 2 unpaired electrons in antibonding p-orbital

> O_3 = diamagnetic molecule

> B_2 = Paramagnetic with 2 unpaired electron in bonding π-orbitals

> C_2 = Diamagnetic molecule

> $NO \longrightarrow \overset{\oplus}{N}O$ (Electron removed from antibonding orbital)

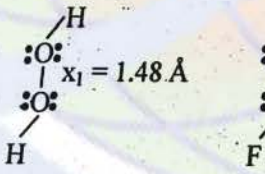
> $CO \longrightarrow \overset{\oplus}{C}O$ (Electron removed from bonding orbital)

3.[3]

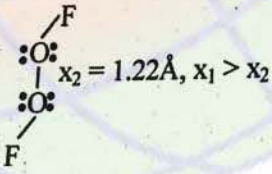
4.[4] NO_2^+ has sp hybrid N and NO_2^- has sp^2 hybrid N

5.[1] Oxides of s block are more basic than d-block

6.[2]



$x_1 = 1.48$ Å



$x_2 = 1.22$Å, $x_1 > x_2$

> According to Bent's Rule in O_2F_2, there is more p-character in O–F bond in comparison to O–H bond in H_2O_2 ; hence s-character in O–O bond is greater in O_2F_2.

7.[3] XeF_4 and ICl_4^- has sp^3d^2 hybridisation and square planar shape

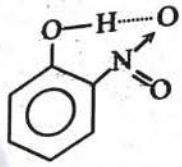
> XeO_4 has zero lp

> SF_4 has one lp

8.[3]

Molecule	Hybridisation
SF_4	sp^3d
XeF_4	sp^3d^2
$SiCl_4$	sp^3
ICl_4^+	sp^3d
I_3^-, XeF_2	sp^3d
ClO_3^-, PO_4^{3-}	sp^3

9.[3]



o-nitrophenol has intramolecular H bonding

10.[2] Rb^+Cl^- has electrostatic attraction

Note

A given Ionic compound is more soluble in water if its hydration energy is high and lattice energy is low.

order of solubility in water →

Alkali metal	Alkaline Earth metal.
$Li_2CO_3 < ---- < Cs_2CO_3$	$BeCO_3 > ----> BaCO_3$
$Li_2SO_4 < ---- < Cs_2SO_4$	$BeSO_4 > ----> BaSO_4$
U ↓ ; solubility ↑	H.E ↑ ; solubility ↑

$K_{sp} \propto$ solubility

★ Electrovalency :-

मतलब No of Atoms

↓ The no. of e⁻, gained or lost by an atom during formation of Ionic bond.

→ electrovalency without sign बोलते हैं

eg: $Na^{+1}Cl^{-1}$

$Ca^{+2}Cl_2^{-1}$

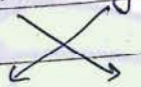
↓↓ For monoatomic Ion's electrovalency equals to its charge or oxidation state.

$Na^{(+1)}$ $Cl^{(-1)}$

(3) For polyatomic ion's electrovalency equals to its cha...

(A) Formula of Ionic Compound -

E.V x y



A B
(+ve) -ve

⇒ $A_y B_x$

note → 'y' and 'x' must be in simple whole no. ratio

x x

A B
+ve -ve

⇒ AB

Naming of Anion

Electrovalency =

Conc lab → For monoatomic anions if mono atomic ... have their lowest possible -ve charge ... their name is ended by -ide

X^-	halide
O^{-2}	oxide
S^{-2}	sulphide
N^{-3}	Nitride
P^{-3}	Phosphide

Date
Page

Na_2S, Sod. Sulphide

Cal. Phosphide, Ca_3P_2

* Contd

For Polyatomic anions,

oxyacid	Name of Anion
-ic acid	-ate
-ous acid	-ite

$HClO_4$, Perchloric Acid	ClO_4^-, Perchlorate
H_2SO_4, Sulphuric Acid	SO_4^{-2}, Sulphate
	HSO_4^-, Bisulphate or hydrogen sulphate
HNO_3, Nitric acid	NO_3^-, Nitrate
H_2SO_3, Sulphurous acid	SO_3^{-2}, Sulphite
	HSO_3^-, bisulphite or hydrogen sulphite
H_2CO_3, Carbonic Acid	CO_3^{-2}, Carbonate
	HCO_3^-, bicarbonate or hydrogen carbonate
H_3PO_4, Phosphoric Acid	PO_4^{-3}, Phosphate
	$H_2PO_4^-$, dihydrogen phosphate
	HPO_4^{-2}, hydrogen phosphate

Na_2SO_3 | Sodium Sulphate ; $Ca_3(PO_4)_2$ | Calcium phosphate

Q.) Formula of a compound is M_2O_3 what is the formula of Nitrate of M?

Sol.)

M_2O_3 (+3) → M (+3) NO_3 (−1)

$\Rightarrow M(NO_3)_2$ Ans

Q.) Formula of a compound is $MHPO_4$. What is the formula of chloride of M?

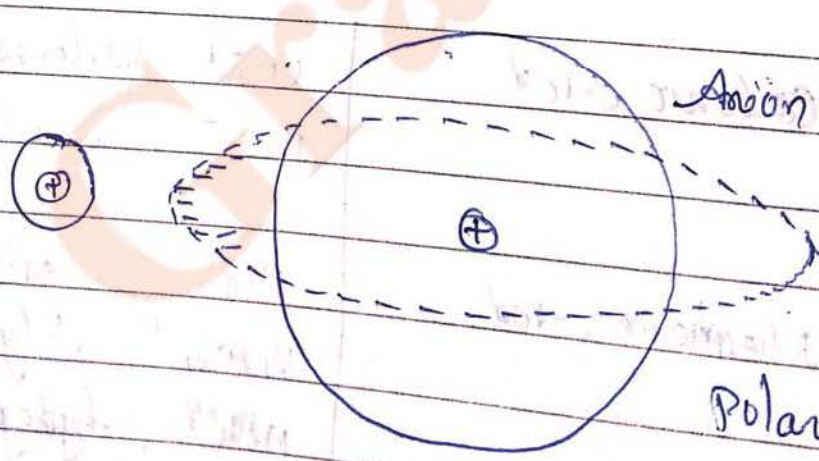
$\underline{M}HPO_4$ (+2) → M (+2) Cl^-

$x+1-3=0$

$\Rightarrow MCl_2$ Ans

★ Covalent character in Ionic compounds (Fajan's rule)

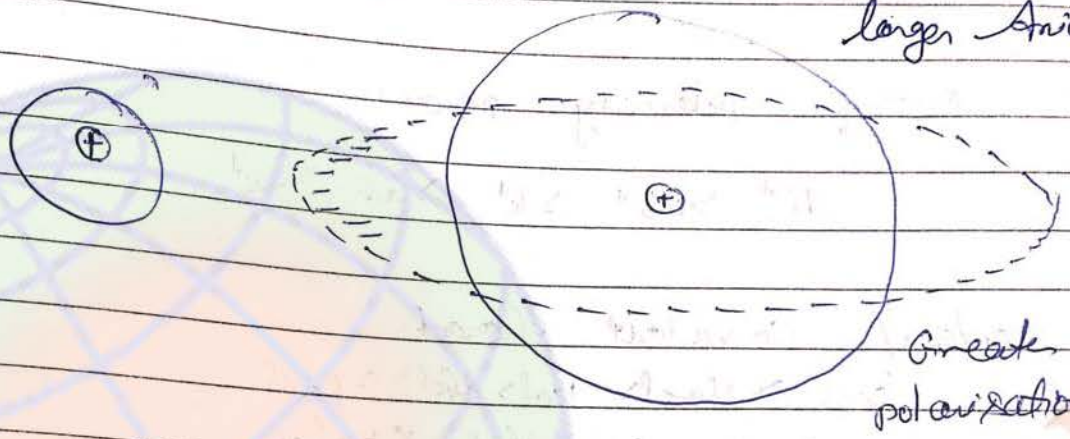
① Covalent character ∝ Polarisation in anion



→ charge का size attraction के कारण small हो जाता है

Polarisation.

Larger anion → Greater polarisation in anion
→ Greater polarisibility of anion.
→ Greater covalent charact.



* order of polarisibility :—

$F^- < Cl^- < Br^- < I^-$

* order of covalent charact. :—

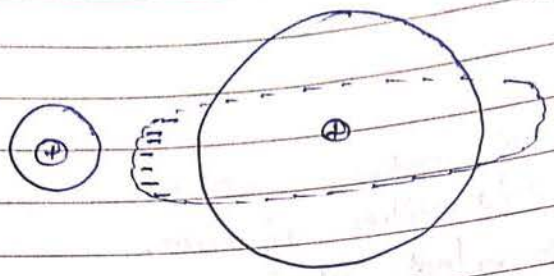
$LiF < LiCl < LiBr < LiI$

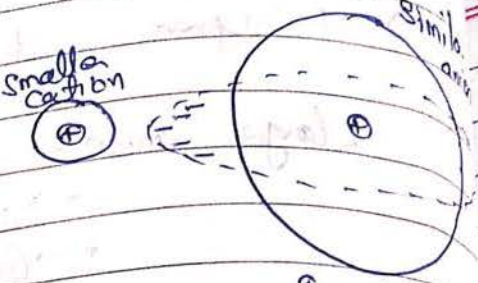
$CuF_2 < CuCl_2 < CuBr_2 < CuI_2$

$BF_3 < BCl_3 < BBr_3 < BI_3$

3) For a given anion—

Smaller cation → Greater Polarising power of cation
→ Greater Polarisation of Anion
→ Greater covalent charact.





order of polarising power -

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

order of Covalent character

LiCl > NaCl > KCl > RbCl > CsCl

NaCl < $MgCl_2$ < $AlCl_3$ < $SiCl_4$

Q1) Arrange in order of Ionic character

KCl, $MgCl_2$, $BeCl_2$, NaCl

Be^{+2}

Na^+ Mg^{+2}

K^+

KCl > NaCl > $MgCl_2$ > $BeCl_2$

Q2) which comp. is most ionic?

a) CsCl b) NaCl c) NaBr d) CaBr

Note:-

(1) In S-block comp. of Berelion (Be^{+2}) are covalent some comp. of Li and Mg are also covalent.

(2) In d-block comp. upto +3 oxidation state Ionic character is greater and at higher oxidation state covalent character is greater.

→ $CuSO_4$

Cu^{+2} ionic SO_4^{-2}

→ $KMnO_4$

K^+ ionic MnO_4^- (+7) covalent

Ex of covalent character :-

MnO (+2) < MnO_2 (+4) < Mn_2O_7 (+7)

$SnCl_2$ (+2) < $SnCl_4$ (+4)

MCl_2 (+2) < MCl_4 (+4)

* Application of fajan's rule :-

(when anion is similar)

$$\text{Ionic Potential } (\phi) = \frac{\text{charge of cation}}{\text{size of cation}}$$

ϕ "↑", Polarising power of cation "↑", covalent ch ↑

$\phi\uparrow$, covalent ch ↑ →

$\phi\downarrow$
Covalent ↓ ch.
↓

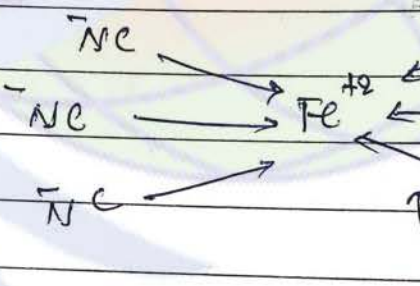
1.) ϕ "↑" ; chance of formation of Co-ordination or Complex Comp. "↑"

(Size of cation ↓ ; chance of formation of Co-ordination Comp.)

eg:-

$K_4[Fe(CN)_6]$

$4K^+$ $[Fe(CN)_6]^{-4}$



covalent charact.

order of chance of formation of ~~Cation~~ complex ~~ratio~~ Comp.

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

$Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$

<2> ϕ ↑, thermal stability of metallic carbonate, sulphate, Nitrates, oxides and hydroxides ↓

(Covalent ch ↑, thermal stability ↓)

order of thermal stability :-

Li_2CO_3 < ---- < Cs_2CO_3

$BeSO_4$ < ---- < $BaSO_4$

$LiNO_3$ < ---- < $CsNO_3$

BeO < ---- < BaO

LiOH < ---- < CsOH

* metallic carbonate -

$$MCO_3 \xrightarrow{\Delta} MO + CO_2 \uparrow$$

(except carbonates of Na^+, K^+, Rb^+, and Cs^+)

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2 \uparrow$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \uparrow$$

* metallic sulphate :-

$$MSO_4 \xrightarrow{\Delta} MO + SO_3 \uparrow \xrightarrow{T > 800^\circ C} SO_2 \uparrow + \frac{1}{2} O_2 \uparrow$$

(except sulphates of Na^+, K^+, Rb^+ and Cs^+)

$$BaSO_4 \xrightarrow{\Delta} BaO + SO_3 \uparrow$$

$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + SO_3$

Ferric sulphate

$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$

R.A O.A

Ferrous sulphate

Brown

Metallic Nitrates:-

$MNO_3 \xrightarrow{\Delta} MO + NO_2 + O_2$

(except nitrate of Na^+, K^+, Rb^+, Cs^+)

$LiNO_3 \xrightarrow{\Delta} Li_2O + NO_2 + O_2$

$Ca(NO_3)_2 \xrightarrow{\Delta} CaO + NO_2 + O_2$

Note:-

$CO_3^{-2} \xrightarrow{\Delta} CO_2$

$SO_4^{-2} \xrightarrow{\Delta} SO_3$

$NO_3^- \xrightarrow{\Delta} NO_2 + O_2$

CO_3^{-2} and SO_4^{-2} salts are not good O.A while NO_3^- salts are good O.A

$NaNO_3 \xrightarrow{\Delta} NaNO_2 + \frac{1}{2}O_2$

(K^+, Rb or Cs^+)

* metallic hydroxides :-

$MOH \xrightarrow{\Delta} MO + H_2O$

(except hydroxides of Na^+, K^+, Rb^+, Cs^+)

$Be(OH)_2 \xrightarrow{\Delta} BeO + H_2O$

$Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + H_2O$

* metallic oxides :-

$MO \xrightarrow{\Delta} M + O_2 \uparrow$

(very few)

$\Rightarrow$ metallic oxides are thermally most stable

Note: Thermal stability of metallic ~~oxides~~ hydrides depend on lattice energy.

* Lattice energy ↑ ; thermal stability ↑

order of thermal stability :

$LiH > NaH > KH > RbH > CsH$

$BaH_2 > MgH_2 > CaH_2 > SrH_2 > BaH_2$

) Q ↑, m.p of metallic halides ↓

(Covalent ch ↑, m.p of halides ↓

★ Order of melting point → in halides of metals →

(a) Cl^-, Br^-, I^-

Fajan's Rule is applicable

$Be^{+2} < Mg^{+2} < Ca^{+2} < Sr^{+2} < Ba^{+2}$

e.g. $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$

b) F^-

$CaF_2 > MgF_2 > SrF_2 > BaF_2 > BeF_2$

★ order of melting point in halides of alkali metals →

a) $NaF > KF > LiF > RbF > CsF$

b) $NaCl > KCl > RbCl > CsCl > LiCl$

c) $NaBr > KBr > RbBr > CsBr > LiBr$

d) $KI > NaI > RbI > CsI > LiI$

Q.) which halide has least m.p.?

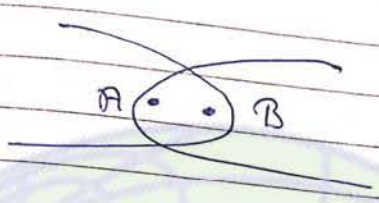
(a) NaF (b) NaCl (c) NaBr (d) NaI

(If cation is similar and anions are different then Fajan's rule is dominating.)

a) Co-valent bond →

a) ~~Ionic~~ Bond that bond stability comes to sharing of e⁻ b/w bonding atom's

b) To form covalent bond ΔE.N must be low (0.1 or less)



c) Polar co-valent compounds are soluble in polar solvent's while non-polar co-valent compounds are soluble in non-polar solvents

d) In general co-valent compounds are bad conductor of heat and electricity.

e) Exception → Compounds having free e⁻'s

eg.→ graphite, I_2, ~~black~~ black P,

f) In some compounds ~~as~~ auto Ionization ~~or~~ self Ionization takes place.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

(c) Aquous solution of polar co-valent

$$HCl \xrightarrow{H_2O} H^+ + Cl^-$$

★ lone pair (LP) / unbonded e⁻ pair / unshared e⁻ pair

Pair of valance e⁻, which do not participate in bonding.

$\ddot{N}H_3$, l.P = 1

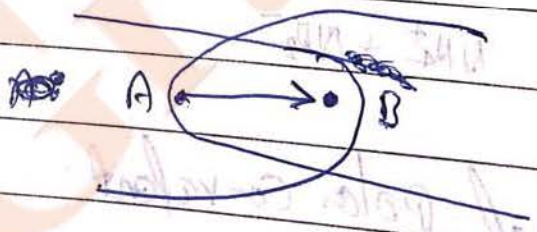
$N\ddot{2}O$: , l.P = 2

CH_4 , l.P = 0

(3) Co-ordinate bond (dative bond) →

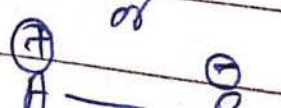
In this bond stability comes of partial transfer and partial sharing of e⁻.

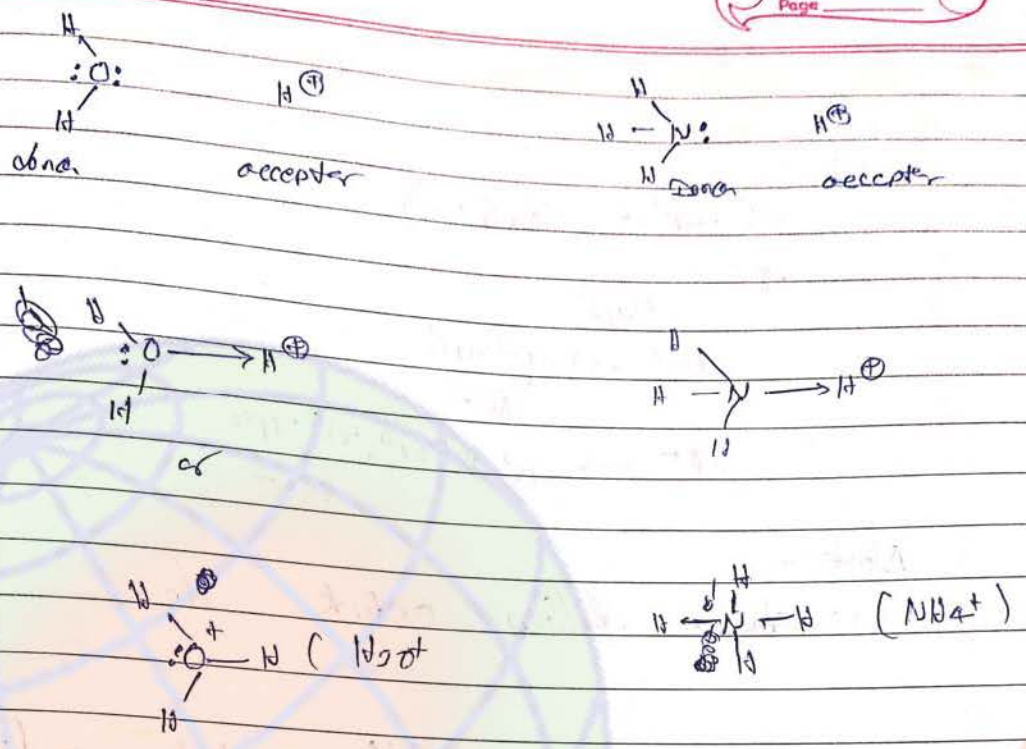
A:	B
l.p	vacant
lewis	orbital
lone	lewis
donor	acid
	acceptor



A → B

or





2 - covalent bond

☆ Lewis octate rule :—

1) As per to Lewis Noble gas have stable e⁻ configuration.

2) 8 e⁻ in outermost shell

3) all other element do to achieve noble gas configuration by sharing e⁻

4) Some element like H, Be do to achieve e⁻ configuration of He (Duplet rule)

5) If Bond Comp following octate rule :—

Note:

(duplet Rule:-)

eg:

NaCl

$Na^+ \rightarrow 1s^2 \underbrace{2s^2 2p^6}_{8e^-}$

$Cl^- \rightarrow 1s^2 2s^2 2p^6 \underbrace{3s^2 3p^6}_{8e^-}$

Note:-

(i) Anions follow octate rule.

(ii) Co-valent compounds follow octate rule if all atoms share $8e^-$s in outermost shell after sharing

(iii) Surrounding atoms attached with central atom follow octate rule.

Central atom: last electrone atom in the formula of a compound.

(except H)

L-2 → 5, 8, 11, 12, 21, 25, 26,
L-3 → 7, 8, 16, 19, 21, 27, 28, 30, 32, 34,
L-4A → 12, 14, 18, 24, 25,
4B → 2, 13,

s-Blocks
L-1 → 1, 2, 3, 5, 9, 12, 13, 16, 14,
20, 22, 23, 25 to 28,
L-2 → 4, 7, 5, 10, 15, 17,
L-3 → 1, 6, 8, 3, 10, 11, 12, 14, 18,
L-3.5 → 1, 2, 6, 8, 3, 10, 11, 12, 14, 18,
21, 27, 24, 25, 34, 36, 38, 40,
4A → 9, 10, 11, 12,

5) No. of covalent bonds to follow octet rule:-

Halogens - 1
"O" - family - 2
"N" - family - 3
"C" - family - 4

IF_4 ✗ ClF_3 ✗ ICl ✓ HI ✗

SF_6 ✗ SF_2 ✓ H_2O ✗

NH_3 ✗ PCl_5 ✗ PCl_3 ✓

CH_4 ✗ CCl_4 ✓

BF_3 ✗ $BeCl_2$ ✗

2) * Exception of octet rule in covalent compounds:-

1) Incomplete octet:-

molecules in which central atom has less than 8 e^- in outermost shell after sharing

e.g. BF_3, $BeCl_2$, etc

2) octet expansion:-

molecule in which central atom has more than 8 e^- in outermost shell after sharing:

eg IF_7, BrF_5, SF_4, PCl_5 etc.

3) molecules having odd no. of e⁻ bonds follow octate rule -
eg NO, NO_2, ClO_2, ClO_3, etc.
↳ These molecules are always paramagnetic

☆ Lewis structure

1) Lewis structure is drawn from molecule which follow octate or duplet rule (not for cyclic compound)

2) Lewis structure give idea about atom's involve in bonding and type of bonds (co-valent and co-ordinate)

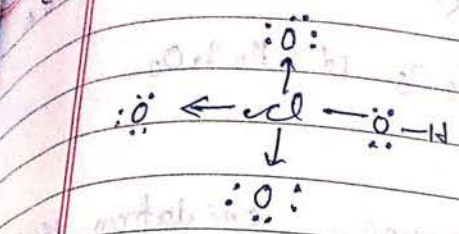
methods: -
write symmetrical skelton -

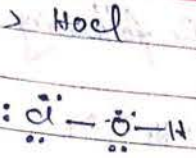
(a) select least EN atom as central atom. (except H)

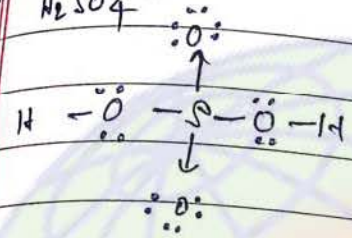
(b) One oxygen atom never bonds with other oxygen atom
exception = O_2, O_3, Peroxide (O–O)

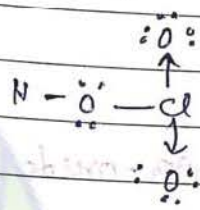
4) In oxyacids -
No of H atom attached with O atom = Basicity of atom

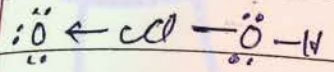
oxyacids	Basicity
H_3PO_3	2
H_3PO_2	1

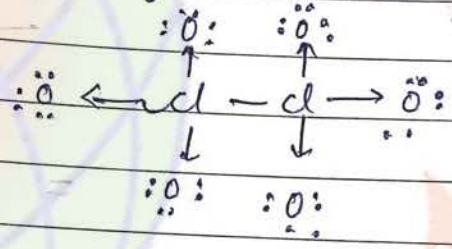
(i) 

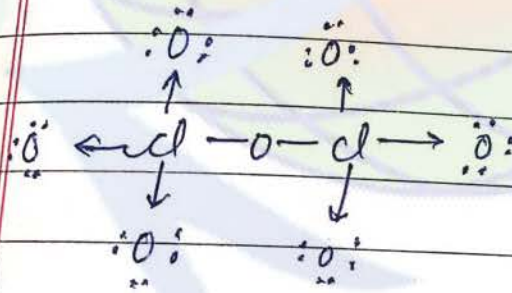
(ii) HOCl 

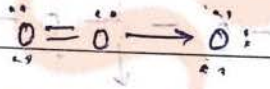
(iii) H_2SO_4 

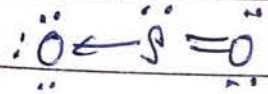
(iv) $HClO_4$ 

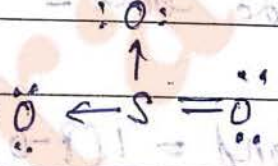
(v) $HClO_3$ 

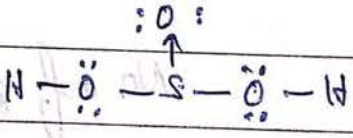
(vi) Cl_2O_6 

(vii) Cl_2O_7 

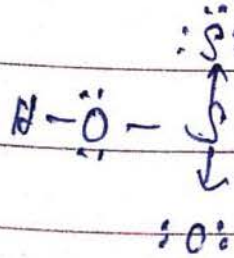
(viii) O_3 

(ix) SO_2 

(x) SO_3 

(xi) H_2SO_3 

(i) Thiosulphenic acid ($H_2S_2O_3$)



Co-ordinate S-S bond

Q) In which of the following oxyacid Per-oxide bond present

(a) $H_2S_2O_8$ (b) $H_2S_2O_7$ (c) $H_2S_2O_6$ (d) $H_2S_2O_3$

Rule → If in an oxygen containing compounds oxidation state of central atom comes more than its highest possible value

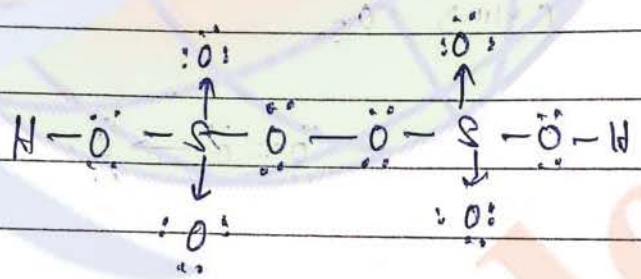
$H_2\overset{+6}{S}_2O_8$

$x = +7$

It contains Per-oxide bond.

$$\text{No of Per-oxide bonds} = \frac{(\text{No. of central atom})(\text{wrong} - \text{correct})\ O.S}{2}$$

$$= \frac{2(7-6)}{2} = 1$$

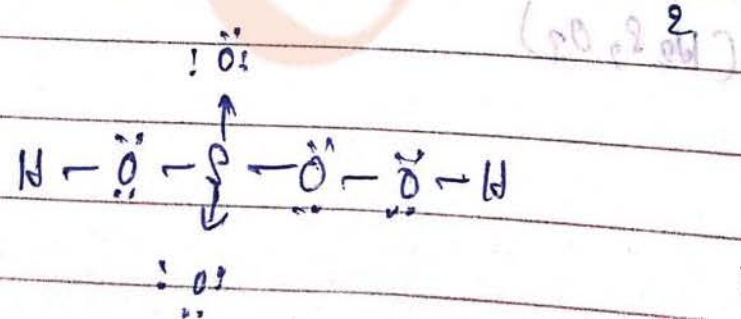


(13) $H_2\overset{+6}{S}O_5$

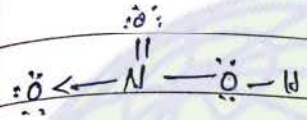
$x = +8$

It contains Per-oxide bond -

$$\text{No. of Per-oxide bond} = \frac{1(8-6)}{2} = 1$$

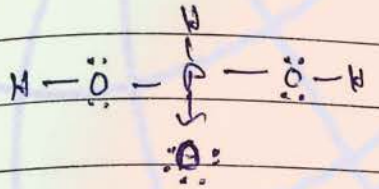


(16) HNO_3

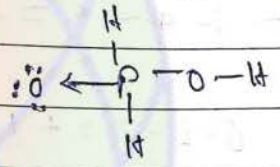


(17) HNO_2

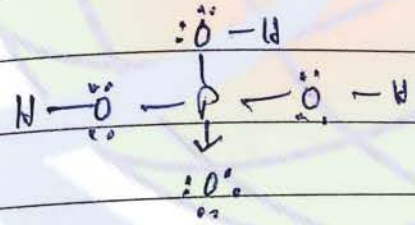
(18) H_3PO_3 (basicity = 2)



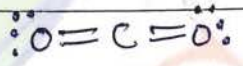
(19) H_3PO_2 (basicity = 1)



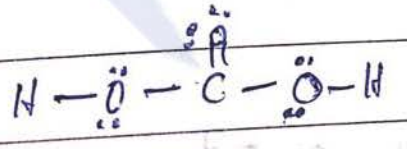
(20) H_3PO_4



(21) CO_2



(22) H_2CO_3



☆ Formal charge →

It is an apparent charge on all atoms in lewis structure.

F.C = No. of valence e⁻ − No. of e⁻ in l.p − No of bonds

Eg O_3

$:\ddot{O}=O \rightarrow \ddot{O}:$

① ② ③

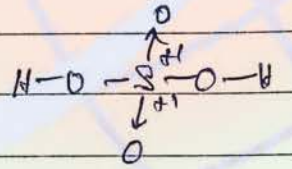
F.C on ① = 6 − 4 − 2 = 0

F.C on ② = 6 − 2 − 3 = +1

F.C on ③ = 6 − 6 − 1 = −1

Q) Calculate F.C of S in H_2SO_4

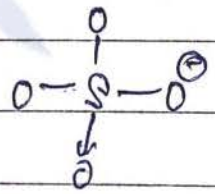
Ans



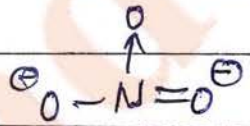
+2 ans

☆ Lewis structure of Polyatomic Ion's →

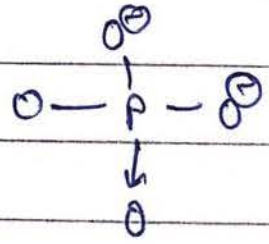
(I) SO_4^{-2}



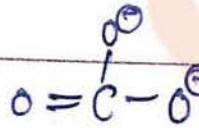
(II) NO_3^-



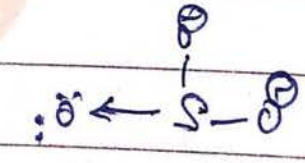
(III) PO_4^{-3}



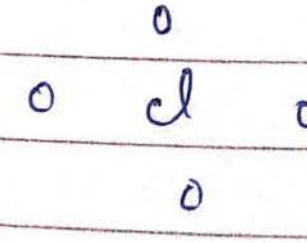
(IV) CO_3^{-2}



(V) SO_3^{-2}



(VI) ClO_4^{-2}



Q) what are the type of bonds in following compounds :-

(1) KNO_3

K^+ ionic NO_3^- — covalent, co-ordinate

(2) $CuSO_4$

Cu^{+2} ionic SO_4^{-2} — covalent, co-ordinate

(3) NaOH

Na^+ ionic OH^- (covalent)

(4) NH_4OH

covalent → NH_4^+ (ionic) OH^- (covalent)

co-ordinate

(5) KCN

K^+ ionic $C \equiv N^{\ominus}$ (covalent)

(6) HCl (g or aq)

covalent

(7) HCl (aq)

ionic

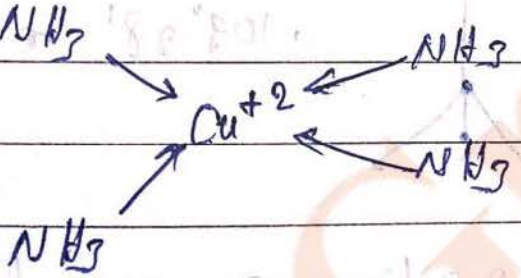
(8) H_2SO_4

(covalent and co-ordinate)

(9) H_2SO_4 (aq)

(ionic, covalent, co-ordinate)

(10) $[Cu(NH_3)_4]SO_4$



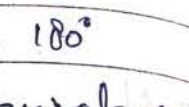
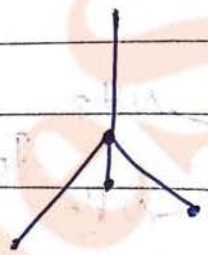
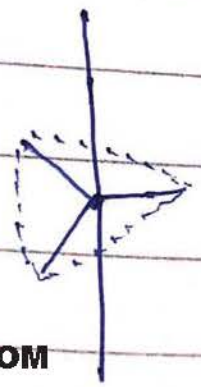
SO_4^{-2} → covalent, co-ordinate.

☆ VESPR theory → (Valence shell e⁻ pair repulsion)

→ shape / geometry and B.A

1.) Acc to this theory geometry of molecules is defined by representation b/w all e⁻ pair in valence shell of central atom.

e.p → l.p + b.p

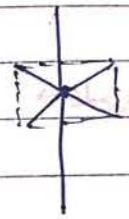
e.p on central atom	Geometry and B.A
2	linear → Both position are equivalent 
3	plane triangle or trigonal planar → all three positions are equivalent 
4	Tetrahedral  → all 4 positions are equivalent → Combination of 4 + face.
5	Trigonal Bipyramidal 

Hey

→ combination of 6-face
→ all 3 positions are not equivalent (+2)
→ 6, 90° angle
→ 3, 120° angle
→ 1, 180° angle

6

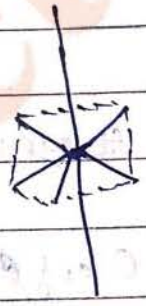
octahedral
or
square Bi Pyramidal



→ combination of 8 face
→ all 8 positions are equivalent
→ 12, 90° angle
3, 180° angle

7

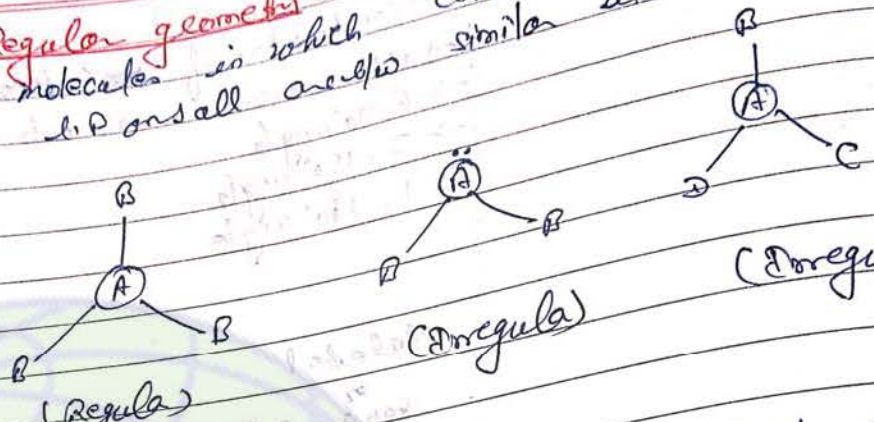
Pentagonal Bi Pyramidal



I.P produce more representation than E.P, Hence ode of representation for various O.P is

$$I.P - I.P > I.P - E.P > E.P - E.P$$

* **Regular geometry →** Molecules in which central atom has no effect of l.p on all are/is similar atom's.



Note → Geometry only depends on σ-bond not on π-bond.

Hence,

On this theory l.p only means σ-bond

→ calculation of l.p and b.p on central atom.

For surrounding atoms :-

H → 1 bond — $M-\overset{\sigma}{H}$

Halogen → 1 bond — $M-\overset{\sigma}{X}$

O or S → 2 bonds — $M=\overset{\sigma\ \pi}{O}$

N → 3 bonds. — $M\equiv\overset{\sigma}{N}$

Compound	l.p	B.p
NH_2	1	3
H_2O	2	2
PCl_3	1	3
XeF_2	3	2

XeF_4	2	4
CO_2	0	2
SO_2	1	2
$POCl_3$	0	4
NCN	0	2
XeO_2F_2	1	4
SO_4^{-2}	0	4
NO_2^+	0	2
NH_4^+	0	4

$ep = b.p + l.p$	Hybridization
2	sp
3	sp^2
4	sp^3
5	sp^3d
6	sp^3d^2 / d^2sp^3 ⇒ for coordinate bond.
7	sp^3d^3 / d^3sp^3

molecules		l.p on central	b.p	e.p = l.p + b.p	Hybridization
1.	$BeCl_2$	0	2	2	sp
2.)	BeF_3	0	3	3	sp^2
3.)	SO_2	1	2	3	sp^2
4)	CH_4	0	4	4	sp^3
5.)	NH_3	1	3	4	sp^3
(6)	H_2O	2	2	4	sp^3
(7)	PCl_5	0	5	5	sp^3d
(8)	SF_4	1	4	5	sp^3d
(9)	ClF_3	2	3	5	sp^3d
(10)	I_3^- / Br^- / ICl_2^- / XeF_2	3	2	5	sp^3d

Hybridised

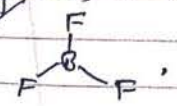
Shape and bond angle

linear

$Cl-Be-Cl$ (Regular), 180°

Plane triangle

Plane triangle

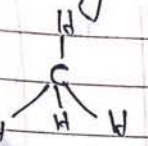

, 120°

Plane triangle


, V-shape/angular/bent, ($< 120°$)
109.5°

tetrahedral

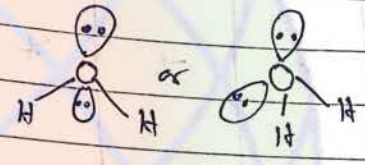
tetrahedral,


, 109°28'

tetrahedral


→ Pyramidal, ($< 109°28'$)
($107°48'$)

tetrahedral

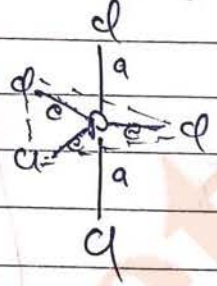

, V-shape/angular/bent, ($< 109°28'$)
104°28'

Trigonal bipyramidal.

Trigonal bipyramidal.

$[PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2]$

→ all 5 bonds are not equivalent.


, 90°, 120°

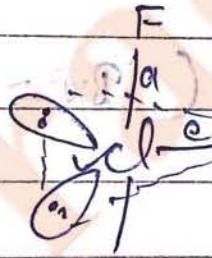
a → axial
e → equatorial
(a > e) (B.L)

))


, T-shape
or
~~Sea-saw shape~~
($< 120°$ or $< 90°$)

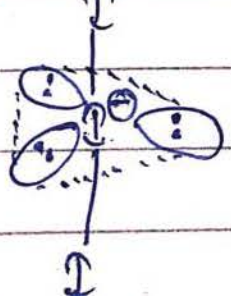
F → All 4 bonds are not equivalent

))


, T-shape ($< 90°$)

F → All 3 bonds are not equivalent

,,

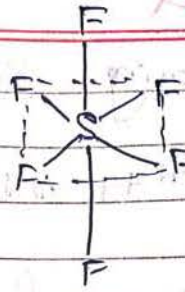

; linear, 180° (Regular)

11)	SF_6	0	6	6	octahedral sp^3d^2
12)	BrF_6	1	5	6	"
13)	XeF_4	2	4	6	square planar
(14)	IF_7	0	7	7	
15)	XeF_6	1	6	7	

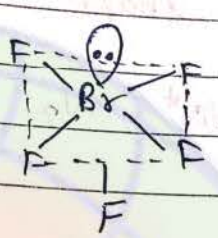
Note:

1) In trigonal bi-pyramidal geometry l.p is present
2) In octahedral geometry two l.p are present at
3) Diatomic molecules (B.P = 1), are al

octahedral.

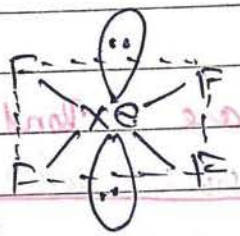
octahedral,  , 90°

~~octahed~~),


, Square pyramidal, (<90°)

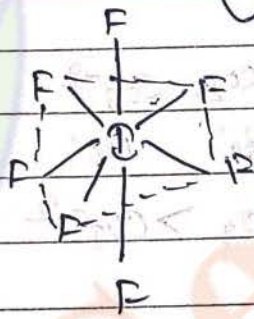
),

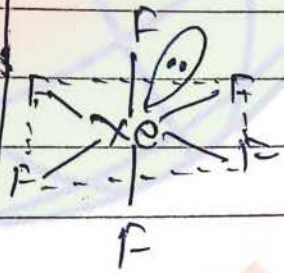
Square planar, (regular)


, (90°) (reg

Pentagonal pyramidal

Pentagonal bipyramidal,


, 72° and 90°


, Distorted octahedral, almost 90°
or
capped octahedral

t "e" (~~eq~~ equitorial position)

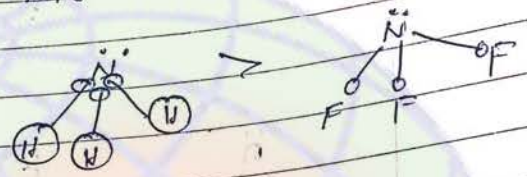
0° angle.

near.

Note → Shape → Geometry → regular, Irregular

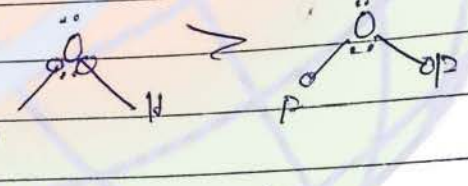
If in above case surrounding atom are similar or surrounding atom's have almost similar size then bond angle depend on electronegativity of central atom

eg1) NH_3 and NF_3



→ (BP - BP repulsion is greater)

eg2) H_2O and F_2O (OF_2)



eg3) $CH_4 \simeq CF_4$

iv) $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

v) $H_2O > H_2S > H_2Se > H_2Te$

Q) Arrange in order of bond angle:—

PCl_3, $AsCl_3$, $SbCl_3$, BCl_3

Sol/n

$BCl_3 > PCl_3 > AsCl_3 > SbCl_3$

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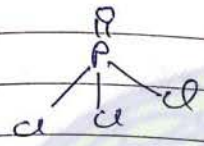
☆ Draw the shape of the following:-

1) PCl_5

l.p = 0 , b.p = 5

sp^3d, Geo → tetra dichedral

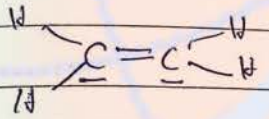


Cl–P–Cl < 109°28' } negligible change
O–P–Cl > 109°28' }

Note → multiple bonds (=, ≡) cause more repulsion than single bond.

Note → Polycentre atom →

$CH_2 = CH_2$ — ethene / ethylene



l.p = 0

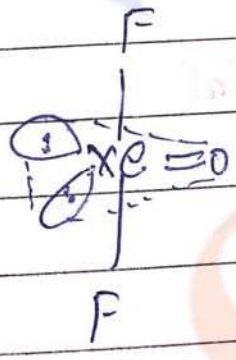
b.p = 3

sp^2

Plane shape

2) $XeOF_2$

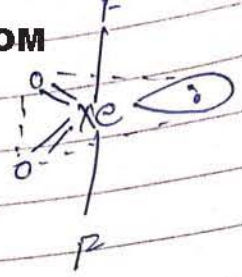
l.p = 2, b.p = 3, sp^3d, Geo → trigonal bipyramidal



T-shape

4) XeO_2F_2

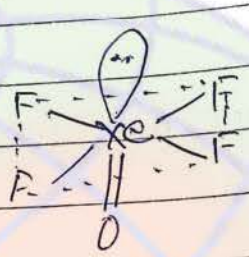
l.p = 1 , b.p = 4, sp^3d, Geo → Trigonal bipyramidal



Square planar shape

(3) $XeOF_4$

l.p = 1, b.p = 5, sp^3d^2, Geo → octahedral



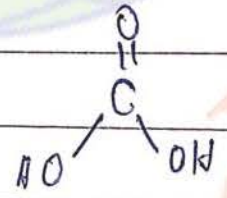
Square pyramidal

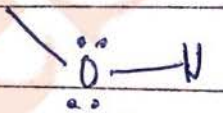
(4)

Shape of oxyacids —

1) H_2CO_3 / $(HO)_2CO$

l.p = 0, b.p = 3, sp^2, Geo ⇒ plane triangle

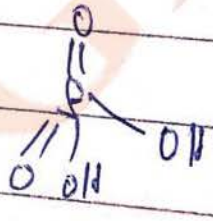




sp^3, V-shape

(2) H_2SO_4 / $(OH)_2SO_2$

l.p = 0, b.p = 4, sp^3, Geo → tetrahedral



(3) H_2SO_3 / $(HO)_2SO$

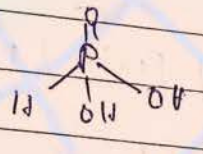
l.p = 1, BP = 3, sp^3, Geo → tetrahedral

Pyramidal

(4) H_3PO_3 (basicity = 2)

$(HO)_2P(O)(H)$

l.p = 0, b.p = 4, sp^3, Geo → tetrahedral

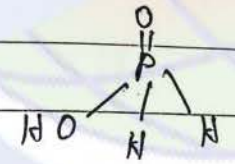


(5) H_3PO_2 (basicity = 1)

~~$(HO)_2P(O)(H)(H)$~~

$(HO)P(O)(H)(H)$

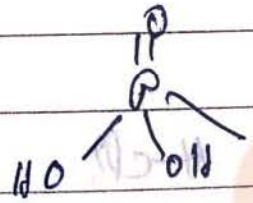
l.p = 0; b.p = 4, sp^3, Geo → tetrahedral



(6) H_3PO_4 (basicity = 3)

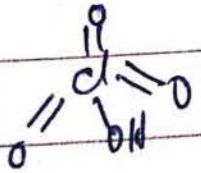
$(HO)_3PO$

l.p = 0, b.p = 4, sp^3, Geo – tetrahedral



7) $HClO_4$ = $(HO)Cl(O)(O)(O)$

l.p = 0, b.p = 4, sp^3, tetrahedral



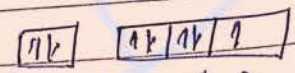
Valence Bond theory (VBT)

overlapping, σ ons π bonds, bond length and bond energy, covalency, lewis octets lone, hybridization.

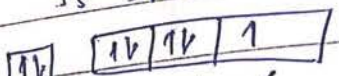
1) According to this theory in a covalent bond unpaired orbitals of valence shell of bonding atoms overlap.

Cl_2

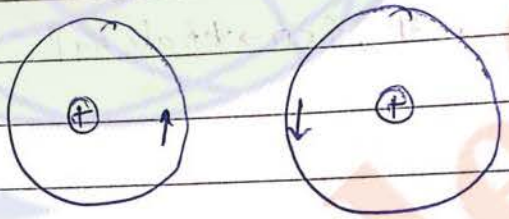
Cl
$3s^2 3p^5$

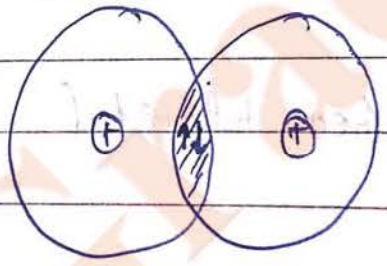


Cl
$3s^2 3p^5$



P-P overlapping





Q) what type of overlaping is present in H-Cl.

Ans S-P overlaping

Date
Page

Type of overlaping :-

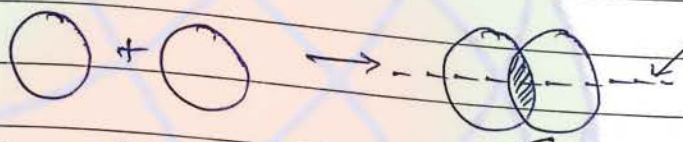
(1) Sigma (σ) bond :-

(a) Coaxial / end-to-end overlaping of unpaired orbitals

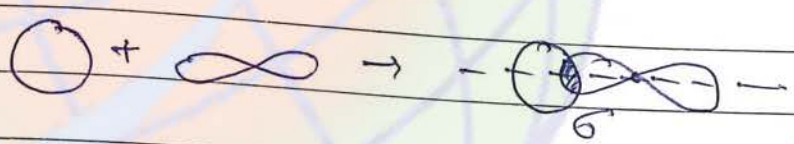
(b) bonded e⁻ density is present at internuclear axis.

* Type of σ bond :-

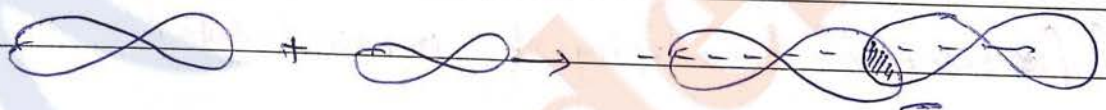
(1) S-S overlaping :-



(2) S-P overlaping



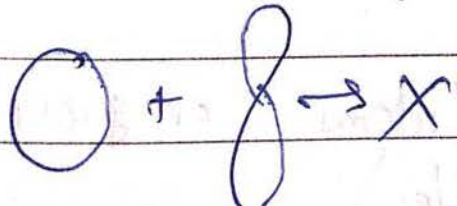
(3) P-P overlaping

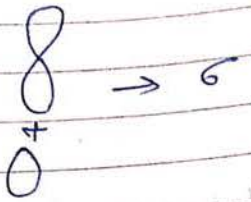


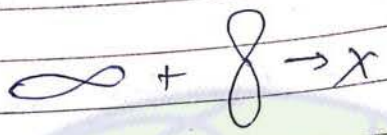
* order of extent of overlaping :-

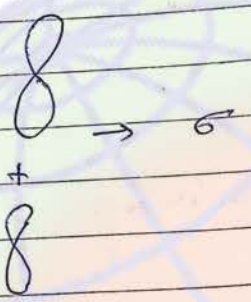
$$S-S < S-P < P-P$$

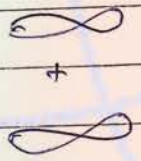
Note → (i) S-orbitals always form σ-bond

(ii)  → X

(III) 

(IV) 

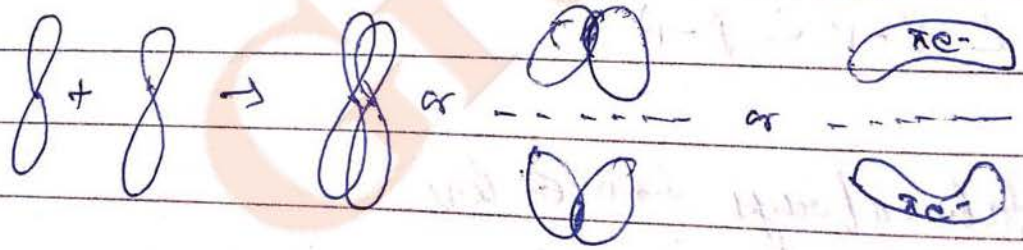
(V) 

VI) 

(2) π-bond →

(a) Co-Lateral (side wise) overlaping of unpaired orbitals.

(b) bonded e⁻ density is present above or below of Internuclear axis. Hence π-bond is weaker than σ-bond



(c) About π-bond free rotation of atoms or group's is not possible (about σ-bond is possible)

Date
Page

Bond length and Bond energy :-

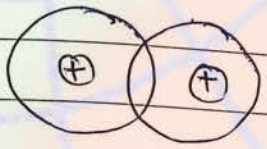
F_2 O_2 N_2

— = ≡

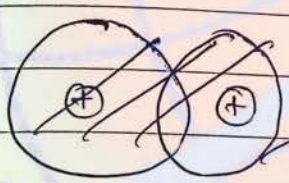
$F_2 < O_2 < N_2$ (B.E)

$F_2 > O_2 > N_2$ (B.L)

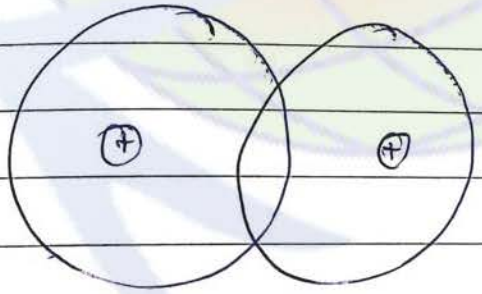
(1) valence shell of bonding atom is closer to the nucleus means greater extent of overlaping hence smaller bond length and higher bond energy.



⇒ more overlaping in smaller atom (i.e. valence shell is close to nucleus)



less overlaping.



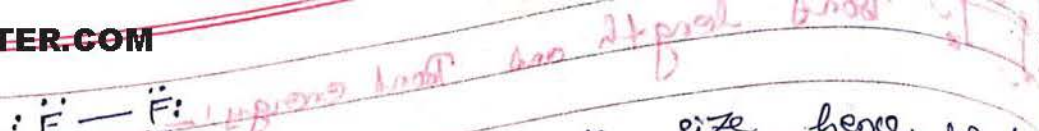
less overlaping.

* Bond strength depends on Bond energy.

Bond length $\propto \frac{1}{\text{overlaping}}$ (always true)

but

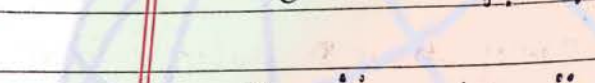
Bond length $\propto \frac{1}{\text{Bond energy}}$ (Not always true)

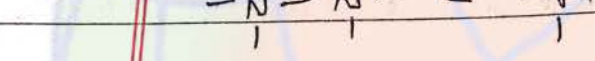


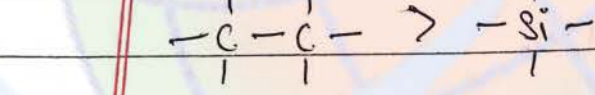
"F" atom has exceptionally small size hence, l.p of both F-atom's in F_2 molecules repel more than expected and its B.E becomes less than expected.

* Order of Bond energy:—

$Cl_2 > Br_2 > F_2 > I_2$







⇒

B	C	N	O	F	
Al	Si	P	S	Cl	
Ga	Ge	As			
Sn					
Tl					

⇒ H - H 104 Kcal/mol

C-C ≃ 102 Kcal/mol

⇒ Catenation:- Formation of long chain of identical atoms of an element is called catenation.

★ Catenation →

~~C has max. tendency of catenation.~~

(i) Tendency of Catenation depends on B.E of single bond b/w identical atoms.

(ii) C has max. tendency of catenation.

(iii) order of tendency of catenation:-

C > Si > Ge > Sn > Pb (carbon family)

S > Se > O > Te (oxygen family)

S-S > Se-Se > O-O > Te-Te (S-family)

★ Co-valency [No. of co-valent bonds] →

(1) Halogens →

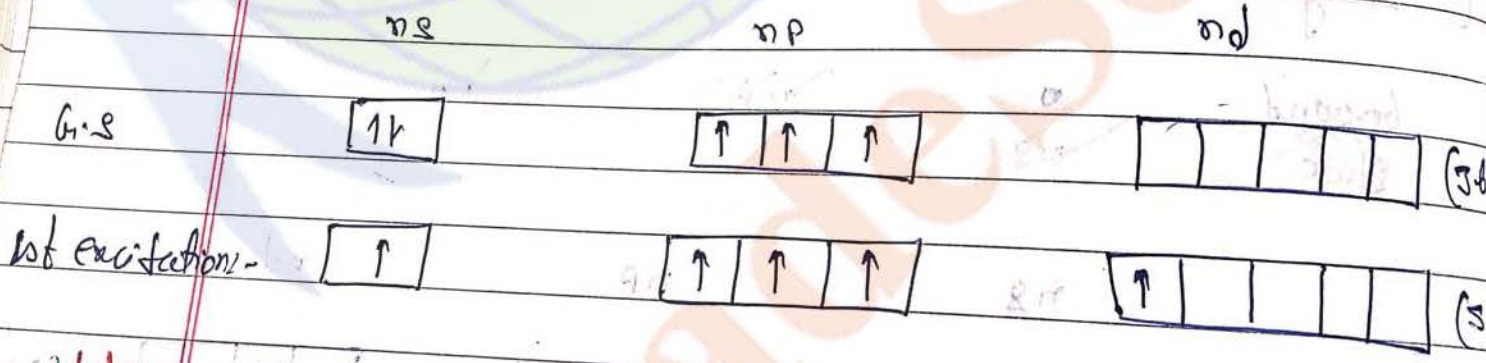
Ground state	ns	np	nd
Ground state:-	↑↓	↑↓ ↑↓ ↑	
st excitation:-	↑↓	↑↓ ↑ ↑	↑
excitation:-	↑↓	↑ ↑ ↑	↑ ↑

3rd excitation:- 

Rule:- excitation possible only vacant orbital and pared electron both are present

(2) oxygen family:-

(3) Nitrogen family:-



Note:- F, O, N show fixed covalency 1, 2, 3 respectively because they are of 2nd period in which d-orbital is absent thus excitation not Possible.

Q) ClF_3 exist but not FCl_3 why ?
SF_6 " " " OF_6 "
PCl_5 " " " NCl_5 "

Sol" due to absent of vacant d-orbitals.

Q) I_3^- exist but F_3^- not why (unlike other halogen F can't form polyhalogen anions why?

Sol" F_3^- $F - \overset{\ominus}{F} - F$

$F^{\ominus}$ 2s: [1↓] 2p: [1↓ | 1↓ | 1↓] (No d-orbital)

⊗ Zero bonds :→ so doesn't exist

I^{-3} $I - \overset{\ominus}{I} - I$

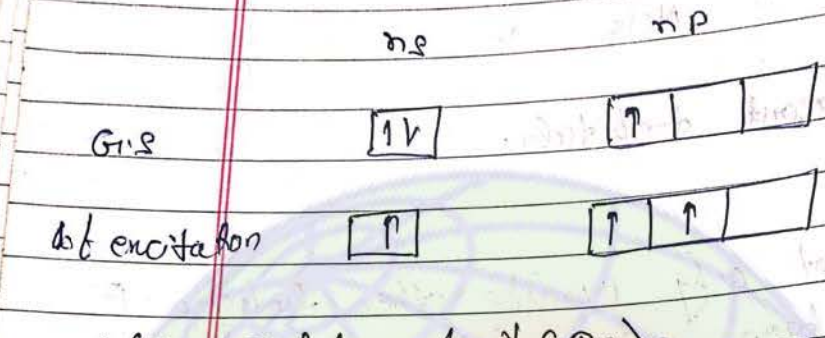
I^{-3} [1↓] [1↓ | 1↓ | 1↓] d-orbital [| | | |]

Exception:- [1↓] [1↓ | 1↓ | ↑] [↑ | | | |] (2 bonds)

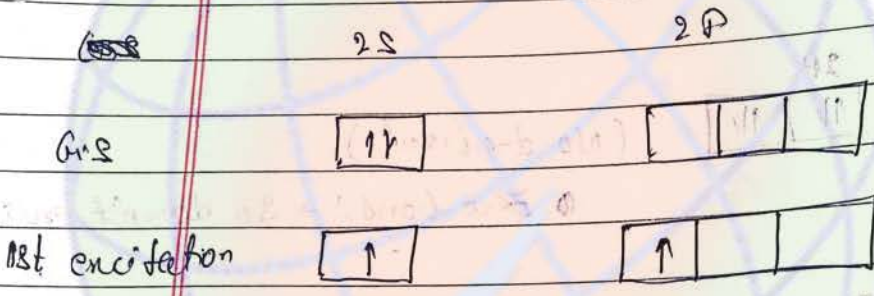
(4) ⇒ Carbon family :-

	ns	np
	[1↓]	[↑ | ↑ |]
Excitation	[↑]	[↑ | ↑ | ↑] (4 bonds)

(5) Boron family:-



(6) Beleium family (Be)



Q) In which molecule central atom is present in its ground state?

(i) $SiCl_4$ (ii) CO_2 (iii) ClF_3 (iv) H_2S

Note: "B" and "C" show fixed covalency 3 and 4 respectively due to small energy difference b/w 2s and 2p subshell.

Lewis base → ↳ l.p donar

(1) In P-block in 2nd period only compound of Boron can behave as lewis acid.

(2) In P-block except 2nd period element can't behave as lewis acid except Boron. and other Period elements of P-block can behave as lewis acid.

Note! — 2nd period elements have fixed covalency.

In halogen, oxygen and Nitrogen family due to absence of vacant orbital (d-orbital) and in carbon, Boron family due to small energy diff "2s" and "2p" subshell

★ Example of co-ordinate bond! —

B	C	N	O	F → Can't act as lewis acid.
Al	Si	P	S	Cl
Ga	Ge	As	Se	Br
In	Sn	Sb	Te	I
Tl	Pb	Bi	Po	At

★ Co-ordinate bond! —

$BF_3 + NH_3 \longrightarrow [H_3N \rightarrow BF_3]$

l.a l.b

vacant orbital, lone pair

$B(CH_3)_3 + N(CH_3)_3 \longrightarrow [(CH_3)_3N \rightarrow B(CH_3)_3]$

l.acid l.base

$H_3BO_3 + OH^- \longrightarrow {}^{\ominus}OH \longrightarrow B(OH)_3$

l.acid l.base $B(OH)_4^-$

$B(OH)_3$

Note:→ (i) If any element form more no. of bond than its possible valency then extra bond is co-ordinate bond.

NH_4^+, H_3O^+, SiF_6^{-2}, BF_4^-, SiF_5^-, AlF_6^{-3}

If we have to find co-ordinate bond then check by both methods:—

(i) Lewis method

(ii) From VBT (Concept of valency)

(ii) 2nd period element can form maximum four bonds. [Co-valent and co-ordinate]; while

3rd period onwards other element can form generally max^m "6" bonds. [more than 6 is only IF_7] covalent and co-ordinate.

Note:→ which can exist!—

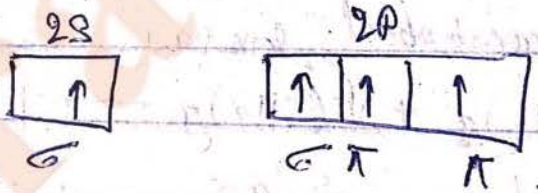
BF_4^-, BF_6^{-3}, CCl_4, CCl_6^{-2} [2nd period element does not form max^m 4 bonds]

(✓) (X) (✓) (X)

* Naming of π-bonds:—

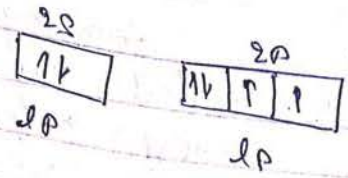
(1) CO_2 $O \overset{\pi}{=} C \overset{\pi}{=} O$ (σ, σ)

C (1st excitation)



[Note:→ σ bonds are marked from right first assume no. of π-bonds then name it.]

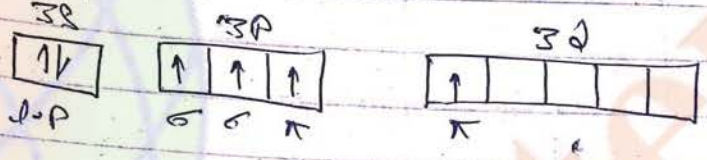
O (Ist excitation)



$2p\pi - p\pi$ - bond. {Paired orbital shows lone pair}

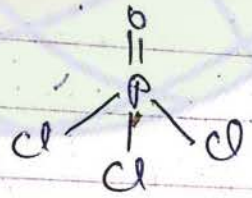
<2> SO_2

S (Ist excitation)

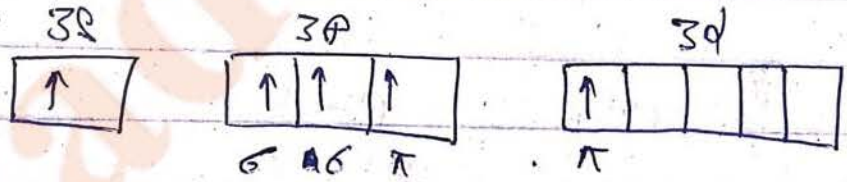


1 - $p\pi - p\pi$
1 - $p\pi - d\pi$

<3> $POCl_3$



P (Ist excitation) :-



1 - $p\pi - d\pi$ bond

Hybridization →

It is defined as intermixing of dissimilar orbitals of valence shell of central atom having almost similar energy to form same no. of new hybrid orbitals having identical shape and size and energy.

* In this process intermixing of orbitals takes place.

Relative intermixing of "s" and "p" orbitals forms "rBT"

	s	p
sp 1:1	$\frac{1}{2}$ 50%	$\frac{1}{2}$ 50%
sp^2 1:2	$\frac{1}{3}$ 33%	$\frac{2}{3}$ 66.67%
sp^3 1:3	$\frac{1}{4}$ 25%	$\frac{3}{4}$ 75%

eg:- CH_4 C—H
$sp^3 - s$

NH_3 N—H
$sp^3 - s$

H_2O O—H
$sp^3 - s$

XeF_2 Xe—F
$sp^3d - p$

* Hybridized orbitals —

Hybrido orbitals ~~regular~~ properly arranged in a regular geometry.

No. of orbitals in Hybridization l.P + b.P	type	Geometry
2	sp	linear
3	sp^2	plane Δ
4	sp^3	tetrahedral
	dsp^2 *	square planner
5	sp^3d / dsp^3 *	trigonal bipyramidal
6	sp^3d^2 / d^2sp^3 *	octahedral
7	sp^3d^3 / d^3sp^3 *	pentagonal bipyramidal

* dsp^2, dsp^3, d^2sp^3, d^3sp^3 only possible in co-ordination compound.

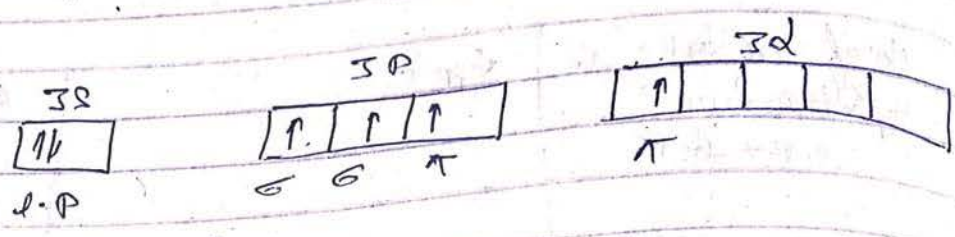
(5) orbitals involve in π-bond do not participate in hybridization.

→ Hybrid orbitals never form π-bond.

→ Hybrid orbitals form π-bond or lone pair.

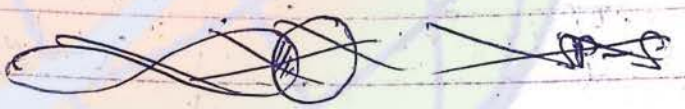
SO_2

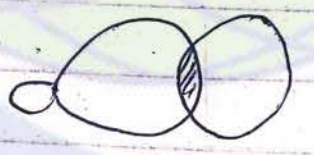
At excitation



(5) Hybrid orbitals provide more effective overlapin than pure atomic orbitals due to extent of overla

$$sp > sp^2 > sp^3 >> p > s$$

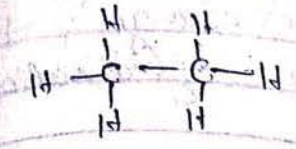




sp-s

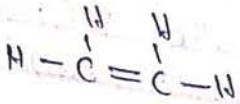
sp^2-s

sp^3-s



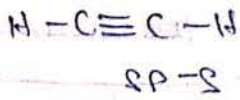
sp^2-s

(ethane)



sp^2-s

(ethene)



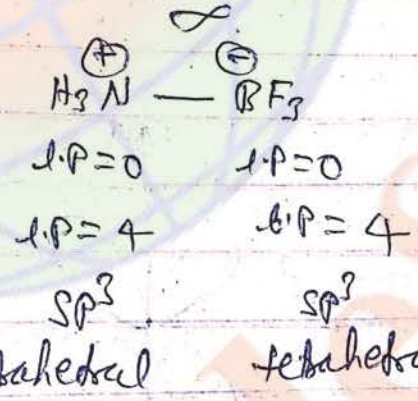
sp-s

(ethyne)

order of C–H (B.L) in ethane > ethene > ethyne.

e) what is the change in hybridization and shape about N and B?

Sol:



H_3N — BF_3

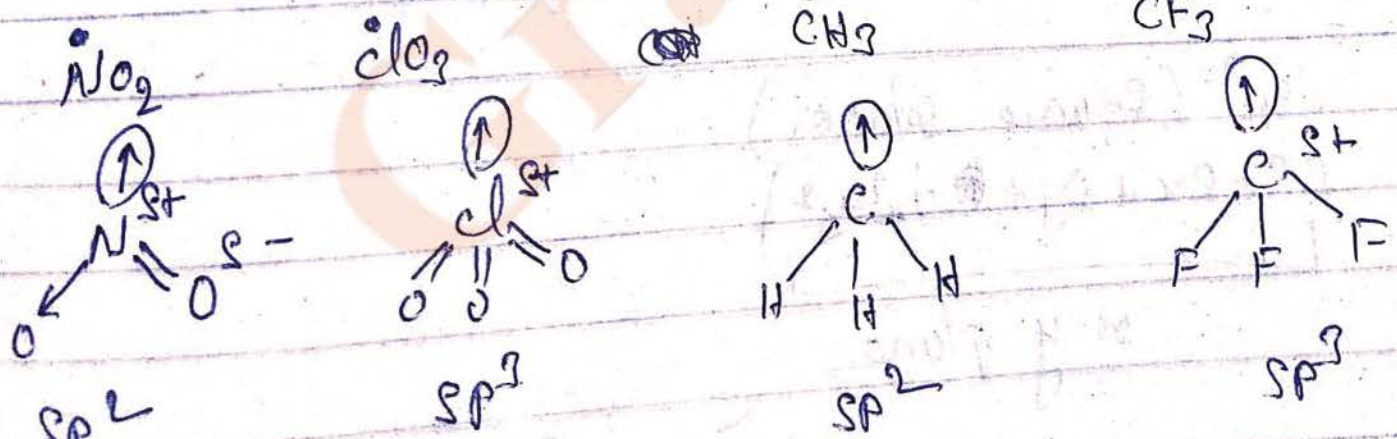
l.p = 0 l.p = 0

b.p = 4 b.p = 4

sp^3 sp^3

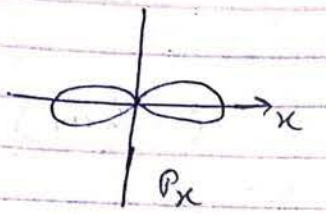
tetrahedral tetrahedral

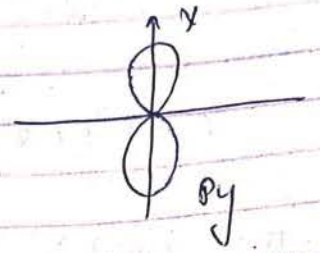
⇒ Hybridization of central atom having one unpaired e⁻

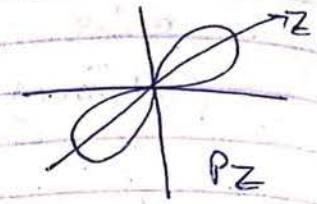


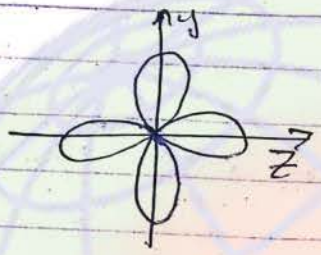
sp^2 sp^3 sp^2 sp^3

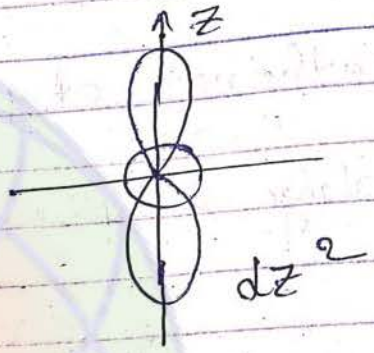
If central atom has 5d (partial (two) charge) then unpaired orbital participate in hybridization.

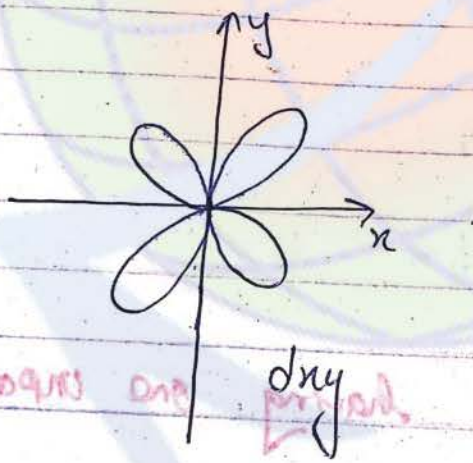


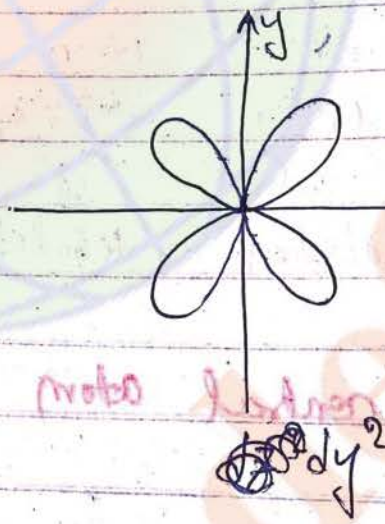


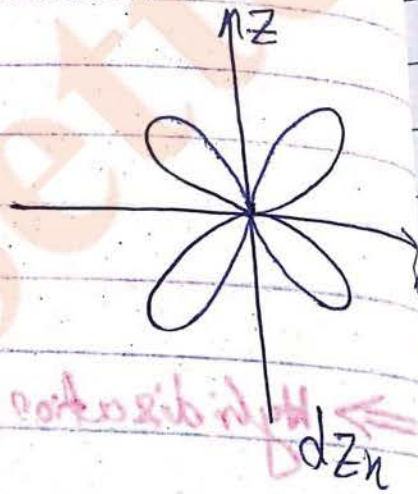












dsp² (square planer)

(S + Px + Py + dx²-y²)

x-y plane

(Square planar) →

$(s + p_x + p_y + d_{x^2-y^2})$

xy plane

2) sp^3d / dsp^3 (trigonal bipyramidal)

$(s + p_x + p_y) + (p_z + p_{z^2})$

xy-plane (z-axis)

3) sp^3d^2 / d^2sp^3 (octahedral)

$(s + p_x + p_y + d_{x^2-y^2}) + (p_z + d_{z^2})$

x-y plane z-axis

4) sp^3d^3 / d^3sp^3 (pentagonal bipyramidal)

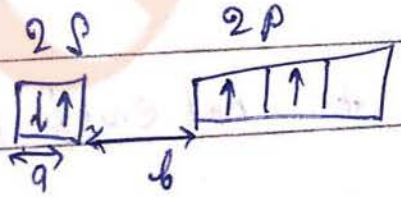
$(s + p_x + p_y + d_{x^2-y^2} + d_{xy}) + (p_z + d_{z^2})$

x-y plane z-axis

Note -

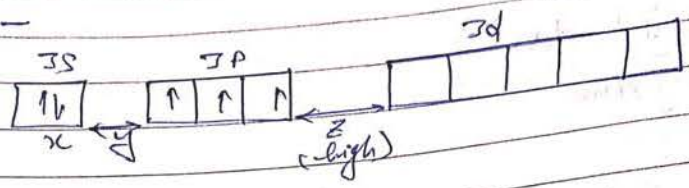
1) In hybridization process intermixing of s and p orbits are well accepted but involvement of d-orbitals is debatiable.

CH_4 →



a + b (low)

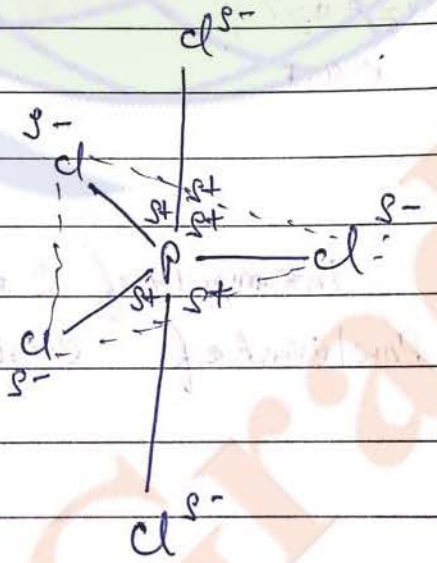
PCl_5 :-

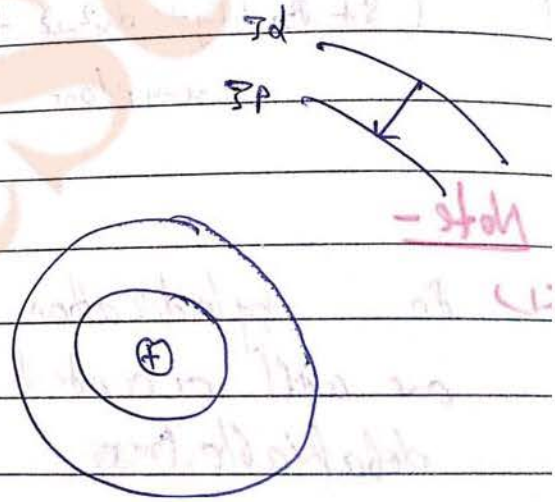


$x+y+z$ (very high)

2) In PCl_5, Cl is more E.N than 'P' Hence "P" acquires partial the charge. Its size reduces and energy differene b/w 3P and 3d subshell also reduces.

3) d-orbital's participate in bonding or in hybridisation when surrounding atom attached to the central atom is highly E.N. (d-orbital contraction)





Q1) PCl_5 exist but PH_5 does not exist why

Q2) PH_3 exist but PH_5 does not exist why.

Valency in hydride -

Halogens → 1 (HF, HCl, HBr, HI)

"O"-family → 2 (H_2O, H_2S, H_2Se, H_2Te)

"N"-family → 3 (NH_3, PH_3, AsH_3, SbH_3, BiH_3)

Rule -

* If in an Ionic compound any P-block element in Present in its lowest possible -ve oxidation state. then it does not form covalent bond with similar atom in that formula of compound.

-1

1) $CaCl_2$

Cl-Cl bond is not present

$Ca^{+2} + 2Cl^-$

2) $Na_2O_2^{-1}$

O-O bond is present

$Na^+ + O_2^{-2}$

(Per-oxide)

3) CaC_2 (calcium carbide)

$Ca^{+2} + C_2^{-2}$

$:\overset{\ominus}{C} \equiv \overset{\ominus}{C}:$

sp sp

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 +$ ethyne $H-C\equiv C-H$

(iv) $Al_4C_3^{-4}$

$4Al^{+3} + 3C^{-4}$

$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$ methane

(v) Mg_2C_3

$2Mg^{+2} + C_3^{-4}$ ($C^{-3}-C\equiv C^-$ or $C^{-2}=C=C^{-2}$)

$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + C_3H_4$

$CH_3-C\equiv CH$ (Propyne)

or

$CH_2=C=CH_2$

(vi) $Be_2C + H_2O \rightarrow$

$2Be^{+2}\ C^{-4}$

$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$ methane

(vii) $Mg_3N_2 + H_2O \longrightarrow$

$3Mg^{+2}\ 2N^{-3}$

$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

(b) $Ca_3P_2 + H_2O \rightarrow$

$3Ca^{+2}$ $2P^{-3}$

$Ca_3P_2 + H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

(c) $AlN^{+3\ -3} + 3H_2O \rightarrow Al(OH)_3 + NH_3$

☆ molecular orbital theory (M.O.T)

1) Acc^n to this theory, molecule is considered as a unit with all e^- are moving under the influence of all nuclei present in molecule

2) When atoms to be bonded come close together their atomic orbitals overlap to form new larger orbitals called as M.

★ Formation of Bonding and antibonding molecular orbital:—

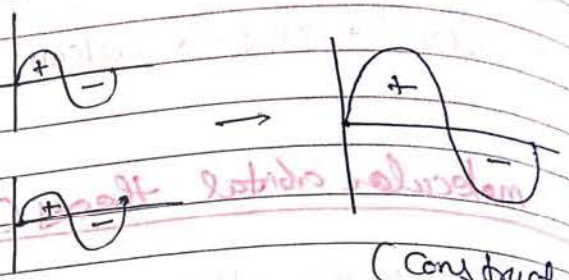
→ LCAO method:—
↳ (linear combination of atomic orbital)

→ only for homonuclear di-atomic molecules.

LCAO (method): — (only for Hetero atom) (Heteronuclear diatomic molecule)

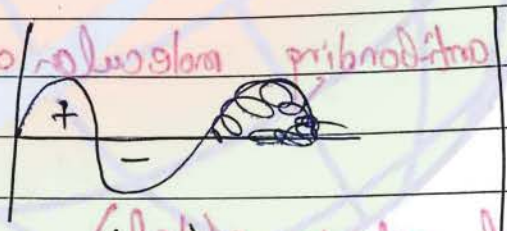
<1> only those A.O overlap which have similar energy and orientation.

0	0
1s	1s
2s	2s
$2p_x$	$2p_x$
$2p_y$	$2p_y$
$2p_z$	$2p_z$

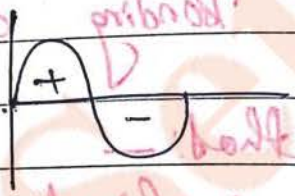


(Constructive Interference)

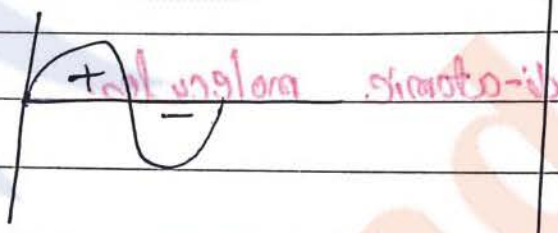
Bonding molecular orbital is formed due to constructive interference of atomic orbital while antibonding molecular orbital is formed due to destructive interference of atomic orbital.

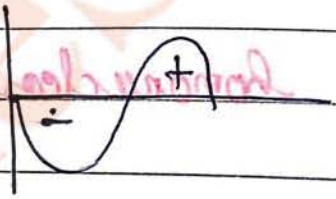


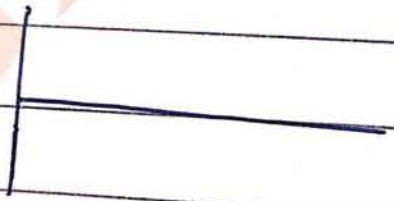
(+)



(−)

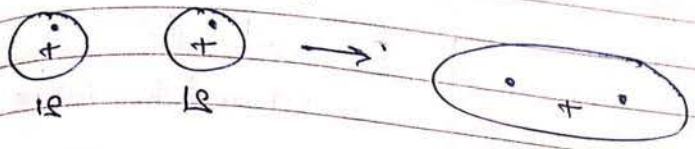


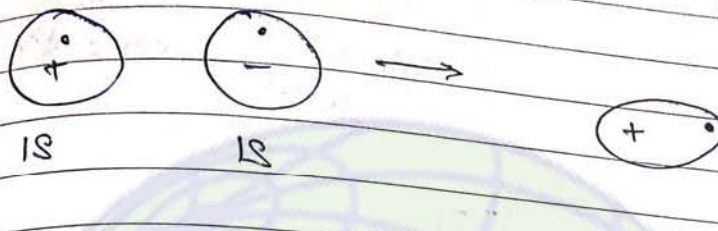




Destructive Interference amplitude = 0

(I) s-s overlaping

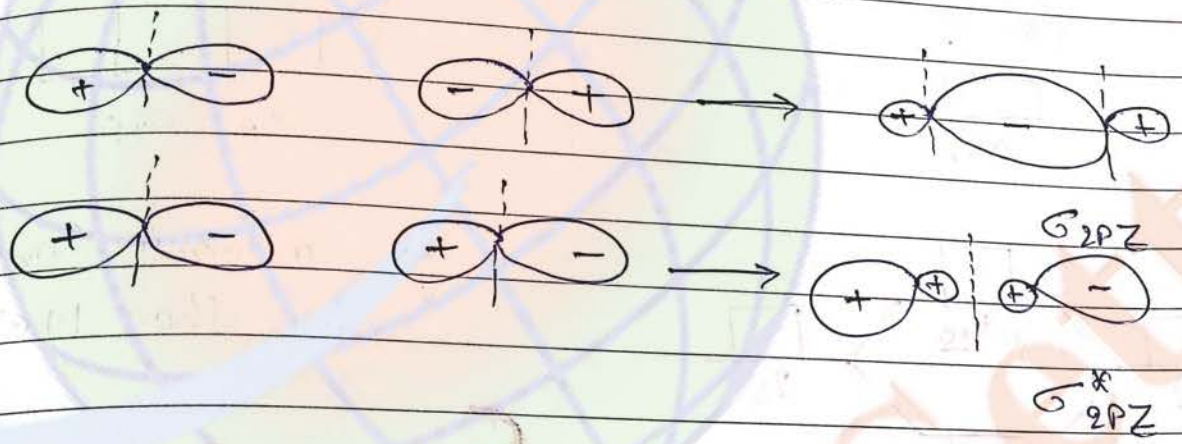




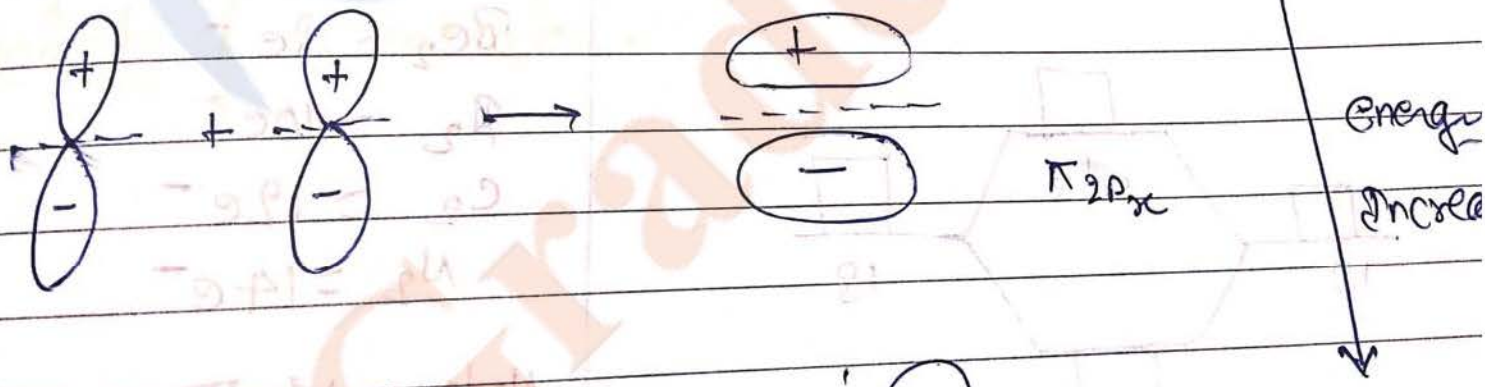
Antibonding molecular orbital

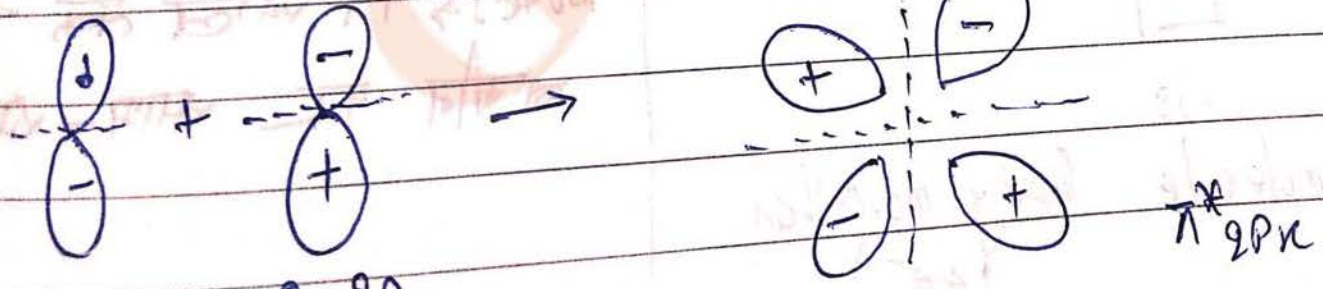
$\sigma^*_{1s} \Rightarrow$ sigma star 1s

(II) p-p overlaping :—



1) π molecular orbital

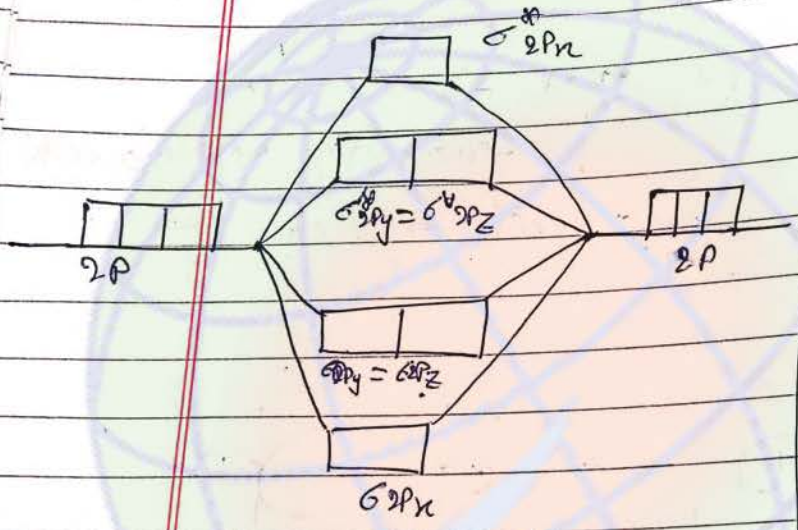


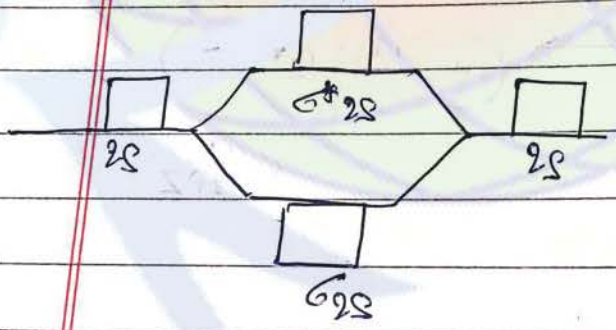


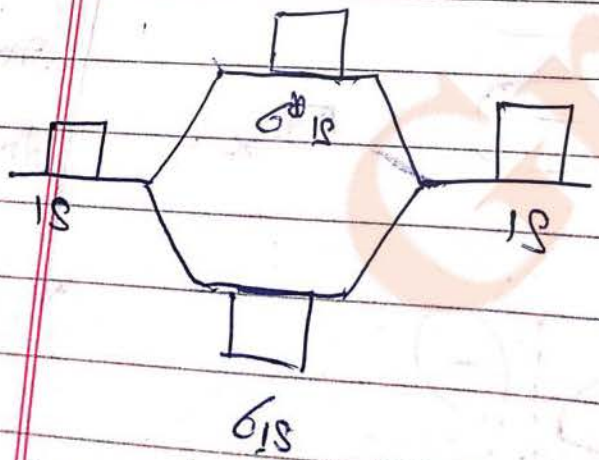
Selection of energy level diagram for di-atomic ions is done on the basis of co-responding neutral diatomic molecule.

• For molecule more than 14 e^-

↳ $O_2 = 16e^-$, $F_2 = 18e^-$, $Ne_2 = 20e^-$



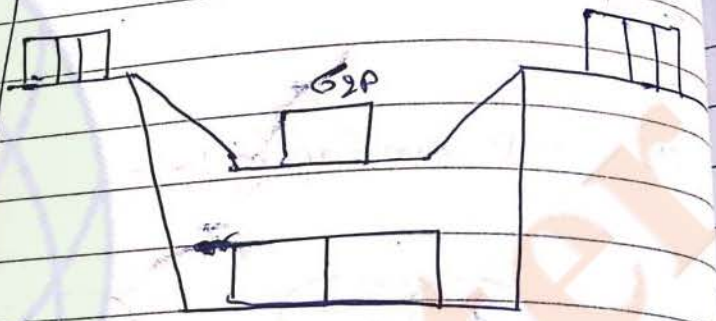




(For molecule having more than

For molecule less than or equal to 14 e-

(structural is similar than before except the portion



for molecule having 14 or less than 14 e^-)

↳ $H_2 = 2e^-$

$He_2 = 4e^-$

$Li_2 = 6e^-$

$Be_2 = 8e^-$

$B_2 = 10e^-$

$C_2 = 12e^-$

$N_2 = 14e^-$

Note :- 14 साल तक बेनी जमीन पर खाए-खाए

M.O depends on:-

(i) Aufbau Principle
(ii) Pauli
(iii) Hund rule.

magnetic Properties:-

(1) magnetic Properties of di-atomic molecule:-

odd no. of e^- → Para ✓
even no. of e^- → diamagnetic (except 10 ans 16 e^-)
(exceptions: O_2 and Br_2)

Note: magnetic Properties direct comp. का molecule का नहीं होता NO of e^- सिर्फ का होता है। क्योंकि एक orbital में max. 2 e^- ही fill किया जा सकता है।

(2) magnetic Properties of polyatomic molecules:-

odd no. of e^- → Para ✓
(eg: NO_2, ClO_3, ClO_2)

even no. of e^- → diamagnetic
eg (O_3, P_6 etc)

stability of molecules:-

N_b = No. of bonding e^-
N_a = No. of antibonding e^-

Case I:- if $N_b > N_a$ → molecule is stable
Case II:- If $N_b = N_a$ → molecule is unstable.

↳ Effect of antibonding is little higher than effect of bonding.
↳ $N_b < N_a$ is possible when molecule is in excited state.

(1) **Bond order** $= \frac{1}{2}(N_b - N_a)$

→ B.O is defined as no. of co-valent bonds b/w two atoms.
→ for odd e⁻ molecule B.O comes fractional (Naming not possible)

(2) B.O. stability of molecules:—

Applicable only when similar molecule have different charge

$$\left\{ \begin{array}{l} \alpha \ \frac{1}{B.L} \\ \alpha \ B.E \ \text{(bond dissociation energy)} \end{array} \right.$$

eg:—

(i) H_2 $\quad \sigma_{1s}^2$

$N_b = 2$, $N_a = 0$

$B.O = \frac{1}{2}(2-0) = 1$

(diatomic)

(ii) H_2^+ $\quad \sigma_{1s}^1$

$N_b = 1$, $N_a = 0$

$B.O = \frac{1}{2}(1-0) = 0.5$

[exist but rare:- because H_2 is more stable]

(iii) H_2^-, σ_{1s}^2 $\sigma^* 1s^1$

$N_b = 2$, $N_a = 1$

$B.O = \frac{1}{2}(2-1) = 0.5$

exist but rare.

Order of stability

σ^*_{2p}
$\pi^*_{2p^1} = \pi^*_{2p^1}$ } remaining e⁻
$\pi_{2p^2} = \pi_{2p^2}$ } 6e⁻ { σ_{2p}, $\pi_{2p} = \pi_{2p}$
σ_{2p^2}
$\sigma^*_{2s^2}$
σ_{1s^2} } 0

K.K { $\sigma^*_{1s^2}$, σ_{1s^2} } 0

Note:

(1) $H_2 > H_2^+ > H_2^-$
→ due to antibonding e⁻ //

Note: →

Imp

B.O ∝ (stability of molecule)
∝ $\left(\frac{1}{B.L}\right)$
∝ (B.L)(Bond dissociation energy)

These relation only applicable similar molecules having different charge.

(4) He_2 σ_{1s^2} $\sigma^*_{1s^2}$

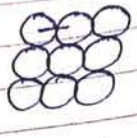
$N_b = N_a = 2$
(unstable.)

(5) Li_2

σ_{1s^2} $\sigma^*_{1s^2}$ σ_{2s^2}

$N_b = 4$, $N_a = 2$

4' (e)


(metallic bond)

Li_2 (may exist in vapour state) } ⇒ Co-valent bond

→ for Na_2 and K_2 also

(6) B_2 (may exist in vapour state), B.O = 1 (Bond in π)

$\sigma 1s^2$ $\sigma^* 1s^2$ $\sigma 2s^2$ $\sigma^* 2s^2$ $\pi 2p_x' = \pi 2p_y'$

or,

KK $\sigma 2s^2$ $\sigma^* 2s^2$ $\pi 2p_x^1$ $\pi 2p_y^1$

(7) N_2 (Diamagnetic)

B.O = 3,

(8) O_2, $16e^-$, Paramagnetic, B.O = 2,

(9) F_2, A.No = 9

9+9 = 18 (Diamagnetic)

B.O = 1

Imp (10) ★ C_2 (may exist in vapour state) //

↳ Diamagnetic

B.O = 2 (Both bonds are π)

Q.11 Arrange the following in order of Bond length

O_2, O_2^+, O_2^-, O_2^{-2}

B.O = 2, 2.5, 1.5, 1

$O_2^+ < O_2 < O_2^- < O_2^{-2}$

M.O.T for heteronuclear di-atomic molecules:—

(1) NO (Paramagnetic)

$15-8 = 7 \Rightarrow \frac{6-1}{2} = \frac{5}{2} = 2.5$

B.O = 2.5

(2) CN^-

$6 + 7 \Rightarrow 14^-$ (even)

(Diatomic) , B.O = 3

(3) NO^-

$8 + 7 \Rightarrow 16^-$ (

Paramagnetic

B.O = 2

(4) CO

$6 + 8 \Rightarrow 14$, Diamagnetic

B.O = 3

Q) Arrange the following in order of bond energy.

NO, NO^-, NO^+

2.5 2 3

$NO^- < NO < NO^+$

Q2) In which of the following process B.O decreases as well as magnetic behavior changes.

(a) $O_2 \longrightarrow O_2^+$

(b) $\overset{2.5}{NO} \longrightarrow \overset{3}{NO^+}$

(c) $\overset{3}{N_2}$ (dia) $\rightarrow \overset{2.5}{N_2^+}$ (para)

(d) $\overset{2.5}{NO}$ (para) $\rightarrow \overset{2}{NO^-}$ (para)

Ans (C)

Q3) $N_2 \rightarrow N_2^+$, for this process one e^- is removed from which molecular orbital

Ans $\sigma 2p_x$ or $\sigma 2p_y$ or $\sigma 2p_z$

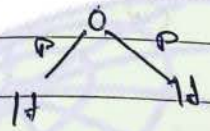
or

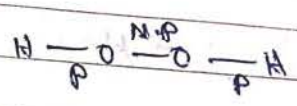
Any 2p molecular orbital. //

(1) A–A , $\Delta E.N = 0$, Non-polar bond

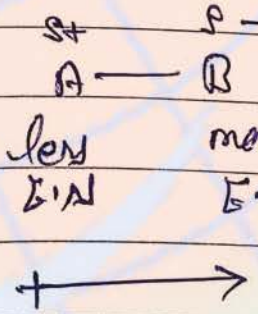
A–B , $\Delta E.N \neq 0$, Polar bond

Cl–Cl (N.P) , H–Cl (P)





(2) In a polar bond →



→ Dipole moment for a bond (μ) = q × d

or

Bond moment

q = charge

d = B.L

→ μ is a vector quantity

→ Unit of "μ" is debye (D).

→ 1D = 10^{-18} esu·cm (C.G.S system)

Dipole moment of di-atomic molecule

~~If bond dipole moment for di-atomic molecules~~
If bond present in di-atomic molecule is polar then molecule is also polar otherwise non-polar.

Polar ($\mu \neq 0$) :- HCl, HBr, CO etc

Non-Polar ($\mu = 0$) :- Cl_2, D_2, O_2 etc.

Dipole moment of polyatomic molecule.—

(1) Resultant D.M of molecule vector sum of Bond moment's of all Individual Polar bonds.

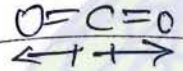
(2) If resultan comes zero then molecule is non-polar other wise polar.

(3) It is not necessary that molecule having Polar bond is also polar.

To determine D.M., VSEPR shape is used.

(4) ~~molecule having regular geometry has zero dipolem~~

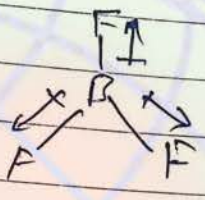
eg: CO_2



$\mu = 0$

Non-Polar

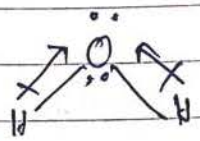
BF_3



$\mu = 0$

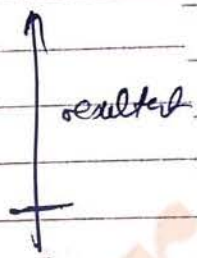
Non-Polar

H_2O



$\mu \neq 0$

Polar



(5) molecules having regula geometry has zero dipole moment (Non-Polar).

$\mu = 0$ (Non-Polar) :→ CS_2, $BeCl_2$, SO_3, CH_4, CCl_4, PCl_5, SF_6, XeF_2, XeF_4, IF_7 etc.

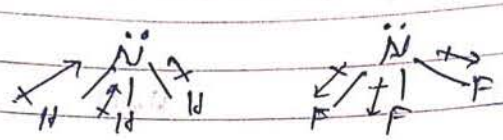
[Regula geometry]

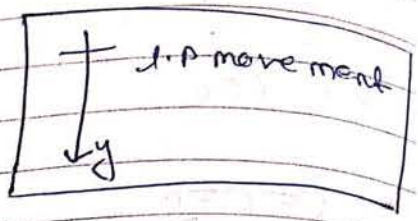
$\mu \neq 0$ (Polar) :— SF_4, ClF_3, H_2S, NH_3, NF_3, SO_2, $POCl_3$, CH_3Cl, CH_2Cl_2, H_2CO_3 ($(HO)_2CO$) etc.

(Irregula geometry)

* Compare dipole moment -

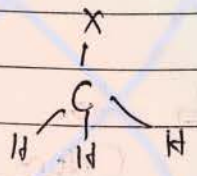
(1) NH_3 and NF_3





$\mu_{NH_3} > \mu(NF_3)$

(2) CH_3F, CH_3Cl, CH_3Br, CH_3I

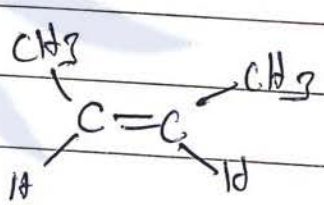


C-F C-Cl C-Br C-I

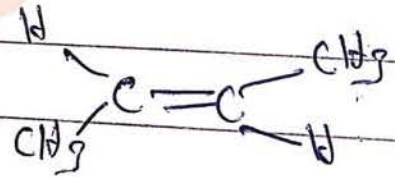
$CH_3Cl > CH_3F > CH_3Br > CH_3-I$ [charge ΔE·A dominat

(F has exceptionally small size)

(3) cis 2 Butene trans 2 butene



$\mu \neq 0$

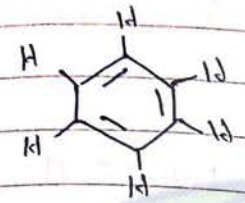


$\mu = 0$

(4)

$\mu = 0$

(5) Benzene



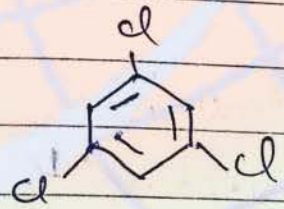
$\mu = 0$

(Non-polar)

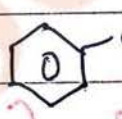
(6) P-dichlorobenzene (1-4)

($\mu = 0$)

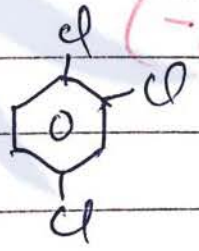
(7) (1-3-5) dichlorobenzene



($\mu = 0$)

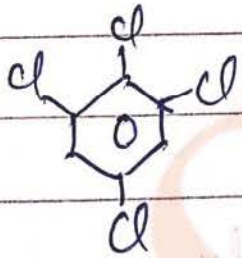
Q) Calculate dipole moment : given  , $\mu = x$

(1)



$\mu = x$

(II)



$\mu = x$

* % Ionic character —

% Ionic character = $\frac{\text{observed dipole moment (actual)}}{\text{expected dipole moment (calculated)}}$

eg:- $\mu_{HCl} = 1.02\ D$, Bond length $= 1.275\ A^0$
calculate % Ionic character in HCl
[$e = 4.8 \times 10^{-10}$ esu]

$\mu = E \cdot d = 4.8 \times 10^{-10} \times 1.275 \times 10^{-8}$
(expected)

H–Cl
$H^+ + Cl^-$

% Ionic character $= \frac{1.02 \times 10^{-18}\ esu\ /cm}{4.8 \times 10^{-10} \times 1.275 \times 10^{-18}} \simeq 17\ \%$

* Resonance (de-localisation of πe^-)

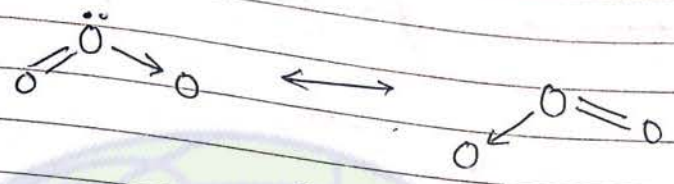
$-M= \longrightarrow \overset{\cdots}{=}M\overset{\cdots}{-}$

sp/sp^2

(I) To show resonance hence structure is made.
(II) Bond participating in reso structure is equal in B.L and B.E
(III) Resonance hybrid (actual structure) is more stable than resonating structure.

example:-

(i) O_3

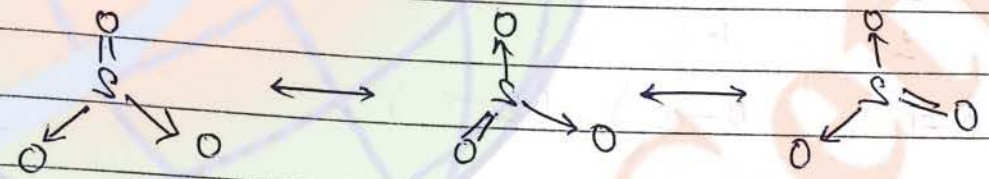


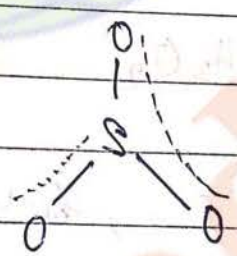
Hybrid structure

Bond order = $1 + 0.5 = 1.5$

1 π-bond is divided into two part so $\frac{1}{2}$ is added. //

(ii) SO_3

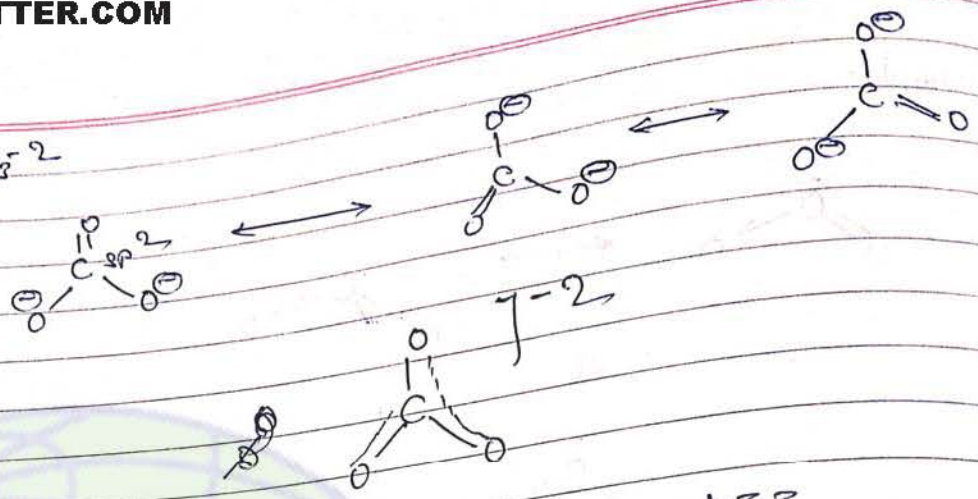




$$B.O = 1 + \frac{1}{3} = \frac{4}{3}$$

1 π bond is divided into 3 parts. //

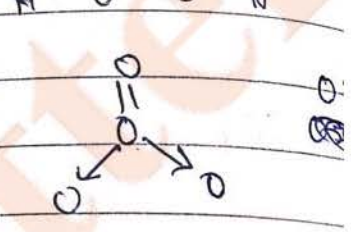
<3> CO_3^{-2}



$B.O = 1 + \frac{1}{3} = \frac{4}{3} = 1.33$

Q) Arrange in Bond order of O–O, B.L

O_2 , O_3 , H_2O_2



B.O ⇒ 2 1.5 1

(O=O) (O⋯O) (O–O)

$O_2 < O_3 < H_2O_2$

Q) Arrange in order of C-O, Bond length.

CO , CO_2 , CO_3^{-2}

B.O 3 2 1.33

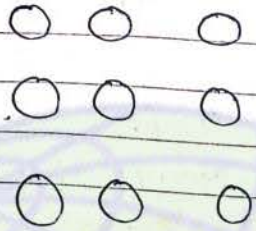
(≡) (=) (⋯)

O=C=O

$[CO < CO_2 < CO_3^{-2}]$

★ Metallic bond →

(i) Such type of Bond is possible in metals.

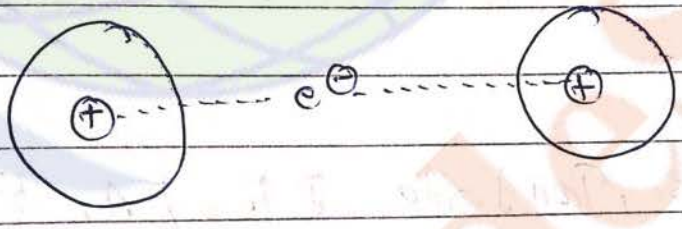


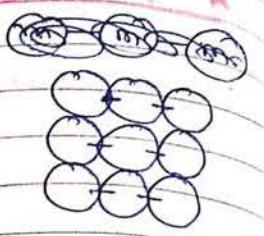
(metallic bond)
(Non-directional)

(ii) metallic bonds are explained on the basis of e⁻ gas model given by Lorentz.

(iii) According to this model metal is network of kernel in which free e⁻ acts as binding force.

(iv) As no. of unpaired e⁻ increase strength of metallic bond increases.



Ionic Compounds	covalent network Compounds	molecular compounds molecule	metallic Compounds
$x^- x^- x^-$ $x^- m^+ x^-$ $x^- x^- x^-$	A–A–A–A–A or A–B–A–B–A–B	AB_2 — AB_2 ↑ covalent bonds ↑ Inter molecular bonds	
→ Physical Prop. depends on strength of Ionic Comp.	→ Physical Prop. depends of strength of co-valent bonds	→ physical Prop. depends on strength of intermolecular bond/—	→ Physical Prop. depends on strength of metallic bonds
$mx / m_2x / mx_2$ (formula unit)	AB / A_2B / AB_2 (formula unit)	AB_2 (molecular formula)/—	(atomic formula)

Note:— For physical properties consider many atom or many molecule.

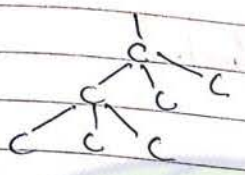
For Bond length, Bond ode, D.E, EA, EN etc. Consid single atom or single compound.

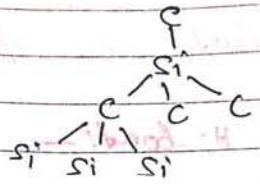
* General ode. of Density m.p and B.p

Covalent Network	> Ionic > metallic > molecular

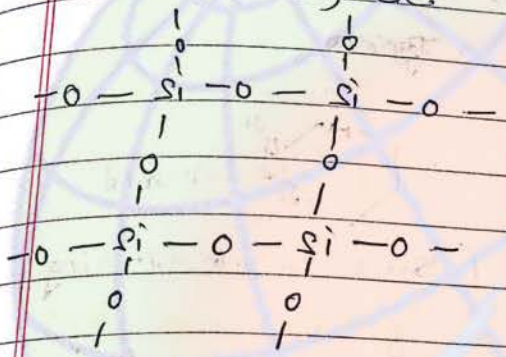
Example of the covalent network compound (selected any five)

(i) Diamond (ii) Graphite (iii) Carborundon (SiC) (iv) silicate.



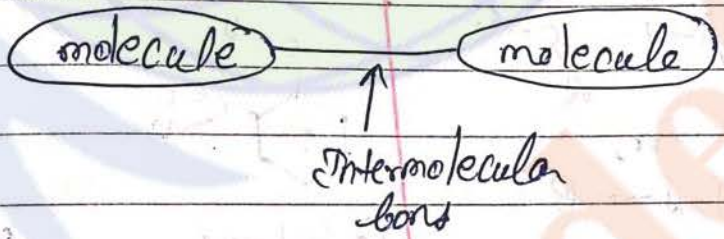


(v) silica (SiO_2) etc.



★ Intermolecular bond :-

⇒ such type of bond is present b/w molecules of molecular compound.



(1) various physical properties of ~~molecules~~ molecule compounds depends on strength of Intermolecular bond

(a) m.p and B.P ∝ Intermolecular bond

(b) Heat of fusion and vaporisation ∝ Intermolecular bond

(c) viscosity ∝ Intermolecular bond

(d) volatility ∝ $\frac{1}{\text{Intermolecular bond}}$

H-Bonding

(1) molecules having F-H, O-H, or N-H bonds are associated due to H-bond.
eg:- H_2O, NH_3, HF, H_2O_2, R-OH, $R-NH_2$, H_2CO_3, $(OH)_2CO$

(2) B.E of H-bond lies b/w 8-42 kJ/mol.

→ Type of H-bond:-

Intermolecular H-bond:-

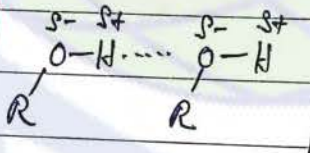
→ b/w molecules

→ Type:-

Homomolecular

→ b/w similar molecules

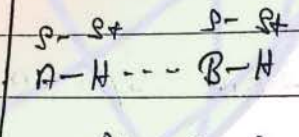
eg:- in pure comp

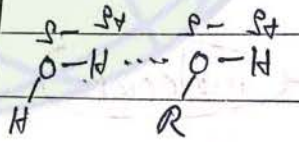


Heteromolecular

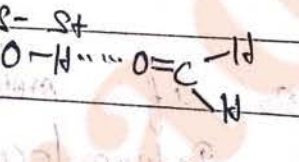
→ b/w diff molecules

eg:- in mixture.





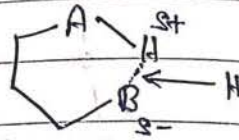
or,



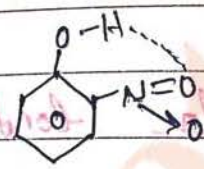
Intramolecular H-bond:-

→ within molecules.

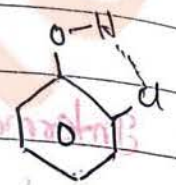
→ ~~Types~~



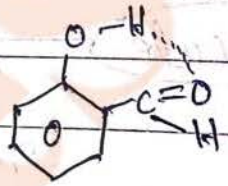
(5 or 6 membered ring)



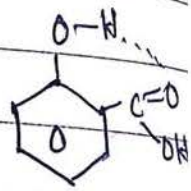
(ONP)



(O-chloro phenol



(O-hydroxy benzaldehyde)



(O-hydroxy benzoic a

Application of H-bond:-

No. of H-bonds per molecule = $2 \times \min\{$ No. of donor site, no of acceptor $\}$

Donar site:- → l.p attached with F, O, or N

Acceptor site:- → H-atoms attached with F, O or N

molecule	Donar site	Acceptor site	No. of H-bond
$H_2\ddot{O}:$	2	2	4
$H-\ddot{F}:$	3	1	2
$\ddot{N}H_3$	1	3	2
$CH_3-\ddot{O}-H$	2	1	2
$CH_3-\overset{\overset{O}{\|\|}}{C}-\ddot{O}-H$	4	1	2

⇒ Orda of extent of net Intermolecular bond:-

$H_2O > HF > NH_3$

⇒ Orda of B.P :-

$H_2O > HF > NH_3$

Q1.) which of the following compounds has least v.p at room temp.

(a) CO_2 (b) C_6H_6 (c) CCl_4 (d) H_2O

Q2.) HF is liquid while HCl, HBr, and HI are gas? why

Sol'n Due to H-bonding

Note:- [HCl, HBr, and HI are monobasic while HF may be di

Q3.) H_2O has greatest boiling point than H_2S? why

Sol'n Due to H-bonding.

Q4) which one has greatest volatility - HF or H_2SO_4 ?

Soln HF, due to H-bonding.

Q5) HF exist in the form of dimer (H_2F_2) in nature, why?

Soln Due to H-bonds.

⇒ HCl, HBr, and HI are monobasic while HF may be di-basic

⇒ Polybasic acids can form Acidic salt

$HCl + NaOH \longrightarrow NaCl + H_2O$

(monobasic) Normal salt.

$H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$

Polybasic (Acidic salt)

$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$

(Normal salt)

$H_2F_2 + KOH \longrightarrow \underline{KHF_2} + H_2O$

Acidic salt.

Q6) KHF_2 exist but not $KHCl_2$, ~~$KHBr_2$~~ $KHBr_2$ and KHI_2

Soln Due to H-bond, HF can exist in the form of dimer (H_2F_2)

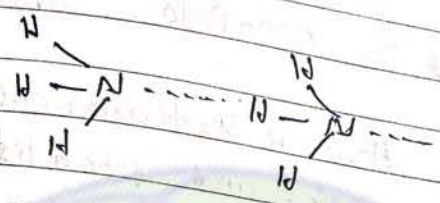
KHF_2,

$\downarrow$ K^+ ionic HF_2^-

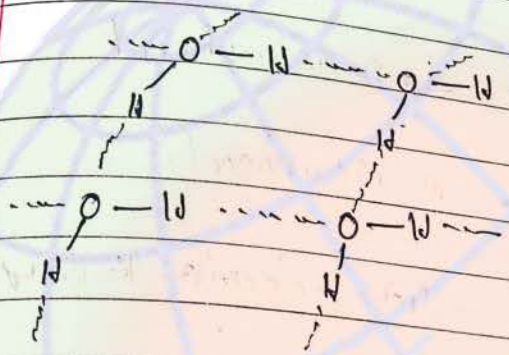
$F^{\ominus} \cdots H - F$

↑ H-bond ↑ covalent

NH_3 :-



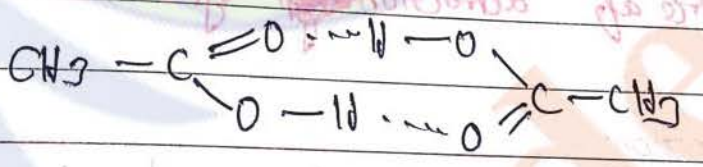
H_2O :-



Volume of ice > water.
Density of ice > water.

⇒ Ice has porous cage like structure.

⇒ CH_3COOH :-



dime.

⇒ B.P ∝ Intermolecular forces
∝ mol. wt (or surface area)

e.) which compound has max^{n} B.P?

(a) $CH_3-CH=CH_2$
(b) CH_3-CH_2-CHO
(c) $CH_3-CH_2-CH_2-OH$
(d) $CH_3-CH_2-CH_2-CH_2-OH$

Reason- Compound which can form H-bond with water are soluble in water.
eg: NH_3 is soluble in H_2O. //

Q) Which comp. has higher solubility in water.?
(a) NaCl (b) NH3 (c) HCl (d) Ar (e) All have equal solubility

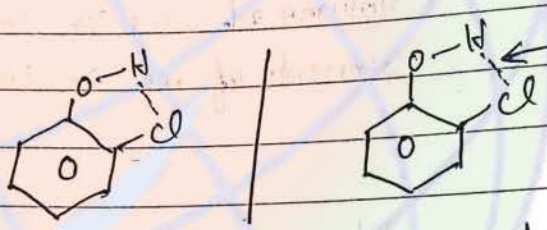
Sol^n order of solubility :-

Ionic > Polar-covalent > non-Polar covalent

⇒ Due to Intermolecular H-bond, Intermolecular bond becomes weaker. Hence, B.P and stability is weak and volatility and V.P ↑

order of B.P :- O-Nitrophenol < P-nitrophenol

order of volatility → O-Nitrophenol > P-Nitrophenol.



(weak Intermolecula bond

★ Vander wall's force of attraction type :→

(1) Ion-dipole attraction :-

attraction b/w anion and a polar molecules

eg Na^+ Cl^-

H^+ Cl^- H-Cl ($\mu \neq 0$)

(+) (δ− Cl) (+ −)

↳ when an ionic compound dissolves in a polar solve

2) Dipole - dipole attraction →

attraction b/w polar molecules :-

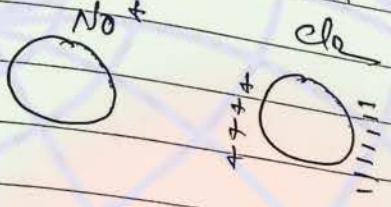
eg HCl ($\mu \neq 0$)

HCl ($\mu \neq 0$)

3) Ion - Induced dipole attraction :-

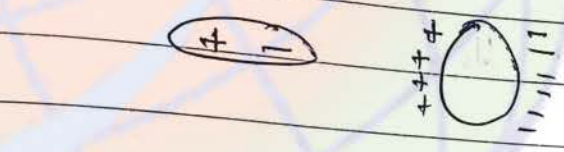
b/w an ion and a non-polar molecule

eg :→



4) Dipole - Induced dipole attraction :-

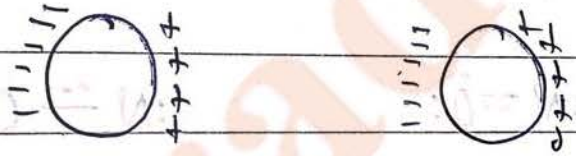
eg: HCl ($\mu \neq 0$) Cl_2 ($\mu = 0$)



5) Induced dipole - Induced dipole attraction :-

(London Dispersion force)

Cl_2 ($\mu = 0$) Cl_2 ($\mu = 0$)



other eg :- Br_2, C_6H_6, CH_4, CCl_4, noble gases etc.

Note For compounds having similar type of van der Waals force of attraction.

[b.p ∝ mol weight]

★ Order of b.p :-

(i) ICl , Br_2
($\mu \neq 0$) ($\mu = 0$)

$ICl > Br_2$

(ii) CH_3I , CH_3Cl , Cl_2 , CH_4
($\mu \neq 0$) ($\mu \neq 0$) ($\mu = 0$) ($\mu = 0$)

$CH_3I > CH_3Cl > Cl_2 > CH_4$

(iii) HF, HCl, HBr, HI

$HF > HI > HBr > HCl$

(iv) H_2O, H_2S, H_2Se, H_2Te

$H_2O > H_2Te > H_2Se > H_2S$

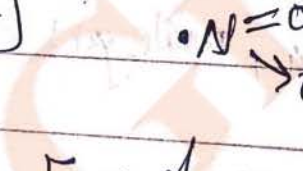
★ Some special bonding :-

1) odd e⁻ bond :-

Such type of bond may possible in molecules having odd no. of e⁻.

NO (15e⁻)

NO_2 (23e⁻)



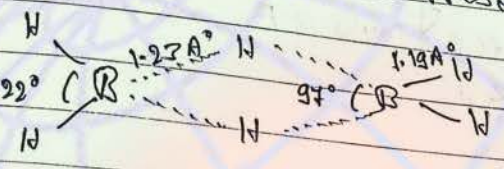
[V-shape
bond angle ≈ 132°]

(2) Banana bonds:-

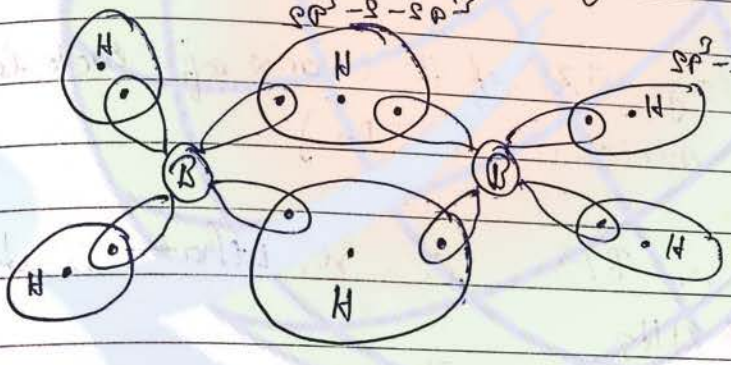
(a) 3 centre - 2e⁻ (3C-2e⁻) bond is called as banana bond.

A — B 2C - 2e⁻
A = B 2C - 4e⁻
A ≡ B 2C - 6e⁻

(b) such type of bond is present in diborane (B_2H_6)



In B_2H_6, hybridisation of B is sp^3.



4, 2C - 2e⁻
2, 3C - 2e⁻

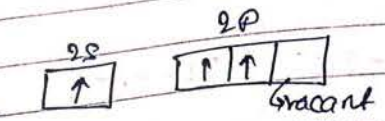
⇒ H - bridge structure
⇒ 4, terminal - H
⇒ 2, Bridge - H
⇒ All H - are not co-planar.

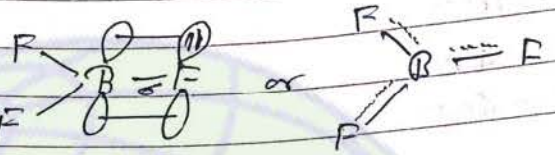
Back bonding →

It is an additional π-bond which is formed b/w atoms both already have a σ-bond and one of the atoms has vacant orbital and other has paired orbital (l.p)

eg:- BF_3

B (1st excitation)





(b) Due to back bonding B-F bond length becomes shorter than expected and BF_3 becomes poor lewis acid than expected

order of lewis strength:-

$BF_3 < BCl_3 < BBr_3 < BI_3$

(Due to larger size of I, chance of back bonding is minimum in BI_3)

Q.) B-F bond length in BF_3 is x, what is its B-L bond in BF_3 are react with NH_3

Soln $BF_3 + NH_3 \longrightarrow [NH_3 \rightarrow BF_3]$

l.a l.b

more than x,

Vacant orbital of B involves in coordinate bond does not involves in back bonding. //

Hydrides :-

1) B-family :-

Hydrides of B

Nido boranes
B_nH_{n+4}
eg B_2H_6 (diborane)
Banana bonds

Arachno boranes
B_nH_{n+6}

2) C-family :-

Hydrides of C are called hydrocarbon.

SiH_4 → Silane
GeH_4 → Germani
SnH_4 → Stannane } rare
PbH_4 → Plumbane }

⇒ Due to Increasment in B.L, down the group stability "↓".

3) N-family

(i) NH_3, PH_3, AsH_3, SbH_3, BiH_3

(ii) Shape :- Pyramidal

(iii) Order of bond angle :-

$\underbrace{NH_3}_{107°48'} > PH_3 > AsH_3 > SbH_3 > \underbrace{BiH_3}_{\text{Almost } 90°}$

(Occ" to E.N of central atom)

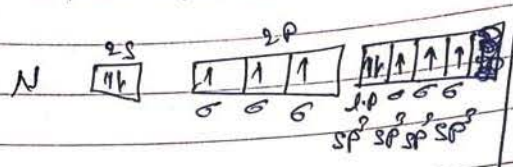
4) O-family

H_2O, H_2S, H_2Se, H_2Te

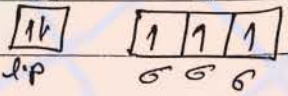
· V-shape

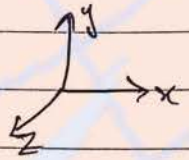
$\underbrace{H_2O}_{104°28'} > H_2S > H_2Se > H_2Te$

In NH_3, hybridisation of N is sp^3,



In other word, there is no hybridisation of central atom. Ther Pure p-orbitals form bonds.





(c) order of acidic strength:-

$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
(acc. to B.L)

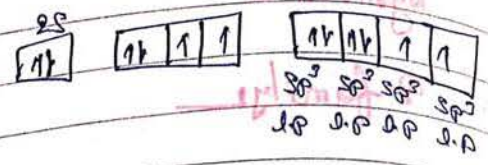
(d) order of basic strength:-

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
(acc to density of l.p on central atom)

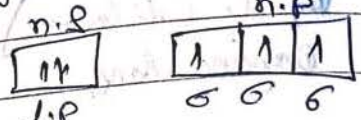
(e) order of thermal stability:-

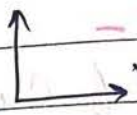
$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
(acc. to B.L)

In H_2O, hybridisation of O is sp^3.



In other three, there is no hybridisation of central atom.





$H_2O < H_2S < H_2Se < H_2Te$

$H_2O > H_2S > H_2Se > H_2Te$

$H_2O > H_2S > H_2Se > H_2Te$

Note:- In covalent compound thermal stability depends on strength of covalent bond

(b) order of reducing power:-
$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
(acc. to B.L)

$H_2O < H_2S < H_2Se < H_2Te$

(g) order of b.p:-
(depends on st. of Intermolecular bonds)
$BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$
(H-bond in NH_3 is weaker than vander wall's force of attn in BiH_3 and SbH_3)

$H_2O > H_2Te > H_2Se > H_2S$

(5) Halogens -

HF, HCl, HBr, HI

(a) order of b.p:-
$HF > HI > HBr > HCl$
(depends on Intermolecular bonds)

(b) order of thermal stability:-
$HF > HCl > HBr > HI$

(c) order of reducing power:-
$HF < HCl < HBr < HI$

(d) order of acidic strength:-
$HF < HCl < HBr < HI$
weak acid — strong acid

(c)

B_2O_3 , Al_2O_3 , Ga_2O_3 , In_2O_3 , Tl_2O_3
or or or or
$B(OH)_3$ $Al(OH)_3$ $Ga(OH)_3$ $In(OH)_3$ $Tl(OH)_3$
or
H_3BO_3
Acidic Amphoteric Basic

(4) Carbon family :-

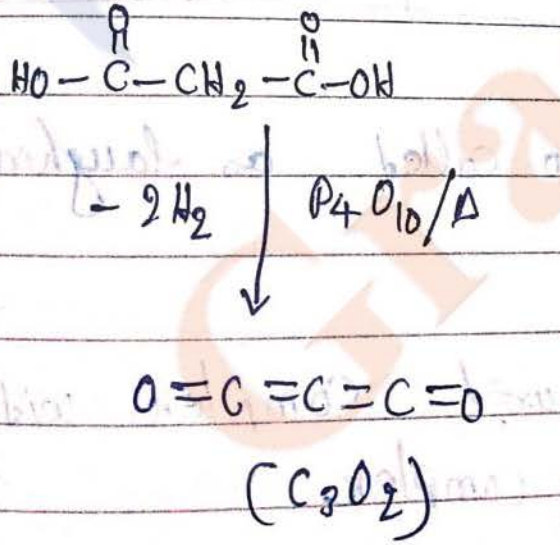
(a) monoxide :-

CO GeO SnO PbO
neutral weak acid Amphoteric

(b) Di-oxide :-

CO_2 SiO_2 GeO_2 SnO_2 PbO_2
Acidic weak acid amphoteric

(c) Carbon ~~dioxide~~ Suboxide (C_3O_2) :-



(C_3O_2)

Note :- P_4O_{10} acts as dehydrating agent.

(3) N-family :-

Oxides of N :-

	Name	structure	mag. Properties	Nature	Physical state and colour
1	Nitrous oxide, N_2O	$\ddot{N} \equiv N \rightarrow \ddot{O}:$	dia	Neutral	Colourless gas
2	Nitric oxide, $\overset{+2}{N}O$	$:\ddot{N}=\ddot{O}:$	Para	"	"
3	Dinitrogen trioxide ($\overset{+3}{N_2}O_3$)	$O \underset{\|}{=} N - N \overset{=O}{\rightarrow} O$	dia	Acidic	In solid state light blue solid
4	Nitrogen di-oxide (NO_2)	$:N \overset{=O}{\rightarrow} O$	Para	"	Reddish brown gas
5	Dinitrogen tetraoxide $\overset{+4}{N_2}O_4$	$O(=O)(\leftarrow O)-N-N(=O)\rightarrow O$	dia	"	Colourless solid
6	Dinitrogen pentaoxide ($\overset{+5}{N_2}O_5$)	$O(=O)(\leftarrow O)-N-O-N(=O)\rightarrow O$	dia	" (most acidic)	"

(1) Nitrous oxides (N_2O) is also called as laughing gas (Cont anaesthesia)

(2) "NO" forms a brown coloured complex with FeSO

Nitric oxide

called as Brown ring complex.

$FeSO_4 \cdot NO$ or $[Fe(H_2O)_5NO]SO_4$

Brown ring complex.

⇒ This rxn is used as differentiation b/w NO and N_2O

(3) $2NO_2(g) \rightleftharpoons N_2O_4(s) + heat$; $\Delta H = -ve$ (exothermic)

∴ rxn exothermic है इसलिए,

temp ↑ to rxn forward direction में proceed होगा, NO_2 का conc ↓ होगा।

so, Paramagnetic ↓ //

T ↑ ; Paramagnetic ↑ ✓

T ↓ ; Paramagnetic ↓ ✓

(4) $\overset{+3}{N_2}O_3 + H_2O \longrightarrow \overset{+3}{H}NO_2$

Nitrous Anhydride

$\overset{+5}{N_2}O_5 + H_2O \longrightarrow \overset{+5}{H}NO_3$

Nitric anhydride

***Y $2NO_2 + H_2O \longrightarrow \overset{+5}{H}NO_3 + \overset{+3}{H}NO_2$

Anhydride of mixture of nitric and nitrous acid.

oxides of P:-

Phosphorous trioxide, (P_4O_6) ; (P_2O_3)

Phosphorous Pentaoxide (P_4O_{10}) ; (P_2O_5)

~~$\overset{+3}{P_4O_6} < \overset{+5}{P_4O_{10}}$ (acidic strength)~~

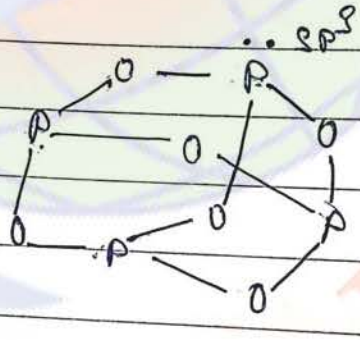
$\overset{+3}{P_4O_6} < \overset{+5}{P_4O_{10}}$ (acidic strength)

$\overset{+3}{P_4O_6} + H_2O \longrightarrow H_3\overset{+3}{P}O_3$

$P_4O_{10} + H_2O \longrightarrow H_3\overset{+5}{P}O_4$

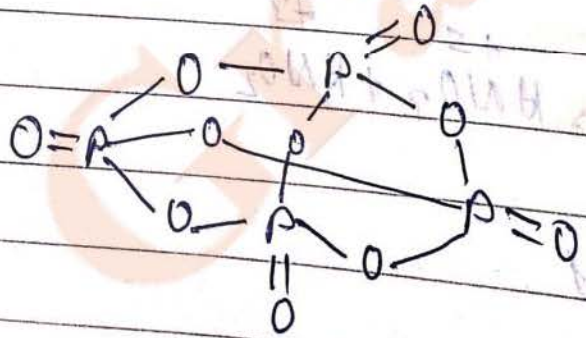
Structure:-

P_4O_6 :-



6, P-P bond
12, P-O-P bond
6, P-O-P linkage
16, l.p

P_4O_{10} :-



4, P=O bond
0, P-P bond
12, P-O Bond
6, P-O-P bond
20 l.p

oxides of S.
sulphur dioxide, $\overset{+4}{SO_2}$
sulphur trioxide, $\overset{+6}{SO_3}$

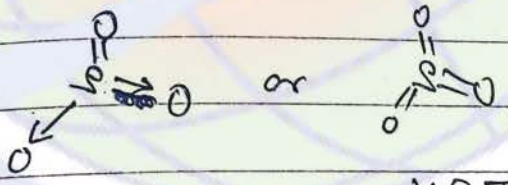
$\overset{+4}{SO_2} < \overset{+6}{SO_3}$ (acidic st)

$SO_2 + H_2O \longrightarrow H_2SO_3$
(Sulphurous anhydride)

$SO_3 + H_2O \longrightarrow H_2SO_4$
(Sulphuric anhydride)

structure of SO_2 :-

(a) Gaseous molecules :-

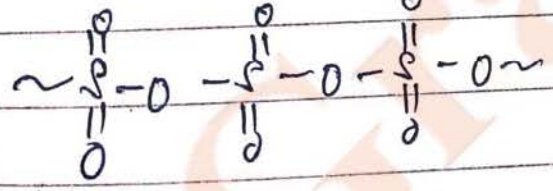


or

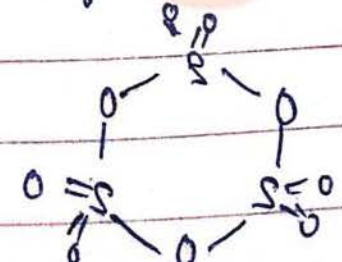
Lewis structure VBT

(b) Solid state :-

Definite chain :-



(c) Cyclic form $(SO_2)_3$



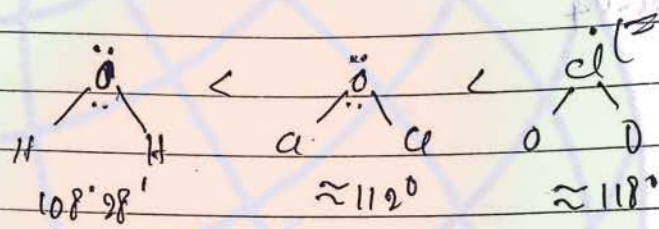
(5) Halogens:-

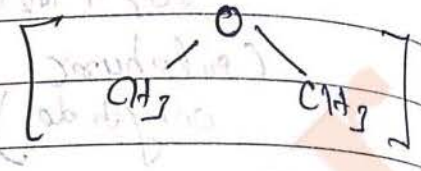
(a) oxide of F:- $\overset{+2}{O}F_2$, $O_2\overset{+1}{F_2}$

(b) oxide of Cl:- Cl_2O, Cl_2O_7 (main oxide)

ClO_2 (Paramagnetic)

$ClO_3 \longrightarrow Cl_2O_3$
(Para) (dia)





⇒ Ionic form of Cl_2O_6 in solid state is:-

ClO_2^+, ClO_4^-

(c) oxide of I:-

$\overset{+5}{I_2O_5}$ (Co-valent oxide) main oxide

I_2O_4 (Ionic oxide
(IO^+, IO_3^-)

I_4O_9 (Ionic oxide)

I^{+3} IO_3^-

$I(IO_3)_3$

form oxy acid.

Hydroxide (oxy acids):-

Halogens:-

due to small size and high E.N one oxyacid of "F" es possible of H-O-F or ~~F-O-H~~ F-O-H which is unstable

Name	Cl	Br	I	Name of anion
1) Hypohalous acid $H\overset{+1}{O}X$ or HXO	HOCl	HOBr	HOI	XO^-, hypohalite
2) Halous acid, $H\overset{+3}{X}O_2$ or (OH)XO	$HClO_2$	—	—	XO_2^-, halite
3) Halic acid, $H\overset{+5}{X}O_3$ or $(HO)XO_2$	$HClO_3$	$HBrO_3$	HIO_3	XO_3^-, halate
4) Perhalic acid, $H\overset{+7}{X}O_4$ / $(HO)XO_3$	$HClO_4$	$HBrO_4$	HIO_4	XO_4^-, perhalate

$NaOI$ → Sod. hypoiodite

$KClO_2$ → Pot. chlorite

$NaIO_3$ → Sod. Iodate

I_4O_9 → Iodine iodate
or
$I(IO_3)_3$

$KBrO_4$ → Pot. Perbromate

* Hypo:- when one o-atom is removed from any [-ous acid]

$H_3PO_4 \rightarrow H_3PO_3$
(Phosphorous acid) (hypophosphorous acid)

* Per:- when one o-atom is added to any [-ic acid]

$H_2SO_4 \rightarrow H_2SO_5$
Sulphuric acid (Per Sulphuric acid)

*** Order of oxidising power:-

$HO\overset{+1}{Cl} > H\overset{+3}{Cl}O_2 > H\overset{+5}{Cl}O_3 > H\overset{+7}{Cl}O_4$

$K\overset{+7}{Mn}O_4 > K\overset{+4}{Mn}O_2$

$K_2\overset{+6}{Cr}_2O_7 > \overset{+3}{Cr}_2O_3$

$H\overset{+5}{N}O_3 > H\overset{+3}{N}O_2$

$H_2\overset{+6}{S}O_4 > H_2\overset{+4}{S}O_3$

⇒ Acidic strength:-

(1) General form of an oxyacids is $(HO)_mZO_n$

m = basicity of acid.
Z = central atom (non-metal)
n = remaining O-atom

$H_3PO_4 / (HO)_3PO$ m = 3

Classmate
Date
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(2) Acidic strength depends on "Z" and "n"

(3) n↑, acidic strength ↑

(4) If "n" is similar and all oxyacids belong to the same group then acid strength depends on E.N of Z.

⇒ order of acidic strength :-

$HOCl < HClO_2 < HClO_3 < HClO_4$

$HNO_2 < H_2SO_4 < HClO_4$

$HOCl > HOBr > HOI$

$HClO_4 > HBrO_4 > HIO_4$

If "n" is similar	If "n" is different
H-O-Cl most E.N	H-O-Cl
H-O-Br	(most difference)

⇒ If n=0, very weak acid
eg HOCl, HOBr, etc.

⇒ n=1, weak acid
eg: $HClO_2$, HNO_2,

⇒ n=2, strong acid
eg: HNO_3, H_2SO_4, etc.

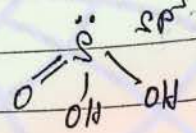
n = 3, very strong acid.

g ↓ → $HClO_4$, etc

o-family →

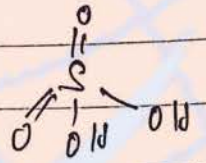
oxy-acid of O :-

1) Sulphurous acid, H_2SO_3 / $(HO)_2SO$



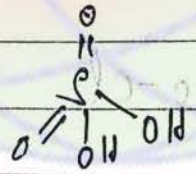
sp^3, Pyramidal

2) Sulphuric acid, H_2SO_4 / $(HO)_2SO_2$

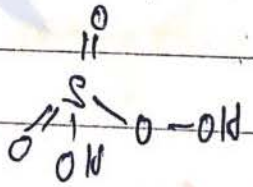


sp^3, tetrahedral

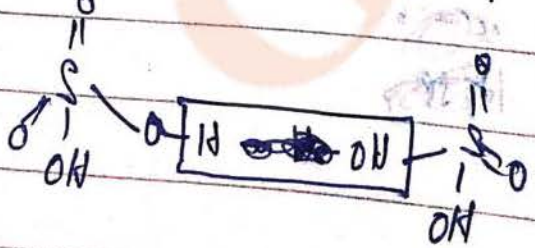
3) Thiosulphuric acid, $H_2S_2O_3$

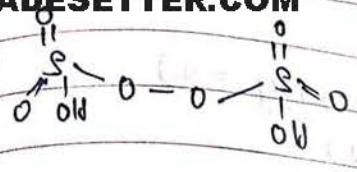


4) Persulphuric acid / Peroxy sulphuric and Caro's acid, H_2SO_5



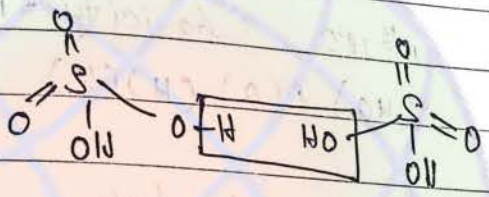
5) Peroxidisulphuric acid / ; marshall acid, $H_2S_2O_8$

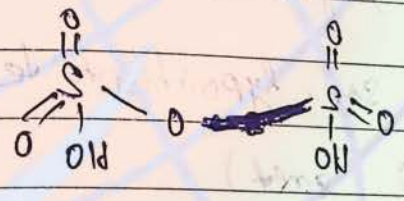




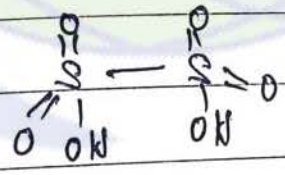
(1) Pyrosulphuric acid/olium, "$H_2S_2O_7$"

Pyro:- when one H_2O molecule is removed from 2 molecule of oxy acid.





(2) Dithionic acid, $H_2S_2O_6$



* N-family →

oxy-acid of N! —

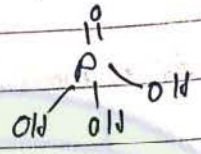
(1) Nitric acid, $\overset{+5}{H}NO_3$

(2) Nitrous acid, $\overset{+3}{H}NO_2$

(1) Phosphorous acid, H_3PO_3 (basicity = 2)

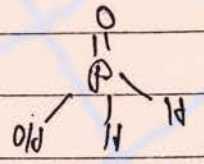
$(OH)_2P(O)(H)$

(2) Phosphoric / orthophosphoric acid, H_3PO_4 / $(OH)_3PO$



(3) Hypophosphorous acid, H_3PO_2 (basicity = 1)

$(HO)P(O)(H)(H)$



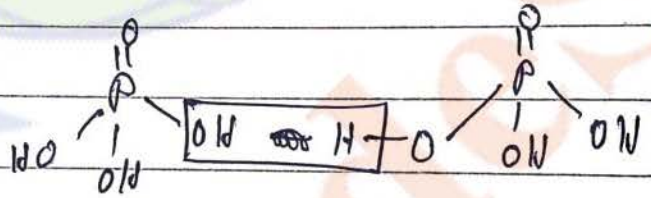
$H_2PO_2^-$, hypophosphite

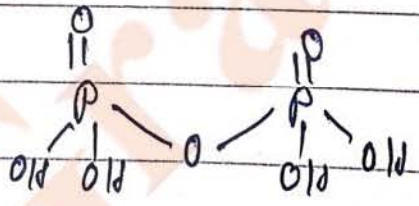
NaH_2PO_2, sod. hypophosphite

(Normal salt)

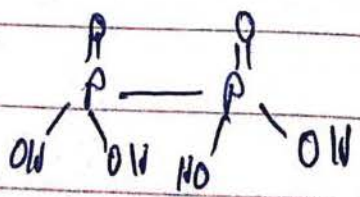
not acid)

(4) Phosphonic acid, $H_4P_2O_7$





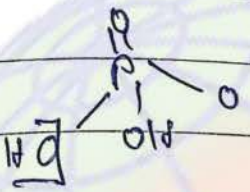
(5) Hypophosphonic acid, $H_4P_2O_6$



(d) meta phosphoric acid $(HPO_3)_n$

↳ Condensation polymer of orthophosphoric acid (H_3PO_4)

as Infinite chain :-



E-C-S → electrochemical series

(high oxidation)

metals

Li

s-block

d-block

p-block

Increasing ↑ value of SRP

change of reduction ↑, change of oxidation ↓

H2

Cu

Ag

Hg

Pt

Au

D2

Br

Cl2

Non-metals

F2

S → P
electrochemical series

classmate
Date
Page 24

Li → लिथियम
K → पोटेशियम
Ca → कैल्शियम
Na → सोडियम
Mg → मैग्नीशियम
Al → एल्युमिनियम

Note :- (i) Li is best reducing agent
(ii) F₂ is best oxidising agent
(iii) ऊपर वाले का oxidation होगा तथा नीचे वाले का Reduction होगा।
(iv) ऊपर वाला metal नीचे वाले metal को displace करेगा।
(v) नीचे वाला Non-metal ऊपर वाला Non-metal को हटाएगा।

H_2O → पानी
Mn → मैंगनीज
Zn → जिंक
Cr → क्रोमियम
Fe^{+2} → आयरन
Co → कोबाल्ट
Ni → निकिल
Sn → टिन
Pb → लेड
H_2 → हाइड्रोजन

AgBr → सिल्वर ब्रोमाइड
AgCl → सिल्वर क्लोराइड (सिल्वर हैलाइड)
Cu^{+2} → कॉपर
Cu^{+1} → कॉपर
I_2 → आयोडीन
$O_2 + 2e^-$ → ऑक्साइड्स

Fe^{+3} → आयरन
Ag → सिल्वर
Hg → मर्करी
NO_3^- → नाइट्रेट
Br_2 → ब्रोमीन
Pt → प्लेटिनम
MnO_2 → मैंगनीज डाइऑक्साइड
$O_2 + 4e^-$ → ऑक्साइड्स
$Cr_2O_7^{-2}$ → काम होगा

Cl_2 → क्लोरीन
Au → गोल्ड
MnO_4^- → मैंगनीज
H_2O_2 → ऑक्सीडाइजिंग एजेंट के लिए
CO
F_2 → फ्लोरीन

* s-block elements :-

(1) IA) → Li, Na, K, Rb, Cs, Fr → +1
IIA) → Be, Mg, Ca, Sr, Ba, Ra → +2
$F^{-1} = -1$.
$Al^{+3} = +3$
$NH_4^+ = +1$.
$Ag^{+1} \rightarrow +1$.
} fixed O.N

(2) O : → −2 to +2

(3) p-block element (Non-metals) :-

max. ON →	+4	+5	+6	+7	
min. ON →	−4	−3	−2	−1	
Groups →	14	15	16	17	18
	C-family	(N-family)	Calogen (O-family)	halogen (F)	Noble gas

(4) Mn → +2 to +7 ; Cr : → +1 to +6

(5) d-block elements :-

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			+1	+1	+1	+1	+1	+1	+1
			+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5	+5	+5			
			+6	+6	+6				
					+7				

Groups →	3	4	5	6	7	8	9	10	11	12

[Lewis Acid → lone pair or Anion acceptor] → Acid → Any sub
[Lewis base → lone pair or Anion donar]

Halides:-

(1) P-family:-

Down the group stability of trihalide decreases while stability of monohalide increases.

(2) Carbon family:-

Down the group stability of tetrahalides decrease and stability of di-halides increase.

(3) Nitrogen family:-

(a) They can form trihalides and pentahalides.
(Nitrogen and Bismuth can not form pentahalides)

N → due to absence of vacant d-orbitals
Bi → due to inert pair effect

(b) PCl_5, acts as chlorinating agent
"sp^3d"

$$PCl_5(g) \xrightarrow{\Delta} PCl_3(g) + Cl_2(g)$$

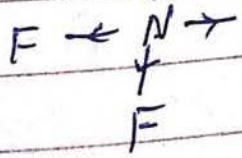
(c) Ionic form of PCl_5 is in solid state.
"sp^3" "sp^3d^2"

$$[PCl_4]^+ [PCl_6]^-$$

$$[PBr_4]Br^-$$

(d) order of lewis basic strength:-

$$\ddot{N}F_3 < \ddot{N}Cl_3 < \ddot{N}Br_3 < \ddot{N}I_3$$



$PCl_5 + H_2O \rightarrow HCl + H_3PO_4$

$PCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_3$

(e) Hydrolysis of trichlorides:—

$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$

$PCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_3$

$SbCl_3 + H_2O \rightarrow 2HCl + SbOCl$ ($SbO^+ Cl^-$)

$BiCl_3 + H_2O \rightarrow 2HCl + BiOCl \downarrow$ ($BiO^+ Cl^-$)
(Pearl white)

$Bi^{+3} + H_2O \rightarrow BiO^+$

Notes—

(1) In hydrolysis of covalent compound H_2O behaves as lewis base.

It donate its l.p to the atom of compound which have vacant orbitals as well as partial the charge.

Q) Hydrolysis of CCl_4 is not possible while Hydrolysis of $SiCl_4$ is possible. why.

Sol) Because Si has vacant orbital as well as partial the charge.

(11) The compound in which partial the charge is greater has greater chance of hydrolysis.

(A) (+)

Some other Properties-

B-family :-

(1) Diagonal relationship b/w "B" and "Si" :-

B C
Al Si

(a) Both B_2O_3 and SiO_2 are acidic. (Similarity) ✓

(b) B can form max. 4 bonds while. ✓
Si can form max 6 bonds. ✓
(difference)

(11) Diagonal relationship b/w Be and Al :-

Be B
mg Al

(a) Both BeO and Al_2O_3 are amphoteric.
(b) Be can form max. 4 bonds while Al can form max. 6 bonds.
(difference)

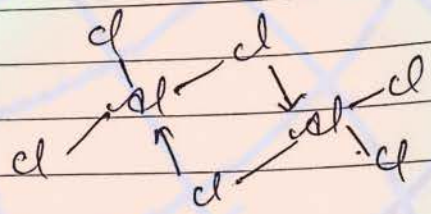
Al (1st excitation)

Be (1st excitation)

(C) chlorides of both Be and Al have bridge structure.

sp^2

$AlCl_3$:—



(dimer)

(in vapour state)

sp

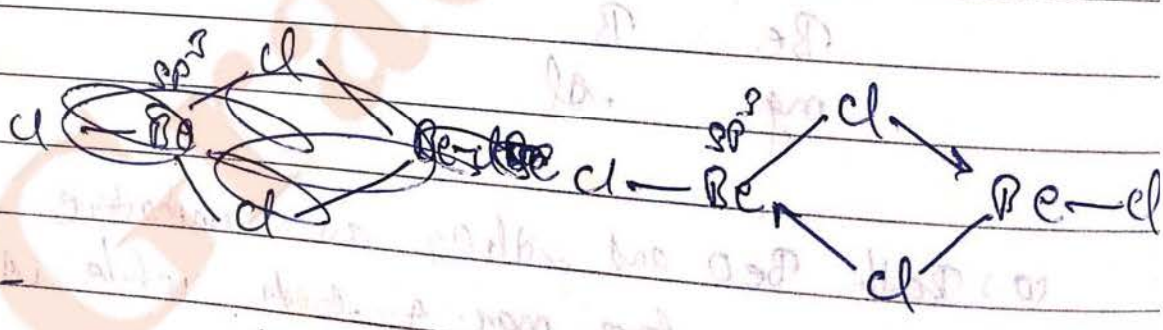
$BeCl_2$:—

$(BeCl_2)_2 \xleftarrow{\text{vapour state}} BeCl_2 \xrightarrow{\text{solid state}} (BeCl_2)_n$

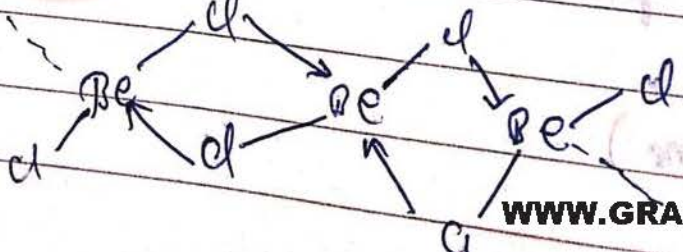
dimer

Polymer

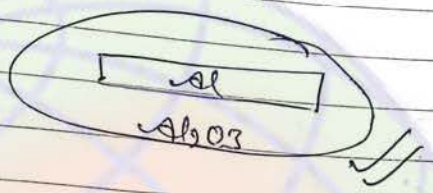
Dimer :—



Polymer :—



(d) Both Be and Al forms layer of their respective oxides on their surface such that they do not react with oxidising agent like HNO_3.



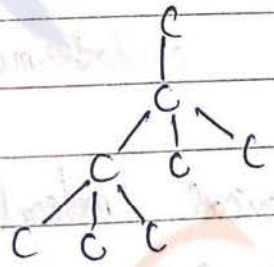
* C-family →

(1) Allotropes of C :-

Crystalline → Diamond, Graphite, fullerene

Amorphous → coal, charcoal, C-black

Diamond :-



covalent network solid

→ Hardest known solid
→ bad conductor of electricity but good conductor of heat.

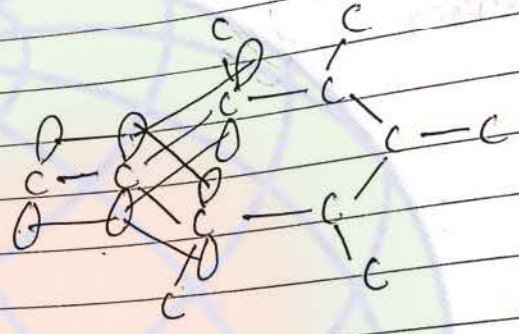
Graphite :-

→ It has layers (sheet-like) structure In each layer one

C-atom is bonded with 3 other C-atoms.

→ b/w layers weak vander waals force of attraction is present Hence, it acts as lubricants

partial $p\pi$-$p\pi$



← planar C

sp^2

→ Due to presence of weakly bonded π-e⁻ graphite acts as conductor of electricity.

→ Thermodynamically, the most stable allotrope of C is graphite.

$$C_{graphite} \longrightarrow C_{(diamond)} \quad ; \quad \Delta H = +ve$$

endothermic

* Fullerenes - There are large spherical molecule having molecular formula [C_{60}, C_{70}, etc]

→ C_{60} is also called as bucky / buckminster ball and it structure like soccer ball.

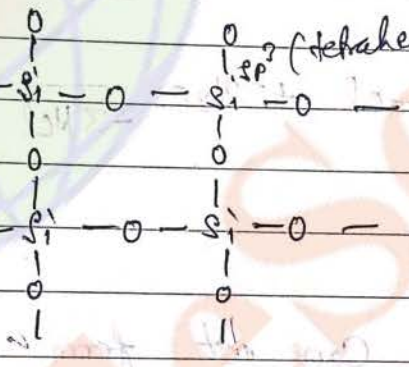
12 Pentagone and 20 hexagone.

Carbon can form stable $p\pi-p\pi$ while due to larger size other elements of this family can't form stable $p\pi-p\pi$ bond.

→ Except carbon other elements, due to presence of vacant d-orbitals, can form $p\pi-d\pi$ back bonding.

Q.) CO_2 is gaseous molecule while SiO_2 is co-valent network solid, why?

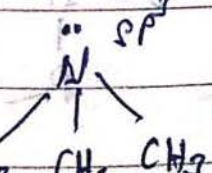
Sol'n Because Si can't form stable $p\pi-p\pi$ bond.

CO_2	SiO_2
$O=\overset{sp}{C}=O$ — CO_2 ↳ weak vander waal's force of attraction.	

Q.) trimethyl amine $((CH_3)_3N)$ is pyramidal while trisilylamine $((SiH_3)_3N)$ is trigonal pyramidal, why?

Si form $p\pi-d\pi$ back bonding with N.

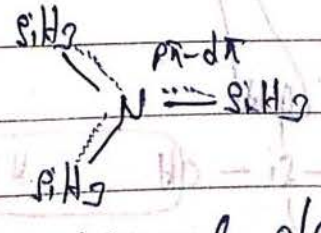
$(CH_3)_3N$



Pyramidal ✓

more basic

$(SiH_3)_3N$



trigonal planar (less basic)

Q3) N_2 exist but not P_2, ...

Q4) O_2 exist " " S_2, why?

Sol^n Due to small size their period element can not form stable $p\pi - p\pi$ bond.

Note:- S_2 and P_2 may exist in vapour state, they have properties like O_2 and N_2 respectively.

<3> Silicones:-

These are ~~organo~~ organosilicone polymers having Si-O-Si linkage.

These are prepared by hydrolysis of alkyl chlorosilane

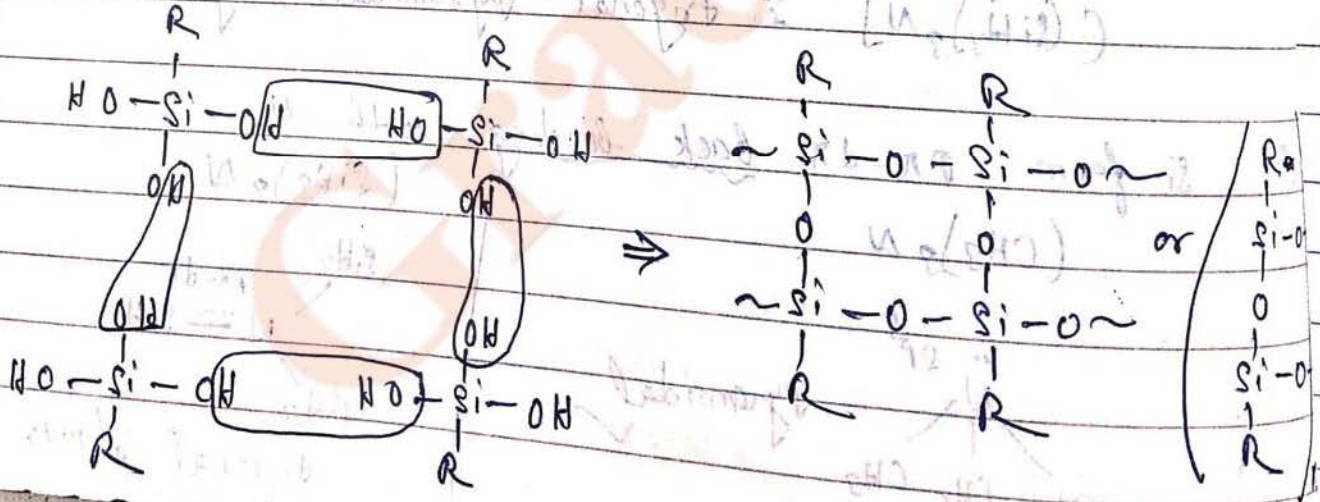
<a> $SiCl_4 + RMgCl \longrightarrow RSiCl_3 + MgCl_2$

[monoalkyl trichloride]

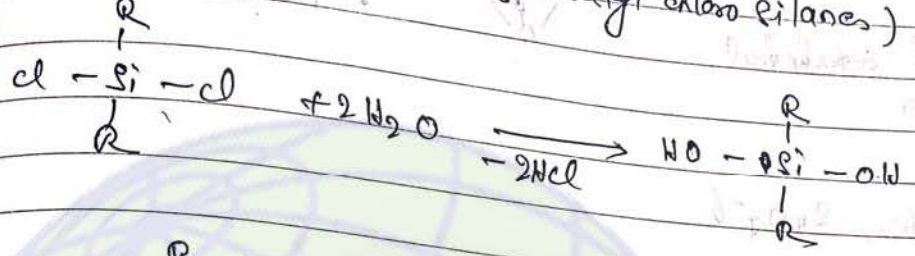
$$Cl-\underset{Cl}{\overset{R}{Si}}-Cl + 3H_2O \xrightarrow[-3HCl]{} HO-\underset{OH}{\overset{R}{Si}}-OH$$

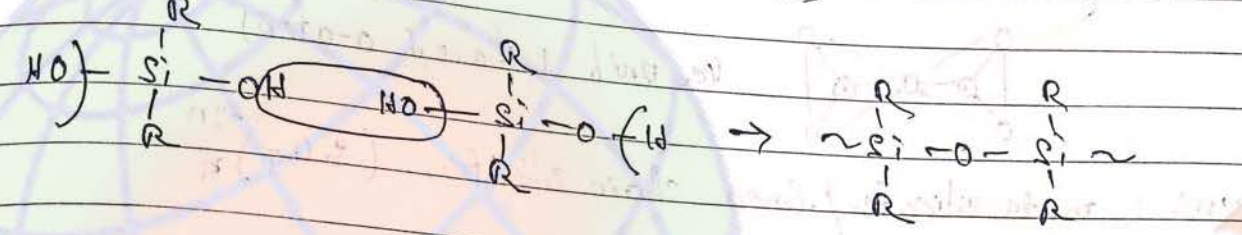
(monoalkyl silanol)

⇒ Si can not form stable $p\pi - p\pi$ bond hence, this silanol undergoes condensation polymerisation to produce silicones.



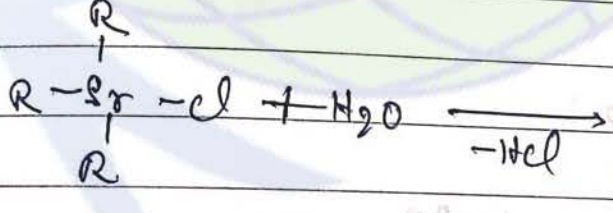
(A) $SiCl_4 + 2\,RMgCl \longrightarrow R_2SiCl_2 + 2MgCl_2$
(dialkyl chloro silanes)



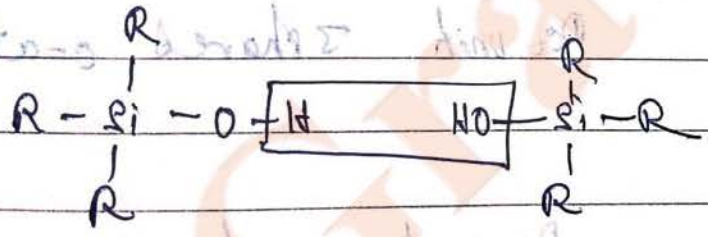


(linear silicones)
$(R_2Si-O)_n$

(C) $SiCl_4 + 3\,RMgCl \longrightarrow R_3SiCl + 3MgCl_2$
(trialkyl chloro silanes)



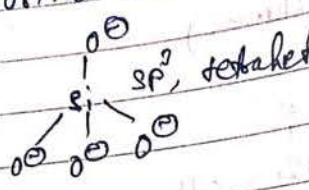
(trialkyl silanol)



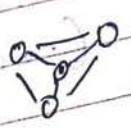
$R_3Si-O-SiR_3$ (dimer)

(7) Silicates :-

(I) orthosilicates, SiO_4^{-4}

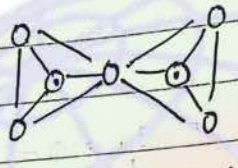


sp^3, tetrahedral



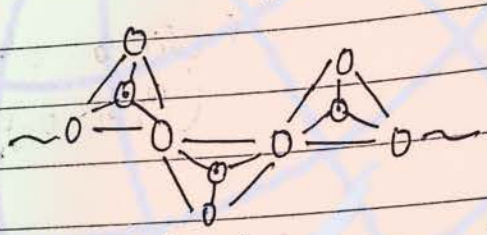
O, oxygen
•, Si

(II) Pyrosilicates, $Si_2O_7^{-6}$



Per unit 1 shared O-atom

(III) meta silicates / linear chain silicates, $(SiO_3)_n^{-2n}$



Per unit 2 shares O-atom

(IV) Cyclic silicates :-

$n=3$	$n=6$
$Si_3O_9^{-6}$	$Si_6O_{18}^{-12}$

(V) 2D-silicates / sheet silicates :-

$(Si_2O_5)^{-2n}$

Per unit 3 shares O-atom,

(VI) 3D-silicates :-

$(SiO_2)_n$ or SiO_2, Per unit 4 shares O-atom

P.

N- family :-

(i) N_2 is colourless, tastless and odourless gas, diamagnetic partially soluble in water

(ii) Due to very high bond energy and absence of bond polarity at ordinary condition N_2 is almost inert.

(iii) Allotropes of phosphorous :-

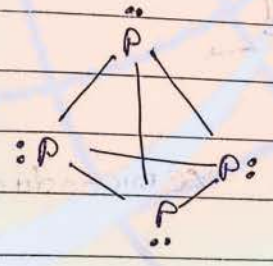
(a) white P :-

→ Poisonous, highly reactive, glows in dark due to auto oxidation. (Phosphorescence)

$$P_4 + SO_2 \longrightarrow P_4O_{10}$$

→ kept in water, otherwise in open air it will catch fire.

→ mol. formula is P_4, shape is tetrahedral, hybridisation is sp^3, bond angle is 60°.



6, P-P bond
4 lp

→ more soluble in organic solvent

→ bad conductor

(b) Red P :-

→ Non-Poisonous, less reactive, does not show Phosphorescence

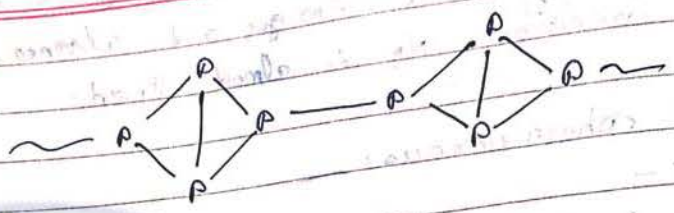
→ used in match making Industries

→ obtained by heating white P upto 240-250°C in absence of air.

→ Insoluble both in water and organic solvent.

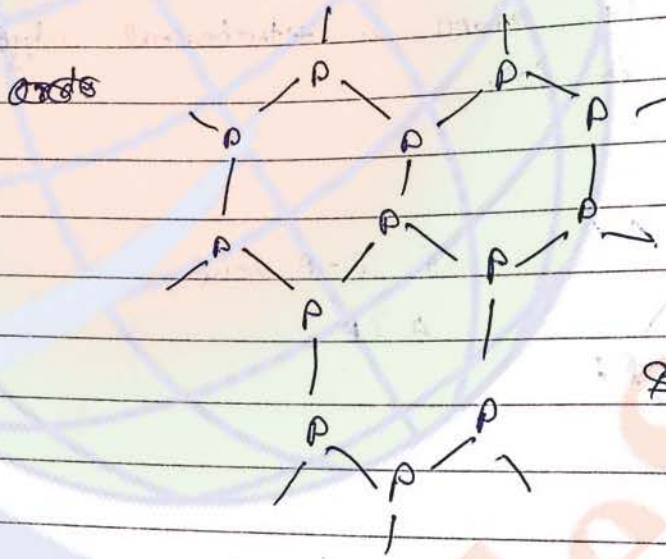
→ In its structure P_4 units are linked to form a linear chain (Polymer).

Note:- Allotropes means different elementary forms of an element.



(c) Black P:-

→ obtained by heating white under high pressure (highly polymeric)



Semiconductor.

Note:→ (i) order of stability:-

Black P > Red P > white P

(ii) order of reactivity:-

Black P < Red P < white P.

(1) There are two allotropes of oxygen:- O_2 and O_3

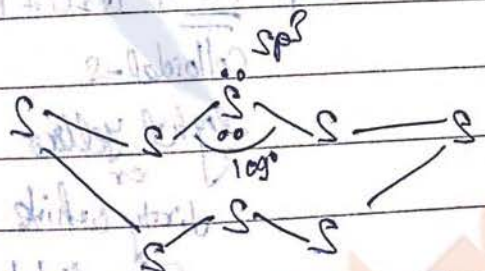
(2) O_2 is colourless, tasteless and odourless gas, paramagnetic, partially soluble in water, liquid O_2 has light blue colour

Gas	absorbent / absorbents
O_3	CCl_4 / turpentine oil / cinnamon oil
O_2	alk. pyrogallol
CO_2 / SO_2	KOH(aq) or any other strong base.
H_2O vap.	anh. $CaCl_2$ / silica gel.

*(3) Allotropes of S:-

(a) Rhombic S

→ crystaline (orthorombic)
→ most stable form.
→ mol. formula is S_8



W/ crown/ boat

→ more soluble in organic solvent
→ bad conductor
→ transparent yellow coloured solid
→

(Rhombic S)

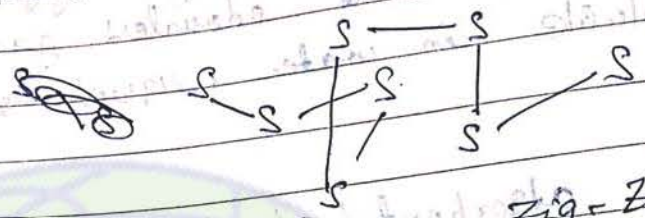
(b) monoclinic S

→ crystaline (monoclinic)
→ mol. formula is S_8.
→ ✓
→ ✓
→ ✓
→ ✓
→

monoclinic S

(c) Plastic S –

→ dark yellow in colour



Zig-Zag
(S)

→ Insoluble both in water and organic solvent.
→ Elastic, can be converted into flexible threads

(d) milk-S: –

white, can be converted into yellow upon heating

(e) Colloidal-S (S-sol): –

obtained by passing H_2S gas into any O.A.

$$KMnO_4 + H_2SO_4 + H_2S^{-2} \longrightarrow \overset{+2}{MnSO_4} + S^0 + H_2O + K_2SO_4$$

O.A — acidic — R.A

S → Colloidal-S
light yellow or dirty white (turbidity)

(1) Physical state and colour :-
$F_2(g)$: → light yellow
$Cl_2(g)$: → greenish yellow
$Br_2(l)$ → Reddish brown
$I_2(s)$ → violet (or Purple)

→ I_2 is violet solid (It emits violet vapour)
→ cause of colour - After absorbing light energy a particle
→ Colour some electrons exist from lower energy m.o to higher energy m.o
→ I_2 conducts electricity (due to large size)

eg :-
Iodine phosphate
$I^{+3}PO_4^{-3}$
IPO_4

Iodine acetate
$I^{+3}\ CH_3COO^-$

$I(CH_3COO)_3$

(2) order of Bond energy :-

$Cl_2 > Br_2 > F_2 > I_2$

(3) order of hydration energy :-

$F^- > Cl^- > Br^- > I^-$

↑
Exceptionally

<4> Order of oxidising power (or, reactivity) :-

$F_2 > Cl_2 > Br_2 > I_2$ (acc. to E.N.)

$\frac{1}{2}X_2(g) \xrightarrow{+\frac{1}{2}B.E} X(g) \xrightarrow[-E.A.]{+e^-} X^-(g) \xrightarrow[-H.E]{+H_2O} X^-(aq)$

Total required energy $= \underbrace{\frac{1}{2}B.E - E.A - H.E}_{\text{minimum}}$

Order of E.E.S.-

I_2

Br_2

Cl_2

F_2

<5> Order of reducing power :- (or reactivity of halides) :-

$F^- < Cl^- < Br^- < I^-$

$HF < HCl < HBr < HI$

$NF_3 < NCl_3 < NBr_3 < NI_3$

Note :-

$F^- \xrightarrow{(X)} F_2$

Not possible

F^- does not act as R.A hence, fluoride of any element is highly stable.

(b) I_2 turns starch paper blue while Br_2 turns starch paper yellow

(c) main source of I_2 (Rare halogen) :-

(a) Kelp (the ash obtained by burning sea weeds) Cl^-, I^-, and SO_4^{-2} of Na^+ and K^+)

(b) caliche / chile salt petre crude salt petre ($NaNO_3$ having $NaIO_3$)

(c) order of solubility in water :-

$F_2 > Cl_2 > Br_2 > I_2$ (acc^n to E.N)

soluble — partially soluble

→ I_2 is soluble in organic solvent (brown or violet colour solution)

Q) An unknown halide salt reacts with Cl_2 to produce a halogen. This halogen forms brown coloured sol^n with $CHCl_3$. Predict unknown halide.

Ans:- $\overset{0}{Cl_2} + \overset{-1}{X^-} \longrightarrow \overset{0}{X_2} + \overset{-1}{Cl^-}$

(Br^-/I^-) (Br_2/I_2)

I^- → Iodide

I_2

* HOCl → Cyanic acid
* The only possible Hydride of Nitrogen which is acidic is Hydrazoic acid (N_3H)

→ I_2 is soluble in KI or NaI.

$$I_2 + \underset{\text{or } NaI}{KI} \longrightarrow \underset{\text{or } NaI_3}{KI_3}$$

or

$$I_2 + I^- \longrightarrow I_3^-$$

↳ covalent and co-ordinate

1.a 1.b

→ To increase solubility of I_2 in water first add KI or NaI into water

(9) Pseudo halide Ion, (Certain anion)

(a) having single -ve charge
(b) made up of 2 or more Σ N atoms (non-metals) at least one of them must be N-atom

CN^- → Cyanide
OCN^- → Cyanate
SCN^- → thiocyanate
N_3^- → Azide

→ Their covalent dimers are called as Pseudo halogen

eg:-
$(CN)_2$, $(OCN)_2$ etc

L-1 → 1, 5, 6, 20, 32, 59, 63, 69, 72,
L-2 → 1 to 5, 9, 12 to 15, 17 to 22, 26 to 28, 29, 30, 31, 32 to 39, 41, 43 to 48,
L-3 → 1 to 5, 9, 12 to 15, 17 to 22, 26 to 28, 29, 30, 31, 32 to 39, 41, 43 to 48
L-4 → A → 1 to 4, 7, 8, 9, 10, 11, 12,
B → 4, 5, 6, 7, 8, 10, 11, 12, 14, 15, 17, 18, 19, 20, 21 to 23, 24, 29, 32, 34

classmate
Page 47

(10) Interhalogen compounds:-

mainly of 4-types:-

(a) AX (ClF)
(b) AX_3 (ClF_3)
(c) AX_5 (BrF_5)
(d) AX_7 (IF_7)

A → less E.N halogen
X → more E.N halogen.

→ Interhalogen compounds are more reactive than constituents halogen (except F_2) because A–X bond is polar while X–X bond is non-polar (ClF is more reactive than F_2 and Cl_2)

Noble gas:-

(i) colourless, tasteless, odourless and monoatomic gas
(ii) Except Rn, other noble gases occur in atmosphere.

(most abundant noble gas in air Ar)

(iii) Claude's Process:-
Industrially, except Rn, other noble gases are isolated by fractional distillation of liquid air.
major product is N_2.
major Product is Ar.

(iv) order of heat of vaporisation:-
(∝ Intermolecular bond)

He < Ne < Ar < Kr < Xe

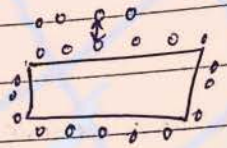
(v) Order of tendency of liquification.
(∝ Intermolecular bond).

He < Ne < Ar < Kr < Xe

(vi) order of extent of adsorption on coconut charcoal.

Extent of adsorption ∝ Intermolecular bond

He < Ne < Ar < Kr < Xe.



Chemical Properties:-

Group 18 (Noble gas)

(i) Due to stable s^2p^6 configuration very high I.E and almost zero E.A noble gas are almost inert.

→ Due to lower I.E and larger size Xe is most reactive noble gas.

→ Some Compounds of Kr are also present.
eg KrF_2.

→ Due to very high I.E, No real compound of He, Ne and Ar are present.

(2) The first real compound of noble gas was made in 1962 by Neil Bartlett

→ He previously used highly oxidising PtF_6 to oxidise O_2.

$$\underset{\text{O.A}}{PtF_6} + \underset{\text{R.A}}{O_2} \longrightarrow O_2^+[PtF_6]^-$$

→ Energy required to remove e^- from both O_2 and Xe is almost similar. Hence in above reaction O_2 can be replaced by Xe.

$$PtF_6 + Xe \longrightarrow Xe^+[PtF_6]^-$$

(3) Xe mainly forms fluorides (because F_2 is most reactive non-metal.)

$$Xe + F_2 \xrightarrow[673K,\ 1\,Bar]{Ni\ tube} XeF_2$$

(2:1)

$$Xe + 2F_2 \xrightarrow[673K,\ 7\,bar]{Ni\ tube} XeF_4$$

(1:5)

$$Xe + 3F_2 \xrightarrow[573K,\ 60\text{-}70\,bar]{Ni\ tube} XeF_6$$

(1:20)

Note-1

Xe fluorides are white crystalline solid. They act as fluorinating agent (can give F^- ion) Hence, can be have as O.A and lewis base.

Note :- Products at high temp also means in absence those products after some time of heating.

<4> Xe fluorides react with F^- ion acceptor like PF_5, AsF_5, SbF_5 etc

$XeF_2 + PF_5 \longrightarrow \underline{Xe}F^+ [PF_6]^-$

l.b l.a

$XeF_4 + SbF_5 \longrightarrow \underline{Xe}F_3^+ [SbF_6]^-$

l.b l.a

$XeF_6 + CsF \longrightarrow Cs^+ [XeF_7]^-$

l.a (Na^+, K^+ or Rb^+)

l.b

<5> Xe fluoride readily hydrolysed -

$2XeF_6 + 2H_2O \rightleftharpoons 2Xe + O_2 + 4HF$

$2XeF_6 + 4H_2O \rightarrow \underline{XeO_3} + Xe + \frac{1}{2}O_2 + 8HF$ (1:2)

$XeF_6 + 3H_2O \rightarrow \underline{XeO_3} + 6HF$

explosive

$XeF_6 + H_2O \xrightarrow{\text{Partial}} XeOF_4 + 2HF$ (2:1)

$XeF_4 + H_2O \xrightarrow{\text{Partial}} XeOF_2 + 2HF$ (0:1)

Note:- mixture of O_2 and He is used by deep-sea divers and it also used in treatment of asthama (He is lightest non-reactive gas)

acid (HX) :-
[HF, HCl, HBr, HI]

* Preparation :-

(I) By direct elemental combination :-

$H_2 + F_2 \longrightarrow 2HF$

$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$

$H_2 + Br_2 \xrightarrow{\Delta} 2HBr$

~~$H_2 + I_2$~~

$H_2 + I_2 \underset{400-500^\circ C}{\overset{Pt}{\rightleftharpoons}} 2HI$ //

(II) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$
(H_2F_2)

(III) Less volatile acid displaces more volatile acid from its salt.

$2NaCl + H_2SO_4(aq) \longrightarrow Na_2SO_4 + 2HCl$
or
$(HO)_2SO_2$
less volatile
more volatile
$\longrightarrow (HF, HNO_3)$

$\Rightarrow$ HBr and HI can not be prepared by using conc because they are very good reducing agent. They further react with conc H_2SO_4.

$2NaI + H_2SO_4(Conc) \longrightarrow Na_2SO_4 + 2HI$

$2HI + H_2SO_4 (conc) \longrightarrow I_2^0 + SO_2 + 2H_2O$

R.A O.A

$2KBr + H_2SO_4$ (conc) $\longrightarrow K_2SO_4 + \ldots$

$2HBr - \overset{+6}{H_2SO_4}$ (conc) $\longrightarrow \overset{0}{Br_2} + \overset{+4}{SO_2} + 2H_2O$

R.A O.A

Order of oxidising power :-

$\overset{+5}{HNO_3} > \overset{+6}{H_2SO_4} > \overset{+5}{H_3PO_4}$

very good O.A Poor O.A very poor O.A (Not act as O.A)

→ HBr and HI can be prepared by using H_3PO_4 because it is less volatile as well as very poor O.

$3NaI + H_3PO_4$ (or $(HO)_3PO$) $\longrightarrow Na_3PO_4 + 3HI$

less volatile more volatile (HF, HCl & HBr)

Properties (Not for HF) :-

1) Reaction as acid :-

$Na_2O + 2HBr \longrightarrow 2NaBr + H_2O$

$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2\uparrow$

(S.B + W.A) H_2CO_3

2) Rex" with NH_3 :-

$NH_3 + HX \longrightarrow NH_4X$

(ammonium halide)

(White fumes)

(3) Reactions as R.A :—

$K\overset{+7}{Mn}O_4 + HCl^{-1} \longrightarrow \overset{+2}{Mn}Cl_2 + Cl_2^0 + H_2O + KCl$

O.A acid / R.A

$K_2\overset{+6}{Cr}_2O_7 + HI^{-1} \longrightarrow \overset{+3}{Cr}I_3 + I_2^0 + H_2O + KI$

O.A acid / R.A

(4) Reactions with halogens :—

$F_2^0 + 2HX^{-1} \longrightarrow X_2^0 + 2HF^{-1}$

(HCl / HBr / HI)

$Cl_2^0 + 2HX^{-1} \longrightarrow X_2^0 + 2HCl^{-1}$

(HBr / HI)

$Br_2 + 2HI^{-1} \longrightarrow I_2^0 + 2HBr^{-1}$

* Properties of halogens :— (F_2, Cl_2, Br_2, I_2) :—

Oxidising Properties :—

(a) F_2 :—

$(F_2 \longrightarrow F^-)$

~~$5F_2^0 + 5H_2O^{-2} \longrightarrow$~~

only chemical rex" to form Ozone.

$5F_2^0 + 5H_2O^{-2} \longrightarrow 10HF^{-1} + O_2^0 \uparrow + O_3^0 \uparrow$

O.A R.A

Note: D_2 can behave both O.A and R.A

(6) Cl_2/Br_2 :-

Aq^n sol^n of Cl_2 is called as "Cl_2 water"

$Cl_2 + H_2O \longrightarrow \overset{-1}{HCl} + \overset{+1}{HOCl}$ (disproportionation rexn)

$\overset{\delta+}{Cl}-\overset{\delta-}{Cl}$

$HOCl \xrightarrow{h\nu} HCl + [O]$

If R.A is present then [O] will attack with it

If R.A is not present then Product will be O_2.

Due to presence of nescent oxygen Cl_2 water acts as very good oxidising agent.

→ $Cl_2 + H_2O \longrightarrow 2HCl + \frac{1}{2}O_2$

→ Cl_2 water act's as bleaching agent:-

In its bleaching action oxidation of objects takes place

→ Any Cl_2 who acts as oxidising agent (Poor O.A than Cl_2 water)

$\underset{[O]}{\underset{\text{moist}}{Cl_2 + H_2O}} + R.A \longrightarrow HCl$

$Cl_2 + R.A \longrightarrow$

Order of oxidising Power:-

$F_2 > Cl_2$ water $> Br_2$ water $> Cl_2 > Br_2 > I_2$

Best O.A — very good O.A — good

$Cl_2 + H_2\overset{-1}{S} \longrightarrow 2HCl + \overset{0}{S}$

$Cl_2 + 2KBr^{-1} \longrightarrow 2KCl + \overset{0}{Br_2}$

$Cl_2 + \overset{+2}{Fe}Cl_2 \longrightarrow \overset{+3}{Fe}Cl_3$

$Cl_2 + \overset{+2}{Sn}Cl_2 \longrightarrow \overset{+4}{Sn}Cl_4$

O.A R.A

$Cl_2 + H_2O + \overset{+4}{S}O_2 \longrightarrow HCl + H_2\overset{+6}{S}O_4$

O.A R.A

$[O]$

$SO_3 + H_2O \longrightarrow H_2SO_4$

$\rightarrow S_2O_3^{-2}$ (thiosulphate) $\rightarrow SO_4^{-2} + S$ on R.A with Cl_2/Br_2 water

$[O]$

$\overset{-2}{S}$

$\overset{+2}{S}$ $\overset{+1}{S}$ $\overset{+2}{S}$

$\overset{0}{S}$

$H_2S_2O_3 + Cl_2 + H_2O \longrightarrow HCl + S + H_2SO_4$

$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow \underset{HCl}{NaCl} + S + Na_2SO_4$

R.A O.A

(c) I_2 (very poor O.A) :—

$$\overset{0}{I_2} + 2Na_2\overset{+2}{S_2}O_3 \longrightarrow \overset{+2.5}{Na_2S_4O_6} + 2NaI$$

O.A R.A

(2) Addition reaction (only with Cl_2) :—

$$\overset{+4}{SO_2}\,(dry) + Cl_2 \longrightarrow \overset{+6}{SO_2Cl_2}$$

R.A (O.A)

or $Cl-\overset{O}{\overset{\|}{\underset{\|}{S}}}(=O)-Cl$ (sulphonyl chloride)

→ SO_2Br_2 and SO_2I_2 are unstable.

$$\left[\overset{+4}{SO_2} + F_2 \longrightarrow \overset{+6}{SO_2F_2} \longrightarrow \overset{+6}{SF_6}\right]$$

$$\overset{+2}{CO} + Cl_2 \longrightarrow \overset{+4}{COCl_2}$$

R.A O.A

or $Cl-\overset{O}{\overset{\|}{C}}-Cl$ (carbonyl chloride) (phosgene)

$$[CO + F_2 \longrightarrow CF_4]$$

(3) Reaction with NH_3 :—

(a) Cl_2 / Br_2 :—

$$\overset{-3}{NH_3} + Cl_2 \longrightarrow \overset{0}{N_2} + HCl/NH_4Cl$$

R.A O.A

$$NH_3(excess) + Cl_2 \longrightarrow N_2 + NH_4Cl$$

$NH_3 + Cl_2$ (excess) $\longrightarrow NCl_3 + HCl$

[$Cl_2 + N_2 \longrightarrow NCl_3$]

(b) F_2 :-

$NH_3 + F_2 \longrightarrow NF_3 + HF$

R.A O.A

(c) I_2 :-

$2NH_3 + 3I_2 \longrightarrow \underbrace{NH_3 \cdot NI_3}_{\text{Black-brown}} \downarrow + 3HI$

$NH_3 \cdot NI_3 \xrightarrow{\Delta} N_2 + I_2 + NH_4I$

[NH_3I_2, I_2I_2, $N_2H_3I_3$ or $NH_3 \cdot NI_3$]

(4) Reaction with alkali (base) :-

[Cl_2, Br_2, I_2]

Rule :→ Non-metal disproportionate in basic medium (except F_2).

$X_2 + OH^-$ (cold/dil) $\longrightarrow X^- + XO^- + H_2O$

(Instantaneous) halide hypohalite

$X_2 + OH^-$ (hot/conc) $\longrightarrow X^- + XO_3^- + H_2O$

(after some time) halate

$I_2 + NaOH$ (dil.) $\longrightarrow NaI + NaOI + H_2O$

$Br_2 + KOH$ (aq.) $\longrightarrow KBr + KBrO_3 + H_2O$

eg.) $Ca(OH)_2 + Cl_2 \longrightarrow CaCl_2 + Ca(OCl)_2 + H_2O$

lime water
(dil. medium)

or

Ca^{+2} Cl^- OCl^-

$CaOCl_2$ (Bleaching powder)

⇒ Formula of bleaching powder -

(a) $CaOCl_2$
(Cal. chloride hypochlorite)

(b) $Ca(OH)_2 + CaCl_2 + Ca(OCl)_2$

Basic mixture of cal. chloride and cal. hypochlorite

⇒ upon standing bleaching powder becomes,

$CaCl_2 + Ca(ClO_3)_2$

⇒ Bleaching powder is a mixed salt

$Ca(OH)_2$

⇒ Due to Presence of OCl^- ion, bleaching power acts as very Powerful O.A.

Group-16 (oxygen-family)

1) oxygen (O_2)

preparation:-

1) claude's Process:

↳ fractional distillation of liquid air

2) By heating various oxysalt's:-

Rule:- If anion of an oxysalt is good O.A then upon heating that salt will liberate O_2 gas.

$$KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2 \uparrow$$

$$K_2Cr_2O_7 \xrightarrow{\Delta} K_2CrO_4 + Cr_2O_3 + O_2 \uparrow$$

1) Halogens: →

$KClO_3 \xrightarrow{MnO_2, \Delta} KCl^{-1} + \frac{3}{2}O_2 \uparrow$ (lab preparation)

$CaOCl_2 \xrightarrow{\Delta} CaCl_2 + \frac{1}{2}O_2 \uparrow$

2) N-family →

$MNO_3 \xrightarrow{\Delta} MO + NO_2 \uparrow + O_2 \uparrow$

(metallic nitrates)

(except nitrates of Na^+, K^+, Rb^+ and Cs^{-1})

$NaNO_3 \xrightarrow{\Delta} NaNO_2 + \frac{1}{2}O_2 \uparrow$

(K^+, Rb^+ and Cs^+)

* metallic oxides:-

→ By heating metallic oxides:-

(a) As we move from top to bottom in E.C.S, thermal stability of metallic oxide ↓, Hence change of O_2 release upon heating ↑,

(b) s-block oxides are thermally most stable

(c) s-block peroxides superoxides can give O_2 gas upon heating

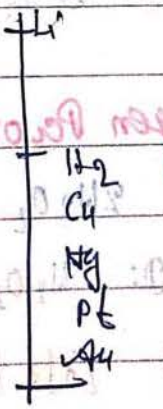
$2HgO \xrightarrow{\Delta} 2Hg + O_2 \uparrow$

$2Ag_2O \xrightarrow{\Delta} 4Ag + O_2 \uparrow$

$MgO \xrightarrow{\Delta} X$

$Ag_2CO_3 \xrightarrow{\Delta} Ag_2O + CO_2 \uparrow$

$Ag_2O \xrightarrow{\Delta} 2Ag + \frac{1}{2}O_2 \uparrow$



$BaO_2^{-1} \xrightarrow{\Delta} BaO^{-2} +$

D. Properties →

Combustion (heating in excess of O_2)

of elements —

$Na + O_2 \xrightarrow{\Delta} Na_2O$ (basic) $\xrightarrow{H_2O}$ NaOH ✓ (PN > 7)

Na metal

$S + O_2 \xrightarrow{\Delta} SO_2$ (acidic) $\xrightarrow{H_2O}$ H_2SO_4 ✓ (PN < 7)

Non-metal

(1) ~~Combustion~~ of Combustion :

(2) of compounds :

$C_2H_6 + O_2 \xrightarrow{\Delta} CO_2 + H_2O$

$H_2S + O_2 \xrightarrow{\Delta} H_2O + SO_2$

★ Ozone →

Ozone layer present in atmosphere does not allow UV rays to come on earth surface.

$O_2 \xrightarrow[U.V]{h\nu} [O] + [O]$

$O_2 + [O] \longrightarrow O_3$

⇒ Green house gases (NO_2, CFC etc) slow down rate of formation of O_3. It is the main cause of depletion of O_3 layer.

★ Hydrogen Peroxide (H_2O_2) :→

$2H_2O_2 \longrightarrow 2H_2O + O_2$

D: $H_2O_2^{-1} \xrightarrow{r.d.s} H_2O + [O]$

D: $[O] + [O] \longrightarrow O_2$

oxidising agent and also reducing agent.

H_2O_2 (-1) → as R.A → O_2^0

H_2O_2 → as O.A → $H_2O + [O]$

$KMnO_4 + H_2SO_4 + H_2O_2 \rightarrow MnSO_4 + O_2 + H_2O + K_2SO_4$

$Cl_2 + \underset{R.A}{H_2O_2} \longrightarrow 2HCl + O_2$

$O_3 + \underset{R.A}{H_2O_2} \longrightarrow 2O_2 + H_2O$

$\overset{-2}{H_2S} + \underset{O.A}{H_2O_2} \longrightarrow 2H_2O + S^0$

$2K\overset{-1}{I} + \underset{O.A}{H_2O_2} \longrightarrow 2KOH + I_2^0$

(3) O_3 is used in refreshing old lead painting / oil-painting.

→ This work can be done by any O.A which can produce [O].

$\overset{-2}{PbS} + \underset{(O.A)}{O_3} \longrightarrow O_2 + \underset{\text{white}}{PbSO_4}$

$PbO + S^0$

$\downarrow [O]$

SO_2

$PbS^{-2} + \underset{O.A}{H_2O_2} \longrightarrow H_2O + PbSO_4$

[H_2O_2 also]

(A-) Test of O_3 (Tailing of Hg) :-

$2Hg + O_3 \xrightarrow{(O.A)} O_2 + Hg_2O$

(A-) Test of H_2O_2 :-

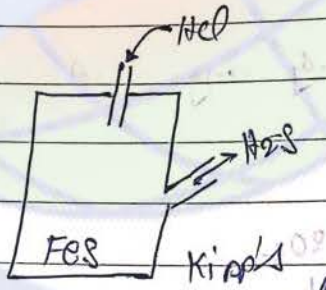
$Cr_2O_7^{-2} + H^+ + H_2O_2 \longrightarrow$
orange red

$CrO_5 + H_2O$
or
$CrO(O_2)_2$
deep blue

Hydrogen sulphide (H_2S) :-
lab Preparation :-

$Na_2S + 2HCl_{(dil)} \longrightarrow 2NaCl + H_2S \uparrow$

metallic sulphide
(S.B + W.A)



Properties :-

1) H_2S is colourless, poisonous gas (highly reactive), having smell of rotten eggs.

Test :-

H_2S turns lead acetate paper black

sulphur dioxide (SO_2) :-
lab Preparation :-

$Na_2SO_3 + 2HCl_{(dil)} \xrightarrow{\Delta} 2NaCl + H_2O + SO_2 \uparrow$

metallic sulphite
(S.B + W.A)

Properties

1) SO_2 is colourless, poisonous gas having suffocating or irritating odour.

Test

SO_2 turns lime water milky & excess of it milkiness disappears

$H_2S + Pb(CH_3COO)_2 \rightarrow PbS\downarrow + 2CH_3COOH$
black

Differences of CO_2 and SO_2 :-

(a) CO_2 is odourless while SO_2 has suffocating odour.

(b) CO_2 can not react with O.A while SO_2 can.

(c) H_2S acts as good R.A
$H_2S^{-2} \rightarrow S^0$

$K_2Cr_2O_7 + H_2SO_4 + H_2S \rightarrow Cr_2(SO_4)_3$

$Cl_2 + H_2S \rightarrow 2HCl + S$

$O_3 + H_2S \rightarrow O_2 + H_2O + S$

$H_2O_2 + H_2S \rightarrow 2H_2O + S$

$Ca(OH)_2 + SO_2 \rightarrow CaSO_3\downarrow + H_2O$
white

$CaSO_3 + H_2O + SO_2 \rightarrow Ca(HSO_3)_2$
soluble.

(c) SO_2 is good R.A but Poor O.A

SO_2 acts as bleaching agent. in its bleaching action reduction of O.C takes place.

SO_2 as O.A $\rightarrow S^0$

SO_2 as R.A $\rightarrow SO_3^{+6}$ / $H_2SO_4^{+6}$ with H_2O / SO_4^{-2} salt (with metal cation)

$2H_2S^{-2} + SO_2^{+4} \rightarrow 3S^0 + 2H_2O$
R.A O.A

$Cl_2 + H_2O + SO_2 \rightarrow HCl + H_2SO_4$
R.A

$O_3 + SO_2 + H_2O \rightarrow O_2 + H_2SO_4$
R.A

$KMnO_4 + H_2SO_4 + SO_2^{+4} \rightarrow MnSO_4^{+2} + H_2O + K_2SO_4$
R.A

$K_2Cr_2O_7 + H_2SO_4 + SO_2 \rightarrow Cr_2(SO_4)_3 + H_2O + K_2SO$
R.A

Sulphuric acid (H_2SO_4) :-

↳ [oil of vitriol / king of chemicals]

Preparation :-

(1) $\overset{+6}{SO_3} + H_2O \longrightarrow \overset{+6}{H_2SO_4}$ + heat ; $\Delta H = -ve$
(highly exothermic)

↳ (unsafe)

(2) Contact process :-

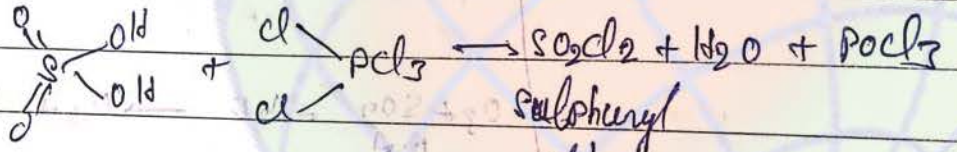
$SO_2(g) + \frac{1}{2} O_2(g) \xrightarrow{Pt/V_2O_5} SO_3(g)$

$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$ (oleum)
(fuming H_2SO_4)

$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$

Properties :-

1) Reaction with PCl_5 :-
PCl_5 is used to detect no. of $-OH$ groups in an unknown compounds.



(2) (a) H_2SO_4 has affinity towards water, hence, acts as dehydra
ag

(b) Skin becomes dry due to H_2SO_4.

(c) mainly dehydrates carbohydrates

dehydration of carbohydrate is called charring.

$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$

Cane sugar (Sucrose) — Black

(3) Conc. H_2SO_4 oxidises some metals and non-metals.

(a) with non-metals :-

H_2SO_4 (Conc) + P_4^0 ⟶ $H_3\overset{+5}{P}O_4$ + SO_2 + H_2O (P_4O_{10})

H_2SO_4 (Conc) + C^0 ⟶ $\overset{+4}{CO_2}$ + $\overset{+4}{SO_2}$ + H_2O

O.A — R.A

(b) with metal above H in ECS :-

$\overset{0}{Mg}$ + $\overset{+1}{H_2}\overset{+6}{S}O_4$ (Conc) ⟶ $\overset{+2}{Mg}SO_4$ + $H_2\uparrow$ ($\overset{+4}{SO_2}\uparrow$)

R.A — O.A

(c) with metals below H in E.C.S :-

$\overset{0}{Cu}$ + $\overset{+1}{H_2}\overset{+6}{S}O_4$ (Conc) ⟶ $\overset{+2}{Cu}SO_4$ + $\overset{+4}{SO_2}\uparrow$ + H_2O

(Ag, Pb) — O.A

R.A

(A) Nitrogen family :-

1) Nitrogen (N_2) :-

Preparation :-

1) Claude's Process :- fractional distillation of liquid air.

2) By heating metallic azides (N_3^-) :- (Pure N_2)

$Ba(N_3)_2 \xrightarrow{\Delta} 3N_2 \uparrow + Ba$

$NaN_3 \xrightarrow{\Delta} \frac{3}{2} N_2 \uparrow + Na$

3) By heating ammonium dichromate or ammonium nitrite.

Rule :- ammonium salts releases NH_3 gas upon heat

$(NH_4)_2 Cr_2O_7 \xrightarrow{\Delta} \overset{0}{N_2} \uparrow + \overset{+3}{Cr_2O_3} \downarrow + N_2O$

colourless green

$\left(\overset{-3}{N}H_3 + \overset{+6}{Cr_2}O_7^{-2} \right)$

RA OA

$NaNO_2 + NH_4Cl \longrightarrow NaCl + \underbrace{NH_4NO_2}_{\text{ammo. nitrite}}$

Sod. nitrite (W.R + S.A) (S.R + W.A)

$NH_4NO_2 \xrightarrow{\Delta} \overset{0}{N_2} \uparrow + 2H_2O$

$\left(\overset{-3}{N}H_3 + \overset{+3}{N}O_2^- \right)$

RA OA

$NH_4NO_3 \xrightarrow{\Delta} N_2O \uparrow + 2H_2O$
ammo. nitrate

Properties:-

1) Birkelands - Eyke Process -

$N_2 + O_2 \xrightarrow[3500°C]{\text{electric arc}} 2NO$

2) Haber's Process:-

$N_2(g) + 3H_2(g) \underset{400-500°C,\ 200atm}{\overset{Fe + MO}{\rightleftharpoons}} 2NH_3(g) + \text{heat}$; $\Delta H = -ve$ (exothermic)

(catalyst: Fe + MO; Promoter)

→ Production of NH_3 can be increased by lowering temp. and increasing pressure.

3) formation of nitride (N^{-3}):-

with s-block (except Na, K, Rb, and Cs) B, Al, etc.

$3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$

$Al + \frac{1}{2}N_2 \xrightleftharpoons{\Delta} AlN$

$\overset{+2}{Mg_3}\overset{-3}{N_2} + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3 \uparrow$

$\overset{+3}{Al}N^{-3} + 3H_2O \longrightarrow Al(OH)_3 + NH_3 \uparrow$

Lab Preparation of NH_3 :-

$2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2NH_3 \uparrow + 2H_2O$

↓ any ammonium salt (acid) ; ↓ base

→ NH_3 obtained by this process is dried by anhydrous CaO (or any other basic dehydrating agent)

Note:- To dehydrate :-

Acidic substance → acidic dehydrating agent
eg :- P_4O_{10}, H_3PO_4, H_2SO_4 etc.

Basic substance :- → Basic dehydrating agent
eg :- CaO, or any other s-block oxides

Test of NH_3 :-

$K_2HgI_4 + KOH \text{ or } NH_4^+ \longrightarrow NH_2 + HgO + HgI_2\downarrow + KI + H_2O$

Nessler's reagent — reddish brown ppt (Iodide of mild ions base)

Properties of HNO_3 :-

(1) Upon standing it, top layers become yellow ~~colour~~ due to release of NO_2 gas.

$$\overset{+1+5-2}{HNO_3} \xrightarrow{h\nu} \overset{+4}{NO_2} \uparrow + \overset{0}{O_2} \uparrow + H_2O$$

(reddish yellow)

(2) Skin becomes dry (corrosive) due to HNO_3 because it reacts with protein of skin to form ~~xantho~~ xanthoprotein and cause yellowness (oxidising property).

(3) HNO_3 oxidising almost all metals. (except noble metals like Au, Pt etc.)

Conc $\overset{+5}{HNO_3} \longrightarrow \overset{+4}{NO_2}$

dil $\overset{+5}{HNO_3} \longrightarrow \overset{+2}{NO}$

$$\overset{0}{Cu} + \overset{+5}{HNO_3}(conc) \longrightarrow Cu(NO_3)_2 + \overset{+4}{NO_2} + H_2O$$

R.A O.A

→ Conc. HNO_3 is better O.A than dil HNO_3.

~~Zn, which is better O.A than dil HNO_3.~~

Zn, which is better R.A than Cu, forms ammonium nitrate (NH_4NO_3) with dil. HNO_3 (No change in Product with conc HNO_3).

$Zn^{0} + HN^{+5}O_3$ (conc) $\longrightarrow Zn^{+2}(NO_3)_2 + NO_2 + H_2O$

$Zn^{0} + HN^{+5}O_3$ (dil) $\longrightarrow Zn(NO_3)_2 + N^{-3}H_4NO_3 + H_2O$

R.A O.A

$N^{-3}H_4NO_3 \xrightarrow{\Delta} N_2O\uparrow + 2H_2O$

(5) with non-metals

$HN^{+5}O_3$ (conc) $+ S^{0} \longrightarrow H_2S^{+6}O_4 + NO_2 + H_2O$

HNO_3 (conc) $+ S \longrightarrow H_2SO_4 + NO_2 + H_2O$

O.A R.A

(6) Noble metals Au, Pt etc. react with aqua-regia

$3HCl + HNO_3 \longrightarrow NaCl + 2H_2O + 2[Cl]$

aqua-regia

because of high reactivity.

$Au^{0} \xrightarrow{[Cl]} AuCl_3 \longrightarrow HAuCl_4$

$Pt \xrightarrow{4[Cl]} PtCl_4 \longrightarrow H_2PtCl_6$

	C.N
Au^{+3}	4
Pt^{+4}	6

P_4O_6 and P_4O_{10} →

Preparation:-

$P_4 + 3O_2$ (limited) $\xrightarrow{\Delta}$ P_4O_6 (slow reaction)

$P_4 + 5O_2 \xrightarrow{\Delta} P_4O_{10}$

(rapid rate)

Properties -

(1) $P_4O_6 + H_2O \longrightarrow H_3PO_4$

$P_4O_6 + H_2O$ (hot) $\longrightarrow H_3PO_4 + PH_3$

$[H_3PO_3 \xrightarrow{\Delta} H_3PO_4 + PH_3]$

$P_4O_{10} + H_2O \longrightarrow H_3PO_4$ / $H_4P_2O_7$ / HPO_3

ortho pyro meta

(2) P_4O_{10} acts as acidic dehydrating agent

$H_2SO_4 + P_4O_{10} \xrightarrow{\Delta} SO_3 + H_3PO_4$ / - -

$(SO_3 + H_2O)$

$HNO_3 + P_4O_{10} \xrightarrow{\Delta} N_2O_5 + H_3PO_4$ / - -

$(N_2O_5 + H_2O)$

Phosphine (PH_3) :-

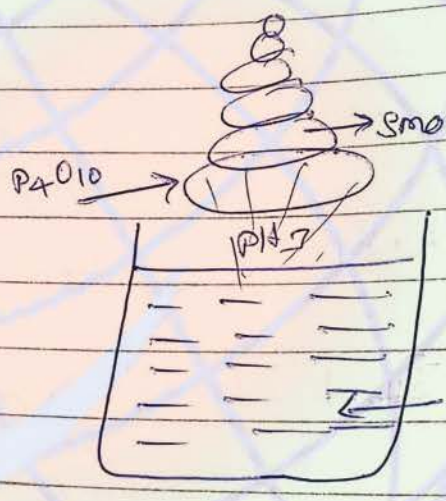
1) $H_3\overset{+3}{P}O_3 \xrightarrow{\Delta} H_3\overset{+5}{P}O_4 + \overset{-3}{P}H_3$

2) $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

3) $\overset{0}{P_4} + NaOH + H_2O \longrightarrow PH_3 + \underbrace{NaH_2\overset{+1}{P}O_2}_{\text{sod. hypophosphite}}$

P_4 — white (Not red)

Caustic soda



→ smoke ring / vortex ring.

(due to impurity P_2H_2, phosphine)

$P_4 + NaOH + H_2O$

Holme's signal → $CaC_2 + Ca_3P_2$

$Ca(OH)_2 + C_2H_2$

$Ca(OH)_2 + PH_3$ (P_2H_4)

Notes:→ Coke = Relatively pure form of coal.

Group 14 (C family) →

1) CO and CO_2 :—

Preparation —

(1) By combustion of C :—

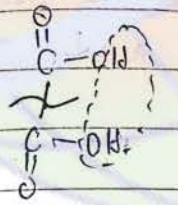
$$C + \frac{1}{2}O_2 \xrightarrow{\text{Incomplete}} \underset{+2}{CO}$$

$$C + O_2 \xrightarrow[\text{(excess)}]{\text{Complete}} \underset{+4}{CO_2}$$

Notes- (i) CO is poisonous gas it forms carbonylcomplex with Fe^{+2} of hemoglobin present in blood.

(ii) Carbogene (95% of O_2 + 5% CO_2) used as antidote of CO.

2)



$$\xrightarrow{H_2SO_4} CO\uparrow + CO_2\uparrow$$

oxalic acid ($H_2C_2O_4$)

3) By heating metallic carbonates and bicarbonates :—

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$$

(except carbonate of Na^+, K^+, Rb^+ and Cs^+)

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2\uparrow$$

(all)

Note:→ Only bicarbonate of Na^+, K^+, Rb^+ and Cs^+ exist in solid state.

* Von-Arkel method is used for Zn, Ti and Boron(B)

(4) By Passing steam on red hot coke:-

$$\underset{\text{(red-hot coke)}}{\overset{0}{C}} + \underset{\text{steam}}{\overset{+1}{H_2O}} \longrightarrow \underset{\text{(water gas/syn gas)}}{\overset{+2}{CO} + \overset{0}{H_2}}$$

(5) By Passing air on red hot coke:-

$$\underset{\text{red-hot coke}}{2C} + \underbrace{4N_2 + O_2}_{\text{air}} \longrightarrow \underbrace{4N_2 + 2CO}_{\text{Producer gas}}$$

Properties -

(1) CO_2 stops burning candle

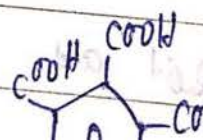
(2) Solid CO_2 is called as dry ice because it directly converts from solid state to gaseous state.

(3) Addition rxn of CO:-

$$CO + Cl_2 \longrightarrow COCl_2$$

$$CO + NaOH \xrightarrow[\text{high Pressure}]{160^\circ C} \underset{\text{(sodium formate)}}{HCOONa} \xrightarrow{H^+} \underset{\text{(formic acid)}}{HCOOH}$$

Note: Graphite forms $C_6(COOH)_6$ with O.A like Conc HNO_3



Group-13 (Boron family):-

Boron(B):-

Preparation:-

Amorphous-B

Borax $\xrightarrow{NaSO_4}$ H_3BO_3 $\xrightarrow[-H_2O]{\Delta}$ $\xrightarrow{+3}$ B_2O_3 $\xrightarrow[(R.A)]{Mg \text{ or } Zn}$ $2\overset{\circ}{B} + 3MgO$ or $3ZnO$ (black powder)

Crystalline-B

(a) Pyrolysis of BI_3 (van-Arkel method):-

$2BI_3 \xrightarrow[W \text{ or } Ta \text{ filament}]{1000^\circ C} 2B + 3I_2 \uparrow$

(b) $B_2H_6 \xrightarrow{\Delta} 2B + 3H_2 \uparrow$

Properties:-

(1) Upon heating with C, it forms an extremly hard solid called boron carbide (B_4C)

*order of hardness:-

Diamond > B_4C > SiC

Norbide, Carborundum

(II) Heating in air:-

$2B + \frac{3}{2}O_2 \xrightarrow{\Delta} B_2O_3$

$2B + N_2 \xrightarrow{\Delta} 2BN$ (Boron nitride)

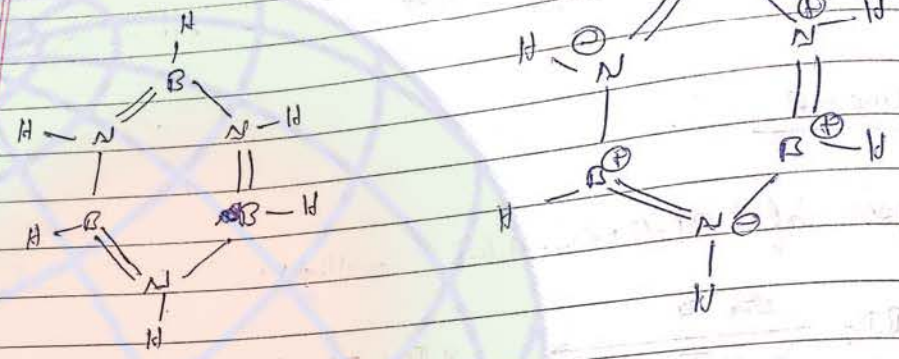
BN → c BN (Harder than diamond, Borazone)

BN → h BN (has similar structure like graphite, Inorganic graphite)

(i.e. c ⇒ Cubic, h → Hexagonal)

$$[2B + 2NH_3 \xrightarrow{\Delta} 2BN + 3H_2\uparrow]$$

Borazine / Borazole / Inorganic benzene, ($B_3N_3H_6$)



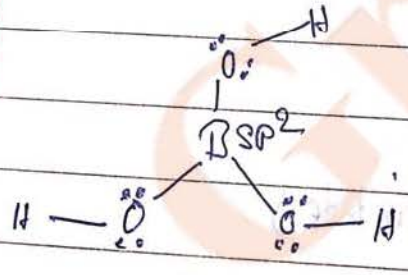
colourless liquid, highly reactive, explode in light (organic benzene is more stable than inorganic benzene)

$$3B_2H_6 + 6NH_3 \xrightarrow{\Delta} 2B_3N_3H_6 + 12H_2\uparrow$$

$$B_2H_6 + NH_3(excess) \xrightarrow{\Delta} BN + H_2$$

★ Boric acid / ortho boric acid :-

H_3BO_3 and $B(OH)_3$



↳ white crystaline solid, soluble in water, used as antiseptic for eyes.

* meta Boric acid (HBO_2 or NBO_2 n-times)

(2) weak mono-basic acid, acts as lewis acid, not as prote or protonic acid.

Prote / Protonic

Prote / Protonic acid :- Acids which can give H^+ from its own formula.

H_3BO_3 or $B(OH)_3$ + H_2O ⇌ $[B(OH)_4]^- + H^+$

lewis acid or arrhenius acid — l.b — mono basic

(3) Test of H_3BO_3 :-

H_3BO_3 or $B(OH)_3$ + C_2H_5OH ⟶ $B(OC_2H_5)_3 + 3H_2O$

Ethyl borate (ester) burns with green flame

lewis acid → $4H_3BO_3$ —Δ, $-4H_2O$→ $4HBO_2$ —Δ, $-H_2O$→ $H_2B_4O_7$ —Δ, $-H_2O$→ $2B_2O_3$ Basic anhydride

arrhenius acid → $4HBO_2$ meta basic acid. → $H_2B_4O_7$ Tetra basic acid

(4) l.b

BO_2^- → meta borate

$NaBO_2$ → sod. meta borate

$B_4O_7^{-2}$ → tetra borate

$Na_2B_4O_7$ → Sod. tetra borate

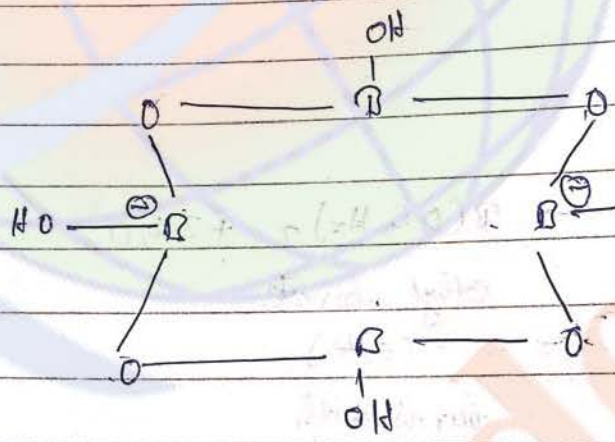
5) $NaOH + H_3BO_3 \rightleftharpoons Na[B(OH)_4] + NaBO_2 + H_2O$

l.b or con. base — l.a or an acid

→ This reaction can be shifted in forward direction by adding cis-1,2-diol.

* Borax or Tincal, $Na_2B_4O_7 \cdot 10H_2O$ or $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ ✓

$B_4O_5(OH)_4^{-2}$



(1) Aqueous solution of Borax behave as buffer and it is basic in nature.

$Na_2B_4O_7 + 7H_2O \longrightarrow \underset{\text{S.A}}{2NaOH} + \underset{\text{W.A}}{4H_3BO_3} / N_2B_4O_7 / HBO_2$

(2) $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$ —

(3) $Na_2B_4O_7 + 2NaOH \longrightarrow 4NaBO_2 + H_2O$

* 2nd Period elements ... Cannot form's alums because they are very small in size and they can form max. 4 bonds //

→ Borax bead test :-

This test is performed to detect some coloured ions like Cr^{+3}, Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2} etc.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\text{strongly heat}} 2NaBO_2 + B_2O_3 + 10H_2O$$

transparent mass (Borax bead)

$$M^{+n} + B_2O_3 \longrightarrow M^{+n}(BO_2)_n$$

metal → metaborate (Colour)

$$Cr^{+3} + B_2O_3 \longrightarrow Cr(BO_2)_3 \text{ green}$$

$$Mn^{+2} + B_2O_3 \longrightarrow Mn(BO_2)_2 \text{ brown}$$

$$Co^{+2} + B_2O_3 \longrightarrow Co(BO_2)_2 \text{ blue}$$

Aluminium chloride, $AlCl_3 \cdot 6H_2O$ or $[Al(H_2O)_6]Cl_3$ } upon heating,

(1) $AlCl_3$ forms in moisture

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl\uparrow$$

(2) Unlike other hydrated salt it does not convert into anhydrous salt upon heating.

$$AlCl_3 \cdot 6H_2O \xrightarrow{\Delta} Al(OH)_3 + HCl\uparrow$$

$$Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + H_2O$$

* Alumina, Al_2O_3 →
  ↳ Amphoteric

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_3 + NaOH \longrightarrow NaAlO_2$$

or $Al(OH)_3$ or Al

Sod. meta aluminate (Soluble)

Q.] Al utensils are not washed by Caustic soda or washing soda (Na_2CO_3). why?

Ans forms soluble meta aluminate.

Alkali metal
(Li, Na, K, Rb, Cs)

1) Flame test
Li → crimson red
*Na → Golden yellow
K → light violet
Rb → violet
Cs → dark violet

2) Reaction with Hydrogen:→

$$M + H_2 \xrightarrow{\Delta} \frac{1}{2} \overset{+1}{M}\overset{-1}{H}$$

$$\overset{+1}{Na}\overset{-1}{H} + H_2O \longrightarrow NaOH + H_2\uparrow$$

3) Reaction with water:-

$$\overset{0}{M} + \overset{+1}{N_2}O \longrightarrow \overset{+1}{M}OH + \frac{1}{2}\overset{0}{H_2}\uparrow$$

Note:-
Na and K are kept in kerosine, Li is not kept in kerosine because it is lighter.

4) Heating in Air :-
→ only lithium (Li) form Nitride (N^{-3})

$$Li + \frac{1}{2} N_2 \xrightarrow{\Delta} Li_3N$$

→
$$2\overset{+1}{M} + \frac{1}{2}\overset{0}{O_2} \xrightarrow{\Delta} M_2O$$

Alkali earth metal

(Be, mg, Ca, Sr, Ba)

1) Be and mg do not give flame test (due to very high IE)

Ca → Brick red

Sr → Crimson red

Ba → Apple green

2)

$$M + H_2 \xrightarrow{\Delta} \overset{+2}{M}\overset{-1}{H_2} \quad (\text{Not } BeH_2)$$

$$\overset{+2}{Ca}\overset{-1}{H_2} + 2H_2O \longrightarrow \overset{+2}{Ca}(\overset{-1}{OH})_2 + 2H_2\uparrow$$

$$BeCl_2 + LiAlH_4 \longrightarrow BeH_2 + LiCl + AlCl_3$$

3)

$$M^0 + 2\overset{+1}{H_2}O \longrightarrow \overset{+2}{M}(OH)_2 + H_2\uparrow$$

Be → steam

mg → hot water

Ca, Sr, Ba → Cold water

4)

→ All alkaline earth metals form Nitrides.

$$3M + N_2 \xrightarrow{\Delta} \overset{+2}{M_3}\overset{-3}{N_2}$$

$$\rightarrow \overset{+2}{M} + \overset{-2}{O_2} \xrightarrow{\Delta} MO$$

NH_2^- → Amide ion.

(3) with excess O_2 :-

$2Na + O_2(excess) \longrightarrow Na_2O_2$ (peroxide) (O^{-1})

(oxone)

$K + O_2(excess) \longrightarrow KO_2$ (superoxide) ($O^{-1/2}$)

(Rb, Cs)

(6) Alkali metals dissolves in liquid ammonia

Alkali metal dissolves in liq. Ammonia to form deep blue solution which is conducting in nature as well as paramagnetic.

(7) $M + (x+y)NH_3(l) \longrightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$

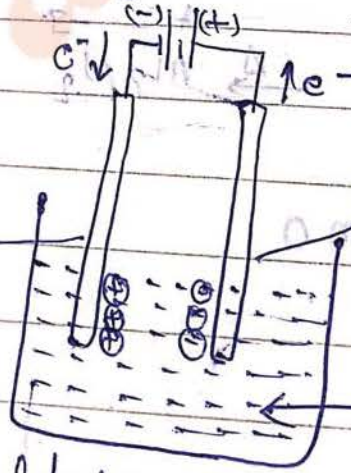
ammoniated cation — ammoniated e^-

after sometime

$M^0 + NH_3 \xrightarrow{\Delta} M^{+1}NH_2 + \frac{1}{2}H_2 \uparrow$

Note :- As concentration of metal is increased in liq. ammonia solution become bronz colour (metallic) and diamagnetic

Note :- Electrolysis :-



(5)

$Sr + O_2$ (excess) $\longrightarrow SrO_2$
(Ba)
(Peroxide)

(6) Alkaline earth metals also dissolves in liquid ammonia to form deep blue black solution.

Imp! → Not Be and mg

Compounds of Na:-

(i) Borax, $Na_2B_4O_7 \cdot 10H_2O$
(ii) Hypo, $Na_2S_2O_3 \cdot 5H_2O$
(iii) Rock salt, NaCl
(iv) chile salt petre, $NaNO_3$
(v) cryolite, Na_3AlF_6
(vi) caustic soda, NaOH
(vii) washing soda, $Na_2CO_3 \cdot 10H_2O$
(viii) soda ash, Na_2CO_3
(ix) Baking soda, $NaHCO_3$
(x) Glauber's salt, $Na_2SO_4 \cdot 10H_2O$
(xi) microcosmic salt, $Na(NH_4)HPO_4 \cdot 4H_2O$

Extraction of Na :-

1) Down's Process :-

(i) Electrolyte :- Fused mixture of NaCl and $CaCl_2$.

⇒ $CaCl_2$ is added to lower down m.p of NaCl.

$NaCl \rightarrow Na^+ + Cl^-$

(ii) Cathode (Fe rod) :-

$Na^+ + e^- \rightarrow Na$

(iii) Anode (Graphite rod) :-

$2Cl^- \rightarrow Cl_2 + 2e^-$

~~Sodium hydroxide (caustic soda, NaOH)~~

Sodium Hydroxide (Caustic Soda, NaOH) :-

Preparation :-

Castner - Kellners Process :-

Electrolyte :- Fused NaCl

$NaCl \rightarrow Na^+ + Cl^-$

Anode: (graphite rod) :- $2Cl^- \longrightarrow Cl_2 + 2e^-$

cathode: (Hg layer) :- $Na^+ + e^- \longrightarrow Na$

$Na + Hg \longrightarrow Na_{(Hg)}$

Amalgam

$Na_{(Hg)} + H_2O \longrightarrow Hg + NaOH + \frac{1}{2} H_2 \uparrow$

Properties:-

(i) Non-metal (concept Fl) disproportionate in NaOH

(ii) Some elements like Be, Zn, B, Al, Si, Ge, Sn, Pb etc form H_2 gas with NaOH

$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2 \uparrow$

(sod. Zincate)

☆ Washing soda:- ($Na_2CO_3 \cdot 10H_2O$)

→ Preparation:-

Ammonia-Soda Process / Solvay process:-

I: $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

II: $NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$

(ammonium bicarbonate)

III: $NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 \downarrow + NH_4Cl$

(Brine Soln) low K_{sp}

IV: $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2 \uparrow$

V: $2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2NH_3 \uparrow + H_2O$

acidic basic

Regeneration of ammonia

S-block.

Raw materials used are lime stone ($CaCO_3$), NH_3 and Brine solution (NaCl)

→ Properties:-

(1) It is called as washing soda it acts as water softner

$$Na_2CO_3 \cdot 10H_2O \xrightarrow[-9H_2O]{373K} Na_2CO_3 \cdot H_2O \xrightarrow[-H_2O]{\Delta} Na_2CO_3$$

Natron → soda ash.

* Baking soda, $NaHCO_3$:-

(1) Preparation by solvay process

(2) $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2 \uparrow$

* Compounds of Ca:-

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

lime ston → lime/quick lime

$$CaO + H_2O \xrightarrow{\Delta} Ca(OH)_2 + heat \quad ; \quad \Delta H = -ve$$

(exothermic)

Solid form → slaked lime

Aqueous form → lime water.

* Plaster of paris (P.O.P) → $(CaSO_4 \cdot \frac{1}{2}H_2O)$

↳ calcium sulphate hemihydrate.

$$2CaSO_4 \cdot 2H_2O \xrightarrow[-3H_2O]{393K} (CaSO_4)_2 \cdot H_2O$$

Gypsom

or

$CaSO_4 \cdot \frac{1}{2}H_2O$

* Cement :-

Composition :-

main Constituent
- Lime (CaO) → 50 - 60%.
- Silica (SiO_2) → 20 - 25%.
- Alumina (Al_2O_3) → 5 - 10%.
- magnesia (MgO) → 2 - 3%.
- Ferric oxide (Fe_2O_3) → 2 - 3%.

vvi * Biological Importance of s-block :-

(1) Mg^{+2} is present in chlorophyll and A.T.P

(2) Calcium is present in Bones and teeth in form phosphate.

(3) Na^+, K^+, Mg^{+2} and Ca^{+2} ions are found in larg proportion in biological fluids.
↳ (like blood, etc.)

(4) These ions (Na^+, K^+, Mg^{+2} and Ca^{+2}) performs various f like blood pressure control, Nerve impulse Condu

Isotopes of Hydrogen :-

Protium	Deuterium	Tritium
$_1H^1$ or H	$_1H^2$ or D	$_1H^3$ or T
ordinary hydrogen	Heavy hydrogen	Radioactive hydrogen
[Isotopes – Having similar atomic number but different no of neutrons]		
(1P, 1e⁻, 0n)	(1P, 1e⁻, 1n)	(1P, 1e⁻, 2n)
more than 99%	almost 0.01%	around 10^{-15}%

* Hydrogen gas (H_2) :-

Preparation -

(i) By electrolysis of acidic or basic water

Cathode: $2H^+ + 2e^- \rightarrow H_2$

(ii) By electrolysis of ionic hydride.

Anode: $2H^- \longrightarrow H_2 + 2e^-$

(iii) From acids -

with metals above "H" in E.C.S

$Mg + 2HCl \longrightarrow MgCl_2 + H_2\uparrow$

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$

[H_2 economy → use of Hydrogen as fuel.]

(iv) Some elements like, Be, Zn, P, Al, Si, Ge, Sn, Pb etc evolve H_2 gas from any hydroxide.

Ex: $Al + NaOH \longrightarrow NaAlO_2 + H_2\uparrow$

(v) From natural gas (or any other hydrocarbon) :-

$$CH_4 + H_2O \xrightarrow[Cr/Ni]{\Delta} \underbrace{CO + H_2}_{\text{water gas or syn gas}} + 2H_2$$

(vi) Bosch Process :-

(a) $CO + H_2 \xrightarrow[Fe_2O_3/Cr_2O_3]{\text{steam } (H_2O)} CO_2 + 2H_2$

CO_2 is absorbed on any basic material like CaO or $Ca(OH)_2$

(b) By hydrolysis of hydrolith (CaH_2) :-

$$CaH_2 + 2H_2O \xrightarrow{Fe_2O_3/Cr_2O_3} Ca(OH)_2 + 2H_2\uparrow$$

Properties :-

(i) lightest, colourless, tasteless and odourless gas, non-polar, partially soluble in water, reactive (B.E = 104 Kilo calorie per mole)

(ii) Very difficult to liquify. (Critical temp =

(iii) H_2 gas can be absorbed on various metallic surfa

Platinum (Pt), Palladium (Pd), Iron, Nickel, Gold etc.

This process is called as occlusion.
↳ (absorption of H_2)

(Colloidal Palladium is the best adsorbent for H_2 gas)

(iv) Reaction with s-block metals :—

$$Na + \frac{1}{2}H_2 \xrightarrow{\Delta} NaH$$

(Ionic hydride)

(v) Rex' with p-block non-metals :—

$$H_2 + Cl_2 \xrightarrow{hv} 2HCl$$

(covalent hydride)

(vi) Rex' of H_2 as reducing agent.

$$R-CH=CH_2 + H_2 \xrightarrow{Pt} RCH_2CH_3$$

• Unsaturated oil (vanaspati oil) :—

$$\text{Unsaturate oil} + H_2 \xrightarrow{Ni} \text{Saturated oil}$$

(Vanaspati oil) (Vanaspati ghee)

* Hydrides :—

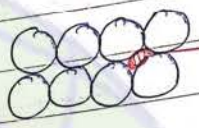
Types :—

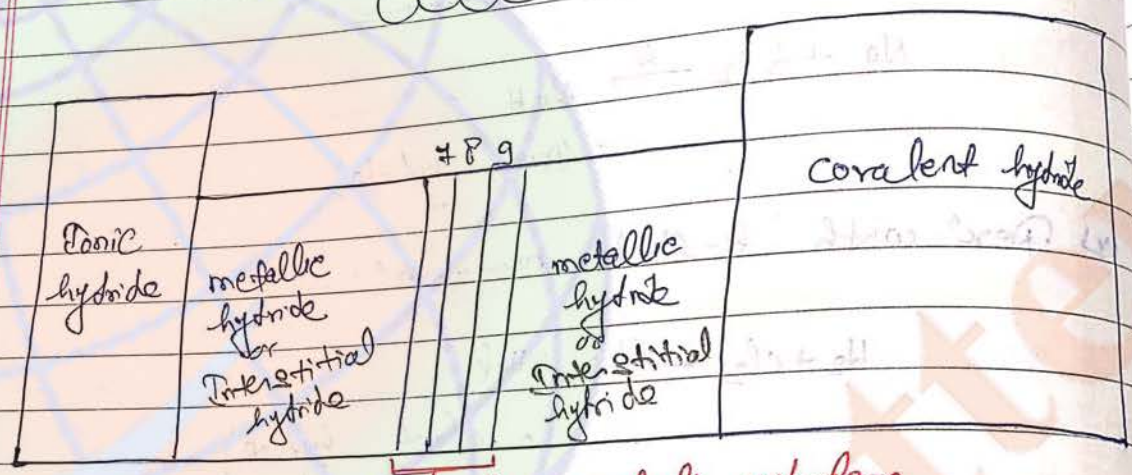
(A) Ionic or salt or saline hydride :—
(with s-block metal)

(B) Covalent or molecular hydride :—
(with p-block non-metals)

(c) metallic or Interstitial or non-stochiometric hydrides (carbon Hydrogen atoms are filled in voids of d or f-block metals.

eg $Ti_{0.83}H$ etc.





These metals not form hydride. So, this is known as hydride gap.//

★ Different type of Hydrogen's →

(1) Atomic hydrogen - (H)

$H_2 \xrightarrow[900°C]{\text{electric arc}} 2H$; $\Delta H = +104$ Kcal/mol

life time = $\frac{1}{3}$rd of a second.

(2) Nascent Hydrogen (H) :-

It is prepared by mixing any metal into any acid in presence of any oxidising agent.

$Zn + 2HCl \rightarrow ZnCl_2 + 2[H]$

If o.A is present then it will attack with o.A

If o.A is not present then Product will be H_2.

$\overset{+3}{FeCl_3}$ (o.A) $\xrightarrow{Zn/HCl} \overset{+2}{FeCl_2}$

$\overset{+3}{FeCl_3} + [H] \longrightarrow HCl + \overset{+2}{FeCl_2}$

(3) Adsorbed Hydrogen (H_2) :-

It is the hydrogen gas adsorbed on various metallic surface

Adsorbed hydrogen

$R-CH=CH_2 \xrightarrow{Pt(H_2)} RCH_2CH_3$

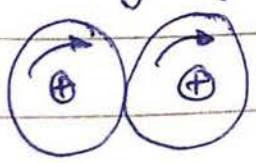
$R-CH=CH_2 + H_2 \xrightarrow{Pt} RCH_2CH_3$

ordinary hydrogen

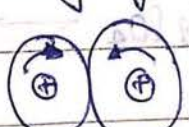
(4) ordinary hydrogen (H_2) :-

It is mixture of ortho hydrogen (H_2) and Para hydrogen (H_2) these are nuclear spin Isomers

ortho hydrogen (H_2) :-



Para hydrogen (H_2) :-



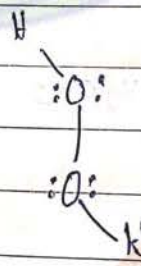
→ Both have similar chemical properties.
→ At room temperature ordinary hydrogen is a mixture of 75% ortho hydrogen and 25% Para hydrogen
→ Ortho hydrogen (H_2) > Para hydrogen (H_2) { stability order }
→ Ortho (H_2) $\xrightarrow{T\uparrow}$ Para (H_2)
Para (H_2) $\xrightarrow{T\uparrow}$ Ortho (H_2)

At absolute zero (0°K) ordinary hydrogen (H_2) is 100%

→ order of reactivity:-

Atomic H > Nascent H > adsorbed H > ordinary H.

Hydrogen Peroxide (H_2O_2):-



half open book structure

Preparation:-

(I) $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow + H_2O_2$

(II) By electrolysis of 50% H_2SO_4
(Industrial Preparation)

$2H_2SO_4 \longrightarrow 2H^+ + 2HSO_4^-$

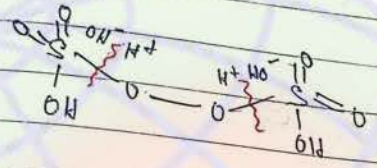
30% H_2O_2 solution.

* Washing soda is ~~removed~~ used to remove all kind of Hardness//

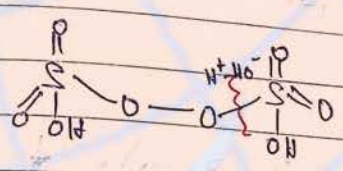
Cathode :→ $2H^+ + 2e^- \rightarrow H_2$

Anode :→ $2HSO_4^- \rightarrow H_2S_2O_8 + 2e^-$

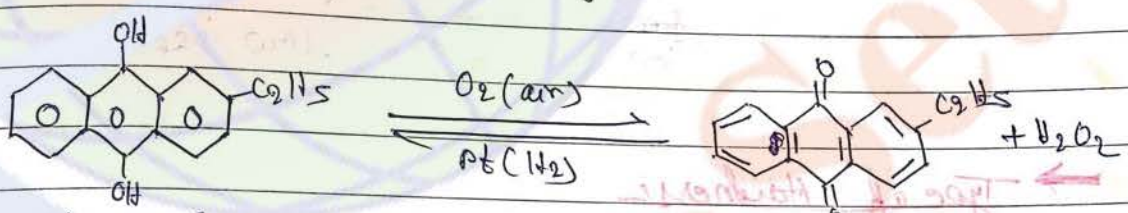
$H_2S_2O_8 + 2H_2O \xrightarrow{\text{Complete}} H_2O_2 + 2H_2SO_4$



$H_2S_2O_8 + H_2O \xrightarrow{\text{Incomplete}} H_2SO_4 + H_2SO_5$



(iii) By auto oxidation of 2-ethylanthraquinol



2-ethyl anthraquinol

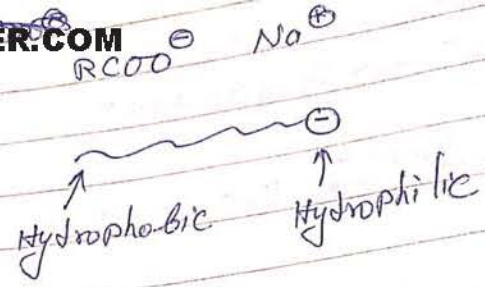
* Hardness of water :-

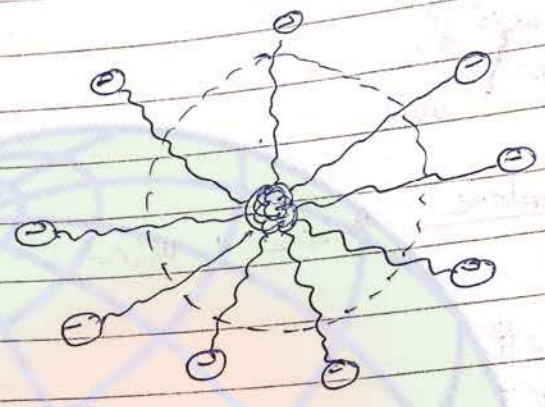
Soft water → water which can easily form foam with soap

Hard water :→ water which can not easily form foam with soap.

* Hardness of water is due to soluble salt of Ca^{+2} and Mg^+

* Soap is sodium salt of fatty acid





$$2RCOO^{\ominus} + \underset{\text{or } Mg^{+2}}{Ca^{+2}} \text{ (free ion)} \longrightarrow \underset{\text{or } Mg(RCOO)_2\downarrow}{Ca(RCOO)_2\downarrow} \text{ (Hard Ka)}$$

⇒ Type of Hardness:-

(1) Temporary hardness:-

Cause It is due to soluble bicarbonates of Ca^{+2} and Mg^{+2}

Removal:-

(i) By heating:-

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

← water ppt
← water bath

(ii) By adding $Ca(OH)_2$ or CaO (clarkes method):-

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

(2) Permanent hardness:-

(a) It is ~~soluble~~ due to soluble sulphate chlorides or nitrates of Ca^{+2} and Mg^{+2}

Removal:-

(i) By adding washing soda:-

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2NaCl$$

$$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3 \downarrow + Na_2SO_4$$

(less Ksp)

~~(ii) By Permanent Proc~~

(ii) By permutite process:-

Permutite process is sodium alumino silicate or Sodium Zeolite (Na_2Z)

$$CaCl_2 + Na_2Z \longrightarrow CaZ \downarrow + 2NaCl$$

$$MgSO_4 + Na_2Z \longrightarrow MgZ \downarrow + Na_2SO_4$$

less Ksp

(iii) By calgon method:-

Calgon is sod. hexametaphosphate

$$Na_6(PO_3)_6$$

$$Na_2[Na_4(PO_3)_6]$$

$$2Ca^{+2} + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + 4Na^+$$

soluble complex

Minerals:- Natural occuring substance in which any metal is present in its native or combined state.

Ores:- minerals from which any metal is extracted easily and economically

Note:- (i) All ores are minerals but all minerals are not ores.
(ii) Less reactive metals like Au, Pt etc is found in native state while more reactive metals are found in combined state.
(iii) Earthy or silicious impurities attached with which are called as Gangue or matrix

Some Important ores and minerals:-

<1> Fe

Haematite, Fe_2O_3
magnetite, Fe_3O_4 ($\overset{+2}{Fe}O$, $\overset{+3}{Fe_2}O_3$)
siderite, $FeCO_3$
Iron pyrite (fools gold), FeS_2

<2> Sn:-

Tin stone / Cassiterite → SnO_2

<3> Cu:-

chalcopyrites / Copper pyrites, $CuFeS_2$
** Copper glance / chalcocite → Cu_2S

Basic Copper carbonate / malachite → $CuCO_3.Cu(OH)_2$

Azurite → $2CuCO_3.Cu(OH)_2$

Cinnabar → HgS

(5) Pb :-

Galena → PbS

Cerrusite → $PbCO_3$

Anglesite → $PbSO_4$

(6) Zn :-

Zinc blend / sphalerite → ZnS

Zincite → ZnO

Calamine → $ZnCO_3$

(7) Al :-

Bauxite → $Al_2O_3 \cdot 2H_2O$

Diaspare → $Al_2O_3 \cdot H_2O$

Corundom → Al_2O_3

~~Cryolite → Na_3AlF_6~~

Cryolite → Na_3AlF_6

(8) Ag :-

Silver glance / argentite → Ag_2S

Horn silver → $AgCl$

(9) Mg :-

magnesite → $MgCO_3$

Dolomite → $MgCO_3 \cdot CaCO_3$

Epsom / Epsomite → $MgSO_4 \cdot 7H_2O$

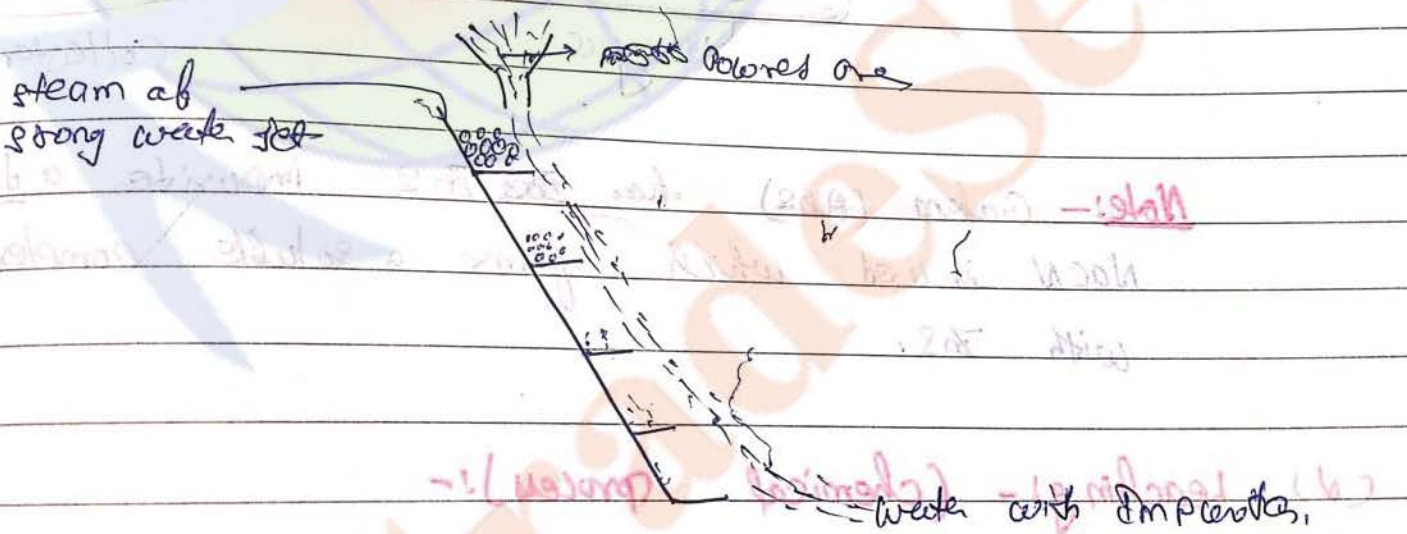
(10) Ca :-
Calcite → $CaCO_3$
Dolomite → $MgCO_3 \cdot CaCO_3$
Gypsom → $CaSO_4 \cdot 2H_2O$

☆ metallurgical operation

Step 1st :- Crushing and Grinding (→ to increase reactive surface area.)

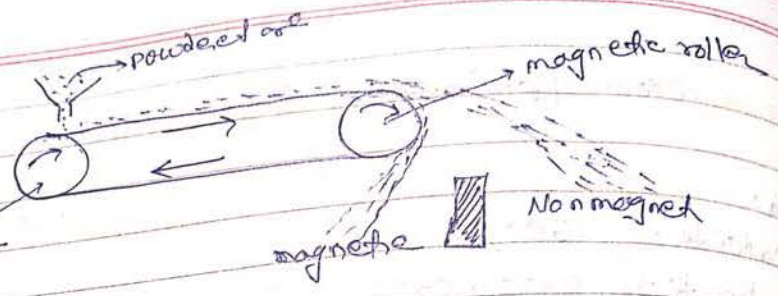
Step 2nd :- Concentration / Beneficiation / Dressing of ore :-
(→ to remove gangue)

(a) washing / Gravity seperation / Levigation :-
mainly used for oxide ore in which impurities are lighter than ore.



magnetic seperation—
used if ore or impurities one is magnetic and other is non-magnetic

Preliminary treatment.

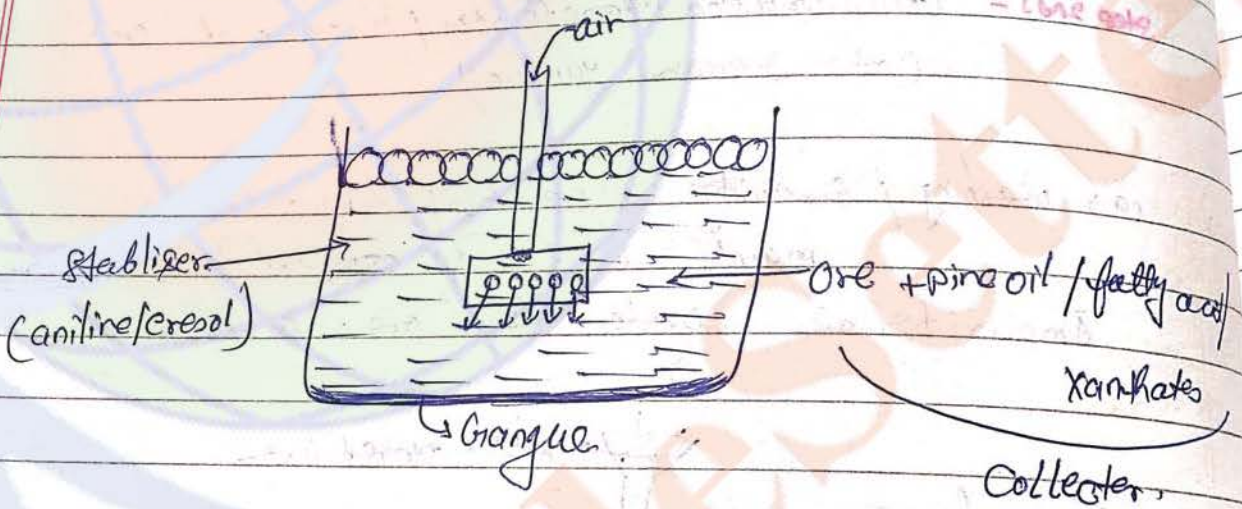


eg:- wolframite ($FeWO_4$) is a magnetic ore and it is seperated from SnO_2 which is non-magnetic.

(C) Froth floatation process:-

→ Very fine powdered ore is required.

→ used for sulphide ore in which ore is wetted by oil and impurities are wetted by water



Note:- Galena (PbS) has ZnS impurities a depressant NaCN is used which forms a soluble complex $Na_2[Zn(CN)_4]$ with ZnS.

(D) Leaching:- (chemical process):-

↳ mainly used for low grade ores like Ag, Au etc.

↳ A suitable regent is used to form complex with metal

Step 3rd :- Preliminary ~~treatment~~ of concentrated ores -

(To remove moisture and volatile impurities and to convert ore into oxide of metal.)

(a) Calcination - Heating of ore in limited supply of air

- mainly used for oxide and carbonate ores.

(b) ~~Roasting~~ Roasting :- Heating of ore ~~in limited supply~~ excess of air.

- mainly used for sulphide ores.

~~more reactive metal~~

Step 4th:-
Reduction to extract metal:-

(A) Hydrometallurgy/ Displacement method:-
Redox takes place in aqueous medium. more reactive metal displaces less reactive metal from its solid

$$CuSO_{4(aq)} + \underset{R.A}{Zn} \longrightarrow \underset{}{Zn^{+2}SO_4(aq)} + Cu$$
O.A

(B) Carbon reduction method/Smelting →

This method is carried out in Blast furnace ore is mixed with coke in blast furnace.

(C) Aluminium reduction method / Alumino thermy / Alumino thermic Process

For some metallic oxides like Cr_2O_3, Mn_3O_4 etc aluminium is used as reducing agent because aluminium is more electropositive than these metals.

$$Cr_2O_3 + Al \longrightarrow Cr + Al_2O_3$$

$$Mn_3O_4 + Al \longrightarrow Mn + Al_2O_3$$
O.A R.A

(D) Electrolytic reduction:-
Highly electropositive metals like Na, Mg, Ca (alkali metals), Al etc. are extracted by electrolysis of their fused salt.

for refining metal

Ga → high temp. thermometer.
Si and Ge → solar cell.

classmate
Date
Page

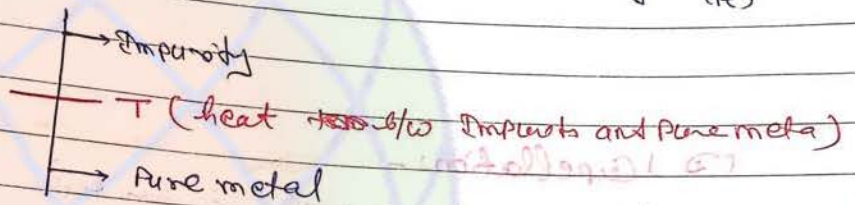
Step 5th! –

Purification or Refining of metals! →

(A) Liquation! —

It is used if impurities have greater melting point than pure metal.

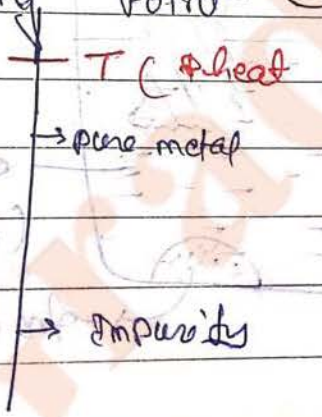
mainly used for tin(Sn), lead(Pb) etc. having Iron Impurities (Fe)

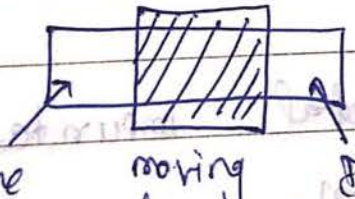


(B) Zone refining! –

This method is used when very high degree of purity is required.
eg Zn, Gallium (Ga), Si, Ge etc.

This method is used when pure metal has greater melting Point than Impurities.





(c) Vapour phase Refining

Mond's Process for Ni

$Ni + 4CO \xrightarrow{\Delta} [Ni(CO)_4] \xrightarrow{\Delta} Ni + 4CO$

(Impure) (volatile) Pure

Van-Arkel Process of Zr or Ti

$Zr/Ti + 2I_2 \xrightarrow{\Delta} ZrI_4/TiI_4 \xrightarrow{\Delta} Zr/Ti + 2I_2$

(Impure) (volatile)

(D) Cupellation:-

Impure Au or Ag is heated with borax and silica in a furnace called as cupel

(कपेल पर गुलाना)

(E) Electrorefining:- (Cu) :→

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

→ more electro (+ve) metal impurities

electrolyte solution

→ Less electro (+ve) impurities like Ag, Au, Pt etc. remains in anode mud.

(F) Poling :-

This method is used when oxide of metal is present as impurity in a metal (In Cu, Cu_2O is present as impurity) molten metal is stired by a green wooden pole Hydrocarbon gas (CH_4) released from pole reduces metal oxide into metal.

$$CH_4 + Cu_2O \rightarrow Cu$$

☆ Thermodynamics in reduction process :-
(Ellingham diagram)

(1) Graph b/w $\Delta G^\circ_{oxidation}$ Vs Temp

(2) For a spontaneous reaction ΔG° of reaction must be -ve

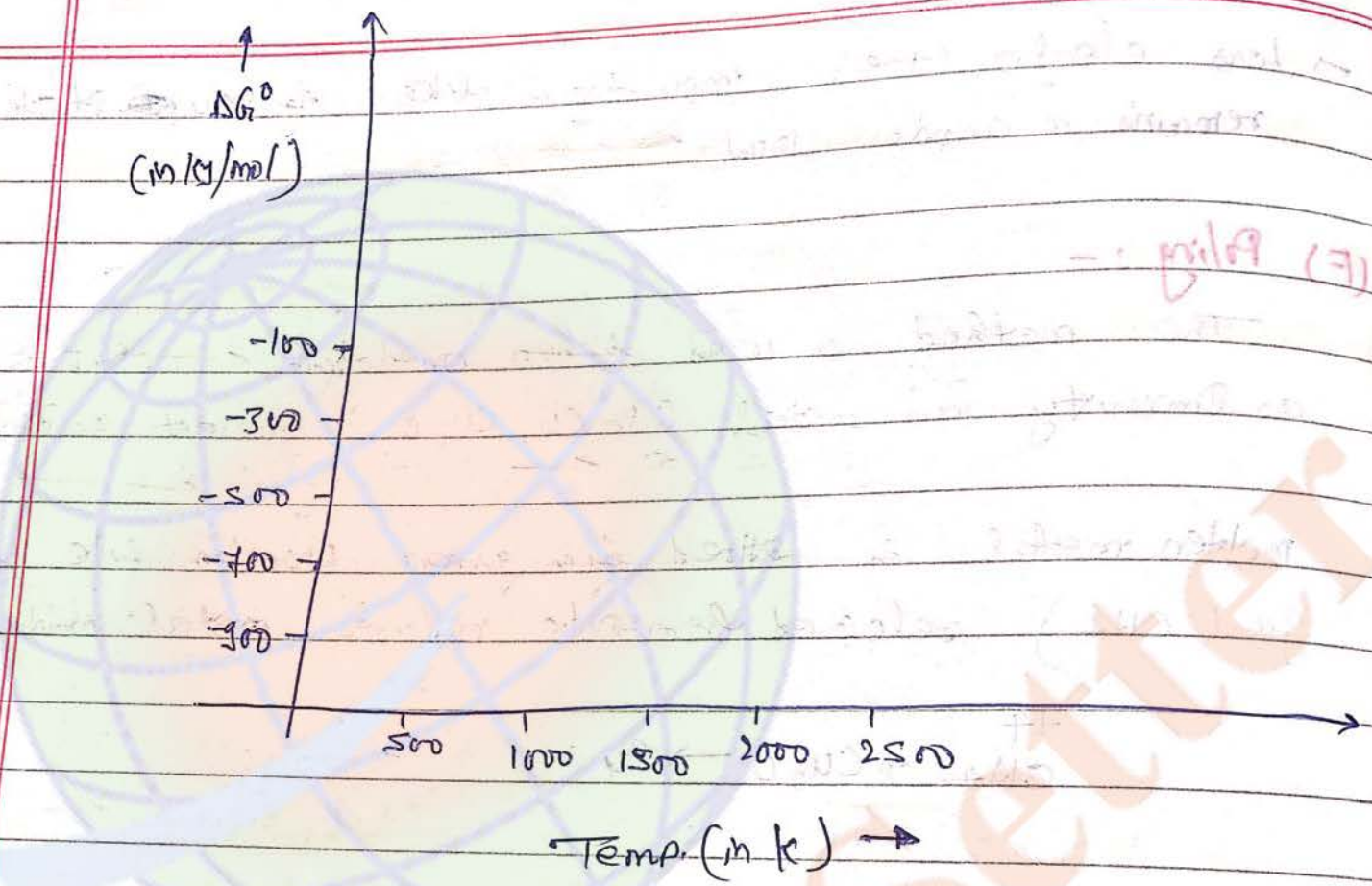
(3) metal present lower in the diagram acts as R.A for metal oxide present higher in this diagram.

Q1.] To reduce ZnO which R.A is better C or CO ?

Soln C

Q2.] To reduce Fe_2O_3 which R.A is better C or CO ?

Ans CO



☆ metallurgy of Silver and gold:→

step 1:- Crushing and Grind.

step 2:→ Conc. by leaching (cyanide process/cyanide leaching/ mac-Arthur-Forrest process)

$$Ag_2S + NaCN + H_2O + O_2 \xrightarrow[\text{hours}]{\text{Several}} Na[\overset{+1}{Ag}(CN)_2] + NaOH + S$$

(Powdered ore) or Au (air) (soluble complex)

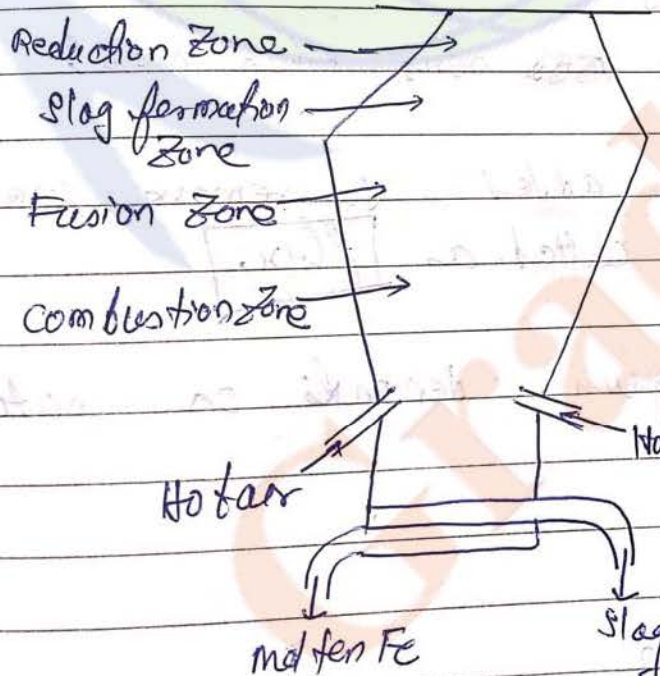
step 4th:- Reduction by hydrometallurgy. (or Displacement method)

$$2\,Na[Ag(CN)_2] + \overset{0}{Zn} \longrightarrow 2\overset{0}{Ag} + Na_2[\overset{+2}{Zn}(CN)_4]$$

O.A R.A

☆ metallurgy of Fe:→

step 4th:- C-reduction process/ smelting



ore is mixed with coke (carbon) and limestone ($CaCO_3$) in blast furnace

Ist:- Combustion Zone:-

$$C + O_2 \xrightarrow{\Delta} CO_2$$

Fusion Zone:-

$$\overset{+4}{CO_2} + \overset{0}{C} \longrightarrow \overset{+2}{CO}$$

$$\underset{O.A}{FeO} + \underset{R.A}{\overset{+2}{CO}} \longrightarrow \overset{0}{Fe} + CO_2$$

Slag formation Zone:-

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_2$$

flux (basic) + impurity (acidic) → slag

Notes:-

(a) Impurities obtained during reduction process is called as slag.

(b) Slag is less dens than metal

(c) The compound added to remove specific Impurities is called as flux.

(d) Selection of flux depends on nature of Impurities.

1 Reduction Zone:-

$$\underset{O.A}{\overset{+3}{Fe_2O_3}} + \underset{R.A}{\overset{+2}{CO}} \longrightarrow \overset{+4}{CO_2} + 2\overset{+2}{FeO}$$

Note:—

(a) molten iron obtained by this process is solidified into small blocks or pigs hence it is called as

Pig iron.

(contains 4% carbon and other impurities like Mn, S, P, Si etc.)

(b) Relatively pure form of iron is called as cast iron (Almost 3% carbon)

(c) Purest form of iron is wrought iron

Metallurgy of copper (Cu)

Step 3rd:- Roasting is carried out in reverberatory furnace

$$2CuFeS_2 + O_2 \longrightarrow \underbrace{Cu_2S + 2FeS}_{\text{matte or } Cu_2S + FeO} + SO_2 \uparrow$$

Step 4th:- Reduction (Bessemerization)

This process is carried out in Bessemer converter air is passed over fused mixture of "matte" flux silica is also added.

$$FeS + O_2 \xrightarrow{\Delta} FeO + SiO_2 \uparrow$$

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

basic flux (acidic)
(impurity) slag

$Cu_2S + O_2 \xrightarrow{\text{Partial}} Cu_2O + SO_2\uparrow$

→ when air supply is turned off

$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2\uparrow$

Cu_2S remaining, Cu_2O formed, blister Cu

→ Self reduction process -

→ S^{-2} ion acts as R.A

→ If complete roasting takes place then c-reduction process can also be used.

* metallurgy of Al :-

step 1st :- Concentration by leaching (Purification of bauxite.)

a) Bayer's process -

→ mainly used for red bauxite (having FeO & Fe_2O_3 impurities)

$Al_2O_3 \cdot 2H_2O + NaOH \longrightarrow NaAlO_2 + H_2O$

(Powdered ore) — soluble (leaving behind impurities.)

$NaAlO_2 + H_2O \xrightarrow{\text{after some time}} Al(OH)_3 + NaOH$

→ To remove excess NaOH, SiO_2 or CO_2 is added.

$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$

(b) Serpeck's process :-

→ mainly used for white bauxite (having SiO_2 impurity)

$$Al_2O_3 \cdot 2H_2O + 3C + N_2 \xrightarrow{\Delta} 3CO + 2AlN + 2H_2O$$

Powdered ore, Coke, air

$$AlN + 3H_2O \longrightarrow Al(OH)_3 \downarrow + NH_3 \uparrow$$

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

Step 4 & 5 :- Reduction (electrolytic reduction)

Hall-Heroult process

electrolyte → fused mixture of Al_2O_3, cryolite (Na_3AlF_6) and fluorspar (CaF_2)

Note :- cryolite and fluorspar are added to lower down m.p and to increase conductivity.

Cathode (Fe tank) $Al^{+3} + 3e^- \rightarrow Al$

Anode (graphite rod)

$$O^{-2} + C \rightarrow CO + 2e^-$$

or

$$2O^{-2} + C \rightarrow CO_2 \uparrow + 4e^-$$

Note :-

Zn → C-reduction process

Sn → C-reduction process

Pb → self reduction / C-reduction process

Co-ordination compounds

Addition compounds :-
when 2 or more stable compounds are allowed to interact to form a new stable compound then that new compound is called as addition compound.

$KCl + MgCl_2 + 6H_2O \longrightarrow KCl.MgCl_2.6H_2O$
(carnallite)

$FeSO_4 + (NH_4)_2SO_4 + 6H_2O \longrightarrow FeSO_4(NH_4)_2SO_4.6H_2O$
mohrs salt

$4KCN + Fe(CN)_2 \longrightarrow K_4[Fe(CN)_6]$
potassium ferro cyanide

Type of addition compound :-

Double salt	Complex salt or Co-ordinate compound
(1) Addition compound which can be completly ionised.	(1) Addition compounds which can not be completly ionises.
$FeSO_4(NH_4)_2SO_4.6H_2O$ $\downarrow H_2O$ $Fe^{+2} + NH_4^+ + SO_4^{-2}$ ↳ It gives test of all ion's.	$K_4[Fe(CN)_6] \xrightarrow{H_2O} 4K^+ + [Fe(CN)_6]^{-4}$ ↳ It does not give test of Fe^{+2} and CN^-

* 3d-series :-

21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$[Ar]4s^2$	$3d^1$	$3d^2$	$3d^3$	$4s^1 3d^5$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$4s^2 3d^{10}$	$3d^{10}$

Type of co-ordination compounds :-

<1> Simple cation and complex anion

$K_4[Fe(CN)_6]$

<2> Complex cation and simple anion

$[Cu(NH_3)_4]SO_4$

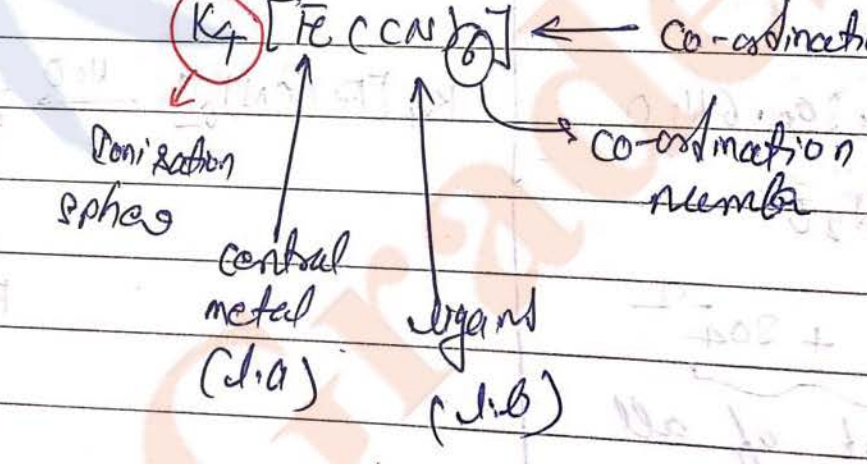
<3> Neutral complex

$[Ni(CO)_4]$

<4> Complex cation and complex anion

$[Pt(Py)_4][PtCl_4]$

☆ Terminology of Co-ordination compounds :-



Note :- <1> In some Compound Ionisation sphere is absent, eg Neutral Complex like

dl,

Note :- → In some compound ionization sphere is absent eg :- Neutral complex like $[Ni(CO)_4]$

1.) Ligands :- → cation, anion or neutral species which can donate their lone pair to central metal are called ligand.

2.) They have lewis base.

3.) The atom of ligand which actually donate its lone pair to central metal is called as donor atom.

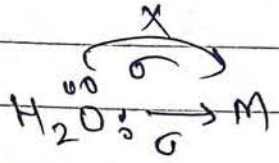
4.) The no. of lone pair donated by a ligand to a central metal is called as No. of donor sites of ligand.

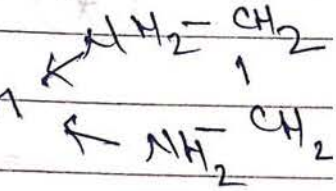
NH_3 No. of donor site = 1

H_2O " " " = 1

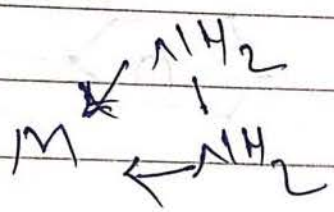
$NH_2CH_2CH_2NH_2$ " " = 2

NH_2 NH_2 " " = 1





Stable



Not stable

Classification of ligand

1.) Monodentated ligand / unidentated ligand
(donar site = 1)

a.) Neutral

- NH_3 ammine
- H_2O aqua / aquo
- CO carbonyl
- NO nitrosyl

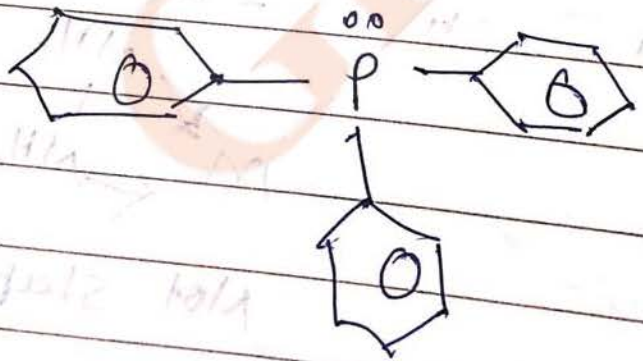
- PH_3 Phosphine

$NH_2\ NH_2$ hydrazine
(N_2H_4)

(*) Py or C_5H_5N Pyridine

(*) PR_3 trialkyl phosphine

PPh_3 triphenylphosphine



$NO_2^{\oplus}$ Nitronium
$NO^{\oplus}$ Nitrosylium / nitrosonium.

c) Anionic

$-C \rightarrow O$

X − halide / halo
(new) (old)

O^{-2} oxo
O_2^{-2} peroxo
O_2^{-} superoxo
OH^{-} hydroxo
OCN^{-} cyanato
S^{-2} sulphido
SO_4^{-2} sulphato
SO_3^{-2} sulphito
$S_2O_3^{-2}$ thiosulphato.

SCN^{-} thio cyanato
NCS^{-} iso thio cyanato

N^{-3} nitrido
N_3^{-} azido
NH_2^{-} amido
NH^{-2} imido
NO_3^{-} nitrato

CN^{-} cyano
NC^{-} isocyano
H^{-} Hydrido

NO_2^{-} nitro / N − Nitro
$ONO^{\ominus}$ nitrito / O-nitro

PO_4^{-3} Phosphato
CO_3^{-2} Carbonate

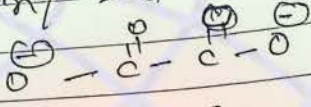
Bidentated Ligand or didentated (donor site = 2)

a.) en ethylenediamine
or
ethane-1,2-diamine

$NH_2 - CH_2 - CH_2 - NH_2$

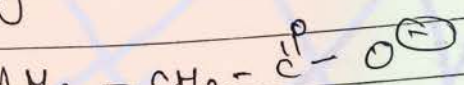
→ Neutral
→ Symmetrical

b.) Ox / $C_2O_4^{-2}$ oxalato



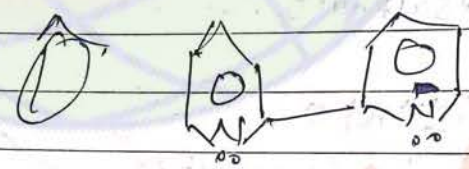
→ charge = 2
→ symmetrical

c.) gly glycinato



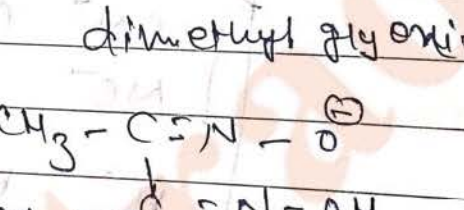
→ charge = −1
→ unsymmetrical

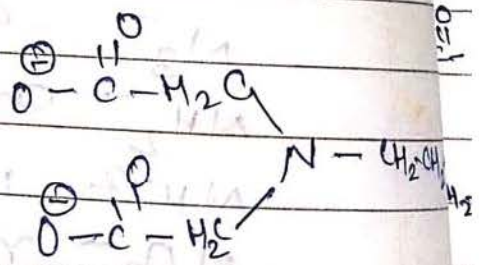
d.) Bipy 2,2-dipyridine



→ neutral
→ Symmetrical

e.) dmg dimethyl glyoximato





charge = −2

→ unsymmetrical

3.) Hexidentated
(donor site = 6)

EDTA ethyl diamine tetra

charge = −4

Ambidentate ligands:- monodented ligand in which more than one atom can donate lone pair as donar. At a time only one can donate its lone pair to central metal.

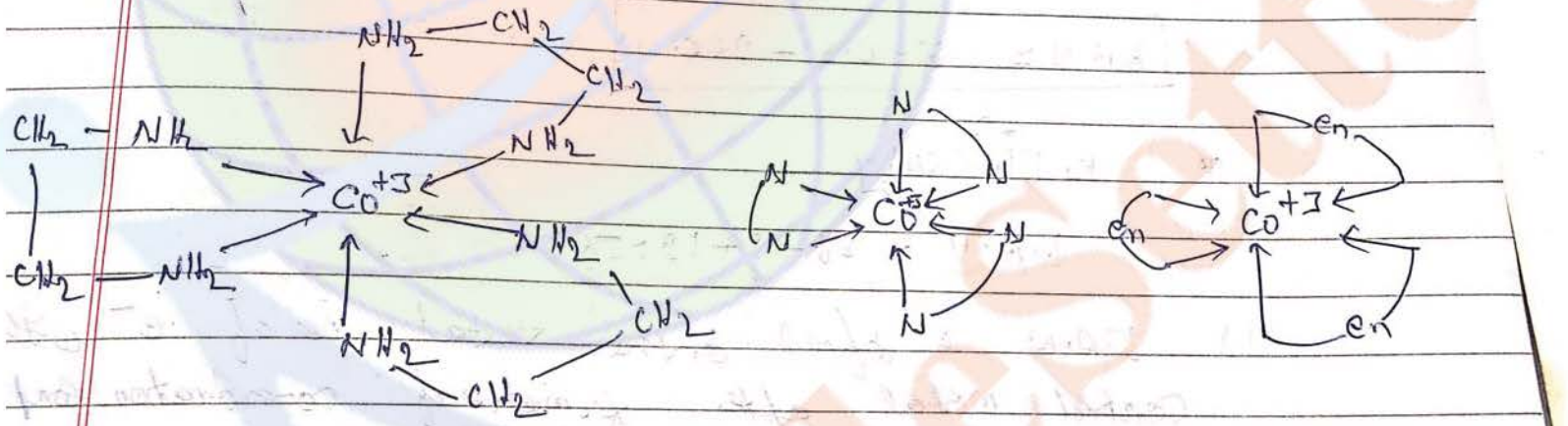
eg. CN^-, NC^-, NO_2^-, ONO^-, SCN^-, NCS^- etc.

Note: <i> All ligands having more than one donar side are collectively called as polydentate or multidentate
<ii> such ligands cause formation of chilate ring hence also called as chilating ligands.

eg

$[Co(en)_3]Cl_3$

$[Co(en)_3]^{+3}$



Co-ordination number:-

It is total no. of σ-bonds (co-ordinate bonds) formed by central metal with all ligands (Not no. of ligands)

$K_4[Fe(CN)_6]$, C.N = 6

$+4 + x - 6 = 0$

$x = 2$

$[Ni^{+2}(gly)_2]$ CN = 4

$[Co^{+3}(en)(H_2O)_2(NO_3)_2]Cl$, CN = 6

$K[Fe^{+3}(EDTA)]$ CN = 6

$NO_3[Cr^{+3}(C_2O_4)]$ CN = 6

$[Ni^{0}(CO)_4]$ CN = 4

~~Fe~~ $[Fe^{+3}Cl_6]^{-3}$ CN = 6

☆ Effective atomic numb (EAN) :-

$$EAN = Z - O.S - 2(C.N)$$

$K_4[Fe^{+2}(CN)_6]$

$EAN = 26 - 2 + 12 = 36$

(1) EAN is defined as the total no of e^- with central metal after formation of co-ordination comp

~~Coordination number~~

(1) $[Cu(NH_3)_4]SO_4$

$EAN = 29 - 2 + 2 \times 4 = 35$

NH_3

(ii) $K_3[Fe(CN)_6]$

$+3 \quad -6 \quad -3$

E.A.N = 26 − 3 + 2 × 6 = 35

(iii) $Ni(CO)_4$

E.A.N = +28 + 0 + 8 = 36

(iv) EAN rule:-

In a stable complex E.A.N of central metal equals to the atomic number of noble gas coming just after that central metal.

(v) many complex do not follow this rule still they are stable it means stability does not depend on E.A.N rule.

Note:-

In metal carbonyls O.S of central metal is zero and they generally follow E.A.N rule.

Q) what is the formula of carbonyl of iron.

Sol:- $Fe(CO)_x$

$36 = 26 - 0 + 2x$

$2x = 10$

$x = 5$

so formula is $Fe(CO)_5$

(ii) $Cr(CO)_x$

Sol^n $18 = 24 - 0 + 2x$

$2x = 12$

$x = 6$

$[Cr(CO)_6]$

☆ Werner's theory:-

1) On the basic of various experiments werner proposes that there are two valencies for a cylindrical metal

(a) Primary valency/ Ionizable linkage
(b) secondary valency/ non-Ionizable linke

(ii) Primary valency is satisfied by anions and it depends on oxidation state of central metal.

(iii) secondary valency is satisfied by ligands and it is co-ordination number of central metal

$CuSO_4 + NH_3(excess) \longrightarrow [Cu(NH_3)_4]^{+2}SO_4$

P.V = +2
S.V = 4

$[Pt(NH_3)_6]^{+4}Cl_4$

P.V = 4
S.V = 6

$[Cr(NH_3)_6]^{+3}Cl_3$

P.V = +3

Note:-

(a) Anionic ligands satisfy both primary and secondary valency

(b) In case of anionic ligands some primary valency converts into secondary valency.

$[Pt(NH_3)_5Cl]Cl_3$

P.V = +3

S.V = 6

$[Cr(NH_3)_4Cl_2]Cl$

P.V = +1

S.V = 6

*** (iv) Each metal ion has fixed S.V (C.N):-

metal	S.V (C.N)
Pt^{+4}, Fe^{+2}, Fe^{+3}, Cr^{+3}, Co^{+3}	6
Au^{+3}, Pt^{+2}, Cu^{+2}, Ni^{+2}, Zn^{+2}, Cr^{+2}, Ca^{+2}, Hg^{+2}	4
Ag^{+1}	2

Note:- for Ni^{+2}; Cl^-, CN^-, H_2O, NH_3

S.V (C.N)
4
6

Thanks

Sol^n

$\Delta T_b = i K_b m$

$1.86 = i \times 1.86 \times 0.5$

$i = 2$

correct structure:—

$[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$

Q.) which equimolal sol^n has highest electrical conductivity :—

(a) $[Co(H_2O)_6]Cl_3$

(b) $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$

(c) $[Co(H_2O)_4Cl_2] \cdot 2H_2O$

electrical conductivity $\propto$ no. of ions

Q.) which of the following can form ppt ($BaSO_4$) with $BaCl_2$.

(1) $[Co(NH_3)_5 \cdot SO_4]Cl$

(2) $[Co(NH_3)_5Cl]SO_4$

Comp + $BaCl_2 \longrightarrow BaSO_4$

$(SO_4^{-2}) + (Ba^{+2})$

So compound is $[Co(NH_3)_5Cl]SO_4$

Q.) $KCl + AgNO_3 \longrightarrow A\downarrow + B$

(white p.p.t)

$A + NH_3$ (sol^n) $\longrightarrow C$

or

NH_4OH (sol^n)

(Complex)

Ans A = AgCl

$AgCl + NH_3$ (excess) $\longrightarrow [Ag^{+2}(NH_3)_2]Cl$

Q.) $CuSO_4(aq) + NH_3(sol) \longrightarrow [Cu(NH_3)_4]SO_4$

(Cuprous ammonium sulphate)

Q.) $Fe^{+2}Cl_2 + KCN$ (excess) $\longrightarrow K_4[Fe(CN)_6]$

$K_4[Fe^{+2}(CN)_6]$

Potassium ferrocyanide

Fe^{+2}

* Pottasium ferricyanide

Fe^{+3}

$K_3[Fe^{+3}(CN)_6]$

Q.) CN of $Ni^{+2} = 4$

$NiCl_2 + KCN \longrightarrow A$ (complex)

$A + KCl$ (excess) $\longrightarrow B$ (complex)

Find "A" and "B"

Solution A :- $K_2[Ni^{+2}(CN)_4]$

$K_2[Ni^{+2}(CN)_4] + KCl$ excess $\longrightarrow K_2[Ni^{+2}Cl_4^-] + KCN$

Note :- Here Cl is excess so it replace CN^- from com

* IUPAC NOMENCEATURE *

Cation is named 1st followed by anion

$K_4[Fe(CN)_6]$ $[Cu(NH_3)]Cl_2$

$[Ni(CO)_4]$ $[Pt(Py)_4][PtCl_4]$

case-(1) if Co-ordination sphere is cationic or neutral

a) ligands are named first followed by central metal with O.S in roman no.

eg - $[Fe^{+3}(ligand)]$

ligand iron (III)

b) if any ligand repeats more than once then before its name

Numerical prefix: di, tri, tetra, etc are used

eg $(NH_3)_6$ - Hexammine

if name of ligand contains already contains already has any numerical prefix then in place of di and tri, bis and tris are used.

$(en)_2$ bis-(ethylene diamine)

$(gly)_2$ di(glycinato)

(c) if more than one type of ligands are present then they are written in alphabatical order. In deciding alphatical order, there is no use of numerical prefix

eg - $(NH_3)_3 Cl_2 Br$ (a, c, b)

triammine dibromidodichloridoplatinum(IV)

1) $[Pt^{+4}(NH_3)_4(H_2O)_2]Cl_4$ (am, aq)

Tetra ammine diaqua platinum(IV) chloride

2) $[Cu^{+2}(NH_3)_4]SO_4$

Tetraammine copper (II) sulphate

3) $[Ni(CO)_4]$

4) $[Co(en)]Cl$

5) $[Ni(gly)_2]$

(6) $[Co^{+3}(en)(H_2O)_2(ONO)_2]Br$

Diaqua ethylenediammine dinitrito cobalt(III) bromide

(7) $[Cu^{+2}(NH_3)_4]^{+2}$

Tetraammine copper(II) ion

(8) Diammine dichloride platinum(II)

$[Pt^{+2}(NH_3)_2Cl_2]$

(9) Tetraaqua dithiocyanato platinum(IV) chloride

$[Pt^{+2}(NH_3)_2Cl_2]$

(10) Tris(ethylenediammine) cobalt(III) sulphate

$[Co^{+3}(en)_3]_2(SO_4)_3$

Case II If co-ordination sphere is anionic then all rules are similar except naming of central metal. Name of central metal is ended by - ate

Zinc - Zincate Chromium - chromate
nickel Nickelate Zirconium - Zirconate
Cobalt cobaltate platinum - Platinate

Iron — ferrate
Copper — cuprate
Gold — aurate
Silver — argentate

(11) $K_3[Fe(CN)_6]$

Potassium hexacyano ferrate(III)

(12) $[FeCl_6]^{-3}$

Hexachloride ferrate III ion.

(13) Sodium tetra cyano nickelate (II)

$Na_2[Ni^{+2}(CN)_4]$

(14) $K[Fe(EDTA)]$

Potassium ethylene diamine tetra au
ferrate (III)

15) $Ca_3[Cr(C_2O_4)]_2$

Calcium trioxalato chromate (III)

6) $[Cr^{+3}(NH_3)_6][Co^{+3}(CN)_6]$

($Cr^{+3}(NH_3)_6$: +ve; $Co^{+3}(CN)_6$: −ve)

Hexammine chromium(III) hexacyano cobaltate(III)

7) $[Pt^{+2}(Py)_4][PtCl_4^{+2}]$

($Pt^{+2}(Py)_4$: +ve; $PtCl_4^{+2}$: −ve)

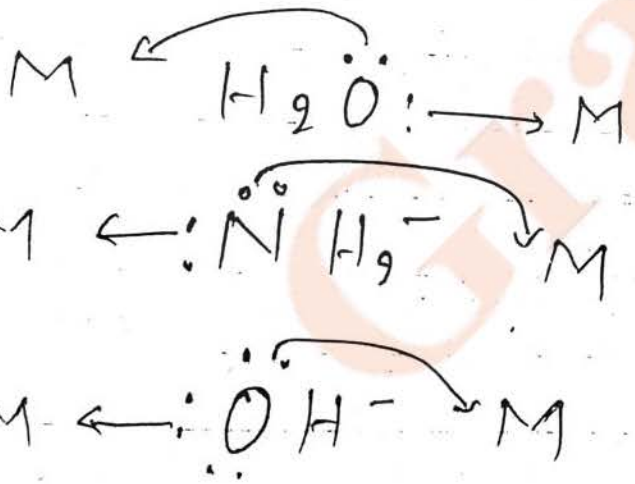
Tetra pyridine platinum(II) tetrachloride platinate(II)

8) $[Pt^{+4}(NH_3)_4Cl_2][PtCl_4^{+2}]$

($Pt^{+4}(NH_3)_4Cl_2$: +ve; $PtCl_4^{+2}$: −ve)

Tetraammine dichloride platinum(IV) tetrachloride platinate(II)

9) Bridge ligands:- Monodentate ligands which can donate its lone pair to more than one central atom.



19) $[(en)_2 Co^{+3}(OH)(NH_2)]Co(en)_2](SO_4)$ (CN=6)

Bis-(ethylene diammine)-μ-amido-μ-hydrono bis ethylene diammine cobalt(III) sulphate.

20) $[(NH_3)_5 Fe^{+3} - OH - Fe^{+3}(NH_3)_5]^{+5}$

μ Hydrono bis-(Pentaammine iron III ion

Bonding in Co-ordination compounds

Valence bond theory (VBT)

(1) M ← L

(2) No of vacant orbitals of central metal participate in bonding = C.N of central metal

(3) These vacant orbitals of central metal undergo hybridisation before bond formation.

C.N	Hybridisation	Geometry
2	sp	linear
4	sp^3	Tetrahedral
4	dsp2	Square planner
6	sp^3d^2 / d^2sp^3	

hybridisation process paired, unpaired or vacant orbitals may participate

Spectrochemical series

$I^- < Br < S^{-2} < Cl^- < NO_3^- < F^- < OH^- < O_n < H_2O < EDTA < NH_3$ and Py $< en < NO_2^- < CN^- < CO$

Weak field ligand.

strong field ligand

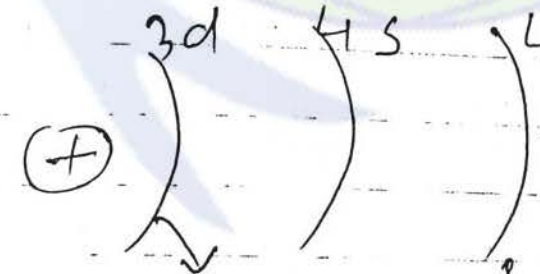
or

Halogen donor < O-donor < N-donor < C donor

weak ligand.

strong ligand

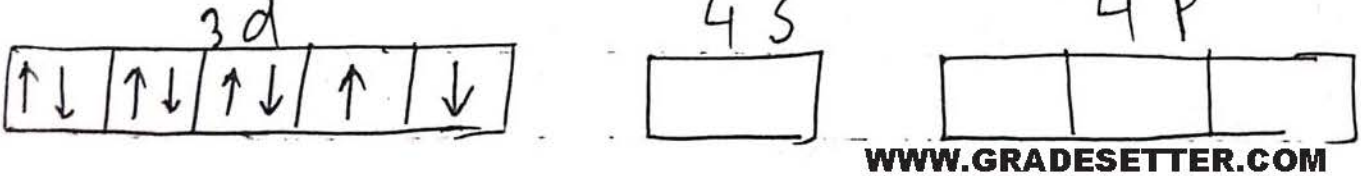
Strong field ligand (S f l) cause pairing of e^- of central metal while in weak field ligand do not cause pairing of e^- of central metal



C.N = 4 (sp^3 / dsp^2)

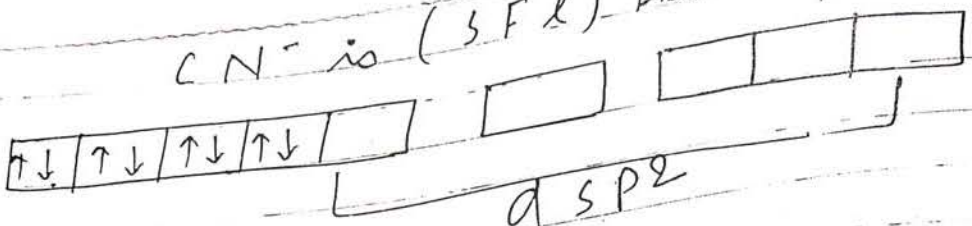
eg (1) $[Ni(CN)_4]^{-2}$

$Ni^{+2} = [Ar]\ 4s^0\ 3d^8$



strong field ligand

CN^- is (S F L) Hence pairing occurs



dsp^2

→ Square planner
→ dia ($\mu_s = 0$)

2) $[NiCl_4]^{-2}$

$Ni^{+2} = (Ar)\ 4s^0\ 3d^8$

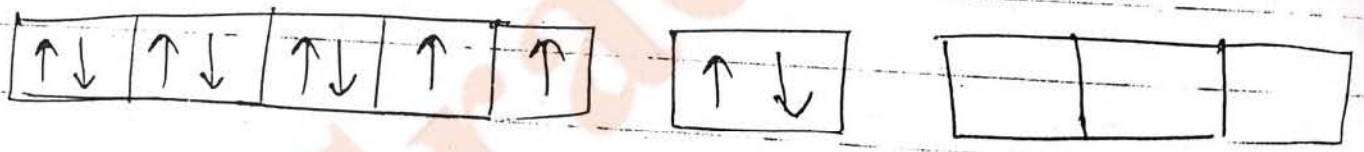
sp^3

Cl^- is W f L, Hence pairing doesn't occ

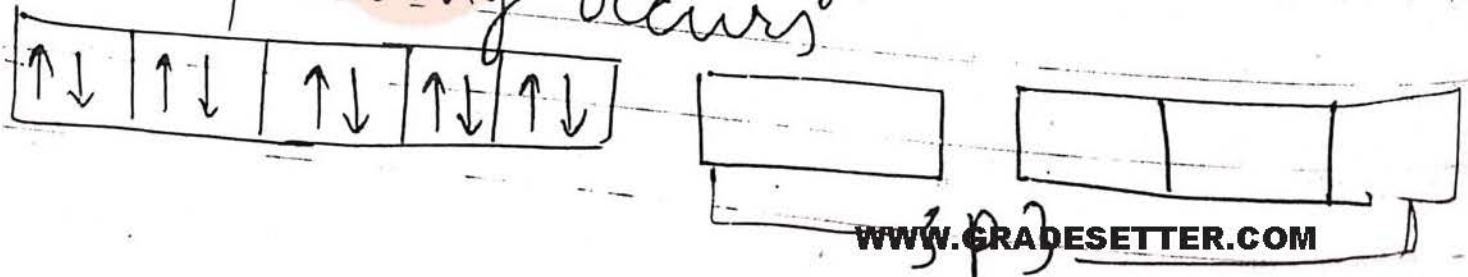
→ Tetrahedral
→ Para ($\mu_s = 2.83$)

3) $[Ni(CO)_4]$

$Ni = [Ar]\ 4s^2\ 3d^8$



CO is S.F.L ligand.
So pairing occurs



sp^3

→ Tetrahedral
→ dia. ($\mu_s = 0$)

4) $[Zn(NH_3)_4]^{+2}$

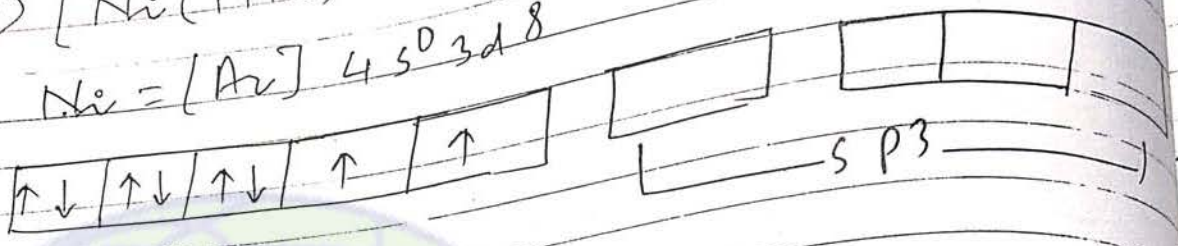
5) $[CrCl_4]^{-2}$

6) $[Co(CN)_4]^{-2}$

weak ligand weak ligand

7) $[Ni(PPH_3)_2Cl_2]$

$Ni = [Ar]\ 4s^0 3d^8$



PPH_3

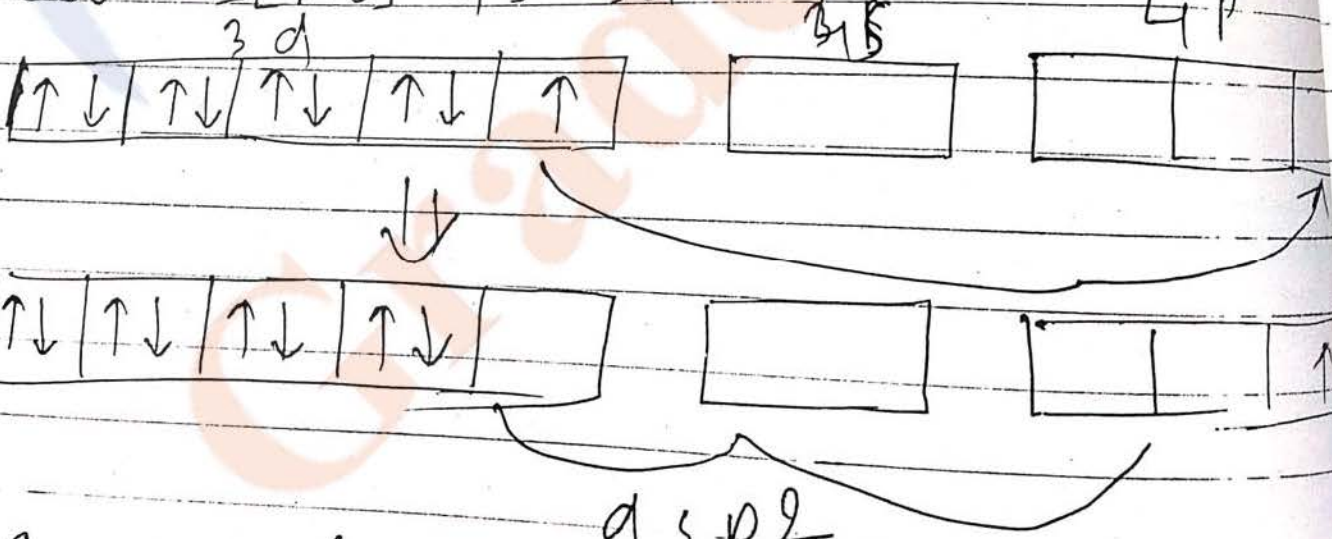
difficult to donate so WF ligand.

→ Tetrahedral

→ Para ($\mu_s = 2.83$)

*** ⑧ $[Cu(NH_3)_4]^{+2}$ exception

$Cu^{+2} = [Ar]\ 4s^0 3d^9$



→ Square planer → Para ($\mu_s = 1.7$

V. VI exception

9) Pt^{+2}, Pd^{+2}, Au^{+3} (d^8)

strong / weak field ligands (pairing always occurs)

→ dsp^2 (square planner)

→ dia ($\mu_s = 0$)

ex- $[PtCl_4]^{-2}$, $[PdCl_4]^{-2}$ etc.

$[Pt(NH_3)_6]Cl_4$

P.V = +4

S.V = 6

$[Cr(NH_3)_6]Cl_3$

P.V = +3

S.V = 6

Note (a) anionic ligand satisfy both primary valency and secondary valency

(b) in case of anonic ligand some Primary Valency converts into secondary Valency

$[Pt(NH_3)_5Cl]Cl_3$

P.V = +3

S.V = 6

$[Cr(NH_3)_4Cl_2]Cl$

P.V = +1

S.V = 6

*

1) According to this theory each metal ion has fixed S.V (C.N)

Metal ion	S.V (C.N)
Pt^{+4}, Fe^{+2} Fe^{+3}, Cr^{+3}, Co^{+3}	6
Fe^{+3}, Cr^{+2}, Co^{+2}, Pt^{+2}, Cu^{+2}, Ni^{+2}, Zn^{+2}, Hg^{+2}	4
Ag^{+}	2

Note:- (a) For Ni^{+2}

H_2O, NH_3	6

(5) Shape / geometry depends on C.N

C.N	geometry
6	Octahedral
4	Tetrahedral / Square Planar
2	linear

$\Rightarrow Cr^{+3}Cl_3 6NH_3$

$[Cr^{+3}(NH_3)_6]Cl_3$

$Pt^{+4}Cl_4 4NH_3$

$[Pt(NH_3)_4Cl_2]Cl_2$

$\Rightarrow CrCl_3 6NH_3 \xrightarrow{H_2O} 3Cl^- + [Cr(NH_3)_6]^{+3}$

4 ions

or

$[Cr(NH_3)_6]Cl_3$

$CrCl_3 6NH_3 + AgNO_3 \longrightarrow AgCl$

excess

$[Cr(NH_3)_6]Cl_3$

$Cl^- + Ag^+ \longrightarrow AgCl$

3 mole excess 3 mole

Q) 1 mole of $CrCl_3 \cdot 5NH_3$ reacts with excess of $AgNO_3$ to form 2 mole of AgCl. Calculate total no of ions present by 1 molecules of ion

$[Cr(NH_3)_5Cl]Cl_2$

9) one mole $CoCl_3 \cdot 5H_2O$ reacts with excess $AgNO_3$ to form 1 mole of AgCl. write correct structural form of coordination compound

$[Co(H_2O)_4Cl_2]Cl \cdot H_2O$

Write all possible structural form of coordination compound having molecular formula $CoCl_3 \cdot 6H_2O$

(a) $[Co(H_2O)_6]Cl_3$

(b) $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$

(c) $[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$

(d) $[Co(H_2O)_3Cl_3] \cdot 3H_2O$

Which of the following equimolar solution has highest electrical conductivity

(a) $[Co(H_2O)_6)Cl_3$

(b) $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$

(c) $[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$

) $[Co(H_2O)_3Cl_3] \cdot 3H_2O$

electrical conductivity ∝ no of ions.

Q) Which of the following compound can form white precipitate of $BaSO_4$ with $BaCl_2$?

(a) $[Co(NH_3)_5SO_4]Cl$

(b) $[Co(NH_3)_5Cl]SO_4$

Comp + $BaCl_2$ $\longrightarrow$ $BaSO_4$

SO_4^{-2} Ba^{+2}

Q) $NaCl + AgNO_3 \longrightarrow$ A ↓ white PPt + B

A + NH_3 (soln) $\longrightarrow$ C

or

NH_4OH (soln)

Soluble complex

A and C ?

Ans – A = AgCl

$AgCl + NH_3$ (excess) $\longrightarrow [Ag^{+1}(NH_3)_2]Cl$

Q) $CuSO_4$ (aq) + NH_3 sol $\longrightarrow [Cu^{+2}(NH_3)_4]$

Cuproammonium sulphate

Q) $FeCl_2$ (aq) + KCN excess $\longrightarrow K_4[Fe^{+2}(CN)_6]$

Potassium ferrocyanide

Fe^{+2} - ferrous
Fe^{+3} - ferric

Pot ferricyanide $K_3[Fe^{+3}(CN)_6]$

⇒ C.N of Ni^{+2} = 4.

$NiCl_2 + KCN_{(excess)} \rightarrow A \Rightarrow K_2[Ni^{+2}(CN)_4]$
(complex)

$A + KCl_{(excess)} \rightarrow B$
complex

Ans - $A = K_2[Ni(CN)_4]$

$K_2[Ni(CN)_4] + KCl_{excess} \rightarrow K_2[Ni^{+2}Cl_4]$
(B)

IUPAC Nomenclature

① Cation is named first followed by anion.

$K_4[Fe(CN)_4]$
① ②

$[Cu(NH_3)_4]Cl_2$
① ②

$[Ni(CO)_4]$
①

$[Pt(Py)_4][PtCl_4]$
① ②

[-1, -1-90, 99.-39. [-2
[-4, -3, 4, 5, 8, 10, 90, 93,

Case 1:- If CO-ordination sphere is cation or neutral:

(a) Ligands are named first followed by central metal with OS in roman

eg [Fe^{+3} (ligand)]
ligand iron (III)

(b) If any ligand repeats more than once then before its name numerical prefix di, tri, tetra etc are used.

eg:- $(NH_3)_6$
hexaammine

→ If name of ligand already has any numerical prefix, then in place of di and tri, bis- and tris are used

eg:- $(en)_2$
bis-(ethylenediamine)

$[Cu(NH_3)_4]SO_4$

Tetraammine copper(II) sulphate

$[Ni^{0}(CO)_4]$

Tetracarbonylnickel(0)

(c) If more than one type of ligands are present then they are written in alphabetical orders

(1) $[Co(en)(H_2O)_2(ONO)_2]Br$
diaqua ethylenediamine nitrito cobalt (III) bromide

(2) Diammine dichloride platinum(II)
$[Pt^{+2}(NH_3)_2Cl_2]$

(3) Tetraaqua dithiocyanato platinum IV chloride
$[Pt^{+4}(H_2O)_4(SCN)_2]Cl_2$

(4) Tris-(ethylene diammine) cobalt(III) sulphate
$[Co^{+3}(en)_3]_2(SO_4)_3$

(5) $[Cu^{+2}(NH_3)_4]^{+2}$
Tetraammine copper (II) ion.

$[Co^{+3}(en)_3]Cl_3$
Tris-(ethylene diamin) cobalt(III) Chloride

Case II - If CO-ordination sphere is anionic then all rules are similar except naming of central metal. Name of central metal is ended by -ate

Zinc - Zincate
Cobalt - cobaltate
nickel - nickelate
Platinum - platinate
Zirconium - Zirconate
Chromium - chromate

Iron - ferrate
Copper - cuprate
silver - argentate
Gold - aurate

(11) $K_3[Fe^{+3}(CN)_6]$
Potassium hexacyanoferrate (III)

(12) Sodium tetracyano nickelate.
$Na_2[Ni(CN)_4]$

13 $[Fe^{+3}Cl_6]^{-3}$
Hexachlorido ferrate (III) ion

(14) $K[Fe^{+3}(EDTA)]$
Potassium ethylene diamine tetra acetato ferrate (

5) $Ca_3[Cr(C_2O_4)_3]_2$ $\quad 6+2n-12=0$, $2n=6$, $n=3$

~~Calcium bisoxalato chromate~~ Calcium trioxalato chromate (III)

6) $[\overset{+3}{Cr}(NH_3)_6][\overset{+3}{Co}(CN)_6]$

(+ve) (−ve)

Hexaammine chromium (III) hexacyano cobaltate (III)

7) $[\overset{+2}{Pt}(Py)_4][\overset{+2}{Pt}Cl_4]$

(+ve) (−ve)

Tetrapyridine platinum(II) tetrachlorido platinate II

8) $[\overset{+4}{Pt}(NH_3)_4Cl_2][\overset{+2}{Pt}Cl_4]$

(+ve) (−ve)

Tetra ammin dichlorido Platinum (IV) tetrachlorido platinate (II)

19) $[(en)_2Co(OH)_2Co(en)_2](SO_4)_2$

C.N = 6 (OH, OH, NH_2, NH_2, en, en) C.N = 6

Bis-(ethylenediamine), cobalt III' μ-amido-μ-hydroxo bis-(ethylene diammine cobalt (III) sulphate

In hybridisation, pair, unpaired or vacant orbital can participate

57 [Ex. 5.3]

(20) $[(NH_3)_5Fe^{+3}-OH-Fe(NH_3)_5]^{+5}$

cis-Hydroxo bis-(penta ammine iron (III))

Bonding in co-ordination Compounds

Valence bond theory (VBT)

(1) M ← L

(2) The no of vacant orbitals of central metal participated in bonding = C.N of central metal.

(3) These vacant orbitals undergo hybridisation before bond formation.

CN	Hybridisation	Geometry
2	sp	Linear
4	sp^3	Tetrahedral
4	dsp^2	Square planar
6	sp^3d^2 / d^2sp^3	Octahedral

spectrochemical series

$I^- < Br^- < S^{-2} < Cl^- < NO_3^- < F^- < OH^- < Ox. < H_2O < EDTA < NH_3 < en < NO_2^- < CN^- < CO$

Weak field ligand

and

Py

Strong field ligand

Halogen donor < 'O' donor < 'N' donor < C-donor

weak field ligand.

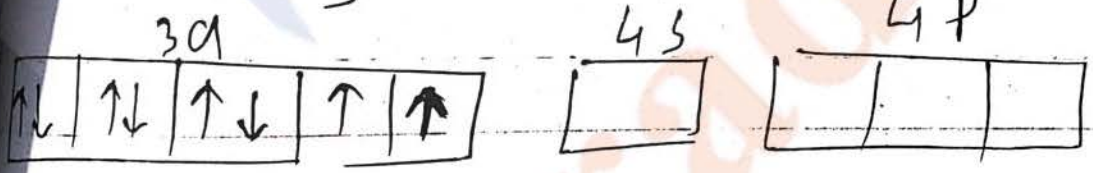
Strong f.l

S.f.l cause pairing of e^- of central metal while W.f.l do not cause pairing of e^- of central

$C.N = 4 \; (dsp^2 / sp^3)$

$[Ni(CN)_4]^{-2}$

$Ni^{+2} = [Ar] \; 4s^0 \; 3d^8$

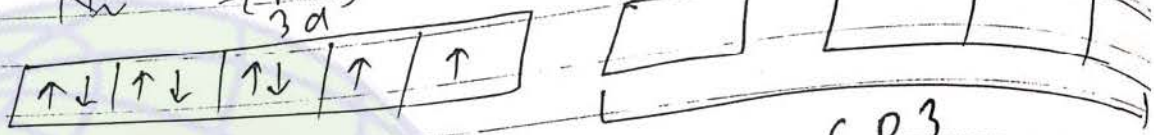


CN^- is s.f.l hence pairing occurs

→ Square planar

(2) $[NiCl_4]^{-2}$

$Ni^{+2} = [Ar]\ 4s^0\ 3d^8$



sp^3

Cl^- is weak hence pairing does not occ

→ Tetrahedral

→ Para ($M_s \simeq 2.83$)

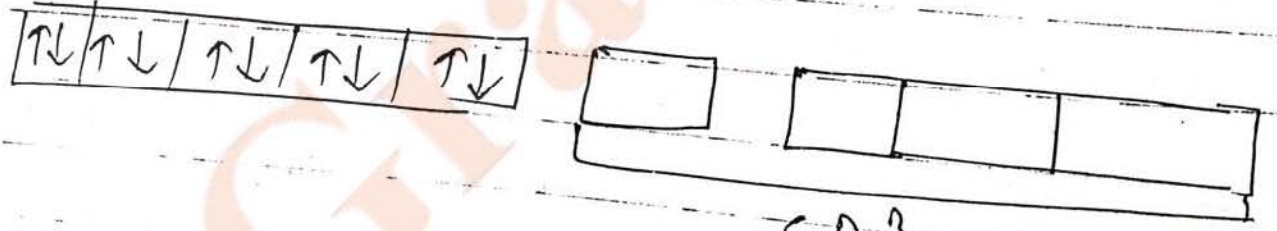
(3) $[Zn(NH_3)_4]^{-2}$

(4) $[Cr(Cl)_4]^{-2}$

(5) $[Co(CN)_4]^{-2}$

(3) $[Zn(NH_3)_4]^{-2}$

$Zn^{+2} = [Ar]\ 4s^0\ 3d^{10}$



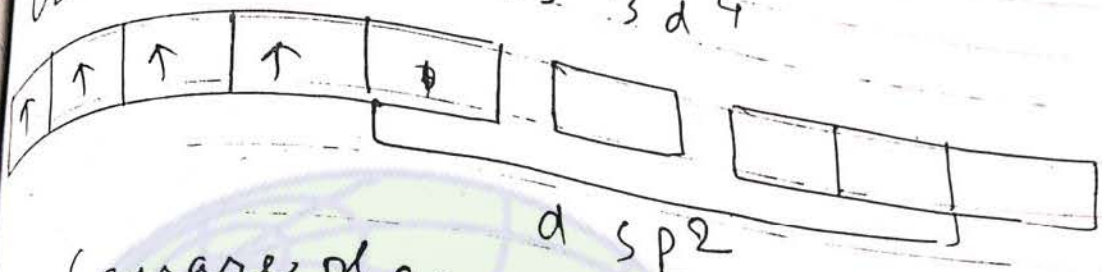
sp^3

→ Tetra Ledral.

→ dia ($M_s = 0$)

$[Cr(Cl)_4]^{-2}$

$Cr^{+2} = [Ar]\ 4s^0\ 3d^4$

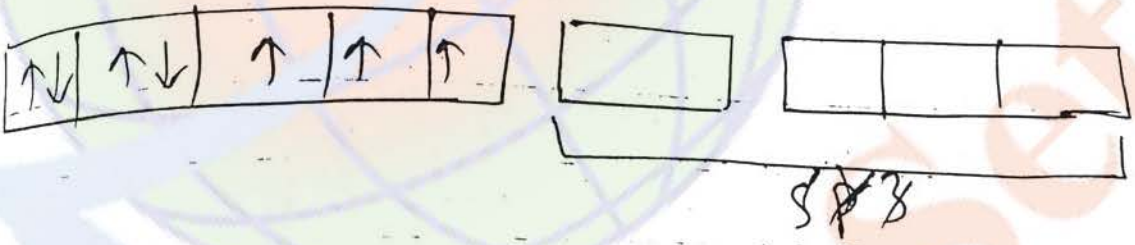


d sp^2

→ Square planar
→ para ($\mu_s = \sqrt{4 \cdot 8}$)

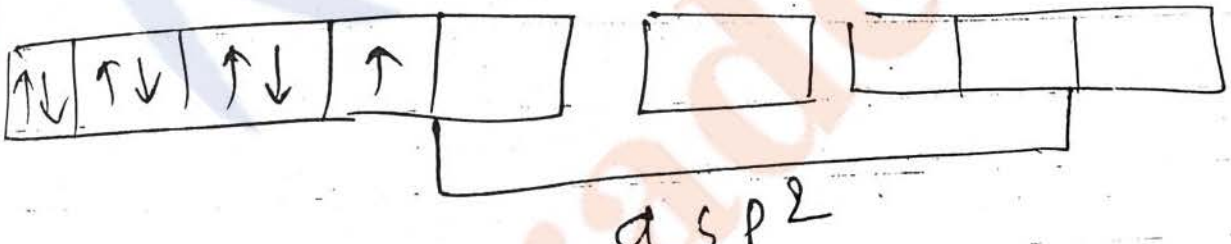
$[Co(CN)_4]^{-2}$

$Co^{+2} = [Ar]\ 4s^0\ 3d^7$



sp^3

CN^- is a strong field ligand

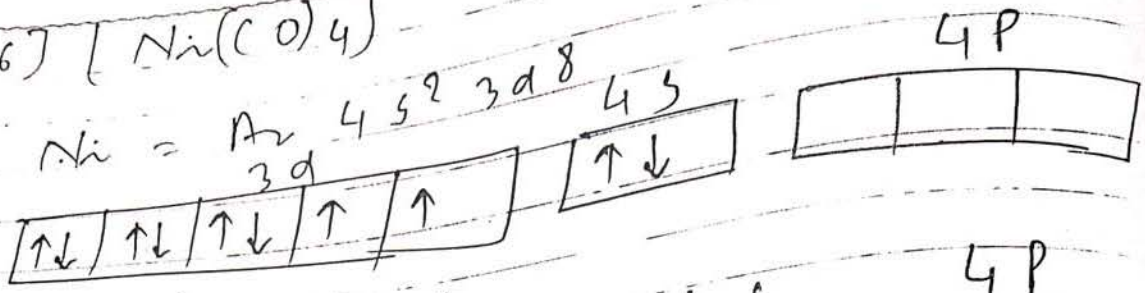


d sp^2

→ Square planar
→ para ($\mu_s = 1.37$)

(6) $[Ni(CO)_4]$

$Ni = Ar\ 4s^2\ 3d^8$



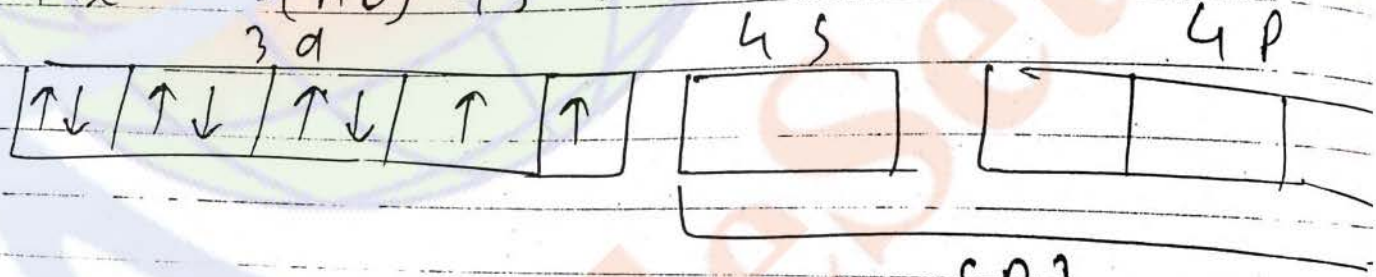
CO is w.f.l

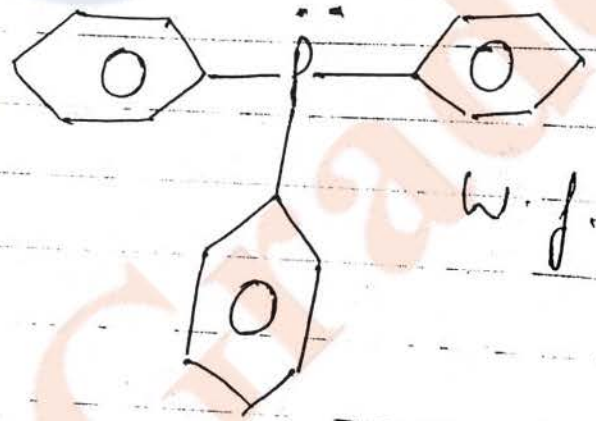
→ Tetrahedral

→ dia ($\mu_s = 0$)

(7) $[Ni(PPh_3)_2Cl_2]$

$Ni^{+2} = (Ar)\ 4s^0\ 3d^8$





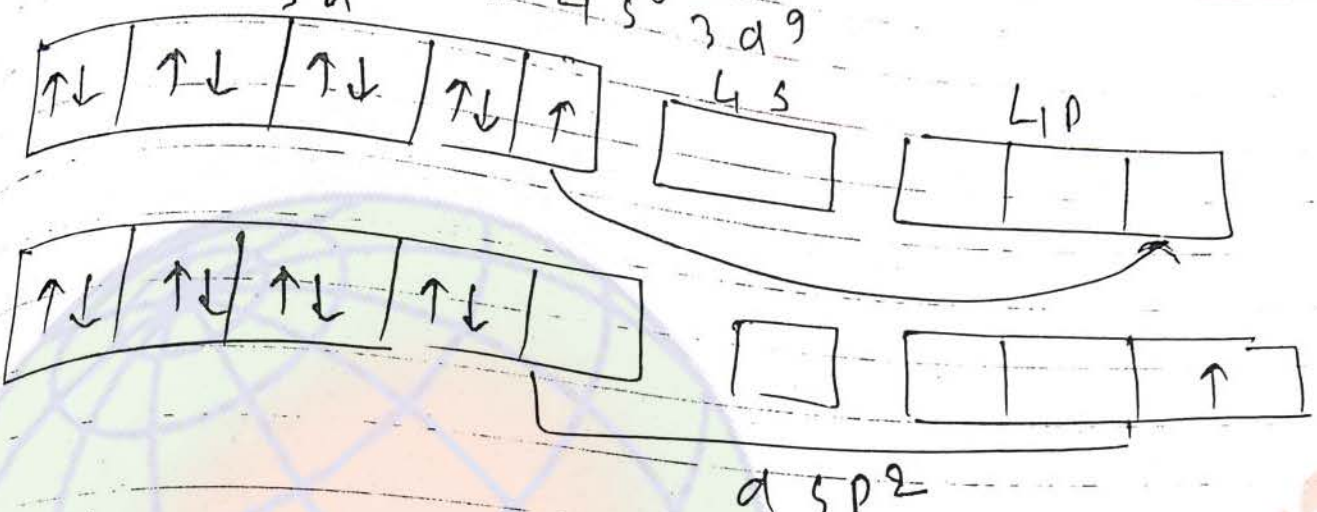
w.f.l

→ Tetrahedral

→ Para ($\mu_s = 2.83$)

$[Cu(NH_3)_4]^{+2}$

$Cu^{+2} = (Ar)\ 4s^0\ 3d^9$



→ square planar

→ para ($\mu_s = 1.73$)

Note - Pt^{+2}, Pd^{+2}, Au^{+3} (d^8)

→ Strong / weak field ligand
(pairing always occurs)

→ dsp^2, square planar

→ dia, $\mu_s = 0$

eg $[PtCl_4]^{-2}$, $[PdCl_4]^{-2}$, etc.

CN = 6 (sp^3d^2 / d^2sp^3)

1) If (n-1) d orbitals participate in hybridisation then complex is called as inner orbital / low spin complex.

(2) Such complex are found due to S.F.L (d^2sp^3)

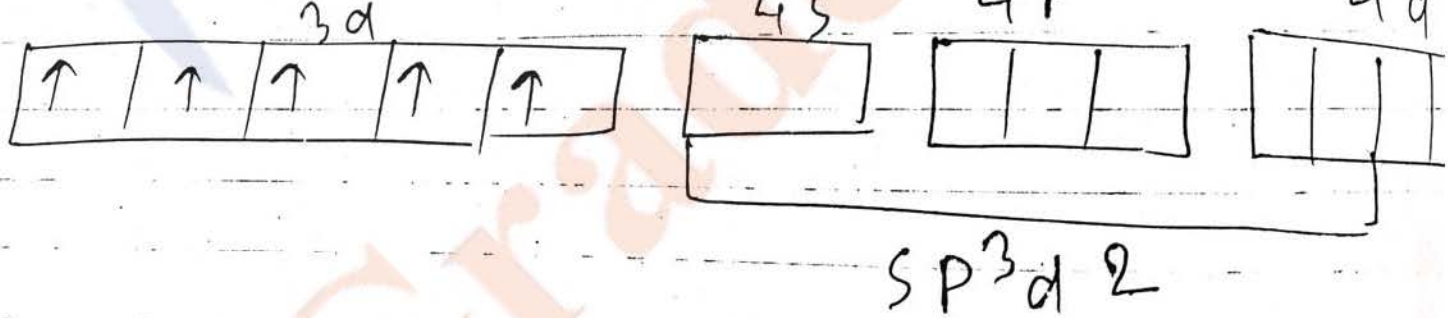
(1) If nd orbitals participate in hybridisation then complex is called as outer orbitals / high spin complex

(2) Such complex are formed due to W.F.L (sp^3d^2)

Total spin = $\pm \frac{1}{2}$ (No of unpaired e^-)

(1) $[FeCl_6]^{-3}$

$Fe^{+3} = [Ar]\ 4s^0\ 3d^5$



sp^3d^2

Cl^- is W.F.L

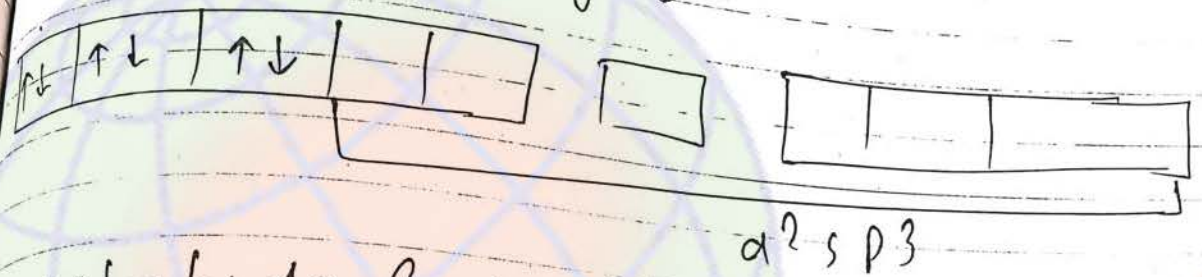
→ Octahedral, para (μ_s = S.O)

→ Outer orbital / high spin complex

$[Co(NH_3)_6]^{+3}$

$Co^{+3} = [Ar]\ 4s^0\ 3d^6$

NH_3 is s.f.l

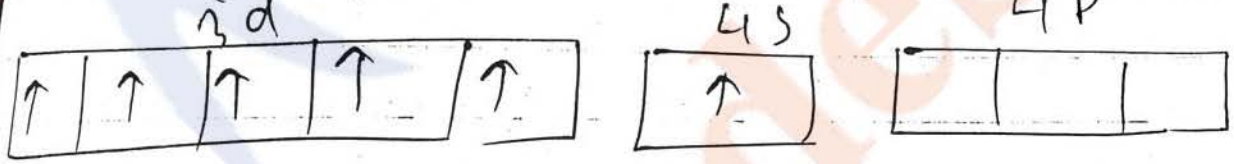


→ octahedral, dia ($\mu_s = 0$)

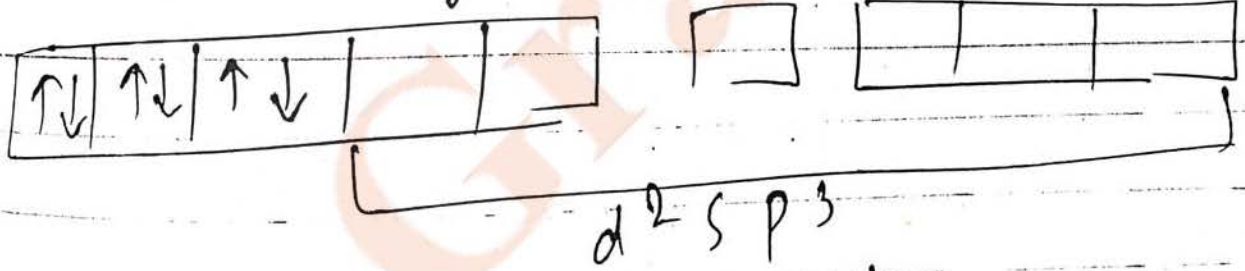
→ inner orbital / low spin complex

3) $[Cr(CO)_6]$

$Cr = [Ar]\ 4s^1\ 3d^5$



CO is S.f.l

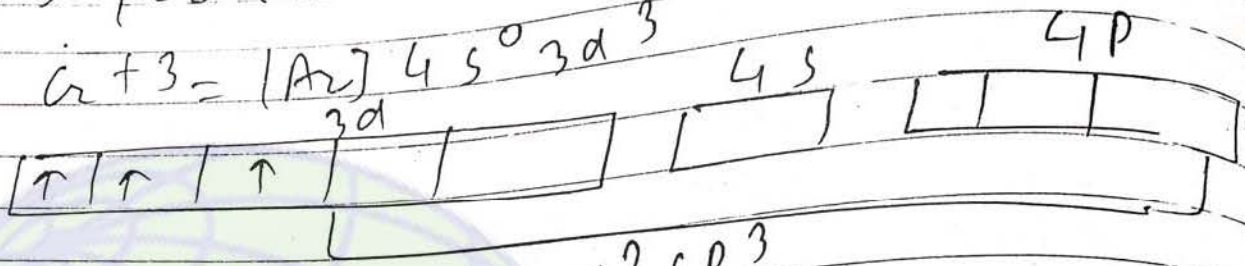


→ octahedral, dia ($\mu_s = 0$)

→ inner orbital / low spin complex.

(4) $[Cr(NH_3)_6]^{+3}$

$Cr^{+3} = [Ar]\ 4s^0\ 3d^3$



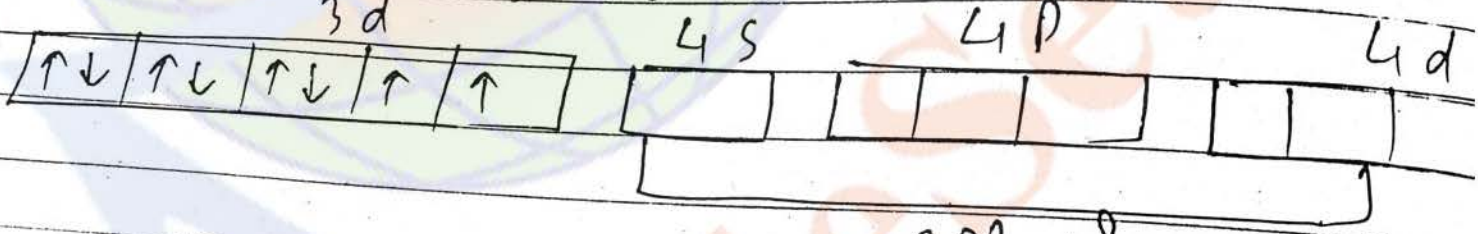
d^2sp^3

→ Octahedral, para ($\mu_s = 3.9$)

→ inner orbital / low spin complex.

(5) $[Ni(NH_3)_6]^{+2}$

$Ni^{+2} = [Ar]\ 4s^0\ 3d^8$



sp^3d^2

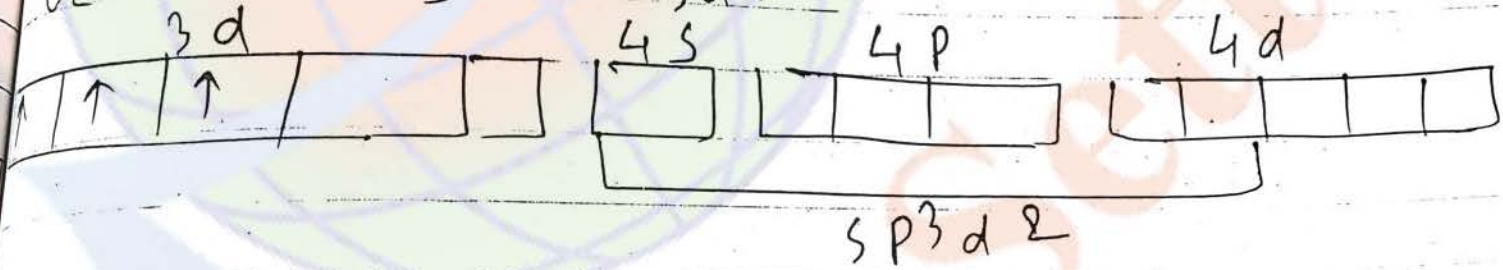
→ Octahedral, para ($\mu_s = 2.83$)

→ Outer orbital / high spin complex

Ex:- In octahedral complex if ligands are strong field then pairing occurs in following case

$[Cr(H_2O)_6]^{+3}$

$Cr^{+3} = [Ar]\ 4s^0\ 3d^3$



H_2O is w.f.l

→ Octahedral, para ($\mu_s \approx 3.9$)

→ Outer orbital / high spin complex

$$[Cr(ox)_3]^{-3}$$

$$d^2sp^3$$

Crystal field theory (CFT)

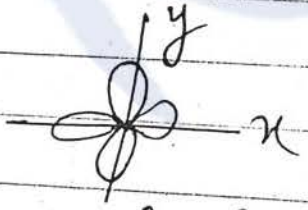
(1) CFT - In this theory anionic ligand are assumed as (-) point charge, central metal assumed as (+)ve point charge (Neutral ligands are assumed as dipole)

(2) The force of attraction b/w central metal and ligands is purely electrostatic

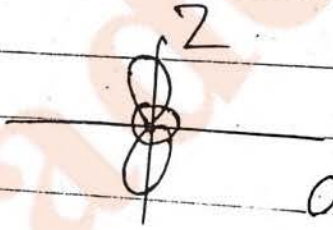
Octahedral crystal field

(1) In $d_{x^2y^2}$ and d_{z^2} orbital valence electron of central metal feel very high repulsion Hence their energy is raised.

(2) In d_{xy}, d_{yz}, d_{xz} orbital, valence electron of central metal feel very less repulsion. Hence their energy is lowered This process is called as d-orbital split

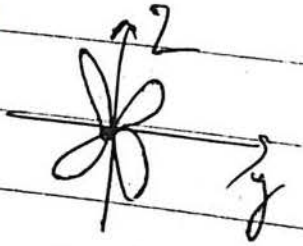


$d_{x^2-y^2}$

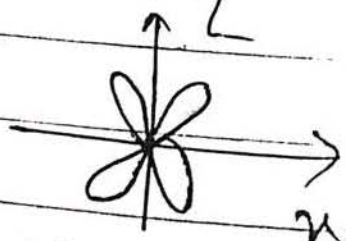


d_{z^2}

d_{xy}

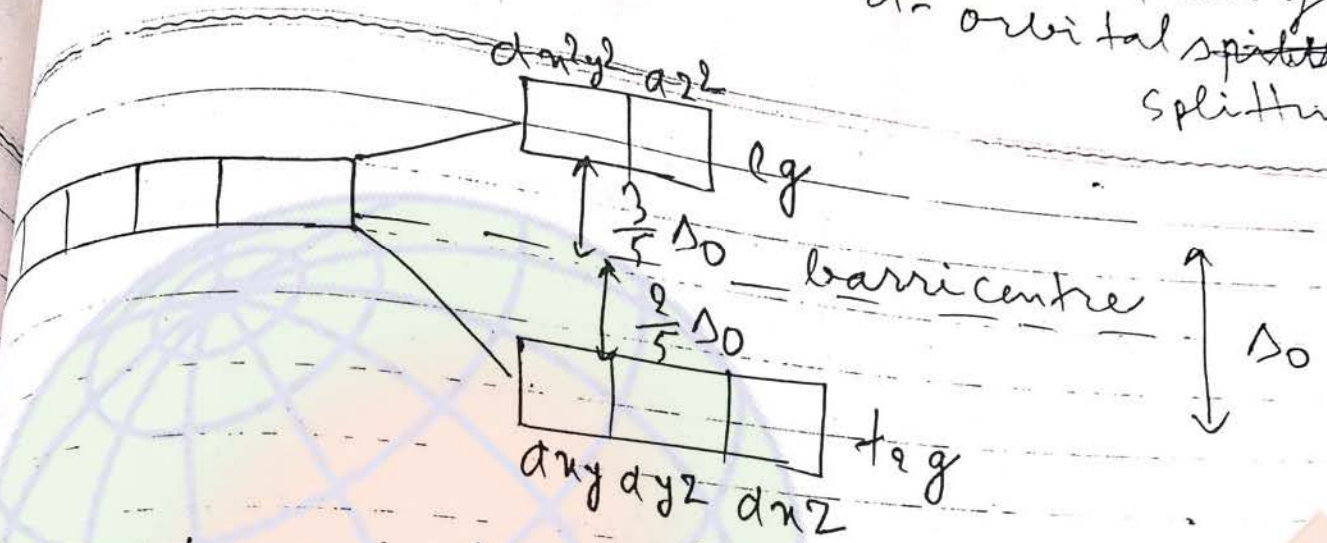


d_{yz}

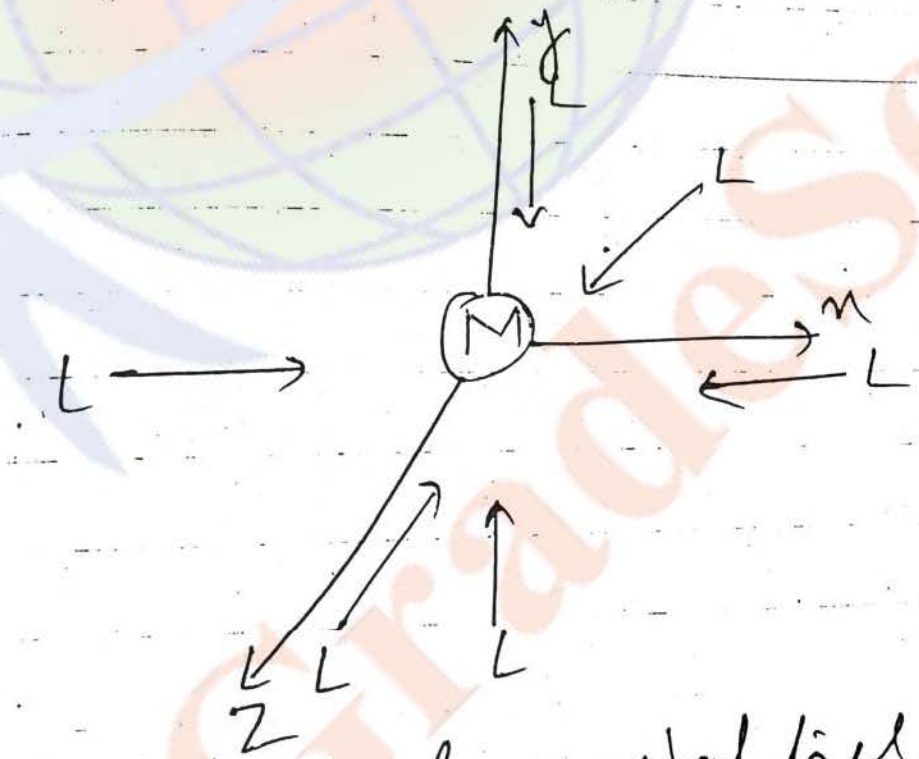


d_{xz}

ter repulsion felt by valence d electron of
al metal means greater d- orbital splitting



Δo = d - orbital splitting in octahedral crystal field.



Octahedral crystal field.

(3) Nature of ligands:-
Stronger is the ligand greater will be the value of Δ
eg $FeCl_6^{-3} < Fe(CN)_6^{-3}$

(4) O.S of central metal:-
O.S ↑, Δ ↑
eg - $Fe^{+3}(CN)_6^{-3} > Fe^{+2}(CN)_6^{-4}$

Stability constant (K_s):-
(1) It is an equilibrium constant of formation of complex.

$$M^{+a} + nL^{-x} \rightleftharpoons ML_n^{-6}$$

$$K_s = \frac{[ML_n^{-6}]}{[M^{+a}][L^{-x}]^n}$$

K_s ↑, stability of complex ↑

(2) Inverse of stability constant is instability constant / dissociation constant

Factor affecting stability complex
① Presence of chelate (chelate effect)
eg $Co(NH_3)_6^{+3} < Co(en)_3^{+3}$

Stability of complex ↑.

eg $NiCl_4^{-2} < Ni(NH_3)_6^{+2}$

Stronger is the ligand greater will be stability of complex.

eg- $FeCl_6^{-3} < Fe(CN)_6^{-3}$

Size of central metal :-

Size ↓ , stability of complex ↑

Order of ionic radius

$Mn^{+2} > Fe^{+2} > Co^{+2} > Ni^{+2} > Cu^{+2} < Zn^{+2}$

Order of stability of complex

$Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$

(Irving William order)

eg $MnCl_4^{-2} < NiCl_4^{-2}$

$Fe^{+3}(CN)_6^{-3} > Fe^{+2}(CN)_6^{-4}$

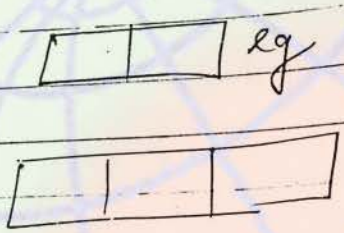
Which complex is most stable ?

$FeCl_6^{-3}$ (b) $Fe(NH_3)_6^{+3}$

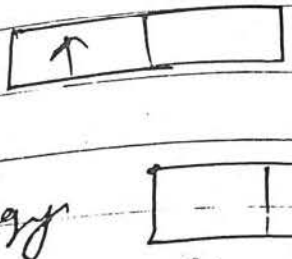
$Fe(C_2O_4)_3^{-3}$ (d) $Fe(CN)_6^{-3}$

Colour in Co-ordination compounds

(1) Acc to C F T unpaired e^- present in t_{2g} orbitals absorb light of a energy of a particular colour and excites to the vacant eg. hence complementary colour is observed in co-ordination compound.
(d-d transition)



$+h\nu$ (light energy of suitable frequency)



$$\Delta = h\nu = \frac{hc}{\lambda}$$

$$\boxed{\Delta \propto \nu \propto \frac{1}{\lambda}}$$

(2) In absence of ligands there is no d-orbital splitting hence compound becomes colourless.

Note: For colour in a compound both ligand and e^- are unpaired.

(3) As Δ changes, colour also changes.

$FeCl_2 \xrightarrow{H_2O} FeCl_2 \cdot 6H_2O$

$FeSO_4 \xrightarrow{H_2O} FeSO_4 \cdot 7H_2O$

SO_4 ka case me one molecule water add hota hai

eg (a) $[Ti(H_2O)_6]Cl_3 \xrightarrow[-6H_2O]{\Delta} TiCl_3$ (anhydrous colourless)

3d¹ violet

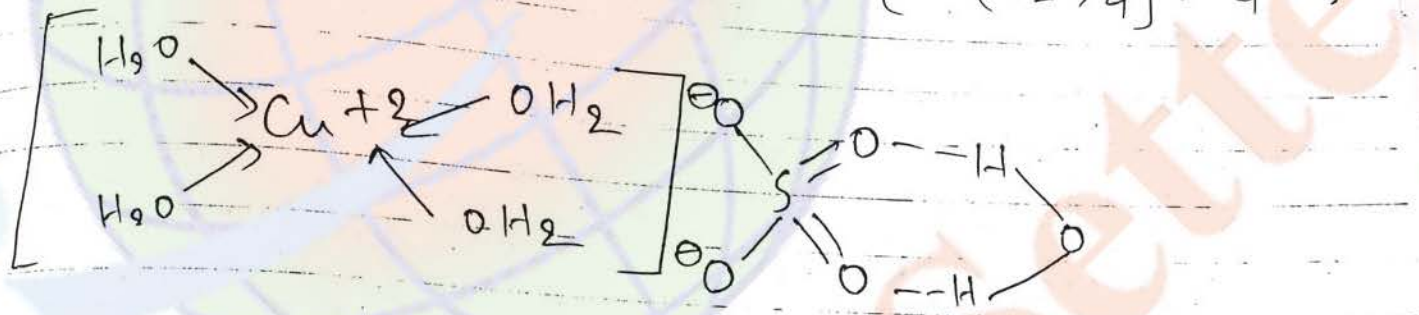
or

$TiCl_3 \cdot 6H_2O$

or

$TiCl_3(aq)$

(b) $CuSO_4$ (anhydrous) $\xrightarrow{H_2O}$ $Cu^{+2}SO_{4aq}$ or $CuSO_4 \cdot 5H_2O$ or $[Cu(H_2O)_4]SO_4 \cdot H_2O$



(c) $CuSO_4(aq) \xrightarrow{NH_3} [Cu(NH_3)_4]SO_4$

light blue — deep blue.

) $CuSO_4(aq) + KCN$ excess → Colourless complex.

(a) $CuCN$

(b) $Cu(CN)_2$

) $K_2[Cu(CN)_4]$

$K_3[Cu^{+1}(CN)_4]$

$3d^{10}$ colourless

(d) $K_2[Cu(CN)_4]$ coloured.

$\downarrow CN^-$ (R.A)

$K_3[Cu^{+1}(CN)_4]$

Note- with Cl^-, CN^-, and SCN^- (+1) O.S of Cu is more stable
$CoCl_3 \cdot 5NH_3$

Isomerism

Types

(1) Structural (due to difference in ligands)
- Ionisation Co-ordination
- Linkage
- Hydrate

(2) Stereo (due to difference in arrangement of ligands)
- Geometrical
- optical

Ionisation isomerism:-

It arised due to exchange of any anionic ligand with anion outside of co-ordinate sphere

eg $[Co(NH_3)_5SO_4]Cl$

$[Co(NH_3)_5Cl]SO_4$

Q) Will $Co(NH_3)_4Br_2Cl$ show ionisation isomerism

Ans- yes $[Co(NH_3)_4Br_2]Cl$

$[Co(NH_3)_4Br Cl]Br$

Co-ordination isomerism
Both cation and anion must be complex
eg $[Cr(NH_3)_6][Co(CN)_6]$
$[Cr(NH_3)_5CN][Co(NH_3)(CN)_5]$

Linkage isomerism:-
Any ligand must be ambident

$[Co(NH_3)_5NO_2]SO_4$
$[Co(NH_3)_5ONO]SO_4$

Hydrate isomerism
It arises due to exchange of H_2O molecules.
$[Co(H_2O)_6]Cl_3$
$[Co(H_2O)_5Cl]Cl_2 H_2O$

Q) What type of isomerism is present in following pairs

(a) $[Co(NH_3)_5SCN]SO_4$ and $[Co(NH_3)_5SO_4]SCN$
Ans- ~~isomerism~~ Ionisation.

(b) $[Co(NH_3)_5SCN]SO_4$ and $[Co(NH_3)_5NCS]SO_4$
Ans- linkage

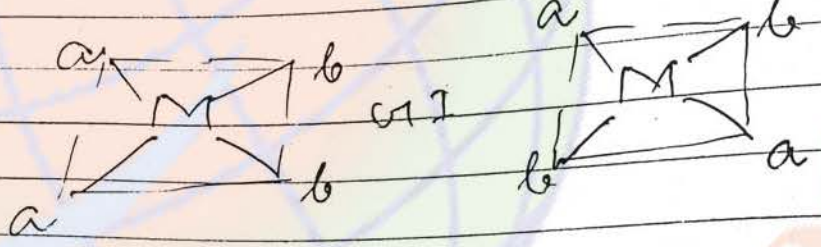
Q(c) What type of isomerism can be shown by
$[Co(NH_3)_5SCN]SO_4$
Ans- Ionisation and linkage.

Geometrical isomerism Cn I

(1). If due to exchange of ligands within co-ordination sphere changes geometry or arrangement of ligands then geometrical isomerism arises (Geometrical isomerism means more than one possible) geometries

(2) Tetrahedral complex do not show Cn I

(3) Octahedral and square planar complex can show Cn I.



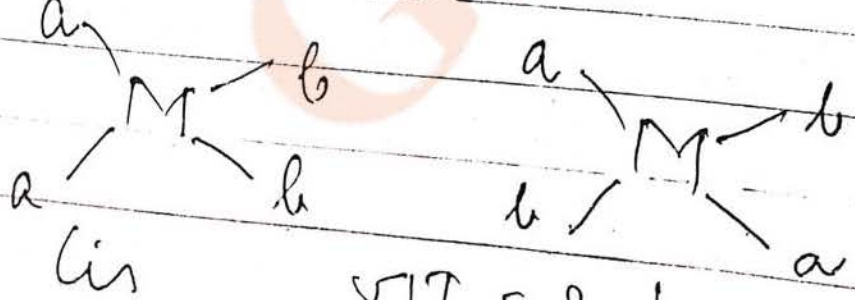
Square planar complex:-

Case I: Ma_2b_2

M → Central metal

a and b are monodentate ligands.

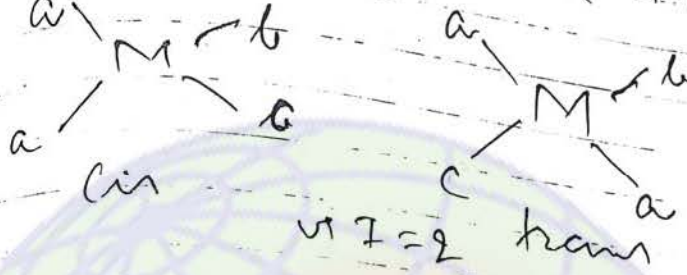
$[Pt(NH_3)_2Cl_2]$



Cn I = 2 trans

Case II Ma_2bc

$[Pt(NH_3)_2ClBr]$ $[Pt(NH_3)(Py)Cl_2]$



VI = 2

Case III $Mabcd$

$[Pt(NH_3)(Py)ClBr]$

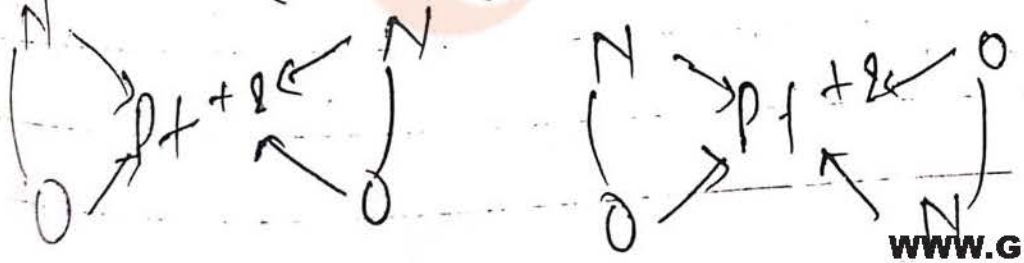
VII = 3

2 cis and 1 trans (w.r.t any 2 ligands)

Case IV $M(ab)_2$

(ab) → unsymmetrical bidentate

$[Pt(gly)_2]$

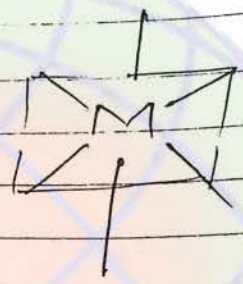


Note:- Ma_4, Ma_3b $M(aa)_2$ complex. do not show G.I

Octahedral complex:-

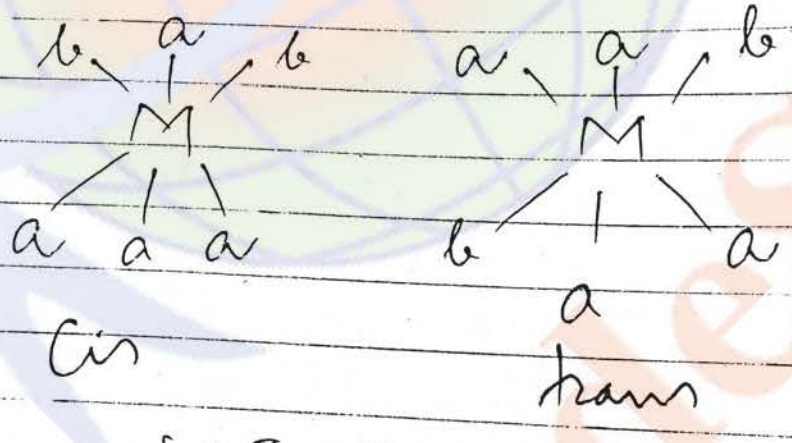
12 - 90° angles

3 - 180° angles.



Case I: Ma_4b_2

$[Co(NH_3)_4Cl_2]^+$



G.I = 2

Case II:- Ma_4bc

$[Co(NH_3)_4ClBr]^+$

G.I = 2

Case III : Ma_3b_3

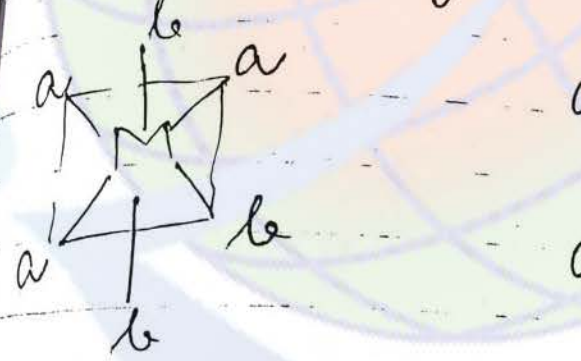
$[Pt(NH_3)_3(NO_2)_3]^+$

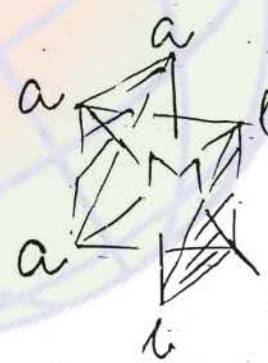
→ 2 GI are possible:

fac (facial) and mer (meridional)

→ In fac isomer any face must have three similar ligands.

→ In mer isomer, meridian must have three similar ligands.





a	b
×4	0
✓3	1
✓2	2
×1	3
×0	4

IV $Mabcdef$

$[Pt(NH_3)(Py)(NO_2)ClBrI]$

GI = 15

Any 2 ligands

12 times 90° angle

3 times 180° angle

Case V $M(ab)_3$

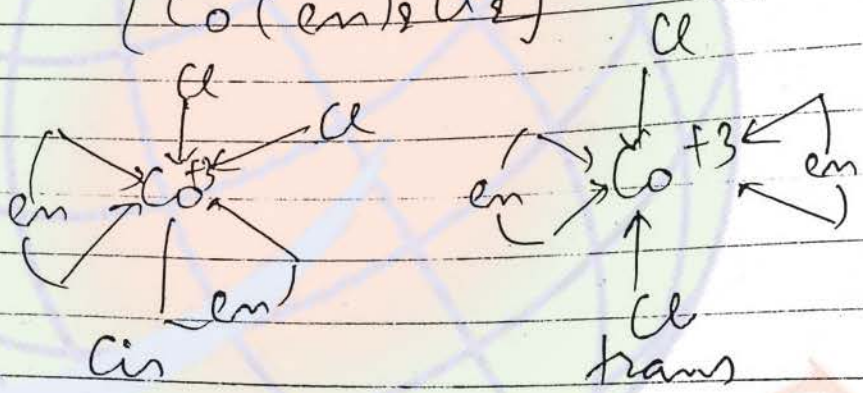
$[P + (gly)_3]^+$

G.I = 2

Similar as Ma_3b_3

Case VI $M(aa)_2b_2$

$[Co(en)_2Cl_2]^+$



G.I = 2

Case VII : $M(aa)_2bc$

$[Co(en)_2ClBr]^+$

G.I = 2

Note – Ma_6, Ma_5b, $M(aa)_3$ complex do not show G.I

Optical isomerism (OI)

1) Co-ordination compound which are non superimposible mirror image of each other are called as optical isomers or optically active or enantiomers.

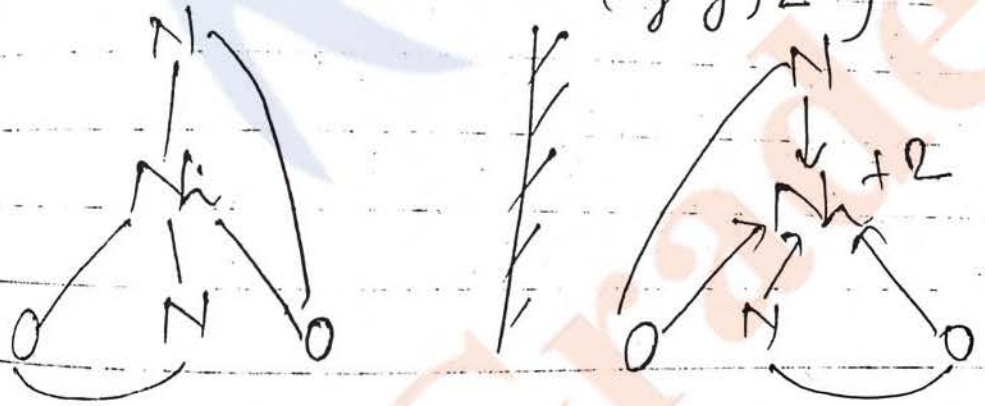
2) They are 2 types :- d and l

3) Optical isomers do not have any plane of symmetry

4) Square planar complex do not show OI

5) Tetrahedral complex Mabcd, M(ab)2 etc show OI

M(ab)2 [Ni(gly)2]



Non superimposible mirror image
Hence optically active.

6:45

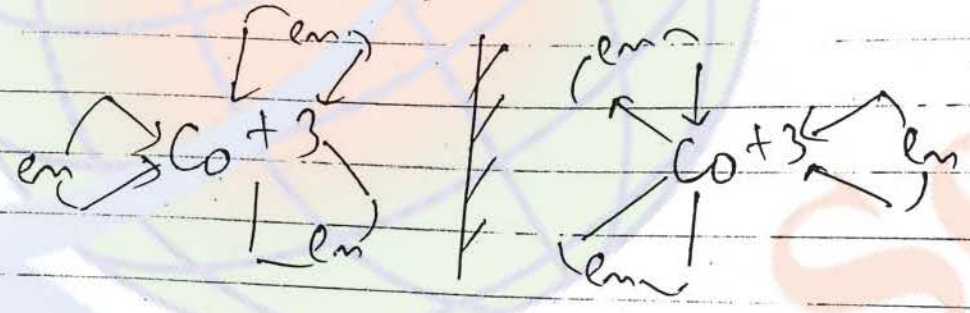
Octahedral :- To show O.I at least one of the geometries must be optically active.

Case I $M(aa)_3$ and $M(ab)_3$

$M(aa)_3$ → Non optically active → SI = 2

$M(ab)_3$ → SI = 2 → optically active = 4 → SI = 4

$[Co(en)_3]^{+3}$



Non superimposible mirror image
Hence optically active

$[Cr(C_2O_4)_3]^{-3}$ $M(aa)_3$ SI ✗ OI ✓

$[Pt(gly)_3]^{+}$ $M(ab)_3$ SI ✓ OI ✓

** Case II ~~$M(aa)_2b_2$ and~~

* Case II : $M(aa)_2bc$ and $M(a_2a)_2bc$

cis → optically active
trans → optically inactive

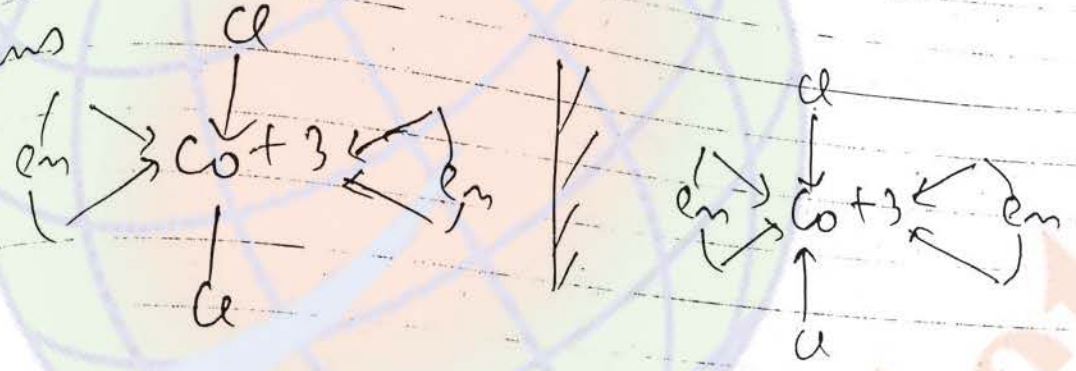
SI = 3

cis → optically active
trans → optically inactive

SI = 3

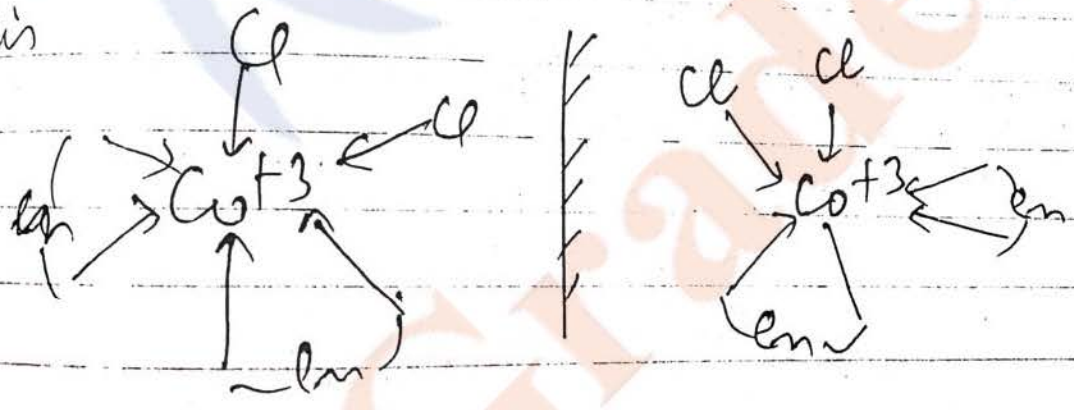
$[Co(en)_2Cl_2]^+$

trans



Superimposible mirror image hence optically inactive

cis



Non superimposible mirror image. Hence optically active

$[Co(en)_2Cl_2]^+$ O.I ✓

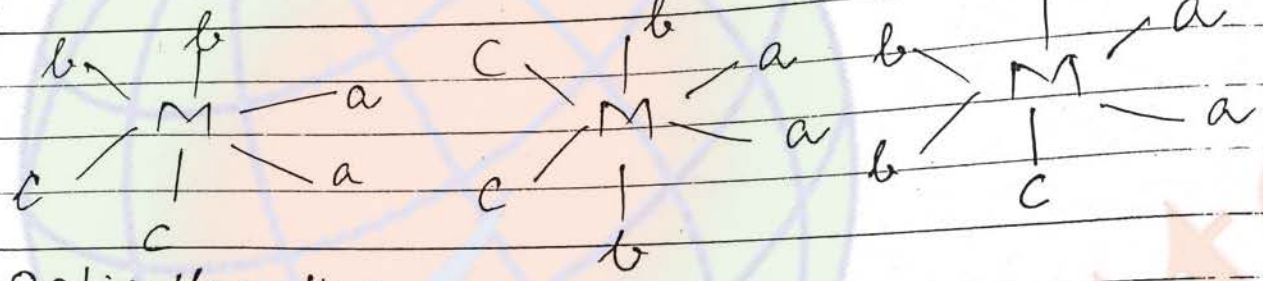
Trans $[Co(en)_2Cl_2]^+$ OI ✗

Cis $[Co(en)_2Cl_2]^+$ OI ✓

Note: Ma_4b_2, Ma_4bc, Ma_3b_3 complexes do not show O.I.

**

Case IV $M(aa)b_2c_2$

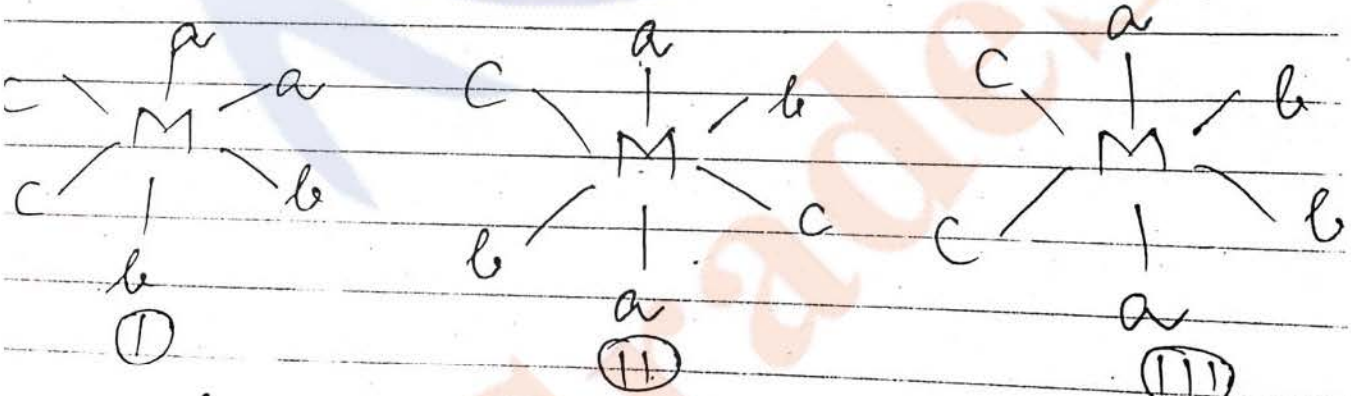


Optically active

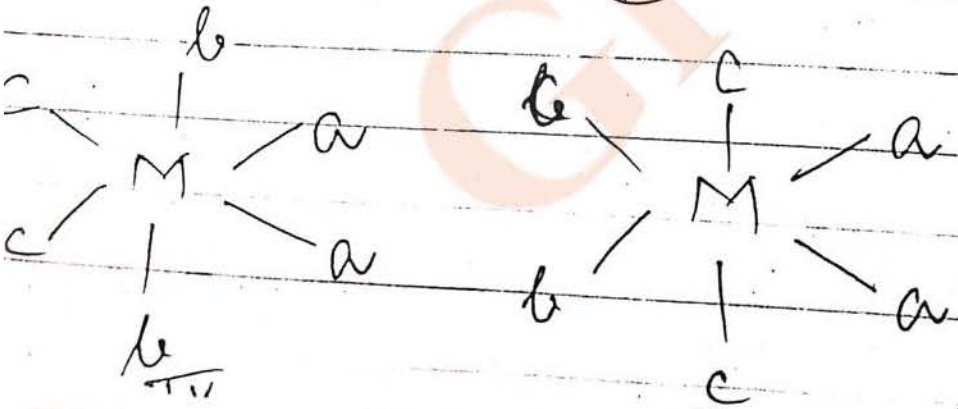
$\sigma I = 3$

Hence S.I = 4

Case (V) $Ma_2b_2c_2$



(I) (II) (III)



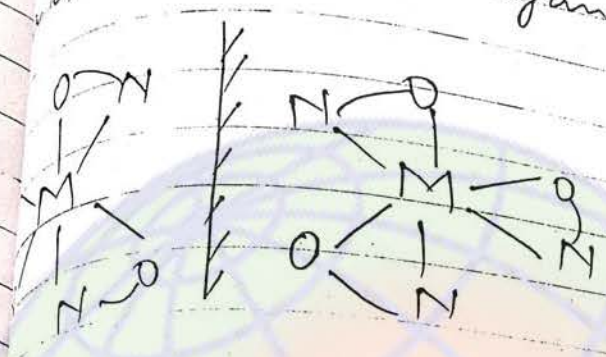
$\sigma I = 5$

only (I) O. active

Hence S.I = 6

Ma_4b_2, Ma_4bc, Ma_3b_3 complex as well as shows
I while $M(ab)_3$ shows O.I

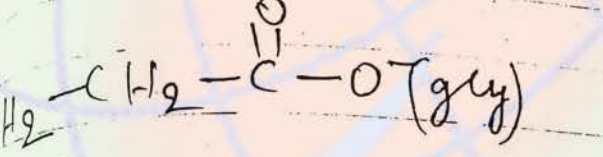
(b) ⇒ Bidentate ligand



a b ⇒ Two monodentate ligand

not

$Pt(gly)_3] \simeq Pt(ab)_3$



Case	G I	O I	S I
Ma_4b_2	✓	X	✓ 2
Ma_4bc	✓	X	✓ 2
Ma_3b_3	✓	X	2
abcdef	✓	✓	3 0
$M(aa)_3$	X	✓	2
$M(ab)_3$	✓	✓	4
$M(aa)_2b_2$	✓	✓	3
$M(aa)_2bc$	✓	✓	3
$M(aa)b_2c_2$	✓	✓	4
$Ma_2b_2c_2$	✓	✓	6