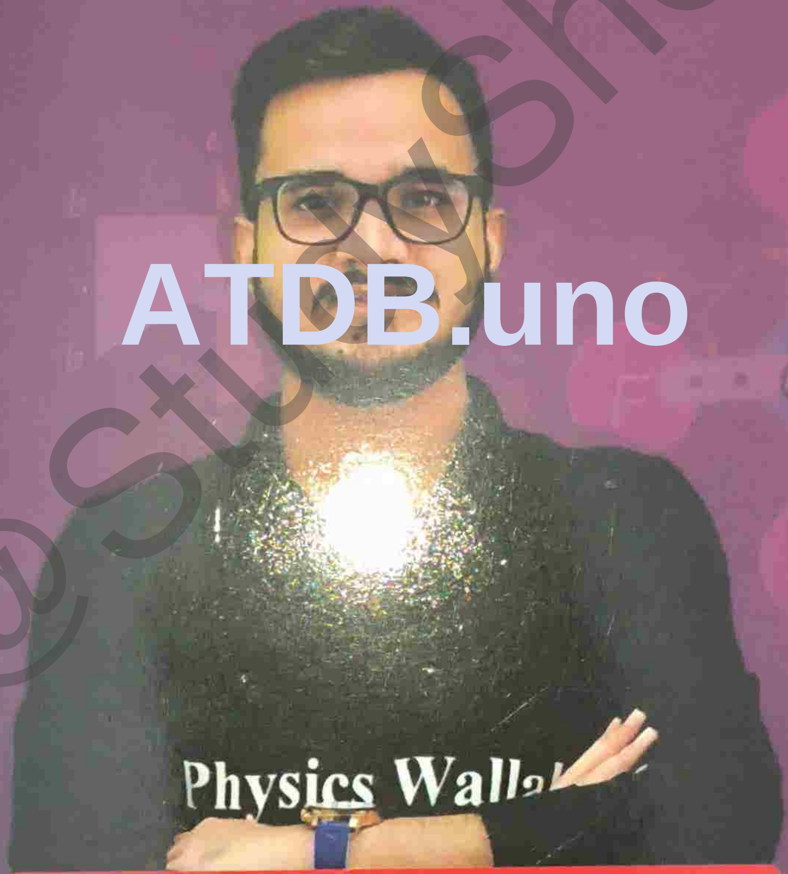
Inorganic Chemistry

Easy Notes

Class Notes in Handwritten Format

Class 11 + 12

NEET + JEE Main



Om Pandey
(IIT - Delhi)

Best Backlog Killer NOTES

Most Creative and Relevant Content | Pure Classroom Feel | Basic to Kattar NEET
JEE Main & JEE Advanced PYQ's | 25 Years NEET PYQ's

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Contents

Special book for -

Future Doctors ❤

मैं ज्वाला हूँ
बुझी राख नहीं,
मैं कर्म के साथ हूँ
किस्मत के हाथ नहीं।

Chapter 1

Classification of Elements and Periodicity in Properties

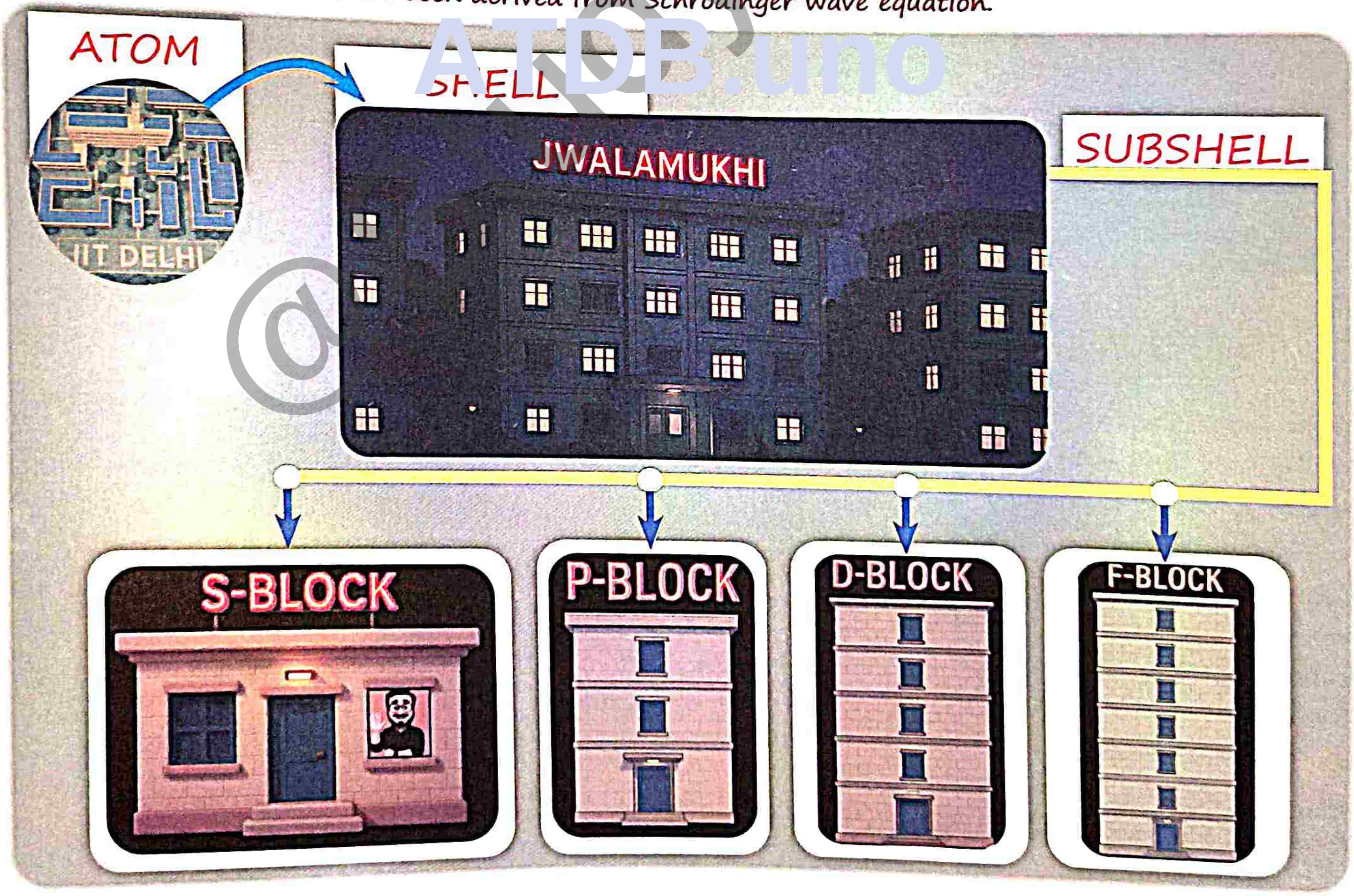
JEE Main & NEET

Syllabus

Modern periodic law and present form of the periodic table, s, p, d and f block elements, periodic trends in properties of elements-atomic and ionic radii, ionization enthalpy, electron gain enthalpy, valence, oxidation states and chemical reactivity.

QUANTUM NUMBERS

The set of four numbers required to defined an electron completely in an atom are called quantum numbers. The first three have been derived from Schrodinger wave equation.

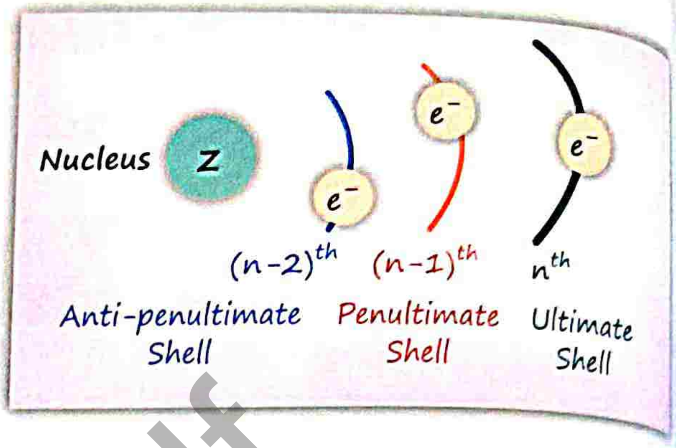


[I] Principal Quantum Number (n)

It describes the size of the electron wave and the total energy of the electron. It has integral values 1, 2, 3, 4... etc. and is denoted by K, L, M, N, ... etc.

Number of subshell present in n^{th} shell = n

n	subshell
1	s
2	s, p
3	s, p, d
4	s, p, d, f



☐ Number of orbitals present in n^{th} shell = n^2

[II] Azimuthal Quantum Number (ℓ)

It describes the shape of electron cloud and the number of subshells in a shell.

◆ It can have values from 0 to [n–1].

◆

Value of l		Subshell
0	⟶	s
1	⟶	p
2	⟶	d
3	⟶	f
4	⟶	g

Note

The notations for the sub-energy levels come from the spectroscopic term that were used to describe the atomic spectra and have the following full form:

s ⟶ sharp
p ⟶ principal
d ⟶ diffused
f ⟶ fundamental
g ⟶ generalized

[III] Magnetic Quantum Number (m)

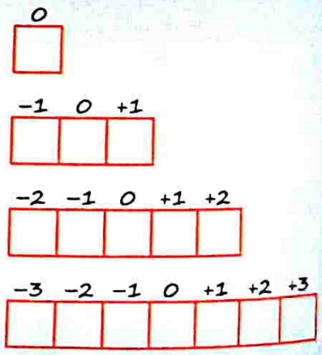
It describes the orientation of an orbital within a subshell. It can have values from –ℓ to +ℓ including zero, i.e., total (2ℓ + 1) values. Each value corresponds to an orbital, s-subshell has one orbital, p-subshell three orbitals (p_x, p_y and p_z), d-subshell five orbitals (d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}) and f-subshell has seven orbitals.

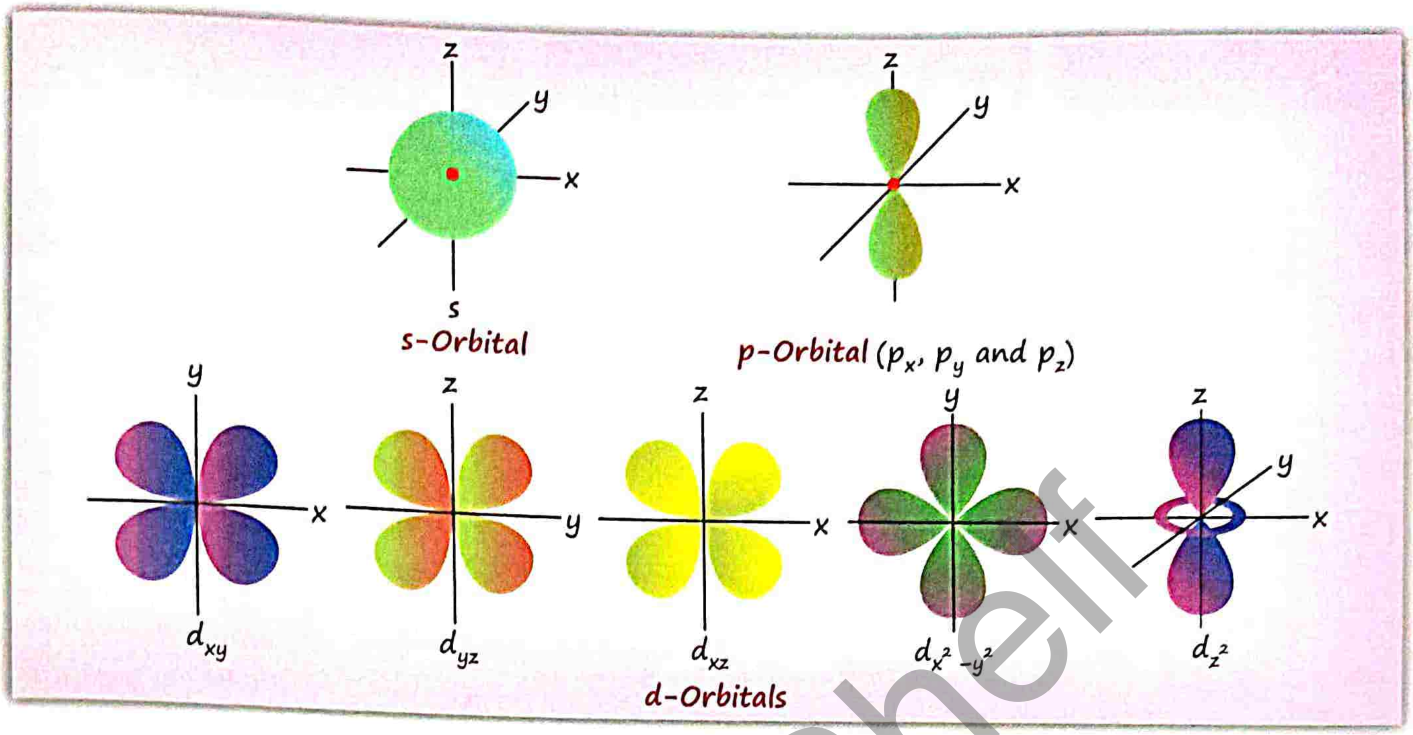
s ⟶ ℓ = 0, m = 0

p ⟶ ℓ = 1, m = –1, 0, +1

d ⟶ ℓ = 2, m = –2, –1, 0, +1, +2

f ⟶ ℓ = 3, m = –3, –2, –1, 0, +1, +2, +3

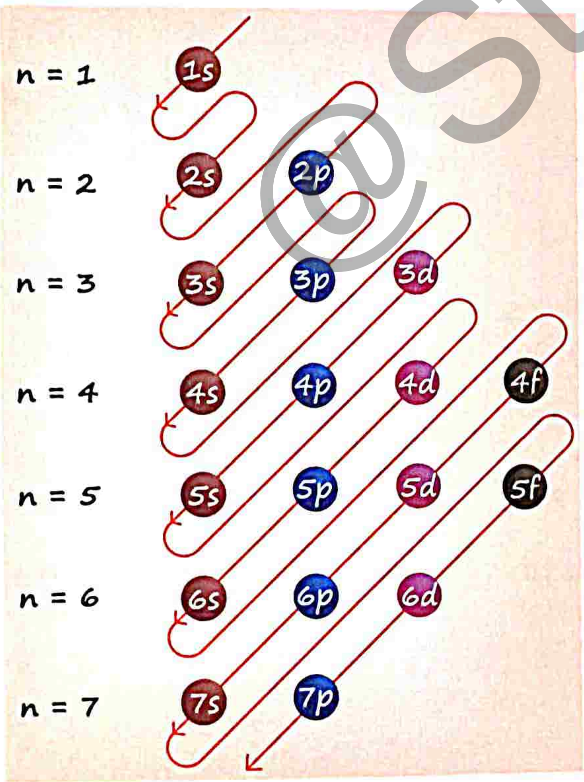




[IV] Spin Quantum Number (s)

It describes the spin of the electron. It has values +1/2 and −1/2. (+) signifies clockwise spinning and (−) signifies anticlockwise spinning.

n+l RULE AND MODERN PERIODIC TABLE

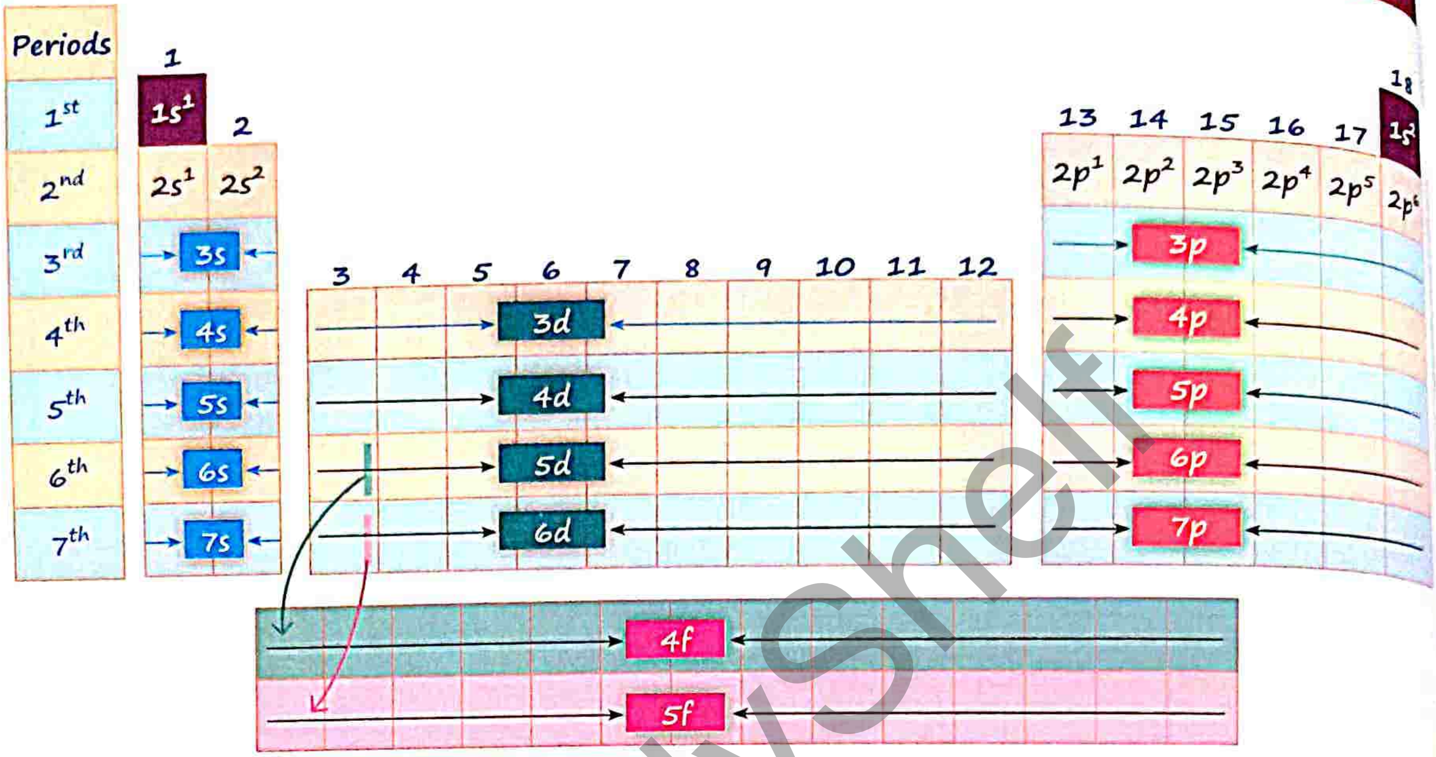


Max. n	Energy Sequence and Set of Subshells	No. of electrons in set of subshell
1	1s	2
2	2s 2p	2 + 6 = 8
3	3s 3p	2 + 6 = 8
4	4s 3d 4p	2 + 10 + 6 = 18
5	5s 4d 5p	2 + 10 + 6 = 18
6	6s 4f 5d 6p	2 + 14 + 10 + 6 = 32
7	7s 5f 6d 7p	2 + 14 + 10 + 6 = 32

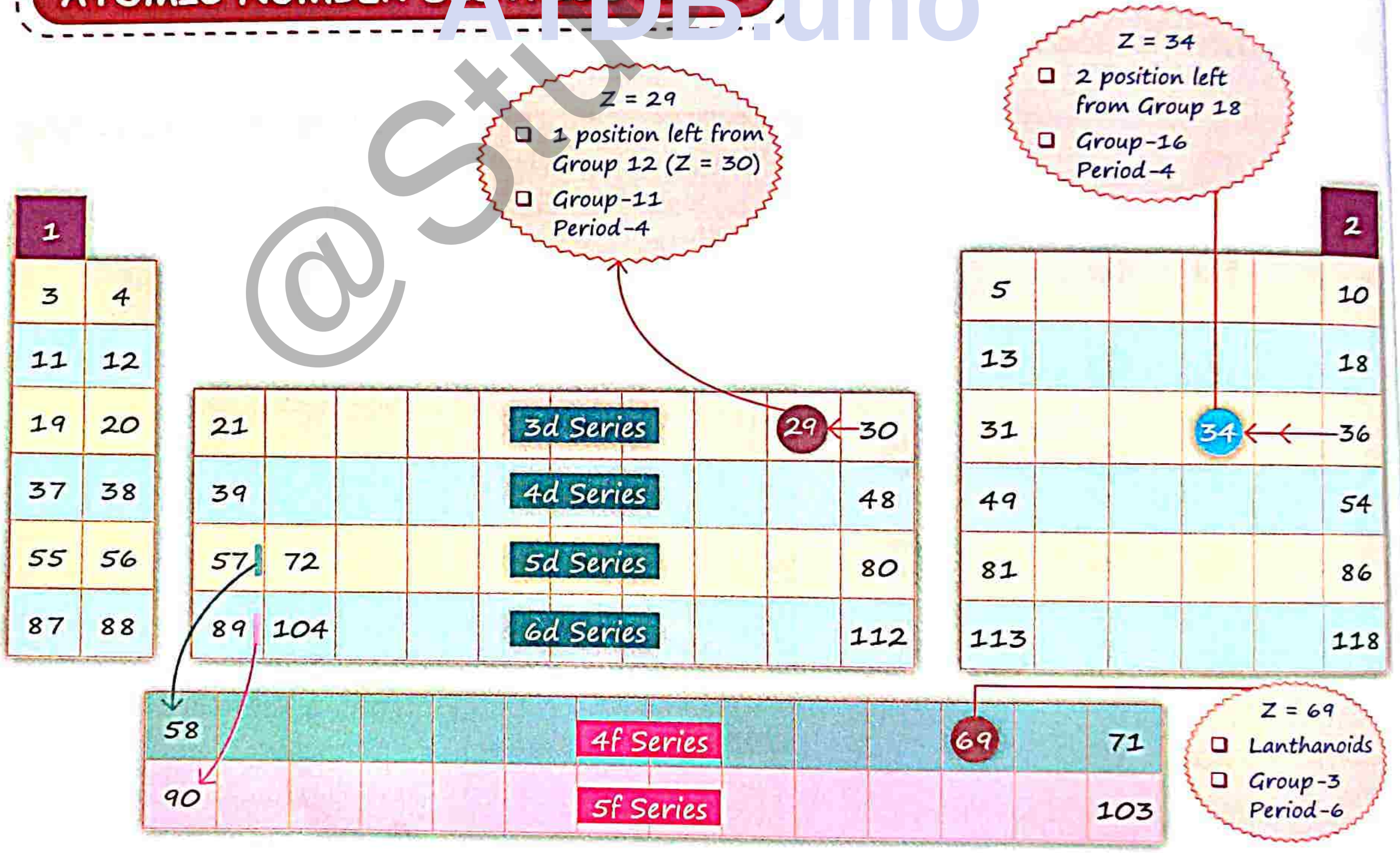
Block: s, p, d, f

7 Periods: Horizontal Rows

18 Groups: Vertical Columns



ATOMIC NUMBER DISTRIBUTION



Z = 29
☐ 1 position left from Group 12 (Z = 30)
☐ Group-11
Period-4

Z = 34
☐ 2 position left from Group 18
☐ Group-16
Period-4

Z = 69
☐ Lanthanoids
☐ Group-3
Period-6

Period Number	Range
1	1-2
2	3-10
3	11-18
4	19-36
5	37-54
6	55-86
7	87-118

La_{57} $Ce_{58} \longrightarrow Lu_{71}$ Hf_{72}

Ac_{89} $Th_{90} \longrightarrow Lr_{103}$ Rf_{104}

Lanthanoid Series

Period No.	6
Group No.	3

Actinoid Series

Period No.	7
Group No.	3

MODERN PERIODIC TABLE

s-Block (ns) d-Block (n − 1)d p-Block (np)

Transition metals (d-Block)

Group Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1 (1s)	H																	He
2 (2s, 2p)	Li	Be											B	C	N	O	F	Ne
3 (3s, 3p)	Na	Mg											Al	Si	P	S	Cl	Ar
4 (4s, 3d, 4p)	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5 (5s, 4d, 5p)	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6 (6s, 4f, 5d, 6p)	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7 (7s, 5f, 6d, 7p)	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

The Rare Earths, (n − 2)f

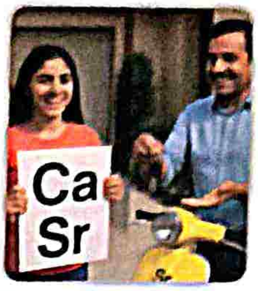
f-Block															
Lanthanide series (4f) Period : 6	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinide series (5f) Period : 7	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

देशी जुगाड़

Alkali Metals (Group-1)

HLiNa ne Ki Rb Cs Fariyad

Alkaline Earth Metals (Group-2)



Beti Mage Car Scooter Baap Razi

Group-13: Boron Family

Bengan Alu Gajar In Thaila

Group-14: Carbon Family

Cahei Sita Ge Suno Prabhu

Group-15: Nitrogen Family

Nana Patekar Aishwarya Sb Bimar

Group-16: Oxygen Family

O S Se Te Po

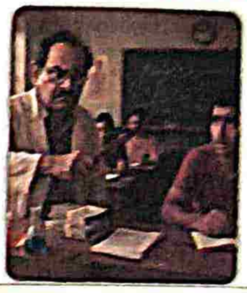
Group-17: Halogen Family

Fir Cal* Bahar I Aunty

Group-18: Inert Gas Family

Heena Neena Aur Kareena
Xerox Rangeen

1st Transition Series: 3d Series



Science Ticher Very Cruel
Mange Fees Copy Niha
Cukker Zindabad

2nd Transition Series: 4d Series

Yari Zra Nibhana
Mout Tc Rukawat Rah
Pde Age Cudo

3rd Transition Series: 5d Series

La HafTa Warna Re
Osama Idher
Pitayi Aur Hogi

4th Transition Series: 6d Series

Ac Rutherford Dube
Sagar me Bohr Hs Mat
Darse Royga Caun

Group-3

ScYLa Ac me
rahti hai

Group-4

Tina Zor Haaf Rafi* hai

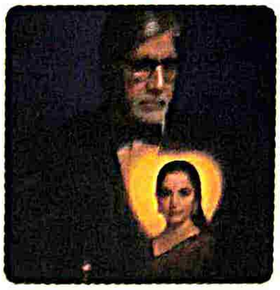
Group-5

Vo Nabab Tha Dabang

Group-6

Crying Moti Wife

Group-7

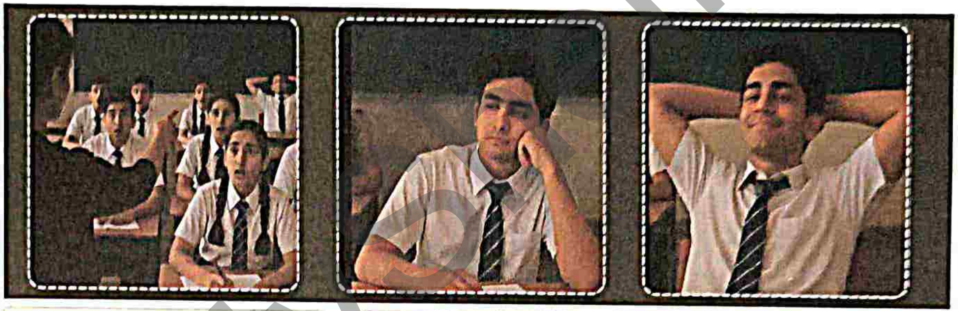


Maan Tac* Rekha

Group-8 and 9

Fer* Rouya Osama Con* Rahega Iran me

Group-10, 11, 12



Nahi Padoge to Pitoge

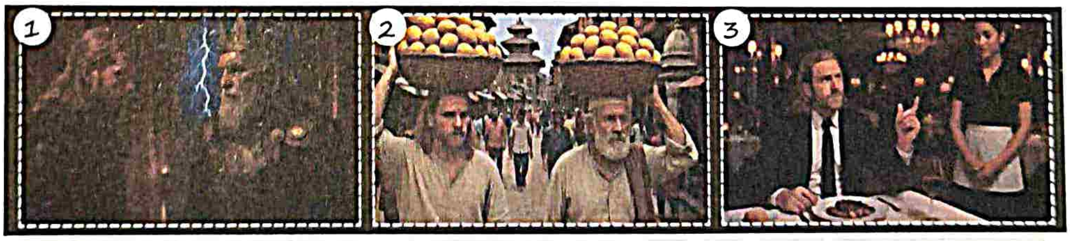
Cyu Aage Aau

Zindagi Cadbury Hogyi

Lanthanoids → Ist Inner Transition Series (Part of Group 3)

Cene Pr Nadiyan Prem Ki Samayi Eu Gadgad Tab Dyl Ho gya Engineer Tum Yebhi Lu

Actinoids → IInd Inner Transition Series (Part of Group 3)



Thor Ke Papa ne U bola Nepal me Purane Am Cam Bikenge Cafe me jana Ease Farmana Madam Noodles Lare

Place of Hydrogen is not fixed in Periodic Table because it shares properties with both alkali metals and halogens.

IUPAC NAME, COMMON NAME AND POSITION OF ELEMENTS HAVING ATOMIC NUMBER 101 TO 118

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

Suffix – ium

101 : Unnilunium (Unu)

102 : Unnilbium (Unb)

105 : Unnilpentium (Unp)

110 : Ununnilium (Uun)

118 : Ununoctium (Uuo)

119 : Ununennium (Uue)

Z = 143
IUPAC Name
↓
Unquadtrium
UQT ♥

Atomic Number 101 to 118

1. Mendeleev [101] ko mila Nobel [102] in Lowrence [103]
2. Rutherford [104] Dube [105] Sea [106] me Bohr [107] Hass [108] Meit [109]
3. Dar [110] se Roe [111] Coper [112]
4. Niho [113] Fle [114] to Mosco [115] to Live [116] Ten [117] Ogan [118]

Atomic Number	Name
101	Mendelevium (Md)
102	Nobelium (No)
103	Lawrencium (Lr)
104	Rutherfordium (Rf)
105	Dubnium (Db)
106	Seaborgium (Sg)
107	Bohrium (Bh)
108	Hassium (Hs)
109	Meitnerium (Mt)

Atomic Number	Name
110	Darmstadtium (Ds)
111	Roentgenium (Rg)
112	Copernicium (Cn)
113	Nihonium (Nh)
114	Flerovium (Fl)
115	Moscovium (Mc)
116	Livermorium (Lv)
117	Tennessine (Ts)
118	Oganesson (Og)

Position in Periodic Table

		101 102 103
Period No.	→	7
Group No.	→	3 (Part of actinoids)

	104	105	106	107	....	118
	↓	↓	↓	↓		↓
Group No. →	4th	5th	6th	7th		18th
Period No. →	7					

1. The IUPAC symbol for the element with atomic number 119 would be–

[8 April, 2019 (Shift-2)]

(a) Unh (b) Uue (c) Uun (d) Une

Sol. (b)

2. Lanthanoids and Actinoids are present in which of the following group–

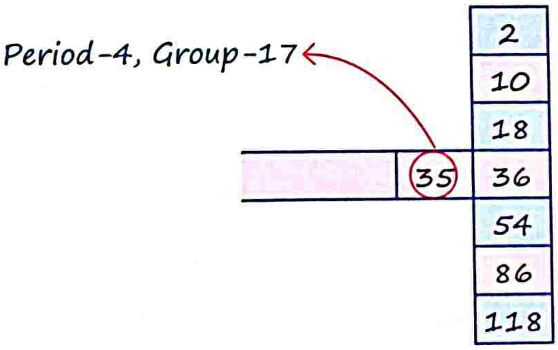
(a) Group 1 (b) Group 3 (c) Group 17 (d) Group 18

Sol. (b)

3. If the atomic number of an element is 35, it will be placed in the periodic table in the–

(a) Group 1 (b) Group 3 (c) Group 17 (d) Group 18

Sol. (c)



4. Match List-I with List-II [30 Jan, 2023 (Shift-1

List-I (Atomic Number)		List-II (Block of Periodic Table)	
(A)	37	(i)	p-block
(B)	78	(ii)	d-block
(C)	52	(iii)	f-block
(D)	65	(iv)	s-block

Choose the correct answer from the options given below:

(a) A-ii, B-iv, C-i, D-iii

(b) A-i, B-iii, C-iv, D-ii

(c) A-iv, B-iii, C-ii, D-i

(d) A-iv, B-ii, C-i, D-iii

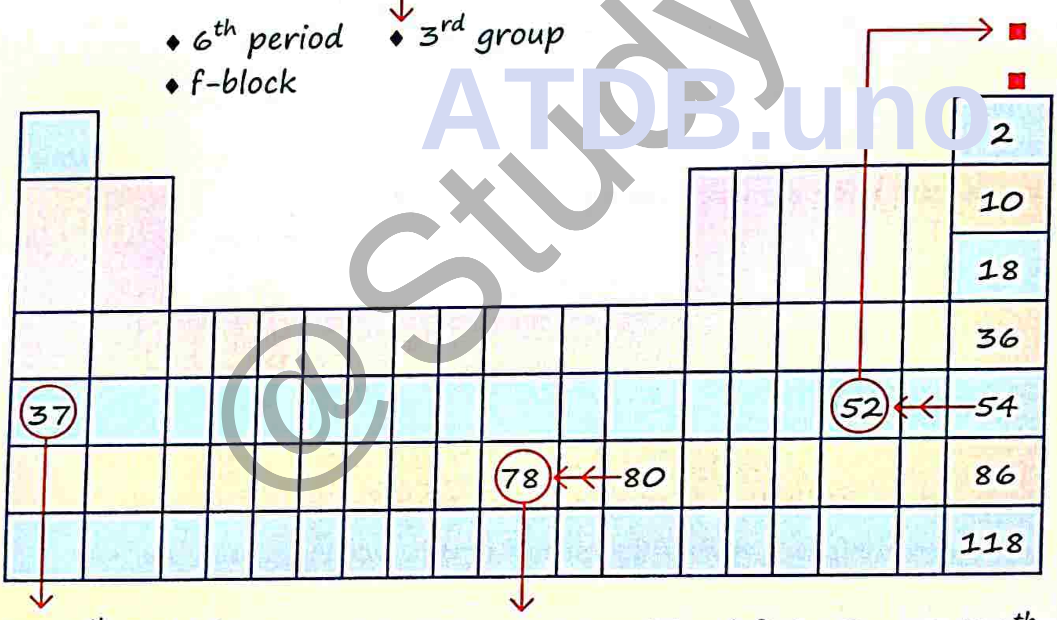
Sol. (d) A-iv, B-ii, C-i, D-iii

- Lanthanoids (58 < 65 < 71)

◆ 6th period ◆ 3rd group

◆ f-block

- 5th period
- 16th group (p-block)



- 5th period
- 1st group (s-block)

- 2 position left to Z = 80 (12th group)
- 10th group, 6th period

5. The element with atomic number 117, 119, 120, 91 will be- [30 Jan, 2023 (Shift-1)]

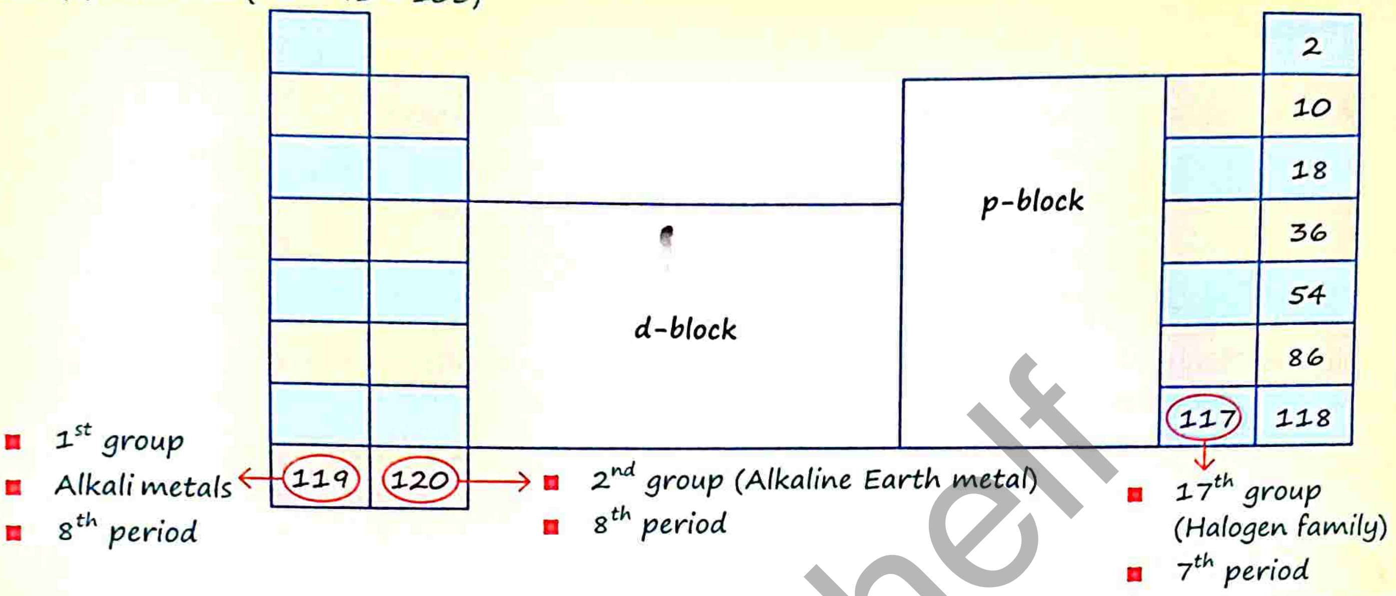
(a) Alkali's

(b) Halogen, Alkali, Alkaline earth metal & Lanthanide

(c) Halogen, Alkali, Alkaline earth metal & Actinide

(d) Transition element, Halogen, Alkali, Alkaline earth metal

Sol. (c) Actinoids (90 < 91 < 103)



6. **The elements with atomic number 101 and 104 belong to, respectively–** [4 Sept, 2020 (Shift-1)]
   (a) Actinoids and Group 4
   (b) Group 11 and Group 4
   (c) Group 6 and Actinoids
   (d) Actinoids and Group 6

Sol. (a)

7. **The element with Z = 120 (not yet discovered) will be an/a** [12 Jan, 2019 (Shift-2)]
   (a) Transition metal
   (b) Inner transition metal
   (c) Alkaline earth metal
   (d) Alkali metal

Sol. (c)

8. **Identify the incorrect match.** [NEET 2016]

	Name		IUPAC Official Name
(A)	Unnilunium	(i)	Mendelevium
(B)	Unniltrium	(ii)	Lawrencium
(C)	Unnilhexium	(iii)	Seaborgium
(D)	Unununium	(iv)	Darmstadtium

(a) A-(i) (b) B-(ii) (c) C-(iii) (d) D-(iv)

Sol. (d) Unununium [111] → Roentgenium

METAL, NON-METAL AND METALLOID

Metal

$M \rightarrow M^+ + e^-$

☐ The metals are characterised by their nature of readily giving up the electron(s) and form shining lustre.

☐ Metals comprises more than 78% of all known elements and appear on the left hand side of the periodic table.

☐ Metals are usually solids at room temperature (except Hg, Ga).

☐ They have high melting and boiling points and are good conductors of heat and electricity.

Non-metal

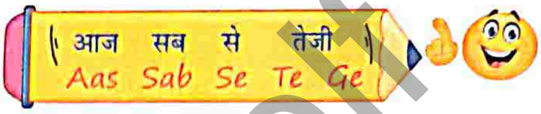
$N + e^- \rightarrow N^-$

- ☐ Non-metals do not lose electrons but take up electrons to form corresponding anions.
- ☐ Non-metals are located at the top right hand side of the periodic table.
- ☐ Non-metals are usually solids, liquids or gases at room temperature with low melting and boiling points. They are poor conductors of heat and electricity.

Metalloids (Semi-metals)

It has been found that some elements which lie at the border of metallic and nonmetallic behavior, possess the properties that are characteristic of both metals and non-metals. These elements are called semi-metals or metalloids.

Examples - As, Sb, Se, Te, Ge



s-BLOCK

Alkali Metals (Group-1) General electronic configuration ⇒ [Inert gas] ns^1	
n = 2	Li_3 : [He] $2s^1$
n = 3	Na_{11} : [Ne] $3s^1$
n = 4	K_{19} : [Ar] $4s^1$
n = 5	Rb_{37} : [Kr] $5s^1$
n = 6	Cs_{55} : [Xe] $6s^1$

Alkaline Earth Metals (Group-2) General electronic configuration ⇒ [Inert gas] ns^2
Be_4 : [He] $2s^2$
Mg_{12} : [Ne] $3s^2$
Ca_{20} : [Ar] $4s^2$
Sr_{38} : [Kr] $5s^2$
Ba_{56} : [Xe] $6s^2$

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

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

p-BLOCK

Group-13: [Inert Gas] ns^2np^1	Group-14: [Inert Gas] ns^2np^2
B_5 : [He] $2s^2\ 2p^1$	C_6 : [He] $2s^2\ 2p^2$
Al_{13} : [Ne] $3s^2\ 3p^1$	Si_{14} : [Ne] $3s^2\ 3p^2$
Ga_{31} : [Ar] $4s^2\ 3d^{10}\ 4p^1$	Ge_{32} : [Ar] $4s^2\ 3d^{10}\ 4p^2$
In_{49} : [Kr] $5s^2\ 4d^{10}\ 5p^1$	Sn_{50} : [Kr] $5s^2\ 4d^{10}\ 5p^2$
Tl_{81} : [Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^1$	Pb_{82} : [Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^2$
Nh_{113} : [Rh] $7s^2\ 5f^{14}\ 6d^{10}\ 7p^1$	Fl_{114} : [Rn] $7s^2\ 5f^{14}\ 6d^{10}\ 7p^2$

Period No. / Group No.	Group 15 (Pnictogens)	Group 16 (Chalcogens)	Group 17 (Halogens)	Group 18 (Inert gas)
1.				He: $1s^2$
2.	N: [He] $2s^2$ $2p^3$	O: [He] $2s^2$ $2p^4$	F: [He] $2s^2$ $2p^5$	Ne: [He] $2s^2$ $2p^6$
3.	P: [Ne] $3s^2$ $3p^3$	S: [Ne] $3s^2$ $3p^4$	Cl: [Ne] $3s^2$ $3p^5$	Ar: [Ne] $3s^2$ $3p^6$
4.	As: [Ar] $4s^2$ $3d^{10}$ $4p^3$	Se: [Ar] $4s^2$ $3d^{10}$ $4p^4$	Br: [Ar] $4s^2$ $3d^{10}$ $4p^5$	Kr: [Ar] $4s^2$ $3d^{10}$ $4p^6$
5.	Sb: [Kr] $5s^2$ $4d^{10}$ $5p^3$	Te: [Kr] $5s^2$ $4d^{10}$ $5p^4$	I: [Kr] $5s^2$ $4d^{10}$ $5p^5$	Xe: [Kr] $5s^2$ $4d^{10}$ $5p^6$
6.	Bi: [Xe] $6s^2$ $4f^{14}$ $5d^{10}$ $6p^3$	Po: [Xe] $6s^2$ $4f^{14}$ $5d^{10}$ $6p^4$	At: [Xe] $6s^2$ $4f^{14}$ $5d^{10}$ $6p^5$	Rn: [Xe] $6s^2$ $4f^{14}$ $5d^{10}$ $6p^6$

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

- ☐ Group 13 to 18
- ☐ General electronic configuration: [inert gas] ns^2 np^{1-6}
- ☐ p-block elements lie on the extreme right of the periodic table.
- ☐ This block includes some metals, all non-metals and metalloids.
- ☐ Representative Elements: s + p block elements except inert gas elements.

d-BLOCK ELEMENTS

Series name ↓ | Group →	3		4	5	6	7	8	9	10	11	12
3d-series	Sc_{21}		Ti_{22}	V	Cr	Mn	Fe	Co	Ni	Cu	Zn_{30}
4d-series	Y_{39}		Zr_{40}	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd_{48}
5d-series	La_{57}	4f Series	Hf_{72}	Ta	W	Re	Os	Ir	Pt	Au	Hg_{80}
6d-series	Ac_{89}	5f Series	Rf_{104}	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn_{112}

Electronic Configuration

3d series: [Ar] 4s 3d

4d series: [Kr] 5s 4d

5d series: [Xe] 6s 5d : for La
[Xe] 6s 5d $4f^{14}$: from Hf → Hg

6d series: [Rn] 7s 6d : for Ac
[Rn] 7s 6d $5f^{14}$: from Rf → Cn

देशी जुगाड़ For Electronic Configuration of 11 Elements ।

Rahgir(Rg) Kyu(Cu) Aage(Ag) Aau(Au) Pitayi(Pt) Croge(Cr), Nabab(Nb) Mout(Mo) Rukawat(Ru) Rah(Rh) Padegi(Pd)

Rg	Cu	Ag	Au	Pt	Cr	Nb	Mo	Ru	Rh

↓ ns^1

Pd

↓ ns°

Sc $4s^2\ 3d^1$	Ti $4s^2\ 3d^2$	V $4s^2\ 3d^3$	Cr $4s^1\ 3d^5$	Mn $4s^2\ 3d^5$	Fe $4s^2\ 3d^6$	Co $4s^2\ 3d^7$	Ni $4s^2\ 3d^8$	Cu $4s^1\ 3d^{10}$	Zn $4s^2\ 3d^{10}$
Y $5s^2\ 4d^1$	Zr $5s^2\ 4d^2$	Nb $5s^1\ 4d^4$	Mo $5s^1\ 4d^5$	Tc $5s^2\ 4d^5$	Ru $5s^1\ 4d^7$	Rh $5s^1\ 4d^8$	Pd $5s^0\ 4d^{10}$	Ag $5s^1\ 4d^{10}$	Cd $5s^2\ 4d^{10}$
La $6s^2\ 5d^1$	Hf $6s^2\ 5d^2$ $4f^{14}$	Ta $6s^2\ 5d^3$ $4f^{14}$	W $6s^2\ 5d^4$ $4f^{14}$	Re $6s^2\ 5d^5$ $4f^{14}$	Os $6s^2\ 5d^6$ $4f^{14}$	Ir $6s^2\ 5d^7$ $4f^{14}$	Pt $6s^1\ 5d^9$ $4f^{14}$	Au $6s^1\ 5d^{10}$ $4f^{14}$	Hg $6s^2\ 5d^{10}$ $4f^{14}$
Ac $7s^2\ 6d^1$	Rf $7s^2\ 6d^2$ $5f^{14}$	Db $7s^2\ 6d^3$ $5f^{14}$	Sg $7s^2\ 6d^4$ $5f^{14}$	Bh $7s^2\ 6d^5$ $5f^{14}$	Hs $7s^2\ 6d^6$ $5f^{14}$	Mt $7s^2\ 6d^7$ $5f^{14}$	Ds $7s^2\ 6d^8$ $5f^{14}$	Rg $7s^1\ 6d^{10}$ $5f^{14}$	Cn $7s^2\ 6d^{10}$ $5f^{14}$

- ☐ Group : 3 to 12
- ☐ General electronic configuration : [inert gas] ns^{0-2} $(n-1)d^{1-10}$ (except, Pd : $4d^{10}5s^{\circ}$)

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

- ☐ All the transition elements are metals.

1^{st} Transition Series	2^{nd} Transition Series
☐ 3d series	☐ 4d series
☐ 10 elements	☐ 10 elements
☐ Starts from $_{21}Sc$ – $_{30}Zn$.	☐ Starts from $_{39}Y$ – $_{48}Cd$
☐ Filling of electrons takes place in 3d subshell.	☐ Filling of electrons takes place in 4d subshell.

3^{rd} Transition Series	4^{th} Transition Series
☐ 5d series	☐ 6d series
☐ 10 elements	☐ 10 elements
☐ Starts from $_{57}La$, $_{72}Hf$ – $_{80}Hg$.	☐ Starts from $_{89}Ac$, $_{104}Rf$ – $_{112}Uub$.
☐ Filling of electrons takes place in 5d subshell.	☐ Filling of electrons takes place in 6d subshell.

Transition Metals

The elements whose atoms or simple ions contain partially filled d-orbitals are called transition metals.

1. Sc is a transition metal because Sc has partially filled d-orbitals.

   Sc : [Ar] $4s^2\ 3d^1$

2. Zn is not a transition metal because Zn and Zn^{2+} both have filled d-orbitals.

   Zn : [Ar] $4s^2\ 3d^{10}$
   Zn^{2+} : [Ar] $3d^{10}$

3. Cu is a transition metal because Cu^{2+} has partially filled d-orbitals.

   Cu : [Ar] $4s^1\ 3d^{10}$
   Cu^{2+} : [Ar] $3d^9$

Note

- ☐ Zn, Cd, Hg are not considered as transition elements because they have filled 'd^{10} configuration' in atomic (M) and ionic (M^{2+}) form.
- ☐ All transition elements are d-block elements but not all d-block elements are transition elements.
  - ◆ Elements in Liquid State at STP – Hg (metal), Br_2 (Non-metal)
  - ◆ Metals in Liquid State (at T < 40°C) – $\underset{Rb}{\underline{\text{Rubi}}}\ \underset{Hg}{\underline{\text{Mar}}}\ \underset{Ga}{\underline{\text{Gayi}}}\ \underset{Fr}{\underline{\text{Fir}}}\ \underset{Cs}{\underline{\text{se}}}$

f-BLOCK ELEMENTS

The f-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium).

Lanthanoids	Ce_{58}	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu_{71}
Actinoids	Th_{90}	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr_{103}

- ☐ They are metals
- ☐ All f-block elements belong to 3rd group.

1st Inner Transition Series – 4f series	2nd Inner Transition Series– 5f series
☐ 14 elements – $_{58}Ce$ to $_{71}Lu$	☐ 14 elements – $_{90}Th$ to $_{103}Lr$
☐ Filling of electrons takes place in 4f subshell.	☐ Filling of electrons takes place in 5f subshell.

Transuranium Elements $Z > 92$

- ☐ The elements coming after uranium are called transuranium elements.

General electronic configuration : [Inert gas] $ns^2 \ (n-2)f^{1-14} \ (n-1)d^{0-1}$

- ☐ When n, (n–1) and (n–2) shells are incompletely filled and last electron enters into f-orbital of anti-penultimate $(n-2)^{th}$ shell, elements of this class are called f-block elements.
- ☐ They are also called as inner transition elements as they contain three incomplete outermost shells and were also referred to as rare earth elements since their oxides were rare in earlier days.

9. The element Z = 114 has been discovered recently. It will belong to which of the following family/group and electronic configuration?

(a) Carbon family, $[Rn]5f^{14}6d^{10}7s^2 7p^2$
(b) Oxygen family, $[Rn]5f^{14}6d^{10}7s^2 7p^4$
(c) Nitrogen family, $[Rn]5f^{14}6d^{10}7s^2 8p^6$
(d) Halogen family, $[Rn]5f^{14}6d^{10}7s^2 7p^5$

Sol. (a)

10. Which of the following is representative group of elements in the periodic table?

(a) Lanthanum (La)
(b) Argon (Ar)
(c) Chromium (Cr)
(d) Aluminium (Al)

Sol. (d)

11. If Z is given (Z = 32, 57, 71, 87), then what will be Period number, Group number, Block, Family, Electronic Configuration?

Sol. Z = 32
- → p-Block
- → Group Number – 14
- → Period – 4 (Carbon family)
- → EC ≡ $[Ar] \ 4s^2 \ 3d^{10} \ 4p^2$

Z = 57
- → d-Block
- → Group Number – 3
- → Period Number – 6
- → EC ≡ $[Xe] \ 6s^2 \ 5d^1$

Z = 71
- → f-Block (Lanthanoids)
- → Group Number – 3
- → Period Number – 6
- → EC ≡ $[Xe] \ 6s^2 \ 5d^1 \ 4f^{14}$

Z = 87
- → Alkali metal
- → s-Block
- → Group 1 [7^{th} Period]
- → EC ≡ $[Rn] \ 7s^1$

Note

If electronic configuration of an element is given and you have to find the position of element in periodic table then add all electrons and find atomic number (For neutral element → Total no. of electrons = atomic number).

- ☐ Through atomic number, you can find the position of element.

12. The IUPAC nomenclature of an element with electronic configuration $[Rn]5f^{14}6d^1 7s^2$ is :

[23 July, 2022 (Shift-1)]

(a) Unnilbium
(b) Unnilunium
(c) Unnilquadium
(d) Unniltrium

Sol. (d) Total number of electrons = 86 + 14 + 1 + 2 = 103 [IUPAC Name – Unniltrium]

13. An atom has electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$, you will place it in-
(a) fifth group (b) fifteenth group (c) second group (d) third group

Sol. (a) Total number of electrons = 2 + 2 + 6 + 2 + 6 + 3 + 2 = 23

14. The characteristics of element X, Y and Z with atomic numbers, respectively, 33, 53 and 83 are:
[16 March, 2021 (Shift-2)]

(a) X and Y are metalloids and Z is a metal
(b) X is a metalloid, Y is a non-metal and Z is a metal
(c) X, Y and Z are metals.
(d) X and Z are non-metals and Y is metalloid

Sol. (b) Metalloid X → 33 [As] Non-metal Y → 53 [I] Metal Z → 83 [Bi]

15. Which among the following electronic configurations belong to main group elements?
[NEET 2025]

A. $[Ne]3s^1$ B. $[Ar]3d^3 4s^2$ C. $[Kr]4d^{10} 5s^2 5p^5$
D. $[Ar]3d^{10} 4s^1$ E. $[Rn]5f^0 6d^2 7s^2$

Choose the correct answer from the option given below:
(a) B and E only (b) A and C only (c) D and E only (d) A, C and D only

Sol. (b) Main group elements = Representative elements

16. The number of d-electrons in Fe^{2+} (Z = 26) is not equal to the number of electrons in which one of the following?
[NEET 2015]
(a) p-electrons in Cl (Z = 17) (b) d-electrons in Fe (Z = 26)
(c) p-electrons in Ne (Z = 10) (d) s-electrons in Mg (Z = 12)

Sol. (a) Number of d-electrons in Fe^{2+} → 6 $[3d^6]$
Number of d-electrons in Fe → 6 $[3d^6]$
Number of s-electrons in Mg → 6 $[1s^2, 2s^2, 3s^2]$
Number of p-electrons in Cl → 11 $[2p^6, 3p^5]$
Number of p-electrons in Ne → 6 $[2p^6]$

EFFECTIVE NUCLEAR CHARGE

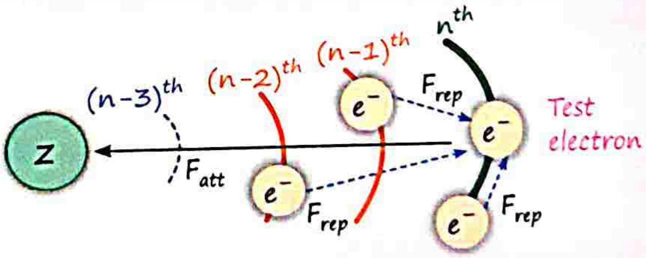
$F_{effective} = F_{att.} - F_{rep.}$

$Z_{eff} = Z - \sigma$

Z_{eff} → औकात of Nucleus

Z → Atomic number

σ → Shielding constant
→ Screening constant
→ Slater's constant



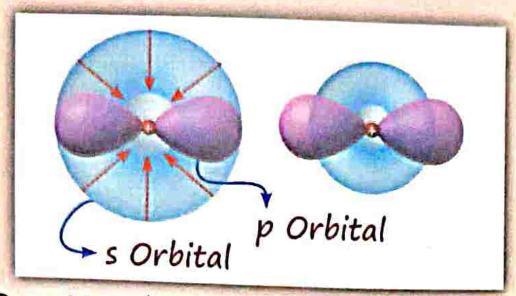
- ❑ Number of inner shell electrons ↑ ⇒ σ ↑ ⇒ Z_{eff} ↓

- ❑ There is a reduction in nuclear charge due to presence of screen b/w test electron and nucleus.
Screening/Shielding Effect: The phenomenon where inner electrons in an atom reduce the attractive force of the nucleus on outer electrons. These inner electrons effectively "screen or shield" the outer electrons from the full nuclear charge.

- ❑ **Effective nuclear charge (Z_{eff}):** The net positive charge experienced by an electron in a multi-electron atom, which is less than the full nuclear charge due to shielding by inner electrons.

PENETRATION EFFECT

- ☐ Penetration Power means the ability of an electron in an orbital to get close to the nucleus.
- ☐ The Penetration effect of s-orbital is the maximum because it is closer to the nucleus than the p, d, and f-orbitals.



Due to spherical shape of s orbital, it is more attracted towards nucleus (centre of sphere) than p orbital having dumb bell shape.

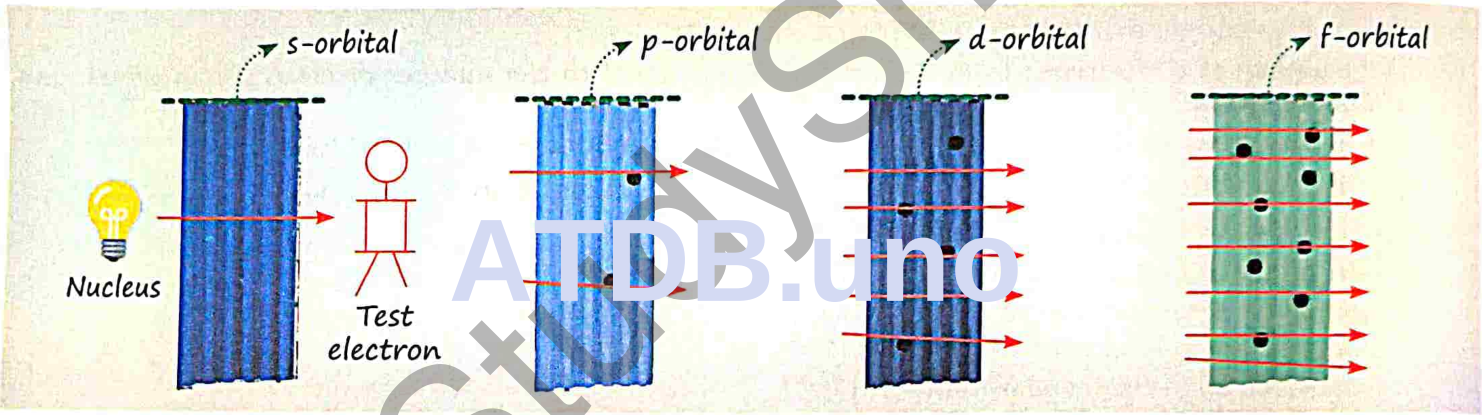
Closeness to the nucleus : s > p > d > f

Penetration effect : s > p > d > f

Screening effect/Shielding effect : s > p > $\boxed{d > f}$ → Poor shielding

Contribution of subshell in shielding constant (σ) :

ns > np > nd > nf



17. The order of screening effect of electrons of s, p, d and f orbitals of a given shell of an atom on its outer shell electrons is :

(a) s > p > d > f (b) f > d > p > s

(c) p > d > s > f (d) f > p > s > d

Sol. (a)

18. Screening effect is not observed in :

(a) He^+ (b) Li^{2+} (c) Be^{3+} (d) In all cases

Sol. (d) Screening effect is not observed in 1 electron system.

Variation of Z_{eff} in Periodic Table

$Z_{eff} = Z - \sigma$

1. $Z_{eff} \propto Z$

2. $Z_{eff} \propto \frac{1}{\sigma} \propto \frac{1}{n_e}$

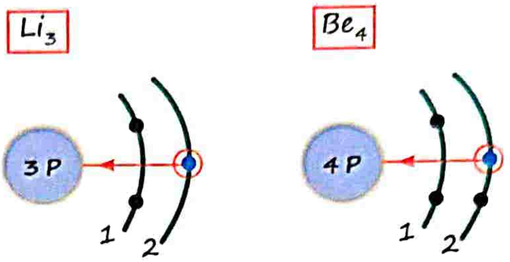
$\boxed{Z_{eff} \propto \frac{Z}{n_e}}$

n_e → Total number of electrons in atom

❑ **Variation in a Period:** Left → Right ⇒ Z_{eff} ↑ [Generally it is valid in all s, p, d and f block]

Z_{eff} : Li < Be

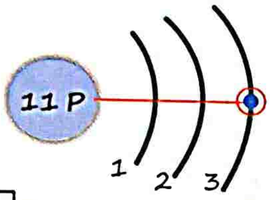
- Same shell number
- No. of protons ↑ : Z_{eff} ↑



❑ **Variation in a Group:** When we move from top to bottom

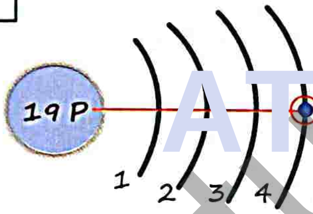
1. Zeff ⇒ Constant [Generally valid in s and p blocks but not always]

Na_{11}



Zeff is constant as no. of proton↑ but distance between nucleus and test electron↑.

K_{19}



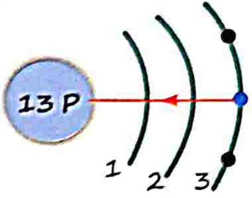
For Example

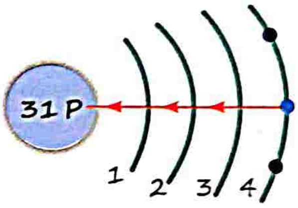
Al_{13} → [Ne] $3s^2$ $3p^1$

Ga_{31} → [Ar] $4s^2$ $\boxed{3d^{10}}$ $4p^1$

Due to poor shielding of $3d^{10}$ electrons, shielding constant σ decreases and Z_{eff}↑

Z_{eff} : Al < Ga

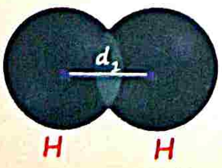
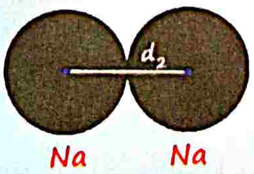
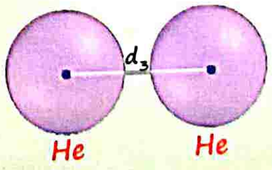




ATOMIC RADIUS

Atomic radius is the average or typical distance from the center of an atom's nucleus to the outermost shell.

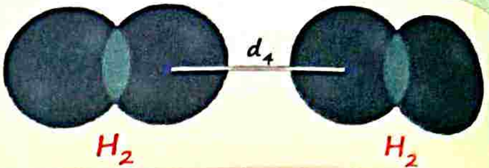
$$\text{Atomic Radius} = \frac{\text{Inter-nuclear Distance}}{2}$$

Covalent Radius	Metallic Radius	vander Waal Radius
◆ Covalent Bond ◆ Non metal – non metal (H)  	◆ Metallic bond ◆ Metal – metal (Na-Na)  	◆ VW – Force of attraction ◆ Inert gas / molecules (He, Ne, Ar) (H_2, Cl_2)  

$r_c = \frac{d_1}{2}$	$r_M = \frac{d_2}{2}$	$r_{vw} = \frac{d_3}{2}$

☐ $d_1 < d_2 < d_3$
☐ $r_c < r_M < r_{vw}$

$(r_{vw})_{H_2} = \frac{d_4}{2}$

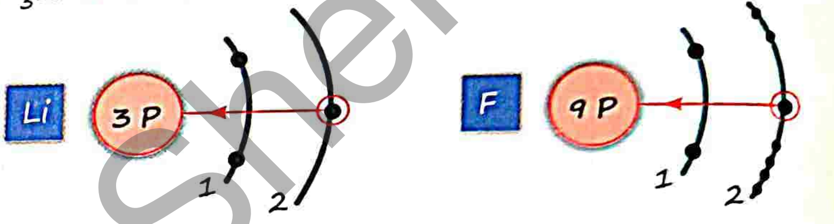


ATOMIC SIZE

☐ **Variation in a Period:** Left → Right ⇒ Z_{eff} ↑ ⇒ Atomic Radius ↓

$_{10}Ne > {}_3Li > Be > B > C > N > O > F$: Atomic Radius

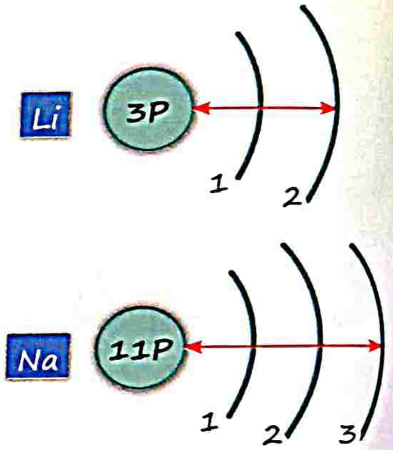
$_{10}Ne$ → vander Waal radii



☐ **Variation in a Group:**

Top ↓ Bottom → Z_{eff} ≈ constant
→ Due to addition of new shell ⇒ Atomic Radius ↑

Period No.	Atomic Size
2	Li
	^
3	Na
	^
4	K
	^
5	Rb
	^
6	Cs



Same Period Elements	Different Period Elements
☐ Left → Right : Atomic Radius ↓	☐ Period Number ↑ : Atomic Radius ↑

◆ $\underbrace{Br}_{n=4} > \underbrace{C > N > F}_{n=2}$

◆ $\underbrace{C}_{n=2} < \underbrace{S < Al}_{n=3} < \underbrace{Ca}_{n=4}$

◆ $\underset{n=2}{B} < \underbrace{\underset{n=3}{P} > \underset{n=3}{S} > \underset{n=3}{Cl}} < \underset{n=4}{Br}$

B < Cl < S < P < Br → Atomic Size

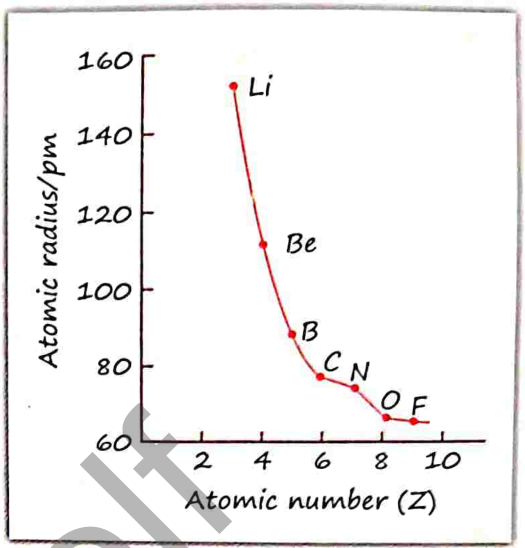
Boron Family

नौटंकी Family

B
^
Al_{13} → [Ne] $3s^2\ 3p^1$
v
Ga_{31} → [Ar] $4s^2\ \boxed{3d^{10}}\ 4p^1$
^
In
^
Tl

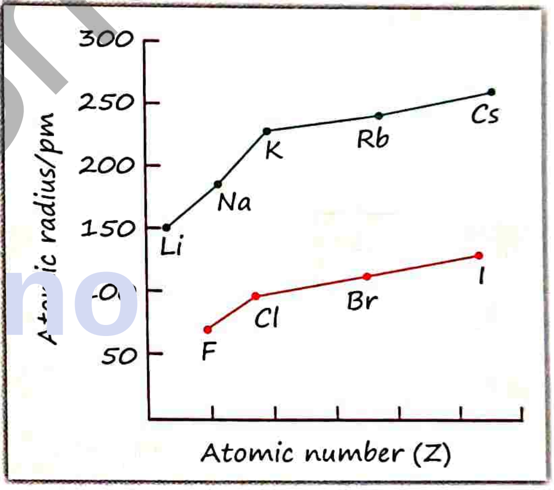
Due to Poor shielding of 3d orbital electrons, Z_{eff} is more in Ga w.r.t Al

→ Z_{eff}↑ : Size↓



Atomic Size Order in s and p Block

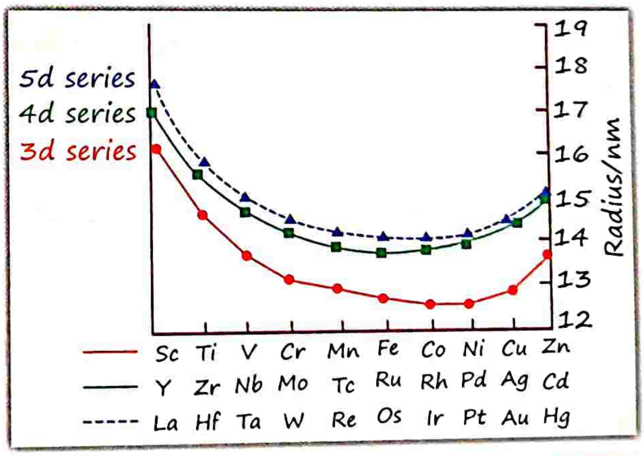
H							He
^							^
Li	Be	B	C	N	O	F	Ne
^	^	^	^	^	^	^	^
Na	Mg	Al	Si	P	S	Cl	Ar
^	^	v	^	^	^	^	^
K	Ca	Ga	Ge	As	Se	Br	Kr
^	^	^	^	^	^	^	^
Rb	Sr	In	Sn	Sb	Te	I	Xe
^	^	^	^	^	^	^	^
Cs	Ba	Tl	Pb	Bi	Po	At	Rn



Atomic Size of 3d Series

There are two factors in order to decide atomic radius of an element.

1. Nuclear charge [Nuclear charge↑ : size↓]
2. Interelectronic repulsion (IER) [IER↑ : size↑]



Elements	Sc → Ti → V → Cr	Mn → Fe → Co → Ni	Cu → Zn
Size	Decreases	Nearly constant	Slightly increases
Reason	Nuclear charge dominates over IER	Nuclear charge ≈ IER	IER dominates over nuclear charge

Lanthanoid Contraction

- ☐ The decrease in atomic or ionic radii from Ce to Lu due to imperfect shielding of 4f e^- from nuclear charge is known as lanthanoid contraction.
- ☐ Lanthanoid contraction is similar to that observed in an ordinary transition series and is attributed to the same cause, the imperfect shielding of one electron by another in the same subshell.
- ☐ The shielding of one 4f electron by another is less than one d electron by another with the increase in nuclear charge along the series. There is fairly regular decrease in the sizes with increasing atomic number.
- ☐ Lanthanoid contraction is applicable on both metal (M) and metal ion (M^{+3}) size orders.

$Ce \rightarrow Lu$
$Ce^{3+} \rightarrow Lu^{3+}$
→ Size decreases

- ☐ Remember → Atomic Radius : Eu > Ce

Effect of Lanthanide Contraction on Size of d-Block Elements

3d →	$_{21}$Sc		$_{22}$Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	∧		∧	∧	∧	∧	∧	∧	∧	∧	∧
4d →	$_{39}$Y		$_{40}$Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	∧		≈	≈	≈	≈	≈	≈	≈	≈	≈
5d →	$_{57}$La	($_{58}$Ce ⟶ $_{71}$Lu)	$_{72}$Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

→ Free from effect of Lanthanide contraction

- ☐ Due to lanthanoid contraction, radii of the members of 5d series are found to be very similar to those of corresponding members of the 4d series.
- ☐ For d-block elements, the trend in atomic radii is: $r_{3d\ series} < r_{4d\ series} \approx r_{5d\ series}$

19. The lanthanide contraction is responsible for the fact that :
(a) Zr and Y have about the same radius
(b) Zr and Nb have similar oxidation state
(c) Zr and Hf have about the same radius.
(d) Zr and Zn have same oxidation state.

Sol. (c)

20. Which of the following has similar atomic radius with respect to Ag :
(a) La (b) Zn (c) Au (d) Rf

Sol. (c)

IONIC RADIUS

Cation → ⊕ vely charged ion

$$Be \xrightarrow{-e^-} Be^+ \xrightarrow{-e^-} Be^{2+}$$

$Z_{eff} \propto \frac{Z}{e} = \frac{4}{4}$ $Z_{eff} \propto \frac{4}{3}$ $Z_{eff} \propto \frac{4}{2}$

Z_{eff} : $Be < Be^+ < Be^{2+}$

Size : $Be > Be^+ > Be^{2+}$

: Mother atom > Cation

◆ $Mg > Mg^+ > Mg^{2+}$: Size

Anion → ⊖ vely charged ion

$$O \xrightarrow{+e^-} O^- \xrightarrow{+e^-} O^{2-}$$

$Z_{eff} \propto \frac{8}{8}$ $Z_{eff} \propto \frac{8}{9}$ $Z_{eff} \propto \frac{8}{10}$

Z_{eff} : $O > O^- > O^{2-}$

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

: Mother atom < Anion

◆ $I < I^-$: Size

ISOELECTRONIC SPECIES

☐ Species having same number of electrons are known as isoelectronic species.

☐ All ions– C^{4-}, N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+} are isoelectronic because they all have 10 electrons.

	C^{4-}	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}
Number of Electrons :	(6 + 4)	(7+3)	(8+2)	(9+1)	(11–1)	(12–2)	(13–3)
Number of Protons :	6	7	8	9	11	12	13
$Z_{eff} \propto \frac{Z}{e}$:	$\frac{6}{10}$ <	$\frac{7}{10}$ <	$\frac{8}{10}$ <	$\frac{9}{10}$ <	$\frac{11}{10}$ <	$\frac{12}{10}$ <	$\frac{13}{10}$
Size :	C^{4-} >	N^{3-} >	O^{2-} >	F^- >	Na^+ >	Mg^{2+} >	Al^{3+}
	Anions				Cations		

☐ Si^{4-}, P^{3-}, S^{2-}, Cl^-, K^+, Ca^{2+}, Sc^{3+} → isoelectronic because they all have 18 electrons.

Size → $Si^{4-} > P^{3-} > S^{2-} > Cl^- > K^+ > Ca^{2+} > Sc^{3+}$

Note

- ☐ H_2S, HCl, Ar, SH^- → Isoelectronic with 18 electrons
- ☐ NH_2^-, NH_3, CH_4, H_2O, OH^-, NH_4^+, NH_2^- → Isoelectronic with 10 electrons
- ☐ CO_3^{2-}, NO_3^-, BO_3^{3-} → Isoelectronic with 32 electrons
- ☐ SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, ClO_4^- → Isoelectronic with 50 electrons
- ☐ $[Ni(CO)_4]$, $[Co(CO)_4]^-$, $[Fe(CO)_4]^{2-}$, $[Fe(CO)_2(NO)_2]$ ⟶ Isoelectronic with 84 electrons

$$\underbrace{28 + 4(6 + 8)}_{84} \quad \underbrace{27 + 4(6 + 8) + 1}_{84} \quad \underbrace{26 + 4(6 + 8) + 2}_{84} \quad \underbrace{26 + 2(6 + 8) + 2(7 + 8)}_{84}$$

Find the order of ionic radius?

- ☐ $S^{2-} > Cl^- > K^+ > Ca^{2+}$: Size
  $[16+2]$ $[17+1]$ $[19-1]$ $[20-2]$: Number of electrons
- ☐ $Te^{2-} > I^-$: Size
  $[52+2]$ $[53+1]$: Number of electrons

Period Number → 2 Period Number → 3

- ☐ $O^{2-} < N^{3-} <$ [illegible] $< P^{3-}$: Size
- ☐ $K^+ > Na^+ > Li^+$: Size [K > Na > Li : Size]
- ☐ $F^- < Cl^- < Br^- < I^-$: Size [I > Br > Cl > F : Size]
- ☐ $O^{2-} < S^{2-} < Se^{2-} < Te^{2-}$: Size

- ☐ $Ar > S^{2-} > Cl^- > K^+ > Ca^{2+}$: Size

vander Waal radii

Note

The smallest anion is F^- and not H^- (ionic radius 208 pm). The radius order of anions is $F^- < Cl^- < Br^- < H^- < I^-$. The exception in the size of H^- is because this is the only anion with z/e ratio = 0.5.

21. Which of the following order is incorrect for size :

(a) $Al > Ga$ (b) $Te^{2-} > I^- > Cs^+ > Ba^{2+}$ (c) $Cr^{3+} < Cr^{6+}$ (d) $Pd \approx Pt$

Sol. (c)

22. The ionic radii (in Å) of N^{3-}, O^{2-} and F^- are respectively :

(a) 1.36, 1.40 and 1.71 (b) 1.36, 1.40 and 1.71

(c) 1.71, 1.40 and 1.36 (d) 1.71, 1.36 and 1.40

Sol. (c) $N^{3-} > O^{2-} > F^-$: size

23. Ionic radii of (IIT JEE 1999)

(a) $Ti^{4+} < Mn^{7+}$ (b) $^{35}Cl^{-} < {}^{37}Cl^{-}$ (c) $K^{+} > Cl^{-}$ (d) $P^{3+} > P^{5+}$

Sol. (d)

24. Among $V(CO)_6$, $Cr(CO)_5$, $Cu(CO)_3$, $Mn(CO)_5$, $Fe(CO)_5$, $[Co(CO)_3]^{3-}$, $[Cr(CO)_4]^{4-}$, and $Ir(CO)_3$, the total number of species isoelectronic with $Ni(CO)_4$ is ________ . (JEE Adv. 2024)

[Given, atomic number: V = 23, Cr = 24, Mn = 25, Fe = 26, Co = 27, Ni = 28, Cu = 29, Ir = 77]

Sol. [1] Total number of electron in $Ni(CO)_4$ = 84

Species	Total electron
$V(CO)_6$	107
$Cr(CO)_5$	94
$Cu(CO)_3$	71
$Mn(CO)_5$	95

Species	Total electron
$Fe(CO)_5$	96
$[Co(CO)_3]^{3-}$	72
$[Cr(CO)_4]^{4-}$	84
$Ir(CO)_3$	119

25. The element expected to form largest ion to achieve the nearest noble gas configuration is: [NEET 2023]

(a) Na (b) O (c) F (d) N

Sol. (d) $N^{3-} > O^{2-} > F^{-} > Na^{+}$: ionic size [All ions have noble gas configuration (Ne)]

26. Which one of the following represents all isoelectronic species? [NEET 2023-Manipur]

(a) $Na^{+}, Cl^{-}, O^{-}, NO^{+}$ (b) N_2O, N_2O_4, NO^{+}, NO

(c) $Na^{+}, Mg^{2+}, O^{-}, F^{-}$ (d) $Ca^{2+}, Ar, K^{+}, Cl^{-}$

Sol. (d)

27. From the following pairs of ions, which one is not an isoelectronic pair? [NEET 2021]

(a) Na^{+}, Mg^{2+} (b) Mn^{2+}, Fe^{3+} (c) Fe^{2+}, Mn^{2+} (d) O^{2-}, F^{-}

Sol. (c)

28. The species Ar, K^{+} and Ca^{2+} contain the same number of electrons. In which order do their radii increase? [NEET 2015]

(a) $Ca^{2+} < Ar < K^{+}$ (b) $Ca^{2+} < K^{+} < Ar$ (c) $K^{+} < Ar < Ca^{2+}$ (d) $Ar < K^{+} < Ca^{2+}$

Sol. (b)

29. Be^{2+} is isoelectronic with which of the following ions? [NEET 2014]

(a) Li^{+} (b) Na^{+} (c) Mg^{2+} (d) H^{+}

Sol. (a)

30. Identify the wrong statement in the following: [NEET 2012 Pre]

(a) Atomic radius of the elements decreases as one moves across from left to right in the 2nd period of the periodic table

(b) Amongst isoelectronic species, smaller the positive charge on the cation, smaller is the ionic radius

(c) Amongst isoelectronic species, greater the negative charge on the anion, larger is the ionic radius

(d) Atomic radius of the elements increases as one moves down the first group of the periodic table.

Sol. (b)

31. **Ionic radii are:** [NEET 2004]

(a) Inversely proportional to square of effective nuclear charge

(b) Directly proportional to effective nuclear charge

(c) Directly proportional to square of effective nuclear charge

(d) Inversely proportional to effective nuclear charge

Sol. (d)

32. **The ions O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+} are isoelectronic. Their ionic radii show:** [NEET 2003]

(a) A significant increase from O^{2-} to Al^{3+}

(b) A significant decrease from O^{2-} to Al^{3+}

(c) An increase from O^{2-} to F^- and then decrease from Na^+ to Al^{3+}

(d) A decrease from O^{2-} to F^- and then increase from Na^+ to Al^{3+}

Sol. (b)

Property	Paramagnetic	Diamagnetic
Unpaired Electrons	Have one or more unpaired electrons	All electrons are paired
Magnetic Behavior	Attracted to an external magnetic field	Repelled by an external magnetic field
Magnetic Moment	Has a net magnetic moment	No net magnetic moment
Examples	Fe^{3+}, Mn^{2+}, NO 23 electrons 15 electrons Entities having odd number of electrons are always paramagnetic.	He, Ne, Zn^{2+}, Mg

IONISATION ENERGY

Minimum energy required to remove an electron from an isolated gaseous atom is known as ionisation energy (IE).

$$A_{(g)} \xrightarrow{\text{Min. Energy}} A^+_{(g)} + e^-$$

Successive IE :

Z_{eff} : B < B^+

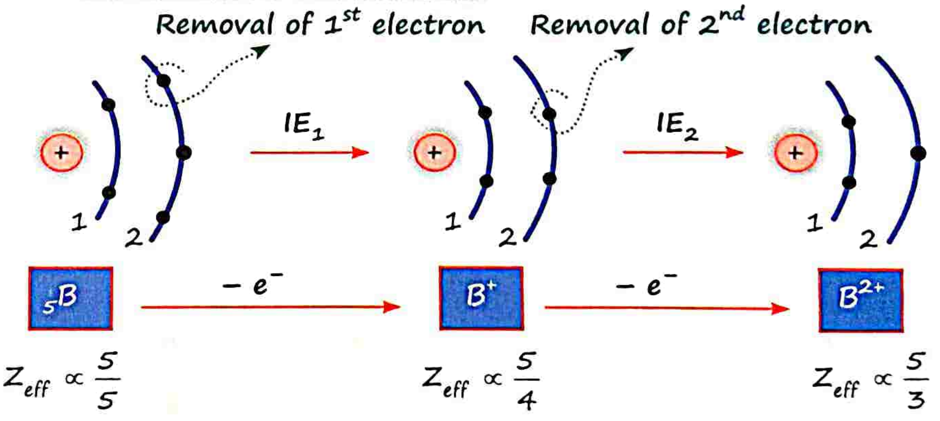
IE : B < B^+

IE_1 of B < IE_2 of B

☐ IE_2 of B = IE_1 of B^+

IE_3 of B = IE_1 of B^{2+}

= IE_2 of B^+



Factors Affecting I.E.

① Z_{eff}

Left → Right ⇒ Z_{eff} ↑ : IE ↑

- ◆ $_3Li < {}_4Be$: IE
- ◆ B < C : IE
- ◆ O < F : IE

② Size

Top
↓
Bottom

→ Size ↑ : IE ↓

Li
∨
Na
∨
K
∨
Rb
∨
Cs

As we move from top to bottom → Size ↑ : IE ↓

Metallic Character

$M \rightarrow M^+ + e^-$

- ◆ Tendency of an element to lose electrons and form positive ions or cations.
- ◆ IE ↓ : Metallic character ↑
- ◆ Metallic character : Cs > Rb > K > Na > Li

③ Electronic Configuration

Half filled / Fully filled subshell → Stable due to high exchange energy.
→ Removal of electron is tough so high IE.

IE : N > O
$2s^2$ $\boxed{2p^3}$ $2s^2$ $\boxed{2p^4}$

Removal of electron from half filled subshell is tough

IE : P > S
$3p^3$ $3p^4$

IE : As > Se
$4p^3$ $4p^4$

$O(2p^4) \rightarrow \boxed{\upharpoonleft\downharpoonright \,|\, 1 \,|\, 1}$ $N(2p^3) \rightarrow \boxed{1 \,|\, 1 \,|\, 1}$

In the oxygen atom, two of the four 2p electrons must occupy the same 2p-orbital, resulting in an increased $e^- - e^-$ repulsion. So, it is easier to remove the fourth 2p electron from oxygen than it is to remove one of the three 2p-electrons from nitrogen.

Comparison of 2nd Ionisation Energy

☐ **Group-1**

Na
$[Ne]\ 3s^1$
$\downarrow IE_1$
$Na^+ \equiv 1s^2\ 2s^2\ \boxed{2p^6}$ → Removal of electron from 2nd shell is tough.
$\downarrow IE_2$
Na^{2+}

Group-2

Mg
$[Ne]\ 3s^2$
$\downarrow IE_1$
$Mg^+ \equiv [Ne]\ \boxed{3s^1}$ → Removal of electron from 3rd shell is easy.
$\downarrow IE_2$
Mg^{2+}

IE_1 : group 1 < group 2
IE_2 : group 1 > group 2

❑ N

$2s^2\ \boxed{2p^3}$ → Half filled

$\downarrow -e^-$

N^+

$2s^2\ 2p^2$

O

$2s^2\ 2p^4$

$\downarrow -e^-$

O^+

$2s^2\ \boxed{2p^3}$ → Half filled

$IE_1 : N > O$
$IE_2 : N < O$
$IE : N^+ < O^+$

❑ Cr

$[Ar]\ 4s^1\ 3d^5$

$-e^- \longrightarrow Cr^+\ [Ar]\ \boxed{3d^5}$

For 2nd IE, removal of e^- from 3rd shell is tough.

Mn

$[Ar]\ 4s^2\ 3d^5$

$-e^- \longrightarrow Mn^+ \equiv [Ar]\ \boxed{4s^1}\ 3d^5$

For 2nd IE, removal of electron from 4th shell is easy.

$IE_2 : Cr > Mn$

4 Penetration Effect

❑ Penetration Effect for different subshell: $s > p > d > f$

- ◆ Be > B : IE

$2s^2 \qquad 2s^2\ \boxed{2p^1}$

$-e^- \longrightarrow$ Removal of e^- from 2p subshell is easy with respect to 2s (Be).

The penetration of a 2s -electron to the nucleus is more than that of a 2p electron; hence the 2p electron of B is more shielded from the nucleus by the inner core of electrons than the 2s electrons of Be.

- ◆ Mg > Al: IE
- ◆ Ca > Ga: IE

33. The correct order of decreasing second ionisation enthalpy of Ti (22), V (23), Cr (24) and Mn (25) is:
(a) Cr > Mn > V > Ti
(b) V > Mn > Cr > Ti
(c) Mn > Cr > Ti > V
(d) Ti > V > Cr > Mn

Sol. (a)

34. **Assertion:** The first ionization energy of Be is greater than that of B.
Reason: 2p orbital is lower in energy than 2s.
(a) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.
(b) Both Assertion and Reason are true but Reason is not correct explanation of Assertion.
(c) Assertion is true but Reason is false.
(d) Assertion is false but Reason is true.

Sol. (c)

35. Four successive members of the first row transition elements are listed below with their atomic numbers. Which one of them is expected to have the highest third ionisation enthalpy?
(a) Vanadium (Z = 23)
(b) Chromium (Z = 24)
(c) Iron (Z = 26)
(d) Manganese (Z = 25)

Sol. (d) Mn $[4s^2 3d^5] \xrightarrow[IE_1]{-e^-} Mn^+ [4s^1 3d^5] \xrightarrow[IE_2]{-e^-} Mn^{2+} [3d^5]$ → Removal of 3rd electron from half filled subshell is tough, so, IE_3 will be highest among all.

36. The set representing the correct order of first ionisation potential is:

(a) K > Na > Li (b) Be > Mg > Ca (c) B > C > N (d) Ge > Si > C

Sol. (b)

37. Reason of lanthanoid contraction is:

(a) Negligible screening effect of f orbitals (b) Increasing nuclear charge

(c) Decreasing nuclear charge (d) Decreasing screening effect

Sol. (a)

☐ **Ionisation Energy:** $ns^1 < \underbrace{ns^2 > np^1}_{\text{due to penetration effect}} < np^2 < \underbrace{np^3 > np^4}_{\text{due to stable electronic configuration } [np^3]} < np^5 < np^6$

$ns^1 < \boxed{np^1 < ns^2} < np^2 < \boxed{np^4 < np^3} < np^5 < np^6$: IE

	$2s^1$	$2s^2$	$2p^1$	$2p^2$	$2p^3$	$2p^4$	$2p^5$	$2p^6$
♦	Li	Be	B	C	N	O	F	Ne
♦	Na	Mg	Al	Si	P	S	Cl	Ar
♦	K	Ca	Ga	Ge	As	Se	Br	Kr

Li < B < Be < C < O < N < F < Ne : IE

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

K < Ga < Ca < Ge < Se < As < Br < Kr : IE

Boron Family

B_5 : $[He]\ 2s^2\ 2p^1$

∨

Al_{13} : $[Ne]\ 3s^2\ 3p^1$

∧

Ga_{31} : $[Ar]\ 4s^2\ \boxed{3d^{10}}\ 4p^1$

poor shielding of 3d electrons

∨

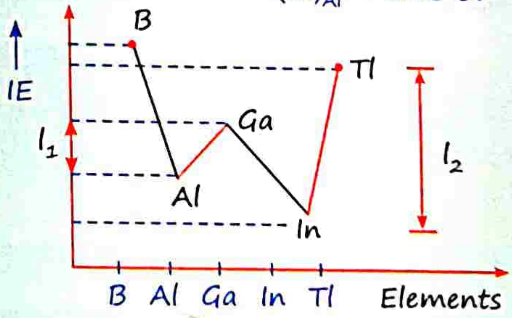
In_{49} : $[Kr]\ 5s^2\ 4d^{10}\ 5p^1$

∧

Tl_{81} : $[Xe]\ 6s^2\ \boxed{4f^{14}}\ 5d^{10}\ 6p^1$

poor shielding of 4f electrons

☐ B > Tl > Ga ≥ Al > In : IE → $(IE)_{Ga} = 5.99$ eV and $(IE)_{Al} = 5.98$ eV



♦ $(IE_{Ga} - IE_{Al} = \ell_1) < (IE_{Tl} - IE_{In} = \ell_2)$

♦ $\Delta IE_{(Ga, Al)} < \Delta IE_{(Tl, In)}$

s Block

Li	Be
∨	∨
Na	Mg
∨	∨
K	Ca
∨	∨
Rb	Sr
∨	∨
Cs	Ba

Highest I.E. : He
Lowest I.E. : Cs

Due to poor shielding of 10 d electrons in Ga

Due to poor shielding of 14 f electrons in Tl & Pb

p Block

B	C	N	O	F	He
∨	∨	∨	∨	∨	∨
Al	Si	P	S	Cl	Ne
∧	∨	∨	∨	∨	∨
Ga	Ge	As	Se	Br	Ar
∨	∨	∨	∨	∨	∨
In	Sn	Sb	Te	I	Kr
∧	∧	∨	∨		∨
Tl	Pb	Bi	Po		Xe

Size → 4d series ≈ 5d series

4d	$_{39}$Y		$_{40}$Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	∧		≈	≈	≈	≈	≈	≈	≈	≈	≈
5d	$_{57}$La	($_{58}$Ce → $_{71}$Lu)	$_{72}$Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Free from the effect of Lanthanoid contraction

Ionisation Energy → 4d series < 5d series

4d	$_{39}$Y		$_{40}$Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	∨		∧	∧	∧	∧	∧	∧	∧	∧	∧
5d	$_{57}$La	($_{58}$Ce → $_{71}$Lu)	$_{72}$Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

The first ionisation energy of 5d elements is higher than that of 4d elements due to a greater Z_{eff} acting on the outer valence electrons, combined with weak shielding by the 4f electrons.

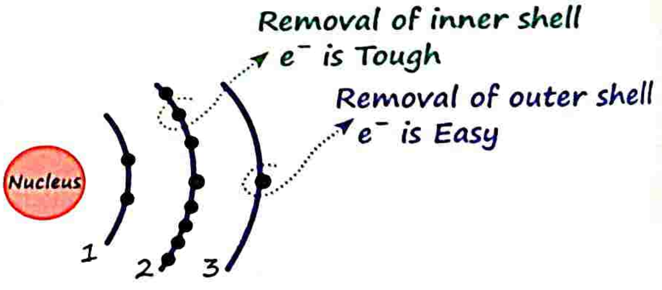
How to find no. of Valence Shell Electrons?

- ☐ Removal of electron from valence shell is easy and from inner shell is tough. So there is a large difference in energies required to remove those electrons.
- ☐ No. of valence electrons = No. of n^{th} ionisation energy just before SUDDEN JUMP

$$A \xrightarrow{-e^-} A^+ \xrightarrow{-e^-} A^{2+} \xrightarrow{-e^-} A^{3+} \xrightarrow{-e^-} A^{4+}$$

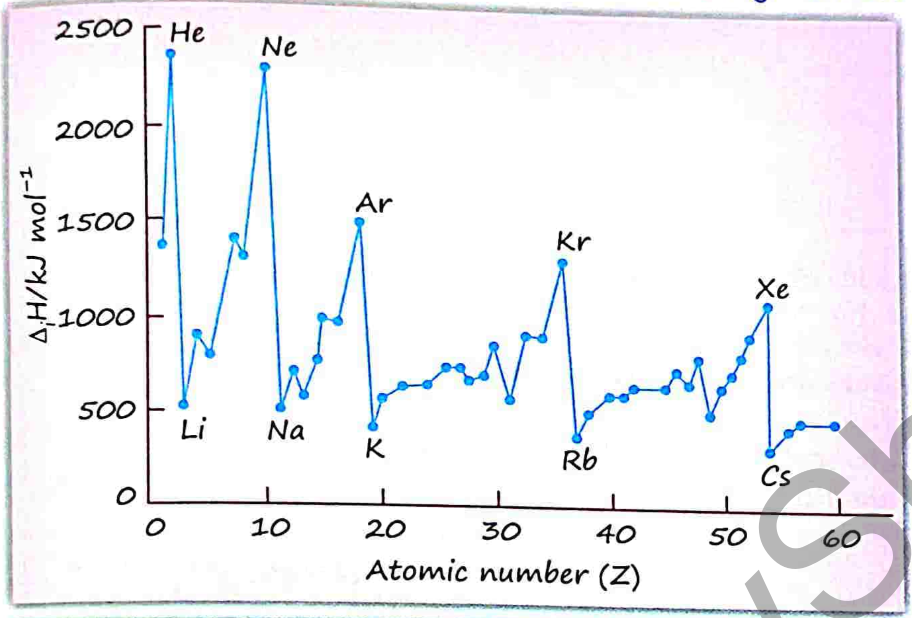
$\boxed{5.1}$ IE_1 $\xrightarrow[\text{Jump}]{\text{Sudden}}$ $\boxed{47.2}$ IE_2 $\boxed{71.6}$ IE_3 $\boxed{98.9}$ IE_4

No. of valence electron = 1 [large difference b/w IE_1 & IE_2]

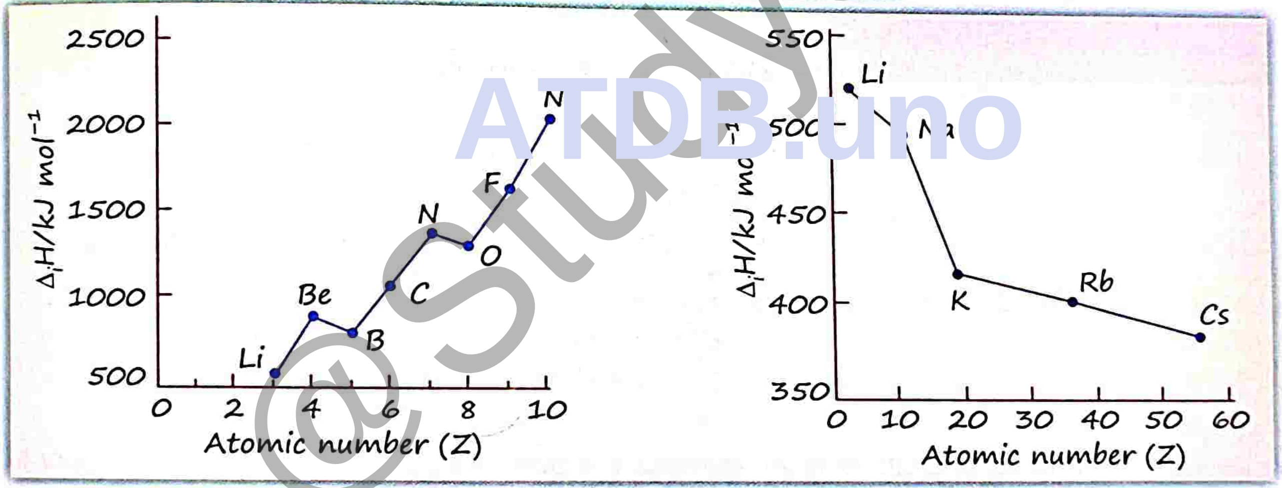


Element	IE_1	IE_2	IE_3	IE_4	IE_5	Number of valence electrons
X	5.98	18.22	28.44 $\xrightarrow[\text{Jump}]{\text{Sudden}}$	119.4	–	3
Y	11.26	26.38	47.44	77.41 $\xrightarrow[\text{Jump}]{\text{Sudden}}$	392.07	4

- If the difference in ionisation energy $\Delta(IE_2 - IE_1)$ is greater than 16 eV atom^{-1}, then the (+1) oxidation state is stable.
  For Na, $\Delta(IE_2 - IE_1) \approx 41$ eV atom^{-1} $\Rightarrow$ Na^+ is more stable.
- If value of $\Delta(IE_2 - IE_1)$ is less than 11 eV atom^{-1} then the (+2) oxidation state is stable.
  For Mg, value of $\Delta(IE_2 - IE_1) \approx 7$ eV atom^{-1} $\Rightarrow$ Mg^{2+} is more stable.



- The periodicity of the graph is quite striking.
- You will find maxima at the noble gases which have closed electron shells and very stable electron configurations.
- Minima occur at the alkali metals and their low ionization enthalpies can be correlated with their high reactivity.



38. Consider the following ionisation enthalpies of two elements 'A' and 'B'. Which of the following statements is correct? [8 April, 2017 (Shift-I)]

Element	Ionization enthalpy (kJ/mol)		
	1st	2nd	3rd
A	899	1757	14847
B	737	1450	7731

(a) Both 'A' and 'B' belong to group-1 where 'B' comes below 'A'
(b) Both 'A' and 'B' belong to group-2 where 'A' comes below 'B'
(c) Both 'A' and 'B' belong to group-2 where 'B' comes below 'A'
(d) Both 'A' and 'B' belong to group-1 where 'A' comes below 'B'

Sol. (c) Both 'A' and 'B' belong to group-2. On moving down the group, the ionisation energy decreases. Since first ionisation energy of B is lower than that of A, 'B' comes below 'A'.

39. Which of the following represents the correct order of metallic character of the given elements? **[24 Jan, 2023 (Shift-2)]**

(a) Si < Be < Mg < K (b) Be < Si < Mg < K (c) K < Mg < Be < Si (d) Be < Si < K < Mg

Sol. (a)

40. Outermost electronic configurations of four element A, B, C, D are given below:

(1) $3s^2$ (2) $3s^2 3p^1$ (3) $3s^2 3p^3$ (4) $3s^2 3p^4$

The correct order of first ionization enthalpy for them is : **[27 July, 2022 (Shift-2)]**

(a) (1) < (2) < (3) < (4) (b) (2) < (1) < (4) < (3)

(c) (2) < (4) < (1) < (3) (d) (2) < (1) < (3) < (4)

Sol. (b) IE → Al < Mg < S < P

(1) $3s^2 \rightarrow Mg$ (2) $3s^2 3p^1 \rightarrow Al$ (3) $3s^2 3p^3 \rightarrow P$ (4) $3s^2 3p^4 \rightarrow S$

41. **Statement-I:** The decrease in first ionization enthalpy from B to Al is much larger than that from Al to Ga.

Statement-II: The d orbitals in Ga are completely filled. **[29 Jan, 2023 (Shift-II)]**

(a) Statement-I is incorrect but Statement-II is correct

(b) Both the Statements I and II are correct

(c) Statement-I is correct but Statement-II is incorrect

(d) Both the Statements I and II are incorrect

Sol. (b)

42. Match List-I with List-II. **[26 Feb, 2021 (Shift-I)]**

	List-I Electronic configuration of elements		List-II ΔH in kJ mol^{-1}
A.	$1s^2 2s^2$	I.	801
B.	$1s^2 2s^2 2p^4$	II.	899
C.	$1s^2 2s^2 2p^3$	III.	1314
D.	$1s^2 2s^2 2p^1$	IV.	1402

Choose the most appropriate answer from the options given below:

(a) (A)-(II), (B)-(III), (C)-(IV), (D)-(I) (b) (A)-(I), (B)-(III), (C)-(IV), (D)-(II)

(c) (A)-(I), (B)-(IV), (C)-(III), (D)-(II) (d) (A)-(IV), (B)-(I), (C)-(II), (D)-(III)

Sol. (a) N > O > Be > B

43. The five successive ionization enthalpies of an element are 800, 2427, 3658, 25024 and 32824 kJ mol^{-1}. The number of valence electrons in the element is: **[3 Sept, 2020 (Shift-II)]**

(a) 4 (b) 2 (c) 5 (d) 3

Sol. (d) Due to large difference in 3rd and 4th ionisation energies, the number of valence electrons is 3.

44. If first ionization enthalpies of elements X and Y are 419 kJ mol^{-1} and 590 kJ mol^{-1}, respectively and second ionization enthalpies of X and Y are 3069 kJ mol^{-1} and 1145 kJ mol^{-1}, respectively. Then correct statement is: **[NEET 2022 Re]**

(a) Both X and Y are alkaline earth metals.

(b) X is an alkali metal and Y is an alkaline earth metal.

(c) X is an alkaline earth metal and Y is an alkali metal.

(d) Both X and Y are alkali metals.

Sol. (b) $X \xrightarrow{419} X^+ \xrightarrow{3069} X^{2+}$ $Y \xrightarrow{590} Y^+ \xrightarrow{1145} Y^{2+}$ $[IE_1 : X < Y, IE_2 : X > Y]$

45. Amongst the elements with following electronic configurations, which one of them may have the highest ionisation energy? **[NEET 2009]**

(a) [Ne] $3s^2 3p^2$ (b) [Ar] $3d^{10} 4s^2 4p^3$ (c) [Ne] $3s^2 3p^1$ (d) [Ne] $3s^2 3p^3$

Sol. (d)

46. With which of the following electronic configuration, an atom has the lowest ionisation enthalpy? **[NEET 2007]**

(a) $1s^2\ 2s^2\ 2p^3$ (b) $1s^2\ 2s^2\ 2p^5\ 3s^1$ (c) $1s^2\ 2s^2\ 2p^6$ (d) $1s^2\ 2s^2\ 2p^5$

Sol. (b)

ELECTRON GAIN ENTHALPY

Enthalpy change in addition of an electron in an isolated gaseous atom is known as electron gain enthalpy.

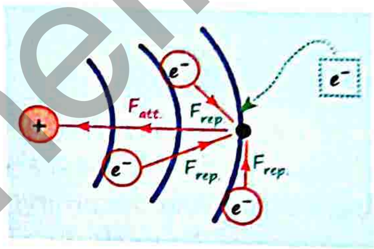
- ☐ Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion.

◆ $F_{att.} > F_{rep.}$: Release of Energy

$$A \xrightarrow{e^-} A^- + \text{Energy}$$

◆ $F_{att.} < F_{rep.}$: Absorption of Energy

$$B \xrightarrow[\text{Energy}]{e^-} B^-$$



Electron Affinity

Tendency of an isolated gaseous atom to add an electron is known as electron affinity.

- ☐ More –ve $\Delta_{eg}H$ ⇒ more electron affinity
- ☐ Less –ve $\Delta_{eg}H$ ⇒ less electron affinity

- ☐ Electron affinity is measured in terms of EGE (ΔH_{eg}).

◆ $H \xrightarrow{+e^-} H^-$ $\Delta_{eg}H = -\ 73$ KJ/mol

$Li \xrightarrow{+e^-} Li^-$ $\Delta_{eg}H = -\ 60$ KJ/mol

→ Electron affinity : H > Li

- ☐ **Formation of multiple ⊖ve anion:** Overall energy change during formation of multiple ⊖ve anion is always ⊕ve.

1. $O \xrightarrow{e^-} O^-$ $\Delta H_1 = -\ 141$ KJ/mol (Exo)

$O^- \xrightarrow[\text{Energy}]{e^-} O^{2-}$ $\Delta H_2 = +\ 844$ KJ/mol (Endo)

$O \xrightarrow{2e^-} O^{2-}$ $\Delta H_1 + \Delta H_2 = +\ 703$ KJ/mol (Endo)

---

2. $N \xrightarrow{3e^-} N^{3-}$ ΔH_{eg} = ⊕ve (Endo)

3. $P \xrightarrow{3e^-} P^{3-}$ ΔH_{eg} = ⊕ve (Endo)

Factor Affecting Electron Affinity

① Z_{eff}

Left → Right : Z_{eff} ↑ : EA ↑

$O_8 < F_9$: EA

② Size

Top ↓ Bottom → Size ↑
→ EA ↓

EA : Cl > Br > I > At

③ Electronic Configuration

☐ Generally for stable electronic configuration (half filled and fully filled) ⇒ $\Delta H = \oplus ve$.

◆ $N \xrightarrow{e^-} N^-$ $(2s^2\ 2p^3)$ $\Delta_{eg}H = \oplus ve$

◆ $Ne \xrightarrow{e^-} Ne^-$ $(2s^2\ 2p^6)$ $\Delta_{eg}H = \oplus ve$

④ Penetration Effect

Addition of electron in s-orbital is more favorable than p-orbital because s-orbital is near to the nucleus and upcoming electron get more attraction by nucleus.

☐ EA : K > Ga
: Rb > In
: Cs > Tl

Li $(2s^1)$ > B $(2s^2\ 2p^1)$

$Li \xrightarrow{+e^-} Li^-\ (2s^2)$

$B \xrightarrow{+e^-} B^-\ (2s^2\ 2p^2)$

Na $(3s^1)$ > Al $(3s^2\ 3p^1)$

Important Points

☐ Generally For neutral atom : $\Delta_{eg}H \equiv (-)ve$

$O \xrightarrow{e^-} O^-$ (Exo)
$C \xrightarrow{e^-} C^-$ (Exo)

☐ But For (Be, Mg, N) (Inert Gas) : $\Delta_{eg}H \equiv (+)ve$

$He \xrightarrow{e^-} He^-$ (Endo)
$Ne \xrightarrow{e^-} Ne^-$ (Endo)
$N \xrightarrow{e^-} N^-$ (Endo)
$Be \xrightarrow{e^-} Be^-$ (Endo)
$Mg \xrightarrow{e^-} Mg^-$ (Endo)

☐ For all cations : $\Delta_{eg}H \equiv (-)ve$

$C^+ \xrightarrow{e^-} C$ (Exo)
$Na^+ \xrightarrow{e^-} Na$ (Exo)

☐ For all anions : $\Delta_{eg}H \equiv (+)ve$

$O^- \xrightarrow{e^-} O^{2-}$ (Endo)
$N^- \xrightarrow{e^-} N^{2-}$ (Endo)

↓

Adding an electron to a negatively charged ion is more difficult because it requires energy to overco the repulsion between the negative charge on atom and electron. This makes the second electron ga enthalpy positive (endothermic).

☐ 1st EGE [ΔH_{eg_1}] may be +ve/−ve. 2nd EGE [ΔH_{eg_2}] is always ⊕ ve.

- ◆ $O \xrightarrow{e^-} O^-$ ΔH_{eg_1} = ⊖ ve
- ◆ $N \xrightarrow{e^-} N^-$ ΔH_{eg_1} = ⊕ ve
- ◆ $O^- \xrightarrow{e^-} O^{2-}$ ΔH_{eg_2} = ⊕ ve
- ◆ $N^- \xrightarrow{e^-} N^{2-}$ ΔH_{eg_2} = ⊕ ve

☐ EA : $\boxed{Ne < Be < N} < \boxed{B < Li < C < O < F}$

$\Delta_{eg}H$ = ⊕ve $\Delta_{eg}H$ = ⊖ve

$\Delta_{eg}H$ = ⊕ve $\Delta_{eg}H$ = ⊖ve

☐ EA : $\boxed{Ar < Mg} < \boxed{Al < Na < P < Si < S < Cl}$

☐ EA : alkali metals > alkaline earth metals

alkali metals:
- $ns^1 \xrightarrow{+e} ns^2$
- Fully-filled electronic configuration is achieved
- $\Delta_{eg}H$ is (−)ve

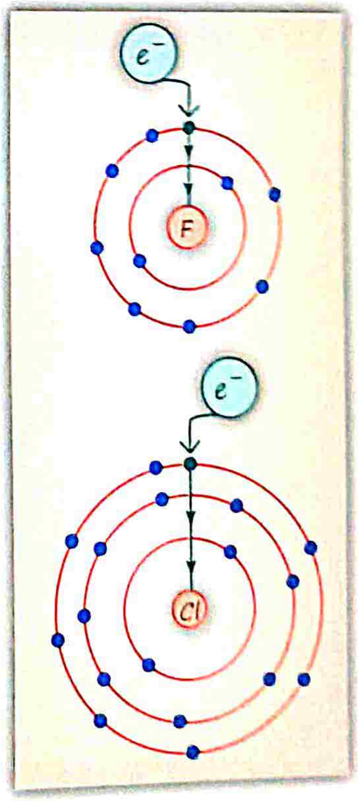
alkaline earth metals:
- $ns^2 \xrightarrow{+e} ns^2\,np^1$
- Fully-filled electronic configuration is disturbed
- $\Delta_{eg}H$ is (+)ve

Comparison b/w Electron Affinity of F & Cl

☐ $\underset{2s^2\,2p^5}{F} \xrightarrow{e^-} \underset{2s^2\,2p^6}{F^-}$ $\Delta_{eg}H = -328$ KJ/mol

☐ $\underset{3s^2\,3p^5}{Cl} \xrightarrow{e^-} \underset{3s^2\,3p^6}{Cl^-}$ $\Delta_{eg}H = -349$ KJ/mol

→ EA ≡ Cl > F



☐ Adding an electron to the 2p-orbital (F) leads to greater repulsion than adding an electron to the larger 3p-orbital (Cl). Hence electron gain enthalpy of the Cl is more negative than F.

Note

◆ B C N O F (Period 2)

$\wedge$ $\wedge$ $\wedge$ $\wedge$ $\wedge$

◆ Al Si P S Cl (Period 3)

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

☐ Order of (−)ve electron gain enthapy: H > Li > Na > $\underbrace{\text{K > Rb > Cs}}_{\text{approx. same value}}$

☐ Order of (−)ve electron gain enthalpy: S > Se > Te > Po > O
Cl > F > Br > I > At

☐ Order of (+)ve electron gain enthalpy: Ne > Ar = Kr > Xe > Rn > He

Noble gases have (+)ve electron gain enthalpy as they have completely filled orbitals of valence shell.

Note

☐ Cl has most (−)ve ΔH_{eg} and Ne has most (+)ve ΔH_{eg} among all elements.

☐ Oxygen has min. EGE in family. EA : S > Se > Te > Po > O

☐ Halogen family has max. EGE in periodic table.

☐ Any element from G−17 has higher EGE wrt other element in periodic table. EA : I > S

47. Find the order of electron affinity in following:

(a) Cl, Br, S, O (b) O, S, Se, I (c) Li, B (d) F, Cl, O, N (e) P, S, Cl, F

Sol. (a) Cl > Br > S > O : ΔH_{eg} (more negative) or electron affinity
(b) I > S > Se > O
(c) Li > B
(d) Cl > F > O > N
(e) Cl > F > S > P

48. In which of the following pairs, electron gain enthalpies of constituent elements are nearly the same or identical? [28 July, 2022 (Shift-1)]

1. Rb and Cs 2. Na and K 3. Ar and Kr 4. I and At

Choose the correct answer from the options given below :

(a) 1 and 2 only (b) 2 and 3 only (c) 1 and 3 only (d) 3 and 4 only

Sol. (c)

49. Inert gases have positive electron gain enthalpy. Its correct order is : [24 Jan, 2023 (Shift-1)]

(a) Xe < Kr < Ne < He
(b) He < Ne < Kr < Xe
(c) He < Xe < Kr < Ne
(d) He < Kr < Xe < Ne

Sol. (c)

50. The first electron gain enthalpy (ΔH_{eg}) of oxygen is −141 kJ/mol, its second electron gain enthalpy is :

(a) Almost the same as that of the first
(b) a more negative value than the first
(c) negative, but less negative than the first
(d) a positive value

Sol. (d)

51. The formation of the oxide in O^{2-} requires first an exothermic and then an endothermic step as shown below :

$$O \longrightarrow O^- \qquad \Delta H_1 = -141 \text{ kJ / mol}$$
$$O^- \longrightarrow O^{2-} \qquad \Delta H_2 = +844 \text{ kJ / mol}$$

This is because:

(a) Oxygen is more electronegative
(b) Oxygen has high electron affinity.
(c) O^- ion will tend to resist the addition of another electron.
(d) O^- ion has comparatively larger size than oxygen atom.

Sol. (c)

52. For electron gain enthalpies of the elements denoted as $\Delta_{eg}H$, the incorrect option is: [1 Feb, 2023 (Shift-II)]

(a) $\Delta_{eg}H(Cl) < \Delta_{eg}H(F)$
(b) $\Delta_{eg}H(Se) < \Delta_{eg}H(S)$
(c) $\Delta_{eg}H(I) < \Delta_{eg}H(At)$
(d) $\Delta_{eg}H(Te) < \Delta_{eg}H(Po)$

Sol. (b) $\Delta_{eg}H$ (S) is more (−)ve value than $\Delta_{eg}H$ (Se).

53. The process that is NOT endothermic in nature is: [4 Sept, 2020 (Shift-II)]

(a) $H_{(g)} + e^- \rightarrow H^-_{(g)}$
(b) $O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)}$
(c) $Na_{(g)} \rightarrow Na^+_{(g)} + e^-$
(d) $Ar_{(g)} + e^- \rightarrow Ar^-_{(g)}$

Sol. (a)

[IIT JEE 2002]

54. Identify the least stable ion amongst the following:

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

Sol. (b) Be^- ion is formed by absorption of energy, so they have high energy → means least stable.

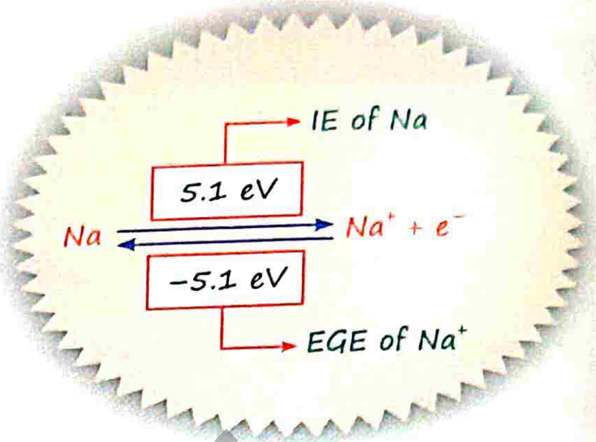
Relation Between I.E. & E.G.E.

☐ $A \underset{EGE}{\overset{IE}{\rightleftharpoons}} A^{+} + e^{-}$

IE of A ≡ | EGE of A$^{\oplus}$|

Order of IE : F > Cl

Order of EA : $F^{+} > Cl^{+}$



☐ $A^{-} \underset{\Delta H_{eg} \text{ of } A}{\overset{\text{IE of } A^{-}}{\rightleftharpoons}} A + e^{-}$

IE of A^{-} = |$\Delta_{eg}H$ of A|

◆ $F^{-} \underset{\text{EA of } F}{\overset{\text{IE of } F^{-}}{\rightleftharpoons}} F + e^{-}$

◆ $Cl^{-} \underset{\text{EA of } Cl}{\overset{\text{IE of } Cl^{-}}{\rightleftharpoons}} Cl + e^{-}$

EA ≡ Cl > F

IE ≡ $Cl^{-} > F^{-}$

Note

If energy is released when an electron is added to an atom, the electron affinity is taken as positive, contrary to thermodynamic convention. If energy has to be supplied to add an electron to an atom, then the electron affinity of the atom is assigned a negative sign. However, electron affinity is defined as absolute zero and, therefore at any other temperature (T) heat capacities of the reactants and the products have to be taken into account in $\Delta_{eg}H = -A - 5/2\ RT$.

55. In which of the following options, the order of arrangement does not agree with the variation of property indicated against it? [NEET 2016-I]

(a) Li < Na < K < Rb (increasing metallic radius)

(b) $Al^{3+} < Mg^{2+} < Na^{+} < F^{-}$ (increasing ionic size)

(c) B < C < N < O (increasing first ionization enthalpy)

(d) I < Br < F < Cl (increasing electron gain enthalpy)

Sol. (c)

56. The formation of the oxide ion, O^{2-} (g) from oxygen atom requires first an exothermic step and then an endothermic step as shown below:

$O\ (g) + e^{-} \rightarrow O^{-}\ (g)\ ;\ \Delta_f H^{o} = -141\ \text{kJ mol}^{-1}$

$O^{-}\ (g) + e^{-} \rightarrow O^{2-}\ (g)\ ;\ \Delta_f H^{o} = +780\ \text{kJ mol}^{-1}$

Thus, process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon. It is due to the fact that, [NEET 2015 Re]

(a) O^{-} ion has comparatively smaller size than oxygen atom

(b) Oxygen is more electronegative

(c) Addition of electron in oxygen results in larger size of the ion

(d) Electron repulsion outweighs the stability gained by achieving noble gas configuration

Sol. (d)

57. Which one of the following arrangements represents the correct order of electron gain enthalpy (with negative sign) of the given atomic species? [NEET 2005]

(a) Cl < F < S < O (b) O < S < F < Cl (c) S < O < Cl < F (d) F < Cl < O < S

Sol. (b)

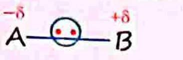
58. What is the value of electron gain enthalpy of Na^+ if IE_1 of Na = 5.1 eV? [NEET 2011 Mains]
(a) +2.55 eV (b) +10.2 eV (c) −5.1 eV (d) −10.2 eV

Sol. (c)

ELECTRONEGATIVITY

☐ Tendency of an atom to attract shared pair of electrons in a covalent bond is known as electronegativity.

−δ : partial ⊖ve charge



Z_{eff} : A > B ⇒ EN : A > B

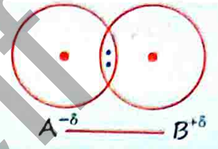
1. Z_{eff} ↑ : EN ↑

$(Z_{eff})_A > (Z_{eff})_B$

$(EN)_A > (EN)_B$

Left → Right ⇒ EN ↑

B < C < N < O < F : EN

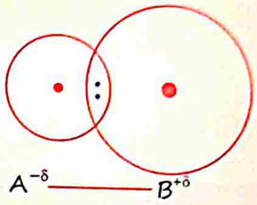


2. Size ↑ : EN ↓

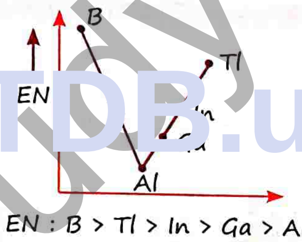
$(Size)_A < (Size)_B$

Top ↓ Bottom → Size ↑ → EN ↓

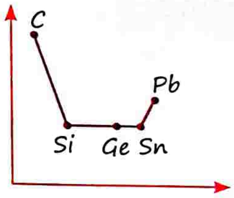
F > Cl > Br > I



Graph of Electronegativity Trends for Group 13 and Group 14 Elements



EN : B > Tl > In > Ga > Al



EN : C > Pb > Si = Ge = Sn

Scale for Electronegativity

- Pauling Scale
- Mulliken Scale
- Allred Rochow Scale

Pauling Scale

CIS (2.5)
HP (2.1)

2.1 H						
1 Li	1.5 Be	2 B	2.5 C	3 N	3.5 O	4 F
0.9 Na	1.2 Mg	1.5 Al	1.8 Si	2.1 P	2.5 S	3 Cl
						2.8 Br
						2.5 I

$Na \xrightarrow{0.3} Mg \xrightarrow{0.3} Al \xrightarrow{0.3} Si \xrightarrow{0.3} P \xrightarrow{0.4} S \xrightarrow{0.5} Cl$

☐ Most electronegative element : F

☐ Second most electronegative element : O

☐ It is based on an empirical relation between energy of a bond and electronegativity.

$$\boxed{\chi_A - \chi_B = 0.208\sqrt{\Delta}\ \text{kcal mol}^{-1}}$$

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

Δ = Extra bond Energy

= Actual bond Energy (A – B) – Calculated bond energy for 100% covalent bond (A – B)

$$\chi_A - \chi_B = 0.208\sqrt{E_{A-B} - \sqrt{E_{A-A} \cdot E_{B-B}}}$$

$$\boxed{\chi_A - \chi_B = 0.101\sqrt{\Delta}\ \text{kJ mol}^{-1}}$$

59. The correct option with respect to the Pauling electronegativity values of the elements is :

(a) Te > Se (b) Ga < Ge (c) Si < Al (d) P > S

Sol. (b)

Mulliken Scale

$$\chi_M = \frac{\text{I.E. + E.A. (eV/atom)}}{2}$$

$$\boxed{\chi_M = 2.8\ \chi_P}$$

I.E. → Ionisation energy of an element in eV/atom

E.A → Electron affinity of an element in eV/atom

χ_M → Electronegativity of an element on Mulliken scale

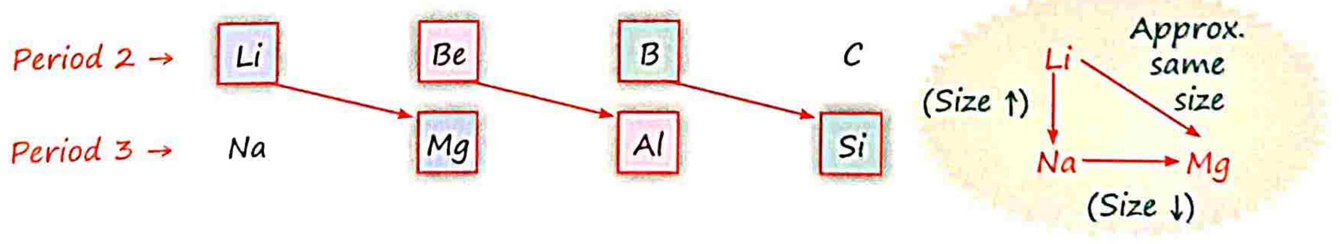
χ_P → Electronegativity of an element on Pauling scale

DIAGONAL RELATIONSHIP

☐ Some elements of certain groups of second period resemble much in properties with the element third period, which are diagonally related in properties.

☐ Diagonal relationship arises because of similar size of atom and ions.

For Example: Atomic size : Li ≈ Mg , Ionic size = $Li^+ > Mg^{2+}$



60. The set of elements that differ in mutual relationship from those of the other sets is :

[17 March, 2021 (Shift-

(a) Li – Mg (b) B – Si (c) Be – Al (d) Li – Na

Sol. (d)

61. Match List-I with List-II

List-I (Elements)		List-II (Properties in their respective groups)	
A.	Cl, S	I.	Elements with highest electronegativity
B.	Ge, As	II.	Elements with largest atomic size
C.	Fr, Ra	III.	Elements which show properties of both metal and non metal
D.	F, O	IV.	Elements with highest negative electron gain enthalpy

Choose the correct answer from the options given below: [08 April, 2024 (Shift-I)]

(a) A-II, B-III, C-IV, D-I
(b) A-III, B-II, C-I, D-IV
(c) A-IV, B-III, C-II, D-I
(d) A-II, B-I, C-IV, D-III

Sol. (c)

62. Arrange the following elements in increasing order of electronegativity: [NEET 2024]

N, O, F, C, Si

Choose the correct answer from the options given below:

(a) $O < F < N < C < Si$
(b) $F < O < N < C < Si$
(c) $Si < C < N < O < F$
(d) $Si < C < O < N < F$

Sol. (c)

OXIDATION STATE

The oxidation state of an atom in a molecule or in an ion is the charge the atom would have if the electron in each bond were located on the more electronegative atom.

Rule:

1.	F : −1	(Li → Cs) Group 1 : +1	(Be → Ra) Group 2: +2	Zn : +2 Al, Sc, Ga : +3
2.	H : +1			
3.	O : −2			
4.	N : −3			
5.	Cl, Br, I : −1			

- Elements in rule −1 ALWAYS show fix oxidation state in all molecules.
- Elements in rules 2, 3, 4, and 5 generally show the listed oxidation state but can also exhibit variable oxidation states in different compounds.
- **Priority of rule: 1 > 2 > 3 > 4 > 5**

Na^+	N^{3-}	NO_3^-	NH_4^+
$x = +1$	$x = -3$	$x + 3(-2) = -1$ then $x = +5$	$x + 4(+1) = +1$ then $x = -3$

LiH	H_2SO_4	Na_2O	Na_2O_2
$(+1) + x = 0$ then $x = -1$	$2(+1) + x + 4(-2) = 0$ then $x = +6$	$2(+1) + x = 0$ then $x = -2$	$2(+1) + 2x = 0$ then $x = -1$

OXIDES & HYDROXIDES

Basic Oxides: $\underset{\text{Basic Oxide}}{Na_2O} + \underset{\text{Acid}}{2HCl} \longrightarrow \underset{\text{Salt}}{2NaCl} + H_2O$

Acidic Oxides: $\underset{\text{Acidic Oxide}}{CO_2} + \underset{\text{Base}}{2NaOH} \longrightarrow \underset{\text{Salt}}{Na_2CO_3} + H_2O$

Amphoteric Oxides:

$$ZnO \xrightarrow{2HCl} ZnCl_2 + H_2O$$

$$ZnO \xrightarrow{2NaOH} Zn(OH)_2 \xrightarrow[NaOH]{Excess} Na_2[Zn(OH)_4]$$

Neutral Oxides: $\underset{\text{Carbon monoxide}}{CO}$ / $\underset{\text{Nitrous oxide}}{N_2O}$ / $\underset{\text{Nitric oxide}}{NO}$

Amphoteric Oxides

- ☐ As(+3) Sb(+3) Cr(+3) V(+5) Te(+4)
  Aas Sab Car Vento Tera
- ☐ Zn Sn Be Al Pb Ga
  Zaan Suno Be Aaliya Pub Gayi

Amphoteric but predominantly acidic → $\overset{+5}{V_2O_5}$

Example → $\overset{+3}{As_2O_3}$ $\overset{+3}{Sb_2O_3}$ $\overset{+3}{Cr_2O_3}$ $\overset{+5}{V_2O_5}$ $\overset{+4}{TeO_2}$

ZnO BeO Al_2O_3 Ga_2O_3 SnO SnO_2 PbO PbO_2 Pb_3O_4 Pb_3O_2

Basic Oxides

- ☐ Most common oxidation states for metals are +1, +2 and +3.
- ☐ Generally oxide of metals are basic in nature but some oxides are amphoteric and acidic also.

Metals

- +1 / +2 / +3 → Basic Oxides: $\overset{+2}{CaO}$, $\overset{+1}{Li_2O}$, $\overset{+2}{MgO}$, $\overset{+3}{V_2O_3}$, $\overset{+2}{CrO}$, $\overset{+2}{MnO}$
- +4 → Amphoteric oxides: $\overset{+4}{TiO_2}$, $\overset{+4}{MnO_2}$, $\overset{+4}{ZrO_2}$
- +6 / +7 → Acidic Oxides: $\overset{+6}{CrO_3}$, $\overset{+7}{Mn_2O_7}$

Acidic Oxides

- ☐ Generally non-metal oxides are acidic except some neutral oxide [CO, NO, N_2O].
- ☐ Metalloid oxides are acidic except those which are considered already in amphoteric.

Non-metal Oxide

Acidic
- B_2O_3
- CO_2
- N_2O_5
- P_2O_5
- Cl_2O_7

Neutral
- CO
- NO
- N_2O

Metalloid Oxide

As
Sb
Se
Te
Ge

- ☐ As_2O_3 (+3) : Amphoteric
  As_2O_5 (+5) : Acidic
- ☐ Sb_2O_3 (+3) : Amphoteric
  Sb_2O_5 (+5) : Acidic
- ☐ TeO_2 (+4) : Amphoteric
- ☐ TeO_3 (+6) : Acidic

Acidic Nature of Oxides

☐ In an oxide, as oxidation state of element increases, acidic nature of oxides increases.

◆ $\overset{+1}{Li_2O} < \overset{+2}{BeO} < \overset{+3}{B_2O_3} < \overset{+4}{CO_2} < \overset{+5}{N_2O_5}$

◆ $\overset{+2}{CO} < \overset{+4}{CO_2}$

◆ $\overset{+1}{Na_2O} < \overset{+2}{MgO} < \overset{+3}{Al_2O_3} < \overset{+4}{SiO_2} < \overset{+5}{P_2O_5} < \overset{+6}{SO_3} < \overset{+7}{Cl_2O_7}$

◆ $\overset{+4}{SO_2} < \overset{+6}{SO_3}$

◆ $\overset{+1}{N_2O} < \overset{+2}{NO} < \overset{+3}{N_2O_3} < \overset{+4}{NO_2} < \overset{+5}{N_2O_5}$

Note

M—O—H like compound will act as acid or as base can be predicted very easily.

a. Acts as a base when

$M—O—H \rightleftharpoons M^+ + OH^-$

$|\chi_O - \chi_M| > |\chi_O - \chi_H|$

☐ Cs—O—H is a base because

$\chi_O - \chi_{Cs} = 3.5 - 0.7 = 2.8$

$\chi_O - \chi_H = 3.5 - 2.1 = 1.4$

b. Acts as an acid when

$M—O—H \rightleftharpoons MO^- + H^+$

$|\chi_O - \chi_H| > |\chi_O - \chi_M|$

☐ Cl—O—H is an acid because

$\chi_O - \chi_{Cl} = 3.5 - 3.1 = 0.34$

$\chi_O - \chi_H = 3.5 - 2.1 = 1.4$

Basic Oxide	Basic hydroxide	Acidic oxide	Acidic hydroxide	Amphoteric oxide	Amphoteric hydroxide
Na_2O	$NaOH$	SiO_2	$Si(OH)_4$	Al_2O_3	$Al(OH)_3$
MgO	$Mg(OH)_2$	B_2O_3	$B(OH)_3$	ZnO	$Zn(OH)_2$
MnO	$Mn(OH)_2$	N_2O_5	HNO_3	BeO	$Be(OH)_2$
CuO	$Cu(OH)_2$	CO_2	H_2CO_3	PbO	$Pb(OH)_2$

63. Three elements X, Y and Z are in the 3rd period of the periodic table. The oxides of X, Y and Z, respectively, are basic, amphoteric and acidic. The correct order of the atomic numbers of X, Y and Z is: [2 Sept, 2020 (Shift-II)]

(a) X < Z < Y (b) Z < Y < X (c) X < Y < Z (d) Y < X < Z

Sol. (c) Atomic number → X (basic oxide) < Y (amphoteric oxide) < Z (acidic oxide)

64. The correct sequence given below containing neutral, acidic, basic and amphoteric oxide each, respectively, is [NEET 2023-Manipur]

(a) NO, ZnO, CO_2, CaO (b) ZnO, NO, CaO, CO_2
(c) NO, CO_2, ZnO, CaO (d) NO, CO_2, CaO, ZnO

Sol. (d)

GENESIS OF PERIODIC CLASSIFICATION

1. Dobereiner's Traids
2. Newland's Law of Octaves
3. Lothar Meyer Classification
4. Mendeleev's Periodic Table
5. Modern Periodic Table

Dobereiner's Traids

3 elements → A, B, C

$$M_B = \frac{M_A + M_C}{2}$$

M_A = atomic mass of A
M_B = atomic mass of B
M_C = atomic mass of C

Dobereiner arranged certain elements with similar properties in groups of three (Triad) in such a way that the atomic mass of the middle element was nearly the same the average atomic masses of the first and the third elements.

Elements	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	Ca	40	Cl	35.5
Na	23	Sr	88	Br	80
K	39	Ba	137	I	127

Be	8
Mg →	24
Ca	40

S	32
Se →	79
Te	127

P	31
As →	75
Sb	120

H	1
F →	19
Cl	35.5

Sc : x
Y → $y = \frac{x + z}{2}$
La : z

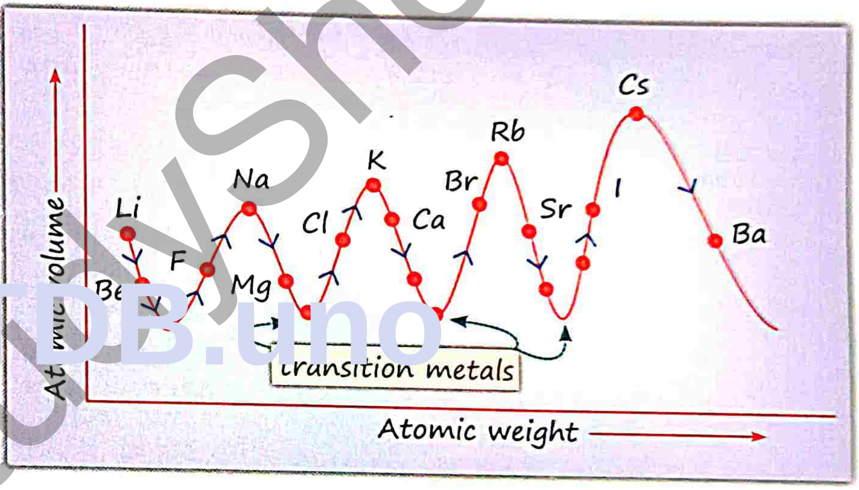
Newland's Law of Octaves

☐ When elements are arranged in order of increasing atomic masses, every 8th element has properties similar to the first. Newlands called it law of octaves because similar relationship exists in the musical notes also.

sa	re	ga	ma	pa	da	ni
H →	Li →	Be →	B →	C →	N →	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe
Co and Ni	Cu	Zn	Y	In	As	Se
Br	Rb	Sr	Ce and La	Zr	–	–

Lothar Meyer Classification

- He calculated the atomic volumes by dividing atomic masses with their densities in solid states.
- He plotted a graph between atomic masses against their respective atomic volumes for a number of elements.
- Elements with similar properties occupied similar positions on the curve.
- Atomic volumes (a physical property) of the elements are the periodic functions of their atomic masses.
- Alkali metals (Li, Na, K, Rb, Cs) having larger atomic volumes occupied the crests.
- Alkaline earth metals (Be, Mg, Ca, Sr, Ba) occupied the positions at about the mid points of the descending portions of the curve.
- The halogens (F, Cl, Br, I) occupied the ascending portions of the curve before the inert gases.
- Transitions elements occupied the troughs.



Mendeleev's Periodic Table

Characteristic of Mendeleev's Periodic Table:

(i) It is based on atomic weight.

(ii) 63 elements were known, noble gases were not discovered.

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

(iv) Horizontal rows are called periods and there were 7 periods in Mendeleev's Periodic table.

(v) Vertical columns are called groups and there were 8 groups in Mendeleev's Periodic table.

(vi) Each group upto VIIth is divided into A & B subgroups. 'A' sub group element are called normal element and 'B' sub groups elements are called transition elements.

(vii) The VIIIth group was consist of 9 elements in three rows (Transition metals group).

(viii) The elements belonging to same group exhibit similar properties.

Fe	Co	Ni
Ru	Rh	Pd
Os	Ir	Pt

Series	Groups of Elements								
	0	I	II	III	IV	V	VI	VII	VIII
1	–	H 1.008	–	–					
2	He 4.0	Li 7.03	Be 9.1	B 11.0	C 12.0	N 14.04	O 16.00	F 19.0	
3	Ne 19.9	Na 23.5	Mg 24.3	Al 27.0	Si 28.4	P 31.0	S 32.06	Cl 35.45	
4	Ar 38	K 39.1	Ca 40.1	Sc 44.1	Ti 48.1	V 51.4	Cr 52.1	Mn 55.0	Fe 55.9 Co 59 Ni 59
5		Cu 63.6	Zn 65.4	Ga 70.0	Ge 72.3	As 75	Se 79	Br 79.95	
6	Kr 81.8	Rb 85.4	Sr 87.6	Y 89.0	Zr 90.6	Nb 94.0	Mo 96.0	–	Ru 101.7 Rh 103.0 Pd 106.5
7		Ag 107.9	Cd 112.4	In 114.0	Sn 119.0	Sb 120.0	Te 127.6	I 126.9	
8	Xe 128	Cs 132.9	Ba 137.4	La 139	Ce 140	–	–	–	
9		–	–	–	–	–	–	–	
10	–	–	–	Yb 173		Ta 183	W 184	–	Os 191 Ir 193 Pt 194.9
11		Au 197.2	Hg 200.0	Tl 204.1	Pb 206.9	Bi 208	–	–	
12	–	–	Ra 224	–	Th 232	–	U 239		
	R	R_2O	RO	R_2O_3	Higher Saline Oxides RO_2	R_2O_5	RO_3	R_2O_7	RO_4
					Higher Gaseous Hydrogen Compounds RH_4	RH_3	RH_2	RH	

Merits of Mendeleev Periodic Table:

- ☐ It has simplified and systematized the study of elements and their compounds.
- ☐ It has helped in predicting the discovery of new elements on the basis of the blank spaces given in its periodic table.
- ☐ Mendeleev predicted the properties of those missing elements from the known properties of the other elements in the same group.

Eka-aluminium – Ga
Eka-silicon – Ge

- ☐ Later, it was found that properties predicted by Mendeleev for these elements and those found experimentally were almost similar.

Demerits in Mendeleev's Periodic Table:

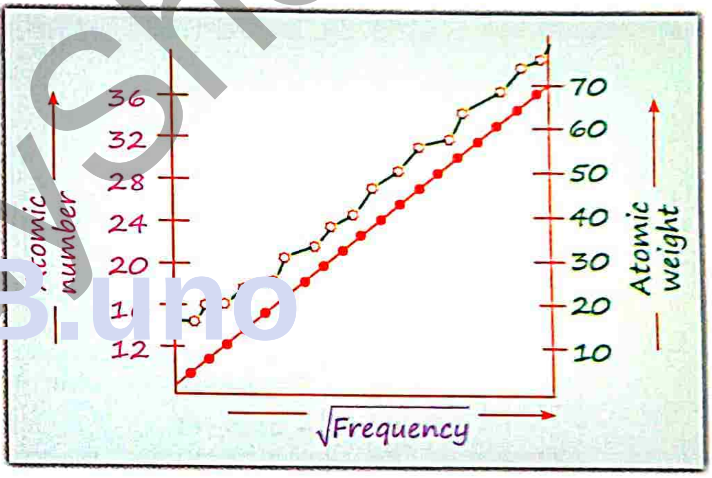
- ☐ Position of hydrogen is uncertain. It has been placed in IA and VIIA groups because of its resemblance with both the groups.
- ☐ No separate positions were given to isotopes.
- ☐ Anomalous positions of lanthanides and actinides in periodic table.
- ☐ Order of increasing atomic weights is not strictly followed.
  Te (127.6) is placed before I (126.9)
- ☐ Similar elements were placed in different groups (Cu in IB and Hg in IIB) and similarly the elements with different properties were placed in same groups (alkali metals in IA and coinage metals in IB).

Modern Periodic Table

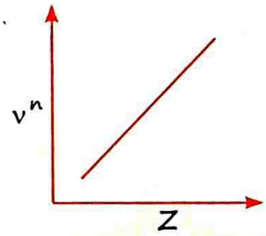
- ☐ Henry Moseley observed regularities in the characteristic X-ray spectra of the elements. A plot of $\sqrt{v}$ (where v is frequency of X-rays emitted) against atomic number (Z) gave a straight line and not the plot of $\sqrt{v}$ vs atomic mass.

◆ $\sqrt{v} \propto Z$

$\boxed{\sqrt{v} = a(Z - b)}$ (a, b : constant)



65. It is observed that characteristic X-ray spectra of elements show regularity. When frequency to the power 'n' i.e. v^n of X-rays emitted is plotted against atomic number 'Z', following graph is obtained. [24 Jan, 2023 (Shift-I)]



The value of 'n' is

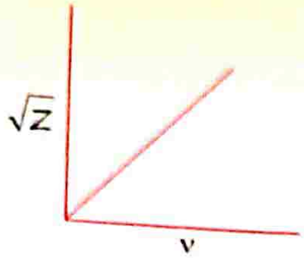
(a) 1 (b) 2 (c) 1/2 (d) 3

Sol. (c)

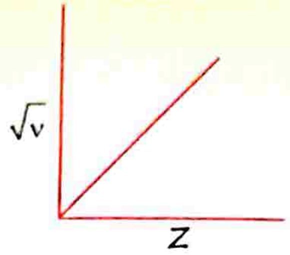
66. Henry Moseley studied characteristic X-ray spectra of elements. The graph which represents his observation correctly is:

(Given: v = frequency of X-ray emitted; Z = atomic number) [8 April, 2023 (Shift-II)]

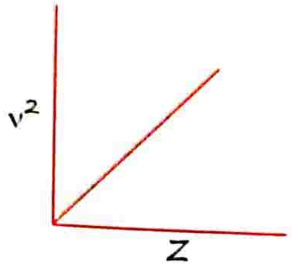
(a)



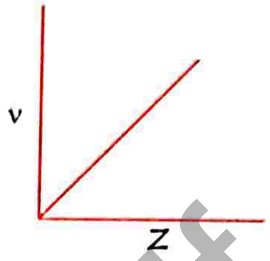
(b)



(c)

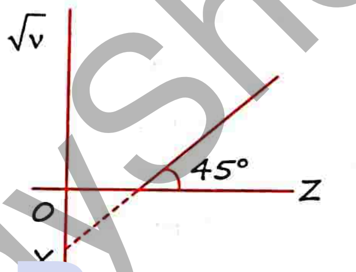


(d)



Sol. (b) $\sqrt{\nu} \propto Z$

67. In the graph between $\sqrt{\nu}$ and Z for the Moseley's equation, the intercept OX is −1 on $\sqrt{\nu}$ axis. What will be in Frequency when atomic number (Z) is 51?



(a) 50 Hz (b) [illegible]0 Hz (c) 2500 Hz (d) None

Sol. (c)

$\sqrt{\nu} = a(z-b)$ $\sqrt{\nu} = az - ab$ $y = mx + c$	Slope (m) = a = tan 45° = 1 $- ab = -1$ $-1.b = -1$ then b = 1	a = 1 & b = 1 $\sqrt{\nu} = a\,(z-b)$ $\sqrt{\nu} = 1\,(z-1)$ $= 51 - 1 = 50$	$\nu = (50)^2 = 2500$ Hz

68. The increasing order of atomic radii of the following Group 13 elements is: (JEE Adv. 2016)

(a) Al < Ga < In < Tl (b) Ga < Al < In < Tl

(c) Al < In < Ga < Tl (d) Al < Ga < Tl < In

Sol. (b)

69. The option(s) with only amphoteric oxides is (are) (JEE Adv. 2020)

(a) NO, B_2O_3, PbO, SnO_2 (b) Cr_2O_3, CrO, SnO, PbO

(c) Cr_2O_3, BeO, SnO, SnO_2 (d) ZnO, Al_2O_3, PbO, PbO_2

Sol. (c) and (d)

70. Which of the following statements are true? [NEET 2025]

A. Unlike Ga that has a very high melting point, Cs has a very low melting point.

B. On Pauling scale, the electronegativity values of N and Cl are not the same.

C. Ar, K^+, Cl^-, Ca^{2+} and S^{2-} are all isoelectronic species.

D. The correct order of the first ionization enthalpies of Na, Mg, Al, and Si is Si > Al > Mg > Na.

E. The atomic radius of Cs is greater than that of Li and Rb.

Choose the correct answer from the options given below:

(a) A, B, and E only
(b) C and E only
(c) C and D only
(d) A, C, and E only

Sol. (b)

71. Match the following: [NEET 2020]

Oxide		Nature	
A.	CO	(i)	Basic
B.	BaO	(ii)	Neutral
C.	Al_2O_3	(iii)	Acidic
D.	Cl_2O_7	(iv)	Amphoteric

Which of the following is correct option?

	(A)	(B)	(C)	(D)
(a)	(ii)	(i)	(iv)	(iii)
(b)	(iii)	(iv)	(i)	(ii)
(c)	(iv)	(iii)	(ii)	(i)
(d)	(i)	(ii)	(iii)	(iv)

Sol. (a)

72. Which of the following oxide is amphoteric in nature? [NEET 2020-Covid]

(a) SiO_2
(b) GeO_2
(c) CO_2
(d) SnO_2

Sol. (d)

Chapter 2

Chemical Bonding and Molecular Structure

JEE Main & NEET

Syllabus

Kossel-Lewis approach to chemical bond formation, the concept of ionic and covalent bonds.

Ionic Bonding: Formation of ionic bonds, factors affecting the formation of ionic bonds; calculation of lattice enthalpy.

Covalent Bonding: Concept of electronegativity, Fajan's rule, dipole moment, Valence Shell Electron Pair Repulsion (VSEPR) theory and shapes of simple molecules.

Quantum mechanical approach to covalent bonding: Valence bond theory- its important features, the concept of hybridization involving s, p and d orbitals, resonance.

Molecular Orbital Theory: Its important features, LCAOs, types of molecular orbitals (bonding, antibonding), sigma and pi-bonds, molecular orbital electronic configurations of homonuclear diatomic molecules, the concept of bond order, bond length and bond energy.

Elementary idea of metallic bonding, hydrogen bonding and its applications.

WHAT IS BOND?

- ☐ Bond ≡ Force of attraction
- ☐ The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.
- ☐ Bond Formation → Exothermic Process

Bond

Strong Bond
(≈ 200 kJ/mole)
(Inter-atomic)

(a) Covalent Bond
(b) Coordinate Bond
(c) Ionic Bond
(d) Metallic Bond

Weak Bond
(4-20 kJ/mole)
(Inter-molecular)

(a) Hydrogen Bond
(b) vander Waal force of attraction

Reason for Bond Formation

- ☐ Tendency to gain stability
- ☐ Tendency to acquire minimum energy
- ☐ Tendency to attain Inert gas configuration

VALENCE ELECTRON & LEWIS SYMBOL

Lewis Symbol → No of dots = no of valence electrons

Group No.	1	2	13	14	15	16	17	18
Valence Electron	1	2	3	4	5	6	7	8
Lewis Symbol	$\cdot Li$	$\cdot Be\cdot$	$\cdot\dot{B}\cdot$	$\cdot\underset{\cdot}{\dot{C}}\cdot$	$:\underset{\cdot\cdot}{N}\cdot$	$:\underset{\cdot\cdot}{O}:$	$:\underset{\cdot\cdot}{\dot{F}}:$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Ne}}:$

Lewis Symbol of Cl → $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$ Lewis Symbol of P → $\cdot\overset{\cdot\cdot}{\underset{\cdot}{P}}:$

Lewis Symbol of S → $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}$ Lewis Symbol of Xe → $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Xe}}:$

OCTET RULE

Atoms can combine either by transfer of electron from one atom to another atom or by sharing of electrons in order to have an octet in their valence shell.

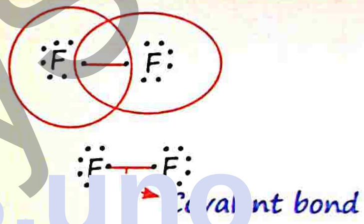
Na : $1s^2\,2s^2\,2p^6\,3s^1$

Na^+ : $1s^2\,\boxed{2s^2\,2p^6}$ ⇒ Set of 8 electrons [Octet]

Cl : $1s^2\,2s^2\,2p^6\,3s^2\,3p^5$

Cl^- : $1s^2\,2s^2\,2p^6\,\boxed{3s^2\,3p^6}$ ⇒ Set of 8 electrons [Octet]

Ionic Bond: The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as electrovalent bond.



F : $1s^2\,2s^2\,2p^5$

After bonding F attain 8 electrons in its valence shell.

Covalent Bond: When two atoms share one electron pair they are said to be joined by a single covalent bond.

H_2 H—H

1. NBE = Zero
2. LP = Zero
3. BP = 1

O_2

1. NBE = 8
2. LP = 4
3. BP = 2

1. Non-bonding Electrons [NBE]
2. Lone Pair [LP]
3. Bond Pair [BP]

N_2

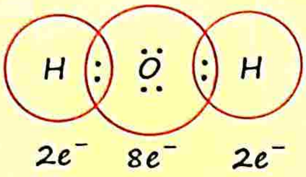
1. LP = 2
2. BP = 3
3. NBE = 4

Selection of Central Atom in a Molecule

Central Atom

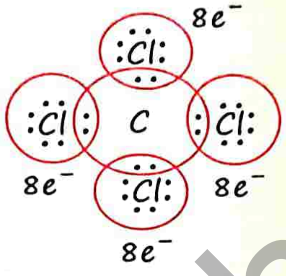
- Less in number
- Least electronegative
- Tendency to form maximum number of bonds

H_2O

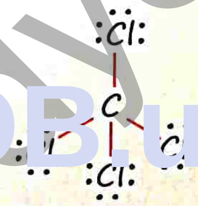


H atoms attain a duplet of electrons and O attain the octet

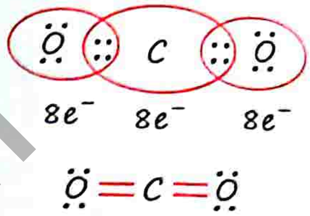
CCl_4



Each of the four Cl atoms along with the C atom attains octet of electrons

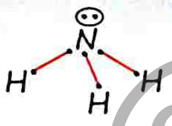


CO_2

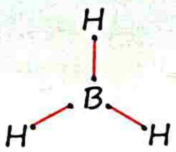


If two atoms share two pairs of electrons, the covalent bond between them is called a double bond.

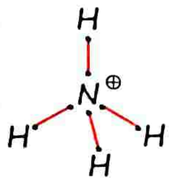
NH_3



BH_3

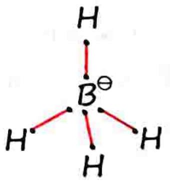


NH_4^+



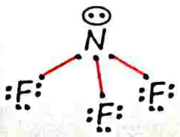
We remove 1e⁻ from nitrogen atom to get N⁺, So N⁺ has 4e⁻ in valence shell.

BH_4^-

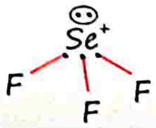


We add 1e⁻ to boron atom to get B⁻.

NF_3

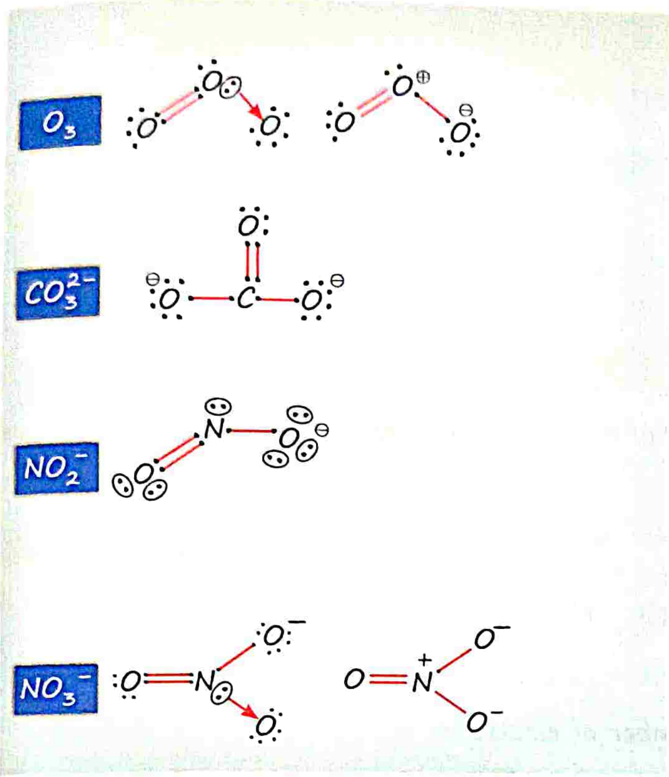


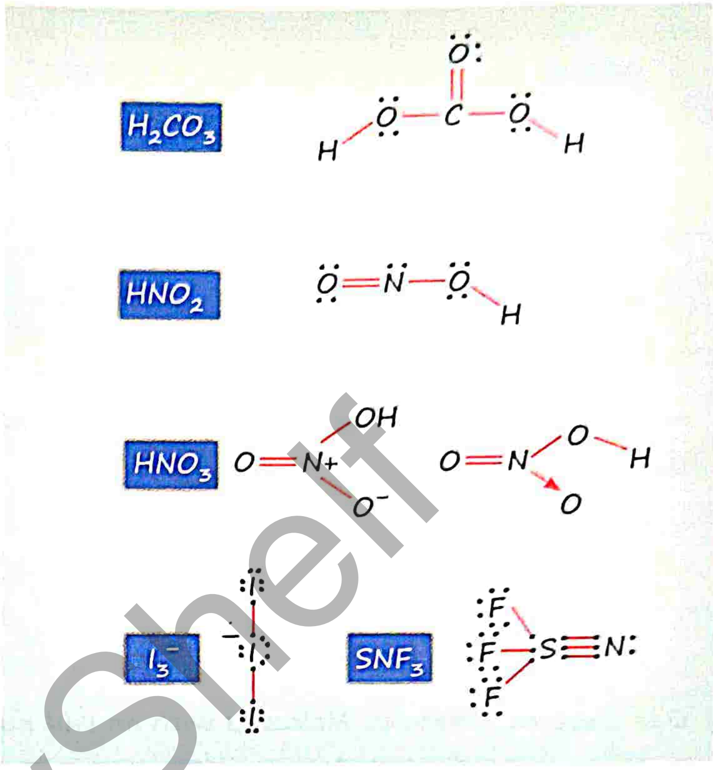
SeF_3^+



Note

F & H can never act as central atom.





Limitations of Octet Rule

1. It applies mainly to 2^{nd} period elements.

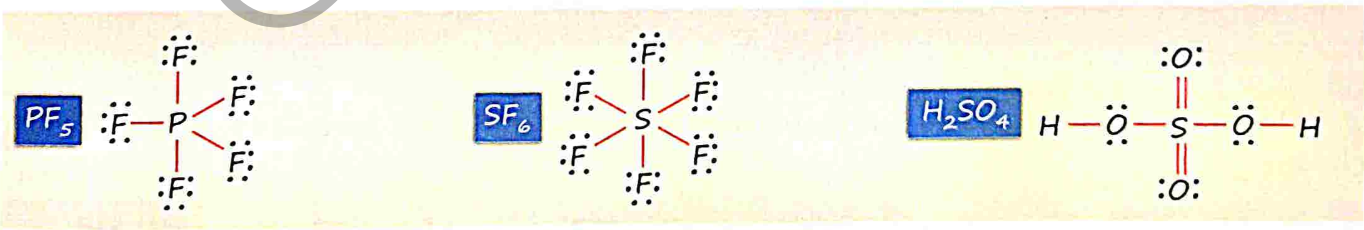
☐ 2^{nd} Period elements [B, C, N, O, F] → s + p subshell in valence shell

→ maximum no. of electrons = 2 + 6 = 8

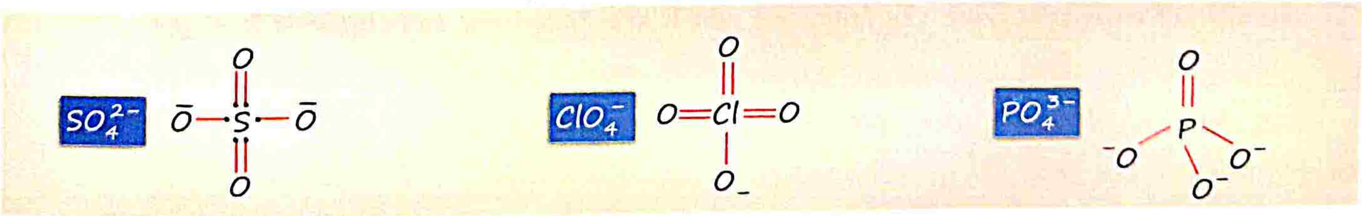
2. Expanded or Super or Hypervalent Octet: Elements in and beyond the 3^{rd} period of periodic table have d orbitals for bonding.

☐ 3^{rd} Period elements [Al, Si, P, S, Cl] → s + p + d subshell in valence shell

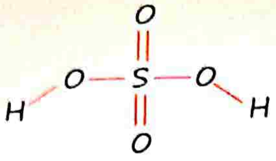
→ maximum no. of electrons = 2 + 6 + 10 = 18



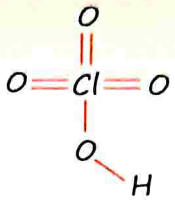
☐ In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet.



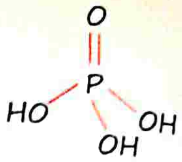
H_2SO_4



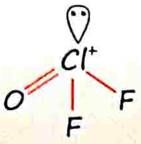
$HClO_4$



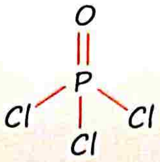
H_3PO_4



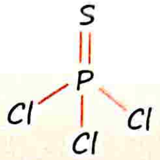
$ClOF_2^+$



$POCl_3$

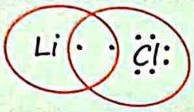


$PSCl_3$



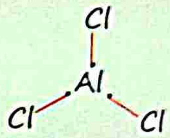
3. **Incomplete Octet:** In some compounds, the number of electrons surrounding the central atom is less than eight.

LiCl



BH_3

$AlCl_3$

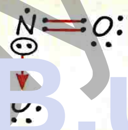


4. **Odd Electron Molecules:** Molecules with an odd number of electrons

NO

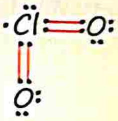
Total no. of electrons in NO = 7 + 8 = 15 (odd)

NO_2



Total no. of electrons in NO_2 = 7 + 8 × 2 = 23 (odd)

ClO_2

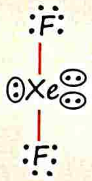


Total no. of electrons in ClO_2 = 17 + 8 × 2 = 33 (odd)

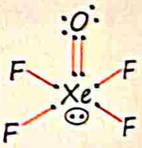
5. **Octet rule is based upon the chemical inertness of noble gases.**

Some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2, KrF_2, $XeOF_4$ etc.

XeF_2



$XeOF_4$



1. The number of molecules or ions from the following, which do not have odd number of electrons are ________.

[29 Jan, 2023 (Shift-I)]

(a) NO_2 (b) ICl_4^- (c) BrF_3 (d) ClO_2 (e) NO_2^+ (f) NO

Sol. [3] ICl_4^-, BrF_3 and NO_2^+ do not have odd number of e^-

2. Number of molecules from the following which are exceptions to octet rule is _____.

[08 April, 2024 (Shift-I)]

CO_2, NO_2, H_2 SO_4, BF_3, CH_4, SiF_4, ClO_2, PCl_5, BeF_2, C_2H_6, $CHCl_3$, CBr_4

Sol. [6] NO_2, H_2SO_4, BF_3, ClO_2, PCl_5, BeF_2

3. Which of the following pair of molecules contain odd electron molecule and an expanded octet molecule? [29 July, 2022 (Shift-I)]
(a) BCl_3 and SF_6 (b) NO and H_2SO_4 (c) SF_6 and H_2SO_4 (d) BCl_3 and NO

Sol. (b)
BCl_3 – electron deficient molécule
SF_6 – expanded octet molecule
NO – odd electron containing molecule
H_2SO_4 – expanded octet molecule

4. Amongst the following, the total number of species NOT having eight electrons around central atom in its outer most shell, is: NH_3, $AlCl_3$, $BeCl_2$, CCl_4, PCl_5 [NEET 2023]
(a) 1 (b) 3 (c) 2 (d) 4

Sol. (b) $AlCl_3$, $BeCl_2$, PCl_5

5. Which of the following species contains equal number of σ and π-bonds? [NEET 2015 Re]
(a) $(CN)_2$ (b) $(CH)_2(CN)_2$ (c) HCO_3^- (d) XeO_4

Sol. (d)

6. Which one of the following molecules contains no π bond? [NEET 2013]
(a) SO_2 (b) NO_2 (c) CO_2 (d) H_2O

Sol. (d)

FORMAL CHARGE (FC)

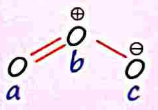
Difference between the number of valence electrons of that atom in free state and the number of electrons assigned to that atom in the Lewis structure.

$$FC = V - N - \frac{B}{2}$$

V = Total number of valence electrons in the free atom

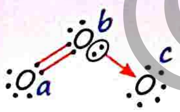
N = Number of non-bonding electrons

B = Number of bonding electrons



	FC
a	zero
b	+1
c	-1

O_3

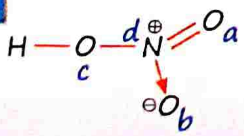


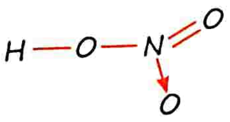
FC on "a"
V = 6
N = 4
B = 4
$\rightarrow FC = 6 - 4 - \frac{4}{2} = 0$

FC on "b"
V = 6
N = 2
B = 6
$\rightarrow FC = 6 - 2 - \frac{6}{2} = +1$

FC on "c"
V = 6
N = 6
B = 2
$\rightarrow FC = 6 - 6 - \frac{2}{2} = -1$

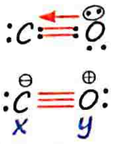
HNO_3





a = 0, b = −1, c = 0, d = +1

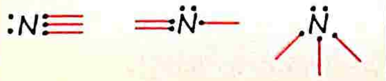
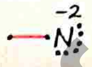
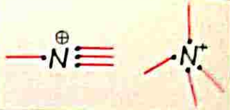
CO

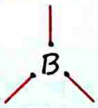
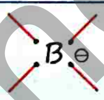
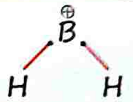


x = −1
y = +1

OP* Points

Formal charge on Oxygen	FC = 0	FC = −1	FC = +1
			

Formal charge on Nitrogen	FC = 0	FC = −1	FC = −2	FC = +1
				

Formal charge on Boron	FC = 0	FC = −1	FC = +1
			

☐ The structure of least energy (most stable) is usually the one with minimal formal charge and most distributed real charge.

CO_2

$\overset{\text{zero}}{O}=\overset{\text{zero}}{C}=\overset{\text{zero}}{O}$

Neutral molecule (No charge) → Stability↑

$\overset{+1}{O}\equiv\overset{\text{zero}}{C}-\overset{-1}{O}$

Molecule with formal charge → Stability↓ → This structure is not acceptable.

$N_3^{\ominus}$

$N\equiv N\odot\rightarrow N$

$\underset{0}{N}\equiv\underset{+1}{N}-\underset{-2}{N}$

Less distributed charge → Less stability

$\underset{-1}{N}=\underset{+1}{N}=\underset{-1}{N}$

More distributed charge → More stability

C_3^{4-}

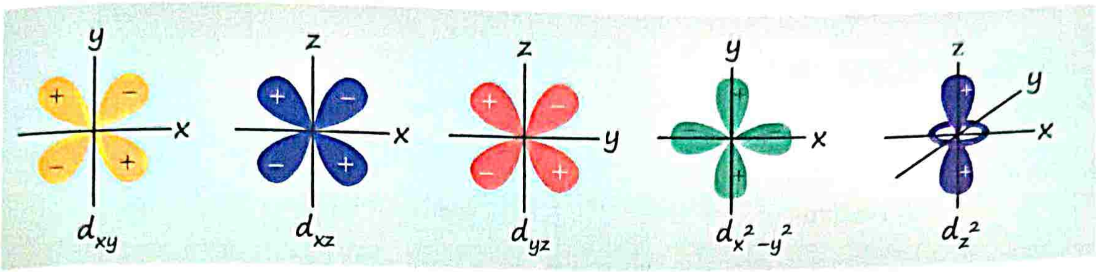
$\underset{-1}{C}\equiv\underset{\text{zero}}{C}-\underset{-3}{C} < \underset{-2}{C}=\underset{\text{zero}}{C}=\underset{-2}{C}$: Stability

NATURE, SHAPE & PHASE OF ATOMIC ORBITAL

☐ s orbital (1 lobe)
☐ Non-directional nature
☐ + or − sign

☐ p orbital (2 lobes)
☐ Directional nature
☐ p_x, p_y, p_z

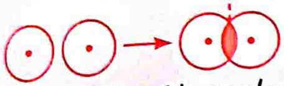
d-Orbital



VALENCE BOND THEORY

$H_a^{\bullet} + H_b \rightarrow H—H$

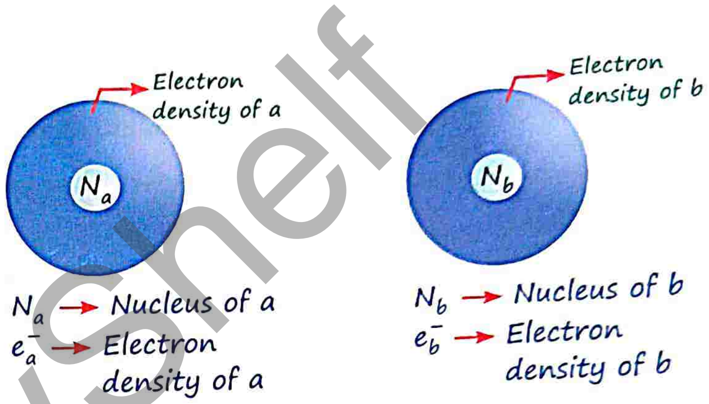
partial merging (overlap)



+ 435.8 KJ/mol

$(1S)_a$ $(1S)_b$ H_2 molecule

Bond Energy

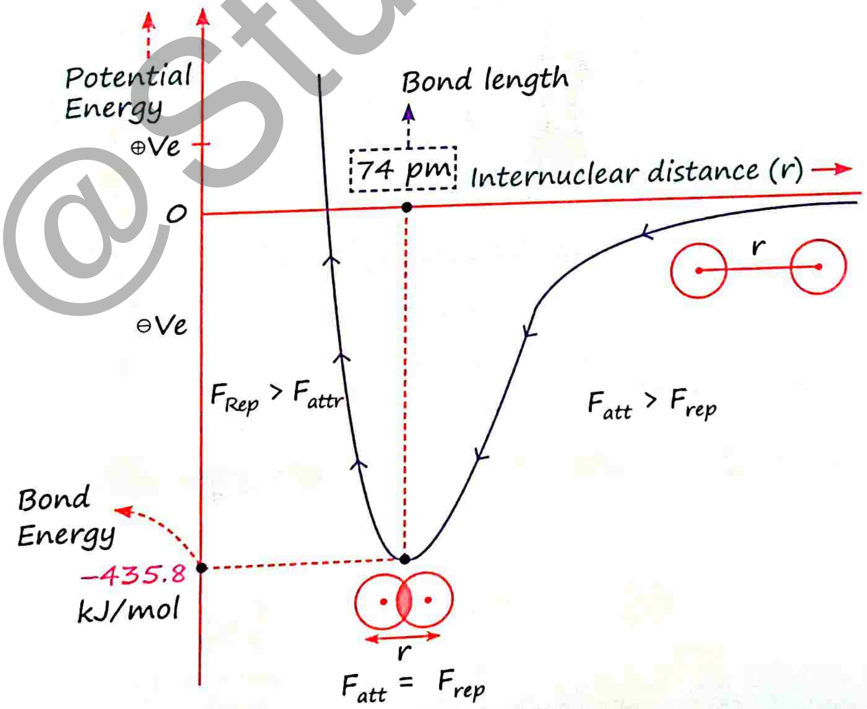


Force of attraction: (i) $(e^-)_a - (N)_b$

(ii) $(e^-)_b - (N)_a$

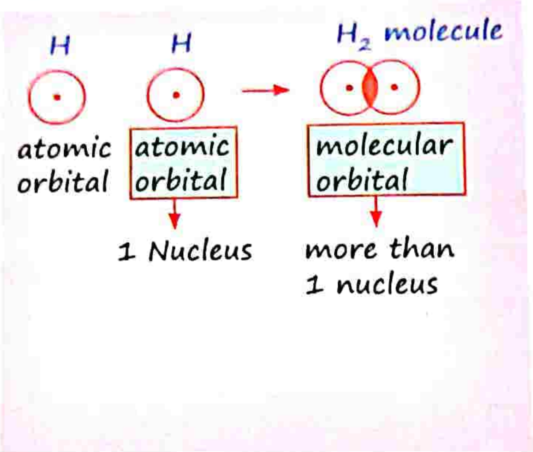
Force of repulsion: (i) $(e^-)_a - (e^-)_b$

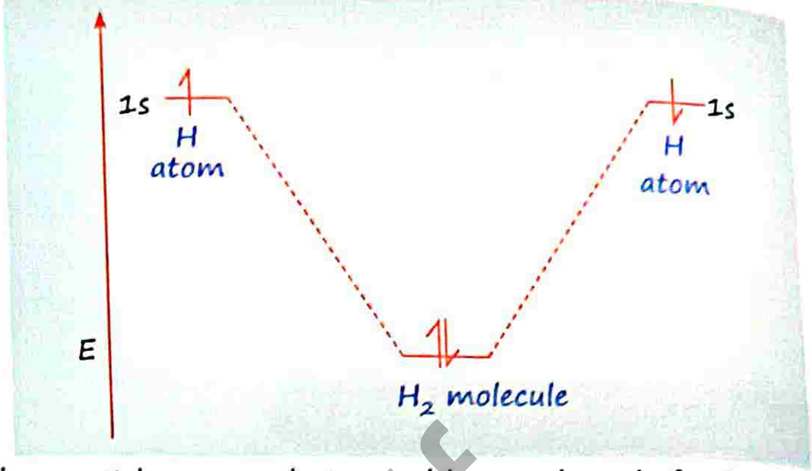
(ii) $(N)_a - (N)_b$



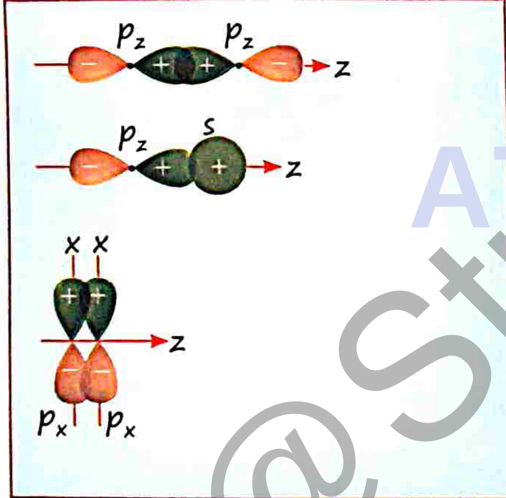
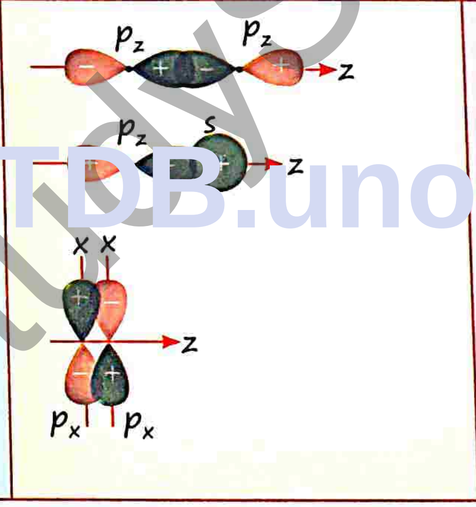
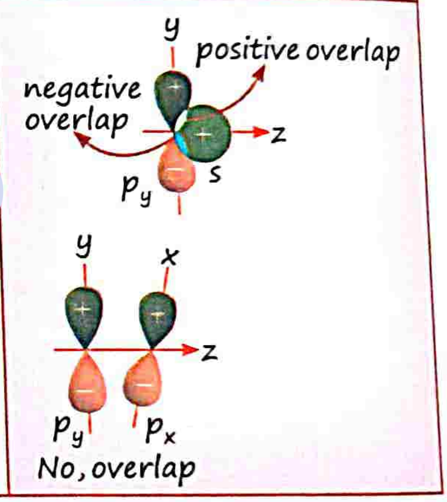
- Energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as bond enthalpy.

- ☐ VBT is an Orbital Overlap Concept.



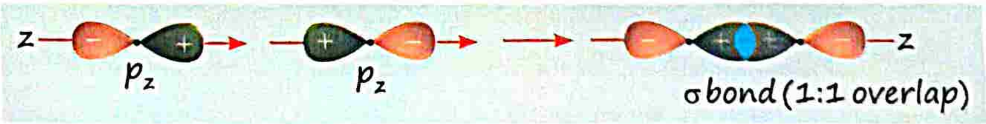


- ☐ Orbitals which are undergoing overlapping must have one electron with opposite spin for formation of covalent bond.

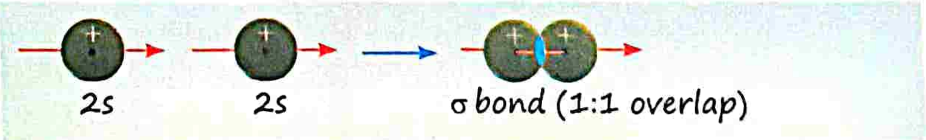
Positive Overlap	Negative Overlap	Zero Overlap
Same phase (sign) Overlap + + – –	Opposite sign Overlap + –	i. No Overlap between 2 orbitals ii. Both positive & negative overlap
		

Sigma Bond

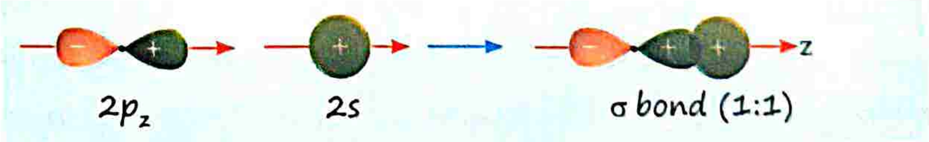
Overlapping along the molecular axis/Head on overlapping



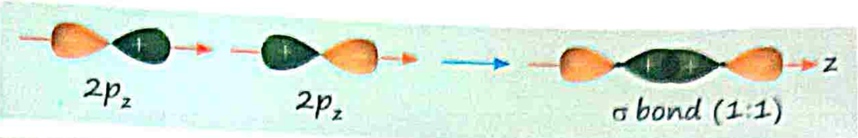
i. s–s overlapping



ii. s–p overlapping



iii. p-p overlapping



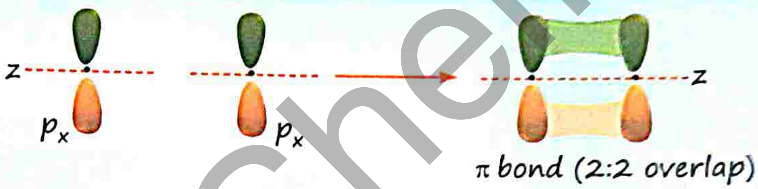
☐ Extent of overlapping ↑ → Strength of bond ↑

Extent of overlapping : 2s – 2s < 2s – 2p < 2p – 2p

Strength: 2s–2s < 2s–2p < 2p–2p

Pi Bond

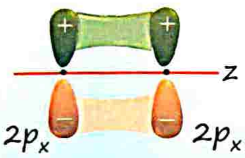
Overlapping $\perp^r$ to molecular axis (Side ways overlapping)



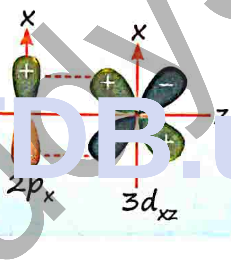
π bond (2:2 overlap)

Strength : σ bond > π bond

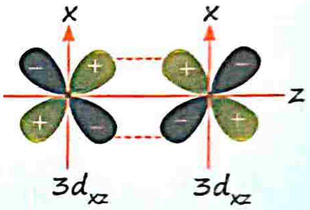
(i) pπ–pπ bond



(ii) pπ–dπ bond



(iii) dπ–dπ bond



☐ Extent of overlapping ↑ : $(n_1 + n_2)$ ↓

Extent of overlapping : 2p–2p > 2p – 3d > 3d – 3d

$n_1 + n_2$: (2 + 2) < (2 + 3) < (3 + 3)

Strength of π bond : 2p–2p > 2p–3d > 3d–3d

Strength of Bond

(i) When $n_1 + n_2$ is same: 2s–2s < 2s–2p < 2p–2p : σ bond strength

$(n_1 + n_2)$→ (2 + 2) (2 + 2) (2 + 2)

(ii) When $n_1 + n_2$ is different:

1s – 1s > 2s – 2s > 3s–3s : σ bond strength

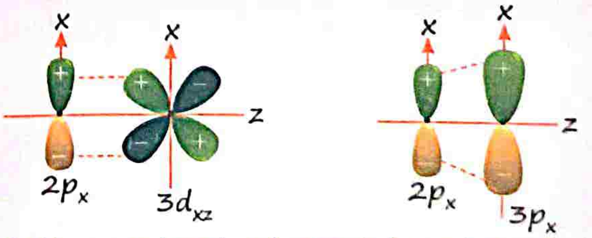
$(n_1 + n_2)$→ (1 + 1) (2 + 2) (3 + 3)

2p – 2p > 2p–3d : π bond strength

$(n_1 + n_2)$→ (2 + 2) (2 + 3)

2p – 3p < 2p – 3d : π bond strength

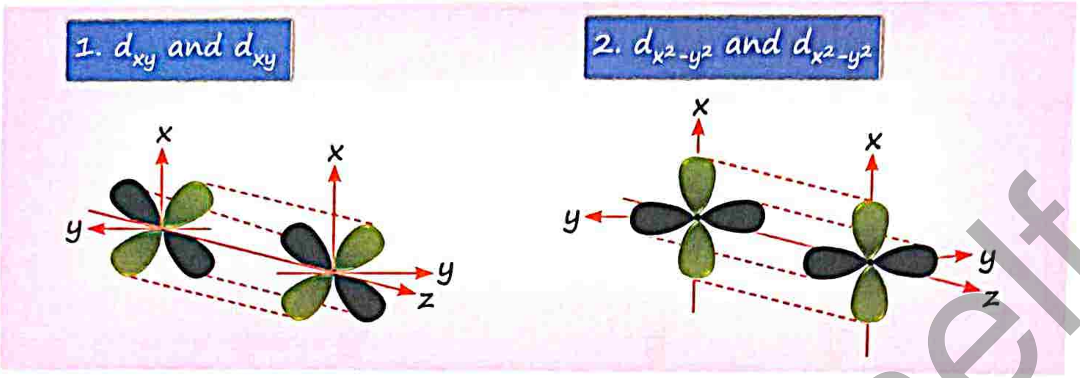
$(n_1 + n_2)$→ (2 + 3) (2 + 3)



Better overlapping in 2p–3d w.r.t 2p–3p

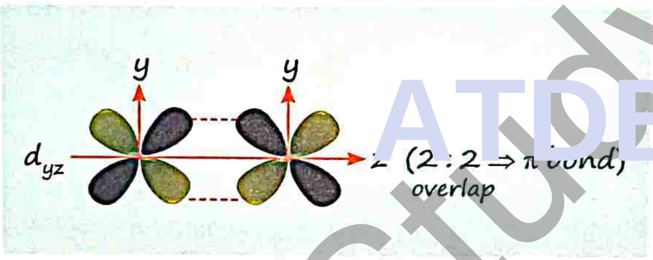
Bonding in d-Orbitals

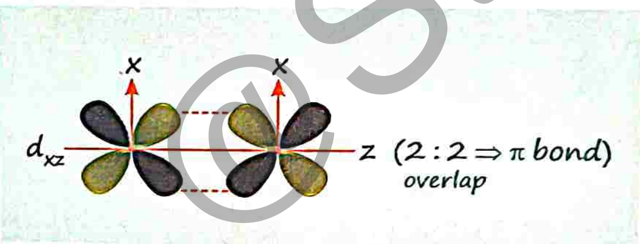
Delta Bond → 4 : 4 overlap


1. d_{xy} and d_{xy}

2. $d_{x^2-y^2}$ and $d_{x^2-y^2}$

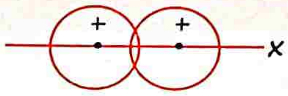
- ☐ Overlapping of 2 $d_{x^2-y^2}$ or 2 d_{xy} orbitals gives a δ bond, when z axis is internuclear axis.



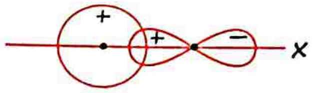


Bond / Orbital	σ	π	δ
s	✓	✗	✗
p	✓	✓	✗
d	✓	✓	✓

s + s = σ bond

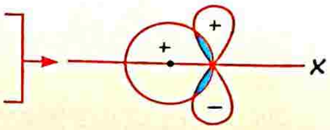


s + p_x = σ bond

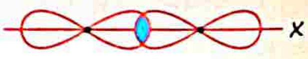


s + p_y = No bond

s + p_z = No bond

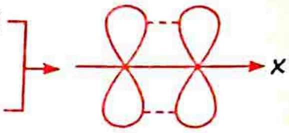


p_x + p_x = σ bond



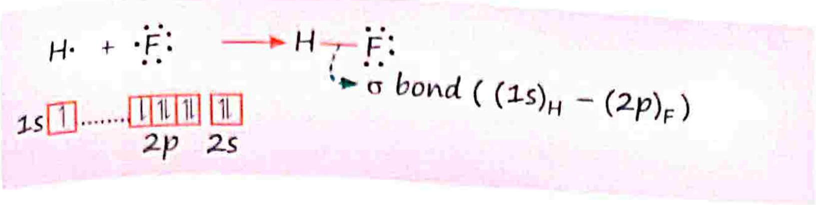
p_y + p_y = π bond

p_z + p_z = π bond

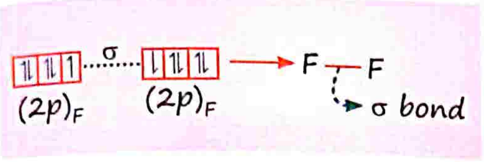


- ☐ Overlapping of orbitals when x axis is internuclear axis.

HF Molecule



F_2 Molecule



7. Draw the type of overlaps between given orbitals, Z is internuclear axis.

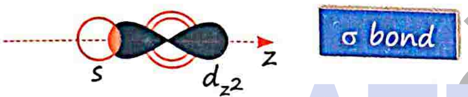
(a) s and d_{z^2}

(b) s and $d_{x^2-y^2}$

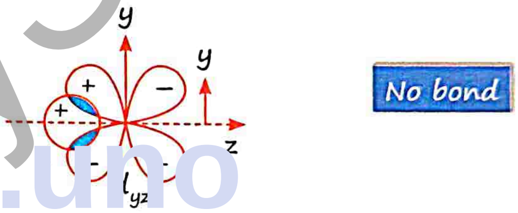
(c) s and d_{yz}

(d) p_z and d_{z^2}

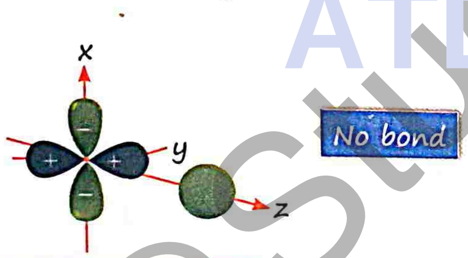
Sol. (a)



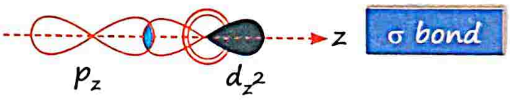
(c)



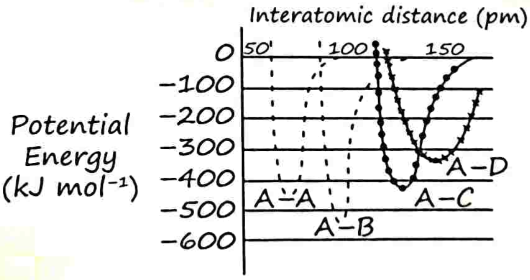
(b)



(d)



8. The intermolecular potential energy for the molecules A, B, C and D given below suggest that: [4 Sept, 2020 (Shift-I)]



(a) A – A has the largest bond enthalpy

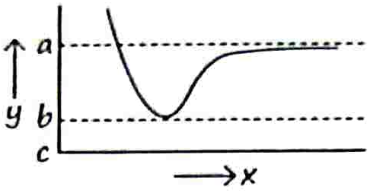
(b) A – D has the shortest bond length

(c) D is more electronegative than other atoms

(d) A – B has the stiffest bond.

Sol. (d) Lower the potential energy, stronger will be the bond. A – B has lowest potential energy which means it has stronger bond.

9. The potential energy (y) curve for H_2 formation as a function of internuclear distance (x) of the H atoms is shown below. [NEET 2020-Covid]



The bond energy of H_2 is

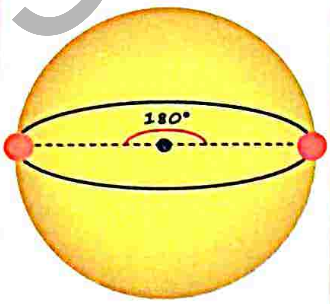
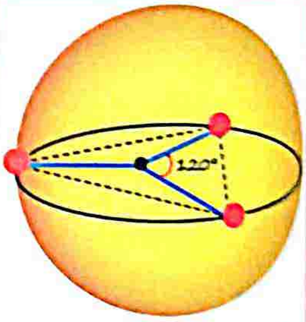
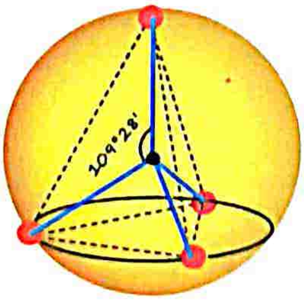
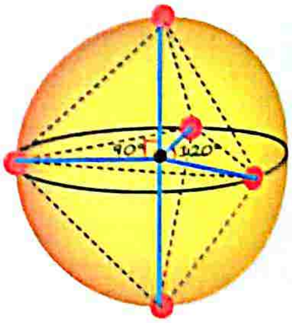
(a) $\frac{(c-a)}{2}$ (b) $\frac{(b-a)}{2}$ (c) $(c-a)$ (d) $(b-a)$

Sol. (d)

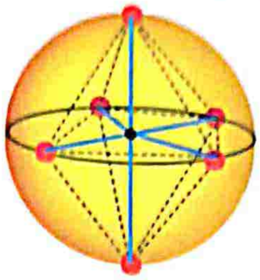
VSEPR THEORY
VALENCE SHELL ELECTRON PAIR REPULSION THEORY

Main Postulates

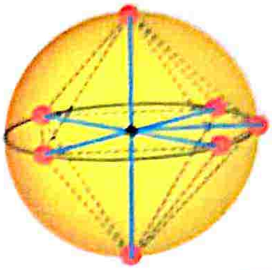
- The shape of a molecule depends upon the number of valence shell electron pairs [bonded or non-bonded] around the central atom.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.

2 electron pairs are localised on spherical surface at maximum distance, when angle between them is 180°.		3 electron pairs are localised on spherical surface at maximum distance, when they are placed at corners at triangle.	
4 electron pairs are localised on spherical surface at maximum distance, when they are placed at corners of tetrahedron.		5 electron pairs are localised on spherical surface of central atom at maximum distance when 3 are placed at equatorial position [at angle 120°] and 2 are placed at axial positon [at angle 90°]	

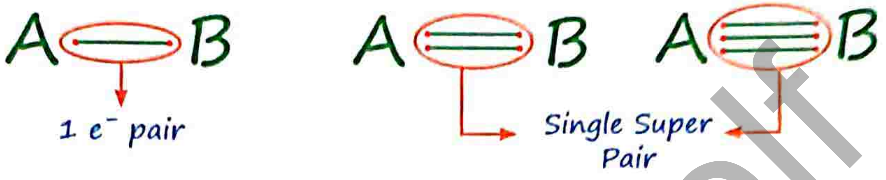
6 electron pairs are localised on spherical surface at maximum distance, when they are placed at corners of octahedron.



7 electron pairs at maximum distance is shown in figure



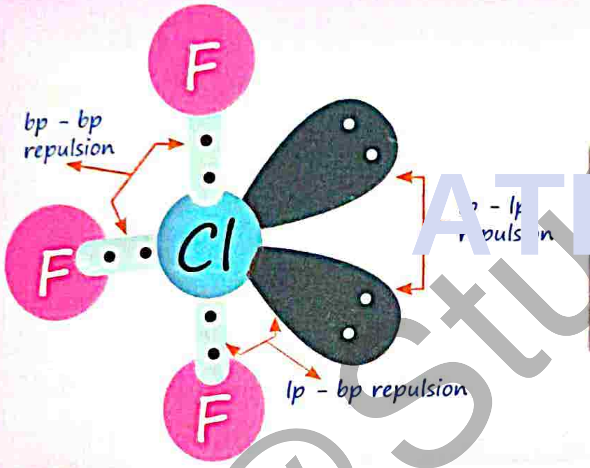
☐ A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.



☐ Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decrease in the order:

Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp)



☐ The lone pair are localized on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons.

☐ We can represent any molecule in AB_xL_y form where, A → Central atom, B → Side atom, L → Lone pair

☐ Number of valence shell electron pair decides the geometry of a molecule.

$$\boxed{\text{Valence shell electron pair [VSEP]} = x + y}$$

AB_2 Type Molecule

CO_2

$\downarrow$

AB_2L_0

$\downarrow$

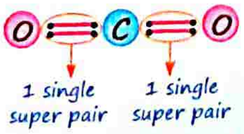
$x = 2$

$y = 0$

☐ Valence shell electron pair = 2

☐ Geometry → Linear

☐ Bond angle → 180°



$BeCl_2$

$\downarrow$

AB_2L_0

$\downarrow$

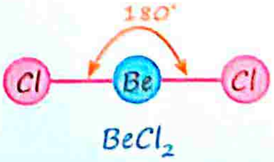
$x = 2$

$y = 0$

☐ Valence shell electron pair = 2

☐ Geometry → Linear

☐ Bond angle → 180°



AB_3 Type Molecule

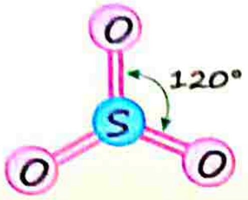
SO_3

AB_3L_0

$x = 3$

$y = 0$

- ☐ Valence shell electron pair = 3 + 0 = 3
- ☐ Geometry → Trigonal planar
- ☐ Bond angle → 120°



SO_2

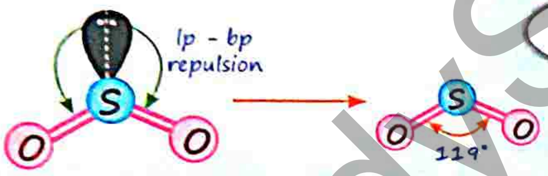
AB_2L_1

$x = 2$

$y = 1$

- ☐ Valence shell electron pair = 2 + 1 = 3
- ☐ Due to lp – bp repulsion, bond angle reduces from 120° to 119°

Structure with lone pair → Geometry
Structure without lone pair → Shape



Geometry → Trigonal planar Shape → Bent

AB_4 Type Molecule

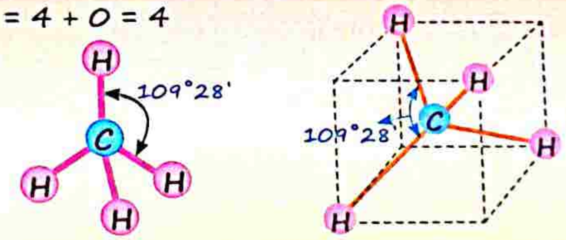
CH_4

AB_4L_0

$x = 4$

$y = 0$

- ☐ Valence shell electron pair = 4 + 0 = 4
- ☐ Geometry → Tetrahedral
- ☐ Bond angle → 109° 28'



C → At body centre of cube

H → At alternate corners of cube

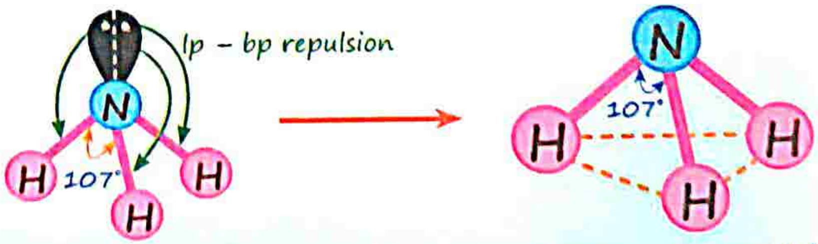
NH_3

AB_3L_1

$x = 3$

$y = 1$

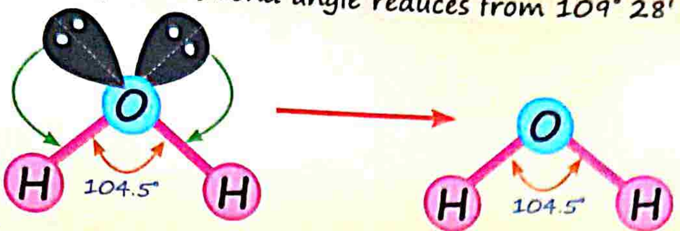
- ☐ Valence shell electron pair = 3 + 1 = 4
- ☐ Due to lp – bp repulsion, bond angle reduces from ideal tetrahedral angle 109° 28' to 107°.



Geometry — Tetrahedral Shape — Pyramidal

H_2O
↓
AB_2L_2
↓
$x = 2$
$y = 2$

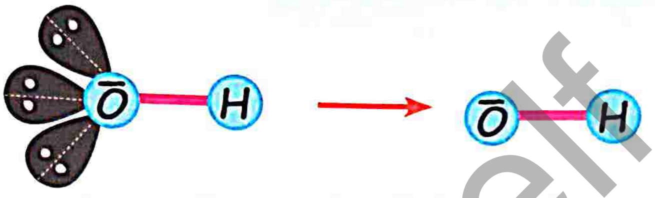
- ☐ Valence shell electron pair = 2 + 2 = 4
- ☐ Due to more lp – bp repulsion, bond angle reduces from 109° 28' to 104.5°



Geometry — Tetrahedral　　Shape — Bent, V-shaped

OH^-
↓
ABL_3
↓
$x = 1$
$y = 3$

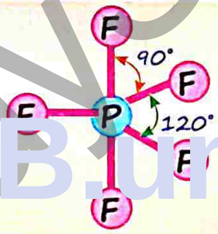
- ☐ Valence shell electron pair = 1 + 3 = 4



Geometry → Tetrahedral　　Shape → linear

AB_5 Type Molecule

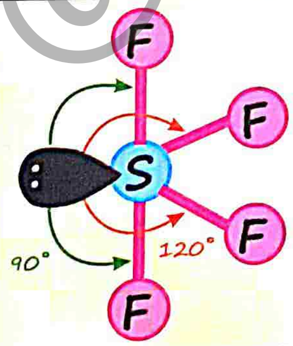
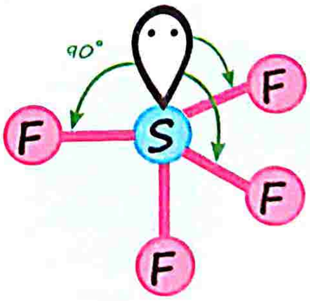
PF_5 → AB_5L_0



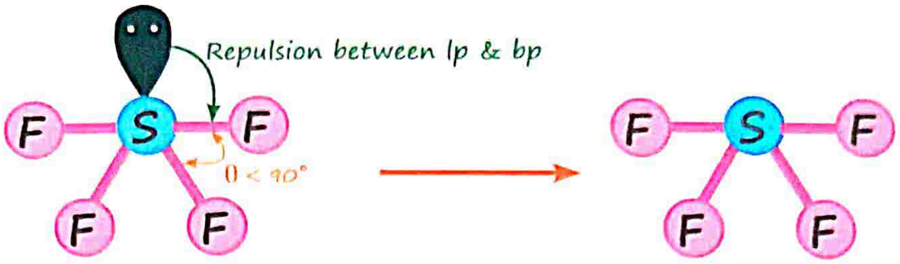
- ☐ Valence shell electron pair = 5 + 0 = 5
- ☐ Geometry → Trigonal bipyramidal
- ☐ θ → 90° and 120°

SF_4 → AB_4L_1

- ☐ Valence shell electron pair = 4 + 1 = 5

Case–1 If lp is present at equatorial position	Case–2 If lp is present at axial position
	
☐ There are 2 lp – bp repulsions at 90° and 2 lp – bp repulsions at 120°.	☐ There are 3 lp – bp repulsions at 90°.
☐ Repulsions at 90° are more effective than 120°. So we are going to compare on the basis of repulsions at 90°.	

- ☐ Case – 1 structure is more favorable than case-2 due to less repulsion.
- ☐ So, case – 1 structure is Acceptable on the basis of postulates of VSEPR theory.



Geometry — TBP

Shape — See Saw

Note

In TBP geometry due to less repulsion, more favorable position for lone pair is equatorial position.

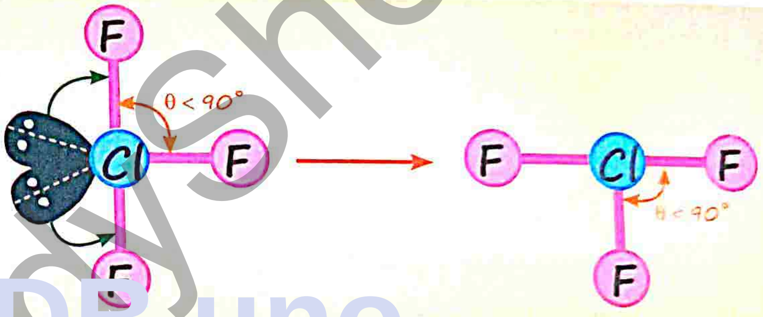
ClF_3

AB_3L_2

$x = 3$

$y = 2$

- ☐ Valence shell electron pair = 3 + 2 = 5



TBP Geometry

Bent T shaped

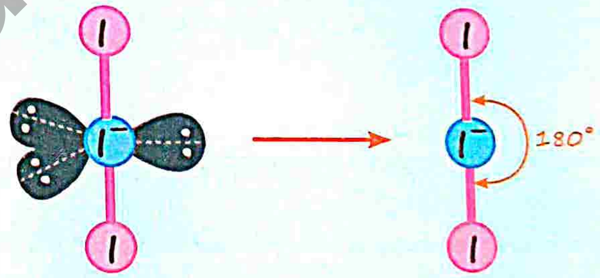
I_3^-

AB_2L_3

$x = 2$

$y = 3$

- ☐ Valence shell electron pair = 2 + 3 = 5



TBP Geometry

Linear shape

AB_6 Type Molecule

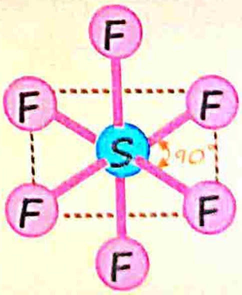
SF_6

AB_6L_0

$x = 6$

$y = 0$

- ☐ Valence shell electron pair = 6 + 0 = 6
- ☐ Geometry → Octahedral
- ☐ Bond angle → 90°



BrF_5

↓

AB_5L_1

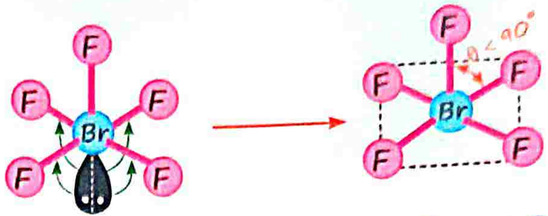
↓

$x = 5$

$y = 1$

- ☐ Valence shell elctron pair = 5 + 1 = 6
- ☐ All bond angles are less than 90°

The lone pair would force the Br–F bond pairs upward, and all Br–F bond angles would contract.



Geometry - Octahedral Shape → Square Pyramidal

XeF_4

↓

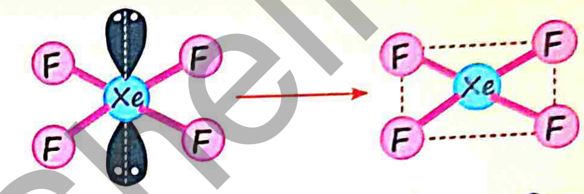
AB_4L_2

↓

$x = 4$

$y = 2$

- ☐ Valence shell electron pair = 4 + 2 = 6
- ☐ Bond angle → 90°



Geometry - octahedral Shape – Square planar

AB_7 Type Molecule

IF_7

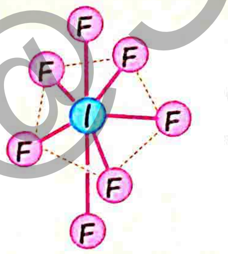
↓

AB_7L_0

↓

$x = 7$

$y = 0$



IF_7 [θ = 72°, 90′]
Pentagonal bipyramidal Geometry

10. In the structure of SF_4, the lone pair of electrons on S is [27 June, 2022 (Shift-II)]

(a) Equatorial position and there are two lone pair – bond pair repulsions at 90°.

(b) Equatorial position and there are three lone pair – bond pair repulsions at 90°.

(c) Axial position and there are three lone pair – bond pair repulsion at 90°.

(d) Axial position and there are two lone pair – bond pair repulsion at 90°.

Sol. (a)

11. Based upon VSEPR theory, match the shape (geometry) of the molecules in List-I with the molecules in List-II and select the most appropriate option. [27 June, 2022 (Shift-I)]

List-I (Shape)			List-II (Molecules)
A.	T-shaped	I.	XeF_4
B.	Trigonal planar	II.	SF_4
C.	Square planar	III.	ClF_3
D.	See-saw	IV.	BF_3

(a) (A)-(I), (B)-(II), (C)-(III), (D)-(IV)
(b) (A)-(III), (B)-(IV), (C)-(I), (D)-(II)
(c) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)
(d) (A)-(IV), (B)-(III), (C)-(I), (D)-(II)

Sol. (b)

12. Match List-I with List-II. [NEET 2024

List-I (Compound)		List-II (Shape/geometry)	
A.	NH_3	I.	Trigonal Pyramidal
B.	BrF_5	II.	Square Planar
C.	XeF_4	III.	Octahedral
D.	SF_6	IV.	Square Pyramidal

Choose the correct answer from the options given below:

(a) A-III, B-IV, C-I, D-II
(b) A-II, B-III, C-IV, D-I
(c) A-I, B-IV, C-II, D-III
(d) A-II, B-IV, C-III, D-I

Sol. (c)

13. Match List - I with List - II: [NEET 2022 Re

List-I (molecules)		List-II (shape)	
A.	NH_3	I.	square pyramidal
B.	ClF_3	II.	trigonal bipyramidal
C.	PCl_5	III.	trigonal pyramidal
D.	BrF_5	IV.	T-shape

Choose the correct answer from the options given below:

(a) A-III, B-IV, C-I, D-II
(b) A-II, B-III, C-IV, D-I
(c) A-III, B-IV, C-II, D-I
(d) A-IV, B-III, C-I, D-II

Sol. (c)

14. Amongst the following, which one will have maximum 'lone pair-lone pair' electron repulsions? [NEET 2022

(a) XeF_2 (b) ClF_3 (c) IF_5 (d) SF_4

Sol. (a)

15. Identify the incorrect statement related to PCl_5 from the following: [NEET 2019

(a) Three equatorial P-Cl bonds make an angle of 120° with each other
(b) Two axial P-Cl bonds make an angle of 180° with each other
(c) Axial P-Cl bonds are longer than equatorial P-Cl bonds
(d) PCl_5 molecule is non-reactive

Sol. (d)

16. Predict the correct order among the following: [NEET 2016-I]
(a) Lone pair – bond pair > bond pair – bond pair > lone pair – lone pair
(b) Lone pair – lone pair > lone pair – bond pair > bond pair – bond pair
(c) Lone pair – lone pair > bond pair – bond pair > lone pair – bond pair
(d) Bond pair – bond pair > lone pair – bond pair > lone pair – lone pair

Sol. (b)

17. Which of the following species has a linear shape? [NEET 2006]
(a) NO_2^- (b) SO_2 (c) NO_2^+ (d) O_3

Sol. (c)

18. In BrF_3 molecule, the lone pairs occupy equatorial positions to minimize: [NEET 2004]
(a) Bond pair-bond pair repulsion only
(b) Lone pair-lone pair repulsion and lone pair-bond pair repulsion
(c) Lone pair-lone pair repulsion only
(d) Lone pair-bond pair repulsion only

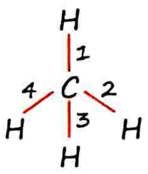
Sol. (b)

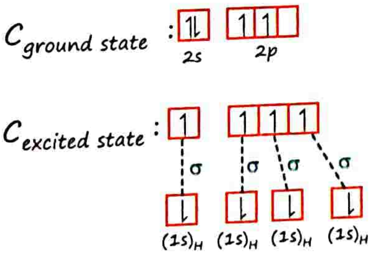
19. BCl_3 is a planar molecule whereas NCl_3 is pyramidal because: [NEET 1995]
(a) Nitrogen atom is smaller than boron atom
(b) BCl_3 has no lone pair but NCl_3 has a lone pair of electrons
(c) B-Cl bond is more polar than N-Cl bond
(d) N-Cl bond is more covalent than B-Cl bond

Sol. (b)

NEED OF NEW CONCEPT → (HYBRIDISATION)

Bonding in CH_4 according to VBT





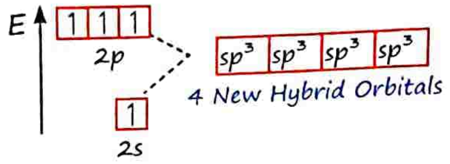
☐ 2 different types of overlapping
→ $(2s)_C - (1s)_H$
→ $(2p)_C - (1s)_H$
☐ 2 Different bond lengths.

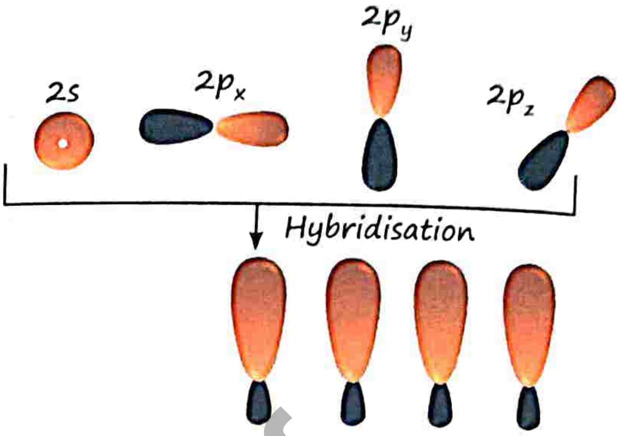
VBT predicts that the 3 bonds formed through s-p overlap would be the same and differ from the 4th bond formed through s-s overlap. This difference in bond types would result in unequal bond lengths which is not what is observed in methane.

Experimental Fact All C — H bonds are same in CH_4. → This fact can be explained by new theory ⇒ Hybridisation

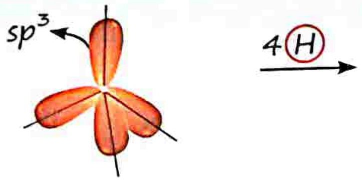
Hybridisation in CH_4

$C_{\text{excited state}}$: $\underset{2s}{\boxed{1}}$ $\underset{2p}{\boxed{1\,|\,1\,|\,1}}$

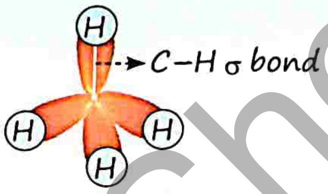




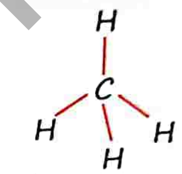
4 hybrid Orbitals (sp^3)



4 sp^3 hybrid orbitals of carbon at 109° 28′



Overlapping between sp^3 hybrid orbital of carbon and 1s atomic orbital of hydrogen



All C—H bonds are equal in length.

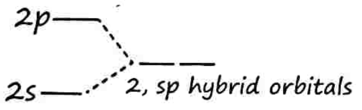
HYBRIDISATION

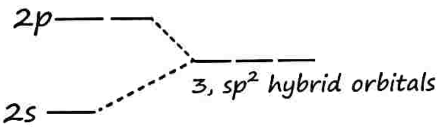
Inter Mixing of pure atomic orbitals before bonding to produce new hybrid orbitals, specially for bonding purpose.

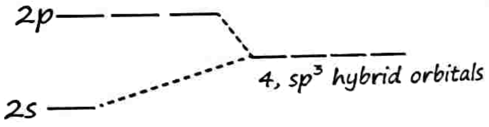
Postulates

(i) It is a hypothetical concept.

(ii) Only those orbitals can take part in hybridisation which have comparable (almost equal) energies.



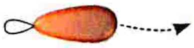




(iii) The number of hybrid orbitals generated will be equal to the number of pure atomic orbitals taking part in hybridisation.

(iv) All 3 type of orbitals (having a pair of electrons $\boxed{1\!\downarrow}$ or having a unpaired electron $\boxed{1}$ or completely empty $\boxed{}$) can take part in hybridisation.

(v) The hybrid orbital generated will be represented by



Bigger lobe will be used for bonding.

Steric Number Rule

Steric number = No. of lone pairs + No. of side atoms

SN	Geometry	Hybridisation	Bond Angle
2	Linear	sp	θ = 180°
3	Trigonal planar	sp^2	θ = 120°
4	Tetrahedral	sp^3	θ = 109° 28′
5	Trigonal bi-pyramidal	sp^3d	θ = 90°, 120°
6	Octahedral	sp^3d^2	θ = 90°
7	Pentagonal bi-pyramidal	sp^3d^3	θ = 90°, 72°

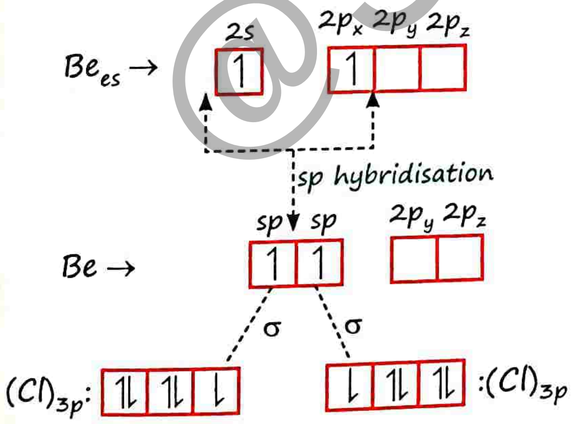
sp Hybridisation

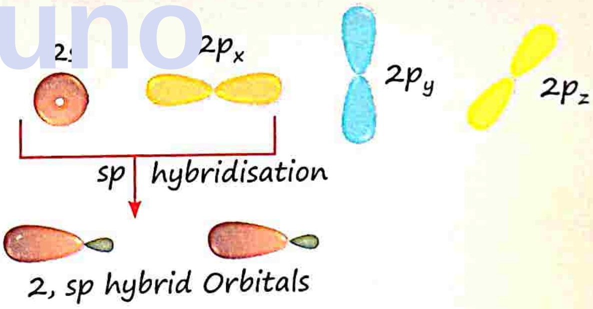
$BeCl_2$ Cl — Be — Cl

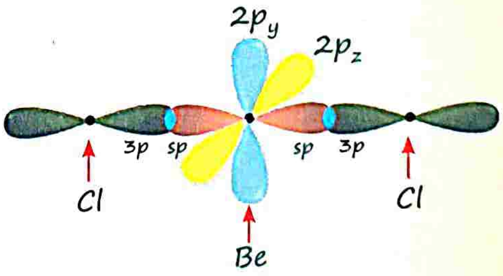
☐ SN = LP + SA = 0 + 2

= ② → sp hybridisation

☐





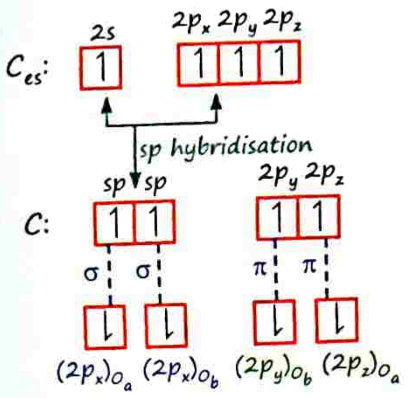


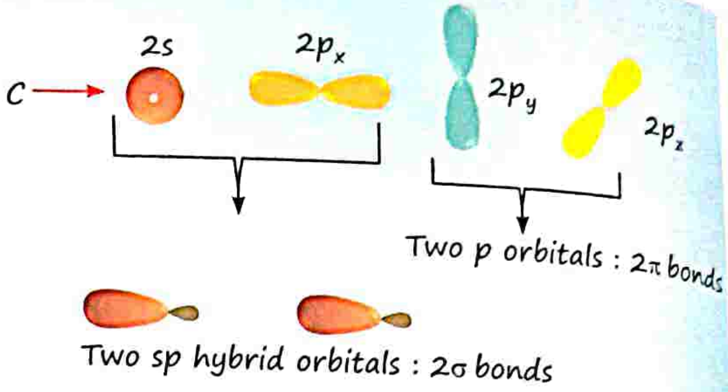
☐ 2 Be — Cl σ bonds : $(sp)_{Be}$ — $(3p)_{Cl}$

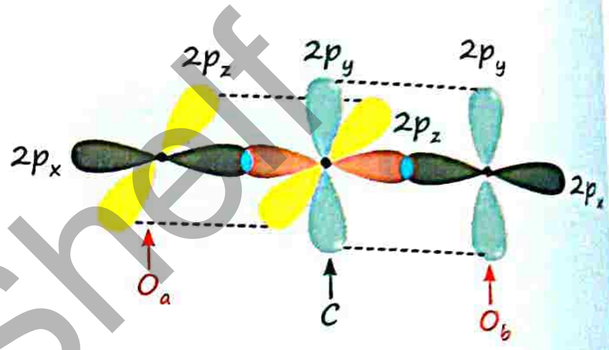
☐ 2 vacant orbitals ($2p_y$ and $2p_z$) at Be.

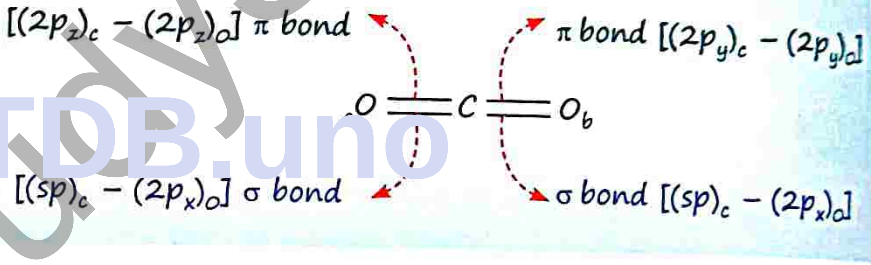
CO_2 $O = C = O$

- ☐ SN = LP + SA
  = 0 + 2
  = 2 → sp hybridisation





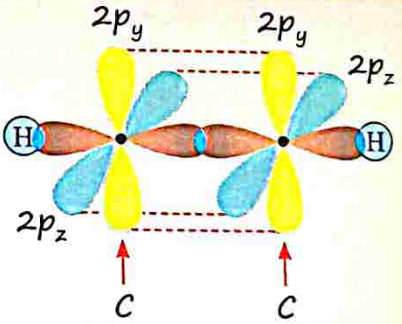




C_2H_2 $H—C \equiv C—H$

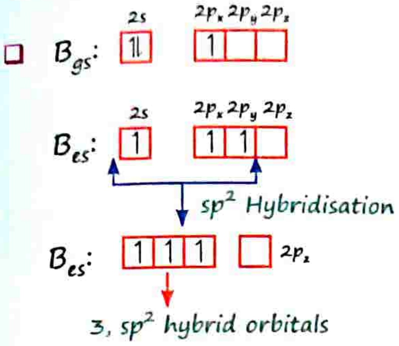
- ☐ 2 C—H σ bonds : $(sp)_C - (1s)_H$
- ☐ 1 C—C σ bond : $(sp)_C - (sp)_C$
- ☐ 2 C—C π bonds : $(2p_y)_C - (2p_y)_C$ and $(2p_z)_C - (2p_z)_C$

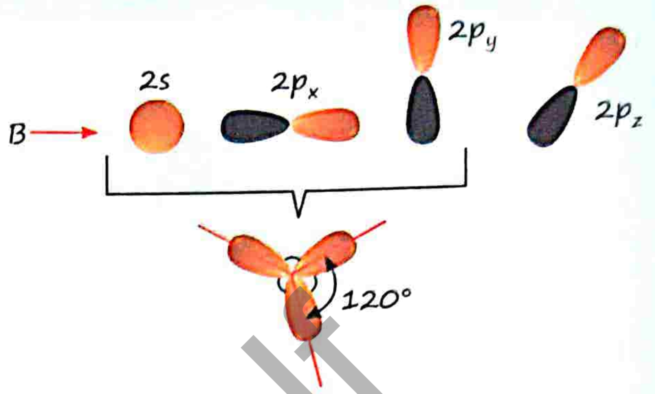
Molecular plane → $\boxed{H— C \equiv C — H}$



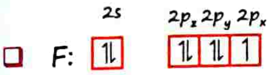
sp^2 Hybridisation

BF_3



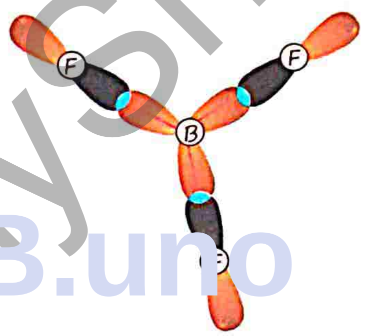


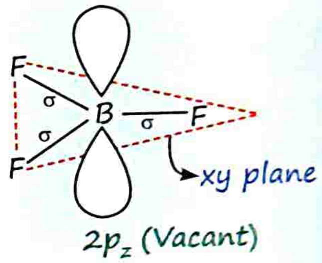
☐ 3 sp^2 hybrid orbitals are arranged at 120° before bonding.



☐ 3 σ B — F bonds: $(sp^2)_B - (2p_x)_F$

☐ $sp^2 \equiv s + p_x + p_y$



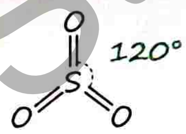


SO_3

☐ SN = 0 + 3 = 3

☐ $hyb^n = sp^2$

☐ Shape = Trigonal planar

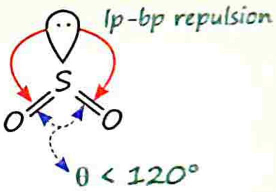


SO_2

☐ SN = 1 + 2 = 3

☐ sp^2

☐ v shaped

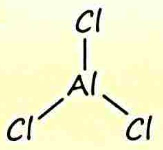


$AlCl_3$

☐ SN = 0 + 3 = 3

☐ sp^2

☐ Trigonal planar

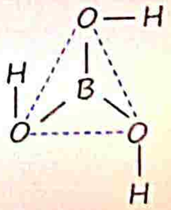


H_3BO_3

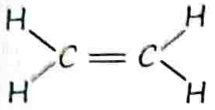
☐ SN = 0 + 3

☐ sp^2

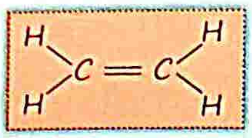
☐ Trigonal planar

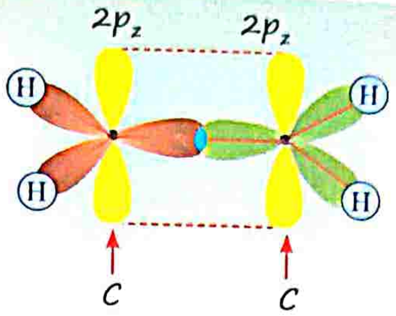


C_2H_4



- ☐ $sp^2 \equiv s + p_x + p_y$
- ☐ 4 C—H σ bonds : $(sp^2)_C - (1s)_H$
- ☐ 1 C—C σ bond : $(sp^2)_C - (sp^2)_C$
- ☐ 1 C—C π bond : $(2p)_C - (2p)_C$
- ☐ Molecular plane →



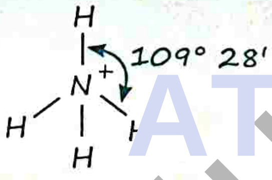


- ☐ Max. no of atoms in a plane = 6

sp^3 Hybridisation → Geometry : Tetrahedral

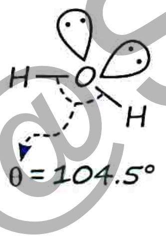
$NH_4^{\oplus}$

- ☐ SN = 0 + 4
- ☐ sp^3
- ☐ Tetrahedral



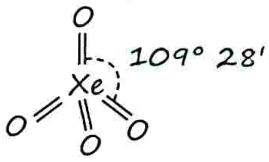
H_2O

- ☐ SN = LP + SA
  = 2 + 2 = 4
- ☐ sp^3
- ☐ V shape



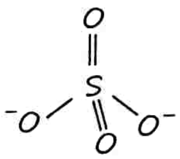
XeO_4

- ☐ SN = 0 + 4 = 4
- ☐ sp^3
- ☐ Tetrahedral



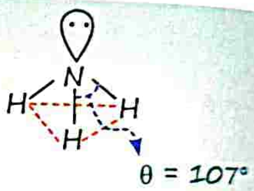
SO_4^{2-}

- ☐ SN = 0 + 4 = 4
- ☐ sp^3
- ☐ Tetrahedral



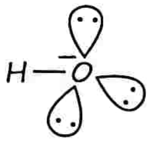
NH_3

- ☐ SN = 1 + 3 = 4
- ☐ sp^3
- ☐ Pyramidal



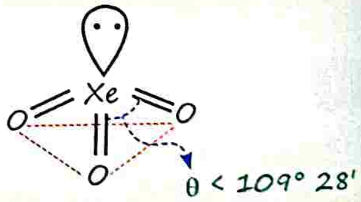
HO^-

- ☐ SN = 3 + 1 = 4
- ☐ sp^3
- ☐ Linear



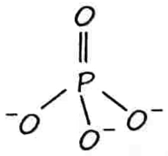
XeO_3

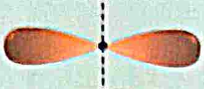
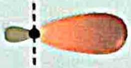
- ☐ SN = 1 + 3 = 4
- ☐ sp^3
- ☐ Pyramidal



PO_4^{3-}

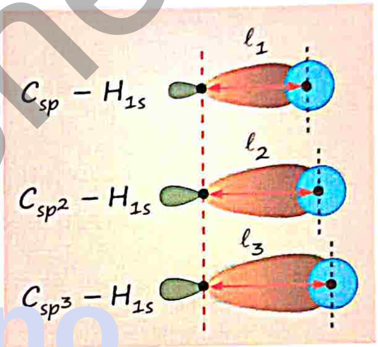
- ☐ SN = 0 + 4 = 4
- ☐ sp^3
- ☐ Tetrahedral



Orbital	% s Character	% p Character
s orbital 	100%	0%
p orbital 	0%	100%
sp hybrid orbital 	50%	50%
sp^2 hybrid orbital 	33.3%	66.6%
sp^3 hybrid orbital 	25%	75%

Bond Length & % s Character

- ☐ % s character: $C_{sp} > C_{sp^2} > C_{sp^3}$
- ☐ Bond length: $\ell_1 < \ell_2 < \ell_3$
- ☐ $\boxed{\text{Bond length} \propto \frac{1}{\%\ s\ \text{character}} \propto \%\ p\ \text{character}}$



Electronegativity & % s Character

- ☐ $\boxed{\text{EN} \propto \%\ s\ \text{character}}$
- ☐ % s character: $C_{sp} > C_{sp^2} > C_{sp^3}$
- ☐ Electronegativity: $C_{sp} > C_{sp^2} > C_{sp^3}$

sp^3d Hybridisation → Geometry: Trigonal bipyramidal (TBP)

PCl_5

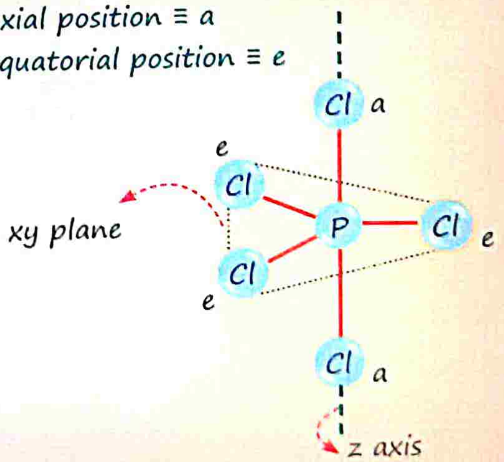
$$sp^3d \equiv \underbrace{s + p_x + p_y}_{[sp^2]_{xy}} + \underbrace{p_z + d_{z^2}}_{[pd]_z}$$

$[sp^2]_{xy}$ ↓ approx 100 % s character ↓ Bond length : $P - Cl_e$

$[pd]_z$ ↓ approx 0 % s character ↓ $P - Cl_a$

Bond length : $P - Cl_e < P - Cl_a$

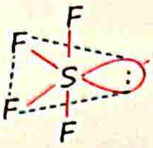
axial position ≡ a
equatorial position ≡ e



Bent's Rule

(1) Lone pair of electron prefers to occupy those hybrid orbitals which has greater % of s character

SF_4

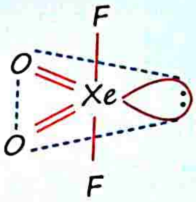


lone pair at equatorial position because it has more % s character than axial position.

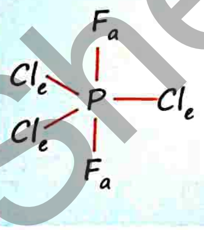
(2) A more electronegative atom prefers to occupy that hybrid orbital which has smaller % of s character (axial position).

XeO_2F_2

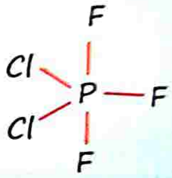
- ☐ SN = LP + SA = 1 + 4 = 5
- ☐ Geometry – TBP
- ☐ Shape – see saw



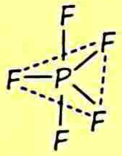
PCl_3F_2



PCl_2F_3

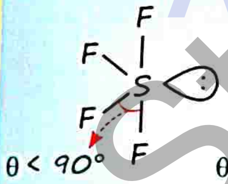


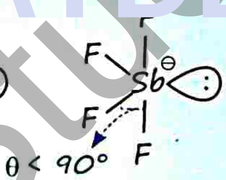
PF_5



- ☐ SN = 0 + 5
- ☐ sp^3d
- ☐ TBP Shape
- ☐ BL : $P{-}F_a > P{-}F_e$

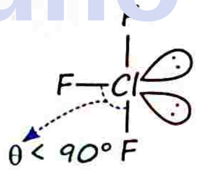
SF_4 **SbF_4^-**





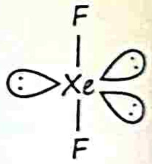
- ☐ SN = 1 + 4 = 5
- ☐ sp^3d
- ☐ See Saw Shape
- ☐ BL : $S{-}F_a > S{-}F_e$

ClF_3



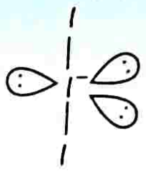
- ☐ SN = 2 + 3 = 5
- ☐ sp^3d
- ☐ Bent T shaped
- ☐ BL : $Cl{-}F_a > Cl{-}F_e$

XeF_2



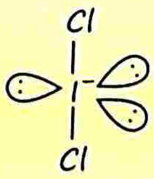
- ☐ SN = 3 + 2 = 5
- ☐ sp^3d
- ☐ Linear Shape

I_3^-



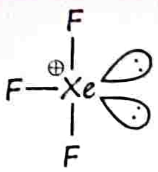
- ☐ SN = 3 + 2 =5
- ☐ sp^3d
- ☐ Linear Shape

ICl_2^-



- ☐ SN = 3 + 2 =5
- ☐ sp^3d
- ☐ Linear Shape

XeF_3^+



- ☐ SN = LP + SA
  = 2 + 3 = 5
- ☐ Bent T shaped

sp^3d^2 Hybridisation: Geometry → Octahedral

AF_6

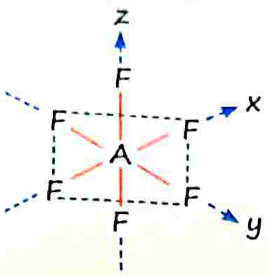
↓

SF_6

PF_6^-

SiF_6^{2-}

AlF_6^{3-}

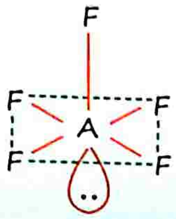


$$sp^3d^2 \equiv \underbrace{s + p_x + p_y + d_{x^2-y^2}}_{\text{xy plane}} \quad \underbrace{p_z + d_{z^2}}_{\text{z axis}}$$

A	S	Si^{2-}	P^-	Al^{3-}
Valence shell electrons	6	4+2	5+1	3+3

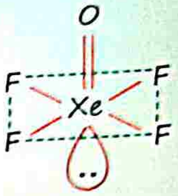
BrF_5, XeF_5^+, ClF_5, IF_5, SF_5^-

- ☐ $:AB_5$ → A = Br, Xe^+, I, Cl, S^-
- ☐ SN = 1 + 5 = 6
- ☐ sp^3d^2
- ☐ Square pyramidal → shape
- ☐ No of bond angles at 90° → zero



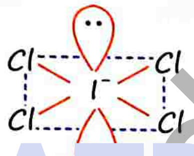
$XeOF_4$

- ☐ SN = 1 + 5 = 6
- ☐ Square pyramidal → shape



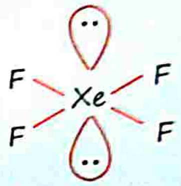
ICl_4^-

- ☐ SN = 2 + 4 = 6 (sp^3d^2)
- ☐ Square planar → shape



XeF_4

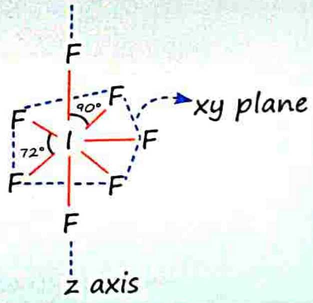
- ☐ Square planar → shape



sp^3d^3 Hybridisation

IF_7

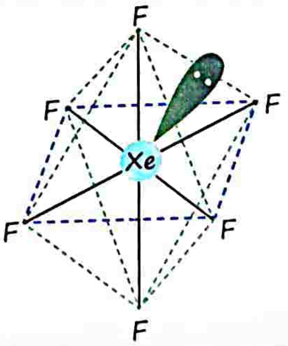
$$\underbrace{s + p_x + p_y + d_{x^2-y^2} + d_{xy}}_{\text{xy plane}} + \underbrace{p_z + d_{z^2}}_{\text{z axis}}$$

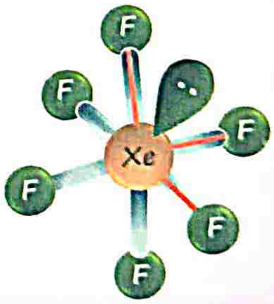


- ☐ SN = LP + SA = 0 + 7 = 7
- ☐ Pentagonal bipyramidal → shape
- ☐ θ → 90°/72°

$XeF_{6(g)}$, IF_6^-, SeF_6^{2-}

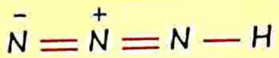
- ☐ SN = LP + SA = 1 + 6 = 7
- ☐ Shape → Distorted octahedral
  Capped octahedral



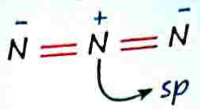


Some Important Molecules-

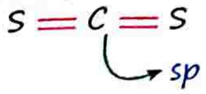
N_3H



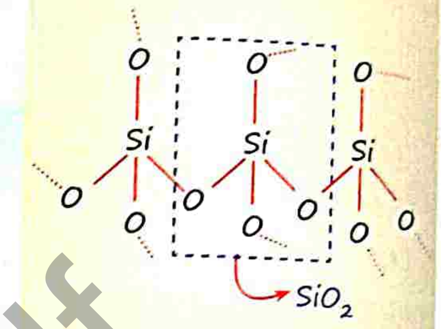
N_3^-



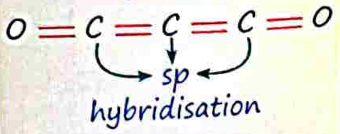
CS_2



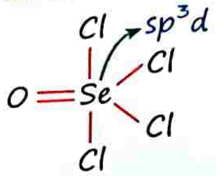
SiO_2



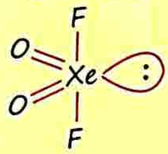
C_3O_2



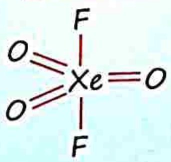
$SeOCl_4$



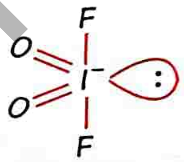
XeO_2F_2



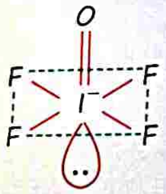
XeO_3F_2



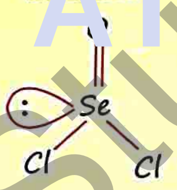
$IO_2F_2^-$



IOF_4^-



$SeOCl_2$



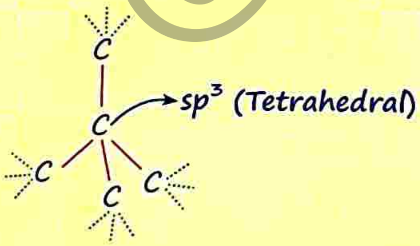
HCP

H — C ≡ P

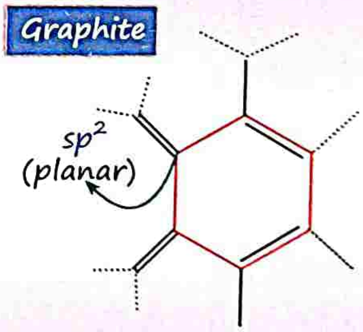
☐ Structure is like HCN

H — C ≡ N

Diamond



Graphite



20. Number of lone pair(s) in $XeOF_4$ is/are (IIT JEE 2004)

(a) 0 (b) 1 (c) 2 (d) 3

Sol. (b)

21. Molecular shape of SF_4, CF_4 and XeF_4 are (IIT JEE 2000)

(a) the same, with 2, 0 and 1 lone pair of electrons respectively

(b) the same, with 1, 1 and 1 lone pair of electrons respectively

(c) the different, with 0, 1 and 2 lone pair of electrons respectively

(d) the different, with 1, 0 and 2 lone pair of electrons respectively

Sol. (d)

22. Based on VSEPR theory, the number of 90° F–Br–F angles in BrF_5 is ______. (IIT JEE 2010)

Sol. [0]

23. The hybridisation of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are (IIT JEE 2000)

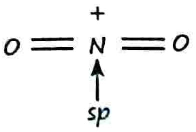
(a) sp, sp^3 and sp^2 respectively

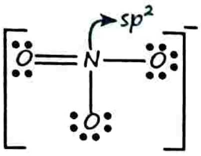
(b) sp, sp^2 and sp^3 respectively

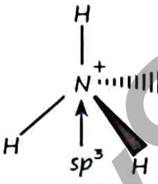
(c) sp^2, sp and sp^3 respectively

(d) sp^3, sp^3 and sp respectively

Sol. (b)







24. Match List–I with List–II: [27 Aug, 2021 (Shift-I)]

List-I (Species)		List-II (Number of lone pair of electrons on the central atom)	
A.	XeF_2	I.	0
B.	XeO_2F_2	II.	1
C.	XeO_3F_2	III.	2
D.	XeF_4	IV.	3

Choose the most appropriate answer from the options given below:

(a) (A)-(IV), (B)-(I), (C)-(II), (D)-(III)

(b) (A)-(III), (B)-(II), (C)-(IV), (D)-(I)

(c) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)

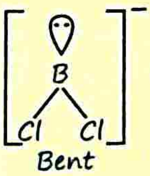
(d) (A)-(IV), (B)-(II), (C)-(I), (D)-(III)

Sol. (d) XeF_2 Lone Pair = 3 XeO_2F_2 Lone Pair = 1 XeO_3F_2 Lone Pair = 0 XeF_4 Lone Pair = 2

25. Amongst the following, the number of species having the linear shape is ____.

XeF_2, I_3^+, C_3O_2, I_3^-, CO_2, SO_2, $BeCl_2$ and BCl_2^- [30 Jan, 2023 (Shift-II)]

Sol. [5] (i)

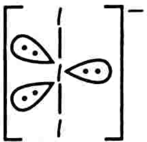


Bent

(ii) Cl—Be—Cl

Linear

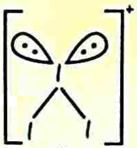
(iii)



Linear

(iv) XeF_2 – Linear

(v)



V-Shape

(vi) CO_2 – Linear (vii) C_3O_2 (O = C = C = C = O) Linear (viii) SO_2 – Bent

26. Which of the following statements is not correct for sigma- and pi-bonds formed between two carbon atoms? [NEET 2003]

(a) Sigma-bond is stronger than a pi-bond

(b) Bond energies of sigma- and pi-bonds are of the order of 264 kJ/mol and 347 kJ/mol, respectively

(c) Free rotation of atoms about a sigma bond is allowed but not in case of a pi-bond

(d) Sigma-bond determines the direction between carbon atoms but a pi-bond has no primary effect in this regard

Sol. (b)

Iso-structural Species and Iso-electronic Species

Iso-structural Species

☐ Species having same shape

$CH_4 \rightarrow SN = 0 + 4$ (Tetrahedral)

$CCl_4 \rightarrow SN = 0 + 4$ (Tetrahedral)

XeF_6 BrF_6^- $SeCl_6^{2-}$ $TeCl_6^{2-}$

☐ Shape → Distorted octahedral

☐ $Xe \equiv Br^- \equiv Se^{2-} \equiv Te^{2-}$

No. of e^- in valence shell → 8

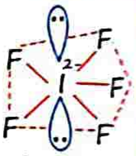
Iso-electronic Species

☐ Species having same no. of electrons

$CH_4 \rightarrow$ no. of $e^- \equiv 6 + 4 \times 1 = 10\ e^-$

$NH_4^+ \rightarrow$ no. of $e^- \equiv 7 + 4 \times 1 - 1 = 10\ e^-$

XeF_5^- IF_5^{2-}



☐ $Xe \equiv I^{2-} \rightarrow 8e^-$ in valence shell

☐ Shape → Pentagonal planar

☐ no. of e^- in $XeF_5^- \equiv 54 + 5 \times 9 + 1 = 100$

☐ no. of e^- in $IF_5^{2-} \equiv 53 + 5 \times 9 + 2 = 100$

Hybridisation in Solid State

(1) $2PCl_{5(s)} \longrightarrow PCl_4^+ PCl_6^-$

☐ hybⁿ of cationic part of $PCl_5 \equiv PCl_4^+ \equiv sp^3$ [Tetrahedral]

☐ hybⁿ of anionic part of $PCl_5 \equiv PCl_6^- \equiv sp^3d^2$ [Octahedral]

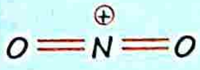
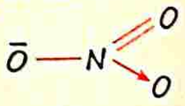
(2) $PBr_{5(s)} \longrightarrow PBr_4^{\oplus}\ Br^{\ominus}$

$PBr_4^{\oplus} \rightarrow sp^3$ hybⁿ [Tetrahedral]

(3) $XeF_{6(s)} \longrightarrow XeF_5^+\ F^-$

$XeF_5^+ \rightarrow sp^3d^2$ [Sq. Pyramidal]

(4) $N_2O_{5(s)} \longrightarrow NO_2^{\oplus}$ $NO_3^{\ominus}$

Cation	Anion
	
☐ sp hybⁿ	☐ sp² hybⁿ
☐ Linear	☐ Trigonal planar

(5) $N_2O_{3(s)} \longrightarrow NO^+\ NO_2^-$

(6) $Cl_2O_{6(s)} \longrightarrow ClO_2^+\ ClO_4^-$

27. Which of the following contains a maximum number of lone pairs on the central atom? (IIT JEE 2005)

(a) ClO_3^- (b) XeF_4 (c) SF_4 (d) I_3^-

Sol. (d)

28. Which of the following are isoelectronic and isostructural?

NO_3^-, CO_3^{2-}, ClO_3^-, SO_3 (IIT JEE 2003)

(a) NO_3^-, CO_3^{2-} (b) SO_3, NO_3^- (c) ClO_3^-, CO_3^{2-} (d) CO_3^{2-}, SO_3

Sol. (a)

29. Among the following species, identify the isostructural pairs.

NF_3, NO_3^-, BF_3, H_3O^+, N_3H (IIT JEE 1996)

(a) [NF_3 , NO_3^-] and [BF_3 , H_3O^+] (b) [NF_3 , HN_3] and [NO_3^- , BF_3]

(c) [NF_3 , H_3O^+] and [NO_3^- , BF_3] (d) [NF_3 , H_3O^+] and [HN_3 , BF_3]

Sol. (c)

30. The sum of the number of lone pairs of electrons on each central atom in the following species is

$[TeBr_6]^{2-}$, $[BrF_2]^+$, SNF_3 and $[XeF_3]^-$

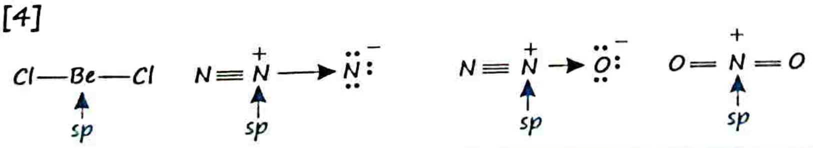
(Atomic numbers : N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54) (JEE Adv. 2017)

Sol. [6]

S.N.	Species	No. of σ – bonds with central atom	No. of LP at central atom
(i)	In $[TeBr_6]^{2-}$	6	1
(ii)	In $[BrF_2]^+$	2	2
(iii)	In SNF_3	4	0
(iv)	In $[XeF_3]^-$	3	3

31. Among the triatomic molecules/ions $BeCl_2$, N_3^-, N_2O, NO_2^+, O_3, SCl_2, ICl_2^-, I_3^- and XeF_2, the total number of linear molecules(s)/ion(s) where the hybridisation of the central atom does not have contribution from the d-orbitals(s) is [atomic number of S = 16, Cl = 17, I = 53 and Xe = 54] (JEE Adv. 2015)

Sol. [4]



32. The linear structure assumed by (IIT JEE 1991)
(a) $SnCl_2$ (b) CS_2 (c) NO_2^+ (d) NCO^-

Sol. (b, c, d) $S=C=S$ Linear $O=\overset{\oplus}{N}=O$ Linear $^{\ominus}O-C\equiv N$ Linear

33. CO_2 is isostructural with (IIT JEE 1986)
(a) $HgCl_2$ (b) C_2H_2 (c) $SnCl_2$ (d) NO_2

Sol. (a, b) CO_2, $HgCl_2$, C_2H_2 are all linear.

34. Among the following which one is a wrong statement? [NEET 2016-II]
(a) SeF_4 and CH_4 have same shape
(b) I_3^+ has bent geometry
(c) PH_5 and $BiCl_5$ do not exist
(d) $p\pi - d\pi$ bonds are present in SO_2

Sol. (a)

35. Among the following, the pair in which the two species are not isostructural is: [NEET 2004]
(a) IO_3^- and XeO_3 (b) BH_4^- and NH_4^+ (c) PF_6^- and SF_6 (d) SiF_4 and SF_4

Sol. (d)

36. XeF_2 is isostructural with [NEET 2013]
(a) $SbCl_3$ (b) $BaCl_2$ (c) TeF_2 (d) ICl_2^-

Sol. (d)

37. Which one of the following pairs is iso-structural (i.e., having the same shape and hybridization)? [NEET 2012 Pre]
(a) $[BF_4^-$ and $NH_4^+]$
(b) $[BCl_3$ and $BaCl_3]$
(c) $[NH_3$ and $NO_3^-]$
(d) $[NF_3$ and $BF_3]$

Sol. (a)

38. In which of the following pairs, the two species are isostructural? [NEET 2007]
(a) SO_3^{2-} and NO_3^-
(b) BF_3 and NF_3
(c) BrO_3^- and XeO_3
(d) SF_4 and XeF_4

Sol. (c)

39. Which of the following is not iso-structural with $SiCl_4$? [NEET 2006]
(a) SCl_4 (b) SO_4^{2-} (c) PO_4^{3-} (d) NH_4^+

Sol. (a)

40. Identify the incorrect statement about PCl_5. [NEET 2024 Re]
(a) PCl_5 possesses two different $Cl-P-Cl$ bond angles
(b) All five $P-Cl$ bonds are identical in length
(c) PCl_5 exhibits sp^3d hybridisation
(d) PCl_5 consists of five $P-Cl$ (sigma) bonds

Sol. (b)

41. The hybridisation of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are: [NEET 2016-II]

(a) sp, sp^3 and sp^2 (b) sp^2, sp^3 and sp (c) sp, sp^2 and sp^3 (d) sp^2, sp and sp^3

Sol. (c)

42. Which of the two ions from the list given below have the geometry that is explained by the same hybridisation of orbitals?

NO_2^-, NO_3^-, NH_2^-, NH_4^+, SCN^- [NEET 2011 Pre]

(a) NO_2^- and NH_2^- (b) NO_2^- and NO_3^-

(c) NH_4^+ and NO_3^- (d) SCN^- and NH_2^-

Sol. (b)

43. The correct order regarding the electronegativity of hybrid orbitals of carbon is: [NEET 2006]

(a) $sp > sp^2 < sp^3$ (b) $sp > sp^2 > sp^3$ (c) $sp < sp^2 > sp^3$ (d) $sp < sp^2 < sp^3$

Sol. (b)

44. Nitrogen form N_2, but phosphorus form P_2, but after some time convert in P_4, reason is: [NEET 2001]

(a) Triple bond present between phosphorous atom

(b) pπ – pπ bonding is weak

(c) pπ – pπ bonding is strong

(d) Multiple bond form easily

Sol. (b)

45. dπ – pπ bond is present in: [NEET 2000]

(a) CO_3^{2-} (b) PO_4^{3-} (c) NO_3^- (d) NO_2^-

Sol. (b)

NO. OF pπ - pπ BONDS/NO. OF pπ - dπ BONDS

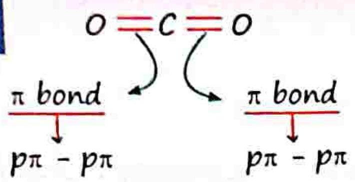
Orbital	π Bond
s	Can not form π bond
p	Can form π bond
d	Can form π bond

Period no = 2	π Bond
s	✗
p	✓
d	→ not available in 2^{nd} period elements.

Period no > 2	π Bond
s	✗
p	✓
d	✓

- ☐ If central atom or side atom is from period no 2 (B,C,N,O) then only p orbital can make π bond.
- ☐ If central atom or side atom is from period no > 2 (Al, Si, P, S, Cl, Xe) then p and d both can make π bond.

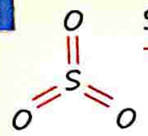
CO_2



☐ overlapping between p orbital of carbon and p orbital of oxygen makes π bond.

☐ No. of pπ - pπ bonds = 2

SO_3



Sulphur (S) ⟶ 6 bonds ⟶ 3 σ bonds + 3 π bonds

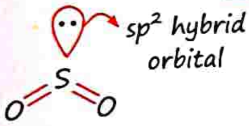
$\boxed{s + p + p}$ + $\boxed{p + d + d}$

$s + p + p$ → 3 sp^2 hybrid orbitals → 3 σ bonds

$p + d + d$ → 3 π bonds → 1 pπ – pπ bond, 2 dπ – pπ bonds

3 π bonds	
Sulphur	Oxygen
1. p	p
2. d	p
3. d	p

SO_2



Sulphur (S) ⟶ 2 σ bonds + 2 π bonds + 1 lone pair

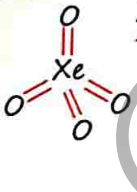
$\boxed{s + p + p}$ + $\boxed{p + d}$

$s + p + p$ → 3 sp^2 hybrid orbitals → 2 σ bonds + 1 lone pair

$p + d$ → 2 π bonds → 1 pπ – pπ bond, 1 dπ – pπ bond

2 π bonds	
Sulphur	Oxygen
1. p	p
2. d	p

XeO_4



Xenon (Xe) ⟶ 4 σ bonds + 4 π bonds

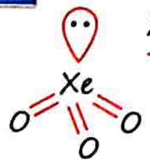
$\boxed{s + p + p + p}$ + $\boxed{d + d + d + d}$

$s + p + p + p$ → 4 sp^3 hybrid orbitals → 4 σ bonds

$d + d + d + d$ → 4 π bonds → 4 dπ – pπ bonds

4 π bonds	
Xenon	Oxygen
1. d	p
2. d	p
3. d	p
4. d	p

XeO_3



Xenon (Xe) ⟶ 3 σ bonds + 3 π bonds + 1 lone pair

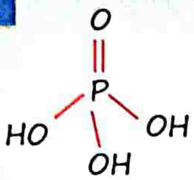
$\boxed{s + p + p + p}$ + $\boxed{d + d + d}$

$s + p + p + p$ → 4 sp^3 hybrid orbitals → 3 σ bonds + 1 lone pair

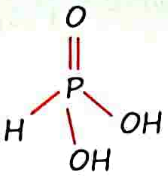
$d + d + d$ → 3 π bonds → 3 dπ – pπ bonds

4 π bonds	
Xenon	Oxygen
1. d	p
2. d	p
3. d	p

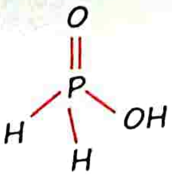
H_3PO_4



H_3PO_3

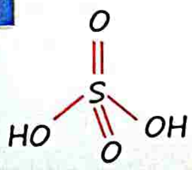


H_3PO_2



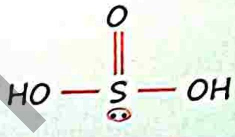
- Hybridisation of P : sp^3
- 1 $p\pi - d\pi$ bond

H_2SO_4



- Hybridisation of S : sp^3
- 2 $p\pi - d\pi$ bond

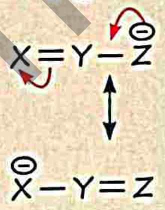
H_2SO_3



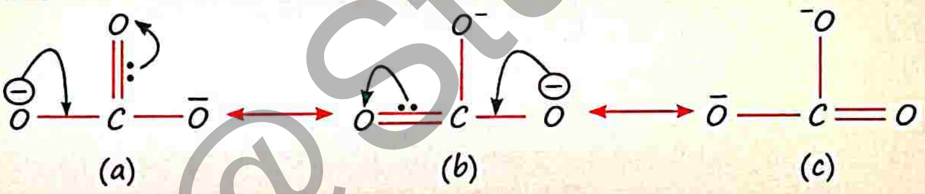
RESONANCE

- Delocalisation of pi electrons
- Conjugation – Necessary condition for resonance

Conjugation

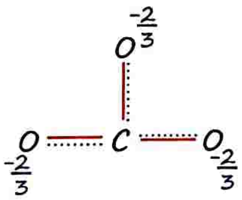


CO_3^{2-}



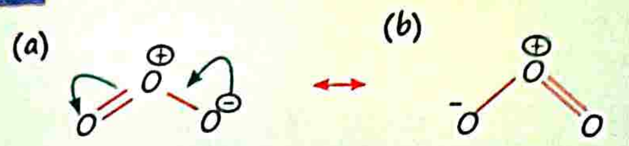
- Resonating structures ≡ a, b, c

◆ Resonance Hybrid ⟶



- No. of bonds b/w 2 atoms [Bond order] $= \frac{\sigma + \pi}{\sigma} = \frac{3+1}{3} = 1.33 \rightarrow 1\sigma$ bond $+ \frac{1}{3}\pi$ bonds.
- Formal charge on oxygen $\equiv \frac{-2}{3}$
- Bond length ≡ All C – O bonds are same due to resonance

O_3



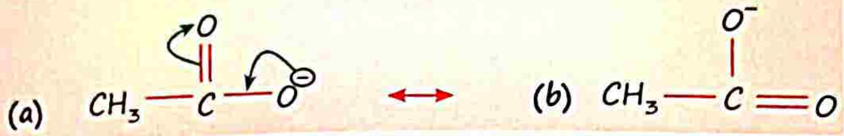
☐ Resonating structures ≡ a & b

☐ Resonance Hybrid ≡

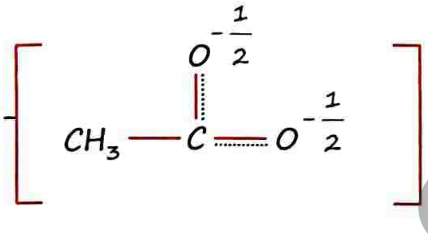
☐ Bond order = $\frac{\sigma + \pi}{\sigma} = \frac{2+1}{2} = 1.5$

☐ Bond length ≡ All O – O bonds are same.

CH_3COO^-

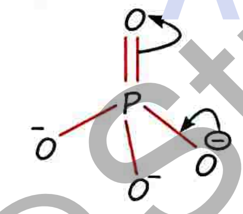
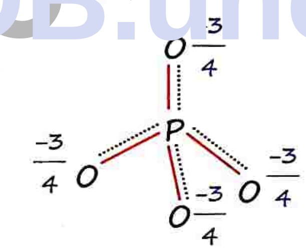
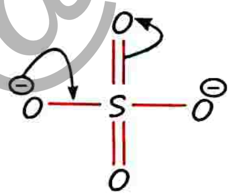
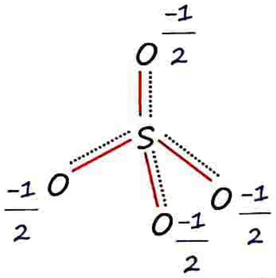
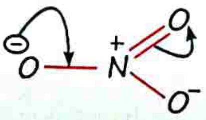
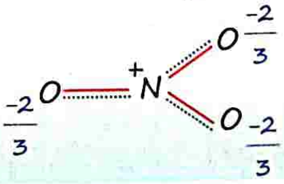


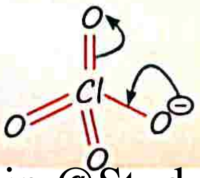
☐ Resonance Hybrid –

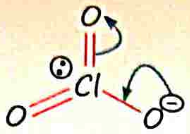
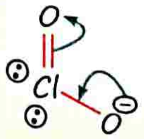
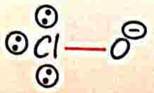


☐ CO bond order = $\frac{\sigma + \pi}{\sigma} = \frac{2+1}{2} = 1.5$

☐ Bond length ≡ All C – O bonds are same

		Resonance Hybrid	Bond Order
PO_4^{3-}			$BO = \frac{\sigma + \pi}{\sigma} = \frac{4+1}{4} = 1.25$
SO_4^{2-}			$BO = \frac{4+2}{4} = 1.5$
NO_3^-			$BO = \frac{\sigma + \pi}{\sigma} = \frac{3+1}{3} = 1.33$

		Formal Charge	Bond Order
$HClO_4 \xrightleftharpoons{-H^+} ClO_4^-$		$\frac{-1}{4}$	$BO = \frac{\sigma + \pi}{\sigma} = \frac{4+3}{4} = 1.75$

$HClO_3 \xrightleftharpoons{-H^+} ClO_3^-$		$\frac{-1}{3}$	$BO = \frac{3+2}{3} = 1.66$
$HClO_2 \xrightleftharpoons{-H^+} ClO_2^-$		$\frac{-1}{2}$	$BO = \frac{2+1}{2} = 1.5$
$HClO \xrightleftharpoons{-H^+} ClO^-$		-1	$BO = 1$

- ☐ Acidity ∝ Stability of conjugate base ∝ $\frac{1}{\text{formal charge}}$
- ☐ Acidic Strength : $a > b > c > d$

(JEE. Adv 2015)

46. The correct statement(s) regarding,
(i) HClO, (ii) $HClO_2$, (iii) $HClO_3$ and (iv) $HClO_4$ is (are)
(a) The number of Cl = O bonds in (ii) and (iii) together is two
(b) the number of lone pair of electrons on Cl in (ii) and (iii) together is three
(c) the hybridisation of Cl in (iv) is sp^3
(d) amongst (i) to (iv), the strongest acid is (i)

Sol. (b, c)

47. In PO_4^{3-} ion, the formal charge on each oxygen atom and P-O bond order respectively are: [NEET 1998]

(a) −0.75, 0.6 (b) −0.75, 1.0 (c) −0.75, 1.25 (d) −3, 1.25

Sol. (c)

DRAGO COMPOUNDS

- ☐ In some cases (like group 15, 16 hydrides from 3rd or higher period), the central atom doesn't participate in hybridisation.
- ☐ Bonding occurs through pure p orbitals, leading to a bond angle of approximately 90°.

NH_3 →	107°	H_2O →	104.5°
PH_3	93.6°	H_2S	92°
AsH_3	91.8°	H_2Se	91°
SbH_3	91.3°	H_2Te	90°

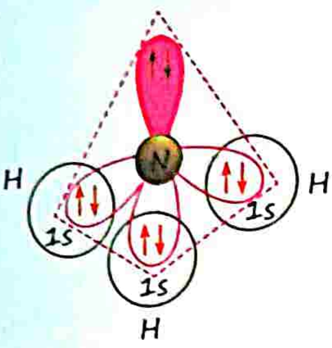
bond angle θ is near to ideal angle 109°28' of sp^3 hybridisation.

bond angle θ ≈ 90° → No, Hybridisation

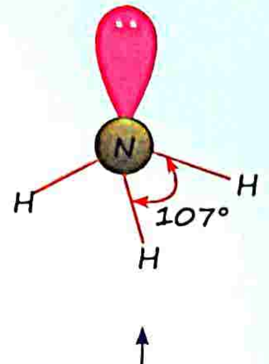
↓

Pure p orbital of central atom overlaps to 1s atomic orbital of side atom H.

Bonding in NH_3

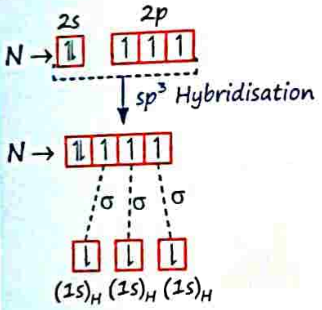


Orbital overlap in NH_3



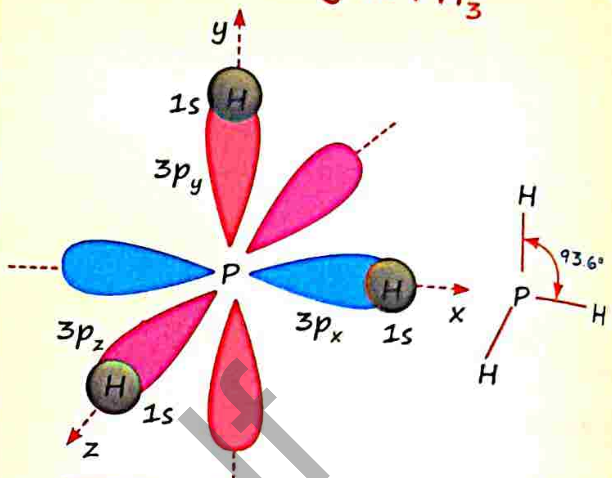
Pyramidal shape

In order to make N– H bonds sp^3 hybrid orbitals of nitrogen overlap with 1s atomic orbital of hydrogens.



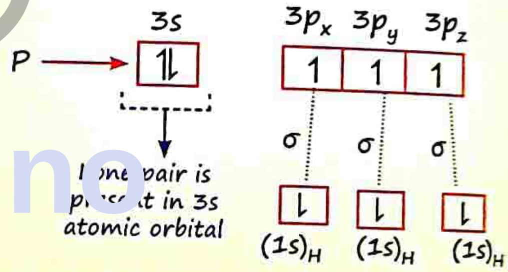
- ☐ 3 N – H σ bonds : $(sp^3)_N$ – $(1s)_H$
- ☐ 1 lone pair in sp^3 hybrid orbital of nitrogen.

Bonding in PH_3



Orbital overlap in PH_3

In order to make P – H bonds p -atomic orbitals (p_x, p_y, p_z) of phosphorus overlap with 1s atomic orbital of hydrogens.



BOND ANGLE

- ☐ Angle between two bonds.

Molecules without Lone Pair

Hybridisation ⟶ θ : sp > sp^2 > sp^3

$\theta : \underset{sp}{\underset{\downarrow}{CO_2}} > \underset{sp^2}{\underset{\downarrow}{CO_3^{2-}}} > \underset{sp^3}{\underset{\downarrow}{CH_4}}$

$\theta : CF_4 = CH_4 = NH_4^+ = XeO_4 = 109°28'$ [sp^3 hybridisation]

$\theta : \underset{sp}{\underset{\downarrow}{NO_2^+}} = \underset{sp}{\underset{\downarrow}{CO_2}} > \underset{sp^2}{\underset{\downarrow}{SO_3}} > \underset{sp^3}{\underset{\downarrow}{XeO_4}}$

$\theta : BF_3 = BCl_3 = BBr_3 = 120°$ [sp^2 hybridisation]

% s character ↓
bond angle ↓

sp	θ = 180°
sp^2	θ = 120°
sp^3	θ = 109° 28'

Molecules with Lone Pair

1. If same Hybridisation ⟶ No of lone pair ↑ : θ ↓

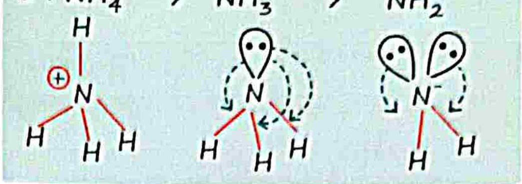
$\theta = CH_4 > \ddot{N}H_3 > H_2\ddot{\ddot{O}}$

↓ sp³ hybⁿ with zero lone pair

↓ sp³ hybⁿ with 1 lone pair

↓ sp³ hybⁿ with 2 lone pairs

$\theta : NH_4^+ > NH_3 > NH_2^-$



2. No. of lone pair : same ⇒ Size of CA ↑ : Bond angle ↓

$\theta : \ddot{N}H_3 > \ddot{P}H_3 > \ddot{As}H_3 > \ddot{Sb}H_3$

$\theta : \ddot{N}Cl_3 > \ddot{P}Cl_3 > \ddot{As}Cl_3 > \ddot{Sb}Cl_3$

$\theta : OF_2 > SF_2$

$\theta : OCl_2 > SCl_2 > SeCl_2 > TeCl_2$

$\theta : NF_3 > PF_3 > AsF_3 > SbF_3$

3. No of lone pair : same

↓

E.N. of S.A. ↑ : Bond angle ↓

$\theta : NH_3 > NF_3$

$\theta : H_2O > OF_2$

☐ Bond pair – bond pair repulsion ↑

☐ Bond angle ↑

☐ θ = 104.5°

☐ Bond pair – bond pair repulsion ↓

☐ Bond angle ↓

☐ θ < 104.5°

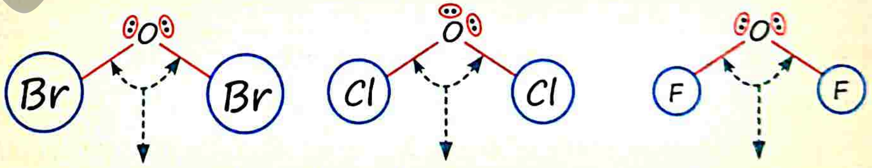
4. No of lone pair : same

↓

Size of S.A. ↑ : Bond angle ↑

$\theta : \ddot{P}Br_3 > \ddot{P}Cl_3 > \ddot{P}F_3$

$\theta : OBr_2 > OCl_2 > OF_2$



θ > 111° θ = 111° θ = 104.5°

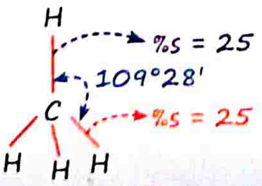
Note

Bent's Rule

% s character ↑ : Bond Angle ↑

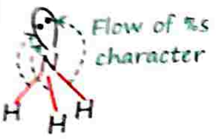
1. Lone pair orbitals must adopt a higher s character to stabilise the unshared, tightly bound nonbonding electrons.

CH_4

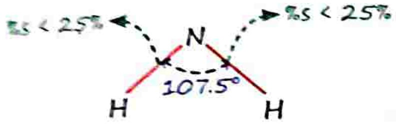


☐ Each C–H bond has 25% s character and bond angle is 109°28'.

NH_3

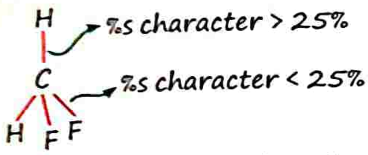


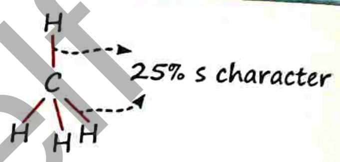
☐ Flow of %s character from N-H bond to lone pair of nitrogen.



☐ %s character decreases in each N-H bond. So, bond angle decreases.

2. Electronegative element prefer hybrid orbital having less s character and more p character while less electronegative substituents prefer hybrid orbital having more s character.





% s character : C – H bond > C – F bond

Bond angle: ∠HCH > ∠HCF > ∠FCF

$\angle HCH = 109°28'$

$$[\angle HCH]_{CH_2F_2} > [\angle HCH]_{CH_4}$$

(IIT JEE 1999)

48. In compounds of type ECl_3, where E = B, P, As or Bi, the angles Cl—E—Cl is in order
(a) B > P = As = Bi (b) B > P > As > Bi (c) B < P = As = Bi (d) B < P < As < Bi

Sol. (b)

49. For OF_2 molecule, consider the following: [30 Jan, 2023 (Shift-I)]
(A) Number of lone pairs on oxygen is 2.
(B) FOF angle is less than 104.5°.
(C) Oxidation state of O is –2.
(D) Molecule is bent 'V' shaped.
(E) Molecular geometry is linear.
Correct options are:
(a) C, D, E only (b) B, E, A only (c) A, C, D only (d) A, B, D only

Sol. (d)

Bond Length

Size ↑ : Bond length ↑

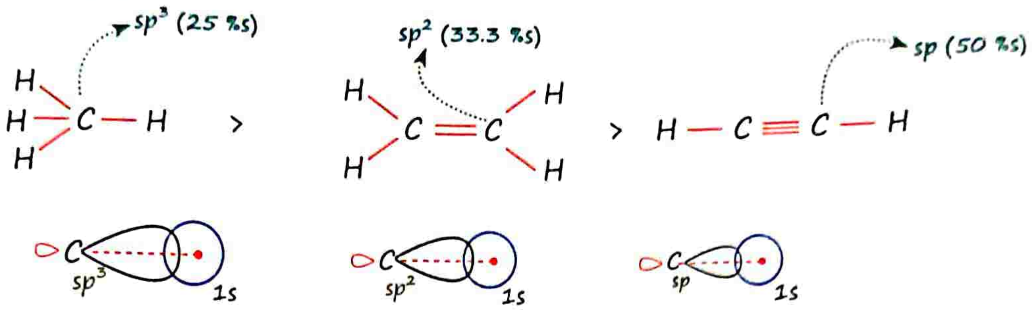
H – F < H – Cl < H – Br < H – I : Bond length
C – F < C – Cl < C – Br < C – I : Bond length

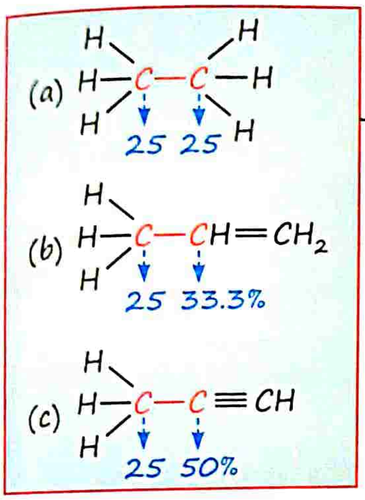
Bond order ↓ : Bond length ↑

$C \equiv C < C = C < C - C$
$C \equiv N < C = N < C - N$ → Bond length
$N \equiv N < N = N < N - N$

%s character↑ : Bond length↓

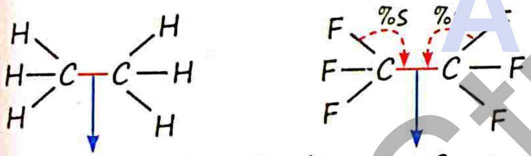
C-H Bond length :





☐ % s character : c > b > a
☐ C—C Bond length : c < b < a

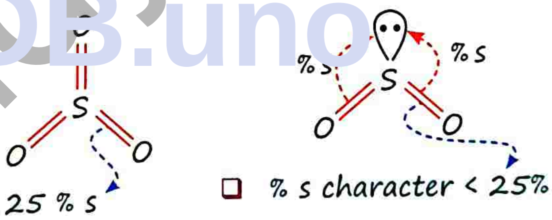
C_2H_6 > C_2F_6 : C—C bond length



less % s character

% s character Concentrates in C– C bond

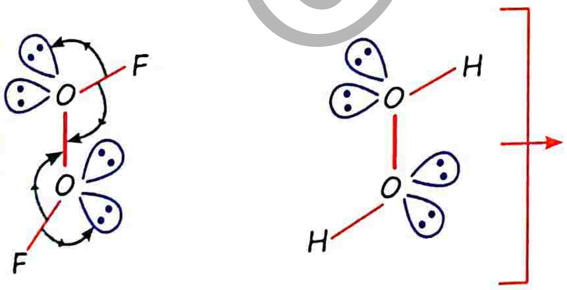
SO_3 < SO_2 : S—O bond length



25 % s character

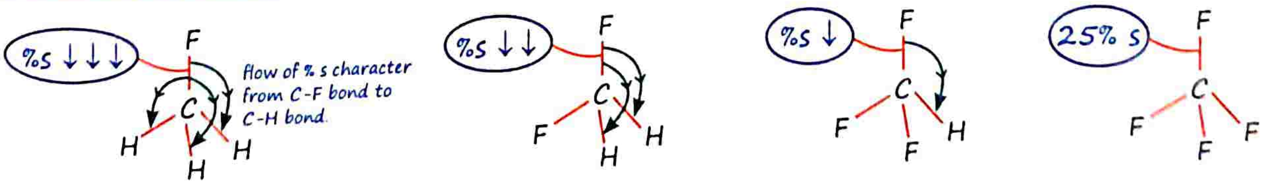
☐ % s character < 25%
☐ Less % s character → more bond length

O_2F_2 < H_2O_2 : O—O bond length



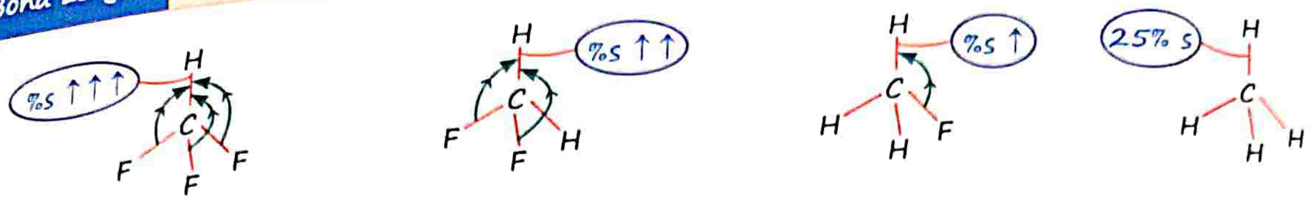
☐ Order of % s character in O – O bond : O_2F_2 > H_2O_2
O – O bond length : O_2F_2 < H_2O_2
☐ % s character : O – F < O – H
Bond length : O – F > O – H

C-F Bond Length: CH_3F > CH_2F_2 > CHF_3 > CF_4

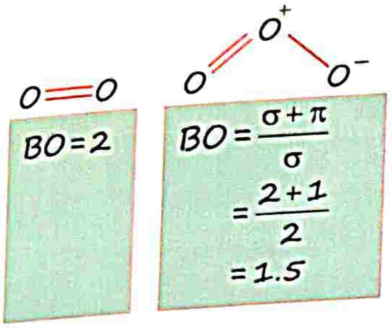


Flow of % s character from C-F bond to C-H bond.

C-H Bond Length: CHF_3 < CH_2F_2 < CH_3F < CH_4

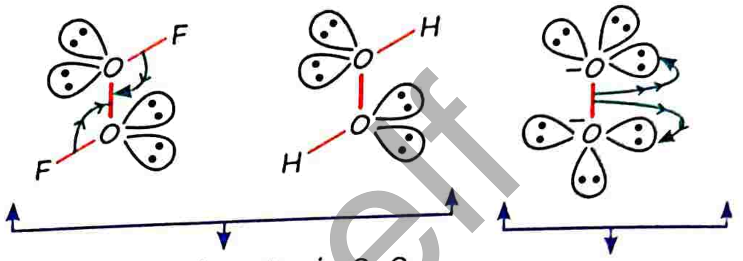


O-O Bond Length: O_2 < O_3 < O_2F_2 < H_2O_2 < Na_2O_2 [$2Na^+ O_2^{2-}$]



$BO = 2$

$$BO = \frac{\sigma + \pi}{\sigma} = \frac{2+1}{2} = 1.5$$

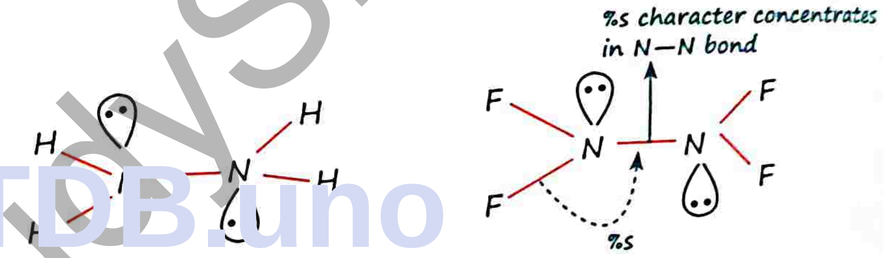


Order of %s character in O–O bond: $O_2F_2 > H_2O_2$

O–O bond length : $O_2F_2 < H_2O_2$

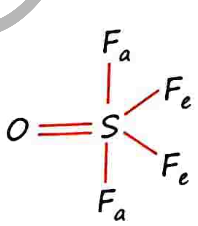
Less %s character in O–O bond in O_2^{2-} than O_2F_2 and H_2O_2.

N-N Bond length: N_2H_4 > N_2F_4

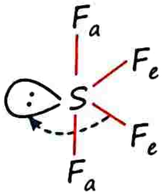


O-F Bond length: O_2F_2 > OF_2

S-F(eq) Bond length: SOF_4 < SF_4



$SOF_4 < SF_4$



50. O–O bond length in H_2O_2 is X than the O–O bond length in F_2O_2. The O–H bond length in H_2O_2 is Y than that of the O–F bond in F_2O_2. [1 Feb, 2023 (Shift-II)]

Choose the correct option for X and Y from the given below.

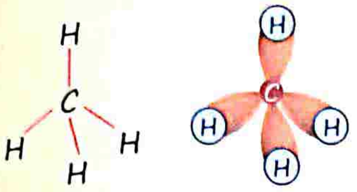
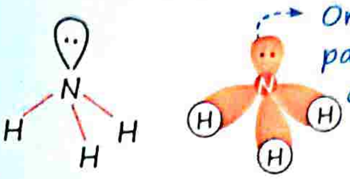
(a) X - shorter, Y - shorter

(b) X - shorter, Y - longer

(c) X - longer, Y - longer

(d) X - longer, Y - shorter

Sol. (d)

Equivalent Hybrid Orbitals	Non-equivalent Hybrid Orbitals
 ☐ All 4 hybrid orbitals are equivalent in energy and size.	 Orbital having lone pair is small in size due to more %s character.
☐ Central atom without lone pair and attached with same side atoms has equivalent hybrid orbitals. Example: XeO_4, $BeCl_2$, BF_3	☐ Central atom with lone pair or attached with different side atoms has non-equivalent hybrid orbitals. Example: $H_2\ddot{O}$, $\ddot{N}H_3$, CH_2F_2

Bond Dissociation Energy

Minimum energy required to break a bond is known as bond dissociation energy.

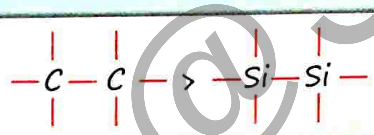
(1) BDE ∝ Bond Order

BDE : $C \equiv C > C = C > C - C$ → Easy to break : BDE ↓

(2) BDE ↓ : Bond Length ↑

☐ Bond length : $C \equiv C > C \equiv N > N \equiv N$ (Size : C > N)

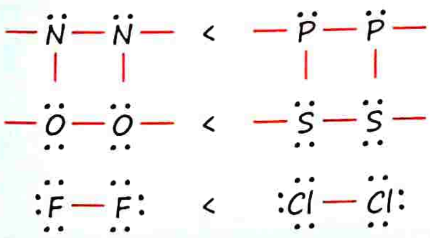
BDE : $C \equiv C < C \equiv N < N \equiv N$

☐ 

Order of bond length: $C - C < Si - Si$

Bond dissociation energy: $C - C > Si - Si$

(3) BDE ↓ : LP-LP Repulsion ↑



☐ In these 3 cases, bonded atoms has/have lone pair(s) so, we are going to consider lone pair-lone pair repulsion as a major factor in order to compare the bond dissociation energy.

☐ Lone pair-lone pair repulsion is more when bonded atoms are small in size, so it will be easy to break the bond.

Note

BDE :	$Cl - Cl$	>	$Br - Br$	>	$F - F$	>	$I - I$
	काला		बन्दर		फिर		India में !

51. The table shown below gives the bond dissociation energies (E_{diss}) for single covalent bonds of carbo atoms with element A, B, C and D. Which element has the smallest atoms? [NEET 1994

Bond	E_{diss} (kJ mol^{-1})
C–A	240
C–B	328
C–C	276
C–D	485

(a) C (b) D (c) A (d) B

Sol. (b)

52. Match List-I with List-II: [NEET 2024 Re

List-I Molecule		List-II Bond enthalpy (kJmol^{-1})	
A.	HCl	I.	435.8
B.	N_2	II.	498
C.	H_2	III.	946.0
D.	O_2	IV.	431.0

Choose the correct answer from the options given below:

(a) A-III, B-IV, C-I, D-II
(b) A-IV, B-I, C-III, D-II
(c) A-IV, B-III, C-II, D-I
(d) A-IV, B-III, C-I, D-II

Sol. (d)

53. The correct order of bond angles in the following compounds/ species is: [NEET 2022 Re

(a) $CO_2 < NH_3 < H_2O < NH_4^+$
(b) $H_2O < NH_3 < NH_4^+ < CO_2$
(c) $H_2O < NH_4^+ < NH_3 < CO_2$
(d) $H_2O < NH_4^+ = NH_3 < CO_2$

Sol. (b)

54. Consider the molecules CH_4, NH_3 and H_2O. Which of the given statement is false? [NEET 2016-

(a) The H–C–H bond angle in CH_4 is larger than the H–N–H bond angle in NH_3
(b) The H–C–H bond angle in CH_4, the H–N–H bond angle in NH_3, and the H–O–H bond ang in H_2O are all greater than 90°.
(c) The H–O–H bond angle in H_2O is larger than the H–C–H bond angle in CH_4
(d) The H–O–H bond angle in H_2O is smaller than the H–N–H bond angle in NH_3

Sol. (c)

55. The correct order of increasing bond length of C – H, C – O, C – C and C = C is: [NEET 2011 Pr

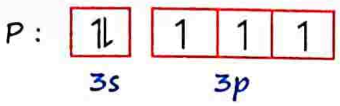
(a) $C-H < C-O < C-C < C=C$
(b) $C-H < C=C < C-O < C-C$
(c) $C-C < C=C < C-O < C-H$
(d) $C-O < C-H < C-C < C=C$

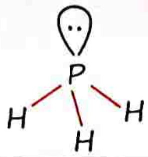
Sol. (b)

PH_3 HAS NO HYBRIDISATION BUT PF_3 & PH_4^+ HAS ? WHY

Complete or partial +ve charge on central atom supports ORBITAL CONTRACTION, which leads hybridisation of atomic orbitals.

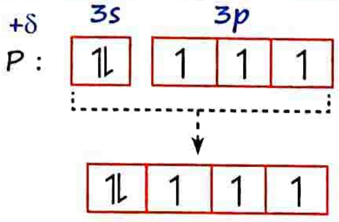
PH_3



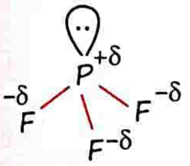


⇒ P in PH_3 has no hybridisation

PF_3

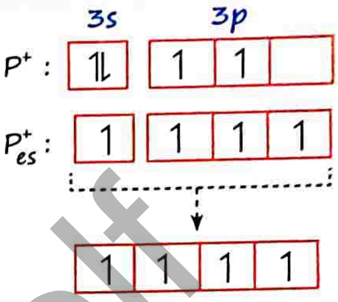


4 sp^3 hybrid orbitals

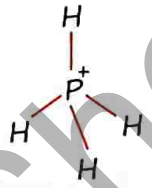


⇒ P in PF_3 is sp^3 hybridised

PH_4^+



4 sp^3 hybrid orbitals

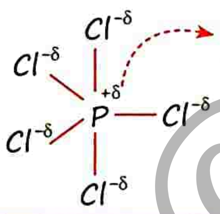


⇒ P in PH_4^+ is sp^3 hybridised

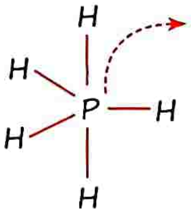
Bond Angle: PH_3 < PF_3 < PH_4^+
[θ ≅ 90°] [θ > 90°] [θ = 109°28']

56. PCl_5 exists but not PH_5 ?

Sol. d-orbital contraction is possible in PCl_5 but not in PH_5.



Partial (+)ve charge on P helps in d orbital contraction



No charge on P.

57. SF_6 exists but not SH_6 ?

Sol. d-orbital contraction is possible in SF_6 but not in SH_6.

EXISTENCE & NON-EXISTENCE

☐ 2nd Period elements → B/C/N/O/F → Can have maximum $8e^-$ in valence shell
→ max. covalency ≡ 4
→ d orbitals are not available
→ Possible hybridisations are – sp, sp^2, sp^3

☐ $3^{rd}/4^{th}/5^{th}/6^{th}/7^{th}$ Period elements → Al/Si/P/S etc.
→ d orbitals are available of bonding
→ Possible hybridisation are sp, sp^2, sp^3, sp^3d, sp^3d^2, sp^3d^3
→ These elements can form more than 4 bonds.

NCl_5
BCl_6^{3-} → N and B can not form more than 4 bonds

PCl_5
$AlCl_6^{3-}$ → P and Al can have covalency more than 4.

Note

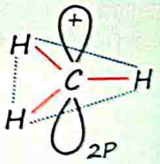
Molecules That Do Not Exist

(1) SF_4, SF_6 & PF_5, exist while OF_4, OF_6, NF_5 do not exist
(2) (a) PI_5(vap) & SCl_6 do not exist
(b) SCl_6 does not exist while $TeCl_6$ exist due to steric effect.
(3) SF_6, PF_5, XeF_6, XeF_4 & XeF_2 exist while SH_6, PH_5, XeH_6, XeH_4, XeH_2 do not exist.

LEWIS BASE AND LEWIS ACID

Lewis Acid → Electron pair acceptor

CA having vacant orbital:	(i) Vacant p orbital: BF_3 $B(OH)_3$ $AlCl_3$	(ii) Vacant d orbital: SiF_4 PCl_5

CA with +ve charge having vacant orbital:	(i) Vacant s orbital: H^+ (ii) Vacant p orbital: CH_3^+ sp^2	

☐ NH_4^+ ⟶ not a Lewis Acid because there is no vacant orbital in N.

Lewis Base → Electron pair donor

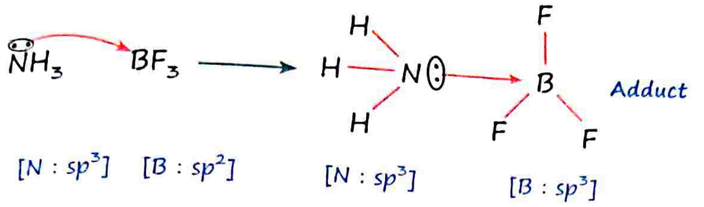
CA with lone pair :	NH_3, PH_3, H_2O
CA with -ve charge :	F^-, Cl^-, OH^-

☐ $F^- + BF_3 \longrightarrow BF_4^-$
[B : sp^2] [B : sp^3]

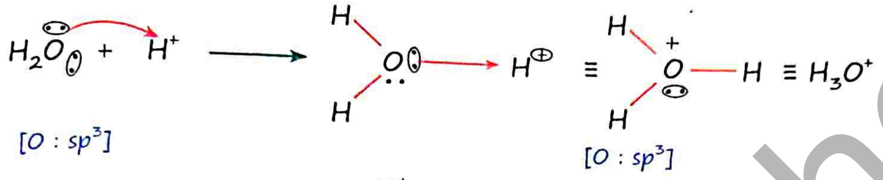
☐ $OH^- + B(OH)_3 \longrightarrow B(OH)_4^-$
[B : sp^2] [B : sp^3]

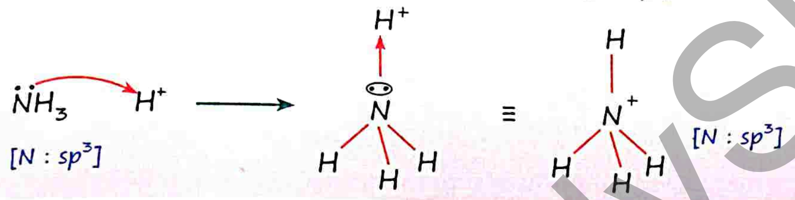
☐ $Cl^- + AlCl_3 \longrightarrow AlCl_4^-$
[Al : sp^2] [Al → sp^3]

☐ $Cl^- + PCl_5 \longrightarrow PCl_6^-$
[P : sp^3d] [P : sp^3d^2]

☐ 

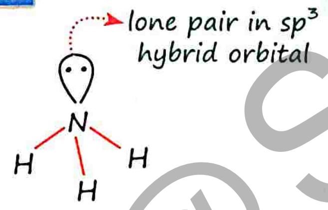
☐ $2F^- + SiF_4 \longrightarrow SiF_6^{2-}$
[Si : sp^3] [Si → sp^3d^2]

☐ 

☐ 

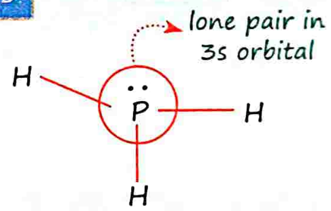
Lewis Basicity NH_3 vs PH_3

NH_3



☐ $H_3N: \longrightarrow H^+ \xrightleftharpoons{K_{b1}} NH_4^+$

PH_3



☐ $H_3P: \longrightarrow H^+ \xrightleftharpoons{K_{b2}} PH_4$

- $K_{b1} >> K_{b2}$
- Lewis basicity : $NH_3 > PH_3$

Order of Lewis basicity is due to fact that lone pair on N is in sp^3 hybrid orbital which is more diffused and directional. But lone pair on P is present in a 's' orbital which is contracted and non-directional.

(IIT JEE 2002)

58. Specify the coordination geometry around and hybridising N and B atoms in a 1 : 1 complex of BF_3 and NH_3.
(a) N: tetrahedral, sp^3; B: tetrahedral, sp^3
(b) N: pyramidal, sp^3; B: pyramidal, sp^3
(c) N: pyramidal, sp^3; B: planar, sp^2
(d) N: pyramidal, sp^2; B: tetrahedral, sp^2

Sol. (a)

HYBRIDISATION IN ODD ELECTRON SPECIES

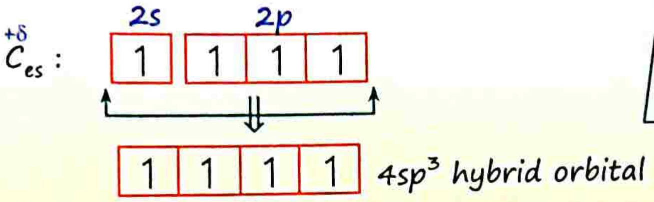
- ☐ When side atoms are more electronegative than central atom then odd electrons are considered in steric number to find hybridisation.

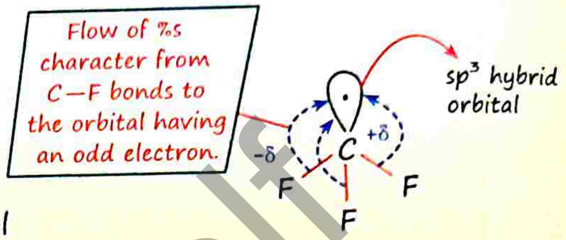
$\dot{C}F_3$

$SN = 1 + 3 = 4 \Rightarrow sp^3$ hybridisation

1 → odd electron

3 → side atoms



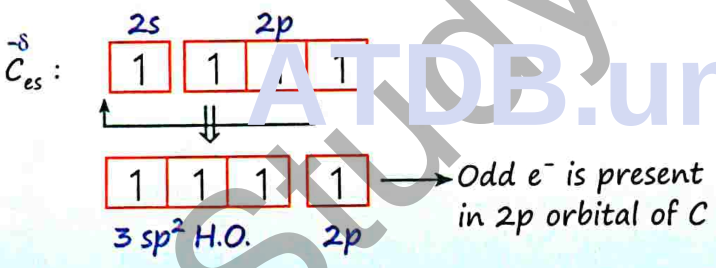


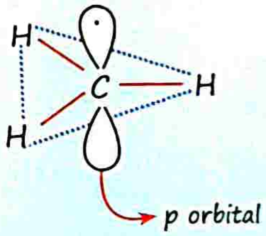
$\dot{C}H_3$

$SN = 0 + 3 = 3 \Rightarrow sp^2$ hybridisation

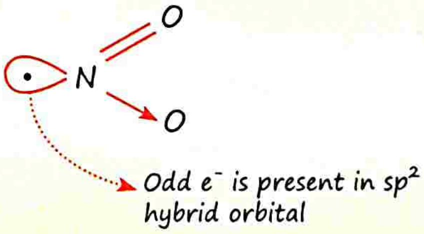
0 → [odd electron is not considered because side atom H is less electronegative than central atom C]

3 → side atoms



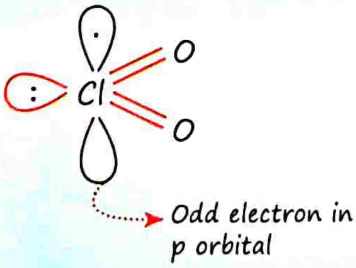


$\dot{N}O_2$



- ☐ $SN = 1 + 2$
  $= 3$
- ☐ sp^2 hybridisation

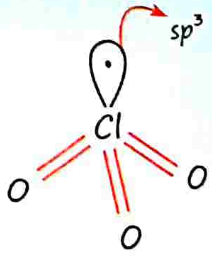
ClO_2



- ☐ $SN = 1 + 2 = 3$
- ☐ sp^2 hybridisation

$\dot{C}lO_3$

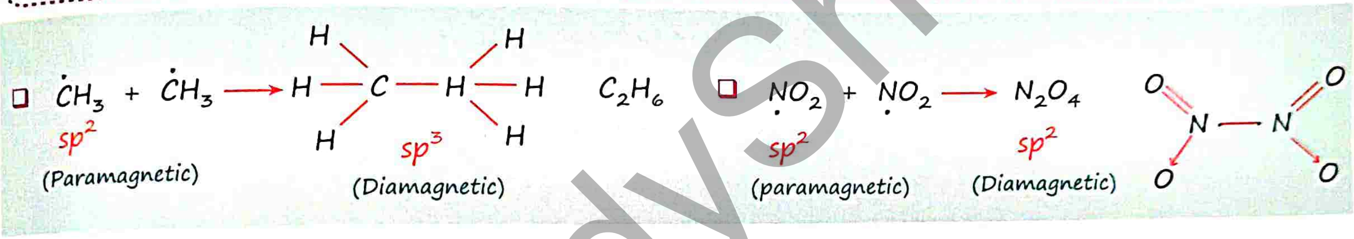
- ☐ $SN = 1 + 3$
  $= 4$
  $= sp^3$



Odd e^- molecule	Orbital having odd electron	hyb^n of central atom
$\dot{C}H_3$	p	sp^2
$\dot{C}F_3$	sp^3	sp^3
$\dot{N}O_2$	sp^2	sp^2
$\dot{Cl}O_3$	sp^3	sp^3
$\dot{Cl}O_2$	p	sp^2

Dimer Formation – Hybridisation Change & Magnetic Behaviour

2 unit



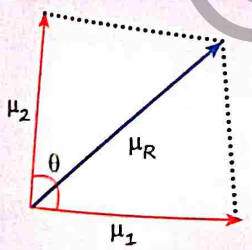
DIPOLE MOMENT

Product of the magnitude of the charge and the distance between the centers of the positive and negative charges.

Dipole moment = charge · distance of separation

$\boxed{\text{Dipole moment } \mu = q \cdot l}$

Dipole moment is a vector quantity when 2 vectors (μ_1 & μ_2) are separated by θ then we can calculate resultant μ_R.



- ☐ $\mu_R^2 = \mu_1^2 + \mu_2^2 + 2\mu_1 \cdot \mu_2 \cos\theta$
- ☐ $\cos\theta \uparrow : \ \mu_R \uparrow$
- ☐ $\theta \uparrow : \cos\theta \downarrow : \ \mu_R \downarrow$

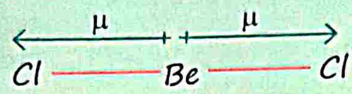
Unit ≡ C . m
≡ esu . cm
≡ Debye [D]
C → Coulomb
m → metre
esu → Electrostatic unit of charge

1 Debye = 10^{-18} esu cm
Charge on e^- → $q_e = 1.6 \times 10^{-19}$ C
$= 4.8 \times 10^{-10}$ esu

Polar Molecule ($\mu_R \neq 0$)	Non-polar Molecule ($\mu_R = 0$)
☐ Hetero-nuclear diatomic	☐ Homonuclear diatomic
☐ Molecule having 2 different atoms	☐ Molecule having 2 same atoms
☐ HCl $\overset{+\delta}{H}$ — $\overset{-\delta}{Cl}$ → Polar bond	☐ H_2, F_2, O_2, N_2 F — F → Non polar bond

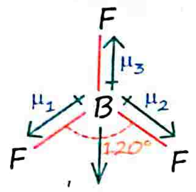
Symmetry and Dipole Moment

A polyatomic molecule having polar covalent bonds and symmetrical structure indicates the zero dipole moment of the molecule.



$BeCl_2$ → Symmetrical molecule

$\mu_{BeCl_2} = 0$



$\mu'_R = \mu$

- ☐ BF_3 → Symmetrical molecule
- ☐ $\mu_{BF_3} = 0$
- ☐ BF_3 → Non polar molecule

$\mu'^2_R = \mu_1^2 + \mu_2^2 + 2\mu_1 \cdot \mu_2 \cos 120°$

$\mu'_R = \mu \quad [\mu_1 = \mu_2 = \mu]$

→ μ'_R is cancelled by μ_3 (= μ)

Symmetrical Molecule

☐ Symmetrical molecules are non-polar molecules. ☐ $(\mu_R)_{molecule} = 0$

1. Molecule having no lone pair on central atom and having same side atoms.

CO_2, CS_2, $BeCl_2(g)$

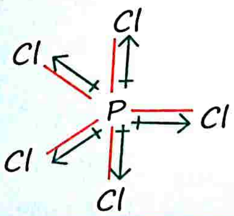
$O = C = O$

$S = C = S$

$Cl — Be — Cl$

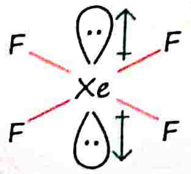
→ Linear $(\mu_R)_{mol} = 0$

BF_3, CH_4, PCl_5, SF_6, IF_7 → $\mu_R = 0$ → Non-Polar molecule



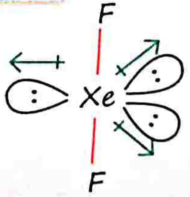
2. Molecule having lone pairs on central atom but in such a way that they can cancel each others dipole moment.

XeF_4



- ☐ Non polar molecule
- ☐ $\mu_R = 0$

XeF_2

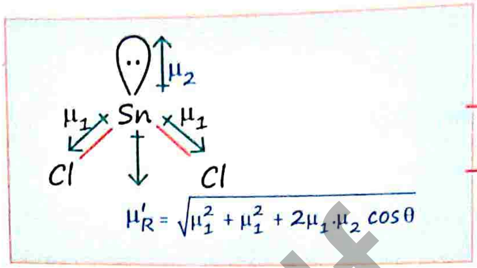


Unsymmetrical Molecule

Molecule having lone pairs on central atom but in such a way that they can not cancel each others dipole moment.

$\ddot{Sn}Cl_2$, $\ddot{Pb}Cl_2$, $\ddot{S}O_2$: Angular mol. : Polar

$\ddot{N}H_3$, $H_2\ddot{\underset{..}{O}}$, $\ddot{N}F_3$, $\ddot{S}F_4$, $H_2\ddot{\underset{..}{S}}$: : Polar molecule

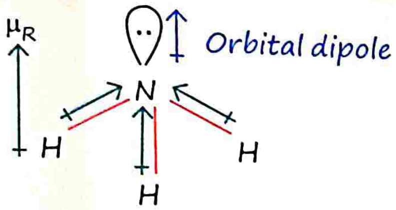
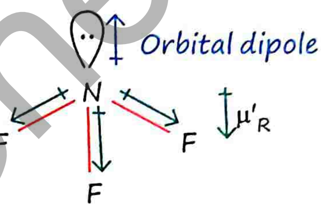


$$\mu'_R = \sqrt{\mu_1^2 + \mu_1^2 + 2\mu_1 \cdot \mu_2 \cos\theta}$$

→ $\mu'_R \neq \mu_2$

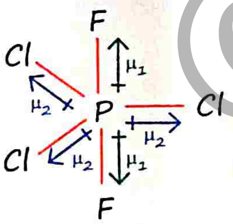
→ $\mu_{SnCl_2} \neq 0$

NH_3 > NF_3 : Dipole moment

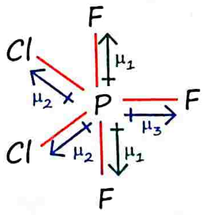
	
In case of NH_3, the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N – H bonds.	In NF_3, the orbital dipole is in the direction opposite to the resultant dipole moment of the three N–F bonds.

The orbital dipole because of lone pair decreases the effect of the resultant N – F bond moments, which results in the low dipole moment of NF_3.

☐ PCl_3F_2 < PCl_2F_3



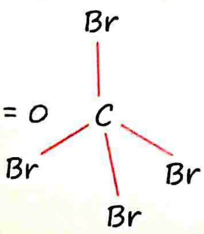
$\mu_R = 0$ (Non Polar)

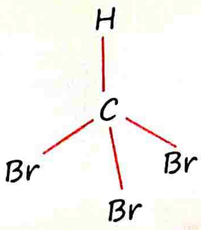


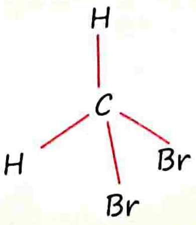
$\mu_R \neq 0$ (Polar molecule)

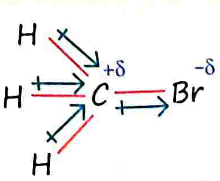
☐ $\mu_R \rightarrow CBr_4$ < $CHBr_3$ < CH_2Br_2 < CH_3Br

$\mu_R = 0$

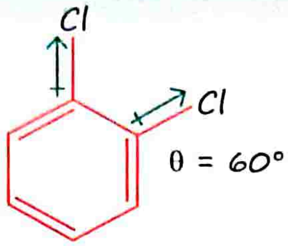


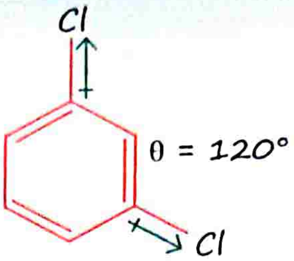


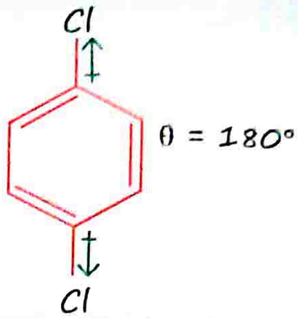




❑ **$\mu_R \uparrow : \theta \downarrow : \cos\theta \uparrow$**

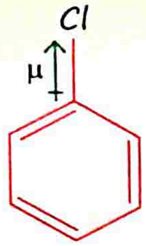




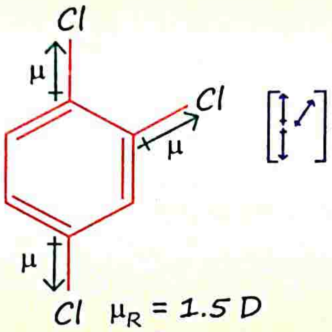


μ_R : ortho - dichlorobenzene > meta-dichlorobenzene > para-dichlorobenzene

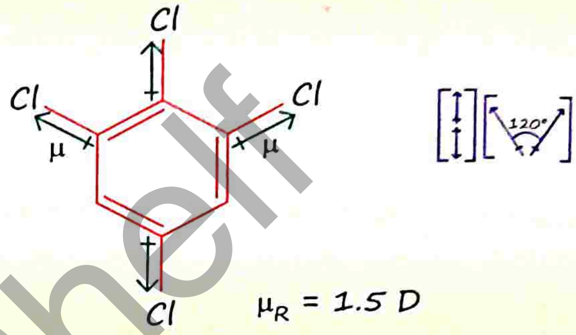
❑



$\mu_R = 1.5\ D$

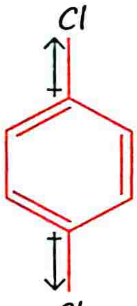


$\mu_R = 1.5\ D$

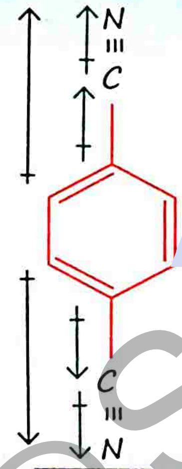


$\mu_R = 1.5\ D$

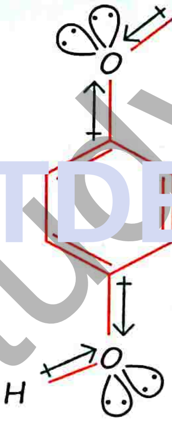
❑



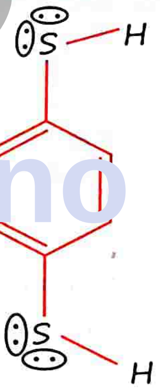
$\mu_R = 0$



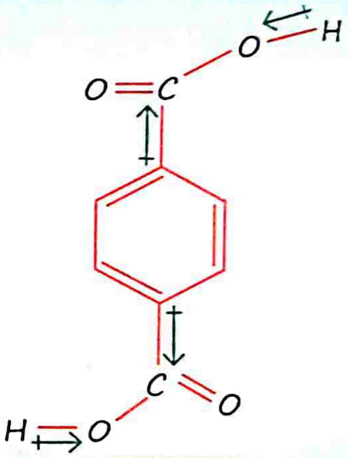
$\mu_R = 0$



$\mu_R \neq 0$

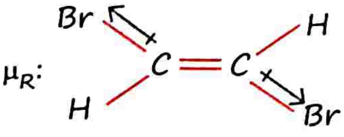


$\mu_R \neq 0$



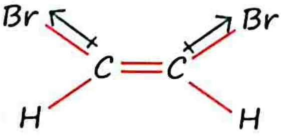
$\mu_R \neq 0$

Cis & Trans

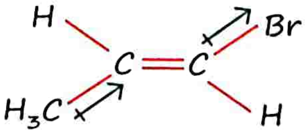


Trans ($\mu = 0$)

<

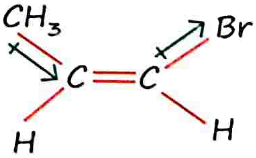


cis ($\mu \neq 0$)



$\mu \neq 0$

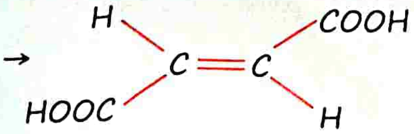
>



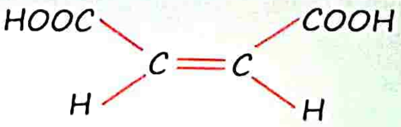
$\mu \neq 0$

: μ_R

$\mu_R \rightarrow$



$\mu_R \neq 0$



$\mu_R \neq 0$

(non-zero dipole moment)

$\mu_R \longrightarrow HF > HCl > HBr > HI$

$\mu_R \longrightarrow CH_3F < CH_3Cl > CH_3Br > CH_3I$

length factor dominates over charge factor.

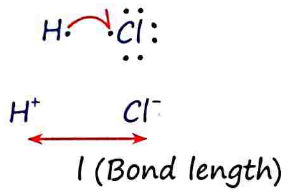
charge factor dominates over length factor

$\mu_R \longrightarrow CH_3-Cl > CH_3F > CH_3Br > CH_3I$

% Ionic Character in Covalent Bond

$$\% \text{ ionic character} = \frac{\mu_{(exp/obs)}}{\mu_{(cal/theo)}} \times 100$$

$\mu_{experiment}$ = given $\longleftarrow$ $\boxed{\overset{+\delta}{H} - \overset{-\delta}{Cl}}$ $\longrightarrow$ $\mu_{calculated} = q.l = (4.8 \times 10^{-10}$ esu). Bond length



☐ For 100% ionic character–
It is assumed that 1 electron is completely transferred from one atom to another.

59. For HCl gas molecule μ = 1.03 D and bond distance = 1.275 Å. Calculate the % ionic character.

Sol. $\mu_{exp} = 1.03$ D

$l = 1.275 \times 10^{-8}$ cm

μ_{cal} = ?

☐ $\mu_{cal} = q_e \cdot l$

$= (4.8 \times 10^{-10}$ esu) . $(1.275 \times 10^{-8}$ cm)

$= (4.8 \times 1.275) . (10^{-18}$esu – cm) $= (4.8 \times 1.275)$D

$$\% \text{ Ionic character} = \frac{1.03}{(4.8 \times 1.275)} \times 100\%$$
$$= 0.1683 \times 100 = 16.83\%$$

60. Among the following, the molecule with the highest dipole moment is (IIT JEE 2003)

(a) CH_3Cl (b) CH_2Cl_2 (c) $CHCl_3$ (d) CCl_4

Sol. (a)

61. Each of the following options contains a set of four molecules. Identify the option(s) where all four molecules possess permanent dipole moment at room temperature. (JEE Adv. 2019)

(a) SO_2, C_6H_5Cl, H_2Se, BrF_5 (b) $BeCl_2$, CO_2, BCl_3, $CHCl_3$

(c) NO_2, NH_3, $POCl_3$, CH_3Cl (d) BF_3, O_3, SF_6, XeF_6

Sol. (a, c)

62. **Which one of the following molecules has maximum dipole moment?** [04 April, 2024 (Shift-I)]

(a) NF_3 (b) CH_4 (c) NH_3 (d) PF_5

Sol. (c)

63. **Given below are two statements: one is labelled as Assertion (A) and the other is labelled as Reason (R).**

Assertion (A): NH_3 and NF_3 molecule have pyramidal shape with a lone pair of electrons on nitrogen atom. The resultant dipole moment of NH_3 is greater than that of NF_3.

Reason (R): In NH_3, the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N–H bonds. F is the most electronegative element.

In the light of the above statements, choose the correct answer from the options given below: [05 April, 2024 (Shift-II)]

(a) Both (A) and (R) are true and (R) is the correct explanation of (A)

(b) (A) is false but (R) is true

(c) (A) is true but (R) is false

(d) Both (A) and (R) are true but (R) is NOT the correct explanation of (A)

Sol. (a)

64. **Which of the following molecules has "NON ZERO" dipole moment value?** [NEET 2024 Re]

(a) CCl_4 (b) HI (c) CO_2 (d) BF_3

Sol. (b)

65. **Identify the correct answer.** [NEET 2024]

(a) Dipole moment of NF_3 is greater than that of NH_3.

(b) Three canonical forms can be drawn for CO_3^{2-} ion

(c) Three resonance structures can be drawn for ozone.

(d) BF_3 has non-zero dipole moment.

Sol. (b)

66. **The correct order of dipole moments for molecules NH_3, H_2S, CH_4 and HF, is:** [NEET 2023-Manipur]

(a) $CH_4 > H_2S > NH_3 > HF$ (b) $H_2S > NH_3 > HF > CH_4$

(c) $NH_3 > HF > CH_4 > H_2S$ (d) $HF > NH_3 > H_2S > CH_4$

Sol. (d)

67. **Which of the following set of molecules will have zero dipole moment?** [NEET 2020]

(a) Boron trifluoride, hydrogen fluoride, carbon dioxide, 1, 3-dichlorobenzene

(b) Nitrogen trifluoride, beryllium difluoride, water, 1, 3-dichlorobenzzene

(c) Boron trifluoride, beryllium difluoride, carbon dioxide, 1,4-dichlorobenzene

(d) Ammonia, beryllium difluoride, water, 1, 4-dichlorobenzene

Sol. (c)

68. **The electronegativity difference between N and F is greater than that between N and H yet the dipole moment of NH_3 (1.5 D) is larger than that of NF_3 (0.2 D). This is because:** [NEET 2006]

(a) In NH_3 as well as in NF_3, the atomic dipole and bond dipole are in the same direction

(b) In NH_3, the atomic dipole and bond dipole are in the same direction whereas in NF_3 these are in opposite directions

(c) In NH_3, as well as NF_3 the atomic dipole and bond dipole are in opposite directions

(d) In NH_3, the atomic dipole and bond dipole are in the opposite directions whereas, in NF_3 these are in the same directions

Sol. (b)

69. Identify the correct orders against the property mentioned

A. $H_2O > NH_3 > CHCl_3$ – dipole moment

B. $XeF_4 > XeO_3 > XeF_2$ – number of lone pairs on central atom

C. $O-H > C-H > N-O$ – bond length

D. $N_2 > O_2 > H_2$ – bond enthalpy

Choose the correct answer from the options given below: [NEET 2025]

(a) A, D only (b) B, D only (c) A, C only (d) B, C only

Sol. (a)

70. H_2O is dipolar, whereas BeF_2 is not. It is because [2004]

(a) H_2O involves hydrogen bonding whereas BeF_2 is a discrete molecule

(b) H_2O is linear and BeF_2 is angular

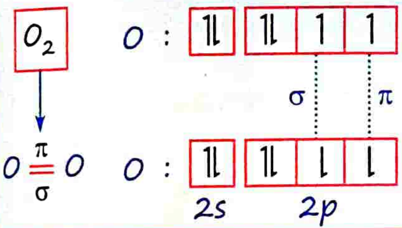
(c) H_2O is angular and BeF_2 is linear

(d) The electronegativity of F is greater than that of O

Sol. (c)

MOLECULAR ORBITAL THEORY

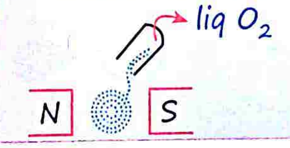
According to VBT



- ☐ All electrons are paired.
- ☐ O_2 is a diamagnetic molecule

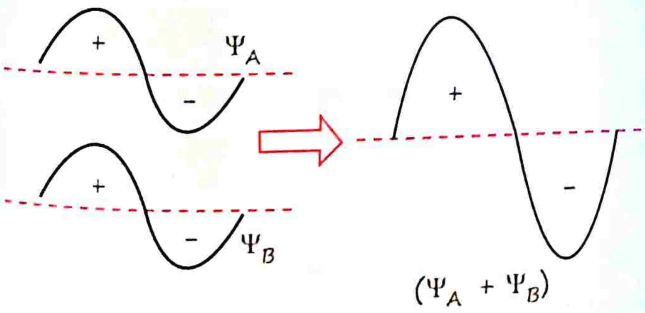
Need of new theory

- ☐ Experimental fact → (i) O_2 is a paramagnetic molecule
  (ii) O_2 has 2 unpaired electrons



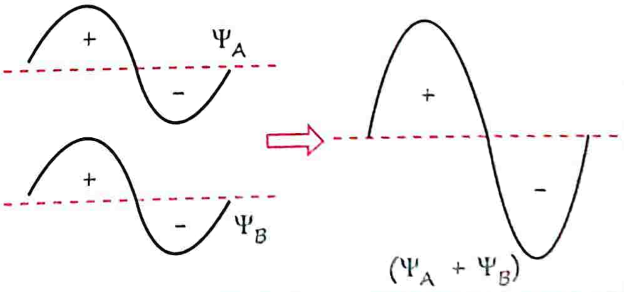
- ☐ Interaction between liq. O_2 and magnetic field.

Valence Bond Theory



Molecular Orbital Theory

☐



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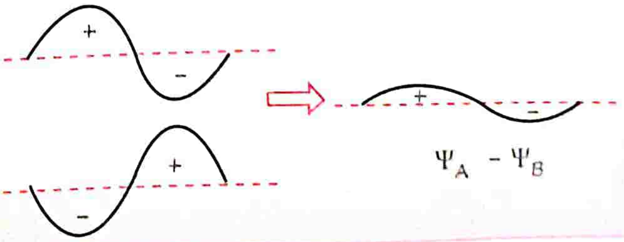
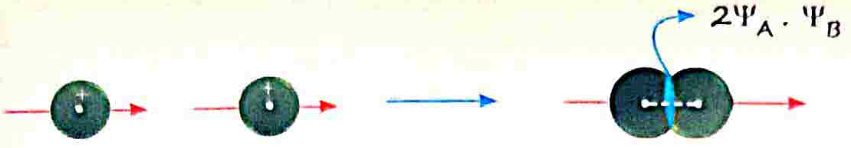


- ☐ VBT & MOT both are quantum mechanical theories of chemical bonding.

VBT



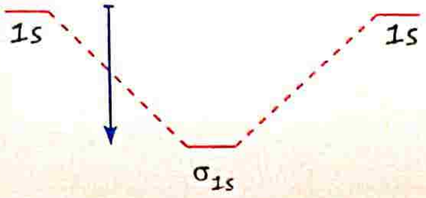
1s atomic orbital Ψ_A^2

1s atomic orbital Ψ_B^2

☐ σ Bonding molecular orbital

☐ σ_{BMO}

$$(\Psi_A + \Psi_B)^2$$
$$\Downarrow$$
$$\Psi^2_A + \Psi^2_B + \underbrace{2\Psi_A \cdot \Psi_B}_{\text{Overlap Integral}}$$



MOT

$\sigma_{1s} \equiv \sigma_{BMO}$

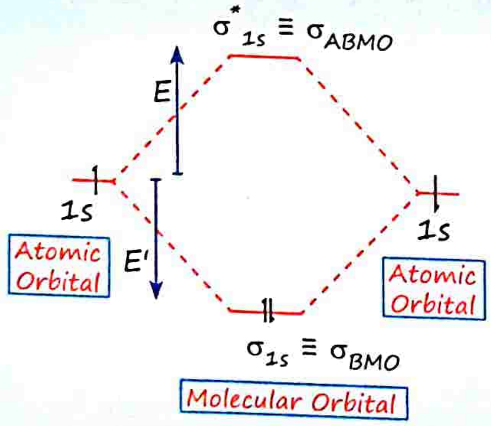
$$(\Psi_A + \Psi_B)^2 = \Psi^2_A + \Psi^2_B + 2\Psi_A \cdot \Psi_B$$

- Energy ↓ : Because electron density ↑ between the nucleus, so force of attraction ↑.

$\sigma^*_{1s} \equiv \sigma_{ABMO}$

$$(\Psi_A - \Psi_B)^2 = \Psi^2_A + \Psi^2_B - 2\Psi_A \cdot \Psi_B$$

- Energy ↑ : Because of no electron density between the nucleus, so force of repulsion ↑ between 2 nucleus

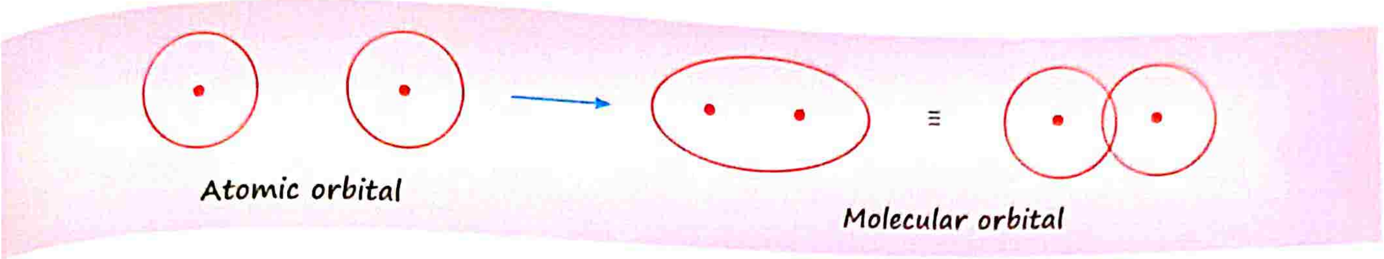


$\boxed{E > E'}$

Energy Order : $\sigma_{1s} < \sigma^*_{1s}$

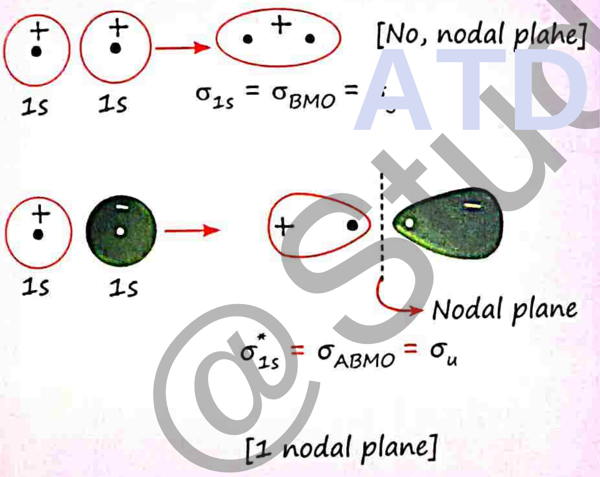
Bond Order = $\dfrac{N_b - N_{ab}}{2}$

$\left[\begin{array}{l} N_b = \text{no. of electrons in bonding molecular orbital} \\ N_{ab} = \text{no. of electrons in anti bonding molecular orbital} \end{array}\right]$



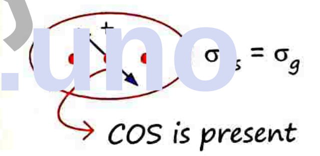
- ☐ An atomic orbital is **monocentric** while a molecular orbital is **polycentric**.
- ☐ Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.
- ☐ The molecular orbitals like the atomic orbitals are filled in accordance with the **Aufbau principle** obeying the **Pauli Exclusion principle** and the **Hund's Rule** of Maximum Multiplicity. But the filling order of these molecular orbitals is always experimentally decided.
- ☐ To construct such molecular orbitals we need to combine the atomic orbitals of the atoms that make up the molecule. This approach is known as the Linear Combination of Atomic Orbitals [LCAO].

➤ s-s overlapping

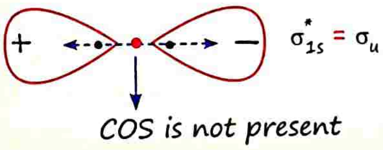


➤ Symmetry Term

- ☐ Gerade: Centre of symmetry is present

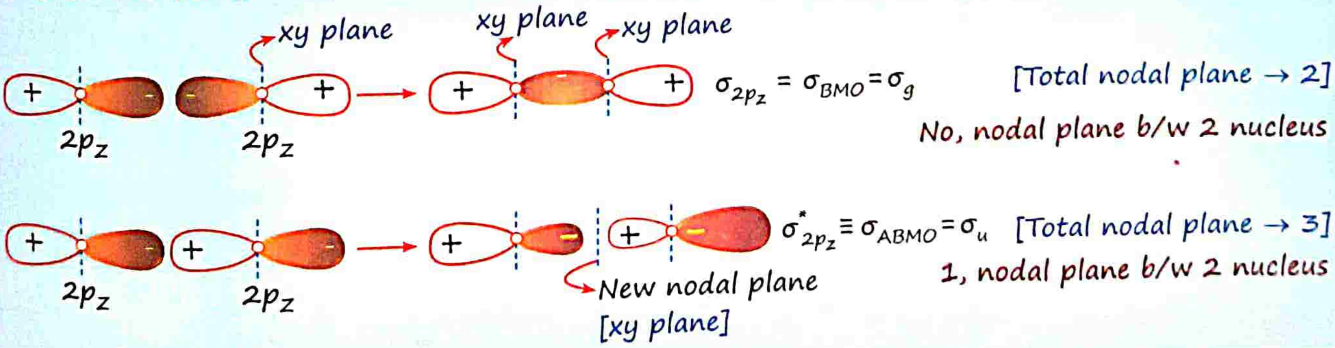


- ☐ Ungerade: COS is not present

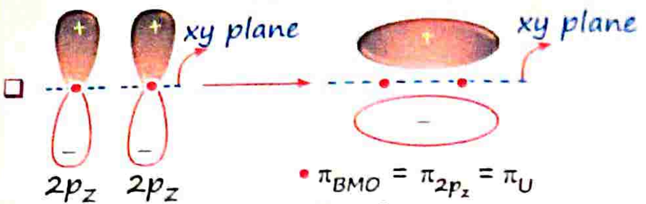


COS : A molecular orbital has a centre of symmetry when, for any molecular orbital in the molecule, an identical lobes (phase-wise, + or –) exists diametrically opposite to this centre at an equal distance.

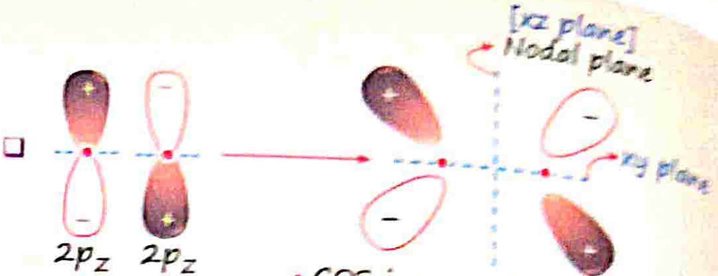
➤ p-p overlapping



➢ p-p overlapping

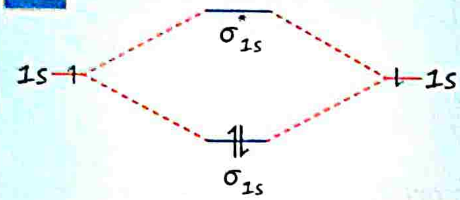
☐ 

- $\pi_{BMO} = \pi_{2p_z} = \pi_U$
- COS is not present
- 1 nodal plane [xy plane]

☐ 

- COS is present
- $\pi^*_{2p_z} = \pi_{ABMO} = \pi_g$
- 2 nodal plane [xy & xz plane]

H_2

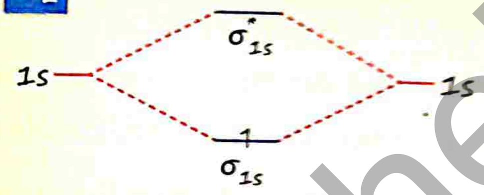


No. of e^- in molecule : 2

Electronic Configuration: σ^2_{1s}

$$\text{Bond Order} = \frac{N_b - N_{ab}}{2} = \frac{2-0}{2} = 1$$

H_2^+

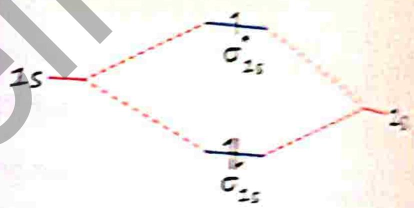


1

σ^1_{1s}

$$BO = \frac{1-0}{2} = 0.5$$

H_2^-



3

$\sigma^2_{1s}\ \sigma^{*1}_{1s}$

$$BO = \frac{2-1}{2} = 0.5$$

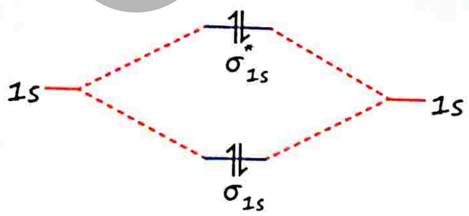
Bond Length: $H_2 < H_2^+ < H_2^-$

Magnetic Behaviour: Diamagnetic — Paramagnetic — Paramagnetic

Note

☐ If bond order is same → $N_{ab}\uparrow$: Bond Length ↑

He_2



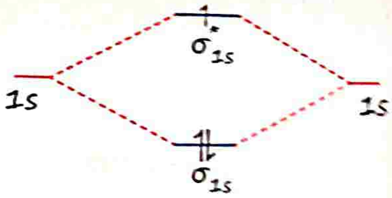
No. of e^- in a molecule → 4

Electronic configuration → $\sigma^2_{1s}\sigma^{*2}_{1s}$

$$\text{Bond Order} \rightarrow \frac{N_b - N_{ab}}{2} = \frac{2-2}{2} = 0$$

Existence → He_2 molecule does not exist because He atoms are not bonded to each other.

He_2^+



3

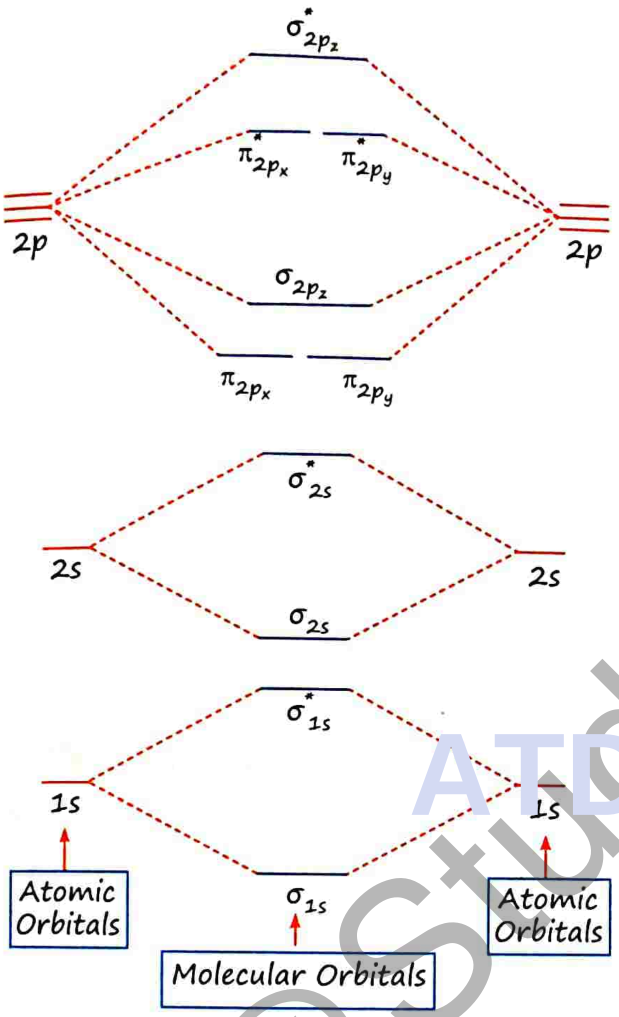
$\sigma^2_{1s}\ \sigma^{*1}_{1s}$

$$BO = \frac{2-1}{2} = 0.5$$

He_2^+ exists

Electronic Configuration

$n \le 14$ [$n \rightarrow$ no. of electrons in molecules, ions]



Energy Increases $\longrightarrow$

- Energy Order: $\sigma_{1s}\ \sigma^*_{1s}\ \sigma_{2s}\ \sigma^*_{2s} \left[\begin{matrix}\pi_{2p_x}\\ \pi_{2p_y}\end{matrix}\right. \sigma_{2p_z} \left[\begin{matrix}\pi^*_{2p_x}\\ \pi^*_{2p_y}\end{matrix}\right. \sigma^*_{2p_z}$
- Due to s-p mixing energy order: $\pi_{2p} < \sigma_{2p}$

$\boxed{B_2} \rightarrow \sigma^2_{1s}\ \sigma^{*2}_{1s}\ \sigma^2_{2s}\ \sigma^{*2}_{2s} \left[\begin{matrix}\pi^1_{2p}\\ \pi^1_{2p}\end{matrix}\right.$

(i) $n \equiv 10$

(ii) $BO \equiv \dfrac{N_b - N_a}{2} = \dfrac{6-4}{2} = 1$

(iii) 2 unpaired e^- ≡ paramagnetic behaviour

$\boxed{C_2} \rightarrow \sigma^2_{1s}\ \sigma^{*2}_{1s}\ \sigma^2_{2s}\ \sigma^{*2}_{2s} \left[\begin{matrix}\pi^2_{2p}\\ \pi^2_{2p}\end{matrix}\right.$

(i) $n \equiv 12$

(ii) $BO \equiv 2$

(iii) Diamagnetic

☐ 4 electrons are present in π_{BMO} which indicates the presence of two π bonds between carbon atoms with no σ bond.

$\boxed{N_2} \rightarrow \sigma^2_{1s}\ \sigma^{*2}_{1s}\ \sigma^2_{2s}\ \sigma^{*2}_{2s} \left[\begin{matrix}\pi^2_{2p}\\ \pi^2_{2p}\end{matrix}\right. \sigma^2_{2p}$

(i) $n \equiv 14$

(ii) $BO \equiv 3$

(iii) Diamagnetic

(iv) HOMO ⟶ Highest occupied MO ⟶ σ_{2p}

(v) LUMO ⟶ Lowest unoccupied MO ⟶ π^*_{2p}

	N_2	N_2^+	N_2^-
N_b	10	9	10
N_{ab}	4	4	5
Bond Order	3	2.5	2.5
Bond Length	$N_2 <$	N_2^+	$< N_2^-$
Bond Strength	$N_2 >$	N_2^+	$> N_2^-$
Bond Dissociation Energy	$N_2 >$	N_2^+	$> N_2^-$
Magnetic Behaviour	Dia	Para	Para
Unpaired e^- is present in	–	σ_{2p}	π^*_{2p}

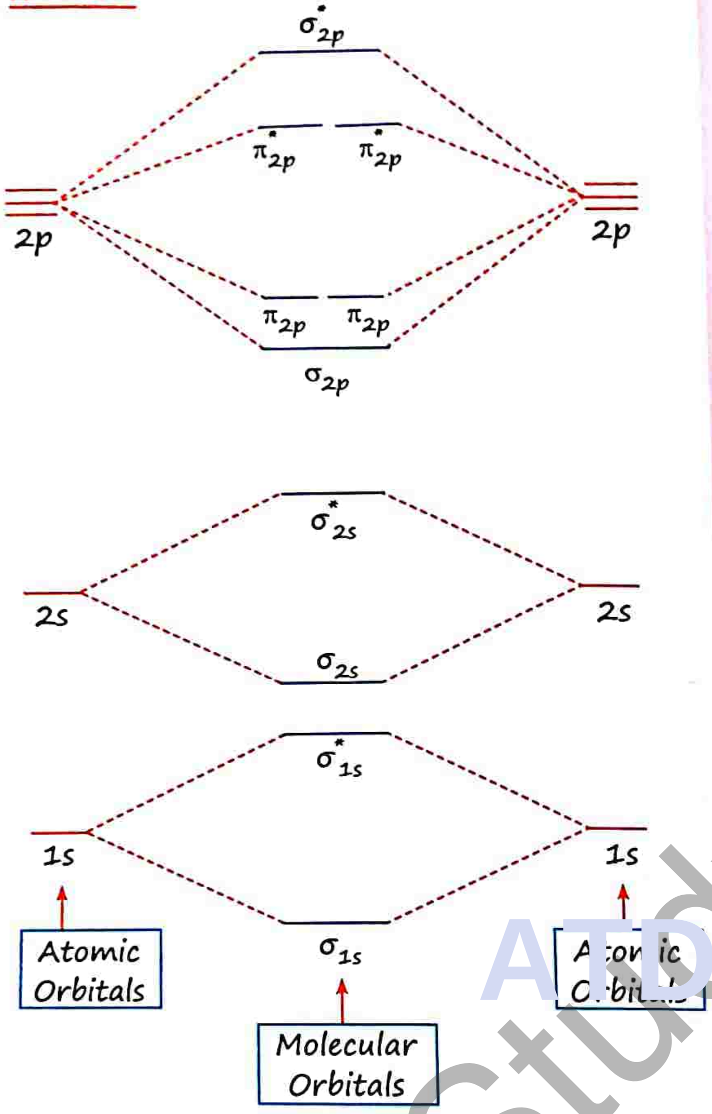
$\boxed{N_2} \xrightarrow[\text{from } \sigma_{2p}]{\text{Remove 1 } e^-} \boxed{N_2^+}$ Energy Order ⟶ $\sigma^2_{1s}\ \sigma^{*2}_{1s}\ \sigma^2_{2s}\ \sigma^{*2}_{2s} \left[\begin{matrix}\pi^2_{2p}\\ \pi^2_{2p}\end{matrix}\right. \sigma^1_{2p}$

☐ We can remove an electron from σ_{2p} molecular orbital of N_2 by applying ionisation energy of N_2 molecule.

$\boxed{N_2} \xrightarrow{\text{Add 1 } e^- \text{ in } \pi^*_{2p}} \boxed{N_2^-}$

Energy Order: $\sigma^2_{1s}\ \sigma^{*2}_{1s}\ \sigma^2_{2s}\ \sigma^{*2}_{2s} \left[\begin{matrix}\pi^2_{2p}\\ \pi^2_{2p}\end{matrix}\right. \sigma^2_{2p} \left[\begin{matrix}\pi^{*1}_{2p}\\ \pi^{*0}_{2p}\end{matrix}\right.$

$n > 14$



Energy Increases →

- **Energy Order:** $\sigma_{1s}\ \sigma^*_{1s}\ \sigma_{2s}\ \sigma^*_{2s}\sigma_{2p_z} \left[\begin{matrix}\pi_{2p_x}\\ \pi_{2p_y}\end{matrix}\right. \left[\begin{matrix}\pi^*_{2p_x}\\ \pi^*_{2p_y}\end{matrix}\right. \sigma^*_{2p_z}$
- **No, s-p mixing** ⟶ Energy: $\sigma_{2p} < \pi_{2p}$

F_2 ⟶ $\sigma^2_{1s}\ \sigma^{*2}_{1s}\ \sigma^2_{2s}\ \sigma^{*2}_{2s}\ \sigma^2_{2p} \left[\begin{matrix}\pi^2_{2p}\\ \pi^2_{2p}\end{matrix}\right. \left[\begin{matrix}\pi^{*2}_{2p}\\ \pi^{*2}_{2p}\end{matrix}\right.$

(i) $n \equiv 18$

(ii) $BO \equiv \frac{10-8}{2} = 1$

(iii) HOMO ⟶ Highest occupied MO ⟶ π^*_{2p}

(iv) LUMO ⟶ Lowest unoccupied MO ⟶ σ^*_{2p}

(v) Colour ⟶ Pale yellow [HOMO to LUMO electronic transition is the reason behind colour]

(vi) Magnetic Behaviour : Diamagnetic

☐ F_2, Cl_2, Br_2 and I_2, all 4 are diamagnetic in nature and are colored (due to transition of electron from HOMO to LUMO ≡ π^* to σ^*).

	O_2^{2+}	O_2^+	O_2	O_2^-	O_2^{2-}
N_b	10	10	10	10	10
N_{ab}	4	5	6	7	8
Bond order	3	2.5	2	1.5	1
Bond length	O_2^{2+} <	O_2^+ <	O_2 <	O_2^- <	O_2^{2-}
Bond strength	O_2^{2+} >	O_2^+ >	O_2 >	O_2^- >	O_2^{2-}
Bond energy	O_2^{2+} >	O_2^+ >	O_2 >	O_2^- >	O_2^{2-}
Magnetic Behaviour	Dia	Para	Para	Para	Dia
No. of Unpaired e^-	0	1	2	1	0

$$O_2^{2+} \xleftarrow{-e^-} O_2^+ \xleftarrow{-e^-} O_2 \xrightarrow{+e^-} O_2^- \xrightarrow{+e^-} O_2^{2-}$$

Electronic Configuration of O_2

$\sigma^2_{1s}\ \sigma^{*2}_{1s}\ \sigma^2_{2s}\ \sigma^{*2}_{2s}\ \sigma^2_{2p} \left[\begin{matrix}\pi^2_{2p}\\ \pi^2_{2p}\end{matrix}\right. \left[\begin{matrix}\pi^{*1}_{2p}\\ \pi^{*1}_{2p}\end{matrix}\right.$

(i) $n = 16$

(ii) Bond order = 2

(iii) 2 unpaired electrons are present in π^*_{2p} → O_2 is paramagnetic in nature

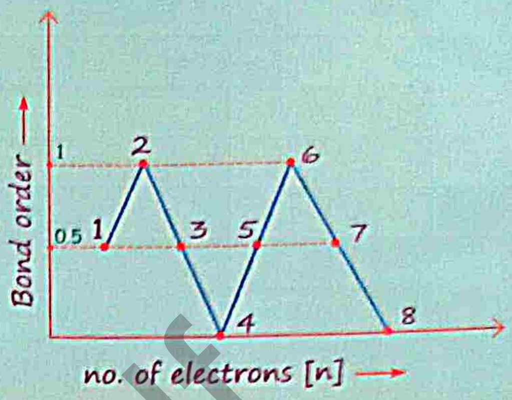
☐ We can remove an electron from π^*_{2p} molecular orbital of O_2 by applying 1st ionisation energy of O_2 molecule.

$$O_2 \xrightarrow{IE_1} O_2^+$$

☐ S_2 molecule is also paramagnetic with 2 unpaired electrons as O_2 molecule.

Note

n	Bond Order	n
14	3	
13	2.5	15
12	2	16
11	1.5	17
10	1	18
9	0.5	19
8	0	20

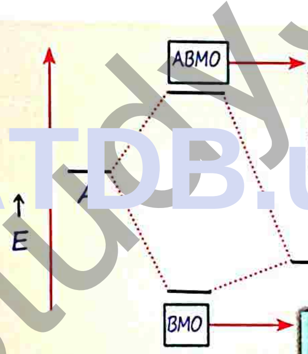


MOT for Heteronuclear Diatomic

AB Type Molecule [CO, NO, CN^-, NO^+]

☐ Electronegativity: A < B

☐ Energy of same orbital: A > B



It has more contribution from atomic orbital of A atom because energywise it is close to A with respect to B.

It has more contribution from atomic orbital of B atom because energywise it is close to B with respect to A.

Isoelectronic Species

N_2	CO	NO^+	CN^-
$(7+7=14e^-)$	$(6+8=14e^-)$	$(7+8-1=14e^-)$	$(6+7+1=14e^-)$

→ Bond order = 3

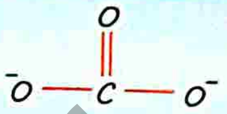
N_2^-	NO
$(14+1=15e^-)$	$(7+8=15e^-)$

→ Bond order = 2.5

Box-1a	BaO_2	O_2	NaO_2
	$Ba^{2+}\ O_2^{2-}$ $(18e^-)$	$(16e^-)$	$Na^+\ O_2^-$ $(17e^-)$
Bond Order →	1	2	1.5
Bond Length [O – O] →	O_2^{2-} >	O_2^- >	O_2

Box-1b	O_2	O_3	$O_2[PtF_6] \rightarrow O_2^+[PtF_6]^-$
	$(16e^-)$		O_2^+ $(15e^-)$
Bond Order →	2	$BO = \frac{\sigma + \pi}{\sigma} = \frac{2+1}{2} = 1.5$	2.5
Bond Length →	O_3 >	O_2 >	O_2^+

Box-2 $KO_2\ [K^+O_2^-]$	O_2	$O_2[BF_4] \rightarrow O_2^+[BF_4]^-$
No. of e^- in oxygen containing species $\rightarrow O_2^-\ (16+1)$	16	$O_2^+\ (16-1)$
Bond Order → 1.5	2	2.5
Bond Length $\rightarrow O_2^+ < O_2 < O_2^-$ [O – O]		

Box-3 Bond Order → $CO\ (6+8 = 14)$ 3	CO_2 2	CO_3^{2-} 1.33  $BO = \frac{\sigma + \pi}{\sigma} = \frac{3+1}{3} = 1.33$
C—O Bond Length $\rightarrow CO < CO_2 < CO_3^{2-}$		

Box-4

☐ **Bond Length:** NO > NO^+

Bond order = 2.5   Bond order = 3

$CO > CO^+$: Bond length

71. Assuming 2s-2p mixing is not operative, the paramagnetic species among the following is (JEE Adv. 2014)
(a) Be_2 (b) B_2 (c) C_2 (d) N_2

Sol. (c) Assuming that no 2s – 2p mixing takes place the MO electronic configuration can be written as

(a) $Be_2 \rightarrow \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2$ (diamagnetic)

(b) $B_2 \rightarrow \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_z^2,$ (diamagnetic)

(c) $C_2 \rightarrow \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_z^2, \pi 2p_x^1, \pi 2p_y^1$ (paramagnetic)

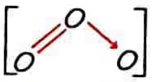
(d) $N_2 \rightarrow \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_z^2, \pi 2p_x^2, \pi 2p_y^2$ (diamagnetic)

72. The species having bond order different from that in CO is- (IIT JEE 2007)
(a) NO^- (b) NO^+ (c) CN^- (d) N_2

Sol. (a)

73. Among the following, the paramagnetic compound is (IIT JEE 2007)
(a) Na_2O_2 (b) O_3 (c) N_2O (d) KO_2

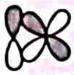
Sol. (d) a → $2Na^+$ [10 e^- : all paired], O_2^{2-} [18 e^- : all paired],

b → O_3 
All electrons are paired

c → N_2O $[N \equiv N \rightarrow O]$
All electrons are paired

d → K^+ [18 e^- : all paired], O_2^- [17 e^- : 1 unpaired]

74. Match the orbital overlap figures shown in Column-I with the description given in Column-II and select the correct answer using the codes given below the Columns. (JEE Adv. 2014)

Column-I		Column-II	
A.		1.	p–d π antibonding
B.		2.	d–d σ bonding
C.		3.	p–d π bonding
D.		4.	d–d σ antibonding

Codes:

	A	B	C	D
(a)	4	3	2	1
(b)	1	2	3	4
(c)	2	3	1	4
(d)	4	1	2	3

Sol. (c)

75. For diatomic molecules, the correct statement(s) about the molecular orbitals formed by the overlap of two $2p_z$ orbitals is(are) (JEE Adv 2022)

(a) σ orbital has a total of two nodal planes.

(b) σ* orbital has one node in the xz-plane containing the molecular axis.

(c) π orbital has one node in the plane which is perpendicular to the molecular axis and goes through the center of the molecule.

(d) π* orbital has one node in the xy-plane containing the molecular axis.

Sol. (a, d)

76. According to molecular orbital theory, which of the following statements is(are) correct? (JEE Adv. 2016)

(a) C_2^{2-} is expected to be diamagnetic

(b) O_2^{2+} is expected to have a longer bond length than O_2

(c) N_2^+ and N_2^- have the same bond order

(d) He_2^+ has the same energy as two isolated He atoms

Sol. (a, c)

77. Among H_2, He_2^+, Li_2, Be_2, B_2, C_2, N_2, O_2^- and F_2, the number of diamagnetic species is (Atomic numbers : H = 1, He = 2, Li = 3, Be = 4, B = 5, C = 6, N = 7, O = 8, F = 9) (JEE Adv. 2017)

Sol. [6] (H_2, Li_2, Be_2, C_2, N_2, F_2) are diamagnetic.

78. During the change of O_2 to O_2^-, the incoming electron goes to the orbital: [10 April, 2019 (Shift-I)]

(a) σ^*2p_z (b) $\pi 2p_y$ (c) π^*2p_x (d) $\pi 2p_x$

Sol. (c)

79. In which of the following processes, the bond order has increased and paramagnetic character has changed to diamagnetic? [9 Jan, 2019 (Shift-II)]

(a) $NO \rightarrow NO^+$ (b) $N_2 \rightarrow N_2^+$ (c) $O_2 \rightarrow O_2^+$ (d) $O_2 \rightarrow O_2^{2-}$

Sol. (a)

☐ $NO \longrightarrow NO^+$
B.O-2.5 3
Para Dia

☐ $N_2 \longrightarrow N_2^+$
B.O-3 2.5
Dia Para

☐ $O_2 \longrightarrow O_2^+$
B.O-2 2.5
Para Para

☐ $O_2 \longrightarrow O_2^{2-}$
B.O-2 1
Para Dia

80. AX is a covalent diatomic molecule where A and X are second row elements of periodic table. Based on molecular orbital theory, the bond order of AX is 2.5. The total number of electrons in AX is _________. (Round off to the nearest integer). [18 March, 2021 (Shift-I)]

Sol. [15] Given: AX ⇒ Diatomic molecule

Bond order is 2.5

According to the given data, the compound is NO.

Total number of electrons in it = 15

($\because$ Number of electrons in N = 7, Number of electron in O = 8)

81. Amongst the following, the number of oxide(s) which are paramagnetic in nature is

$Na_2O, KO_2, NO_2, N_2O, ClO_2, NO, SO_2, Cl_2O$ (Nearest Integer) [27 July, 2022 (Shift-I)]

Sol. [4] Paramagnetic species = KO_2, NO_2, ClO_2, NO

82. Match List-I with List-II. [27 July, 2022 (Shift-II)]

	List-I		List-II
A.	$\psi_{MO} = \psi_A - \psi_B$	I.	Dipole moment
B.	$\mu = Q \times r$	II.	Bonding molecular orbital
C.	$\frac{N_b - N_a}{2}$	III.	Anti-bonding molecular orbital
D.	$\psi_{MO} = \psi_A + \psi_B$	IV.	Bond order

Choose the correct answer from the options given below

(a) (A)-(II), (B)-(I), (C)-(IV), (D)-(III) (b) (A)-(III), (B)-(IV), (C)-(I), (D)-(II)

(c) (A)-(III), (B)-(I), (C)-(IV), (D)-(II) (d) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)

Sol. (c)

83. The linear combination of atomic orbitals to form molecular orbitals takes place only when the combining atomic orbitals

A. have the same energy

B. have the minimum overlap

C. have same symmetry about the molecular axis

D. have different symmetry about the molecular axis

Choose the most appropriate from the options given below: [31 Jan, 2024 (Shift-I)]

(a) A, B, C only (b) A and C only (c) B, C, D only (d) B and D only

Sol. (b)

84. Bonding in which of the following diatomic molecule(s) become(s) stronger, on the basis of MO Theory, by removal of an electron? [25 June, 2022 (Shift-I)]

(A) NO (B) N_2 (C) O_2 (D) C_2 (E) B_2

Choose the most appropriate answer from the options given below:

(a) (A), (B), (C) only
(b) (B), (C), (E) only
(c) (A), (C) only
(d) (D) only

Sol. (c)

85. Given below are two statements:

Statement-I: A π bonding MO has lower electron density above and below the inter-nuclear axis.

Statement-II: The π* antibonding MO has a node between the nuclei.

In the light of the above statements, choose the most appropriate answer from the options given below: [01 Feb, 2024 (Shift-II)]

(a) Both Statement-I and Statement-II are false
(b) Both Statement-I and Statement-II are true
(c) Statement-I is false but Statement-II is true
(d) Statement-I is true but Statement-II is false

Sol. (c) A pi bonding molecular orbital exhibits higher electron density both above and below the internuclear axis.

86. Given below are two statements: [NEET 2025]

Statement-I: A hypothetical diatomic molecule with bond order zero is quite stable.

Statement-II: As bond order increases, the bond length increases.

In the light of the above statements, choose the most appropriate answer from the options given below:

(a) Both Statement-I and Statement-II are true
(b) Both Statement-I and Statement-II are false
(c) Statement-I is true but Statement-II is false
(d) Statement-I is false but Statement-II is true

Sol. (b)

87. The correct order of energies of molecular orbitals of N_2 molecule is: [NEET 2023]

(a) $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma 2p_z < \sigma^* 2p_z$

(b) $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

(c) $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

(d) $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \sigma^* 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y)$

Sol. (b)

88. Which one of the following statements is incorrect related to Molecular Orbital Theory? [NEET 2023-Manipur]

(a) The π* antibonding molecular orbital has a node between the nuclei.
(b) In the formation of bonding molecular orbital, the two election waves of the bonding atoms reinforce each other.
(c) Molecular orbitals obtained from $2P_x$ and $2P_y$ orbitals are symmetrical around the bond axis.
(d) A π-bonding molecular orbital has larger electron density above and below the internuclear axis.

Sol. (c)

89. Which amongst the following is incorrect statement? [NEET 2022]

(a) O_2^+ ion is diamagnetic.

(b) The bond orders of O_2^+, O_2, O_2^- and O_2^{2-} are 2.5, 2, 1.5 and 1, respectively

(c) C_2 molecule has four electrons in its two degenerate π molecular orbitals.

(d) H_2^+ ion has one electron.

Sol. (a)

90. Identify a molecule which does not exist. [NEET 2020]

(a) Li_2 (b) C_2 (c) O_2 (d) He_2

Sol. (d)

91. Which of the following diatomic molecular species has only π bonds according to Molecular Orbital Theory? [NEET 2019]

(a) O_2 (b) N_2 (c) C_2 (d) Be_2

Sol. (c)

92. Consider the following species: [NEET 2018]

CN^+, CN^-, NO and CN

Which one of these will have the highest bond order?

(a) NO (b) CN^- (c) CN (d) CN^+

Sol. (b)

93. The correct bond order in the following species is: [NEET 2015]

(a) $O_2^{2+} < O_2^- < O_2^+$ (b) $O_2^{2+} < O_2^+ < O_2^+$ (c) $O_2^- < O_2^+ < O_2^{2+}$ (d) $O_2^{2+} < O_2^+ < O_2^-$

Sol. (c)

94. Which of the following is paramagnetic? [NEET 2013]

(a) CO (b) O_2^- (c) CN^- (d) NO^+

Sol. (b)

95. Four diatomic species are listed below. Identify the correct order in which the bond order is increasing in them: [NEET 2012 Mains]

(a) $He_2^+ < O_2^- < NO < C_2^{2-}$ (b) $NO < O_2^- < C_2^{2-} < He_2^+$

(c) $O_2^- < NO < C_2^{2-} < He_2^+$ (d) $C_2^{2-} < He_2^+ < O_2^- < NO$

Sol. (a)

96. During change of O_2 to O_2^- ion, the electron adds on which one of the following orbitals? [NEET 2012 Mains]

(a) π* orbital (b) π orbital (c) σ* orbital (d) σ orbital

Sol. (a)

97. Main axis of a diatomic molecule is z, molecular orbital p_x and p_y overlaps to form, which of the following orbital? [NEET 2001]

(a) π molecular orbital (b) σ molecular orbital

(c) δ molecular orbital (d) No bond will form

Sol. (a)

98. The number of anti-bonding electrons pairs in O_2^{2-} molecular ion on the basis of molecular orbital theory is (atomic no. of O is 8): [NEET 1998]

(a) 3 (b) 2 (c) 5 (d) 4

Sol. (d)

99. N_2 and O_2 are converted into monocations, N_2^+ and O_2^+ respectively. Which is wrong? [NEET 1997]

(a) In O_2^+, paramagnetism decreases. (b) N_2^+ becomes diamagnetic.
(c) In N_2^+, the N–N bond weakens. (d) In O_2^+, the O–O bond order increases.

Sol. (b)

100. The correct order of C–O bond length among: CO, CO_3^{2-}, CO_2 is: [NEET 2007]

(a) $CO < CO_3^{2-} < CO_2$ (b) $CO_3^{2-} < CO_2 < CO$
(c) $CO < CO_2 < CO_3^{2-}$ (d) $CO_2 < CO_3^{2-} < CO$

Sol. (c)

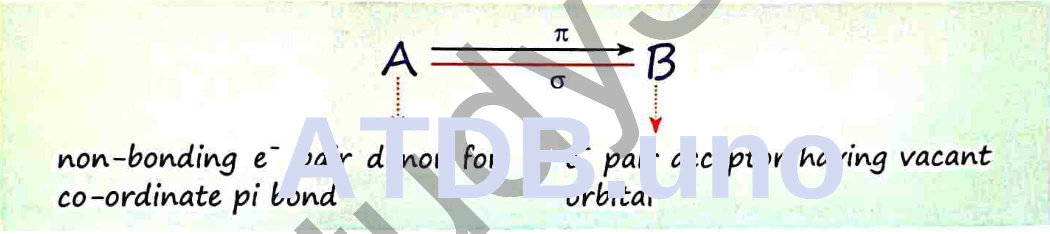
101. The correct order in which the O—O bond length increases in the following is: [NEET 2005]

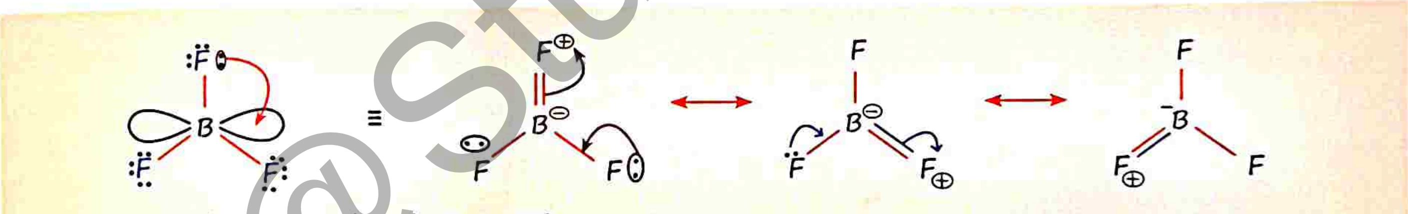
(a) $H_2O_2 < O_2 < O_3$ (b) $O_3 < H_2O_2 < O_2$ (c) $O_2 < O_3 < H_2O_2$ (d) $O_2 < H_2O_2 < O_3$

Sol. (c)

BACK BONDING

- ☐ Coordinate pi bond

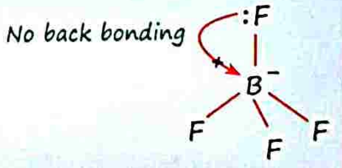




Back bond → π bond (Pπ − Pπ)

- ☐ Back bonding increases the bond strength and decreases the bond length.

B—F Bond length: $BF_3 < BF_4^-$



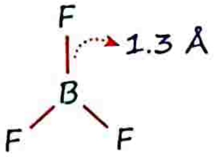
Condition for Excellent Back Bonding

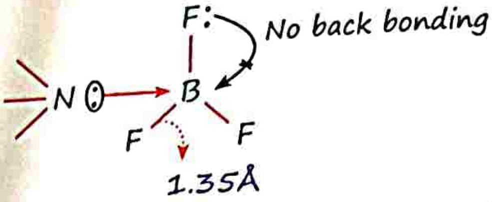
1. One atom from 2nd period
2. Second atom from 2nd/3rd period

π bond strength [back bond strength] : 2p – 2p > 2p – 3d > 2p – 3p > 3p – 3p

102. The B – F bond length in $Me_3N.BF_3$ is 1.35 Å, much longer than 1.30 Å in BF_3. Explain?

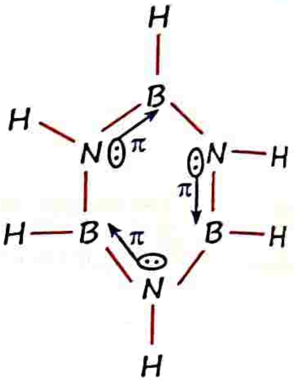
Sol.



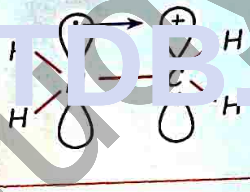
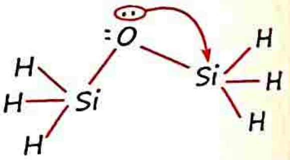
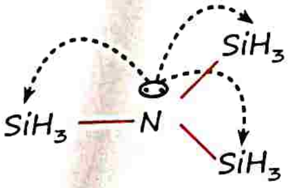
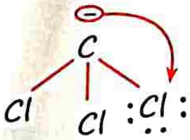
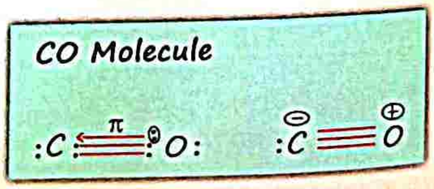


- back bonding from F to B → small B – F bond
- No back bonding → large B – F bond

Inorganic Benzene ($B_3N_3H_6$)



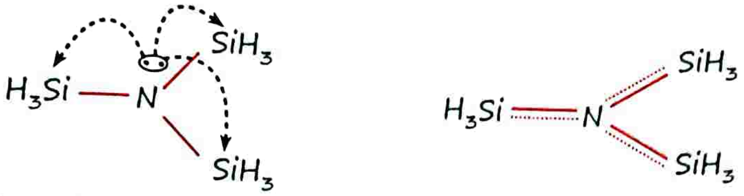
☐ Back bonding from N to B.
☐ 3π bonds [6π electrons]
☐ All nitrogen and boron are sp^2 hybridised.
☐ Molecule is planar.
☐ It is an aromatic compound and isoelectronic as benzene [C_6H_6].

(1)	$\overset{\ominus}{N}H_2—\overset{+}{C}H_2$ (2p – 2p : pπ – pπ bond) 	(2)	$:\ddot{C}l—\overset{\ominus}{C}H_2$ (3d – 2p : dπ – pπ bond)
(3)	$SiH_3—\overset{\ominus}{O}$ (3d – 2p : dπ – pπ bond)	(4)	$O(SiH_3)_2$  (dπ – pπ back bonding)
(5)	 (pπ – dπ back bonding)	(6)	$SiH_3—\ddot{N}=C=O$ (dπ – pπ back bonding)
(7)	 (pπ – dπ back bonding)	(8)	**CO Molecule** 

(JEE Adv. 2005)

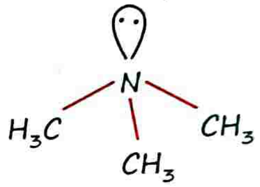
103. Trisilylamine is a planar molecule and does not act as a Lewis base while trimethylamine is pyramidal and act as Lewis base!

Sol. $N(SiH_3)$ → Trisilylamine



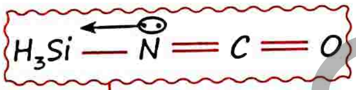
- Back bonding from N to Si
- Lone pair on nitrogen is delocalised as it is participating in back bonding with Si, so does not act as lewis base.
- Steric no = LP + SA = 0 + 3 = 3
- sp^2 hybridisation (planar molecule)

$N(CH_3)_3$ → Trimethylamine

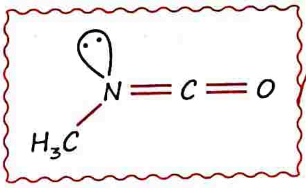


- No back bonding
- Lone pair is localised on nitrogen, so act as lewis base
- Steric No = LP + SA = 1 + 3 = 4
- sp^3 hybridisation (pyramidal shape)

104. Silyl isocyanate (SiH_3NCO) is linear but methyl isocyanate (CH_3NCO) is bent explain!

Sol. 

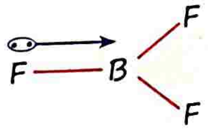
- Steric number of N : LP + SA = $\underset{\underset{LP}{\downarrow}}{\underline{0}} + \underset{\underset{SA}{\downarrow}}{\underline{2}} = 2$
- sp hyb^n : Linear
- Back bonding from N to Si

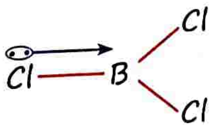


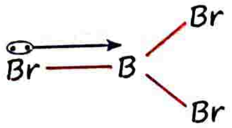
- No back bonding
- SN ≡ 1 + 2 ≡ 3
- sp^2 hyb^n
- Bent shape

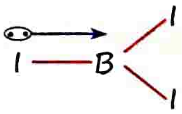
Lewis Acidic Character

$BF_3 < BCl_3 < BBr_3 < BI_3$: Lewis Acidity [Lone pair accepting tendency]









Extent of overlapping: 2p – 2p > 3p – 2p > 4p – 2p > 5p – 2p

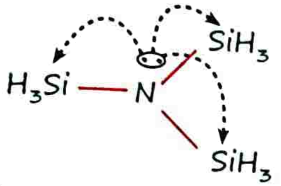
(Back Bonding)

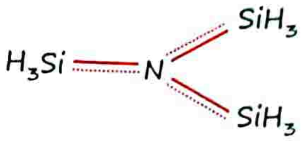
Lewis acidity: BF_3 < BCl_3 < BBr_3 < BI_3

(JEE Adv. 2005)

103. Trisilylamine is a planar molecule and does not act as a Lewis base while trimethylamine is pyramidal and act as Lewis base!

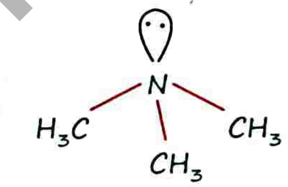
Sol. $N(SiH_3)$ → Trisilylamine





- ◆ Back bonding from N to Si
- ◆ Lone pair on nitrogen is delocalised as it is participating in back bonding with Si, so does not act as lewis base.
- ◆ Steric no = LP + SA = 0 + 3 = 3
- ◆ sp^2 hybridisation (planar molecule)

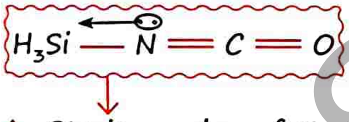
$N(CH_3)_3$ → Trimethylamine



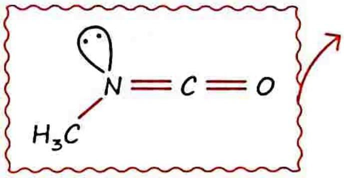
- ◆ No back bonding
- ◆ Lone pair is localised on nitrogen, so act as lewis base
- ◆ Steric No = LP + SA = 1 + 3 = 4
- ◆ sp^3 hybridisation (pyramidal shape)

104. Silyl isocyanate (SiH_3NCO) is linear but methyl isocyanate (CH_3NCO) is bent explain!

Sol.



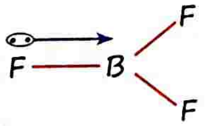
- ◆ Steric number of N : LP + SA = $\underset{\text{LP}}{0} + \underset{\text{SA}}{2} = 2$
- ◆ sp hyb^n : Linear
- ◆ Back bonding from N to Si

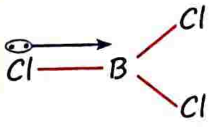


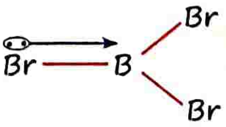
- ◆ No back bonding
- ◆ SN ≡ 1 + 2 ≡ 3
- ◆ sp^2 hyb^n
- ◆ Bent shape

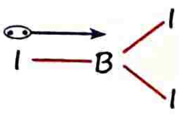
Lewis Acidic Character

$BF_3 < BCl_3 < BBr_3 < BI_3$: Lewis Acidity [Lone pair accepting tendency]







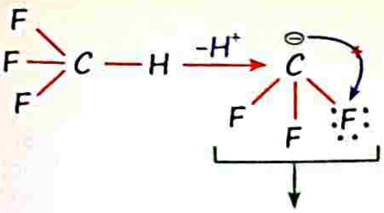


Extent of overlapping: 2p – 2p > 3p – 2p > 4p – 2p > 5p – 2p
(Back Bonding)

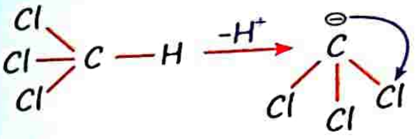
Lewis acidity: BF_3 < BCl_3 < BBr_3 < BI_3

Acidic Nature

Fluoroform CHF_3 < Chloroform $CHCl_3$

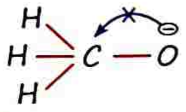


- No back bonding
- Carbanion is stabilised by -I effect of F.



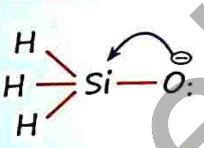
- Conjugate base is stable due to back bonding

Methanol CH_3OH < Silanol $SiH_3—OH$



- No back bonding

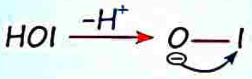
<

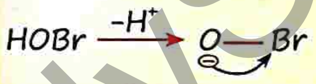


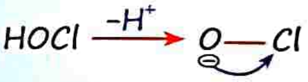
Stability of conjugate base

- Stable due to back bonding

HOI < HOBr < HOCl







$\bar{O}—I$ < $\bar{O}—Br$ < $\bar{O}—Cl$: Stability of conjugate base

(IIT JEE. 1996)

105. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order.

ClOH (I), BrOH (II), IOH (III)

(a) I > II > III (b) II > I > III (c) III > II > I (d) I > III > II

Sol. (a)

DIMER FORMATION

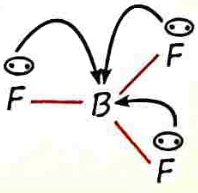
mer ≡ Unit,

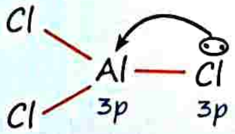
mono-mer ≡ Single Unit

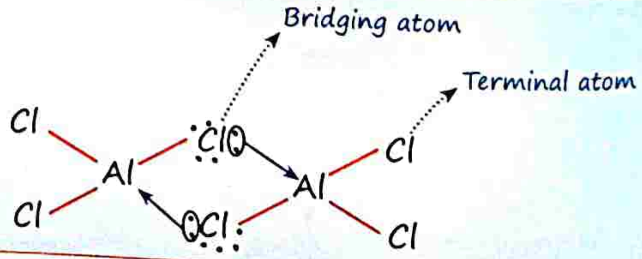
Dimer ≡ Combination of 2 unit

Poly-mer ≡ Combination of more than 2 unit

BF_3 vs $AlCl_3$

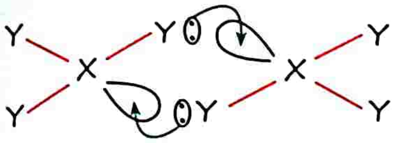
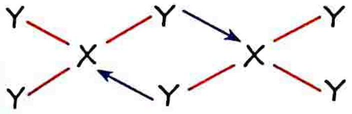
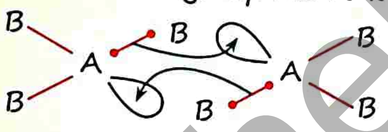
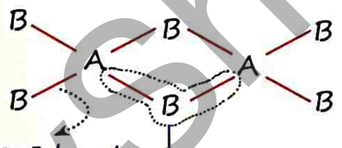




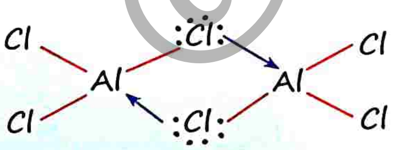
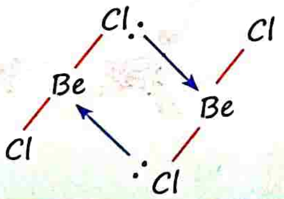


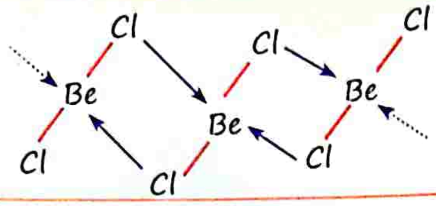
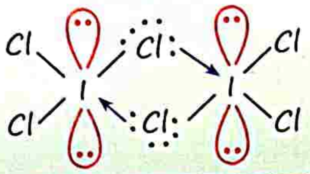
❑ monomer is stable due to excellent back bonding [2p - 2p]	❑ Monomer is not stable because back bonding from Cl to Al [3p - 3p] is not so good ❑ Dimer formation takes place through bridge bonding to attain stability ❑ $[AlCl_3]_2 \equiv Al_2Cl_6$

BRIDGE BONDING

Type-1	Type-2
❑ Side atom has lone pair (Br, Cl)   ❑ All bonds have $2e^-$ in it [2 centre - $2e^-$ bond]	❑ Side atom or group has no lone pair ($-H$, $-CH_3$, $-C_6H_5$)   2C - $2e^-$ bond → Banana bond → 3C - $2e^-$ bond → Electron deficient bond

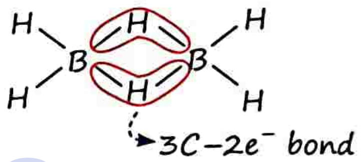
Type-1

Type-1	Hybridisation	Max. No. of atom in same plane
$\boxed{Al_2Cl_6}$  	Al − Cl → Al $sp^3 - sp^3 - sp^3$	6 [2Al , 4Cl] ↓ Terminal
$\boxed{BeCl_2 \text{ at high temperature}} \rightarrow$ Monomer Cl − Be − Cl	Be → sp (Linear)	3
$\boxed{BeCl_2 \text{ in vapour phase}} \rightarrow$ Dimer  	❑ Be → sp^2 (planar) ❑ Be − Cl → Be $sp^2 - sp^3 - sp^2$	6

BeCl$_2$ in solid phase → Polymer 	☐ Be → sp^3 (Tetrahedral) ☐ Be − Cl → Be $sp^3 - sp^3 - sp^3$	−
I$_2$Cl$_6$ in solid phase → Planar molecule 	☐ I − Cl − I $sp^3d^2 - sp^3 - sp^3d^2$	8 [2I and 6Cl]

Type-2

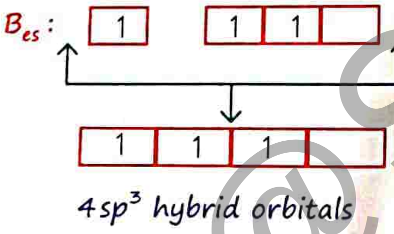
Diborane: $[BH_3]_2 = B_2H_6$

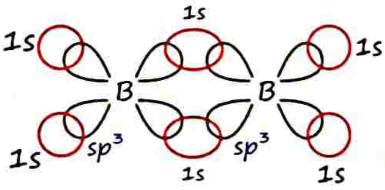


☐ B—H—B bond ≡ banana bond ≡ 3C − 2e⁻ bond

≡ Electron deficient bond

☐ Hybridisation of B → sp^3

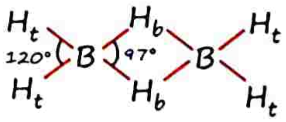




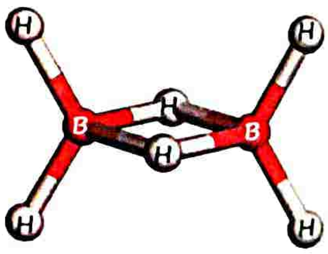
☐ B—H—B ⇒ $sp^3 - 1s - sp^3$

$\boxed{< H_tBH_t = 120°} \rightarrow \theta\uparrow : \%s\uparrow : \%p\downarrow$: Bond length↓

$\boxed{< H_bBH_b = 97°} \rightarrow \theta\downarrow : \%s\downarrow : \%p\uparrow$: Bond length↑



☐ Terminal B-H bonds have less p-character when compared to bridging bonds.

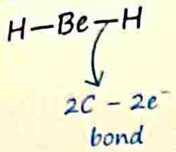


☐ Bond Length: $B—H_t < B - H_b$

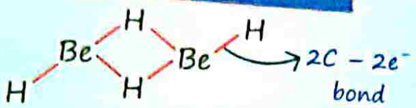
☐ Bond Angle: $H_tBH_t > H_bBH_b$

☐ Max. No. of atoms in same plane: 6[2B, 4H_t]

BeH_2 : Monomer

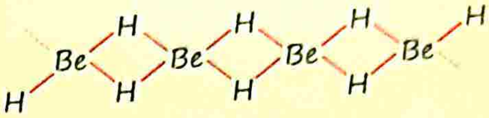


Be_2H_4 : Dimer



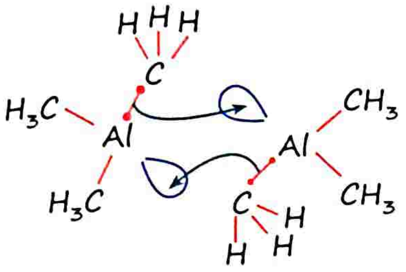
- ☐ Be—H—Be : 3C – 2e⁻ bond

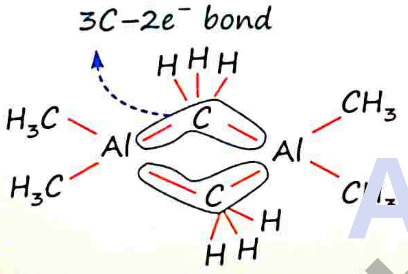
$[BeH_2]_n$: Polymer



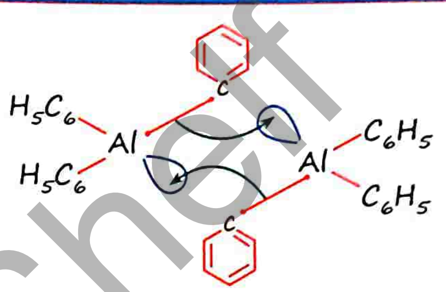
- ☐ Be—H—Be : 3C – 2e⁻ bond

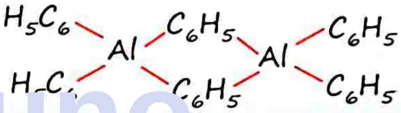
$Al_2(CH_3)_6$ Al—C—Al ≡ $sp^3–sp^3–sp^3$





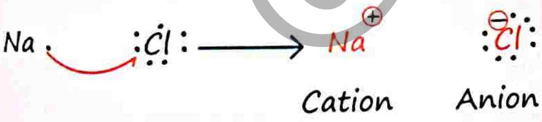
$Al_2(C_6H_5)_6$ Al—C—Al ≡ $sp^3–sp^2–sp^3$ ≡ 3C–2e⁻ bond





IONIC BONDING

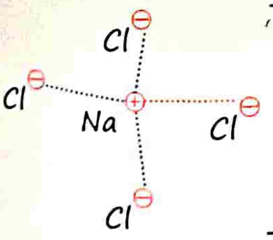
- ☐ The chemical bond formed between two or more atoms as a result of transfer of one or more electrons between them.



Electrostatic force of attraction between cation and anion ≡ Ionic Bond

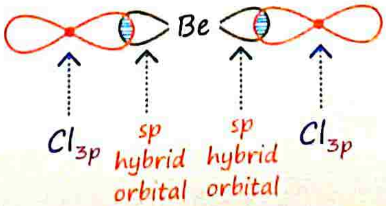
≡ Electrovalent bond

- ☐ Ionic bond (electrovalent bond) is non-directional in nature but covalent bond is directional in nature.



→ Here force of attraction does not depend on direction of interaction between anion and cation

$BeCl_2$ → Covalent molecule

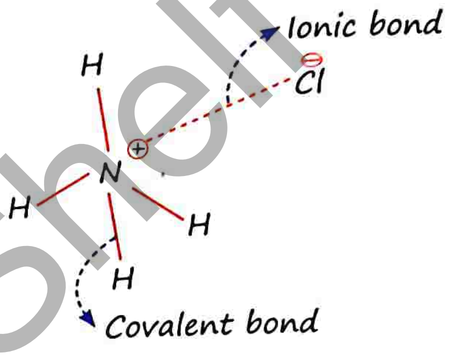


→ Direction of overlapping plays an important role to form covalent bond

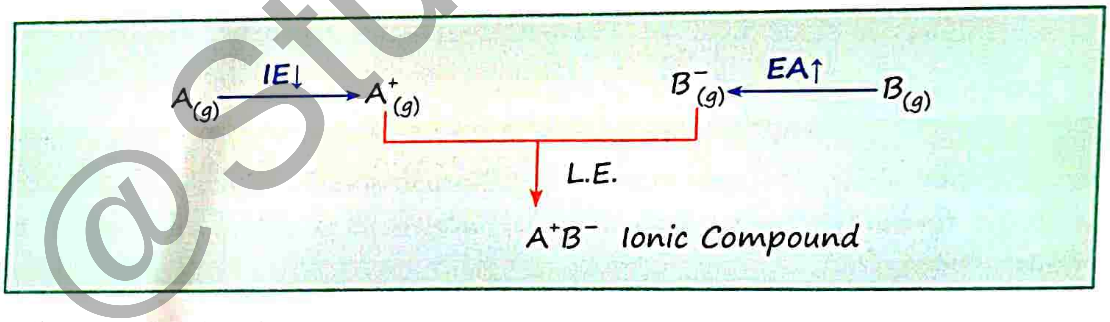
Ionic Compounds

A^+ Cation	B^- Anion
(a) Metal (Na, Mg)	(a) Non-Metal (B, C, N, S, O, F)
(b) Group of atoms having (+)ve charge $NH_4^{\oplus}$	(b) Group of atoms having (−)ve charge SO_4^{2-}, PO_4^{3-}

$NaF \longrightarrow$	Na^+	F^-
$KCl \longrightarrow$	K^+	Cl^-
$CaO \longrightarrow$	Ca^{2+}	O^{2-}
$NH_4Cl \longrightarrow$	NH_4^+	Cl^-
$Na_2SO_4 \longrightarrow$	$2Na^+$	SO_4^{2-}



Favourable Condition for Ionic Bond



(i) Less Ionisation Energy for A

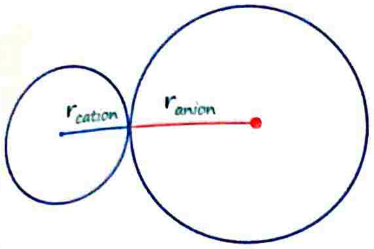
(ii) More Electron Affinity for B

(iii) Energy released because of the combination of cation (A^+) and anion (B^-) should be high. This energy is also defined in terms of lattice enthalpy.

LATTICE ENERGY

☐ Energy which is released when the component ions (in gas phase) were brought together from infinity to make the lattice of the crystal.

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} + \text{Lattice Energy}$$



$r = r_{cation} + r_{anion} \equiv$ Internuclear Distance

$$\boxed{\text{Lattice Energy} \propto \frac{q_1 \cdot q_2}{r}}$$

Factors Affecting LE

(i) Charge ↑ : LE ↑

(ii) Size ↑ : LE ↓

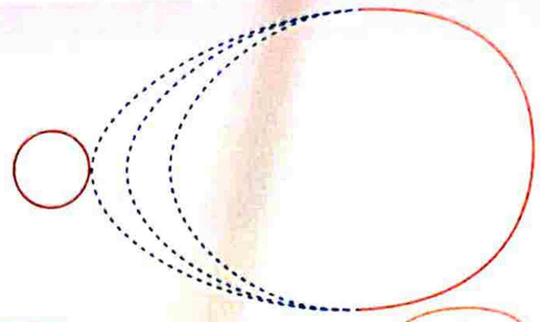
1. LE $\propto q_1 \cdot q_2$
2. LE $\propto \dfrac{1}{r_{cation} + r_{anion}}$

पहले charge
फिर size

LE	→	NaF (1×1)	>	NaCl (1×1)							[size: $F^- < Cl^-$] → $q_1 \cdot q_2$
LE	→	Na_2O (1×2)	<	MgO (2×2)	<	Al_2O_3 (3×2) → $q_1 \cdot q_2$					
LE	→	NaCl (1×1)	<	$MgCl_2$ (2×1)	<	$AlCl_3$ (3×1) → $q_1 \cdot q_2$					
LE	→	LiCl	>	NaCl	>	KCl	>	RbCl	>	CsCl	(Size: $Li^+ < Na^+ < K^+ < Rb^+$)
LE	→	AlN (3×3)	>	Al_2O_3 (3×2)	>	AlF_3 (3×1) → $q_1 \cdot q_2$					

FAJAN'S RULE

- ☐ There is no compound which is 100% ionic.
- ☐ Covalent character in ionic compound can be explained with the help of Fajan's rule.
- ☐ The negative charge of an isolated anion is evenly distributed, but in the presence of a cation, the anion's negative charge density is distorted. This distortion of e^- cloud is known as **polarisation**.
- ☐ **Polarising power** → a cation's ability or power to distort the electron density of an anion towards itself, or to pull the electron density of an anion towards itself.
- ☐ **Polarisability** → tendency for an anion to become polarised.



Cation
↓
Polarising Power ↑
(i) Small size
(ii) More charge
(iii) Pseudo inert gas configuration of cation

Anion
↓
Polarisability ↑
(i) Large size
(ii) More charge

Polarising power of cation ↑
Polarisability of anion ↑
→ Polarisation ↑ → Covalent character ↑

Polarising power of cation → $Li^+ > Na^+ > K^+$
• $Be^{2+} > Mg^{2+} > Ca^{2+}$
• N[illegible] Mg^{2}[illegible]

Polarisability of anion → $F^- < Cl^- < Br^- < I^-$
• $N^{3-} > O^{2-} > F^-$

Covalent character → $LiCl > NaCl > KCl > RbCl > CsCl$
$\xrightarrow{\hspace{6em}}$
Size of cation ↑ : Polarisation ↓ : Covalent character ↓

☐ $BeCl_2$ $MgCl_2$ $CaCl_2$ $SrCl_2$ $BaCl_2$
$\xrightarrow{\hspace{10em}}$
Size of cation ↑ : Polarisation ↓ : Covalent character ↓

☐ LiF $LiCl$ $LiBr$ LiI
$\xrightarrow{\hspace{6em}}$
- Size of anion ↑
- Polarisation ↑
- Covalent character ↑

☐ $NaCl < MgCl_2 < AlCl_3$ — Covalent character
Na^+ Mg^{+2} Al^{+3}
$\xrightarrow{\hspace{6em}}$
- Charge of cation ↑
- Polarisation ↑
- Covalent character ↑

☐ $AlF_3 < Al_2O_3 < AlN$ — Covalent character
F^- O^{-2} N^{-3}
$\xrightarrow{\hspace{6em}}$
- Charge on anion ↑
- Polarisation ↑
- Covalent Character ↑

Ionic Character

☐ AlN < Al_2O_3 < AlF_3 → less covalent character
more ionic character

☐ AlF_3 > $AlCl_3$
Ionic compound (Al^{3+} $3F^-$)
Covalent compound

☐ $BeCl_2$ < $MgCl_2$
Covalent molecule
Ionic compound (Mg^{2+} $2Cl^-$)

☐ BeF_2 > $BeCl_2$
(F—Be—F) (Cl—Be—Cl)
[BeF_2 has more ionic character than $BeCl_2$ but both are covalent molecules]

Note

☐ Cation having pseudo-inert gas configuration, has more polarising power than other cations.

CuCl > NaCl : Covalent character

$\begin{bmatrix}\text{d block} \\ \text{metal}\end{bmatrix}$ > $\begin{bmatrix}\text{s block} \\ \text{metal}\end{bmatrix}$

- Z_{eff} : Cu^+ > Na^+
  Cu^+: [Ar]$3d^{10}$ ↓ Pseudo inert gas configuration
  Na^+: [Ne] ↓ Inert gas configuration
- Polarising power : Cu^+ > Na^+

Melting point ↑ : Ionic character ↑

☐ Melting point of covalent compound < melting point of ionic compound.

r_+ ↑ : Ionic character ↑ $BeCl_2$ < $MgCl_2$ < $CaCl_2$: M.P.

r_- ↑ : Ionic character ↓ CaF_2 > $CaCl_2$ > $CaBr_2$ > CaI_2 : M.P.

Colour

☐ The colour of some compounds can be explained on the basis of polarisation of their bigger negative anion.

☐ The bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.

1. AgCl is white but AgBr, AgI is yellow.	⇒	Polarisation : AgCl < AgBr < AgI → more polarisation, more intensity of colour
2. $SnCl_2$ is white but SnI_2 is red.	⇒	Polarisation : $SnCl_2$ < SnI_2
3. $PbCl_2$ is white but PbI_2 is yellow.	⇒	Polarisation : $PbCl_2$ < PbI_2

106. The number of following factors which affect the percent covalent character of the ionic bond is___ [8 April, 2023 (Shift-

(A) Polarising power of cation
(B) Extent of distortion of anion
(C) Polarisability of the anion
(D) Polarising power of anion

Sol. [3] Acc. to Fajan's rule a compound is said to be covalent having smaller cation, larger anion and having high charge density. A, B and C are factors which affect the percent covalent character of the ionic bond according to Fajan's rule

107. Which of the following is least ionic? [31 Jan, 2024 (Shift-

(a) $BaCl_2$ (b) $AgCl$ (c) KCl (d) $CaCl_2$

Sol. (b) $AgCl < CaCl_2 < BaCl_2 < KCl$ (ionic character)

Reason: Ag^+ has pseudo inert gas configuration.

108. Arrange the bonds in order of increasing ionic character in the molecules LiF, K_2O, N_2, SO_2 and ClF_3. [01 Feb, 2024 (Shift-

(a) $ClF_3 < N_2 < SO_2 < K_2O < LiF$
(b) $LiF < K_2O < ClF_3 < SO_2 < N_2$
(c) $N_2 < SO_2 < ClF_3 < K_2O < LiF$
(d) $N_2 < ClF_3 < SO_2 < K_2O < LiF$

Sol. (c) Increasing order of ionic character

$N_2 < SO_2 < ClF_3 < K_2O < LiF$

The degree of ionic character in a bond depends on the difference in electronegativity, which determines the bond polarity.

109. Order of Covalent bond; [24 Jan, 2023 (Shift-

(A) $KF > KI$; $LiF > KF$
(B) $KF < KI$; $LiF > KF$
(C) $SnCl_4 > SnCl_2$; $CuCl > NaCl$
(D) $LiF > KF$; $CuCl < NaCl$
(E) $KF < KI$; $CuCl > NaCl$

(a) C, E only (b) B, C only (c) B, C, E only (d) A, B only

Sol. (c)

THERMAL STABILITY

☐ $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2 \uparrow$ — Li_2CO_3 is thermally unstable

☐ $Na_2CO_3 \xrightarrow{\Delta}$ No Reaction — Na_2CO_3 is thermally stable

☐ Thermally stable → Strong lattice → (i) Lattice Energy ↑
(ii) Ionic Character ↑

Anions

Monoatomic anions

F^- Cl^- Br^- I^- O^{2-} H^-

Apply Lattice Energy concept to get order for thermal stability

$LiCl > NaCl > KCl > RbCl > CsCl$

size of cation ↑
Lattice Energy ↓
Thermal stability ↓

$LiH > NaH > KH > RbH > CsH$

Polyatomic anions

SO_4^{2-}, NO_2^-, CO_3^{2-}, OH^-, NO_3^-

Apply ionic character concept to get order for thermal stability

$Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Rb_2SO_4 < Cs_2SO_4$

size of cation ↑
Ionic character ↑
Thermal stability ↑

$Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$

$BeO > MgO > CaO > SrO > BaO$

$\underbrace{Be^{2+}\ O^{2-}}_{\text{Monoatomic anion}}$

Lattice Energy ↓
Thermal stability ↑

$BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$

$\underbrace{Be^{2+}\ CO_3^{2-}}_{\text{Polyatomic anion}}$

Ionic character ↑
Thermal stability ↑

$\underbrace{Li^+\ \bar{O}H}_{\text{Polyatomic anion}}$

$LiOH < NaOH < KOH < RbOH < CsOH$

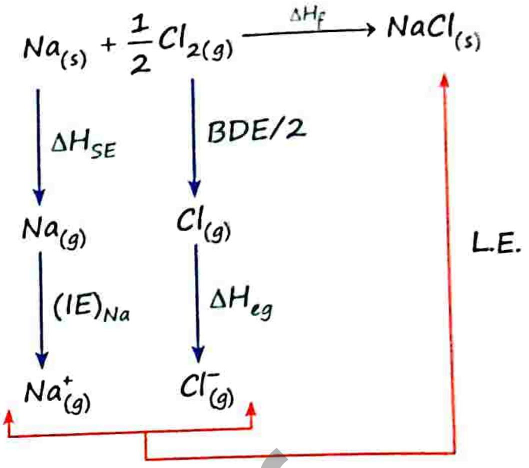
HEAT OF FORMATION

- ☐ Amount of heat released when 1 mole of substance is formed by its elements in pure and stable state.

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

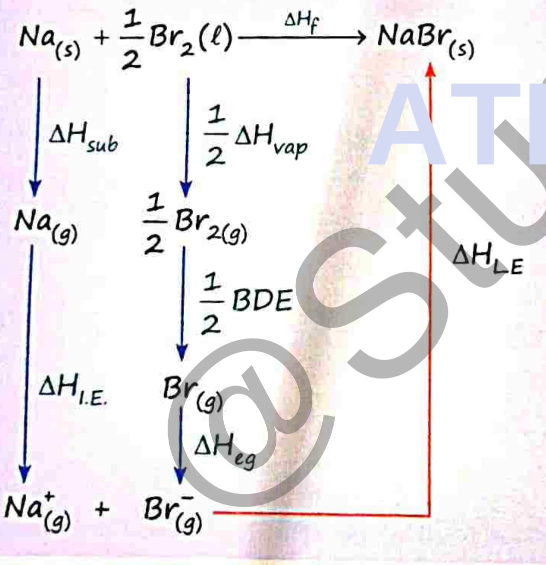
BORN-HABER CYCLE

- ☐ ΔH_f → Heat of formation of NaCl
- ☐ $[\Delta H_{SE}]_{Na}$ → Sublimation energy of Na
- ☐ BDE → Bond dissociation energy of 1 mole Cl_2 molecule
- ☐ ΔH_{eg} → Electron gain enthalpy of $Cl_{(g)}$
- ☐ ΔH_{IE} → Ionisation Energy
- ☐ ΔH_{LE} → Lattice Energy

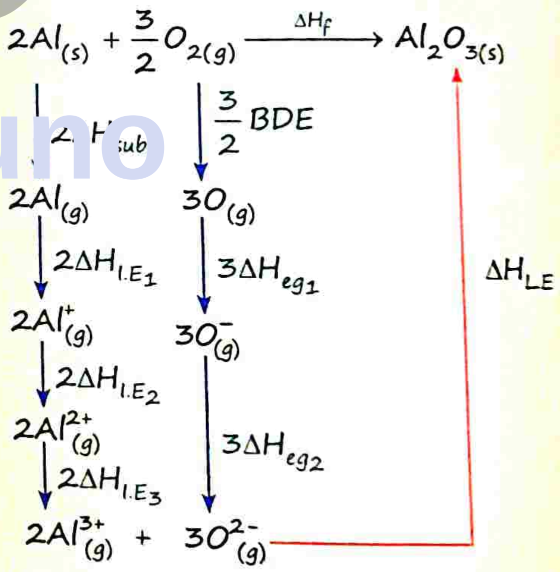


$$\underset{\substack{\downarrow\\(Exo)\\\downarrow\\\Delta H \to \ominus ve}}{\Delta H_f} \equiv \underset{\substack{\downarrow\\(Endo)\\\downarrow\\\oplus ve}}{(\Delta H_{SE})_{Na}} + \underset{\substack{\downarrow\\(Endo)\\\downarrow\\\oplus ve}}{(IE)_{Na}} + \underset{\substack{\downarrow\\(Endo)\\\downarrow\\\oplus ve}}{\left(\frac{BDE}{2}\right)_{Cl_2}} + \underset{\substack{\downarrow\\(Exo)\\\downarrow\\\ominus ve}}{(\Delta H_{eg})_{Cl}} + \underset{\substack{\downarrow\\(Exo)\\\downarrow\\\ominus ve}}{(L.E.)_{NaCl}}$$

Born Haber Cycle for NaBr



Born Haber Cycle for $Al_2O_{3(s)}$



$$\Delta H_f = 2\Delta H_{sub} + 2\Delta H_{I.E_1} + 2H_{I.E._2} + 2\Delta H_{I.E_3} + \frac{3}{2}BDE + 3\Delta H_{eg_1} + 3\Delta H_{eg_2} + \Delta H_{L.E.}$$

110. Arrange the following in the increasing order of their covalent character.

(a) NaF, Na_3N and Na_2O

(b) NaCl, $MgCl_2$, $AlCl_3$, $SiCl_4$ and PCl_5

Sol. (a) $NaF < Na_2O < Na_3N$

(b) $NaCl < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$: Covalent character

$[Na^+ < Mg^{2+} < Al^{3+} < Si^{4+} < P^{5+}$: Charge]

111. $SnCl_4$ has melting point $-15°C$ whereas $SnCl_2$ has melting point $535°C$. Why?

Sol. Covalent character : $SnCl_4 > SnCl_2$ [Charge : $Sn^{+4} > Sn^{+2}$]

According to Fajan's rule, as charge on cation increases, its polarising power increases resulting in to the greater polarisation of anion. Thus, covalent character increases and melting point decreases.

112. Which of the following is in order of increasing covalent character?

(a) $CCl_4 < BeCl_2 < BCl_3 < LiCl$
(b) $LiCl < CCl_4 < BeCl_2 < BCl_3$
(c) $LiCl < BeCl_2 < BCl_3 < CCl_4$
(d) $LiCl < BeCl_2 < CCl_4 < BCl_3$

Sol. (c) As charge on cations increases, their polarising power increases and thus covalent character increases.

$$\overset{+1}{Li}Cl < \overset{+2}{Be}Cl_2 < \overset{+3}{B}Cl_3 < \overset{+4}{C}Cl_4$$

113. Which of the following combination of ion will have highest polarisation?

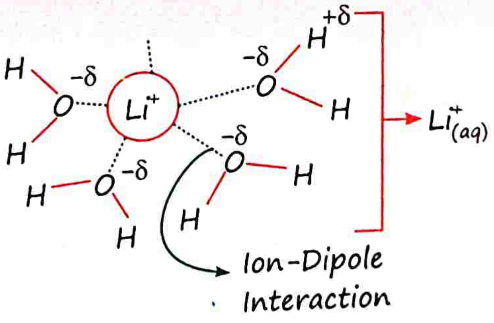
(a) Fe^{2+}, Br^-
(b) Ni^{4+}, Br^-
(c) Ni^{2+}, Br^-
(d) Fe^{3+}, Br^-

Sol. (b) Increase in oxidation state (Ni^{4+}) increases the polarising power of cation and thus increases the polarisation of Br^- ions.

HYDRATION ENERGY

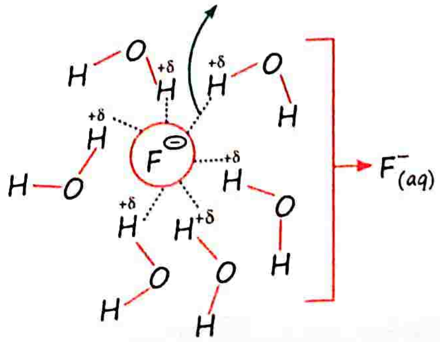
Hydration energy is the amount of energy released when one mole of ions undergoes hydration.

☐ $Li^+_{(g)} \xrightarrow{H_2O} Li^+_{(aq)} + (\Delta H_{hy})_{Li^+}$

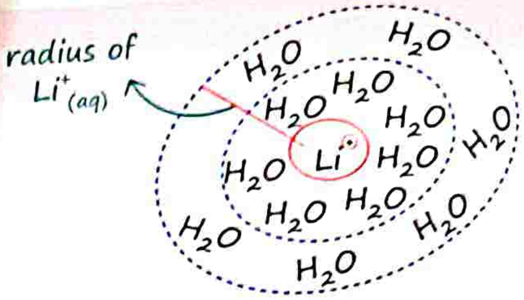


☐ $F^-_{(g)} \xrightarrow{H_2O} F^-_{(aq)} + (\Delta H_{hy})_{F^-}$

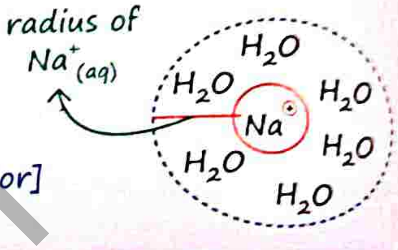
$$\boxed{\text{Hydration Energy} \propto \frac{\text{charge }(q)}{\text{size }(r)}}$$



Radius$_{(g)}$: $Li^+ < Na^+$
Radius$_{(aq)}$: $Li^+_{(aq)} > Na^+_{(aq)}$
Mobility : $Li^+_{(aq)} < Na^+_{(aq)}$



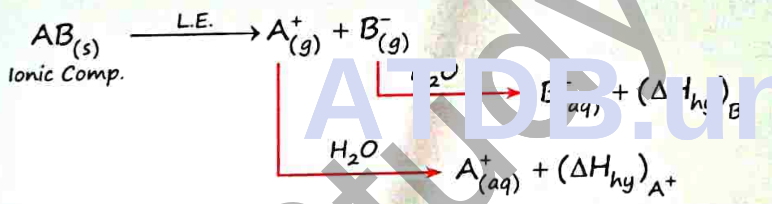
Ion Dipole Interaction : $Li^+ > Na^+$
Hydration Energy : $Li^+ > Na^+$
Hydration Energy : $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ [Size factor]
: $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ [Size factor]
: $Na^+ < Mg^{2+}$ [Charge factor]

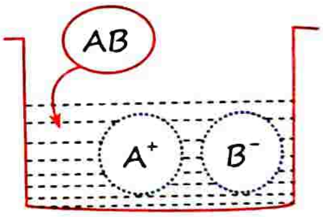


Solubility in Water

2 factors are responsible:

(i) Lattice energy of ionic compounds (ii) Hydration energy of component ions

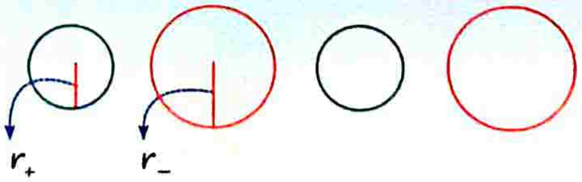




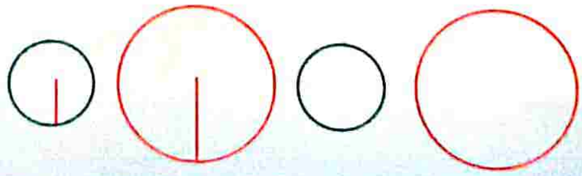
- ☐ Ionic Compound is soluble: $LE < [(\Delta H_{hy})_{A^+} + (\Delta H_{hy})_{B^-}]$
- ☐ Ionic Compound is insoluble: $LE > [(\Delta H_{hy})_{A^+} + (\Delta H_{hy})_{B^-}]$
- ☐ High solubility of NaCl → $(LE)_{NaCl} < [(\Delta H_{hy})_{Na^+} + (\Delta H_{hy})_{Cl^-}]$

$$NaCl_{(s)} \xrightarrow{L.E.} Na^+_{(g)} + Cl^-_{(g)} \xrightarrow{H_2O} Na^+_{(aq)} + Cl^-_{(aq)}$$

- ☐ Perfect lattice: $r_+ \approx r_-$
  → Solubility ↓↓



- ☐ Imperfect lattice: $r_+ < r_-$
  → Solubility ↑



- ☐ Extent of solubility $\propto |r_- - r_+|$

- ☐ Solubility : LiF < CsF
  Low solubility of LiF is due to its high lattice enthalpy
- ☐ Solubility : LiI > CsI
  Low solubility of CsI is due to smaller hydration enthalpy of its two ions (Cs^+, I^-)

Anion

Small size → F^-, OH^-, O^{2-}

Large size → I^-, Br^-, SO_4^{2-}, NO_3^-, NO_2^-, CO_3^{2-}

$\boxed{Li^+ \quad F^- / OH^-} \rightarrow r_+ \approx r_- \rightarrow$ less soluble

$\boxed{Cs^+ \quad I^-, Br^-, NO_3^-, NO_2^-} \rightarrow r_+ \approx r_- \rightarrow$ less soluble

- ☐ LiOH < NaOH < KOH < RbOH < CsOH
- ☐ $Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2 < \boxed{Be(OH)_2}$ → Be compounds are generally more soluble than others due to high hydration of Be^{2+} ion.

$\boxed{2Li^+ \quad CO_3^{2-}/SO_4^{2-}}$ → $2r_+ \approx r_-$ → Solubility ↓

$\boxed{2Cs^+ \quad CO_3^{2-}/SO_4^{2-}}$ → $2r_+ > r_-$ → Solubility ↑

- ☐ $Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Rb_2SO_4 < Cs_2SO_4$
- ☐ $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$
- ☐ $LiHCO_3 < NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$ $\boxed{\text{Same order for : } CO_3^{2-} = HCO_3^-}$

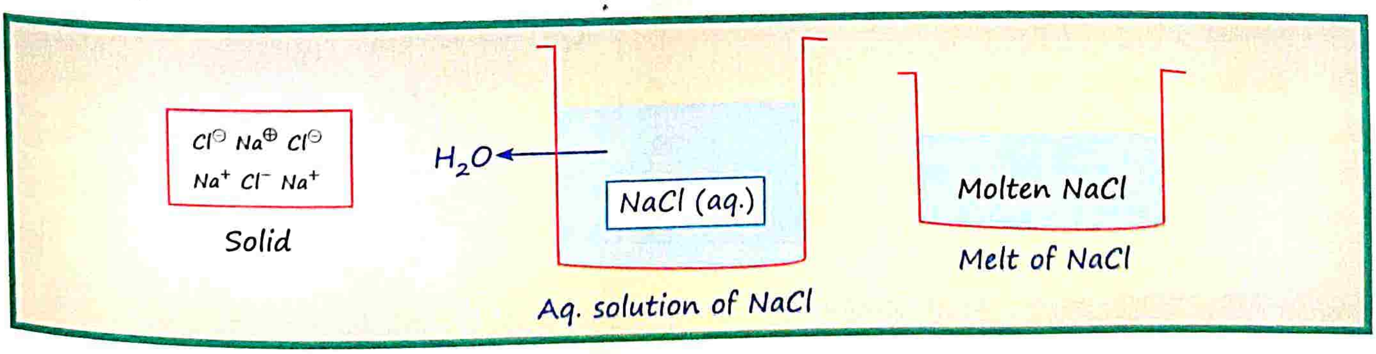
$\boxed{Be^{2+} \quad CO_3^{2-}/SO_4^{2-}} \rightarrow r_+ < r_- \rightarrow$ Solubility ↑

$\boxed{Ba^{2+} \quad CO_3^{2-}/SO_4^{2-}} \rightarrow r_+ \approx r_- \rightarrow$ Solubility ↓

- ☐ $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$
- ☐ $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

Properties of Ionic Compound

- ☐ **Physical state :** At room temperature, ionic compounds exist either in solid state or in solution phase but not in gaseous state.



- ❑ **Electrical conductivity :** Ionic solids are almost non-conductors. All ionic solids are good conductors in molten state & in aqueous solutions because their ions are free to move.
- ❑ **Solubility of ionic compounds :** Soluble in polar solvents like water which have high dielectric constant (like H_2O, C_2H_5OH).

ISOMORPHISM

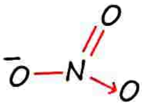
- ❑ Crystals of different ionic compounds having similar crystal structures are known to be isomorphs to each other and the phenomenon is known as isomorphism.

Example: $FeSO_4 \cdot 7H_2O$ & $MgSO_4 \cdot 7H_2O$ are isomorphs.

Crystals having same shape of anion are isomorphs

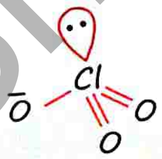
- $BaSO_4$ & $KMnO_4$ → isomorphs
  → Both anions SO_4^{2-} and MnO^-_4 are tetrahedral in shape.
- $NaNO_3$ & $NaClO_3$ → not isomorphs
  → Because anions have different shape.

- $Na^+ NO_3^-$



(Planar)

- $Na^+ ClO_3^-$



(Pyramidal)

114. Which of the following compounds has the lowest melting point? [NEET 2011 Pre]
(a) CaF_2 (b) $CaCl_2$ (c) $CaBr_2$ (d) CaI_2
Sol. (d)

115. Among the following which one has the highest cation to anion size ratio? [NEET 2010 Mains]
(a) CsI (b) CsF (c) LiF (d) NaF
Sol. (b)

116. The sequence of ionic mobility in aqueous solution is: [NEET 2008]
(a) $Na^+ > K^+ > Rb^+ > Cs^+$ (b) $K^+ > Na^+ > Rb^+ > Cs^+$
(c) $Cs^+ > Rb^+ > K^+ > Na^+$ (d) $Rb^+ > K^+ > Cs^+ > Na^+$
Sol. (c)

117. Among the following, which compound will show the highest lattice energy? [NEET 1993]
(a) KF (b) NaF (c) CsF (d) RbF
Sol. (b)

118. In the case of alkali metals, the covalent character decreases in the order: [NEET 2009]
(a) MF > MCl > MBr > MI (b) MF > MCl > MI > MBr
(c) MI > MBr > MCl > MF (d) MCl > MI > MBr > MF
Sol. (c)

119. Among LiCl, $BeCl_2$, BCl_3 and CCl_4, the covalent bond character follows the order: [NEET 1990]
(a) $BeCl_2 > BCl_3 > CCl_4 < LiCl$ (b) $BeCl_2 < BCl_3 < CCl_4 < LiCl$
(c) $LiCl < BeCl_2 < BCl_3 < CCl_4$ (d) $LiCl > BeCl_2 > BCl_3 > CCl_4$
Sol. (c)

INTER MOLECULAR FORCE OF ATTRACTION

Polar (H_2O, HCl) ← **Molecules** → Non-polar (Cl_2, O_2, CO_2)

1. Interaction between Polar molecules
   - Dipole - dipole attraction
2. Interaction between Polar & non polar molecules
   - Dipole - induced dipole attraction
3. Interaction between non-polar molecules
   - Instantaneous induced dipole - induced dipole attraction [IID-ID]
   - Dispersion force
   - London force

$\overset{+\delta}{H}-\overset{-\delta}{Cl}\cdots\cdots\overset{+\delta}{H}-\overset{-\delta}{Cl}$

$\overset{-\delta}{Cl}-\overset{+\delta}{H}\cdots\cdots\overset{-\delta\delta}{Cl}-\overset{+\delta\delta}{Cl}$

$\overset{-\delta\delta}{Cl}-\overset{+\delta\delta}{Cl}\cdots\cdots\overset{-\delta\delta\delta}{Cl}-\overset{+\delta\delta\delta}{Cl}$

☐ Vander Waal force of attraction includes 1st, 2nd and 3rd interactions.

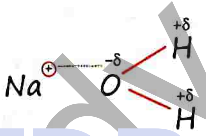
Order of Inter-molecular Forces

(a) Ion - ion attraction

$Na^+\cdots\cdots Cl^-$

v

(b) Ion - dipole attraction



v

(c) Dipole - dipole attraction

$\overset{+\delta}{H}-\overset{-\delta}{Cl}\cdots\cdots\overset{+\delta}{H}-\overset{-\delta}{Cl}$

v

(d) Ion-induced dipole attraction

$Na^{\oplus}\cdots\cdots\overset{-\delta\delta}{O}=\overset{+\delta\delta}{O}$

v

(e) Dipole-induced dipole attraction

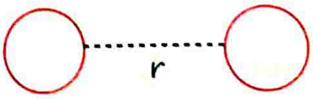
$\overset{-\delta}{Cl}-\overset{+\delta}{H}\cdots\cdots\overset{-\delta\delta}{Cl}-\overset{+\delta\delta}{Cl}$

v

(f) Ins. Induced dipole - induced dipole

$\overset{-\delta\delta}{Cl}-\overset{+\delta\delta}{Cl}\cdots\cdots\overset{-\delta\delta\delta}{Cl}-\overset{+\delta\delta\delta}{Cl}$

Energy & Distance Relationship between 2 Interacting Particles



1. Ion-ion attraction $E \propto \frac{1}{r}$
2. Ion-dipole attraction $E \propto \frac{1}{r^2}$
3. Dipole-dipole attraction $E \propto \frac{1}{r^3}$
4. Ion-induced dipole attraction $E \propto \frac{1}{r^4}$
5. Dipole - induced dipole attraction
6. Ins. Induced dipole - induced dipole

(5, 6) → $E \propto \frac{1}{r^6}$

These forces are always attractive and interaction energy is inversely proportional to the sixth power of the distance between two interacting particles ($1/r^6$ where r is the distance between two particles).

120. Identify type of Interaction present between following species

(1) Xe and H_2O (2) Na^+ and Br_2 (3) Br_2 and Br_2 (4) CO_2 and CO_2 (5) CCl_4 and CCl_4
(6) K^+ and Cl^- (7) Li^+ and H_2O (8) H_2S and H_2S (9) Ne and Ne (10) I^- and I_2

Sol. 1. Xe , H_2O → Dipole-induced dipole
[non polar-polar]

2. Na^+, Br_2 → Ion-induced dipole
[ion-nonpolar]

3. Br_2, Br_2 → London force/IID-ID
[nonpolar - nonpolar]

4. CO_2, CO_2 → IID-ID
[nonpolar - nonpolar]

5. CCl_4, CCl_4 → IID-ID
[nonpolar - nonpolar]

6. $K^{\oplus}$, $Cl^{\ominus}$ → Ion-ion attraction
[ion - ion]

7. Li^+, H_2O → Ion-dipole attraction
[ion - polar molecule]

8. H_2S , H_2S → Dipole-dipole attraction
[polar – polar molecule]

9. Ne , Ne → London force
[nonpolar - nonpolar]

10. I^- , I_2 → Ion-induced dipole attraction
[ion - nonpolar molecule]
$I^{\ominus}\cdots\cdots I^{+\delta} - I^{-\delta} \Rightarrow I_3^-$ ion

121. The interaction energy of London forces between two particles is proportional to r^x, where r is the distance between the particles. The value of x is: **[26 Aug, 2021 (Shift-II)]**

(a) −3 (b) −6 (c) 6 (d) 3

Sol. (b) $E \propto r^{-6}$ where E is the interaction energy of London forces.
Thus, $x = -6$.

122. Which one of the following is the correct order of interactions? **[NEET 1993]**

(a) Covalent < hydrogen bonding < Van Der Waals' < dipole-dipole
(b) Van Der Waals' < hydrogen bonding < dipole < covalent
(c) Van Der Waals' < dipole-dipole < hydrogen bonding < covalent
(d) Dipole-dipole < Van Der Waals' < hydrogen bonding < covalent.

Sol. (b)

Vander Waal Force of Attraction

Molecular mass ↑ : Vander Waal force ↑
: Boiling Point ↑

Order of Boiling Point

PH_3	H_2S	HCl
^	^	^
AsH_3	H_2Se	HBr
^	^	^
SbH_3	H_2Te	HI

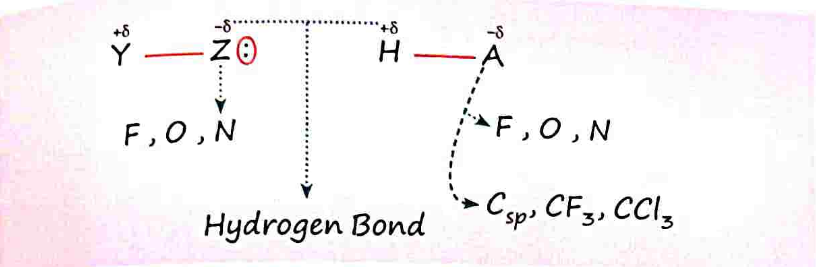
Size of the atom ↑ : Vander Waal force ↑ : BP ↑

He < Ne < Ar < Kr < Xe : BP/MP

Lowest B.P. (4.2 K) of any known substance

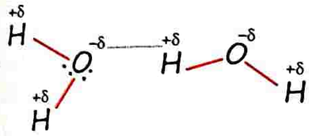
	Boiling Point (K)	Melting Point (K)
He	4.216	0.95
Ne	27.1	24.7
Ar	87.29	83.6
Kr	120.85	115.8
Xe	166.1	161.7
Rn	211.5	202.2

HYDROGEN BONDING

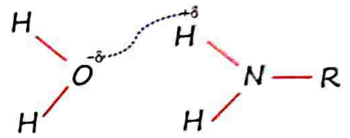


Force of attraction : H– bonding > Van der Waals force of attraction

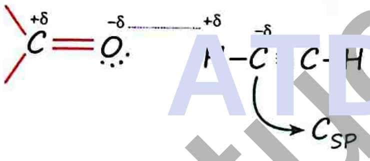
Water



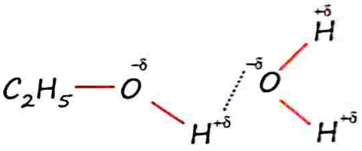
Water & Amine



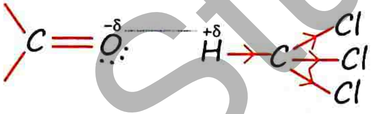
Acetone and Acetylene



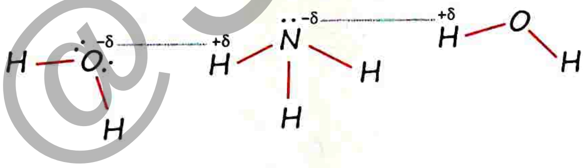
Water & Alcohol

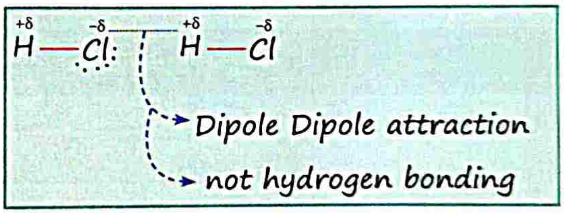


Acetone & Chloroform



Water & Ammonia





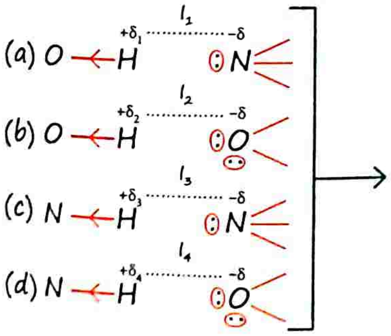
Dipole Dipole attraction

not hydrogen bonding

Extent of H-bonding

Extent of H-bonding ↑ : (i) Partial (+)ve charge on H ↑

(ii) Electron density on Z ↑



Extent of H-bonding : a > b > c > d

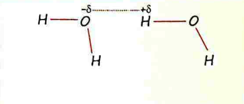
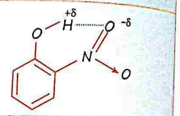
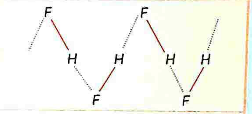
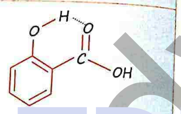
Bond length : $l_1 < l_2 < l_3 < l_4$

Order for partial charge : $(\delta_1 = \delta_2) > (\delta_3 = \delta_4)$

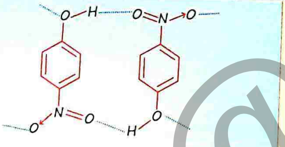
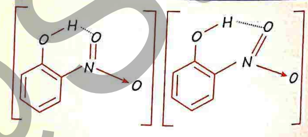
- ☐ $K[HF_2]$

$$K^+[HF_2]^- \equiv \overset{+}{K}\,\underbrace{\overset{\ominus}{F}\cdots\cdots}_{y}\underbrace{\overset{+\delta}{H}—\overset{-\delta}{F}}_{x}$$ [Bond length : x = y]

Types of Hydrogen Bonding

Inter-molecular H-bonding		**Intra-molecular H-bonding**	
H-bonding between molecules		H-bonding within a molecule	
H_2O		o-Nitrophenol	
$(HF)_n$ Solid or liquid		Salicylic Acid	
☐ The hydrogen bonds in HF link the F atom of one molecule with the H-atom of another molecule, thus forming a zig-zag chain $(HF)_n$ in both the solid and also in the liquid.			

Boiling Point

p-Nitrophenol	>	**o-Nitrophenol**
		
☐ Association of molecules due to inter-molecular H-bonding ⇒ BP ↑ ☐ The intermolecular hydrogen bonding in p-nitrophenol requires more energy to break the intermolecular forces, resulting in a higher boiling point.		☐ It exists as discrete molecules which are held together by weak van der waals forces of attraction. A small amount of energy is required to break these forces of attraction. So, less boiling point.

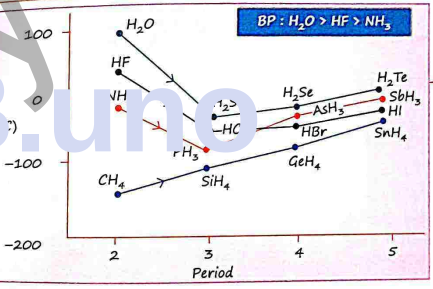
Order of Boiling Point

NH_3, H_2O and HF → Inter-molecular hydrogen bonding ⇒ BP ↑

Top → Bottom
: Molecular Mass ↑
: Vander Waal Force of attraction ↑
: BP ↑

CH_4	**NH_3**	PH_3	**H_2O**	H_2S	**HF**	HCl
^		^		^		^
SiH_4	PH_3	AsH_3	H_2S	H_2Se	HCl	HBr
^		^		^		^
GeH_4	AsH_3	NH_3	H_2Se	H_2Te	HBr	HI
^		^		^		^
SnH_4	SbH_3	SbH_3	H_2Te	H_2O	HI	HF

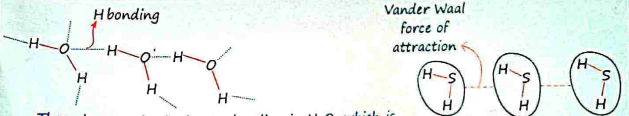
It has stronger intermolecular force of attraction (H-bonding) than others (having vander Waal force of attraction).



- ☐ Sudden increase in boiling point of NH_3, H_2O and HF is due to hydrogen bonding. H_2O > HF > NH_3

Physical State

(i) H_2O is liquid but H_2S is gas at room temperature.

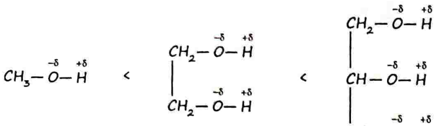


There is extensive hydrogen bonding in H_2O, which is absent in H_2S. Molecules of H_2S are held together only by weak van der Waal's forces of attraction. Hence, H_2O exists as a liquid while H_2S as a gas.

(ii) HF is liquid but HCl is gas. Think why?

B.P. & Viscosity

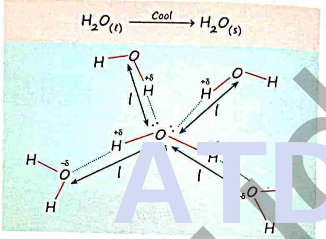
→ No. of Hydrogen bonds per molecule ↑ : viscosity ↑
: BP ↑



$CH_3-\overset{-\delta}{O}-\overset{+\delta}{H} \;<\; \begin{matrix} CH_2-\overset{-\delta}{O}-\overset{+\delta}{H} \\ | \\ CH_2-\overset{-\delta}{O}-\overset{+\delta}{H} \end{matrix} \;<\; \begin{matrix} CH_2-\overset{-\delta}{O}-\overset{+\delta}{H} \\ | \\ CH-\overset{-\delta}{O}-\overset{+\delta}{H} \\ | \\ CH_2-\overset{-\delta}{O}-\overset{+\delta}{H} \end{matrix}$

WATER

- ☐ No. of water molecules attached to 1 H_2O molecule = 4

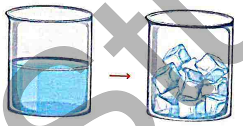


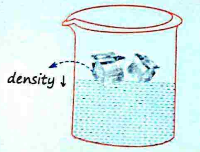
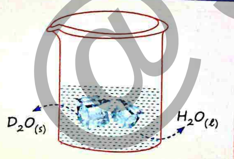
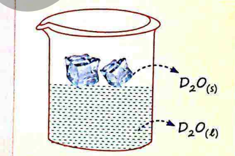
- ☐ Tetrahedrally bonded to a water molecule in solid state.

  Density : $H_2O_{(s)} < H_2O_{(\ell)}$

  Volume : $H_2O_{(s)} > H_2O_{(\ell)}$

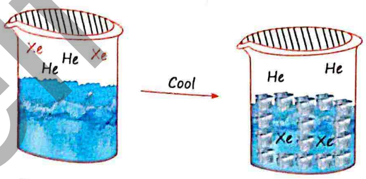
- ☐ Volume of ice is more because of open cage like crystal structure, form by association of water molecules with the help of hydrogen bond.



$H_2O_{(s)}$ in $H_2O_{(\ell)}$	$D_2O_{(s)}$ in $H_2O_{(\ell)}$	$D_2O_{(s)}$ in $D_2O_{(\ell)}$
 Ice [H_2O (s)] floats on water	 D_2O (s) sinks into water	 D_2O (s) floats on heavy water

- ☐ Due to open structure, ice is capable of forming Clatherates.

Clatherates compounds
↓
Cage like compounds



- ☐ Noble gas hydrate (clathrate compound): Ar, Kr, Xe can form clathrate compounds but He, Ne cannot due to their smaller size.

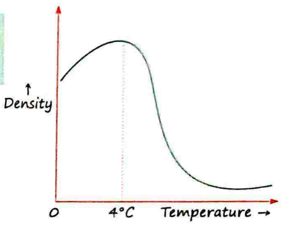
$Xe\cdot 6H_2O$
$Ar\cdot 6H_2O$
$Kr\cdot 6H_2O$
→ formed only where water freezes at high pressure together with noble gas

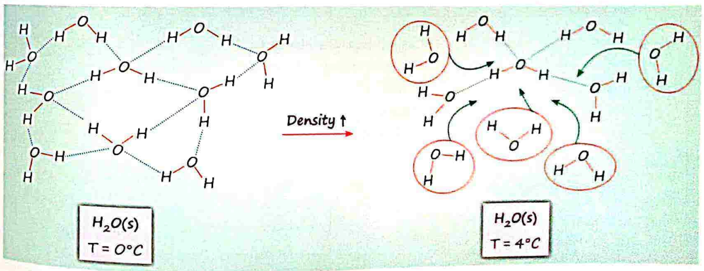
Variation of Density with Temperature

H_2O (T = 0°C) $\xrightarrow{\text{Density}\uparrow}$ H_2O (T = 4°C) $\xrightarrow{\text{Density}\downarrow}$ H_2O (T > 4°C)

- ☐ In this temperature region (0°C to 4°C), some of the ice melts and hence some H_2O molecule go into the cages of remaining ice structure.

  So, volume decreases, density increases becoming max at 4°C but beyond this temp thermal effects become dominating volume increases then density decreases.





(IIT JEE 2000)

123. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is
- (a) H_2O because of hydrogen bonding
- (b) H_2Te because of higher molecular weight
- (c) H_2S because of hydrogen bonding
- (d) H_2Te because of lower molecular weight

Sol. (a) H_2O displays higher boiling point (in spite of lower molecular weight) on account of strong hydrogen bonding, while H_2S, H_2Se and H_2Te do not display H-bonding.

124. The correct statement/s about Hydrogen bonding is/are : [04 April, 2024 (Shift-II)]
- A. Hydrogen bonding exists when H is covalently bonded to the highly electronegative atom.
- B. Intermolecular H bonding is present in o-nitrophenol
- C. Intramolecular Hs bonding is present in HF.
- D. The magnitude of H bonding depends on the physical state of the compound.
- E. H-bonding has powerful effect on the structure and properties of compounds.

Choose the correct answer from the options given below:

(a) A only (b) A, D, E only (c) A, B, D only (d) A, B, C only

Sol. (b)

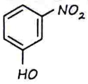
125. If the boiling point of H_2O is 373 K, the boiling point of H_2S will be: [3 Sep 2020 Shift-

(a) more than 373 K (b) less than 300 K

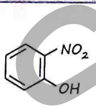
(c) greater than 300 K but less than 373 K (d) equal to 373 K

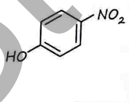
Sol. (b) Boiling point of H_2S is 213K.

126. Intramolecular hydrogen bonding is present in [NEET 2024]

(a) 

(b) HF

(c) 

(d) 

Sol. (c)

127. In X – H– – –Y, X and Y both are electronegative elements: [NEET 2001]
- (a) Electron density on X will increase and on H will decrease
- (b) In both electron density will increase
- (c) In both electron density will decrease
- (d) On X electron density will decrease and on H increases

Sol. (a)

128. Strongest hydrogen bond is shown by: [NEET 1992]

(a) Water (b) Ammonia

(c) Hydrogen fluoride (d) Hydrogen sulphide

Sol. (c)

129. Which one shows maximum hydrogen bonding? [NEET 1990]

(a) H_2O (b) H_2Se (c) H_2S (d) HF

Sol. (a)

130. Match the compounds of Xe in Column-I with the molecular structure in Column-II. [NEET 2020-Covid]

Column-I		Column-II	
(A)	XeF_2	(i)	Square planar
(B)	XeF_4	(ii)	Linear
(C)	XeO_3	(iii)	Square pyramidal
(D)	$XeOF_4$	(iv)	Pyramidal

(a) A-ii B-i C-iv D-iii
(b) A-ii B-i C-iii D-iv
(c) A-ii B-iv C-iii D-i
(d) A-ii B-iii C-i D-iv

Sol. (a)

131. Match the Xenon compounds in Column-I with its structure in Column-II and assign the correct code: [NEET 2019]

Column-I		Column-II	
(A)	XeF_4	(i)	Pyramidal
(B)	XeF_6	(ii)	Square planar
(C)	$XeOF_4$	(iii)	Distorted octahedral
(D)	XeO_3	(iv)	Square pyramidal

Code:

	A	B	C	D
(a)	i	ii	iii	iv
(b)	ii	iii	iv	i
(c)	ii	iii	i	iv
(d)	iii	iv	i	ii

Sol. (b)

132. Which of the following pairs of compounds is isoelectronic and isostructural? [NEET 2017-Delhi]

(a) IF_3, XeF_2 (b) $BeCl_2$, XeF_2 (c) TeI_2, XeF_2 (d) IBr_2^- , XeF_2

Sol. (d)

133. The correct geometry and hybridization for XeF_4 are: [NEET 2016-II]

(a) Planar triangle, sp^3d^3 (b) Square planar, sp^3d^2

(c) Octahedral, sp^3d^2 (d) Trigonal bipyramidal, sp^3d

Sol. (b)

134. Match the compound given in Column-I with the hybridization and shape given in Column-II and mark the correct option. [NEET 2016-I]

Column-I		Column-II	
(A)	XeF_6	(i)	Distorted octahedral
(B)	XeO_3	(ii)	Square planar
(C)	$XeOF_4$	(iii)	Pyramidal
(D)	XeF_4	(iv)	Square pyramidal

Code:

	(A)	(B)	(C)	(D)
(a)	(iv)	(i)	(ii)	(iii)
(b)	(i)	(iii)	(iv)	(ii)
(c)	(i)	(ii)	(iv)	(iii)
(d)	(iv)	(iii)	(i)	(ii)

Sol. (b)

135. In which of the following pairs, both the species are not isostructural? [NEET 2015 Re]

(a) XeF_4, XeO_4 (b) $SiCl_4$, PCl_4^+

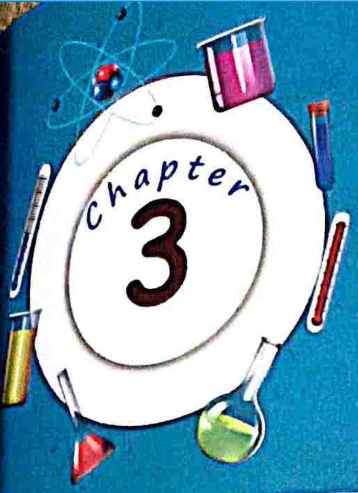
(c) Diamond, silicon carbide (d) NH_3, PH_3

Sol. (a)

136. XeF_2 is isostructural with: [NEET 2013]

(a) TeF_2 (b) ICl_2^- (c) $SbCl_3$ (d) $BaCl_2$

Sol. (b)



Chapter 3

Coordination Compounds

JEE Main & NEET

Syllabus

Introduction to coordination compounds. Werner's theory, ligands, coordination number, denticity, chelation, IUPAC nomenclature of mononuclear coordination compounds, isomerism, Bonding: Valence bond approach and basic ideas of Crystal field theory, colour and magnetic properties, importance of coordination compounds (in qualitative analysis, extraction of metals and in biological systems).

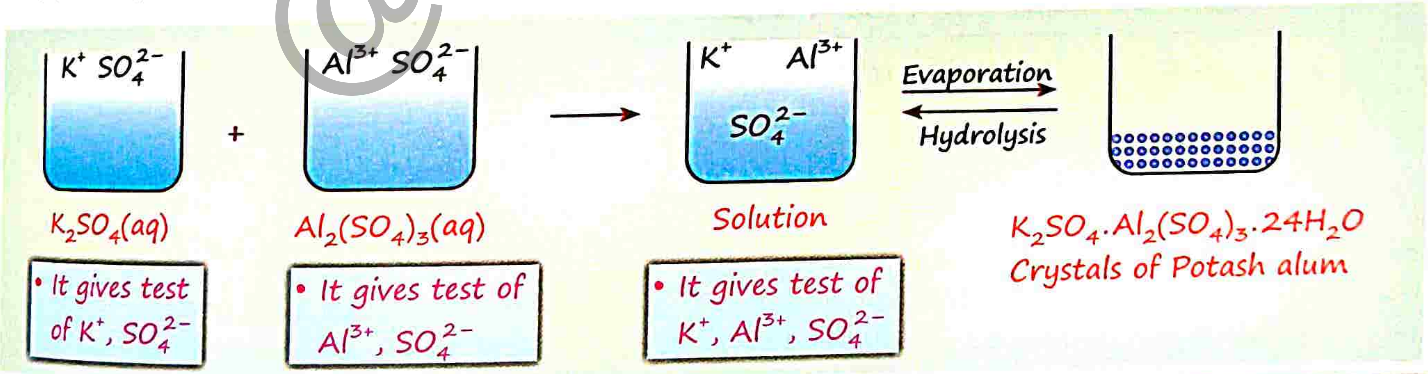
ADDITION COMPOUNDS

- Combination of two or more stable compounds
- There are 2 types of addition compounds: (i) Double salts and (ii) Coordination Compounds

1. **Double Salts:** Ions in addition compound, don't lose their identity in aq. solution.

(a) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ [Potash Alum] (b) $KCl \cdot MgCl_2 \cdot 6H_2O$ [Carnallite]

(c) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ [Mohr's salt/FAS (Ferrous ammonium sulphate)]



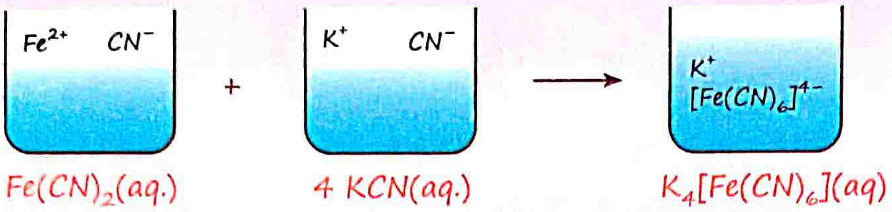
$$KCl_{(aq.)} + MgCl_{2(aq.)} \xrightarrow{Cool} \underset{\text{Carnallite (solid)}}{KCl \, . \, MgCl_2 . \, 6H_2O} \xrightarrow[\text{Solution}]{\text{Aq.}} \text{Test of } K^+, Mg^{2+}, Cl^- \text{ ions.}$$

$$FeSO_{4\,(aq)} + (NH_4)_2SO_{4\,(aq)} \xrightarrow{Cool} \underset{\text{Mohr's Salt (solid)}}{FeSO_4 \, . \, (NH_4)_2SO_4.6H_2O} \xrightarrow[\text{Solution}]{\text{Aq.}} \text{Test of } Fe^{2+}, SO_4^{2-}, NH_4^+.$$

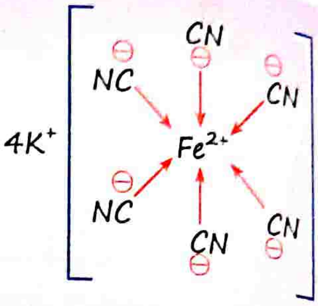
2. Coordination Compounds:

Some ions in addition compound, lose their identity in aq. solution.

(a) $K_4[Fe(CN)_6]$ (b) $[Cu(NH_3)_4]\ SO_4$

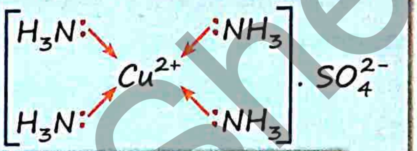


- It gives test of Fe^{+2}, CN^-
- It gives test of K^+, CN^-
- It does not give test of Fe^{+2}, CN^- because Fe^{2+} forms a complex ion with CN^-.



$CuSO_{4(aq.)} + 4\overset{\circ\circ}{N}H_{3(g)} \longrightarrow [Cu(NH_3)_4]SO_4$

Deep blue Solution



- It does not give test of Cu^{2+} and NH_3

1. Which of the following are the example of double salt ? (2023/01 Feb Shift-1)

(I) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (II) $CuSO_4 \cdot 4NH_3 \cdot H_2O$

(III) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ (IV) $Fe(CN)_2 \cdot 4KCN$

Choose the correct answer.

(a) I and III only (b) I and II only (c) I, II and IV only (d) II and IV only

Sol. (a)

$Fe(CN)_2 \cdot 4KCN$	$K_4[Fe(CN)_6] \rightarrow$ Coordination complex
$CuSO_4 \cdot 4NH_3$	$[Cu(NH_3)_4]SO_4 \rightarrow$ Coordination complex
$KCl.MgCl_2 \cdot 6H_2O$	Double salt (known as Carnallite)
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Double salt (known as Mohr's salt)

2. Which of the following forms a set of complex and a double salt, respectively ? [NEET 2023-Manipur]

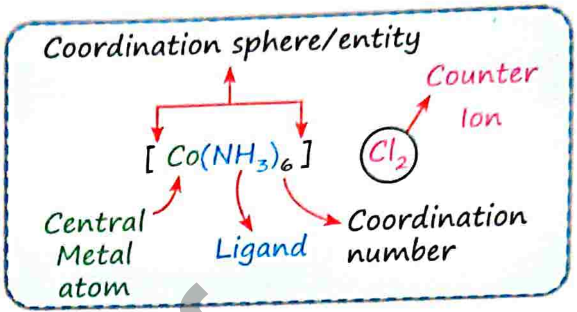
(a) $CuSO_4 \cdot 5H_2O$ and $CuCl_2 \cdot 4NH_3$ (b) $PtCl_2 \cdot 2NH_3$ and $PtCl_4 \cdot 2HCl$

(c) $K_2PtCl_2 \cdot 2NH_3$ and $KAl(SO_4)_2 \cdot 12H_2O$ (d) $NiCl_2 \cdot 6H_2O$ and $NiCl_2(H_2O)_4$

Sol. (c)

TERMINOLOGY AND ITS DEFINITION

1. Coordination Entity/Sphere: The central atom/ion and the ligands attached to it are enclosed in square brackets are collectively known as co-ordination entity or co-ordination sphere.



2. Ligand: The donor atoms ions or molecules which donate a pair of electrons to the central metal atom/ion are called ligands.

For example: $[Co(NH_3)_6]^{2+}$

Here, NH_3 is a ligand because it donates lone pair of electron to Co^{+2} ion.

3. Denticity: No. of coordinate bonds that a ligand can form with Metal

Monodentate → Ligand having only 1 donor site.

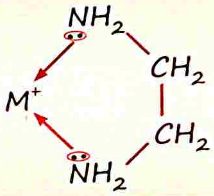
Example: F^- / Cl^- / Br^- / I^- / H_2O / NH_3 etc.

- It is also called unidentate ligand.

Bidentate → When a ligand can bind through 2 donor sites.

Example: Ethane-1, 2-diamine: (en)

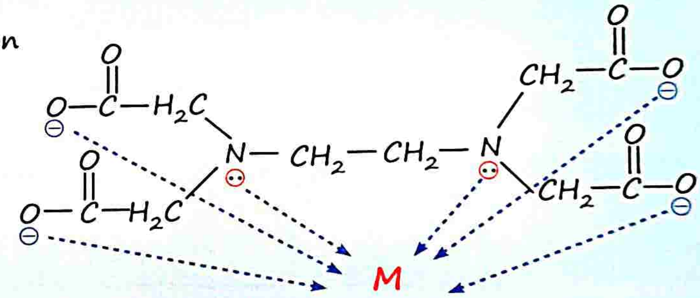
$NH_2 - CH_2 - CH_2 - NH_2$



Polydentate ligand → When a ligand can bind metal ion/atom through more than 2 donor sites.

Example: $EDTA^{4-}$: Ethylene diamine tetraacetate ion

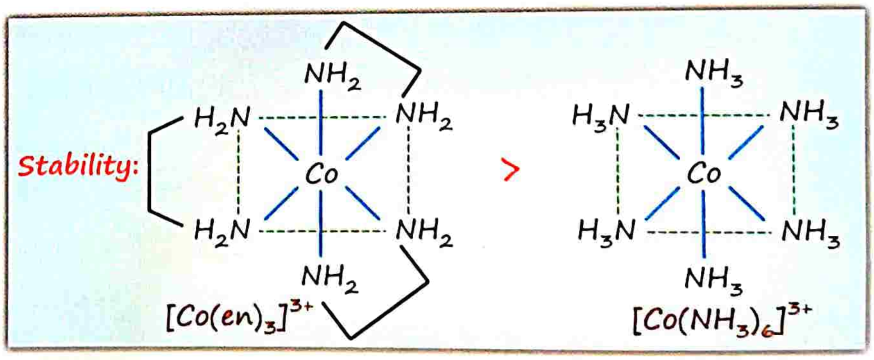
- 4 ⊖ve charges
- Hexadentate ligand



4. Chelation: Ring Formation

A bidentate/polydentate ligand containing donor atoms positioned in such a way that, they coordinate with the central metal ion forming a **5 or 6 membered ring**. This ring formation is known as chelation.

- The ligand which chelates the metal ion is known as chelating ligand.
- As a result of chelate effect, the stability of the complex increases.



ING OF LIGANDS

Naming of oxy-acids:

Group 15	Group 16	Group 17
+5 (ic acid)	+6 (ic acid)	+7 (per.....ic acid)
+3 (ous acid)	+4 (ous acid)	+5 (ic acid)
+1 (Hypo....ous acid)		+3 (ous acid)
		+1 (Hypo....ous acid)

+5 HNO_3 Nitric acid	+5 H_3PO_4 Phosphoric acid	+6 H_2SO_4 Sulphuric acid	+7 $HClO_4$ Perchloric acid
+3 HNO_2 Nitrous acid	+3 H_3PO_3 Phosphorous acid	+4 H_2SO_3 Sulphurous acid	+5 $HClO_3$ Chloric acid
+1 $H_2N_2O_2$ Hyponitrous acid	+1 H_3PO_2 Hypophosphorous acid	$H_2S_2O_3$ Thiosulphuric acid	+3 $HClO_2$ Chlorous acid
			+1 $HClO$ Hypochlorous acid

Anions →
ic acid → ate ion → ato [IUPAC name]
ous acid → ite ion → ito [IUPAC name]

	Ligand [General Name]	IUPAC Name		Ligand [General Name]	IUPAC Name
HNO_3 Nitric acid	NO_3^- Nitrate ion	Nitrato	H_3PO_4 Phosphoric acid	PO_4^{3-} Phosphate ion	Phosphato
HNO_2 Nitrous acid	NO_2^- Nitrite ion	Nitrito	$HClO_4$ Perchloric acid	ClO_4^- Perchlorate ion	Perchlorato
H_2SO_4 Sulphuric acid	SO_4^{2-} Sulphate ion	Sulphato	$HClO_3$ Chloric acid	ClO_3^- Chlorate ion	Chlorato

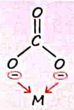
$H_2S_2O_3$ Thio sulphuric acid	$S_2O_3^{2-}$ Thiosulphate ion	Thiosulphato	$HClO_2$ Chlorous acid	ClO_2^- chlorite ion	Chlorito
H_2SO_3 Sulphurous acid	SO_3^{2-} Sulphite ion	Sulphito	$HClO$ Hypo chlorous acid	ClO^- Hypochlorite ion	Hypochlorito

Ligand	IUPAC Name	Ligand	IUPAC Name
F^-	Fluorido	O^{2-}	Oxo/oxido
Cl^-	Chlorido	O_2^{2-}	Peroxido/peroxo
I^-	Iodido	O_2^-	Superoxo
Br^-	Bromido	N^{3-}	Nitrido
NH_2^-	Amido	N_3^-	Azido
NH^{2-}	Imido	S^{2-}	Sulphido
OH^-	Hydroxido	H^-	Hydrido
CN^-	Cyano / cyanido	$\underset{\text{Dioxygen}}{O_2} \xrightarrow{+e^-} \underset{\text{Superoxide}}{O_2^-} \xrightarrow{+e^-} \underset{\text{Peroxide}}{O_2^{2-}} \longrightarrow \underset{\text{Oxide}}{O^{2-}}$	
H_2O	Aqua	C_5H_5N	Pyridine
CO	Carbonyl	CH_3-NH_2	Methylamine
NO	Nitrosyl	NO^+	Nitrosonium
NH_3	Ammine	$N_2H_5^+$	Hydrazinium
PPh_3	Triphenylphosphine	$\underset{\text{Hydrazine}}{\ddot{N}H_2 - \ddot{N}H_2} \xrightarrow{H^+} \underset{\text{Hydrazinium ion}}{\ddot{N}H_2 - \overset{\oplus}{N}H_3}$	

Bidentate Ligand

CO_3^{2-} → Carbonate ion

- ☐ IUPAC: Carbonato
- ☐ 2 ⊖ve charge
- ☐ 4 membered ring

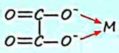


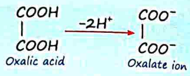
$H_2CO_3 \xrightarrow{-2H^+} CO_3^{2-}$

Carbonic acid   Carbonate ion

Ox^{2-} → Oxalate ion ($C_2O_4^{2-}$)

- ☐ Oxalato
- ☐ 2⊖ve charge
- ☐ Symmtrical ligand
- ☐ 5 membered ring

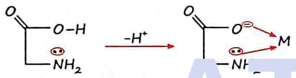




Oxalic acid   Oxalate ion

Gly^- → Glycinate ion

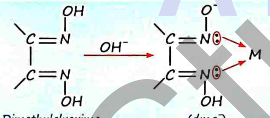
- ☐ Glycinato
- ☐ 1 ⊖ve charge
- ☐ 5 membered ring
- ☐ Unsymmetrical ligand



Glycine   lycinate io

dmg^- → Dimethylglyoximate ion

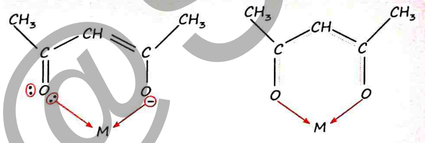
- ☐ Charge ≡ -1
- ☐ 5 membered ring

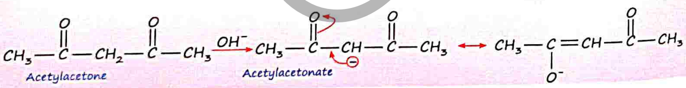


Dimethylglyoxime   (dmg⁻)

$acac^-$ → Acetylacetonate ion

- ☐ Charge ≡ -1
- ☐ 6 membered ring
- ☐ Symmetrical ligand



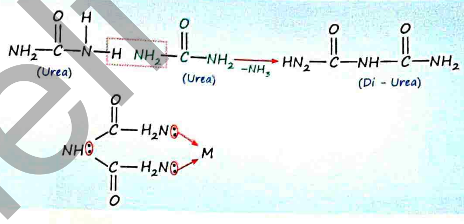


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{OH^-} CH_3-\overset{O}{\overset{\|}{C}}-\underset{\ominus}{CH}-\overset{O}{\overset{\|}{C}}-CH_3 \longleftrightarrow CH_3-\underset{O^-}{\underset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3$$

Acetylacetone   Acetylacetonate

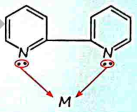
Di-urea → Biurate

- ☐ Symmetrical ligand
- ☐ 6 membered ring
- ☐ Neutral ligand



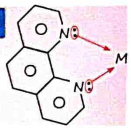
dipy → Dipyridyl

- ☐ Neutral ligand
- ☐ 5 membered ring



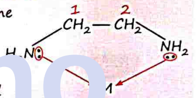
o-phen → Ortho-phenanthroline

- ☐ Neutral ligand
- ☐ 5 membered ring



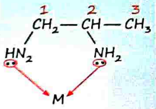
en → Ethylene diamine

- ☐ Ethane-1,2-diamine
- ☐ Neutral ligand
- ☐ 5 membered ring
- ☐ Symmetrical ligand



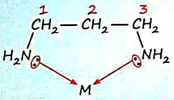
pn → Propylene diamine

- ☐ Propane-1,2-diamine
- ☐ Neutral ligand
- ☐ 5 membered ring
- ☐ unsymmetrical ligand



tn → Trimethylene diamine

- ☐ Propane-1, 3-diamine
- ☐ Neutral ligand
- ☐ 6 membered ring
- ☐ Symmetrical ligand

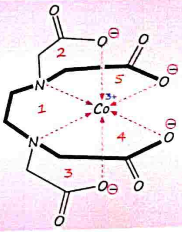


Polydentate Ligands

$EDTA^{4-}$ → Ethylenediamine tetraacetate ion Denticity ≡ 6

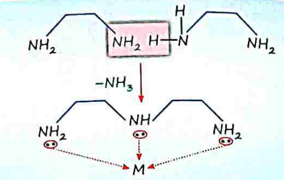
$[Co(EDTA)]^-$

- ☐ Oxidation state of Co ≡ +3
- ☐ No of 5 membered rings ≡ 5
- ☐ No of O-M-O bond angles ≡ 6
- ☐ No of N-M-N bond angles ≡ 1



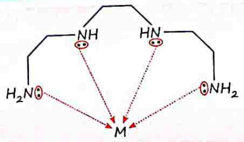
dien → Diethylene triamine

- ☐ Denticity ≡ 3
- ☐ No of 5 membered rings ≡ 2



trien → Tri-ethylene tetraamine

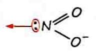
- ☐ Denticity ≡ 4
- ☐ No of 5 membered rings ≡ 3



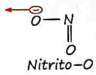
Ambidentate Ligand

Ligands that have more than one kind of donor sites.

NO_2^-

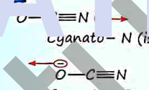


Nitrito–N



Nitrito–O

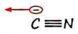
OC



Cyanato – N (isocyanate ion)

Cyanato – O

CN^-



- ☐ Cyanido – C
- ☐ Cyanide ion $[CN^-]$

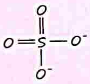
- ☐ Cyanido – N
- ☐ Isocyanide ion (NC^-)

Flexidentate Ligand

A polydentate ligand with different denticity in different coordination compounds.

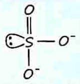
SO_4^{2-}

[D = 1, 2]
denticity

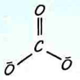


SO_3^{2-}

[D = 1, 2]

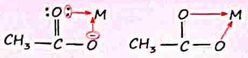


CO_3^{2-}

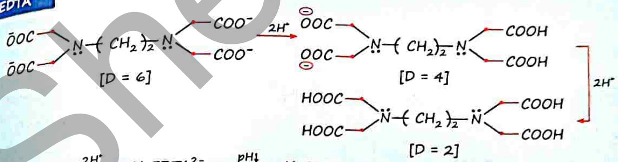


CH_3COO^-

[D = 1, 2]



$EDTA^{4-}$



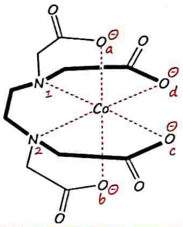
☐ $EDTA^{4-} \xrightarrow[\text{low pH}]{2H^+} \underset{(D=4)}{H_2EDTA^{2-}} \xrightarrow{pH\downarrow} H_4EDTA$

(JEE Adv. 2013)

3. EDTA is ethylenediaminetetraacetate ion. The total number of N – Co – O bond angles in $[Co(EDTA)]^{1-}$

Sol. (8)

N – [illegible]
$N_1 - Co - O_d$
3. $N_1 - Co - O_b$
4. $N_1 - Co - O_c$
5. $N_2 - Co - O_a$
6. $N_2 - Co - O_d$
7. $N_2 - Co - O_b$
8. $N_2 - Co - O_c$



4. Ethylene diaminetetraacetate ion is a/an: [NEET 2024 Re]
   (a) hexadentate ligand
   (b) ambidentate ligand
   (c) monodentate ligand
   (d) bidentate ligand

Sol. (a)

5. Which of the following is not an ambidentate ligand? [NEET 2024 Re]
   (a) $C_2O_4^{2-}$
   (b) SCN^-
   (c) NO_2^-
   (d) CN^-

Sol. (a)

6. Which complex compound is most stable? [NEET 2023]
   (a) $[Co(NH_3)_6]_2(SO_4)_3$
   (b) $[Co(NH_3)_4(H_2O)Br](NO_3)_2$
   (c) $[Co(NH_3)_3(NO_3)_3]$
   (d) $[CoCl_2(en)_2]NO_3$

Sol. (d)

7. Ethylene diaminetetraacetate (EDTA) ion is: [NEET 2021]
   (a) Unidentate ligand
   (b) Bidentate ligand with two "N" donor atoms
   (c) Tridentate ligand with three "N" donor atoms
   (d) Hexadentate ligand with four "O" and two "N" donor atoms

Sol. (d)

Homoleptic and Heteroleptic Complexes

Homo-leptic complex Same Ligand	Hetero-leptic complex Different Ligand
Complex in which a metal is bound to only one kind of donor ligands. $[Co(H_2O)_6]^{2+}$: only one type of ligand	Complex in which a metal is bound to more than one kind of donor ligands. $[Co(H_2O)_4Br_2]$: Two different ligands.

8. Which of the following complex is homoleptic? [01 Feb, 2024 (Shift-I)]
   (a) $[Ni(CN)_4]^{2-}$ (b) $[Ni(NH_3)_2Cl_2]$ (c) $[Fe(NH_3)_4Cl_2]^+$ (d) $[Co(NH_3)_4Cl_2]^+$

Sol. (a)

9. Given below are two statements: [NE[illegible] 2024]
   Statement I: $[Co(NH_3)_6]^{3+}$ is a homoleptic complex w[illegible]reas [C[illegible]$(NH_3)_4Cl_2]^+$ i[illegible]eroleptic complex.
   Statement II: Complex $[Co(NH_3)_6]^{3+}$ has only one kind of ligands but $[Co(NH_3)_4Cl_2]^+$ has more than one kind of ligands.
   In the light of the above statements, choose the correct answer from the options given below:
   (a) Statement I is true but Statement II is false.
   (b) Statement I is false but Statement II is true.
   (c) Both Statement I and Statement II are true.
   (d) Both Statement I and Statement II are false.

Sol. (c)

Coordination Number

No. of ligand donor atoms to which the metal is directly bonded.

Coordination number = No. of ligands × Denticity

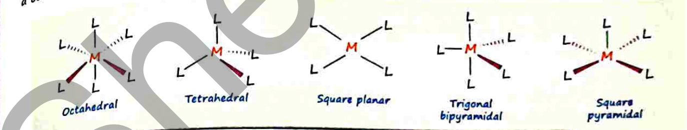
$[Co(NH_3)_6]^{3+}$ ⇒ Coordination number = No. of ligands × Denticity = 6 × 1 = 6

$[Co(en)_3]^{2+}$ ⇒ Coordination number = 3 × 2 = 6

$[Ni(NH_3)_4]^{2+}$ ⇒ Coordination number = 4 × 1 = 4

Coordination Polyhedron

The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a co-ordination polyhedron about the central atom.



Shapes of Different Coordination Polyhedra

M represents the central atom/ion and L, a unidentate ligand.

Oxidation State of Central Metal

If x is the oxidation state of central metal then

x + sum of charges on total ligands = charge on coordination sphere

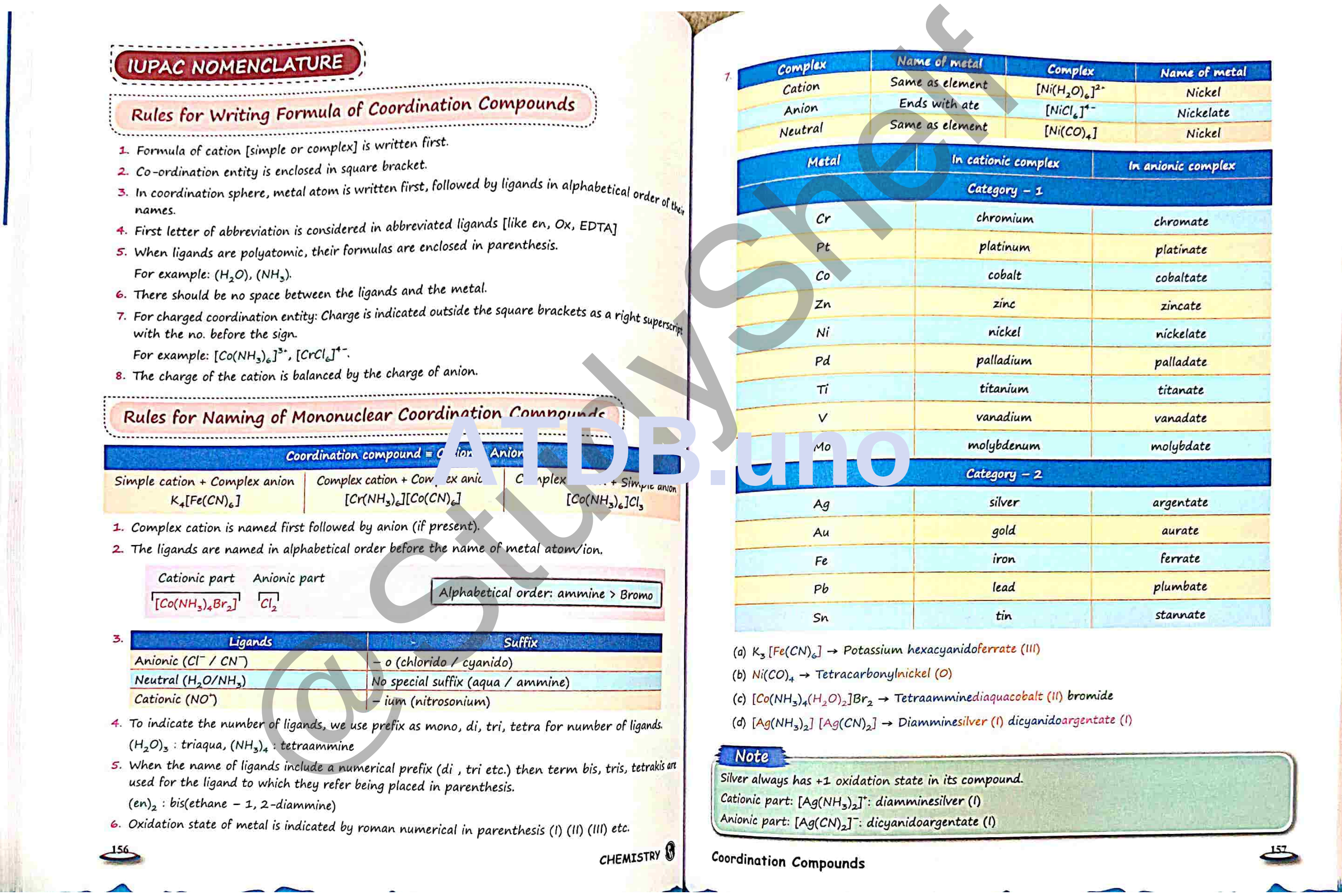
1.	[C[illegible]NH_3[illegible]$]^{3+}$	x [illegible] 6 (charge on NH_3) = + 3 x [illegible] 6 × 0 = + 3, then x = + 3
2.	$K_2[Ni(CN)_4]$	2(charge on K^+) + x + 4 (charge on CN^-) = 0 2(1) + x + 4 (−1) = 0 then x = +2
3.	$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$	oxidation state of Cr + 6(charge on H_2O) + 3(charge on Cl^-) = 0 x + 6(0) + 3(−1) = 0, then x = +3
4.	$Ni(CO)_4$	oxidation state of Ni + 4 (charge on CO) = 0 x + 4 (0) = 0 then x = 0

10. The coordination environment of Ca^{2+} ion in its complex with $EDTA^{4-}$ is: [09 April, 2024 (Shift-II)]
    (a) tetrahedral (b) octahedral (c) square planar (d) trigonal prismatic

Sol. (b)

11. The sum of coordination number and oxidation number of the metal M in the complex $[M(en)_2(C_2O_4)]Cl$ (where en is ethylenediamine) is: [NEET 2015 Re]
    (a) 6 (b) 7 (c) 8 (d) 9

Sol. (d)



IUPAC NOMENCLATURE

Rules for Writing Formula of Coordination Compounds

1. Formula of cation [simple or complex] is written first.
2. Co-ordination entity is enclosed in square bracket.
3. In coordination sphere, metal atom is written first, followed by ligands in alphabetical order of their names.
4. First letter of abbreviation is considered in abbreviated ligands [like en, Ox, EDTA]
5. When ligands are polyatomic, their formulas are enclosed in parenthesis.
   For example: (H_2O), (NH_3).
6. There should be no space between the ligands and the metal.
7. For charged coordination entity: Charge is indicated outside the square brackets as a right superscript with the no. before the sign.
   For example: $[Co(NH_3)_6]^{3+}$, $[CrCl_6]^{4-}$.
8. The charge of the cation is balanced by the charge of anion.

Rules for Naming of Mononuclear Coordination Compounds

Coordination compound ≡ Cation + Anion		
Simple cation + Complex anion $K_4[Fe(CN)_6]$	Complex cation + Complex anion $[Cr(NH_3)_6][Co(CN)_6]$	Complex cation + Simple anion $[Co(NH_3)_6]Cl_3$

1. Complex cation is named first followed by anion (if present).
2. The ligands are named in alphabetical order before the name of metal atom/ion.

Cationic part	Anionic part
$[Co(NH_3)_4Br_2]$	Cl_2

Alphabetical order: ammine > Bromo

3.

Ligands	Suffix
Anionic (Cl^- / CN^-)	– o (chlorido / cyanido)
Neutral (H_2O/NH_3)	No special suffix (aqua / ammine)
Cationic (NO^+)	– ium (nitrosonium)

4. To indicate the number of ligands, we use prefix as mono, di, tri, tetra for number of ligands.
   $(H_2O)_3$: triaqua, $(NH_3)_4$: tetraammine
5. When the name of ligands include a numerical prefix (di , tri etc.) then term bis, tris, tetrakis are used for the ligand to which they refer being placed in parenthesis.
   $(en)_2$: bis(ethane – 1, 2-diammine)
6. Oxidation state of metal is indicated by roman numerical in parenthesis (I) (II) (III) etc.

7.

Complex	Name of metal	Complex	Name of metal
Cation	Same as element	$[Ni(H_2O)_6]^{2+}$	Nickel
Anion	Ends with ate	$[NiCl_6]^{4-}$	Nickelate
Neutral	Same as element	$[Ni(CO)_4]$	Nickel

Metal	In cationic complex	In anionic complex
Category – 1		
Cr	chromium	chromate
Pt	platinum	platinate
Co	cobalt	cobaltate
Zn	zinc	zincate
Ni	nickel	nickelate
Pd	palladium	palladate
Ti	titanium	titanate
V	vanadium	vanadate
Mo	molybdenum	molybdate
Category – 2		
Ag	silver	argentate
Au	gold	aurate
Fe	iron	ferrate
Pb	lead	plumbate
Sn	tin	stannate

(a) $K_3[Fe(CN)_6]$ → Potassium hexacyanidoferrate (III)
(b) $Ni(CO)_4$ → Tetracarbonylnickel (O)
(c) $[Co(NH_3)_4(H_2O)_2]Br_2$ → Tetraamminediaquacobalt (II) bromide
(d) $[Ag(NH_3)_2]$ $[Ag(CN)_2]$ → Diamminesilver (I) dicyanidoargentate (I)

Note

Silver always has +1 oxidation state in its compound.
Cationic part: $[Ag(NH_3)_2]^+$: diamminesilver (I)
Anionic part: $[Ag(CN)_2]^-$: dicyanidoargentate (I)

8. If there is any water of crystallization, it is to included in the name. For example, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ → Tetraaquadichloridochromium (III) chloride-2-water or Tetraaquadichloridochromium (III) chloride dihydrate

S.No.	Formula of Complex Compound	IUPAC Name
1.	$K_3[Co(NO_2)_6]$	Potassium hexanitrito-N-cobaltate(III)
2.	$[Ni(dmg)_2]$	Bis(dimethylglyoximato)nickel(II)
3.	$Na_2[Fe(CN)_5(NO^+)]$	Sodium pentacyanidonitrosoniumferrate(II)
4.	$[Fe(H_2O)_5(NO^+)]SO_4$	Pentaaquanitrosoniumiron(I)sulphate
5.	$[Cu(CN)_4]^{3-}$	Tetracyanidocuperate(I)ion
6.	$[Co(NH_3)_5(CO_3)]Cl$	Pentaamminecarbonatocobalt(III) chloride
7.	$[Cr(CO)_5(PPh_3)]$	Pentacarbonyltriphenylphosphinechromium(O)
8.	$(NH_4)[Cr(NH_3)_2(NCS)_4]$	Ammonium diamminetetra(thiocyanato-N) chromate (III)
9.	$[Pt(NH_3)_2Cl_4]$	Diamminetetrachloridoplatinum (IV)
10.	$[NiCl_2(PPh_3)_2]$	Dichloridobis(triphenylphosphine)nickel (II)
11.	$[Cr(NH_3)_3(H_2O)_3]Cl_3$	Triamminetriaquachromium (III) chloride
12.	$[Pt(NH_3)_5Cl]Br_3$	Pentaamminechloridoplatinum (IV) bromide
13.	$(NH_4)_2[Ni(C_2O_4)_2(H_2O)_2]$	Ammonium diaquadioxalatonickelate (II)
14.	$[Pt(H_2NCH_2CH_2NH_2)_2Cl_2]Cl_2$	Dichloridobis(ethylenediamine)platinum (IV) chloride
15.	$Fe(CO)_5$	Pentacarbonyliron (O)
16.	$[Rh(NH_3)_5I]I_2$	Pentaammineiodidorhodium (III) iodide
17.	$[Fe(C_2O_4)_3]^{3-}$	Trioxalatoferrate(III) ion
18.	$[Cu(NH_3)_4]SO_4$	Tetraamminecopper(II) sulphate
19.	$NaCr(OH)_4$: Na^+ $[Cr(OH)_4]^-$	Sodium tetrahydroxidochromate (III)
20.	$[Co(gly)_3]$	Triglycinatocobalt(III)
21.	$[Fe(H_2O)_5(SCN)]^{2+}$	Pentaaquathiocyanato-S-iron(III) ion
22.	$K_2[HgI_4]$	Potassium tetraiodidomercurate (II)
23.	$Co[Hg(SCN)_4]$	Cobalt (II)tetrathiocyanato-S-mercurate(II)
24.	$Fe_4[Fe(CN)_6]_3$	Iron (III) hexacyanidoferrate(II)

S.No.	IUPAC Name	Formula of Complex Compound
1.	Dicyanidoaurrate(I)ion	$[Au(CN)_2]^-$
2.	Sodium hexafluoridoaluminate(III)	$Na_3[AlF_6]$
3.	Diamminetriaquahydroxidochromium(III) nitrate	$[Cr(NH_3)_2(H_2O)_3(OH)](NO_3)_2$
4.	Barium dihydroxidodinitrito-O-oxalatozirconate (IV)	$Ba[Zr(OH)_2(ONO)_2(ox)]$
5.	Decacarbonyldimanganese (O)	$[(CO)_5Mn-Mn(CO)_5]$
6.	Pentaamminedinitrogenruthenium(II) chloride	$[Ru(NH_3)_5N_2]Cl_2$
7.	Tetrapyridineplatinum(II) tetrachloridoplatinate (II)	$[Pt(py)_4][PtCl_4]$

12. As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is (IIT JEE 2012)
(a) tetraaquadiaminecobalt (III) chloride (b) tetraaquadiamminecobalt (III) chloride
(c) diaminetetraaquacobalt (III) chloride (d) diamminetetraaquacobalt (III) chloride

Sol. (d)

13. The IUPAC name for $[Ni(NH_3)_4][NiCl_4]$ is (IIT JEE 2008)
(a) Tetrachloronickel (II), tetraamminenickel (II)
(b) Tetraamminenickel (II) tetrachloronickel (II)
(c) Tetraamminenickel (II) tetrachloronickelate (II)
(d) Tetrachloronickel (II) tetraamminenickelate (O)

Sol. (c)

14. Homoleptic complex from the following complexes is: [NEET 2023]
(a) Triamminetriaquachromium (III) chloride
(b) Potassium trioxalatoaluminate (III)
(c) Diamminechloridonitrito – N- platinum(II)
(d) Pentaamminecarbonatocobalt (III) chloride

Sol. (b)

15. The IUPAC name of the complex- $[Ag(H_2O)_2][Ag(CN)_2]$ is: [NEET 2022]
(a) diaquasilver(I) dicyanidoargentate(I) (b) dicyanidosilver(II) diaquaargentate(II)
(c) diaquasilver(II) dicyanidoargentate(II) (d) dicyanidosilver(I) diaquaargentate(I)

Sol. (a)

TESTS TO CONFIRM STRUCTURE OF COORDINATION COMPOUNDS

Aq. $AgNO_3$ Test

☐ $[Cr(NH_3)_5Cl]Cl_{2(aq)} \xrightarrow[\text{excess}]{AgNO_3} 2AgCl\downarrow$ (White ppt.)

$[Cr(NH_3)_5Cl]Cl_2 \equiv [Cr(NH_3)_5Cl]^{2+}2Cl^-$

[2 moles of white ppt (AgCl) indicates that $2Cl^-$ ions are outside the coordination sphere]

☐ $[Cr(NH_3)_5Cl]Br_{2(aq)} \xrightarrow[\text{excess}]{AgNO_3} 2AgBr\downarrow$ (Yellow ppt.)

$[Cr(NH_3)_5Cl]Br_2 \equiv [Cr(NH_3)_5Cl]^{2+}2Br^-$

[2 moles of yellow ppt (AgBr) indicates that $2Br^-$ ions are outside the coordination sphere]

$BaSO_4$ Test

☐ $[Cr(NH_3)_5Cl]SO_{4(aq)} \xrightarrow[\text{excess}]{BaCl_2(aq.)} BaSO_4\downarrow$ (White)

$[Cr(NH_3)_5Cl]SO_4 \equiv [Cr(NH_3)_5Cl]^{2+}SO_4^{2-}$

[White ppt with $BaCl_2$ indicates presence of SO_4^{2-} ion outside the coordination sphere]

☐ $[Cr(NH_3)_5(SO_4)]Cl \xrightarrow[\text{excess}]{Ba(NO_3)_2}$ No ppt

This indicates that SO_4^{2-} ion [illegible] not present outside the coordination sphere.

16. Mixture X = 0.02 mole of $[Co(NH_3)_5SO_4]Br$ and 0.02 mole of $[Co(NH_3)_5Br]SO_4$ was prepared in 2L of solution.

1L of mixture X+ excess $AgNO_3 \rightarrow Y$

1L of mixture X+ excess $BaCl_2 \rightarrow Z$

Number of moles of Y and Z are (IIT JEE 2003)

(a) 0.01, 0.01 (b) 0.02, 0.01 (c) 0.01, 0.02 (d) 0.02, 0.02

Sol. (a) In 1L of solution, 0.01 mole of each $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$ will be present. Adding of excess of $AgNO_3$ will give 0.01 mole of AgBr. On adding of excess $BaCl_2$, 0.01 mole of $BaSO_4$ will be formed.

17. The correct order of the stoichiometries of AgCl formed when $AgNO_3$ in excess is treated with the complexes: $CoCl_3.6NH_3$, $CoCl_3.5NH_3$ $CoCl_3.$ $4NH_3$ respectively is: (MR^+) [NEET 2017-Delhi]

(a) 2AgCl, 3AgCl, 1AgCl (b) 1AgCl, 3AgCl, 2AgCl

(c) 3AgCl, 1AgCl, 2AgCl (d) 3AgCl, 2AgCl, 1AgCl

Sol. (d)

18. Cobalt(III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test for chloride ions with silver nitrate at 25°C? [NEET 2015]

(a) $CoCl_3.4NH_3$ (b) $CoCl_3.5NH_3$ (c) $CoCl_3.6NH_3$ (d) $CoCl_3.3NH_3$

Sol. (d)

Molar Conductivity Measurement

☐ Molar conductivity $\propto$ No. of Charges

	No. of Charges	Molar Conductivity (ohm^{-1} cm^2 mol^{-1})
LiCl	Li^+ $Cl^- \equiv 2$	112
$MgCl_2$	Mg^{2+} $2Cl^- \equiv 4$	260.8
$LaCl_3$	La^{3+} $3Cl^- \equiv 6$	393.5

☐ a. $[Cr(NH_3)_4Cl_2]Cl \equiv [Cr(NH_3)_4Cl_2]^+Cl^- \longrightarrow$ No. of charges = 2

b. $[Cr(NH_3)_5Cl]Cl_2 \equiv [Cr(NH_3)_5Cl]^{2+}2Cl^- \longrightarrow$ No. of charges = 4

Order of molar conductivity: a < b

19. Consider the following complexes:

(i) K_2PtCl_6 (ii) $PtCl_4{\cdot}2NH_3$ (iii) $PtCl_4{\cdot}3NH_3$ (iv) $PtCl_4{\cdot}5NH_3$

their electrical conductance in aqueous solutions are:

(a) 2[illegible], [illegible] 97, 404 (b) 404, 0, 97, 256

(c) 2[illegible], [illegible], 0, [illegible] (d) 404, 97, 256, 0

Sol. (a) The electrical conductance of the complexes depend upon the number of ions given by them in the aqueous solutions.

(i) $K_2[PtCl_6] \xrightleftharpoons{aq} 2K^+ + [PtCl_6]^{2-}$

(ii) $[Pt(NH_3)_2Cl_4] \xrightleftharpoons{aq} [Pt(NH_3)_2Cl_4]$

(iii) $[Pt(NH_3)_3Cl_3]Cl \xrightleftharpoons{aq} [Pt(NH_3)_3Cl_3]^+ + Cl^-$

(iv) $[Pt(NH_3)_5Cl]Cl_3 \xrightleftharpoons{aq} [Pt(NH_3)_5Cl]^{3+} + 3Cl^-$

Cryoscopic Measurement

The reduction in the freezing point of solvents due to the addition of solutes (salt).

☐ Depression in freezing point $\propto$ no of particles

☐ LiCl $\rightarrow Li^+ + Cl^-$ $\Rightarrow$ No of particles ≡ 2

$MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$ $\Rightarrow$ No of particles ≡ 3

Depression in freezing point: LiCl < $MgCl_2$

☐ a. $[Cr(NH_3)_5Cl]Cl_2 \Rightarrow$ No of particles ≡ 3

b. $[Cr(NH_3)_4Cl_2]Cl \Rightarrow$ No of particles ≡ 2

Depression in freezing point: a > b

20. Arrange the following compounds in order of increasing molar conductivity.

(a) $K[Co(NH_3)_2(NO_2)_4]$ (b) $[Cr(NH_3)_3(NO_2)_3]$

(c) $[Cr(NH_3)_5(NO_2)](NO_2)_2$ (d) $[Cr(NH_3)_6]Cl_3$

Sol. As the charge increases, molar conductivity increases.

(a) $K[Co(NH_3)_2(NO_2)_4] \rightarrow$ Charge = 2 (b) $[Cr(NH_3)_3(NO_2)_3] \rightarrow$ Charge = 0

(c) $[Cr(NH_3)_5(NO_2)](NO_2)_2 \rightarrow$ Charge = 4 (d) $[Cr(NH_3)_6]Cl_3 \rightarrow$ Charge = 6

(b) < (a) < (c) < (d) : Molar conductivity

Establishing the Structure of Complexes

Formula	Cryoscopic measurement	Molar conductivity	Structure
$CoCl_3 \cdot 6NH_3$	4 particles	6 charges	$[Co(NH_3)_6]^{3+}\ 3Cl^-$
$CoCl_3 \cdot 5NH_3$	3 particles	4 charges	$[Co(NH_3)_5Cl]^{2+}\ 2Cl^-$
$CoCl_3 \cdot 4NH_3$	2 particles	2 charges	$[Co(NH_3)_4Cl_2]^+ Cl^-$
$CoCl_3 \cdot 3NH_3$	1 particle	0 charge	$[Co(NH_3)_3Cl_3]$
$Co(NO_2)_3\ KNO_2 \cdot 2NH_3$	2 particles	2 charges	$K^+\ [Co(NH_3)_2(NO_2)_4]^-$
$Co(NO_2)_3 \cdot 2KNO_2 \cdot NH_3$	3 particles	4 charges	$2K^+\ [Co(NH_3)(NO_2)_5]^{2-}$
$Co(NO_2)_3 \cdot 3KNO_2$	4 particles	6 charges	$3K^+\ [Co(NO_2)_6]^{3-}$

Dehydrating Agents-Conc. H_2SO_4, P_2O_5

- ☐ $[Cr(H_2O)_4Cl_2]Cl \xrightarrow{\text{Conc } H_2SO_4}$ No reaction [No loss of weight]

  Molar Mass ≡ x g/mol

- ☐ $[Cr(H_2O)_4Cl_2]Cl.H_2O \xrightarrow[H_2SO_4]{\text{Conc}} [Cr(H_2O)_4Cl_2]Cl + H_2O$ [Loss of 1 mole H_2O ≡ loss of 18 g/mol]

  Molar Mass ≡ y Molar Mass ≡ y – 18 g/mol

- ☐ $[Cr(H_2O)_4Cl_2]Cl.2H_2O \xrightarrow[H_2SO_4]{\text{Conc}} [Cr(H_2O)_4Cl_2]Cl + 2H_2O$ [Loss of 2 moles of H_2O ≡ loss of 36 g/mol]

  Molar Mass ≡ z z – 2 × 18 ≡ Z – 36 g/mol

Loss of weight by using dehydrating agent → c > b > a

21. Which of the following complexes will be dehydrated to relatively minimum extent by conc. H_2SO_4 under identical condition.

(a) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (b) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

(c) $[Cr(H_2O)_6]Cl_3$ (d) All of these

Sol. (c) Under identical conditions, the complex $[Cr(H_2O)_6]Cl_3$ will be dehydrated the least by concentrated H_2SO_4 because the water molecules are directly coordinated to the metal ion, making them less likely to be removed.

22. Complex A has a composition of $H_{12}O_6Cl_3Cr$. If the complex on treatment with conc. H_2SO_4 loses 13.5% of its original mass, the correct molecular formula of A is:
[Given: atomic mass of Cr = 52 amu and Cl = 35 amu]
[03 Sep, 2020 (Shift-II)]

(a) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$
(b) $[Cr(H_2O)_6]Cl_3$
(c) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
(d) $[Cr(H_2O)_3Cl_3] \cdot H_2O$

Sol. (a) Here, conc. H_2SO_4 acts as a dehydrating agent.
Molar mass of given complex = 265 g/mol
On treating with conc. H_2SO_4 the mass lost by the complex is:

$$= \frac{13.5}{100}(265) \approx 36g = 2 \text{ moles of } H_2O$$

Hence, the formula of the complex = $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

WERNER'S THEORY

Werner was the first to formulate his idea about the structures of coordination compounds. The main postulates are:

1. In coordination compounds metals show two types of valency:
   (a) Primary Valency (b) Secondary Valency
2. The primary valencies are normally ionisable and are satisfied by negatively charged ions.
3. The secondary valencies are non-ionisable. These are satisfied by neutral molecules or negatively charged ions.
4. The ions/groups bounded by secondary valency to metal have spatial arrangements corresponding to different coordination number.

VALENCIES OF METAL

Primary Valency

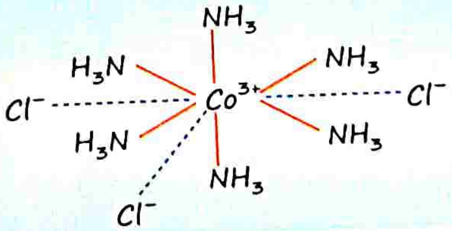
- ☐ Ionisable Valency
- ☐ Non-directional in nature
- ☐ Primary valencies are satisfied by negatively charged ions.
- ☐ Primary valency ≡ oxidation state of metal.
- ☐ It is represented by dotted line (......)

Secondary Valency

- ☐ Non-ionisable Valency
- ☐ Directional in nature
- ☐ Secondary valencies are satisfied by neutral molecules or negatively charged charged ions or both
- ☐ Secondary valency ≡ coordination number of metal.
- ☐ It is represented by solid line (_____).

Example: $\boxed{CoCl_3.6NH_3 = [Co(NH_3)_6]Cl_3}$

Primary Valency → 3
Secondary valency → 6



Modern Formulation

Primary valency ≡ oxidation state of metal. Secondary valency ≡ coordination number of metal.

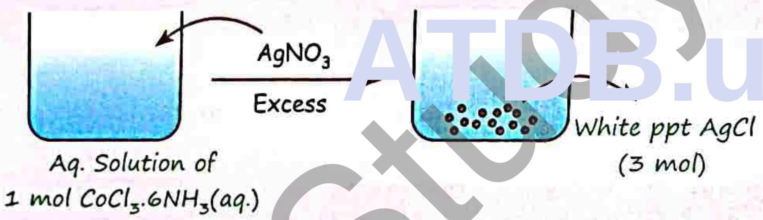
Complex	Primary Valency/Oxidation state	Secondary Valency/Coordination No.
$[Co(NH_3)_6]Cl_3$	3 (this valency is satisfied by $3Cl^-$)	6 (this valency is satisfied by $6NH_3$)
$[Co(NH_3)_5Cl]Cl_2$	+3 (this valency is satisfied by $3Cl^-$)	5 + 1 = 6 (this valency is satisfied by $5NH_3$ and $1Cl^-$)
$[Co(NH_3)_4Cl_2]Cl$	+3 (this valency is satisfied by $3Cl^-$)	4 + 2 = 6 (this valency is satisfied by $4NH_3$ and $2Cl^-$)

Experiments

1. Precipitation Reaction with $AgNO_3$

In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of chloride ions could be precipitated as AgCl on adding excess $AgNO_3$ solution but some remained in solution.

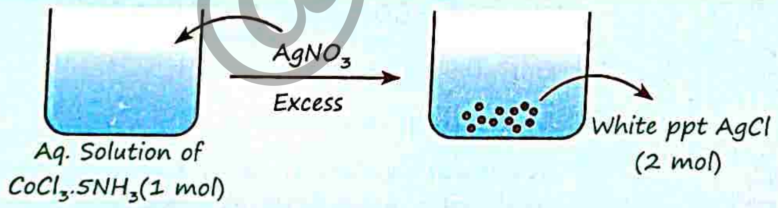
(a)



☐ It means that 3 mol Cl^- were present in aq. solution of $CoCl_3.6NH_3$

$$CoCl_3.6NH_3 \equiv [Co(NH_3)_6]Cl_3 \equiv [Co(NH_3)_6]^{3+}.3Cl^- \xrightarrow[Excess]{AgNO_3} 3\ AgCl\downarrow$$

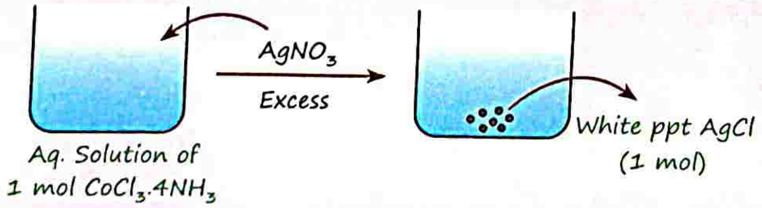
(b)



☐ It means that 2 mol Cl^- were present in aq. Solution of $CoCl_3.5NH_3$

$$CoCl_3.5NH_3 \equiv [Co(NH_3)_5Cl]Cl_2 \equiv [Co(NH_3)_5Cl]^{2+}\ 2Cl^- \xrightarrow[Excess]{AgNO_3} 2AgCl\downarrow$$

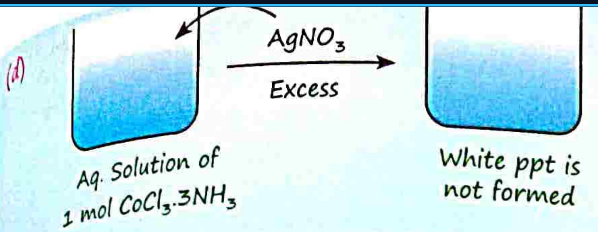
(c)



☐ It means that 1 mol Cl^- was present in aq. Solution of $CoCl_3.4NH_3$

$$CoCl_3.4NH_3 \equiv [Co(NH_3)_4Cl_2]Cl \equiv [Co(NH_3)_4Cl_2]^{+}Cl^- \xrightarrow[Excess]{AgNO_3} AgCl\downarrow$$

(d)



☐ It means that Cl^- was not present in aq. Solution of $CoCl_3.3NH_3$

$$CoCl_3.3NH_3 \equiv [Co(NH_3)_3Cl_3] \xrightarrow[\text{Excess}]{AgNO_3} \text{ppt is not formed.}$$

2. Measurement of Conductivity

Conductivity of a solution is proportional to no. of ions present in solution.

	$CoCl_3.6NH_3$	$CoCl_3.5NH_3$	$CoCl_3.4NH_3$
Modern Representation	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_4Cl_2]Cl$
Ions in aq. solution	$[Co(NH_3)_6]^{3+}$ $3Cl^-$	$[Co(NH_3)_5Cl]^{2+}$ $2Cl^-$	$[Co(NH_3)_4Cl_2]^+$ Cl^-
Solution conductivity corresponds to	1 : 3 Electrolyte	1 : 2 Electrolyte	1 : 1 Electrolyte
No. of ions in aq. solution	4	3	2

Order of conductivity: $CoCl_3.6NH_3 > CoCl_3.5NH_3 > CoCl_3.4NH_3$

	(a) $CrCl_3.6H_2O$	(b) $CrCl_3.5H_2O$	(c) $CrCl_3.4H_2O$	(d) $CrCl_3.3H_2O$
Modern Representation	$[Cr(H_2O)_6]Cl_3$	$[Cr(H_2O)_5Cl]$ Cl_2	$[Cr(H_2O)_4Cl_2]$ Cl	$[Cr(H_2O)_3Cl_3]$
Ions	$[Cr(H_2O)_6]^{3+}$, $3Cl^-$	$[Cr(H_2O)_5Cl]^{2+}$, $2Cl^-$	$[Cr(H_2O)_4Cl_2]^+$, Cl^-	$[Cr(H_2O)_3Cl_3]$
No of particles	4	3	2	1
Depression in freezing point	a > b > c > d			
No of charges	6	4	2	0
Molar Conductivity	a > b > c > d			

23. An octahedral complex with the formula $CoCl_3 . nNH_3$ upon reaction with excess of $AgNO_3$ solution given 2 moles of AgCl. Consider the oxidation state of Co in the complex is 'x'. The value of "x + n" is ______ . [08 April, 2024 (Shift-I)]

(a) 3 (b) 6 (c) 8 (d) 5

Sol. (c) $[Co(NH_3)_5Cl]Cl_2$ + excess $AgNO_3 \rightarrow 2AgCl$ (2 moles)

- $x + 0 - 1 - 2 = 0$ then $x = +3$

∴ The oxidation state (x) of Co = +3 and n = 5

Therefore, x + n = 8

24. The conductivity of a solution of complex with formula $CoCl_3(NH_3)_4$ corresponds to 1 : 1 electrolyte, then the primary valency of central metal ion is ________. [27 July, 2022 (Shift-I)]

Sol. [3] Complex is $[Co(NH_3)_4Cl_2]Cl$

Primary valency = oxidation no. = +3.

25. Complex X of composition $Cr(H_2O)_6Cl_n$ has a spin only magnetic moment of 3.83 BM. It reacts with $AgNO_3$ and shows geometrical isomerism. The IUPAC nomenclature of X is: [9 Jan, 2020 (Shift-II)]

(a) Dichloridotetraquachromium (IV) chloride dihydrate

(b) Hexaaquachromium (III) chloride

(c) Tetraaquadichloridochromium (III) chloride dihydrate

(d) Tetraaquadichloridochromium (IV) chloride dihydrate

Sol. (c) $Cr(H_2O)_6Cl_n \longrightarrow \mu_{spin} = 3.83$ B.M.

From data of magnetic moment it is clear that 3 unpaired electrons are present, so oxidation number of Cr should be +3.

- Complex shows geometrical isomerism and reacts with $AgNO_3$ therefore, formula of complex is $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$.

IUPAC Name: Tetraaquadichloridochromium(III) chloride dihydrate.

26. The primary and secondary valencies of cobalt respectively in $[Co(NH_3)_4Cl_2]$ are: (2023/24 Jan/Shift-1)

(a) 3 and 5 (b) 2 and 6 (c) 2 and 8 (d) 3 and 6

Sol. (b)

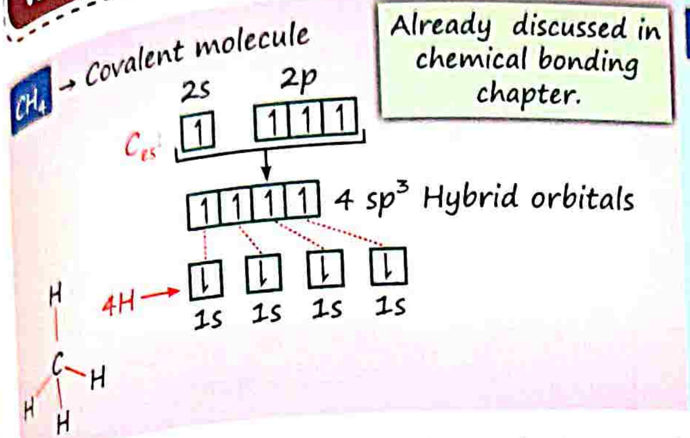
27. Write the modern representation and secondary valency of following compounds, if moles of AgCl precipitated with excess of $AgNO_3$ is given?

$PtCl_2.2NH_3$, $CoCl_3.4NH_3$, $PtCl_4.2HCl$, $NiCl_2.6H_2O$, $PdCl_2.4NH_3$

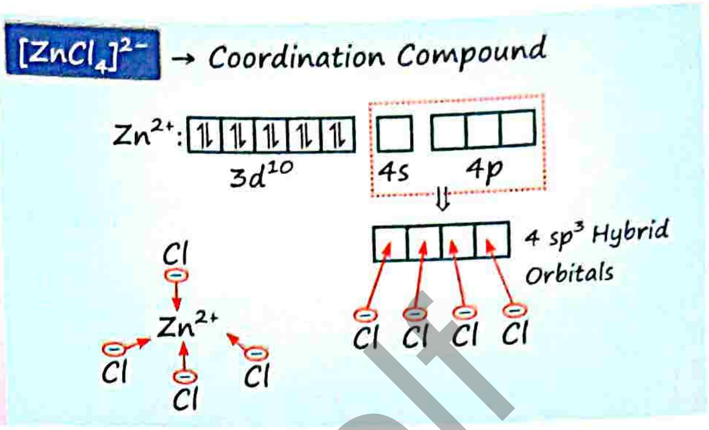
Sol.

Molecular Formula	Moles of AgCl precipitated with excess of $AgNO_3$	Compound	Secondary valency (Coordination number)
$PtCl_2.2NH_3$	0	$[Pt(NH_3)_2Cl_2]$	4
$CoCl_3.4NH_3$	1	$[Co(NH_3)_4Cl_2]Cl$	6
$PtCl_4.2HCl$	0	$H_2[PtCl_6]$	6
$NiCl_2{\cdot}6H_2O$	2	$[Ni(H_2O)_6]Cl_2$	6
$PdCl_2.4NH_3$	2	$[Pd(NH_3)_4]Cl_2$	4

VALENCE BOND THEORY



Already discussed in chemical bonding chapter.



- According to VBT, the central metal atom or ion uses its vacant s, p and d orbitals to undergo hybridization, forming a set of hybrid orbitals (vacant).
- The vacant hybrid orbitals of the metal then overlap with the filled orbitals of the ligands, which are electron-pair donors. This overlap leads to the formation of coordinate covalent bonds, where the electron pair is donated by the ligand to the metal.

Coordination number	Type of hybridisation	Shape of complex	Types of d-orbitals
4	sp^3	Tetrahedral	-
4	dsp^2	Square planar	$d_{x^2-y^2}$
4	d^3s	Tetrahedral	d_{xy}, d_{yz}, d_{xz}
6	sp^3d^2	Octahedral	$d_{x^2-y^2} \cdot d_{z^2}$
6	d^2sp^3	Octahedral	$d_{x^2-y^2}, d_{z^2}$

Note

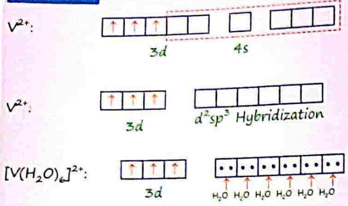
Every type of hybridisation involves s orbital. So, it is necessary to vacate the s orbital of central metal before hybridisation.

Hybridisation in Octahedral Complex

Inner Orbital Complex

If inner (n-1) d orbitals of metal are used in hybridization with outer 's' and 'p' orbitals then such hybridization is known as inner orbital hybridization. A complex having such hybridization is known as inner orbital complex (IOC).

$[V(H_2O)_6]^{2+}$ V^{2+} : $[Ar]4s^0\ 3d^3$



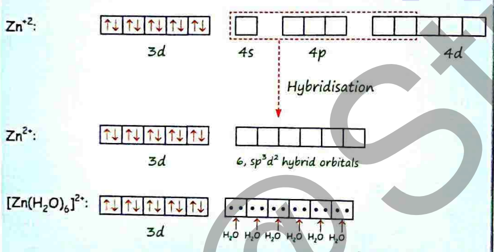
- ☐ Two 3d orbitals are vacant in V^{2+} ion.
- ☐ So, two 3d orbitals, one 4s and three 4p orbitals are going to take part in hybridisation.

- ☐ After hybridization six d^2sp^3 hybrid orbitals are obtained. Now these hybrid orbitals are ready to accept electron pair from ligand.
- ☐ Here, $6H_2O$ ligands are donating lone pair in 6 vacant hybrid orbitals.
- ☐ In this hybridization, inner (n-1) d-orbitals are used (3d). So $[V(H_2O)_6]^{2+}$ is an IOC.

Outer Orbital Complex

If outer (n = valence shell) nd orbitals of metal are taking part in hybridization with 'ns' and 'np' orbitals then such hybridization is known as outer orbital hybridization. And complex having such hybridization is known as outer orbital complex [OOC].

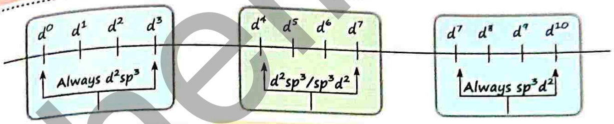
$[Zn(H_2O)_6]^{2+}$ Zn^{2+} : $4s^0\ 3d^{10}$



- ☐ No vacant orbital in 3d subshell. So, hybridization will be between 1 orbital of 4s, 3 orbitals of 4p and 2 orbitals of 4d.
- ☐ After hybridization six vacant sp^3d^2 hybrid orbitals are available for bonding.
- ☐ Here, $6H_2O$ ligands are donating lone pair in 6 vacant hybrid orbitals.

- ☐ Inner orbital complex : d^2sp^3 : Low spin complex : Spin paired complex.
- ☐ Outer orbital complex : sp^3d^2 : High spin complex : Spin free complex.

d-Scale for Hybridisation (Octahedral)



Because two inner d-orbitals are always available for hybridisation

Both type of hybridisation are possible. It can be determined by value of magnetic moment or magnetic behaviour.

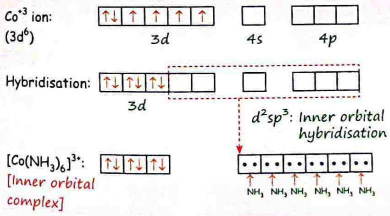
Because two inner d-orbitals are not available for hybridisation

For d^4 complex			
Complex	Magnetic Behaviour/Moment	Hybridisation	Type of complex
$[Mn(CN)_6]^{3-}$	Paramagnetic with 2 electrons (magnetic moment = 2.82)	d^2sp^3	Inner orbital complex
$[MnCl_6]^{3-}$	Paramagnetic with 4 electrons (magnetic moment = 4.89 BM)	sp^3d^2	Outer orbital complex

For d^5 complex			
Complex	Magnetic Behaviour/Moment	Hybridisation	Type of complex
$[Fe(CN)_6]^{3-}$	Paramagnetic with 1 electrons (magnetic moment = 1.73)	d^2sp^3	Inner orbital complex
$[FeF_6]^{3-}$	Paramagnetic with 5 unpaired electrons (magnetic moment = 5.92 BM)	sp^3d^2	Outer orbital complex

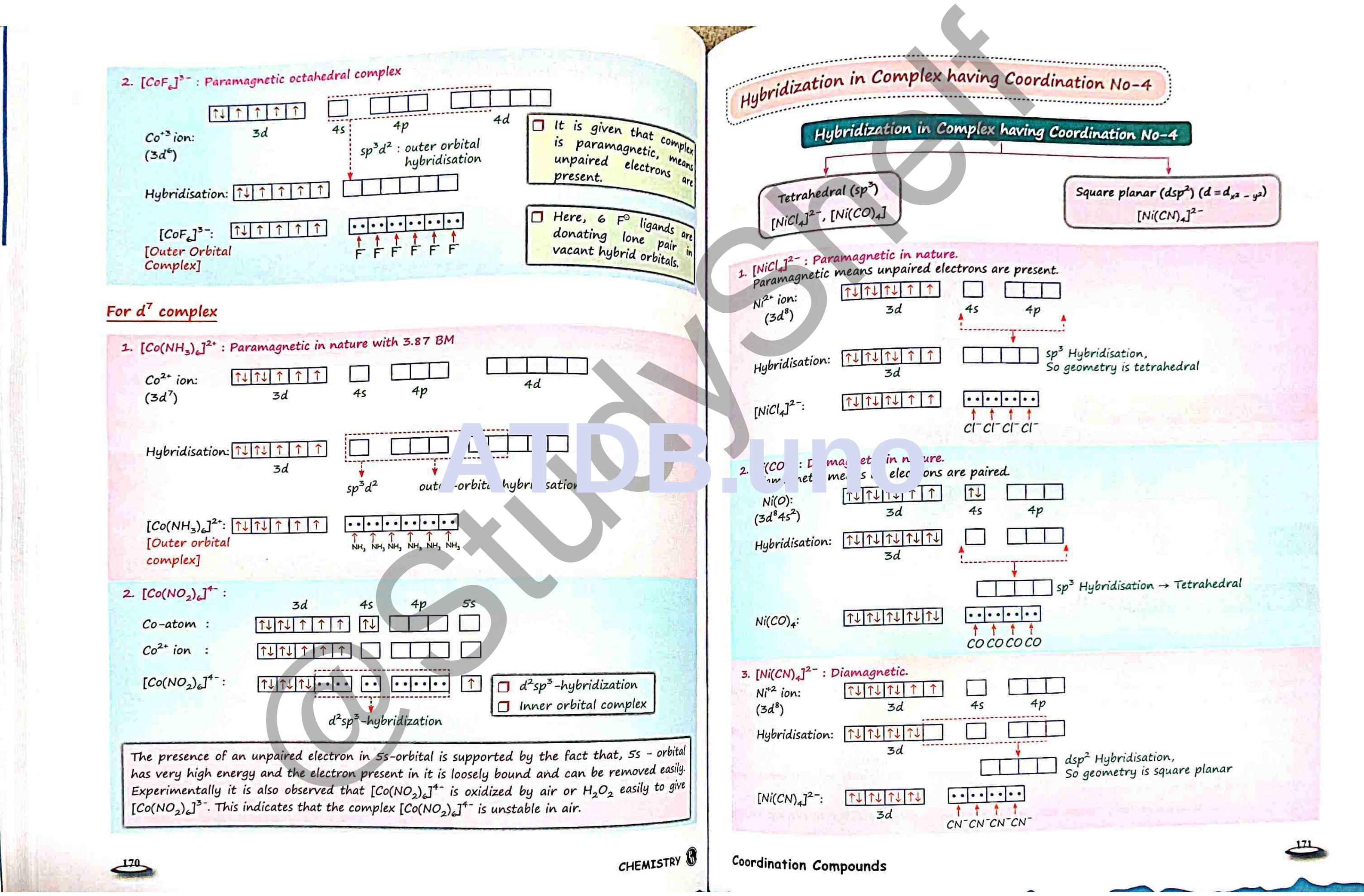
For d^6 complex

1. $[Co(NH_3)_6]^{3+}$: Diamagnetic in nature.



- ☐ It is given that complex is diamagnetic, so all electrons should be paired

- ☐ Here, 6 NH_3 ligands are donating lone pair in vacant hybrid orbitals.



2. $[CoF_6]^{3-}$: Paramagnetic octahedral complex

sp^3d^2 : outer orbital hybridisation

[Outer Orbital Complex]

☐ It is given that complex is paramagnetic, means unpaired electrons are present.

☐ Here, 6 $F^{\ominus}$ ligands are donating lone pair in vacant hybrid orbitals.

For d^7 complex

1. $[Co(NH_3)_6]^{2+}$: Paramagnetic in nature with 3.87 BM

outer-orbital hybridisation

[Outer orbital complex]

2. $[Co(NO_2)_6]^{4-}$:

d^2sp^3-hybridization

☐ d^2sp^3-hybridization
☐ Inner orbital complex

The presence of an unpaired electron in 5s-orbital is supported by the fact that, 5s - orbital has very high energy and the electron present in it is loosely bound and can be removed easily. Experimentally it is also observed that $[Co(NO_2)_6]^{4-}$ is oxidized by air or H_2O_2 easily to give $[Co(NO_2)_6]^{3-}$. This indicates that the complex $[Co(NO_2)_6]^{4-}$ is unstable in air.

Hybridization in Complex having Coordination No-4

Hybridization in Complex having Coordination No-4

Tetrahedral (sp^3)
$[NiCl_4]^{2-}$, $[Ni(CO)_4]$

Square planar (dsp^2) ($d \equiv d_{x^2-y^2}$)
$[Ni(CN)_4]^{2-}$

1. $[NiCl_4]^{2-}$: Paramagnetic in nature.
Paramagnetic means unpaired electrons are present.

sp^3 Hybridisation,
So geometry is tetrahedral

2. $Ni(CO)_4$: Diamagnetic in nature.
Diamagnetic means all electrons are paired.

sp^3 Hybridisation → Tetrahedral

3. $[Ni(CN)_4]^{2-}$: Diamagnetic.

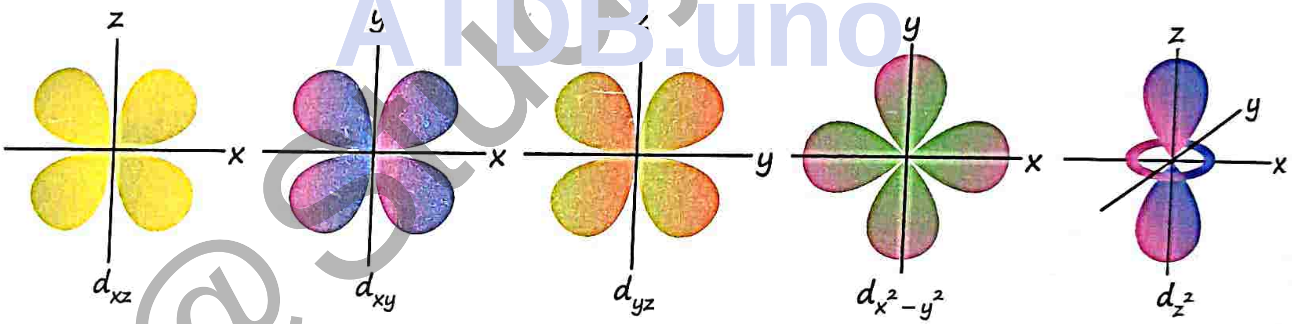
dsp^2 Hybridisation,
So geometry is square planar

Limitation of VBT

1. It involves no. of assumptions.
2. It does not explain colour of coordination compounds.
3. It does not give explanation of kinetic and thermodynamic stabilities of complex.
4. It does not distinguish between weak and strong ligands.

Metal	Coordination Number	Metal	Coordination Number
Cu^+	2, 4	Fe^{2+}	6
Ag^+	2	Fe^{3+}	6
Au^+	2, 4	Co^{2+}	4, 6
Cu^{2+}	4, 6	Co^{3+}	6
Pt^{2+}	4	Al^{3+}	6
Pd^{2+}	4	Pt^{4+}	6
Mg^{2+}	6	Pd^{4+}	6
Ni^{2+}	4, 6		

SHAPES OF d-ORBITALS

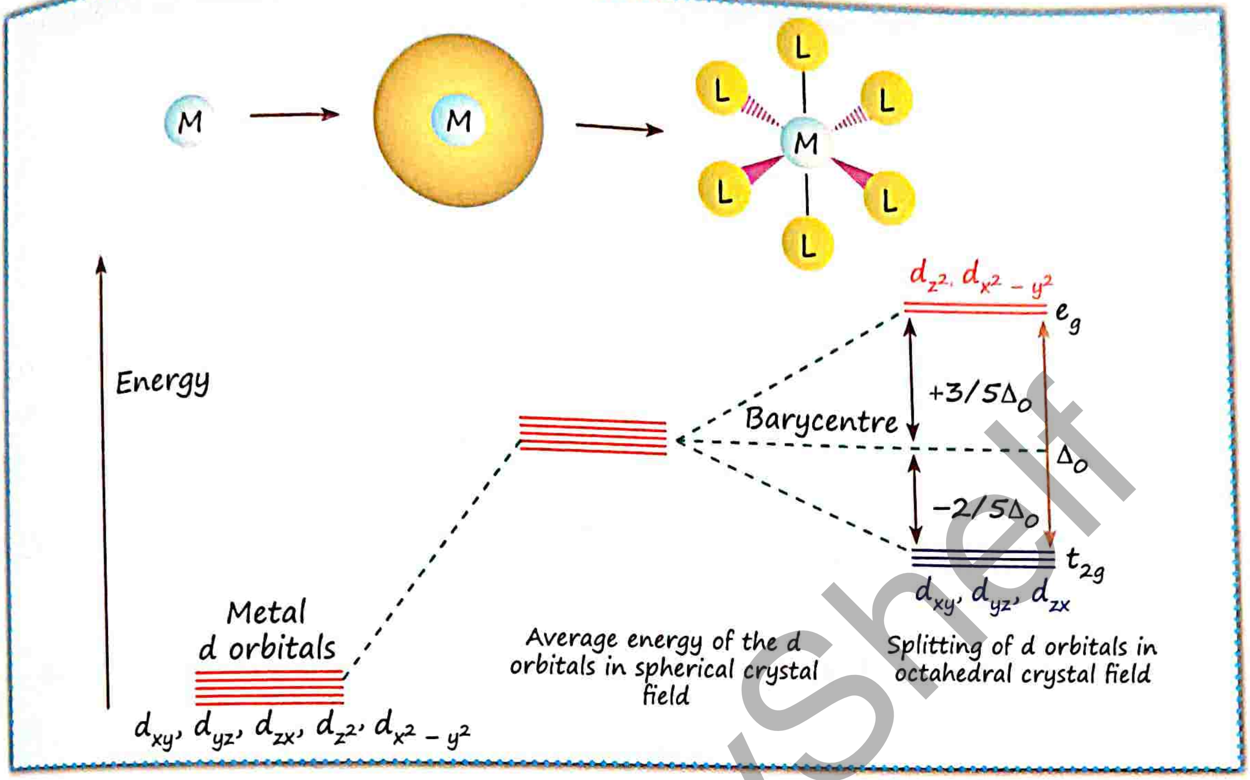


CRYSTAL FIELD THEORY

Crystal Field Splitting in Octahedral Complexes

- ☐ Under the influence of 6 ligands degeneracy of d orbitals has been removed due to ligand-metal electron repulsions in octahedral complex.
- ☐ Removal of degeneracy gives three orbitals [d_{xy}, d_{yz}, d_{zx} = t_{2g} set] of lower energy and two orbitals of higher energy [d_{z^2}, $d_{x^2-y^2}$ = e_g set].
- ☐ $d_{x^2-y^2}$ and d_{z^2} orbitals point towards the axes along the direction of the ligand, will experience more repulsion and will be raised in energy.
- ☐ d_{xy}, d_{yz}, d_{zx} orbitals are directed between axes, will be lowered in energy relative to average energy (in the spherical crystal field).

- Splitting of degenerate levels due to the presence of ligands in a definite geometry is called **Crystal field splitting** and the energy separation is denoted by Δ_o [Crystal field splitting energy].

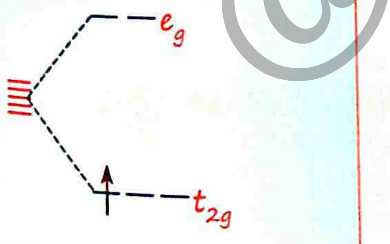
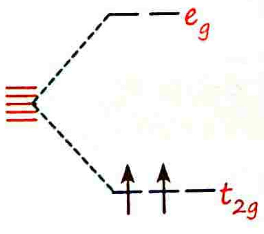
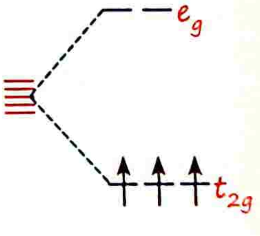


- Crystal Field Stabilization Energy $\text{CFSE}_{(\text{octahedral})} = [-0.4n_{(t_{2g})} + 0.6n_{(e_g)}]\Delta_o$

where $n_{(t_{2g})}$ and $n_{(e_g)}$ are the number of electrons occupying the t_{2g} and e_g orbitals respectively.

d Orbital Splitting in an Octahedral Crystal Field

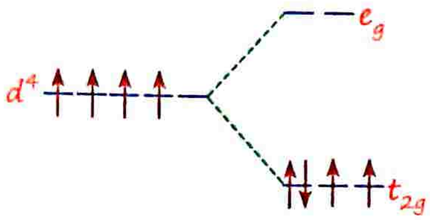
The extent of splitting depends upon the field produced by ligand and charge on metal ion.

d^1 Configuration	d^2 Configuration	d^3 Configuration
		
Electronic configuration: $t_{2g}^1e_g^0$ No. of unpaired electrons = 1 Magnetic moment $= \sqrt{1(1+2)}$ BM $= 1.73$ BM Example: $[Ti(H_2O)_6]^{3+}$ CFSE = $1 \times -0.4\ \Delta_o = -0.4\Delta_o$	Electronic configuration: $t_{2g}^2e_g^0$ No. of unpaired electrons = 2 Magnetic moment $= \sqrt{2(2+2)}$ BM $= 2.82$ BM Example: $[Ti(H_2O)_6]^{2+}$ CFSE = $2 \times -0.4\ \Delta_o = -0.8\Delta_o$	Electronic configuration: $t_{2g}^3e_g^0$ No. of unpaired electrons = 3 Magnetic moment $= \sqrt{3(3+2)}$ BM $= 3.87$ BM Example: $[V(H_2O)_6]^{2+}$ CFSE = $3 \times -0.4\ \Delta_o = -1.2\Delta_o$

Pairing Energy: The energy required to force the two unpaired electrons in one orbital is called the pairing energy (P).

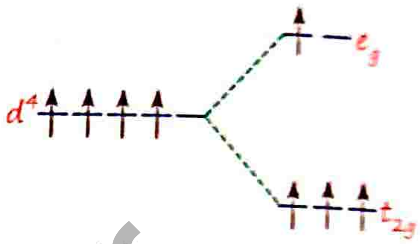
d^4 Configuration

(i) If Δ_o > P [P = pairing energy]



- ☐ If the crystal field splitting parameter (Δ) is large because of strong-bonding ligands, then the pairing energy will be smaller, and the complex will be low-spin.
- ☐ 4^{th} electron enters into t_{2g} orbital and configuration = $t_{2g}^4 e_g^0$
- ☐ Ligands for which Δ_o > P are known as strong field ligand. [SFL]
- ☐ No. of unpaired electron = 2
- ☐ Magnetic moment = $\sqrt{2(2+2)}$ = 2.83 BM
- ☐ CFSE = 4 × – $0.4\Delta_o$ + P = $-1.6\Delta_o$ + P
- ☐ Example: $[Cr(CN)_6]^{4-}$

(ii) If Δ_o < P



- ☐ If the crystal field splitting parameter (Δ) is small because of weak-bonding ligands, then the pairing energy will be larger and the complex will be high-spin.
- ☐ 4^{th} electron enters into one of e_g orbitals giving the configuration $t_{2g}^3 e_g^1$.
- ☐ Ligands for which Δ_o < P are known as weak field ligand. [WFL]
- ☐ No. of unpaired electrons = 4
- ☐ Magnetic moment = $\sqrt{4(4+2)}$ = 4.89 BM
- ☐ CFSE = 3 × – $0.4\Delta_o$ + 1 × $0.6\Delta_o$ = $-0.6\Delta_o$
- ☐ Example: $[Cr(H_2O)_6]^{2+}$

Spectrochemical Series

- ☐ If ligands are arranged in a series (in the order of increasing field strength) then that series is called spectrochemical series.

Halogen donors < Oxygen donors < Nitrogen donors < Carbon donors

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$ [NCERT]

d series	Charge on metal	Ligands	Field strength
3d series Sc → Zn	+2	I^- to en	Weak
	+3	I^- to H_2O	Weak*
	+4	I^- to CO	Strong
4d series Y → Cd	+2 / +3 / +4	I^- to CO	Strong
5d series La → Hg	+2 / +3 / +4	I^- to CO	Strong

* For Co^{3+} all oxygen / nitrogen / carbon donor ligands are strong field ligand.

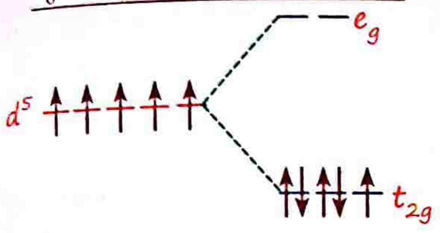
$[Co(NH_3)_6]^{2+}$: NH_3 as WFL with Co^{+2} : $\Delta_o < P$
$[Co(NH_3)_6]^{3+}$: NH_3 as SFL with Co^{+3} : $\Delta_o > P$
$[Co(H_2O)_6]^{+3}$: H_2O as SFL with Co^{+3} : $\Delta_o > P$
$[Ni(H_2O)_6]^{2+}$: H_2O as WFL with Ni^{+2} : $\Delta_o < P$
$[NiCl_6]^{4-}$: Cl^- as WFL with Ni^{+2} : $\Delta_o < P$
$[NiF_6]^{2-}$: F^- as SFL with Ni^{+4} : $\Delta_o > P$

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_2^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < CH_3C \equiv N < EDTA^{4-} < py < NH_3 < en < bipy < NO_2^- < PPh_3 < CN^- < CO$

(The donor atoms are indicated by bold letters.)

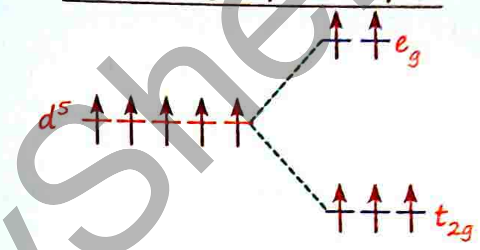
d^5 System

$\Delta_o > P$: Low Spin Complex



Electronic configuration = $t_{2g}^5 e_g^o$
No. of unpaired electrons = 1
Magnetic moment = $\sqrt{1(1+2)}$ BM = 1.73 BM
CFSE = $5 \times -0.4\Delta_o + 2\ P = -2.0\ \Delta_o + 2\ P$
Example = $[Fe(CN)_6]^{3-}$

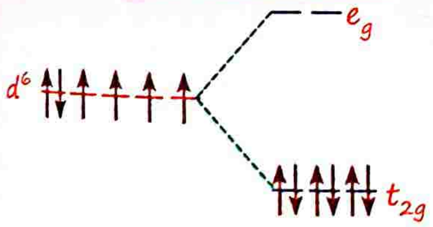
$\Delta_o < P$: High Spin Complex



Electronic configuration = $t_{2g}^3 e_g^2$
No. of unpaired electrons = 5
Magnetic moment = $\sqrt{5(5+2)}$ BM = 5.91 BM
CFSE = $3 \times -0.4\Delta_o + 2 \times 0.6\ \Delta_o = 0$
Example = $[FeF_6]^{3-}$

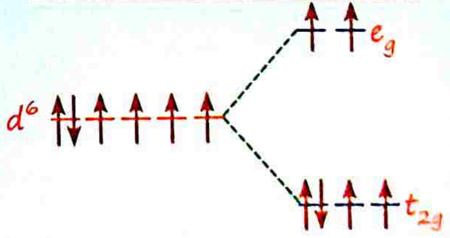
d^6 System

$\Delta_o > P$: Low Spin Complex



Electronic configuration = $t_{2g}^6 e_g^o$
No. of unpaired electrons = 0 (Diamagnetic)
Magnetic moment = 0
CFSE = $6 \times -0.4\Delta_o + 2\ P = -2.4\ \Delta_o + 2\ P$
Example = $[Co(C_2O_4)_3]^{3-}/[Co(NH_3)_6]^{3+}$

$\Delta_o < P$: High Spin Complex

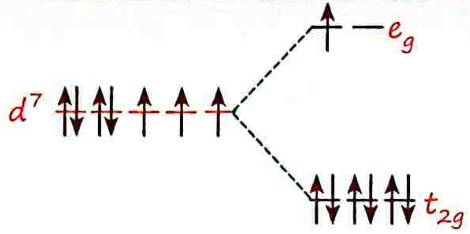


Electronic configuration = $t_{2g}^4 e_g^2$
No. of unpaired electrons = (Paramagnetic : 4 unpaired electrons)
Magnetic moment = $\sqrt{4(4+2)}$BM = 4.89 BM
CFSE = $4 \times -0.4\Delta_o + 2 \times 0.6\ \Delta_o = -0.4\ \Delta_o$
Example = $[CoF_6]^{3-}$

Complex	Configuration	Δ_o (cm^{-1})	P (cm^{-1})	Predicted	Found
$[Fe^{II}(H_2O)]^{2+}$	d^6	10400	17600	High spin	High spin
$[Fe^{II}(CN)_6]^{4-}$	d^6	32850	17600	Low spin	Low spin
$[Co^{III}F_6]^{3-}$	d^6	13000	21000	High spin	High spin
$[Co^{III}(NH_3)_6]^{3+}$	d^6	23000	21000	Low spin	Low spin

d^7 System

$\Delta_o > P$: Low Spin Complex



Electronic configuration = $t_{2g}^6 e_g^1$

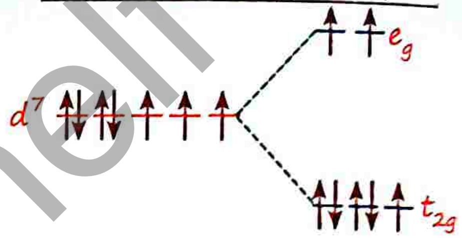
No. of unpaired electrons = Paramagnetic with 1 unpaired electron

Magnetic moment = $\sqrt{1(1+2)}$BM = 1.73 BM

CFSE = $6 \times -0.4\Delta_o + 1 \times 0.6\Delta_o + P = -1.8\Delta_o + P$

Example = $[Co(CN)_6]^{4-}$

$\Delta_o < P$: High Spin Complex



Electronic configuration = $t_{2g}^5 e_g^2$

No. of unpaired electrons = Paramagnetic with 3 unpaired electrons

Magnetic moment = $\sqrt{4(4+2)}$BM = 3.87 BM

CFSE = $5 \times -0.4\Delta_o + 2 \times 0.6\Delta_o = -0.8\Delta_o$

Example = $[Co(NH_3)_6]^{2+}$

CFSE and Electronic Arrangements in Octahedral Complexes

Number of d electrons	Arrangement in weak ligand field				Arrangement in strong ligand field			
	t_{2g}	e_g	CFSE Δ_o	Spin only magnetic moment μ_s(BM)	t_{2g}	e_g	CFSE Δ_o	Spin only magnetic moment μ_s(BM)
d^1	[↑][ ][ ]	[ ][ ]	−0.4	1.73	[↑][ ][ ]	[ ][ ]	−0.4	1.73
d^2	[↑][↑][ ]	[ ][ ]	−0.8	2.83	[↑][↑][ ]	[ ][ ]	−0.8	2.83
d^3	[↑][↑][↑]	[ ][ ]	−1.2	3.87	[↑][↑][↑]	[ ][ ]	−1.2	3.87
d^4	[↑][↑][↑]	[↑][ ]	−0.6	4.90	[⇅][↑][↑]	[ ][ ]	−1.6	2.83
d^5	[↑][↑][↑]	[↑][↑]	0	5.92	[⇅][⇅][↑]	[ ][ ]	−2.0	1.73
d^6	[⇅][↑][↑]	[↑][↑]	−0.4	4.90	[⇅][⇅][⇅]	[ ][ ]	−2.4	0.00
d^7	[⇅][⇅][↑]	[↑][↑]	−0.8	3.87	[⇅][⇅][⇅]	[↑][ ]	−1.8	1.73
d^8	[⇅][⇅][⇅]	[↑][↑]	−1.2	2.83	[⇅][⇅][⇅]	[↑][↑]	−1.2	2.83
d^9	[⇅][⇅][⇅]	[⇅][↑]	−0.6	1.73	[⇅][⇅][⇅]	[⇅][↑]	−0.6	1.73
d^{10}	[⇅][⇅][⇅]	[⇅][⇅]	0	0	[⇅][⇅][⇅]	[⇅][⇅]	0	0

Δ_o depends on

(i) Charge on metal ⇒ Charge on metal ↑ : Δ_o↑

(ii) d Series ⇒ Δ_o : 3d Series < 4d Series < 5d Series

(iii) Position of ligand in spectrochemical series.

Crystal field splittings by various ligands

Complex	Absorption peak	
	(cm^{-1})	$(kJ\ mol^{-1})$
$[Cr^{III}Cl_6]^{3-}$	13640	163
$[Cr^{III}(H_2O)_6]^{3+}$	17830	213
$[Cr^{III}(NH_3)_6]^{3+}$	21680	259
$[Cr^{III}(CN)_6]^{3-}$	26280	314

Δ_o crystal field splittings in one group

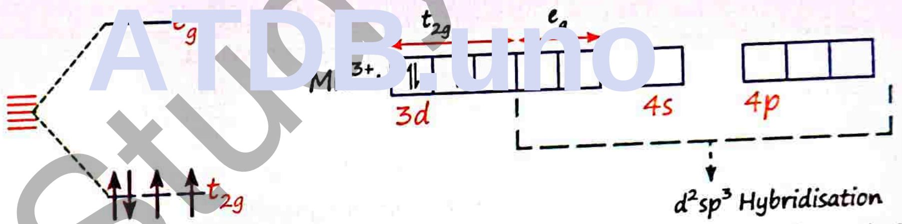
	(cm^{-1})	$(kJ\ mol^{-1})$
$[Co(NH_3)_6]^{3+}$	24800	296
$[Rh(NH_3)_6]^{3+}$	34000	406
$[Ir(NH)_3)_6]^{3+}$	41000	490

Prediction of Hybridisation with Help of CFT

$[Mn(CN)_6]^{3-}$

☐ Mn^{3+} : $3d^4$

☐ CN^- : Strong field ligand

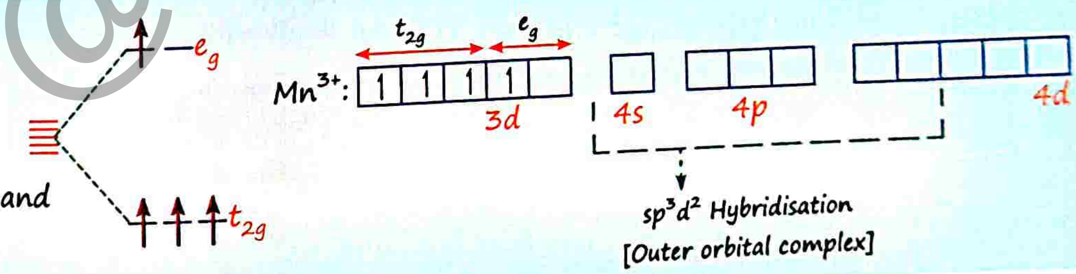


d^2sp^3 Hybridisation
[Inner orbital complex]

$[MnCl_6]^{3-}$

☐ Mn^{3+} : $3d^4$

☐ Cl^- : Weak field ligand

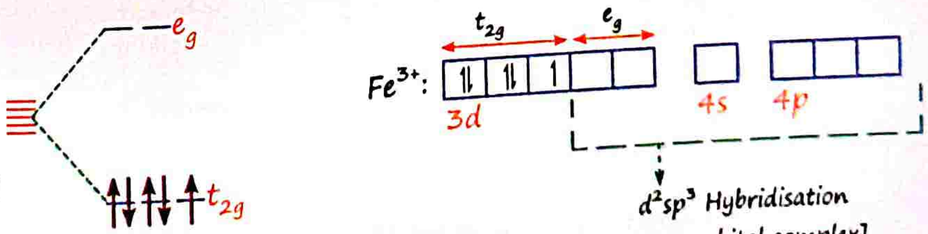


sp^3d^2 Hybridisation
[Outer orbital complex]

$[Fe(CN)_6]^{3-}$

☐ Fe^{3+} : $3d^5$

☐ CN^- : Strong field Ligand

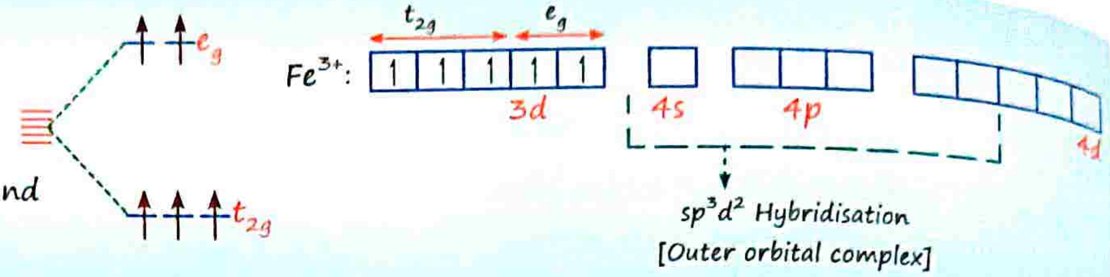


d^2sp^3 Hybridisation
[Inner orbital complex]

$[FeF_6]^{3-}$

☐ Fe^{+3} : $3d^5$

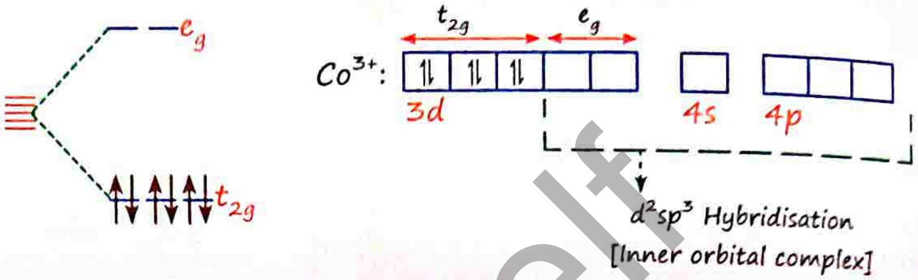
☐ F^- : Weak field ligand



$[Co(C_2O_4)_3]^{3-}$

☐ Co^{3+} : $3d^6$

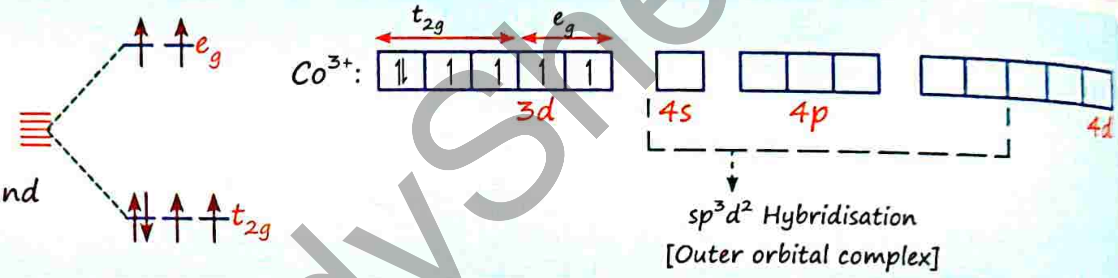
☐ $C_2O_4^{2-}$: Strong field Ligand



$[CoF_6]^{3-}$

☐ Co^{3+} : $3d^6$

☐ F^- : Weak field ligand



28. $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$ are respectively known as [01 Feb, 2024 (Shift-II)]

(a) Spin free Complex, Spin paired Complex

(b) Spin paired Complex, Spin free Complex

(c) Outer orbital Complex, Inner orbital Complex

(d) Inner orbital Complex, Spin paired Complex

Sol. (b)

29. Match List-I with List-II

List-I Complex		List-II Crystal Field splitting energy (Δ_o)	
(A)	$[Ti(H_2O)_6]^{2+}$	(I)	−1.2
(B)	$[V(H_2O)_6]^{2+}$	(II)	−0.6
(C)	$[Mn(H_2O)_6]^{3+}$	(III)	0
(D)	$[Fe(H_2O)_6]^{3+}$	(IV)	−0.8

Choose the correct answer from the options given below: [10 April, 2023 (Shift-II)]

(a) (A) – (II), (B) – (IV), (C) – (I), (D) – (III) (b) (A) – (IV), (B) – (I), (C) – (II), (D) – (III)

(c) (A) – (IV), (B) – (I), (C) – (III), (D) – (II) (d) (A) – (II), (B) – (IV), (C) – (III), (D) – (I)

Sol. (b)

30. The metal d-orbital that can directly facing the ligands in $K_3[Co(CN)_6]$ are

[12 Jan, 2019 (Shift-I)]

(a) d_{xy} and $d_{x^2-y^2}$ (b) $d_{x^2-y^2}$ and d_{z^2} (c) d_{xz}, d_{yz} and d_{z^2} (d) d_{xy}, d_{xz} and d_{yz}

Sol. (b)

31. For a d^4 metal ion in an octahedral field, the correct electronic configuration is

[06 Sep, 2020 (Shift-II)]

(a) $t_{2g}^4 e_g^0$ when $\Delta_O < P$ (b) $t_{2g}^3 e_g^1$ when $\Delta_O > P$

(c) $t_{2g}^2 e_g^2$ when $\Delta_O < P$ (d) $t_{2g}^3 e_g^1$ when $\Delta_O < P$

Sol. (d)

32. The Crystal Field Stabilization Energy (CFSE) of $[CoF_3(H_2O)_3]$ $(\Delta_O < P)$ is

[04 Sep, 2020 (Shift-II)]

(a) $-0.8\ \Delta_O$ (b) $-0.8\ \Delta_O + 2P$ (c) $-0.4\ \Delta_O$ (d) $-0.4\ \Delta_O + P$

Sol. (c) $[CoF_3(H_2O)_3] \Rightarrow Co^{3+} \Rightarrow d^6$ or $t_{2g}^4 e_g^2$, CFSE = $[4 \times -0.4 + 2 \times 0.6]\ \Delta_O = -0.4\ \Delta_O$

33. The crystal field stabilization energy (CFSE) value, for $[Ti(H_2O)_6]^{3+}$ that has absorption maximum at 492 nm is

(a) $20{,}325\ cm^{-1}$ (b) $12,195\ cm^{-1}$ (c) $10,162\ cm^{-1}$ (d) $8,130\ cm^{-1}$

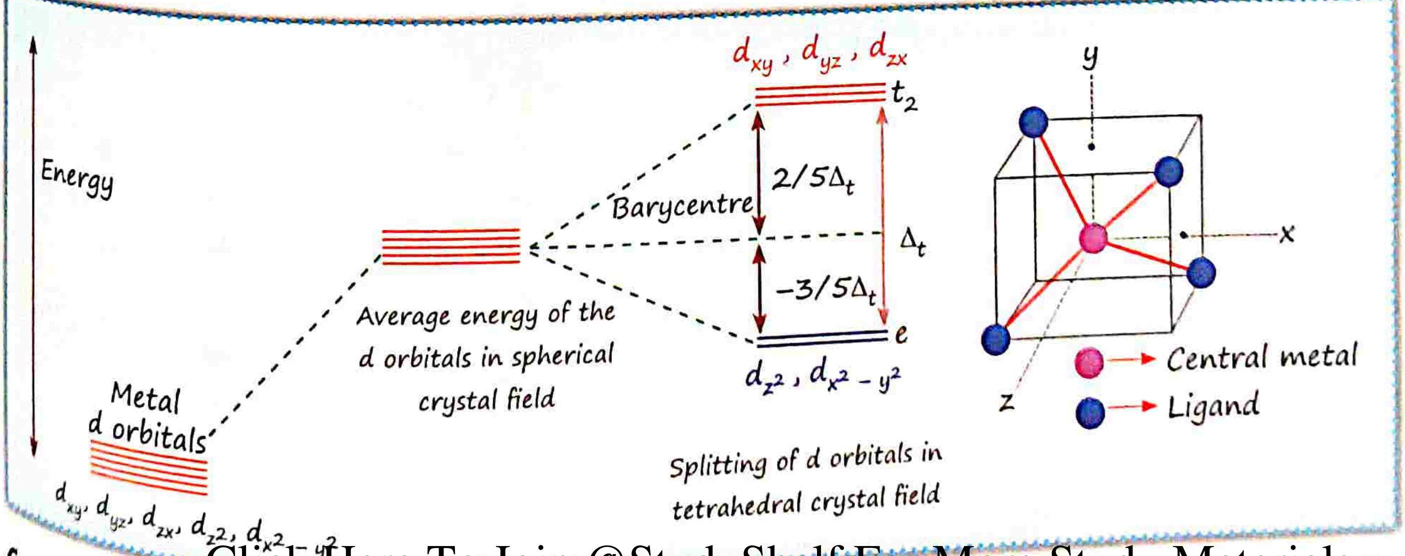
Sol. (d) Absorption maximum, $\lambda = 492\ nm = 492 \times 10^{-7}\ cm$

$$\Delta_O = \frac{1}{\lambda} = \frac{1}{492 \times 10^{-7}} = 20325\ cm^{-1}$$

$$CFSE = -0.4 \times 1 \times \Delta_0 = -0.4\ \Delta_0 = -0.4 \times 20325 = -8130\ cm^{-1}$$

Crystal Field Splitting in Tetrahedral Complexes

- In tetrahedral coordination entity formation the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting.
- For tetrahedral complexes, only four ligands located between the axes. (4 ligands are shown at alternate corner of the cube and metal at bodycentre).
- None of the orbitals points directly at the tetrahedral ligands. However, the $d_{x^2-y^2}$ and d_{z^2} orbitals (along the Cartesian axes) overlap with the ligands less than the d_{xy}, d_{xz}, and d_{yz} orbitals.
- By analogy with the octahedral case, the energy diagram for the d orbitals in a tetrahedral crystal field can be predicted as shown in following diagram.



Splitting of d orbitals in tetrahedral crystal field

- ☐ The orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are not observed.
- ☐ $CFSE_{(tetrahedral)} = +0.4n_{(t_2)} - 0.6n_{(e)}$
  Where $n_{(t_2)}$ and $n_{(e)}$ are the number of electrons occupying the t_2 and e orbitals respectively

CFSE and Electronic Arrangements in Tetrahedral Complexes

Number of d electrons	Arrangement of electrons		Spin only magnetic moment	$(CFSE)_{Tetrahedral}$
	e	t_2	μ(BM)	Δ_t
d^1	↑ ☐	☐ ☐ ☐	1.73	-0.6
d^2	↑ ↑	☐ ☐ ☐	2.83	-1.2
d^3	↑ ↑	↑ ☐ ☐	3.87	-1.2 + 0.4 = - 0.8
d^4	↑ ↑	↑ ↑ ☐	4.90	-1.2 + 0.8 = -0.4
d^5	↑ ↑	↑ ↑ ↑	5.92	-1.2 + 1.2 = 0.0
d^6	↑↓ ↑	↑ ↑ ↑	4.90	-1.8 + 1.2 = - 0.6
d^7	↑↓ ↑↓	↑ ↑ ↑	3.87	-2.4 + 1.2 = -1.2
d^8	↑↓ ↑↓	↑↓ ↑ ↑	2.83	-2.4 + 1.6 = -0.8
d^9	↑↓ ↑↓	↑↓ ↑↓ ↑	1.73	-2.4 + 2.0 = -0.4
d^{10}	↑↓ [illegible]	[illegible] [illegible] ↑↓	0.00	-2.4 + 2.4 = 0.0

d^8 configuration

$[NiCl_4]^{2-}$

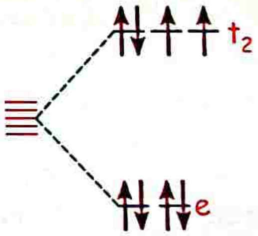
Oxidation state of Ni: $x - 4 = -2 \Rightarrow x = -2 + 4 = +2$

Electronic configuration of Ni: $[Ar]3d^8\ 4s^2$

Electronic configuration of Ni^{2+}: $[Ar]3d^8$

No. of unpaired electrons = 2

Electronic configuration: $e^4t_2^4$



34. The values of the crystal field stabilization energies for a high spin d^6 metal ion in octahedral and tetrahedral fields, respectively, are [05 Sep, 2020 (Shift-I)]

(a) $-1.6\ \Delta_o$ and $-0.4\ \Delta_t$ (b) $-2.4\ \Delta_o$ and $-0.6\ \Delta_t$

(c) $-0.4\ \Delta_o$ and $-0.27\ \Delta_t$ (d) $-0.4\ \Delta_o$ and $-0.6\ \Delta_t$

Sol. (d) Octahedral → $[4 \times -0.4\ \Delta_o + 2 \times 0.6\Delta_o]$ Tetrahedral → $[3 \times -0.6\ \Delta_o + 3 \times 0.4\Delta_o]$

35. The correct order of the spin-only magnetic moments of the following complexes is:

(I) $[Cr(H_2O)_6]Br_2$ (II) $Na_4[Fe\ (CN)_6]$

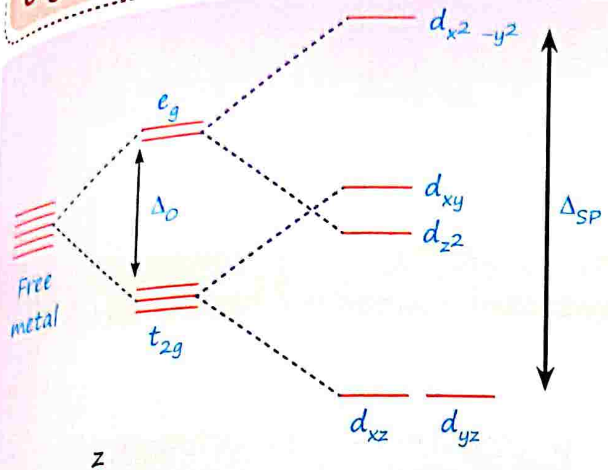
(III) $Na_3[Fe(C_2O_4)_3](\Delta_o > P)$ (IV) $(Et_4N)_2[CoCl_4]$ [09 Jan, 2020 (Shift-II)]

(a) (III) > (I) > (IV) > (II) (b) (III) > (I) > (II) > (IV)

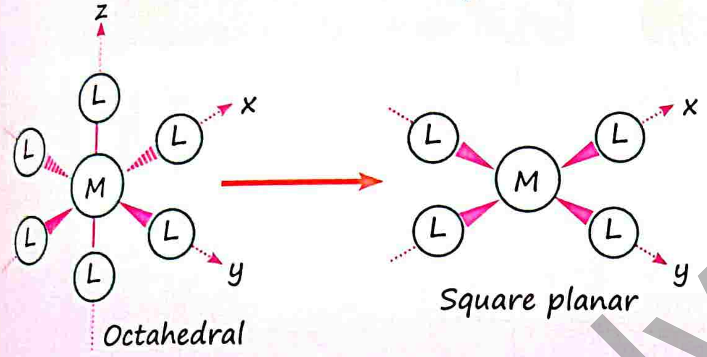
(c) (I) > (IV) > (III) > (II) (d) (II) ≈ (I) > (IV) > (III)

Sol. (c) No. of unpaired electrons ⇒ (I) 4 (II) Zero (III) 1 (IV) 3

Crystal Field Splitting in Square Planar Complex

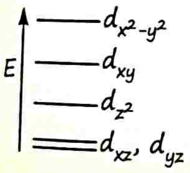


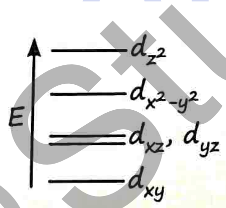
Energy order for sq. planar Complex:
$d_{x^2-y^2} > d_{xy} > d_{z^2} > (d_{xz} = d_{yz})$

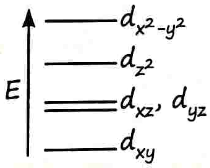


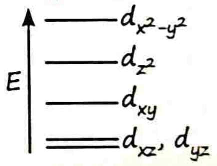
☐ Removal of 2 axial ligands (along the z axis) from an octahedral complex leads to form square planar complex

36. Complete removal of both the axial ligands (along the z-axis) from an octahedral complex leads to which of the following splitting patterns? (relative orbital energies not on scale)
[12 April, 2019 (Shift-I)]

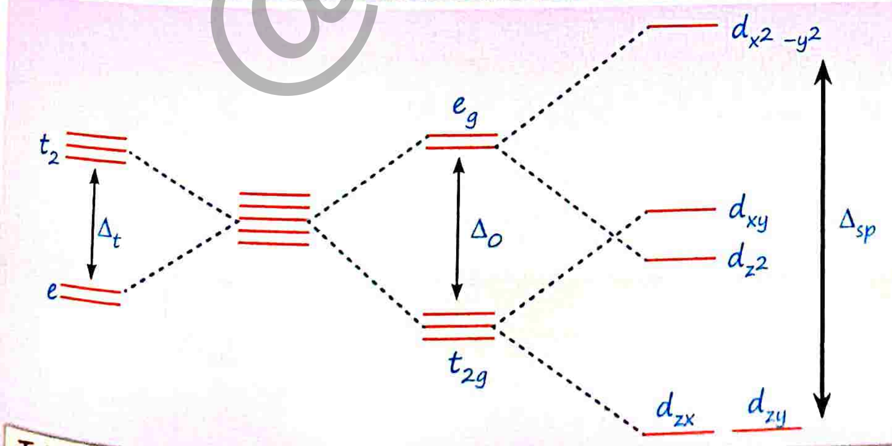
(a)


(b)


(c)


(d)


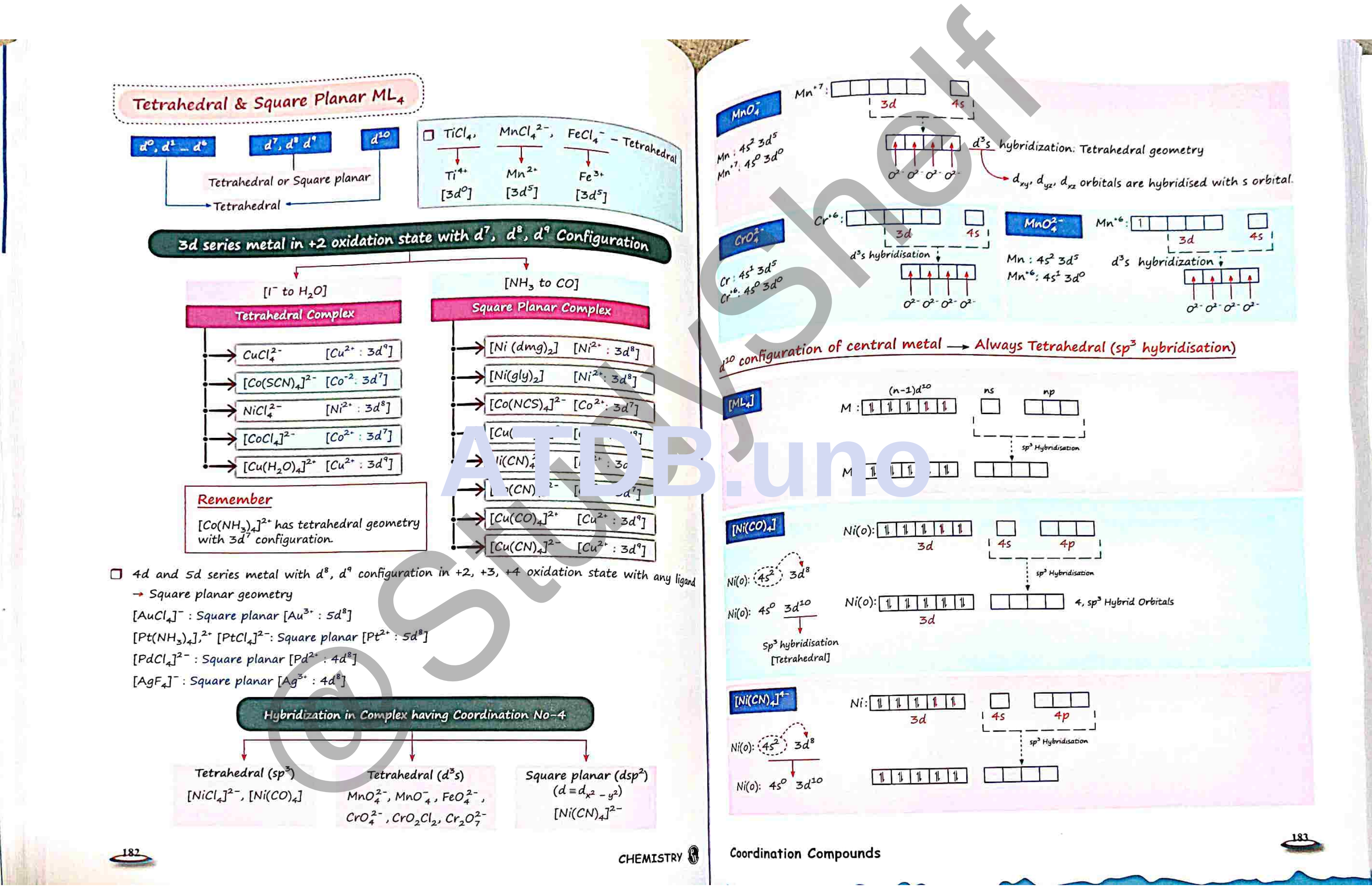
Sol. (a)



$\Delta_{sp} > \Delta_O > \Delta_t$
$\Delta_{sp} = 1.3\ \Delta_O$
$\Delta_t = 4/9\ \Delta_O$

Tetrahedral	Octahedral	Square Planar
($\Delta_t << P$)	1. ($\Delta_O >> P$)	($\Delta_{sp} >> P$)
	2. ($\Delta_O << P$)	

P → pairing energy



Tetrahedral & Square Planar ML_4

$d^0, d^1 - d^6$ → Tetrahedral

d^7, d^8, d^9 → Tetrahedral or Square planar

d^{10} → Tetrahedral

☐ $TiCl_4$, $MnCl_4^{2-}$, $FeCl_4^-$ – Tetrahedral

Ti^{4+} $[3d^0]$; Mn^{2+} $[3d^5]$; Fe^{3+} $[3d^5]$

3d series metal in +2 oxidation state with d^7, d^8, d^9 Configuration

$[I^-$ to $H_2O]$ Tetrahedral Complex		$[NH_3$ to $CO]$ Square Planar Complex	
$CuCl_4^{2-}$	$[Cu^{2+} : 3d^9]$	$[Ni(dmg)_2]$	$[Ni^{2+} : 3d^8]$
$[Co(SCN)_4]^{2-}$	$[Co^{-2} : 3d^7]$	$[Ni(gly)_2]$	$[Ni^{2+} : 3d^8]$
$NiCl_4^{2-}$	$[Ni^{2+} : 3d^8]$	$[Co(NCS)_4]^{2-}$	$[Co^{2+} : 3d^7]$
$[CoCl_4]^{2-}$	$[Co^{2+} : 3d^7]$	[Cu([illegible]	[illegible]
$[Cu(H_2O)_4]^{2+}$	$[Cu^{2+} : 3d^9]$	[illegible]	[illegible]
		[illegible]	[illegible]
		$[Cu(CO)_4]^{2+}$	$[Cu^{2+} : 3d^9]$
		$[Cu(CN)_4]^{2-}$	$[Cu^{2+} : 3d^9]$

Remember

$[Co(NH_3)_4]^{2+}$ has tetrahedral geometry with $3d^7$ configuration.

☐ 4d and 5d series metal with d^8, d^9 configuration in +2, +3, +4 oxidation state with any ligand → Square planar geometry

$[AuCl_4]^-$: Square planar $[Au^{3+} : 5d^8]$

$[Pt(NH_3)_4]^{2+}$, $[PtCl_4]^{2-}$: Square planar $[Pt^{2+} : 5d^8]$

$[PdCl_4]^{2-}$: Square planar $[Pd^{2+} : 4d^8]$

$[AgF_4]^-$: Square planar $[Ag^{3+} : 4d^8]$

Hybridization in Complex having Coordination No-4

Tetrahedral (sp^3)	Tetrahedral (d^3s)	Square planar (dsp^2) ($d \equiv d_{x^2-y^2}$)
$[NiCl_4]^{2-}$, $[Ni(CO)_4]$	MnO_4^{2-}, MnO_4^-, FeO_4^{2-}, CrO_4^{2-}, CrO_2Cl_2, $Cr_2O_7^{2-}$	$[Ni(CN)_4]^{2-}$

MnO_4^-

$Mn : 4s^2\,3d^5$
$Mn^{+7} : 4s^0\,3d^0$

Mn^{+7} : 3d 4s

d^3s hybridization. Tetrahedral geometry

O^{2-} O^{2-} O^{2-} O^{2-}

d_{xy}, d_{yz}, d_{xz} orbitals are hybridised with s orbital.

CrO_4^{2-}

$Cr : 4s^1\,3d^5$
$Cr^{+6} : 4s^0\,3d^0$

Cr^{+6} : 3d 4s

d^3s hybridisation

O^{2-} O^{2-} O^{2-} O^{2-}

MnO_4^{2-}

$Mn : 4s^2\,3d^5$
$Mn^{+6} : 4s^1\,3d^0$

Mn^{+6} : 1 3d 4s

d^3s hybridization

O^{2-} O^{2-} O^{2-} O^{2-}

d^{10} configuration of central metal → Always Tetrahedral (sp^3 hybridisation)

$[ML_4]$

M : $(n-1)d^{10}$ ns np

sp^3 Hybridisation

M

$[Ni(CO)_4]$

Ni(0): 3d 4s 4p

sp^3 Hybridisation

Ni(0): 3d 4, sp^3 Hybrid Orbitals

Ni(0): $4s^2$ $3d^8$

Ni(0): $4s^0$ $3d^{10}$

Sp^3 hybridisation [Tetrahedral]

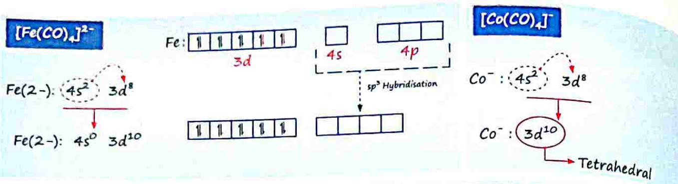
$[Ni(CN)_4]^{4-}$

Ni : 3d 4s 4p

sp^3 Hybridisation

Ni(0): $4s^2$ $3d^8$

Ni(0): $4s^0$ $3d^{10}$



Metal	Ligand	Complex/ML_4	d Configuration
Zn	Cl	$[ZnCl_4]^{2-}$	$Zn^{+2}/3d^{10}$
Hg	I	$[HgI_4]^{2-}$	$Hg^{2+}/5d^{10}$
Cd	Cl	$[CdCl_4]^{2-}$	$Cd^{2+}/4d^{10}$
Zn	CN	$[Zn(CN)_4]^{2-}$	$Zn^{+2}/3d^{10}$
Cu	py	$[Cu(py)_4]^{+}$	$Cu^{+}/3d^{10}$
Cu	CN	$[Cu(CN)_4]^{3-}$	$Cu^{+}/3d^{10}$

sp^3 hybridisation

Tetrahedral Geometry

37. The structure of the complexes $[Cu(NH_3)_4](ClO_4)_2$ and $[Cu(NH_3)_4](ClO_4)$ in solution respectively
(a) square planar and tetrahedral (b) tetrahedral and square pyramidal
(c) octahedral and trigonal bipyramidal (d) tetrahedral and square planar

Sol. (a) $[Cu(NH_3)_4]^{2+} \cdot 2ClO_4^- \longrightarrow Cu^{2+}\ (3d^9)$ with $NH_3 \longrightarrow$ Square planar
$[Cu(NH_3)_4]^{+} \cdot ClO_4^- \longrightarrow Cu^{+}\ (3d^{10})$ with $NH_3 \longrightarrow$ Tetrahedral

38. Match List-I with List-II.

List-I (Complex ion)		List-II (Spin only magnetic moment in B.M.)	
A.	$[Cr(NH_3)_6]^{3+}$	I.	4.90
B.	$[NiCl_4]^{2-}$	II.	3.87
C.	$[CoF_6]^{3-}$	III.	0.0
D.	$[Ni(CN)_4]^{2-}$	IV.	2.83

Choose the correct answer from the options given below: [08 April, 2024 (Shift-II)]
(a) (A)-(I), (B)-(IV), (C)-(II), (D)-(III) (b) (A)-(IV), (B)-(III), (C)-(I), (D)-(II)
(c) (A)-(II), (B)-(IV), (C)-(I), (D)-(III) (d) (A)-(II), (B)-(III), (C)-(I), (D)-(IV)

Sol. (c)

39. The number of complexes from the following with no electrons in the t_2 orbital is _____.
$TiCl_4$, $[MnO_4]^-$, $[FeO_4]^{2-}$, $[FeCl_4]^-$, $[CoCl_4]^{2-}$ [05 April, 2024 (Shift-II)]
(a) 3 (b) 1 (c) 4 (d) 2

Sol. (a) Three complexes have zero number of electrons in t_2 orbital

$TiCl_4 \Rightarrow Ti^{+4}$ $e^0t_2^0$
$MnO_4^- \Rightarrow Mn^{+7}$ $e^0t_2^0$
$FeO_4^{2-} \Rightarrow Fe^{+6}$ $e^2t_2^0$
$FeCl_4^- \Rightarrow Fe^{+3}$ $e^2t_2^3$
$CoCl_4^{2-} \Rightarrow Co^{+2}$ $e^4t_2^3$

40. Match List-I with List-II

List-I		List-II	
A.	$K_2[Ni(CN)_4]$	I.	sp^3
B.	$[Ni(CO)_4]$	II.	sp^3d^2
C.	$[Co(NH_3)_6]Cl_3$	III.	dsp^2
D.	$Na_3[CoF_6]$	IV.	d^2sp^3

Choose the correct answer from the options given below: [09 April, 2024 (Shift-II)]
(a) A-III, B-I, C-II, D-IV (b) A-III, B-II, C-IV, D-I
(c) A-I, B-III, C-II, D-IV (d) A-III, B-I, C-IV, D-II

Sol. (d)

41. The species that has a spin-only magnetic moment of 5.9 BM, is (T_d = tetrahedral) [06 Sep, 2020 (Shift-I)]
(a) $[MnBr_4]^{2-}$ (T_d) (b) $[NiCl_4]^{2-}$ (T_d) (c) $Ni(CO)_4$ (T_d) (d) $[Ni(CN)_4]^{2-}$ (square planar)

Sol. (a) $Mn^{2+} : 3d^5 \longrightarrow$ 5 unpaired electrons

42. The compound having tetrahedral geometry is (IIT JEE 2004)
(a) $[Ni(CN)_4]^{2-}$ (b) $[Pd(CN)_4]^{2-}$ (c) $[PdCl_4]^{2-}$ (d) $[NiCl_4]^{2-}$

Sol. (d)

43. Among $[Ni(CO)_4]$, $[NiCl_4]^{2-}$, $[Co(NH_3)_4Cl_2]Cl$, $Na_3[CoF_6]$, Na_2O_2 and CsO_2, the total number of paramagnetic compounds is (JEE Adv. 2016)
(a) 2 (b) 3 (c) 4 (d) 5

Sol. (b)

- $[Ni(CO)_4] \rightarrow sp^3 \rightarrow$ 0 unpaired electron, as all electrons are paired.
- $[NiCl_4]^{2-} \rightarrow 3d^8 \rightarrow sp^3 \rightarrow$ 2 unpaired electron.
- $[Co(NH_3)_4Cl_2]Cl \rightarrow 3d^6 \rightarrow d^2sp^3 \rightarrow$ 0 unpaired electron, as all electrons are paired.
- $Na_3[CoF_6] \rightarrow 3d^6 \rightarrow sp^3d^2 \rightarrow$ 4 unpaired electron.
- Na_2O_2 has O_2^{2-} ions and in this, 0 unpaired electron is present.
- CsO_2 has O_2^- ion and in this, 1 unpaired electron is present.

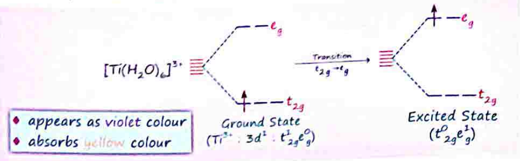
44. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^-, CN^- and H_2O, respectively, are (IIT JEE 2011)
(a) octahedral, tetrahedral and square planar
(b) tetrahedral, square planar and octahedral
(c) square planar, tetrahedral and octahedral
(d) octahedral, square planar and octahedral

Sol. (b) $[NiCl_4]^{2-} \longrightarrow$ Tetrahedral, $[Ni(CN)_4]^{2-} \longrightarrow$ Square planar, $[Ni(H_2O)_6]^{2+} \longrightarrow$ Octahedral

COLOUR IN COORDINATION COMPLEX

- ☐ Colour of any compound is complementary colour of absorbed light. We can predict complementary colour of any colour by COLOUR WHEEL.

- ☐ If any sample absorbs red colour then it appears as green.



- ☐ When light of certain frequency falls on the complex, it absorbs light from visible range for transition of electrons from lower d energy level to higher d energy level. This transition is called d-d transition of electron.
- ☐ Strong field ligands cause a large split in the energies of d orbitals of the central metal atom.

- Absorbed energy for transition (E) ↑ ⇒ Large splitting ⇒ field strength ↑
- Absorbed wavelength of light for transition (λ) ↓ ⇒ field strength ↑

(a) $[Co(CN)_6]^{3-}$
(b) $[Co(NH_3)_6]^{3+}$
(c) $[Co(NH_3)_5(H_2O)]^{3+}$
(d) $[CoCl(NH_3)_5]^{2+}$

Field strength: $CN^- > NH_3 > H_2O > Cl^-$
Absorbed energy for transition: a > b > c > d
Absorbed wavelength of light for transition: a < b < c < d
Observed wavelength of light for transition: a > b > c > d
(Because absorbed and observed colours are complementary)

(e) $[Cu(H_2O)_4]^{2+}$: It has tetrahedral geometry ($\Delta_t < \Delta_o$). So less energy is required for transition than octahedral (a, b, c and d) complexes.

Absorbed wavelength for transition : a < b < c < d < e

Note

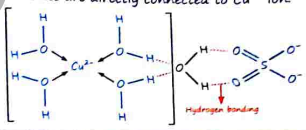
- ☐ The colours observed from electronic transitions within the d orbitals of transition metal ions are common in everyday life. For example–
  - **Ruby** is composed of aluminium oxide (Al_2O_3) with approximately 0.5–1% Cr(III) ions (Cr^{3+}, d^3). These Cr^{3+} ions are randomly distributed in positions normally occupied by Al^{3+}. We can consider these chromium(III) ions as octahedral complexes embedded within the alumina lattice. The colours in rubies arises from d-d electronic transitions occurring at these chromium(III) sites.
  - In **emerald**, Cr^{3+} ions occupy octahedral sites in the mineral beryl ($Be_3Al_2Si_6O_{18}$).

- ☐ In absence of ligand crystal field splitting does not occur and hence the substance is colourless.
  - $\underset{\text{violet}}{[Ti(H_2O)_6]Cl_3} \xrightarrow[-6H_2O]{\Delta} TiCl_3$ (colourless)
  - $\underset{\text{Blue}}{CuSO_4.5H_2O} \xrightarrow[-5H_2O]{\Delta} CuSO_4$ (colourless)

Blue Vitriol ($CuSO_4 \cdot 5H_2O$)

$CuSO_4 \cdot 5H_2O \equiv [Cu(H_2O)_4]SO_4 \cdot H_2O$: 4 water molecules are directly connected to Cu^{2+} ion.

Hybridisation and geometry: Tetrahedral, sp^3



45. The secondary valency and the number of hydrogen bonded water molecule(s) in $CuSO_4.5H_2O$, respectively are [18 March, 2021 (Shift-II)]
(a) 6 and 4 (b) 4 and 1 (c) 5 and 1 (d) 6 and 5

Sol. (b) Secondary valency = Coordination number = 4, H-bonded water molecule=1

46. Given below are two statements: [29 June, 2022 (Shift-II)]
Statement-I: In $CuSO_4.5H_2O$, Cu-O bonds are present.
Statement-II: In $CuSO_4.5H_2O$, ligands coordinating with Cu(II) ion are O- and S- based ligands.
In the light of the above statements, choose Correct answer from the options given below:
(a) Both Statement-I and Statement-II are correct.
(b) Both Statement-I and Statement-II are incorrect.
(c) Statement-I is correct but Statement-II is incorrect.
(d) Statement-I is incorrect but Statement-II is correct.

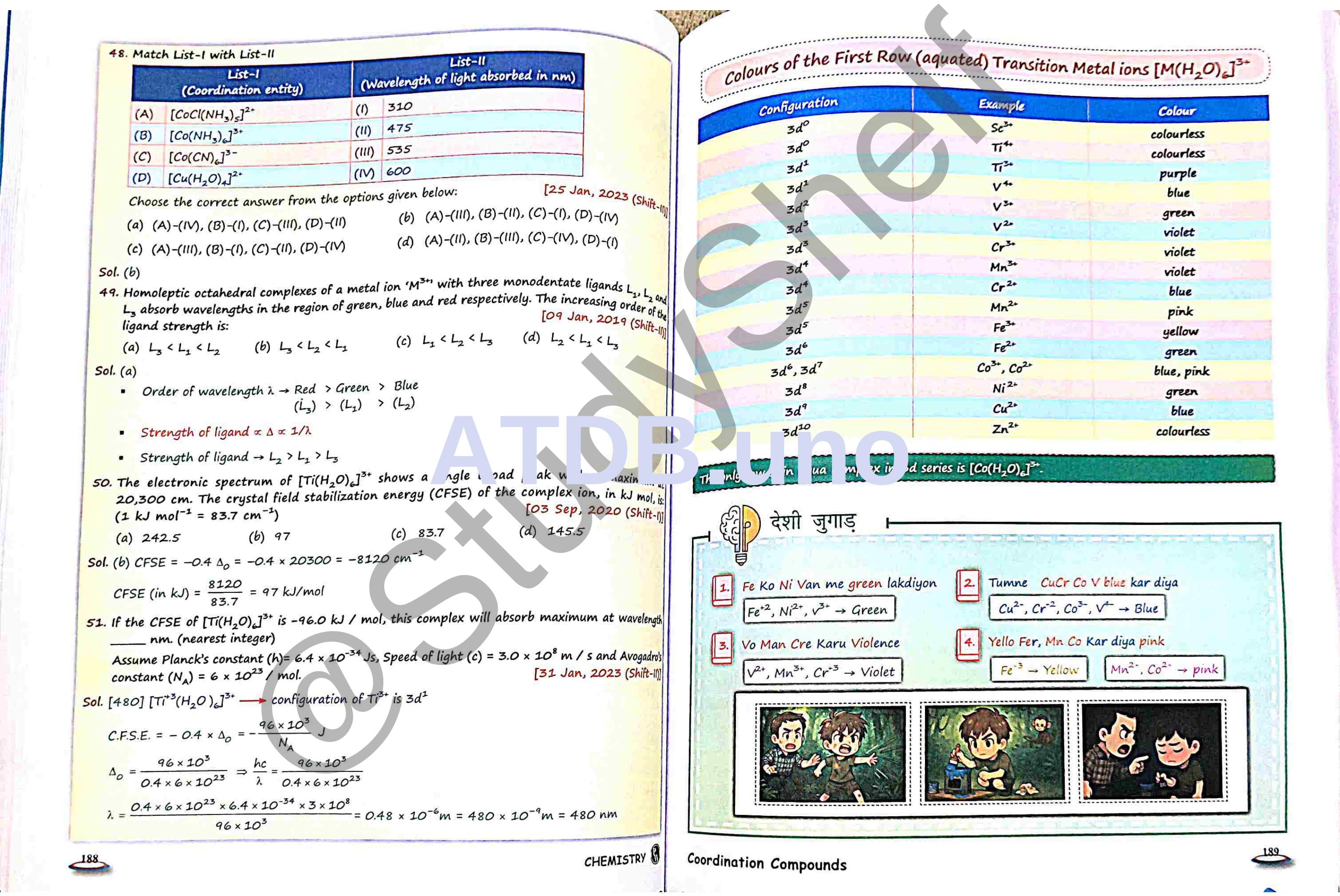
Sol. (c)

(IIT JEE 1983)

47. Type of bonds present in $CuSO_4 \cdot 5H_2O$ are only
(a) Electrovalent and covalent
(b) Electrovalent and coordinate covalent
(c) Electrovalent, covalent and coordinate covalent
(d) Covalent and coordinate covalent

Sol. (c)

Coordination Comp.	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
a. $[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
b. $[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green	Red
c. $[Co(NH_3)_6]^{3+}$	475	Blue	Yellow Orange
d. $[Co(CN)_6]^{3-}$	310	Ultraviolet	Pale Yellow
e. $[Cu(H_2O)_4]^{2+}$	600	Red	Blue



48. Match List-I with List-II

List-I (Coordination entity)		List-II (Wavelength of light absorbed in nm)	
(A)	$[CoCl(NH_3)_5]^{2+}$	(I)	310
(B)	$[Co(NH_3)_6]^{3+}$	(II)	475
(C)	$[Co(CN)_6]^{3-}$	(III)	535
(D)	$[Cu(H_2O)_4]^{2+}$	(IV)	600

Choose the correct answer from the options given below: [25 Jan, 2023 (Shift-II)]

(a) (A)-(IV), (B)-(I), (C)-(III), (D)-(II)
(b) (A)-(III), (B)-(II), (C)-(I), (D)-(IV)
(c) (A)-(III), (B)-(I), (C)-(II), (D)-(IV)
(d) (A)-(II), (B)-(III), (C)-(IV), (D)-(I)

Sol. (b)

49. Homoleptic octahedral complexes of a metal ion 'M^{3+}' with three monodentate ligands L_1, L_2 and L_3 absorb wavelengths in the region of green, blue and red respectively. The increasing order of the ligand strength is: [09 Jan, 2019 (Shift-II)]

(a) $L_3 < L_1 < L_2$
(b) $L_3 < L_2 < L_1$
(c) $L_1 < L_2 < L_3$
(d) $L_2 < L_1 < L_3$

Sol. (a)

- Order of wavelength $\lambda \rightarrow$ Red > Green > Blue
  $(L_3) > (L_1) > (L_2)$
- Strength of ligand $\propto \Delta \propto 1/\lambda$
- Strength of ligand $\rightarrow L_2 > L_1 > L_3$

50. The electronic spectrum of $[Ti(H_2O)_6]^{3+}$ shows a single broad peak with maximum at 20,300 cm. The crystal field stabilization energy (CFSE) of the complex ion, in kJ mol, is: $(1\ kJ\ mol^{-1} = 83.7\ cm^{-1})$ [03 Sep, 2020 (Shift-I)]

(a) 242.5
(b) 97
(c) 83.7
(d) 145.5

Sol. (b) $CFSE = -0.4\ \Delta_o = -0.4 \times 20300 = -8120\ cm^{-1}$

$$CFSE\ (in\ kJ) = \frac{8120}{83.7} = 97\ kJ/mol$$

51. If the CFSE of $[Ti(H_2O)_6]^{3+}$ is -96.0 kJ / mol, this complex will absorb maximum at wavelength _____ nm. (nearest integer)

Assume Planck's constant (h) = 6.4×10^{-34} Js, Speed of light (c) = 3.0×10^8 m / s and Avogadro's constant $(N_A) = 6 \times 10^{23}$ / mol. [31 Jan, 2023 (Shift-II)]

Sol. [480] $[Ti^{+3}(H_2O)_6]^{3+} \longrightarrow$ configuration of Ti^{3+} is $3d^1$

$$C.F.S.E. = -0.4 \times \Delta_o = -\frac{96 \times 10^3}{N_A} J$$

$$\Delta_o = \frac{96 \times 10^3}{0.4 \times 6 \times 10^{23}} \Rightarrow \frac{hc}{\lambda} = \frac{96 \times 10^3}{0.4 \times 6 \times 10^{23}}$$

$$\lambda = \frac{0.4 \times 6 \times 10^{23} \times 6.4 \times 10^{-34} \times 3 \times 10^8}{96 \times 10^3} = 0.48 \times 10^{-6} m = 480 \times 10^{-9} m = 480\ nm$$

Colours of the First Row (aquated) Transition Metal ions $[M(H_2O)_6]^{3+}$

Configuration	Example	Colour
$3d^0$	Sc^{3+}	colourless
$3d^0$	Ti^{4+}	colourless
$3d^1$	Ti^{3+}	purple
$3d^1$	V^{4+}	blue
$3d^2$	V^{3+}	green
$3d^3$	V^{2+}	violet
$3d^3$	Cr^{3+}	violet
$3d^4$	Mn^{3+}	violet
$3d^4$	Cr^{2+}	blue
$3d^5$	Mn^{2+}	pink
$3d^5$	Fe^{3+}	yellow
$3d^6$	Fe^{2+}	green
$3d^6, 3d^7$	Co^{3+}, Co^{2+}	blue, pink
$3d^8$	Ni^{2+}	green
$3d^9$	Cu^{2+}	blue
$3d^{10}$	Zn^{2+}	colourless

The only low spin aqua complex in 3d series is $[Co(H_2O)_6]^{3+}$.

देशी जुगाड़

1. Fe Ko Ni Van me green lakdiyon
   $Fe^{+2}, Ni^{2+}, V^{3+} \rightarrow$ Green
2. Tumne CuCr Co V blue kar diya
   $Cu^{2-}, Cr^{-2}, Co^{3-}, V^{+} \rightarrow$ Blue
3. Vo Man Cre Karu Violence
   $V^{2+}, Mn^{3+}, Cr^{+3} \rightarrow$ Violet
4. Yello Fer, Mn Co Kar diya pink
   $Fe^{-3} \rightarrow$ Yellow
   $Mn^{2-}, Co^{2-} \rightarrow$ pink

Influence of the Ligand on Colour

$$\underset{\text{Green}}{[Ni(H_2O)_6]^{2+}_{(aq.)}} + en_{(aq.)} \xrightarrow[-2H_2O]{} \underset{\text{Pale blue}}{[Ni(H_2O)_4en]^{2+}} \xrightarrow[-2H_2O]{+en} \underset{\text{Blue/purple}}{[Ni(H_2O)_2(en)_2]^{2+}} \xrightarrow[-2H_2O]{en} \underset{\text{Violet}}{[Ni(en)_3]^{2+}}$$

CHARGE TRANSFER SPECTRA

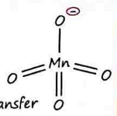
Ligand to Metal Charge Transfer Spectra [LMCT]

If the transfer of an electron takes place from the ligand to metal, then charge transfer is called ligand to metal charge transfer.

Purple Colour

MnO_4^-

Mn^{+7} : d^0 → No d–d transition

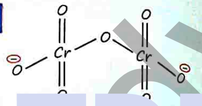


MnO^-_4: Colour is due to electron transfer from $O^{2-} \rightarrow Mn^{+7}$.

Red Orange Colour

$Cr_2O_7^{2-}$

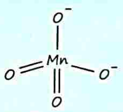
Cr^{+6} : d^0



Green Colour

MnO_4^{2-}

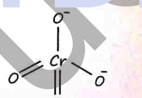
Mn^{+6} : d^1



Yellow Colour

CrO_4^{2-}

Cr^{+6} : d^0



Metal to Metal Charge Transfer Spectra [MMCT]

In these transitions-electron transfer takes place from an atom of lower oxidation state to an another atom of higher oxidation state.

1. $Fe^{2+} + [\overset{III}{Fe}(CN)_6]^{3-} \rightarrow \overset{II}{Fe}_3[\overset{III}{Fe}(CN)_6]_2$ — Ferrous ferricyanide [Turn bulls blue]
2. $Fe^{3+} + [\overset{II}{Fe}(CN)_6]^{4-} \rightarrow \overset{III}{Fe}_4[\overset{II}{Fe}(CN)_6]_3$ — Ferric ferrocyanide [Prussian blue]
3. Pb_3O_4 **(red colour)** $\equiv PbO_2 \cdot 2PbO$

> Red lead (Pb_3O_4) contains Pb(II) and Pb(IV). Due to electron transfer from Pb(II) to Pb(IV), it gives intense red colour.

52. Consider the following complexes.

$[CoCl(NH_3)_5]^{2+}$,	$[Co(CN)_6]^{3-}$,	$[Co(NH_3)_5(H_2O)]^{3+}$,	$[Cu(H_2O)_4]^{2+}$
(A)	(B)	(C)	(D)

The correct order of A, B, C and D in terms of wavenumber of light absorbed is: [06 April, 2024 (Shift-I)]

(a) C < D < A < B (b) D < A < C < B (c) A < C < B < D (d) B < C < A < D

Sol. (b) As the ligand field strength increase, light of more energy is absorbed. Ligand strength can be determined by spectrochemical series.

Also, Energy ∝ wave number ($\bar{\upsilon}$)

53. Which of the following cannot be explained by crystal field theory? [24 Jan, 2023 (Shift-II)]

(a) The order of spectrochemical series
(b) Magnetic properties of transition metal complexes
(c) Colour of metal complexes
(d) Stability of metal complexes

Sol. (a)

54. Match List-I with List-II

List-I		List-II	
A.	$[Cu(NH_3)_6]^{2+}$	I.	–0.6
B.	$[Ti(H_2O)_6]^{3+}$	II.	–2.0
C.	$[Fe(CN)_6]^{3-}$	III.	–1.2
D.	$[NiF_6]^{4-}$	IV.	–0.4

Choose the correct answer from the options given below: [12 April, 2023 (Shift-I)]

(a) A-I, [illegible] C-I[illegible] D-[illegible]
(b) A-II, B-III, C-I, D-IV
(c) A-I, B-II, C-IV, D-III
(d) A-III, B-IV, C-I, D-II

Sol. (a)

55. Assertion (A): $[CoCl(NH_3)_5]^{2+}$ absorbs at lower wavelength of light with respect to $[Co(NH_3)_5(H_2O)]^{3+}$

Reason (R): It is because the wavelength of the light absorbed depends on the oxidation state of the metal ion.

In the light of the above statements, choose the correct answer from the options given below: [11 April, 2023 (Shift-II)]

(a) (A) is false but (R) is true.
(b) (A) is true but (R) is false.
(c) Both (A) and (R) are true and (R) is the correct explanation of (A).
(d) Both (A) and (R) are true and (R) is NOT the correct explanation of (A).

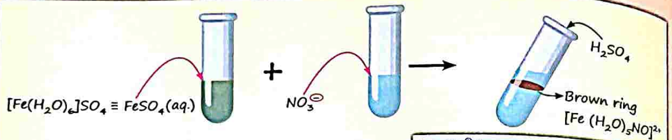
Sol. (a)

LIMITATION OF CFT

1. Crystal field theory assumed that ligands are point charges. It follows that anionic ligands should exert the greatest splitting effect but these ligands actually are found at the low end of the spectrochemical series.
2. Further, it does not take into account the covalent character of bonding between the ligand and the central atom

Discussion About Some Important Complexes

Brown Ring Complex ⇒ $[Fe(H_2O)_5NO]^{2+}$



☐ $NO^{\oplus}$ is present in complex.
☐ Oxidation state of Fe ≡ +1

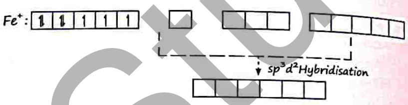
☐ $\overset{+5}{NO_3^-} + Fe^{2+} \xrightarrow{H^+} \overset{+2}{NO} + Fe^{+3}$
[O.A.] [R.A.]

$[Fe(H_2O)_6]^{2+} + NO \xrightarrow[-H_2O]{} [Fe(H_2O)_5NO]^{2+}$

$Fe^{2+} \leftarrow \ddot{N}O \xrightarrow[\text{transfer spectra}]{\text{ligand to metal charge}} \overset{\oplus}{Fe} \leftarrow \overset{\oplus}{NO}$

$[Fe(H_2O)_5NO]^{2+}$

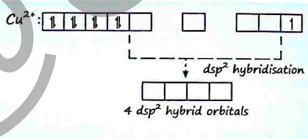
☐ Fe^+ : $4s^1\ 3d^6$
: $3d^7\ 4s^0$



☐ Hybridisation = sp^3d^2
☐ No of unpaired electrons = 3
☐ Magnetic Moment = $\sqrt{3(3+2)}$ BM
= 3.87 BM

$[Cu(NH_3)_4]^{2+}$

☐ Square planar
$[Cu^{2+} : 3d^9]$



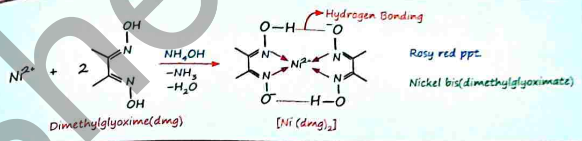
☐ Hybridization = dsp^2
☐ No of unpaired electrons = 1
☐ Colour = deep Blue

$[Ni(dmg)_2]$

Important for JEE Main and NEET both

☐ dmg^- → -1 charge
→ Bidentate (nitrogen donor ligand)

☐ $Ni^{2+} : 3d^8$



☐ Complex acquires stability through chelation and intramolecular H-bonding.

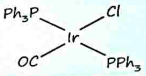
☐ Hybridisation & Geometry = Square planar/dsp^2
☐ No of unpaired electrons = Zero
☐ Colour = Rosy Red / Scarlet Red
☐ Types of bonds = H-bond, Covalent, Co-ordinate bond
☐ Types of rings = 5 and 6 membered
☐ No of rings = 4 [Two ⑤ and Two ⑥ membered rings]

[R[illegible](PP[illegible])$_3$] Wi[illegible]nso[illegible] [illegible]alyst: Chloridotris(triphenylphosphine)rhodium(I)

[illegible]xid[illegible]te Rh [illegible] +[illegible]

$\underline{Rh^+ : 4d^8}$
↓
dsp^2 [Square planar]

$[IrCl(CO)(PPh_3)_2]$ Vaska complex: Trans-carbonylchloridobis(triphenylphosphine) iridium(I)



$\underline{Ir^+ = 5d^8}$
↓
dsp^2[Square planar]

$Na_2[Fe(CN)_5NO]$ Sodium Nitroprusside

Oxidation state of NO ≡ +1
If oxidation state of Fe is x.
(2×1) + x + 5(−1) + (+1) = 0, then x = 2

$Na_4[Fe(CN)_5NOS]$ Sodium thionitroprusside

Oxidation state of NOS ≡ −1
If oxidation state of Fe is x.
(4×1) + x + 5(−1) + (−1) = 0, then x = 2

56. Identify from the following species in which d^2sp^3 hybridization is shown by central atom: [27 Jan, 2024 (Shift-II)]

(a) $[Co(NH_3)_6]^{3+}$ (b) BrF_5 (c) $[PtCl_4]^{2-}$ (d) SF_6

Sol. (a)

57. Which of the following are paramagnetic? [NEET 2025]

A. $[NiCl_4]^{2-}$ B. $Ni(CO)_4$ C. $[NiCN)_4]^{2-}$

D. $[Ni(H_2O)_6]^{2+}$ E. $Ni(PPh_3)_4$

Choose the correct answer from the options given below:

(a) A and C only (b) B and E only (c) A and D only (d) A, D and E only

Sol. (c)

58. The correct order of the wavelength of light absorbed by the following complexes is, [NEET 2025]

A. $[Co(NH_3)_6]^{3+}$ B. $[Co(CN)_6]^{3-}$ C. $[Cu(H_2O)_4]^{2+}$ D. $[Ti(H_2O)_6]^{3+}$

Choose the correct answer from the options given below:

(a) B < D < A < C (b) B < A < D < C (c) C < D < A < B (d) C < A < D < B

Sol. (b)

59. Given below are two statements: [NEET 2024]

Statement I: Both $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$ complexes are octahedral but differ in their magnetic behaviour.

Statement II: $[Co(NH_3)_6]^{3+}$ is diamagnetic whereas $[CoF_6]^{3-}$ is paramagnetic.

In the light of the above statements, choose the correct answer from the options given below:

(a) Statement I is true but Statement II is false.

(b) Statement I is false but Statement II is true.

(c) Both Statement I and Statement II are true.

(d) Both Statement I and Statement II are false.

Sol. (c)

60. The order of energy absorbed which is responsible for the color of complexes [NEET 2022]

A. $[Ni(H_2O)_2(en)_2]^{2+}$ B. $[Ni(H_2O)_4(en)]^{2+}$ and C. $[Ni(en)_3]^{2+}$ is :

(a) B > A > C (b) A > B > C (c) C > B > A (d) C > A > B

Sol. (d)

61. Match List-I with List-II. [NEET 2021]

List-I		List-II	
(A)	$[Fe(CN)_6]^{3-}$	(i)	5.92 BM
(B)	$[Fe(H_2O)_6]^{3+}$	(ii)	0 BM
(C)	$[Fe(CN)_6]^{4-}$	(iii)	4.90 BM
(D)	$[Fe(H_2O)_6]^{2+}$	(iv)	1.73 BM

Choose the correct answer from the options given below.

(a) A-ii B-iv C-iii D-i
(b) A-i B-iii C-iv D-ii
(c) A-iv B-i C-ii D-iii
(d) A-iv B-ii C-i D-iii

Sol. (c)

62. Which of the following is the correct order of increasing field strength of ligands to form coordination compounds? [NEET 2020]

(a) $SCN^- < F^- < CN^- < C_2O_4^{2-}$ (b) $F^- < SCN^- < C_2O_4^{2-} < CN^-$

(c) $CN^- < C_2O_4^{2-} < SCN^- < F^-$ (d) $SCN^- < F^- < C_2O_4^{2-} < CN^-$

Sol. (d)

63. Match the coordination number and type of hybridisation with distribution of hybrid orbitals in space based on Valence bond theory. [NEET 2020-Covid]

Coordination number and type of hybridisation		Distribution of hybrid orbitals in space	
(A)	4, sp^3	(i)	Trigonal bipyramidal
(B)	4, dsp^2	(ii)	Octahedral
(C)	5, sp^3d	(iii)	Tetrahedral
(D)	6, d^2sp^3	(iv)	Square planar

Select the correct option:

(a) A-iii B-iv C-i D-ii
(b) A-iv B-i C-ii D-iii
(c) A-iii B-i C-iv D-ii
(d) A-ii B-iii C-iv D-i

Sol. ([illegible])

64. What is the correct electronic configuration of the central atom in $K_4[Fe(CN)_6]$ based on crystal field theory? [NEET 2019]

(a) $t_{2g}^4 e_g^2$ (b) $t_{2g}^6 e_g^0$ (c) $e^3t_{2g}^3$ (d) $e^4t_{2g}^2$

Sol. (b)

65. The geometry and magnetic behaviour of the complex $[Ni(CO)_4]$ are? [NEET 2018]

(a) Square planar geometry and diamagnetic (b) Tetrahedral geometry and diamagnetic

(c) Tetrahedral geometry and paramagnetic (d) Square planar geometry and paramagnetic

Sol. (b)

66. Correct increasing order for the wavelengths of absorption in the visible region for the complexes of Co^{3+} is: [NEET 2017-Delhi]

(a) $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(H_2O)_6]^{3+}$ (b) $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(H_2O)_6]^{3+}$

(c) $[Co(H_2O)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$ (d) $[Co(H_2O)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$

Sol. (b)

67. Pick out the correct statement with respect to $[Mn(CN)_6]^{3-}$ [NEET 2017-Delhi]

(a) It is dsp^2 hybridised and square planar (b) It is sp^3d^2 hybridised and octahedral

(c) It is sp^3d^2 hybridised and tetrahedral (d) It is d^2sp^3 hybridised and octahedral

Sol. (d)

68. The hybridisation involved in complex $[Ni(CN)_4]^{2-}$ is (Atomic Number Ni = 28) [NEET 2015 Re]

(a) d^2sp^3 (b) dsp^2 (c) sp^3 (d) d^2sp^2

Sol. (b)

69. Which of these statements about $[Co(CN)_6]^{3-}$ is true? [NEET 2015]

(a) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a low-spin configuration

(b) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a high-spin configuration

(c) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a high-spin configuration

(d) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a low-spin configuration

Sol. (d)

70. Among the following complexes the one which shows zero crystal field stabilization energy (CFSE) is: [NEET 2014]

(a) $[Fe(H_2O)_6]^{3+}$ (b) $[Co(H_2O)_6]^{2+}$ (c) $[Co(H_2O)_6]^{3+}$ (d) $[Mn(H_2O)_6]^{3+}$

Sol. (a)

71. A magnetic moment of 1.73 BM will be shown by one among the following: [NEET 2013]

(a) $[Cu(NH_3)_4]^{2+}$ (b) $[Ni(CN)_4]^{2-}$ (c) $TiCl_4$ (d) $[CoCl_6]^{4-}$

Sol. (a)

72. Low spin complex of d^6 - cation in an octahedral field will have the following energy: [NEET 2012 Mains]

(a) $\frac{-2}{5}\Delta_o + P$ (b) $\frac{-12}{5}\Delta_o + P$ (c) $-\frac{12}{5}\Delta_o + 3P$ (d) $\frac{-2}{5}\Delta_o + 2P$

Sol. (c)

73. Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour? [NEET 2012 Pre]

(a) $[Co(NH_3)_6]^{3+}$ (b) $[Ni(NH_3)_6]^{2+}$ (c) [illegible]$(NH_3)_6]^{2+}$ (d) [illegible]$]^{3+}$

Sol. (b)

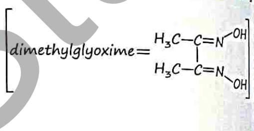
74. Red precipitate is obtained when ethanol solution of dimethylglyoxime is added to ammonical Ni (II). Which of the following statements is not true? [NEET 2012 Mains]

(a) Red complex has a square planar geometry

(b) Complex has symmetrical H-bonding

(c) Red complex has a tetrahedral geometry

(d) Dimethylglyoxime functions as bidentate ligand



Sol. (c)

75. Of the following complex ions, which is diamagnetic in nature? [NEET 2011 Pre]

(a) $[CoF_6]^{3-}$ (b) $[NiCl_4]^{2-}$ (c) $[Ni(CN)_4]^{2-}$ (d) $[CuCl_4]^{2-}$

Sol. (c)

76. Which of the following complex compounds will exhibit highest paramagnetic behaviour? [NEET 2011 Mains]

(Atomic Number Ti = 22, Cr = 24, Co = 27, Zn = 30)

(a) $[Co(NH_3)_6]^{3+}$ (b) $[Zn(NH_3)_6]^{2+}$ (c) $[Ti(NH_3)_6]^{3+}$ (d) $[Cr(NH_3)_6]^{3+}$

Sol. (d)

77. The d-electron configurations of Cr^{2+}, Mn^{2+}, Fe^{2+} and Co^{2+} are d^4, d^5, d^6 and d^7 respectively. Which one of the following will exhibit minimum paramagnetic behaviour? [NEET 2011 Pre, 2007]

(Atomic Number Cr = 24, Mn = 25, Fe = 26, Co = 27)

(a) $[Cr(H_2O)_6]^{2+}$ (b) $[Mn(H_2O)_6]^{2+}$ (c) $[Fe(H_2O)_6]^{2+}$ (d) $[Co(H_2O)_6]^{2+}$

Sol. (d)

78. Crystal field stabilization energy for high spin d^4 octahedral complex is: [NEET 2010 Pre]

(a) $-0.6\Delta_o$ (b) $-1.8\Delta_o$ (c) $-1.6\Delta_o + P$ (d) $-1.2\Delta_o$

Sol. (a)

79. Which of the following complex ion is not expected to absorb visible light? [NEET 2010 Pre]

(a) $[Ni(H_2O_6)]^{2+}$ (b) $[Ni(CN)_4]^{2-}$ (c) $[Cr(NH_3)_6]^{3+}$ (d) $[Fe(H_2O)_6]^{2+}$

Sol. (b)

80. Which of the following complex ions is expected to absorb visible light? [NEET 2009]

(Atomic number Zn = 30, Sc = 21, Ti = 22, Cr = 24)

(a) $[Ti\,(en)_2\,(NH_3)_2]^{4+}$ (b) $[Cr\,(NH_3)_6]^{3+}$

(c) $[Zn\,(NH_3)_6]^{2+}$ (d) $[Sc\,(H_2O)_3\,(NH_3)_3]^{3+}$

Sol. (b)

81. Out of TiF_6^{2-}, CoF_6^{3-}, Cu_2Cl_2 and $NiCl_4^{2-}$ (Z of Ti = 22, Co = 27, Cu = 29, Ni = 28), the colourless species are: [NEET 2009]

(a) Cu_2Cl_2 and $NiCl_4^{2-}$ (b) TiF_6^{2-} and Cu_2Cl_2

(c) CoF_6^{3-} and $NiCl_4^{2-}$ (d) TiF_6^{2-} and CoF_6^{3-}

Sol. [illegible]

82. In which of the following coordination entities the magnitude of Δ_o (CFSE in octahedral field) will be maximum: (atomic number Co = 27)? [NEET 2008]

(a) $[Co(C_2O_4)_3]^{3-}$ (b) $[Co(H_2O)_6]^{3+}$ (c) $[Co(NH_3)_6]^{3+}$ (d) $[Co(CN)_6]^{3-}$

Sol. (d)

83. Which of the following complexes exhibits the highest paramagnetic behaviour? Where gly = glycine, en = ethylenediamine and bpy = bipyridyl moities. (Atomic number Ti = 22, V = 23, Fe = 26, Co = 27): [NEET 2008]

(a) $[Ti(NH_3)_6]^{3+}$ (b) $[V(gly)_2(OH)_2(NH_3)_2]^{+}$

(c) $[Fe(en)(bpy)(NH_3)_2]^{2+}$ (d) $[Co(Ox)_2(OH)_2]^{-}$

Sol. (c)

84. $[Cr(H_2O)_6]Cl_3$ (atomic number of Cr = 24) has a magnetic moment of 3.83 BM, the correct distribution of 3d electrons in the chromium of the complex is: [NEET 2006]

(a) $3d^1_{x^2-y^2}, 3d^1_{z^2}, 3d^1_{xz}$ (b) $3d^1_{xy}, 3d^1_{x^2-y^2}, 3d^1_{yz}$

(c) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{xz}$ (d) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{z^2}$

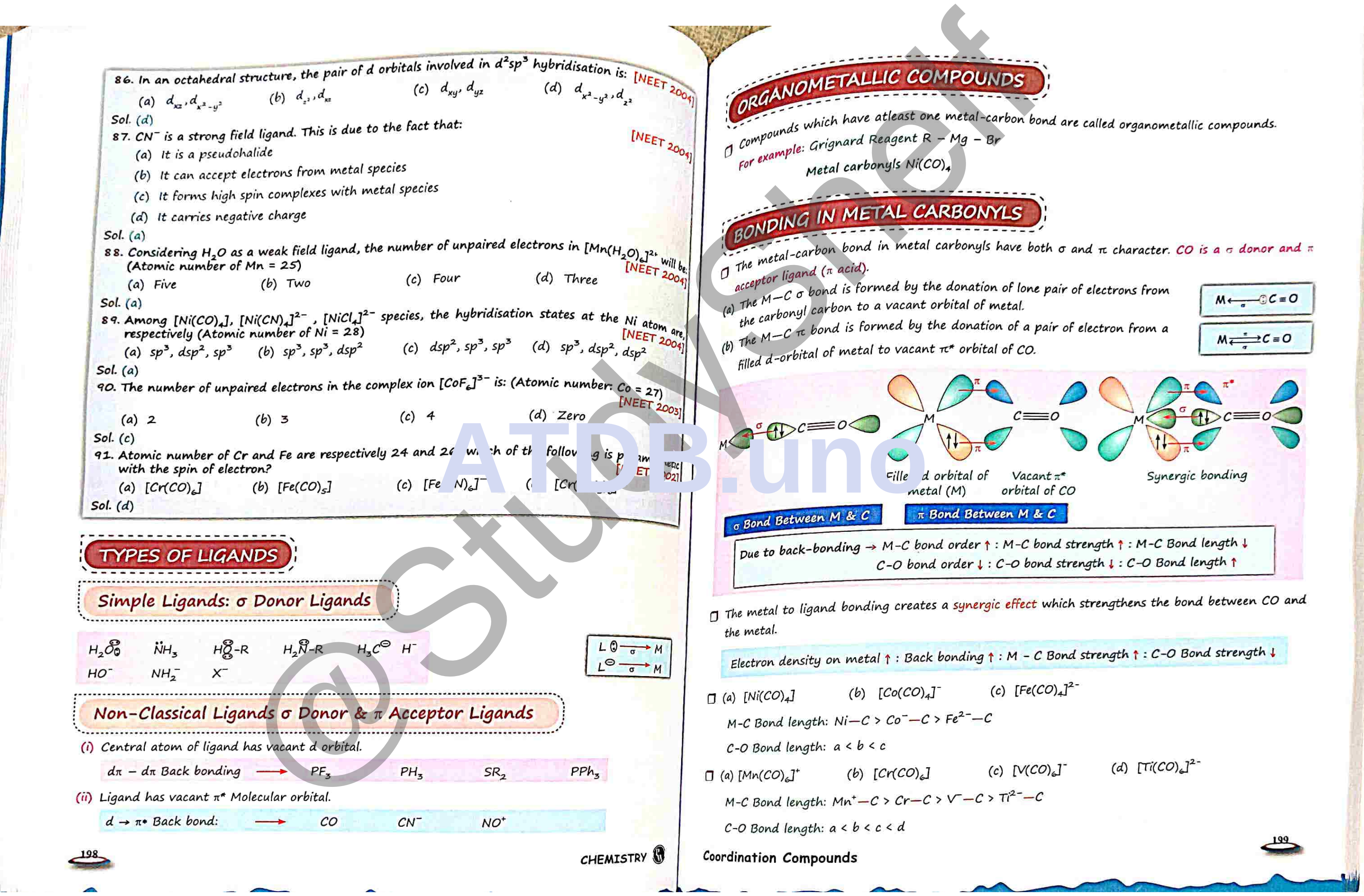
Sol. (c)

85. Which one of the following is an inner orbital complex as well as diamagnetic in behaviour? [NEET 2005]

(Atomic number: Zn = 30, Cr = 24, Co = 27, Ni = 28)

(a) $[Zn\,(NH_3)_6]^{2+}$ (b) $[Cr\,(NH_3)_6]^{3+}$ (c) $[Co\,(NH_3)_6]^{3+}$ (d) $[Ni\,(NH_3)_6]^{2+}$

Sol. (c)



86. In an octahedral structure, the pair of d orbitals involved in d^2sp^3 hybridisation is: [NEET 2004]
(a) $d_{xz}, d_{x^2-y^2}$ (b) d_{z^2}, d_{xz} (c) d_{xy}, d_{yz} (d) $d_{x^2-y^2}, d_{z^2}$

Sol. (d)

87. CN^- is a strong field ligand. This is due to the fact that: [NEET 2004]
(a) It is a pseudohalide
(b) It can accept electrons from metal species
(c) It forms high spin complexes with metal species
(d) It carries negative charge

Sol. (a)

88. Considering H_2O as a weak field ligand, the number of unpaired electrons in $[Mn(H_2O)_6]^{2+}$ will be: (Atomic number of Mn = 25) [NEET 2004]
(a) Five (b) Two (c) Four (d) Three

Sol. (a)

89. Among $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$, $[NiCl_4]^{2-}$ species, the hybridisation states at the Ni atom are, respectively (Atomic number of Ni = 28) [NEET 2004]
(a) sp^3, dsp^2, sp^3 (b) sp^3, sp^3, dsp^2 (c) dsp^2, sp^3, sp^3 (d) sp^3, dsp^2, dsp^2

Sol. (a)

90. The number of unpaired electrons in the complex ion $[CoF_6]^{3-}$ is: (Atomic number: Co = 27) [NEET 2003]
(a) 2 (b) 3 (c) 4 (d) Zero

Sol. (c)

91. Atomic number of Cr and Fe are respectively 24 and 2[illegible] w[illegible]ch of th[illegible] follov[illegible]g is p[illegible]am[illegible]etic with the spin of electron? [[illegible]ET [illegible]021]
(a) $[Cr(CO)_6]$ (b) $[Fe(CO)_5]$ (c) $[Fe$[illegible]$N)_6]^-$ ([illegible]) $[Cr($[illegible]

Sol. (d)

TYPES OF LIGANDS

Simple Ligands: σ Donor Ligands

$H_2\ddot{O}$ $\ddot{N}H_3$ $H\ddot{O}-R$ $H_2\ddot{N}-R$ $H_3C^{\ominus}$ H^-
HO^- NH_2^- X^-

$L \overset{\cdot\cdot}{} \xrightarrow[\sigma]{} M$
$L^{\ominus} \xrightarrow[\sigma]{} M$

Non-Classical Ligands σ Donor & π Acceptor Ligands

(i) Central atom of ligand has vacant d orbital.

$d\pi - d\pi$ Back bonding ⟶ PF_3 PH_3 SR_2 PPh_3

(ii) Ligand has vacant π* Molecular orbital.

$d \rightarrow \pi^*$ Back bond: ⟶ CO CN^- NO^+

ORGANOMETALLIC COMPOUNDS

☐ Compounds which have atleast one metal-carbon bond are called organometallic compounds.
For example: Grignard Reagent R – Mg – Br
Metal carbonyls $Ni(CO)_4$

BONDING IN METAL CARBONYLS

☐ The metal-carbon bond in metal carbonyls have both σ and π character. CO is a σ donor and π acceptor ligand (π acid).

(a) The M—C σ bond is formed by the donation of lone pair of electrons from the carbonyl carbon to a vacant orbital of metal.

$M \xleftarrow[\sigma]{} :C \equiv O$

(b) The M—C π bond is formed by the donation of a pair of electron from a filled d-orbital of metal to vacant π* orbital of CO.

$M \underset{\sigma}{\overset{\pi}{\rightleftarrows}} C \equiv O$

M σ C≡O
M π π C≡O
Filled d orbital of metal (M)
Vacant π* orbital of CO
M π π* σ π C≡O
Synergic bonding

σ Bond Between M & C

π Bond Between M & C

Due to back-bonding → M–C bond order ↑ : M–C bond strength ↑ : M–C Bond length ↓
C–O bond order ↓ : C–O bond strength ↓ : C–O Bond length ↑

☐ The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

Electron density on metal ↑ : Back bonding ↑ : M – C Bond strength ↑ : C–O Bond strength ↓

☐ (a) $[Ni(CO)_4]$ (b) $[Co(CO)_4]^-$ (c) $[Fe(CO)_4]^{2-}$

M-C Bond length: $Ni—C > Co^-—C > Fe^{2-}—C$

C-O Bond length: a < b < c

☐ (a) $[Mn(CO)_6]^+$ (b) $[Cr(CO)_6]$ (c) $[V(CO)_6]^-$ (d) $[Ti(CO)_6]^{2-}$

M-C Bond length: $Mn^+—C > Cr—C > V^-—C > Ti^{2-}—C$

C-O Bond length: a < b < c < d

(JEE Adv. 2007)

92. Among the following metal carbonyls, the C – O bond order is lowest in:

(a) $[Mn(CO)_6]^+$ (b) $[V(CO)_6]^-$ (c) $[Cr(CO)_6]$ (d) $[Fe(CO)_5]$

Sol. (d) The C–O bond order is lowest in $[Fe(CO)_5]$ because iron in the 0 oxidation state has a strong ability for back-donation to the 5 CO ligands (other complexes have 6 CO ligands), which weakens the C–O bond. This results in the lowest bond order among the given complexes.

93. The bond length in CO is 1.128 A°, what will be the order of bond length of CO in CO^+ and $Fe(CO)_5$ with respect to free CO?

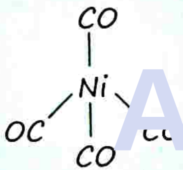
Sol.

CO^+
bond Order > 3
(Bond order is approximately 3.5 for CO^+ according to MOT)

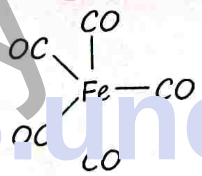
Free $C \equiv O$
bond Order = 3

$Fe(CO)_5$
$Fe \leftarrow C \equiv O$
Bond order < 3
(due to back bonding)

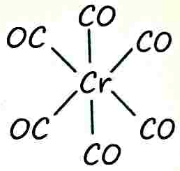
C—O Bond length : $Fe(CO)_5 > CO > CO^+$



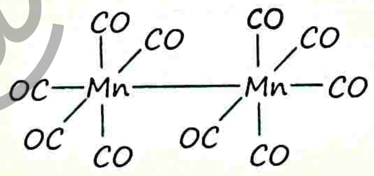
$Ni(CO)_4[sp^3]$
Tetrahedral



$Fe(CO)_5[dsp^3]$
Trigonal bipyramidal

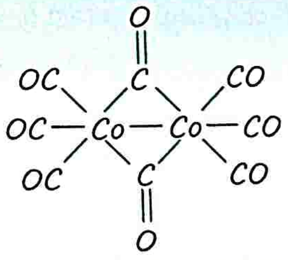


$Cr(CO)_6[d^2sp^3]$
Octahedral



$[Mn_2(CO)_{10}]$

Number of metal to metal bond [Mn – Mn]: 1
Number of bridging CO: 0
Number of terminal CO: 10



$[Co_2(CO)_8]$

Number of metal to metal bond [Co – Co]: 1
Number of bridging CO: 2
Number of terminal CO: 6

94. In which one of the following metal carbonyls, CO forms a bridge between metal atoms?

[29 Jan, 2024 (Shift-

(a) $[Co_2(CO)_8]$ (b) $[Mn_2(CO)_{10}]$ (c) $[Os_3(CO)_{12}]$ (d) $[Ru_3(CO)_{12}]$

Sol. (a)

95. The number of bridging CO ligand(s) and Co–Co bond (s) in $Co_2(CO)_8$ respectively are: [11 Jan, 2019 (Shift-II)]

(a) 2 and 1 (b) 2 and 0 (c) 0 and 2 (d) 4 and 0

Sol. (a)

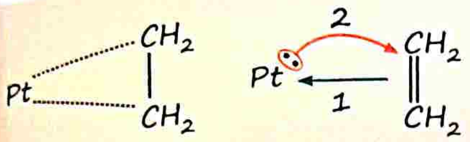
96. Low oxidation state of metals in their complexes are common when ligands: [27 July, 2022 (Shift-II)]

(a) have good π-accepting character (b) have good σ-donor character

(c) are having good π-donating ability (d) are having poor σ-donating ability

Sol. (a)

π DONOR AND π ACCEPTOR LIGANDS



1. Donation of π e^- from C_2H_4 to Pt
2. Donation of e^- from Pt (d e^-) to π* of C_2H_4.

Hepticity of Ligand

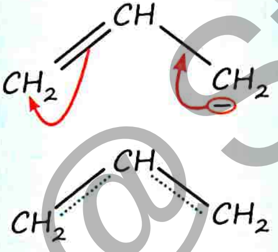
☐ No of atoms involved in donation of π electron.

C_2H_4

☐ $\eta^2-C_2H_4$

☐ $2e^-$ donor

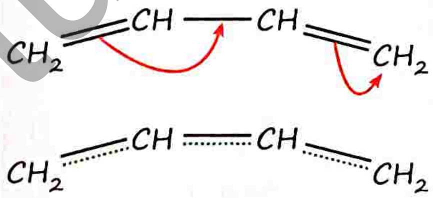
$C_3H_5^-$



☐ $\eta^3-C_3H_5^-$

☐ $4e^-$ Donor

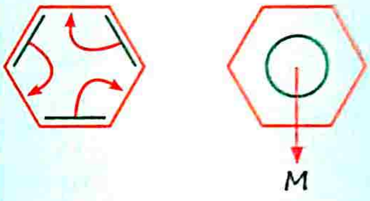
C_4H_6



☐ $\eta^4-C_4H_6$

☐ $4e^-$ Donor

C_6H_6



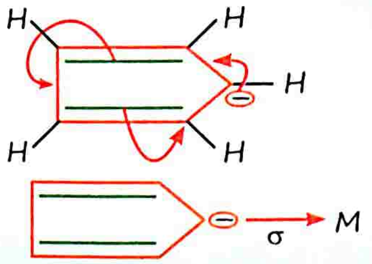
☐ $\eta^6-C_6H_6 \equiv \pi-C_6H_6$

☐ $6e^-$ Donor

$C_5H_5^-$ → Cyclopentadienyl [cp]

1. $\pi-C_5H_5^-$ → $6e^-$ donor

2. $\sigma-C_5H_5^-$ → $2e^-$ donor

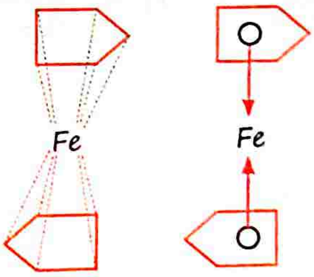


Ferrocene

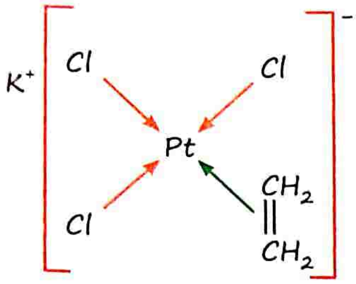
$Fe(C_5H_5)_2$

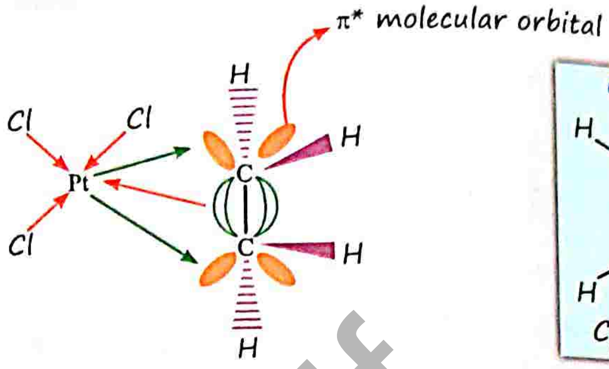
$Fe(Cp)_2$

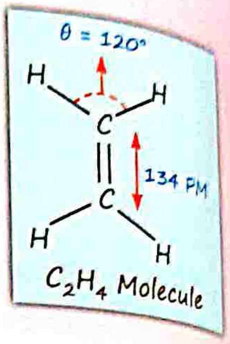
Oxidation state of Fe +2(charge on cp) = 0



Zeise's Salt $K^+ [PtCl_3(\eta^2 - C_2H_4)]^-$







C_2H_4 Molecule

- ☐ Square planar complex (Pt^{2+} : $5d^8$ / dsp^2)
- ☐ C–C Bond length in Zeise Salt = 137.5 pm
  C–C Bond length in free C_2H_4 = 134 pm → donation of electron density from Pt to π* of C_2H_4 makes C–C bond weak in Zeise salt

EFFECTIVE ATOMIC NUMBER

EAN = Z − n + [2 × CN]
CN → Coordination number
n → Oxidation state of metal
Z → Atomic no. of metal

Sidgwick EAN Rule:–

The metal complexes are stable when EAN is equal to the nearest noble gas configuration.

$[Cr(CO)_6]$	EAN = 24 – 0 + (6 × 2) = 36 ≡ [Kr]
$[Pd(NH_3)_6]^{4+}$	EAN = 46 – 4 + (6 × 2) = 54 ≡ [Xe]
$[PtCl_6]^{2-}$	EAN = 78 – 4 + (6 × 2) = 86 ≡ [Rn]

- ☐ $[Pt(NH_3)_4]^{2+}$ EAN = 78 – 2 + (4 × 2)
- ☐ $[Ti(\sigma-C_5H_5)_2(\pi-C_5H_5)_2]$ EAN = 22 – 4 + 16 = 34

  If x is the oxidation state of Ti.

  x + 2(– 1) + 2(– 1) = 0 then x = 4

$\sigma-C_5H_5$: $2e^-$ donor
$\pi-C_5H_5$: $6e^-$ donor

- ☐ $[Fe(\pi-C_5H_5)_2]$ EAN = 26 – 2 + 12 = 36

  Oxidation state of Fe is x, then

  x + 2(–1) = 0 ⇒ x = 2
- ☐ $[Fe(CO)_2(NO)_2]$ EAN = 26 – 0 + (2 × 2 + 2 × 3] = 36
  - ◆ All donations contribute two electrons, while NO is considered as a 3-electron donor.

Effective Atomic Numbers of Some Metals in Complexes

Atom	Atomic number	Complex	Electrons lost in ion formation	Electrons gained by coordination	EAN
Fe	26	$[Fe(CN)_6]^{4-}$	2	12	36
Fe	26	$[Fe(CO)_5]$	0	10	36
Co	27	$[Co(NH_3)_6]^{3+}$	3	12	36
Ni	28	$[Ni(CO)_4]$	0	8	36
Cu	29	$[Cu(CN)_4]^{3-}$	1	8	36
Fe	26	$[Fe(CN)_6]^{3-}$	3	12	35
Ni	28	$[Ni(NH_3)_6]^{2+}$	2	12	38
Pd	46	$[PdCl_4]^{2-}$	2	8	52
Co	27	$[Co(CO)_4]^-$	-1	8	36
V	23	$[V(CO)]^-$	-1	12	36

☐ $[Mn(CO)_6]$ can act as a reducing agent.

$$\underset{\substack{\text{EAN = 37}\\ \text{(Reducing Agent)}}}{[Mn(CO)_6]} \xrightarrow{-e^-} \underset{\substack{\text{EAN = 36}\\ \text{(Stable)}}}{[Mn(CO)_6]^+}$$

☐ $[V(CO)_6]$ can act as oxidizing agent.

$$\underset{\substack{\text{EAN = 35}\\ \text{(oxidising agent)}}}{[V(CO)_6]} \xrightarrow{+e^-} \underset{\substack{\text{EAN = 36}\\ \text{(Stable)}}}{[V(CO)_6]^-}$$

☐ $[Mn(CO)_5]$ undergoes dimerization to attain the noble gas configuration.

$$\underset{\substack{\text{EAN = 35}\\ \text{(Unstable)}}}{2\,Mn(CO)_5} \longrightarrow \underset{\text{EAN=36}}{(CO)_5Mn} - \underset{\text{EAN = 36}}{Mn(CO)_5}$$

☐ The number of CO molecule attached in mononuclear carbonyls can be predicted.

$Fe(CO)_x$ $\quad 26 - 0 + [x \,.\, 2] = 36$
$x = 5$

$Ni(CO)_y$ $\quad 28 - 0 + [y \times 2] = 36$
$y = 4$

$Cr(CO)_z$ $\quad 24 - 0 + [z \times 2] = 36$
$z = 6$

97. $Mn_2(CO)_{10}$ is an organometalic compound due to the presence of **[12 Jan, 2019 (Shift-I)]**

(a) Mn – C bond (b) Mn – Mn bond (c) Mn – O bond (d) C – O bond

Sol. (a)

98. $[Mn_2(CO)_{10}]$ and $[Co_2(CO)_8]$ structures have [NEET 2024

A. Metal-Metal linkage
B. Terminal CO groups
C. Bridging CO groups
D. Metal in zero oxidation state

Choose the correct answer from the options given below

(a) Only A, B, C (b) Only B, C, D (c) Only A, C, D (d) Only A, B, D

Sol. (d)

99. Given below are two statements: one is labelled as Assertion (A) and the other is labelled as Reason (R). [NEET 2021

Assertion (A): The metal carbon bond in metal carbonyls possesses both σ and π character.

Reason (R): The ligand to metal bond is a π bond and metal to ligand bond is a σ bond.

In the Light of the above statements, choose the most appropriate answer from the options given below:

(a) (A) is not correct but (R) is correct

(b) Both (A) and (R) are correct and (R) is the correct explanation of (A)

(c) Both (A) and (R) are correct but (R) is not the correct explanation of (A)

(d) (A) is correct but (R) is not correct

Sol. (d)

100. Iron carbonyl, $Fe(CO)_5$ is [NEET 20

(a) Tetranuclear (b) Mononuclear (c) Dinuclear (d) Trinuclear

Sol. (b)

101. Which of the following has longest C–O bond length? (Free C–O bond length in CO is 1.12 [NEET 2016

(a) $[Mn(CO)_6]^+$ (b) $Ni(CO)_4$ (c) $[Co(CO)_4]^-$ (d) $[Fe(CO)_4]^{2-}$

Sol. (d)

102. Which of the following carbonyl's will have the strongest C – O bond? [NEET 2011 Mains]

(a) $V(CO)_6^-$ (b) $Fe(CO)_5$ (c) $Mn(CO)_6^+$ (d) $Cr(CO)_6$

Sol. (c)

103. Which of the following does not have a metal- carbon bond? [NEET 2004]

(a) C_2H_5MgBr (b) $K[Pt(C_2H_4)Cl_3]$ (c) $Ni(CO)_4$ (d) $Al(OC_2H_5)_3$

Sol. (d)

104. Among the following, which is not the π-bonded organometallic compound? [NEET 2003]

(a) $K[PtCl_3(\eta^2-C_2H_4)]$ (b) $Fe(\eta^5-C_5H_5)_2$

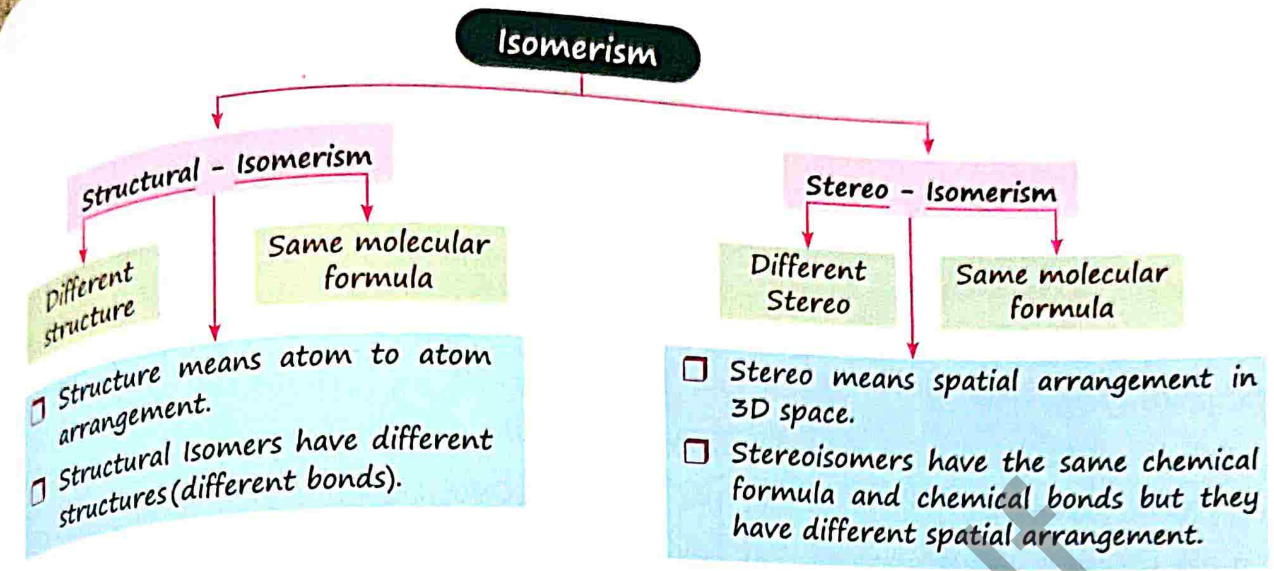
(c) $Cr(\eta^6-C_6H_6)_2$ (d) $(CH_3)_4Sn$

Sol. (d)

ISOMERISM

Isomers are two or more compounds that have the same chemical formula but a different arrangement of atoms. Because of the different arrangement of atoms, they differ in one or more physical or chemical properties. Two principal types of isomerism are known among coordination compounds.

(a) Structural isomerism (b) Stereoisomerism



- ☐ Structure means atom to atom arrangement.
- ☐ Structural Isomers have different structures (different bonds).

- ☐ Stereo means spatial arrangement in 3D space.
- ☐ Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement.

STRUCTURAL ISOMERISM

(i) Ionisation Isomerism

Isomers having same molecular formula but give **different ions in solution** are known as ionisation isomers and this phenomena is known as Ionisation Isomerism.

Example-

☐ $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ are ionisation isomers because they give different ions in aqueous solution.

$$[Co(NH_3)_5Br]SO_4 \longrightarrow [Co(NH_3)_5Br]^{2+} + SO_4^{2-}$$

$$[Co(NH_3)_5SO_4]Br \longrightarrow [Co(NH_3)_5SO_4]^{+} + Br^{-}$$

☐ 1. $[Co(en)_2(NO_2)Cl]\ SO_4$
2. $[Co\ (en)_2(NO_2)\ (SO_4)]\ Cl$
3. $[Co(en)_2Cl\ (SO_4)]\ NO_2$

→ Ionisation isomers

(ii) Solvate Isomerism

Isomers having same molecular formula but **different no. of water molecules as ligands and as free solvent molecules** are known as solvate isomers and this phenomena is known as solvate isomerism.

Example-

$[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ and $[Cr(H_2O)_3Cl_3].3H_2O$

(iii) Linkage Isomerism

Isomers having same molecular formula but **different linkage between metal and ligand** are known as linkage isomers and this phenomena is known as linkage isomerism.

Example-

☐ (a) $[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$

(b) $[Cr(NH_3)_5(NCS)]Br_2$ and $[Cr(NH_3)_5(SCN)]Br_2$

☐ (a) $[Co(en)_2(NCS)(NO_2)]Cl \rightarrow$ 4 linkage isomers

1.	NCS^-	NO_2^-
2.	NCS^-	ONO^-
3.	SCN^-	NO_2^-
4.	SCN^-	ONO^-

(b) $[Co(en)_2(NCS)(ONO)]Cl$

(c) $[Co(en)_2(SCN)(NO_2)]Cl$

(d) $[Co(en)_2(SCN)(ONO)]Cl$

☐ 4 linkage isomers are possible for square planar $[Pd\ FCl\ (SCN)\ (NO_2)]^{2+}$ –

(a) $[Pd\ FCl\ (SCN)\ (NO_2)]^{2+}$ (b) $[Pd\ FCl\ (SCN)\ (ONO)]^{2+}$

(c) $[Pd\ FCl\ (NCS)\ (NO_2)]^{2+}$ (d) $[Pd\ FCl\ (NCS)\ (ONO)]^{2+}$

(iv) Coordination Isomerism

This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

Example-

a. $[Co(en)_3][Cr(CN)_6]$ and $[Cr(en)_3]\ [Co(CN)_6]$ b. $[Pt(NH_3)_4][CuCl_4]$ and $[Cu(NH_3)_4][PtCl_4]$

Q. Find total structural isomers in $[Co(en)_2(NCS)(NO_2)]Cl$ complex

Ans.

$[Co(en)_2\ (NCS)(NO_2)]Cl$ $[Co(en)_2Cl(NO_2)]\ NCS$ $[Co(en)_2(NCS)Cl]NO_2$

$[Co(en)_2\ (NCS)\ (ONO)]Cl$ $[Co(en)_2Cl\ (ONO)]\ NCS$ $[Co(en)_2(SCN)Cl]NO_2$

$[Co(en)_2(SCN)\ (NO_2)]Cl$

$[Co(en)_2\ (SCN)(ONO)]Cl$

Total No. of structural isomers ≡ 8

105. Match List-I with List-II. [NEET 2024]

	List-I (Complex)		List-II (Type of isomerism)
A.	$[Co(NH_3)_5(NO_2)]Cl_2$	I.	Solvate isomerism
B.	$[Co(NH_3)_5(SO_4)]Br$	II.	Linkage isomerism
C.	$[Co(NH_3)_6][Cr(CN)_6]$	III.	Ionization isomerism
D.	$[Co(H_2O)_6]Cl_3$	IV.	Coordination isomerism

Choose the correct answer from the options given below:

(a) A-I, B-IV, C-III, D-II (b) A-II, B-IV, C-III, D-I

(c) A-II, B-III C-IV, D-I (d) A-I, B-III, C-IV, D-II

Sol. (c)

106. Type of isomerism exhibited by compounds $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ and the value of coordination number (CN) of central metal ion in all these compounds, respectively is: [NEET 2023-Manipur]

(a) Geometrical isomerism, CN = 2 (b) Optical isomerism, CN = 4

(c) Ionisation isomerism, CN = 4 (d) Solvate isomerism, CN = 6

Sol. (d)

107. Match List-I with List-II: [NEET 2022 Re]

	List-I (Complexes)		List-II (Types)
A.	$[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5\ ONO]Cl_2$	I.	ionization isomerism
B.	$[Cr(NH_3)_6][Co(CN)_6]$ and $[Cr(CN)_6][Co(NH_3)_6]$	II.	coordination isomerism
C.	$[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]\ SO_4$	III.	linkage isomerism
D.	$[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2.\ H_2O$	IV.	solvate isomerism

Choose the correct answer from the options given below:

(a) A-IV, B-III, C-II, D-I (b) A-III, B-I, C-II, D-IV

(c) A-[illegible], B-II, C-IV, D-I (d) A-III, B-II, C-I, D-IV

Sol. [illegible]

108. The complexes $[Co(NH_3)_6]$, $[Cr(CN)_6]$ and $[Cr(NH_3)_6]$, $[Co(CN)_6]$ are the examples of which type of isomerism? [NEET 2011 Pre]

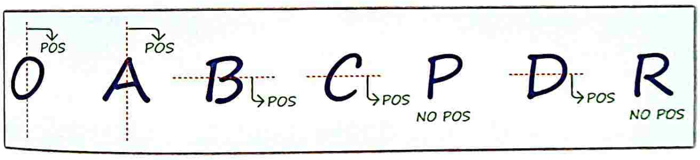
(a) Geometrical isomerism (b) Linkage isomerism

(c) Ionization isomerism (d) Coordination isomerism

Sol. (d)

PLANE OF SYMMETRY (POS)

A plane of symmetry is an imaginary plane that bisects a molecule into halves that are mirror images of each other.



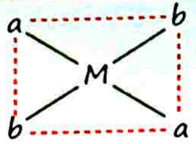
POS and Anti-pairs in Square Planar Complex

a, b, c, d ... → monodentate ligand [Cl^-, NH_3 etc.]

AA → Symmetrical bidentate ligand [en]

AB → Unsymmetrical bidentate ligand [gly^-]

Complex-1



☐ a is Anti to a → (aa)

∠ aMa = 180°

☐ b is Anti to b → (bb)

∠ bMb = 180°

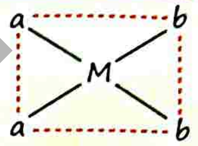
☐ Anti pair → (aa) (bb) for complex-1

90°

180° 180°

☐ POS is present.

Complex-2



☐ a is Anti to b → (ab)

∠ aMb = 180°

☐ a is Anti to b → (ab)

∠ aMb = 180°

☐ Anti pair → (ab) (ab) for complex-2

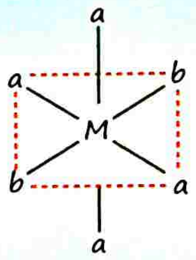
90°

180° 180°

☐ POS is present.

POS and Anti-pairs in Octahedral Complex

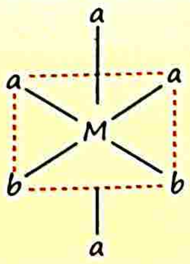
Complex-1



☐ Anti pair → (aa) (aa) (bb)

☐ POS is present.

Complex-2



☐ Anti pair → (aa) (ab) (ab)

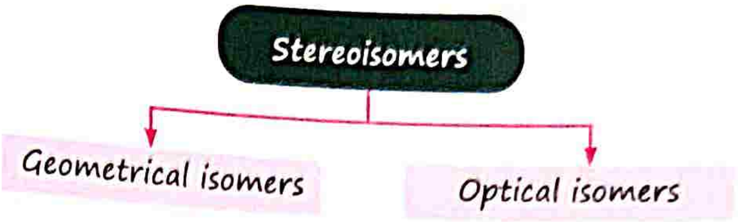
☐ POS is present.

STEREOISOMERS

Isomers having –

Different arrangement of the atoms in space (3D)

or Different spatial arrangement of atoms / ligands.



GEOMETRICAL ISOMERISM

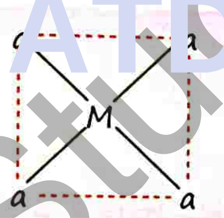
Same molecular formula but different geometry.

- ☐ Bond angles must be different between 2 ligands (θ = 90° /(180°)
- ☐ When similar groups are present in adjacent position, it is cis.
- ☐ When they are present in opposite position, it is trans.
- ☐ It occurs in square planar compounds and octahedral compounds.
- ☐ In case of cis, bond angle (θ) should be 90° but in Trans form, θ should be 180°.

No. of geometrical isomers ⇒ No. of set of anti-pairs

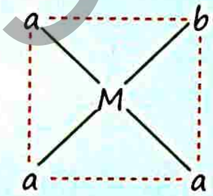
Geometrical Isomerism in Square Planar Complex

Ma_4 (aa) (aa)



☐ No geometrical isomer

Ma_3b (aa) (ab)

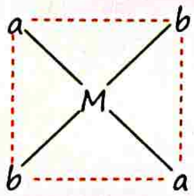


☐ No geometrical isomer

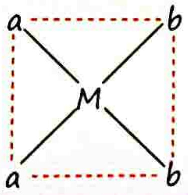
Ma_2b_2 (i) (aa) (bb)

(ii) (ab) (ab)

Example – $[Pt(NH_3)_2Cl_2]$



(i) Trans

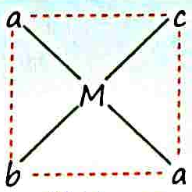


(ii) Cis

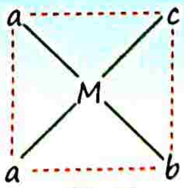
Ma_2bc (i) (aa) (bc)

(ii) (ab) (ac)

Example – $[Pd(NH_3)_2ClBr]$



(i) Trans



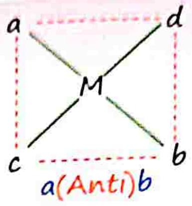
(ii) Cis

→ 2 geometrical isomers ←

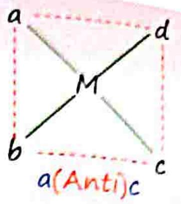
Mabcd (i) (ab)(cd)

(ii) (ac) (bd)

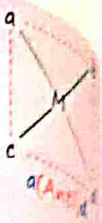
(iii) (ad) (cb)



a(Anti)b



a(Anti)c

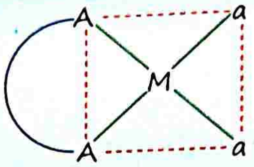


a(Ant

Example– [Pt NH_3 Br Cl Py] → 3 geometrical isomers

M(AA)a_2 (Aa)(Aa)

Example– [Pt (en)Cl_2]



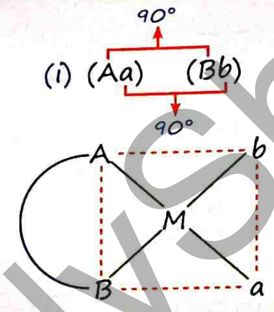
☐ No geometrical isomer is possible.

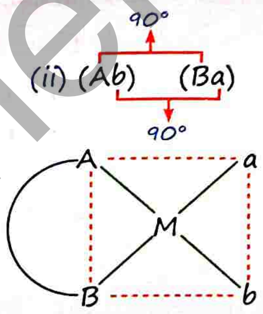
☐ ∠AMA = 90° (always).

M(AB)ab (i) (Aa)(Bb)

(ii) (Ab) (Ba)

Example– [Pd (gly) (NH_3)Cl]





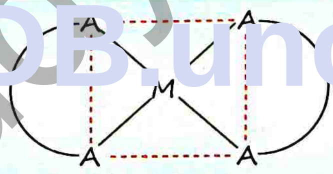
180°

(iii) (AB) (ab)

– This is not possible because ∠AMB should always be equal to 90° (not 180°).

$M(AA)_2$ (AA)(AA)

Example– $[Pt (en)_2]^{2+}$

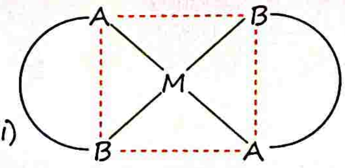


$M(AB)_2$ (i) (AA)(BB)

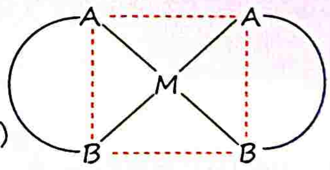
(ii) (AB) (BA)

Example– $[Pt (gly)_2]$

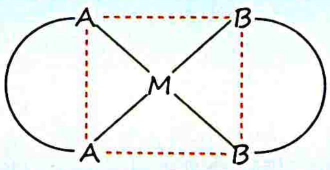
(i)



(ii)

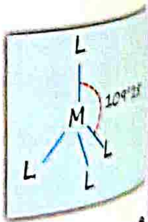


M(AA)(BB) (AB)(AB)



Geometrical Isomerism in Tetrahedral Complex

Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands (L) attached to the central metal atom (M) are the same with respect to each other (all bond angles are same in tetrahedral complex).



OPTICAL ISOMERISM IN COMPLEX HAVING 4 LIGANDS

4 different groups round the central metal ion are not the only requirement to make the complex to show mirror-image isomerism but the molecule should be asymmetric (it should have no plane of symmetry).

Note

- Optically active compounds - Chiral Compound
- Optically active compounds can rotate plane polarised light.

Optical Isomerism in Square Planar Complex

- Generally, square planar complexes have plane of symmetry. So they can not show optical isomerism.

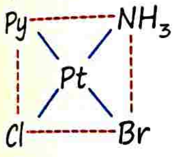
109. The complex, $[Pt(Py)(NH_3)BrCl]$ will have how many geometrical isomers? [NEET 2011 Pre]

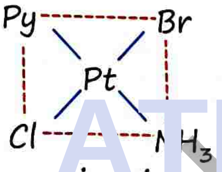
(a) 2 (b) 3 (c) 4 (d) 0

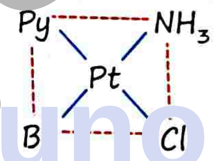
Sol. (b)

110. Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?

Sol.







None of the above will show optical isomerism because these platinum compounds are square planar and have plane of symmetry.

111. The total number of isomers for a square planar complex $[M(F)(Cl)(SCN)(NO_2)]$ is [10 Jan, 2019 (Shift-I)]

(a) 16 (b) 8 (c) 4 (d) 12

Sol. (d)

- 4 linkage isomers are possible for square planar $[M\ F\ Cl\ (SCN)\ (NO_2)]$–

1. $[M\ F\ Cl\ (SCN)\ (NO_2)]$
2. $[M\ F\ Cl\ (SCN)\ (ONO)]$
3. $[M\ F\ Cl\ (NCS)\ (NO_2)]$
4. $[M\ F\ Cl\ (NCS)\ (ONO)]$

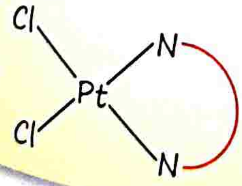
- Through every linkage isomers we can make 3 gemetrical isomers. So total = 4 x 3 = 12.

112. The species that can have a trans-isomer is:
(en = ethane-1, 2-diamine, ox = oxalate) [10 April, 2019 (Shift-I)]

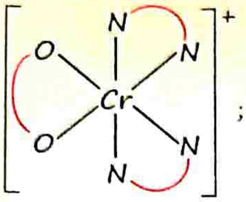
(a) $[Pt(en)Cl_2]$ (b) $[Cr(en)_2(ox)]^+$ (c) $[Zn(en)Cl_2]$ (d) $[Pt(en)_2Cl_2]^{2+}$

Sol. (d)

(a)

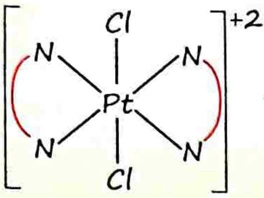


no trans isomer possible because bidentate ligand will be co-ordinating only at 90° angle in square planar complex

(b) 

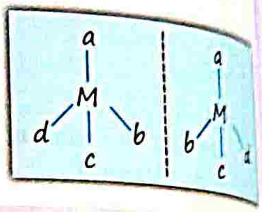
; no trans isomer possible

(c) $[Zn(en)Cl_2]$ → Tetrahedral → sp^3 hybridized so no trans possible

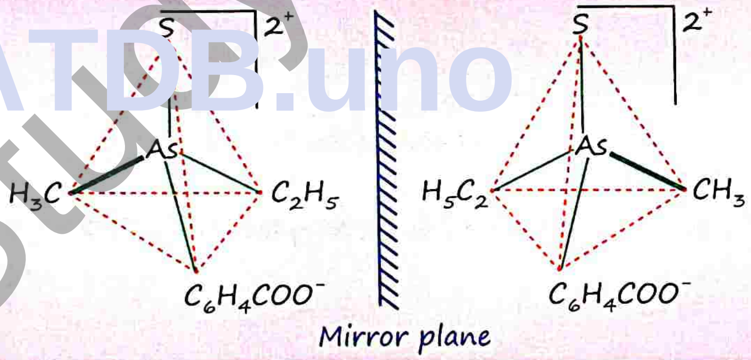
(d) 

Trans is possible

Optical Isomerism in Tetrahedral Complex



- ☐ Tetrahedral complexes are optically active only when all ligands are different.
- ☐ For example $[As(III)(CH_3)(C_2H_5)(S)(C_6H_4COO)]^{2+}$, shows optical isomerism.



113. The number of possible optical isomers for the complexes MA_2B_2 with sp^3 and dsp^2 hybridized metal atom, respectively, is:

Note: A and B unidentate neutral and unidentate monoanionic ligands, respectively.

[7 Jan, 2020 (Shift-II)]

(a) 0 and 0 (b) 2 and 2 (c) 0 and 2 (d) 0 and 1

Sol. (a) POS is present in MA_2B_2 in both tetrahedral (sp^3) and square planar (dsp^2).

114. The metal atom present in the complex MABXL (where A, B, X and L are unidentate ligands and M is metal) involves sp^3 hybridization. The number of geometrical isomers exhibited by the complex is:

[05 April, 2024 (Shift-II)]

(a) 4 (b) 0 (c) 2 (d) 3

Sol. (b) Tetrahedral complex (sp^3) does not show geometrical isomerism.

(IIT JEE 2010)

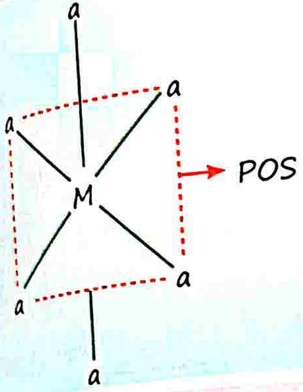
115. Total number of geometrical isomers for the complex $[RhCl(CO)(PPh_3)(NH_3)]$ is

Sol. [3] Complex is square planar with 4 different ligands.

GEOMETRICAL & OPTICAL ISOMERISM IN OCTAHEDRAL COMPLEX

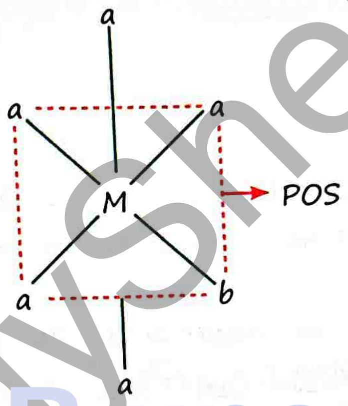
☐ GI → Geometrical isomers
☐ OI → Optical isomers
☐ SI → Stereo-isomers

Ma$_6$ (aa) (aa) (aa)



GI = 0
OI = 0
SI = 0

Ma$_5$b (aa) (aa) (ab)



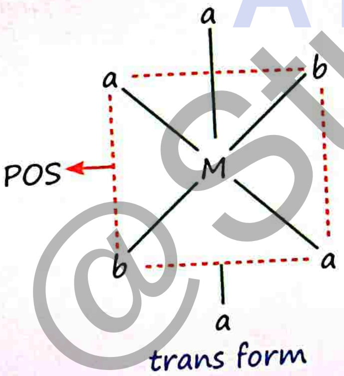
GI = 0
OI = 0
SI = 0

Ma$_4$b$_2$

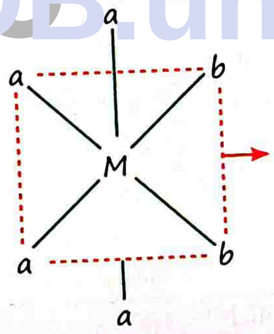
180°

1. (aa) (aa) (bb)
2. (aa) (ab) (ab)

90°



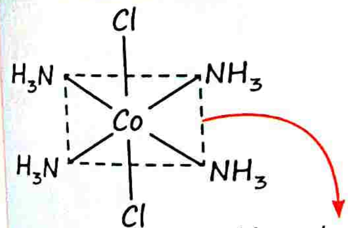
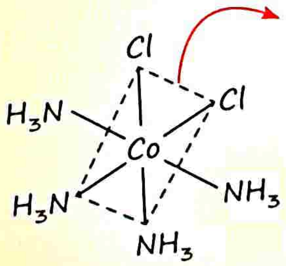
trans form



Cis form

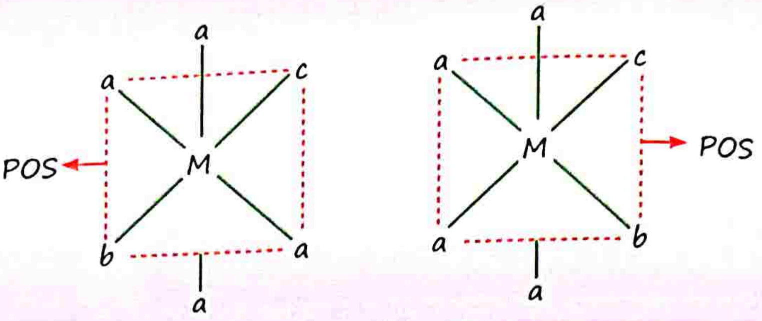
GI = 2
OI = 0
SI = 2

Plane of symmetry and optical activity in geometrical isomers of $[Co(NH_3)_4Cl_2]$.

Trans form	Cis form
 This plane bisects the molecule in 2 equal halves. So it has POS. ☐ Optically Inactive Compound.	 Here, Plane of symmetry is present because this plane bisects the molecule in 2 equal halves. ☐ Optically Inactive Compound

Ma_4bc

1. (aa) (aa) $\overset{180^\circ}{(bc)}$
2. (aa) $\underbrace{(ab)\ (ac)}_{90^\circ}$



GI = 2
OI = 0
SI = 2

Ma_3b_3

1. (a a) (a b) (b b) → meridional
2. (ab) (ab) (ab) → facial

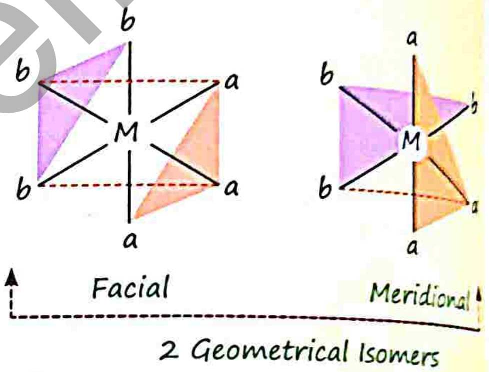
Facial [fac]: All 3 same ligands are at the corner of face of octahedron

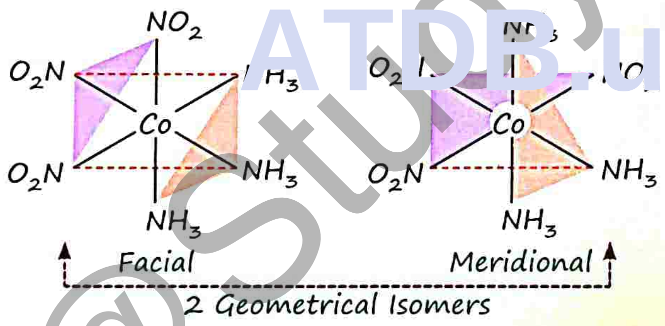
Bond angle between same ligands ⇒ θ = 90° (but θ ≠ 180°)

Meridional [mer]: All 3 same ligands are on the same plane that bisects octahedron

Bond angle between same ligands ⇒ (θ = 90° & θ = 180°)

Example: $[Co(NH_3)_3(NO_2)_3]$

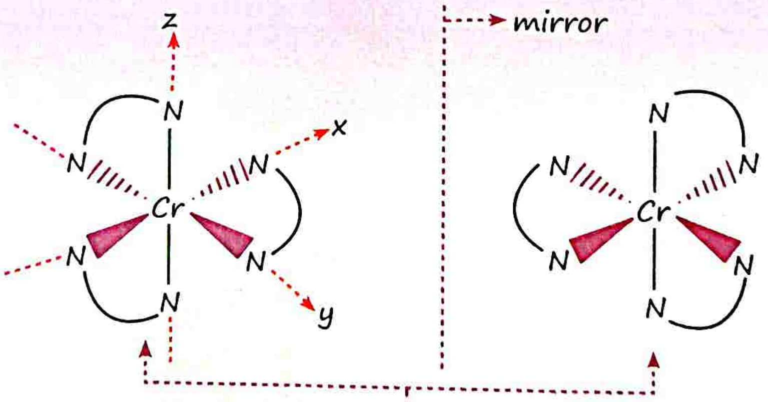




$M(AA)_3$

(A A) (A A) (A A)

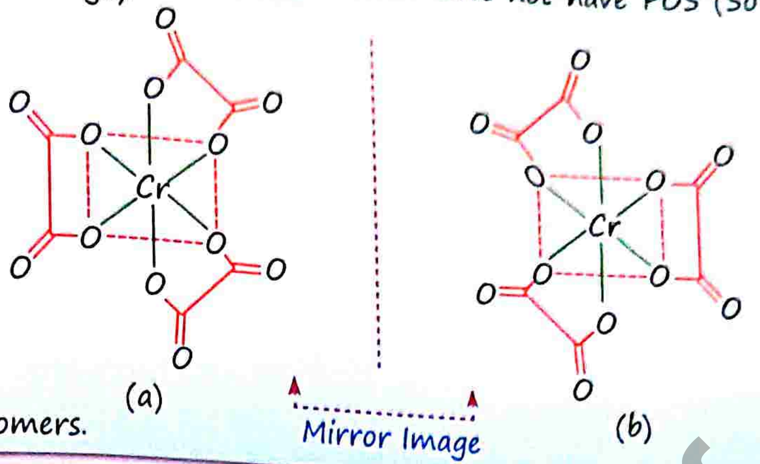
☐ $[Cr(en)_3]$



☐ Enantiomeric Pair

☐ POS is absent.

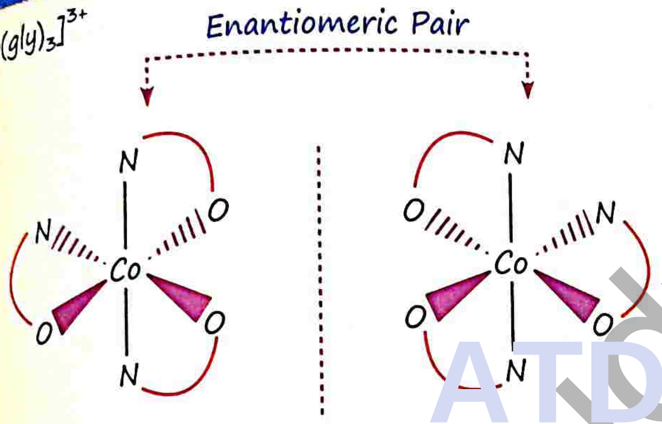
☐ $[Cr(C_2O_4)_3]^{3-}$ is an optically active compound because it does not have POS (So it is non-superimposable on its mirror image).



- (a) and (b) are optical isomers.

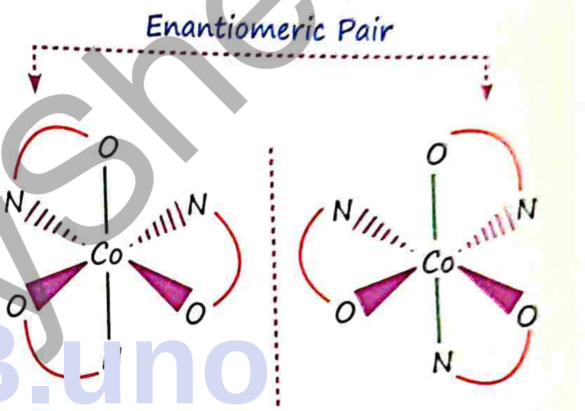
$[M(AB)_3]^{3+}$ → (i) (AB) (AB) (AB) (ii) (AB) (A A) (B B)

☐ $[Co(gly)_3]^{3+}$



☐ θ = 180°, 90°
☐ meridional

☐ POS is absent
☐ optically active

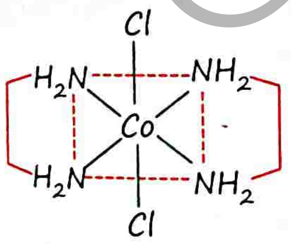


☐ θ = 90°
☐ Facial

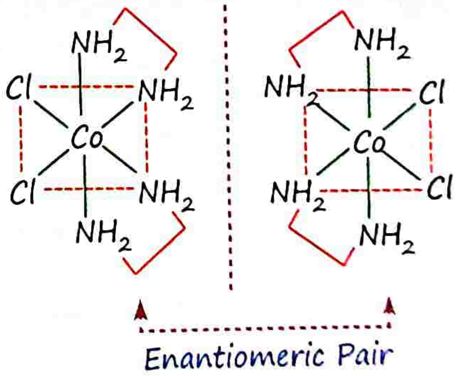
☐ POS is absent
☐ Optically active

GI = 2, Enantiomeric pairs = 2 OI = 4 SI = 4

$[M(AA)_2a_2]$ → (i) (A A) (A A) (a a) (ii) (A A) (A a) (A a)



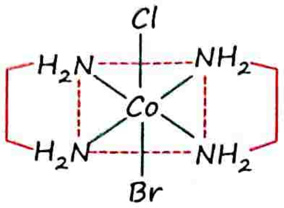
Trans form is optically inactive because it has plane of symmetry.



Cis form is optically active because it does not have plane of symmetry.

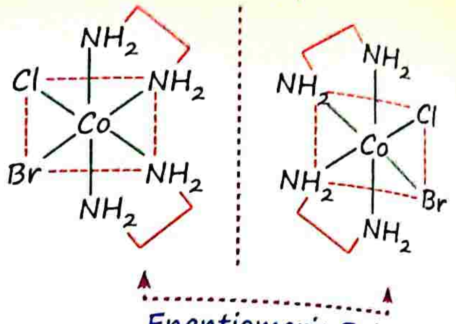
Geometrical isomers → 2
Optical isomers → 2
] → Stereoisomers : 3

[M(AA)$_2$ab] → (i) (A A) (A A) (a b)



Trans form is optically inactive because it has plane of symmetry.

(ii) (A A) (A a) (A b)

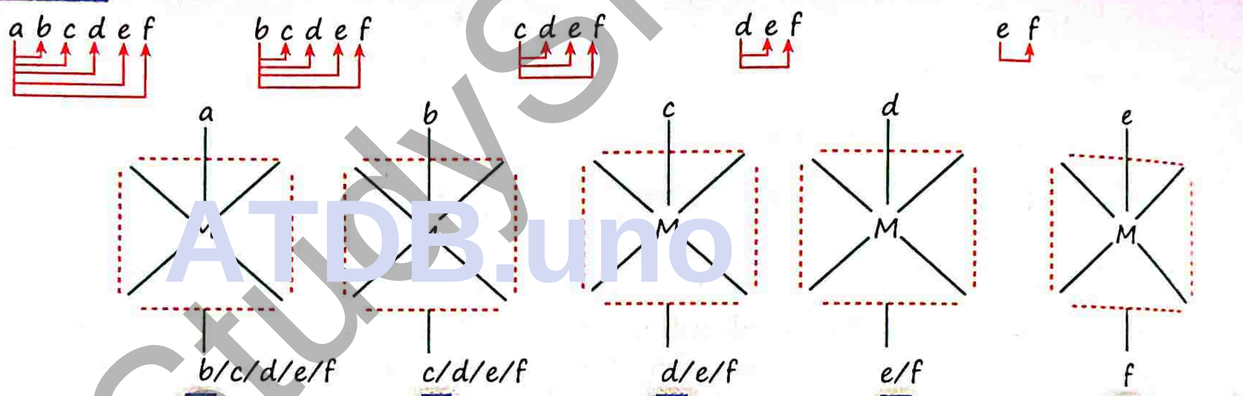


Enantiomeric Pair

Cis form is optically active because it does not have plane of symmetry.

Geometrical isomers → 2
Optical isomers → 2
→ Stereoisomers → 3

Mabcdef



5 + 4 + 3 + 2 + 1 =

☐ All 15 geometoical isomers are optically active becaouse it has no POS.

GI = 15 Enantiomeric pairs = 15 OI = 30 SI = 30

116. The Cl–Co–Cl bond angle values in a fac$[Co(NH_3)_3Cl_3]$ complex is/are: [30 Jan, 2023 (Shift-

(a) 90° & 180° (b) 90° (c) 180° (d) 90° & 120°

Sol. (b)

117. Indicate the complex/complex ion which did not show any geometrical isomerism: [26 Aug, 2021 (Shift-

(a) $[Co(NH_3)_3(NO_2)_3]$ (b) $[CoCl_2(en)_2]$ (c) $[Co(NH_3)_4Cl_2]^+$ (d) $[Co(CN)_5(NC)]^{3-}$

Sol. (d)

118. If Ni^{2+} is replaced by Pt^{2+} in the complex $[NiCl_2Br_2]^{2-}$, which of the following properties a expected to get changed? [11 April, 2023 (Shift-

A. Geometry
B. Geometrical isomerism
C. Optical isomerism
D. Magnetic properties

(a) A, B and C (b) A, B and D (c) A and D (d) B and C

Sol. (b) $[NiBr_2Cl_2]^{2-}$ — tetrahedral ($3d^8$: paramagnetic)
$[PtBr_2Cl_2]^{2-}$ — Square planar ($5d^8$: diamagnetic)

119. Match List-I with List-II:

	List-I		List-II
(A)	$[Co(NH_3)_6][Cr(CN)_6]$	(I)	Linkage isomerism
(B)	$[Co(NH_3)_3(NO_2)_3]$	(II)	Solvate isomerism
(C)	$[Cr(H_2O)_6]Cl_3$	(III)	Coordination isomerism
(D)	cis – $[CrCl_2(ox)_2]^{3-}$	(IV)	Optical isomerism

Choose the correct answer from the options given below: [17 March, 2021 (Shift-II)]

(a) (A)-(IV), (B)-(II), (C)-(III),(D)-(I)
(b) (A)-(I), (B)-(II), (C)-(III), (D)-(IV)
(c) (A)-(II), (B)-(I), (C)-(III), (D)-(IV)
(d) (A)- (III), (B)-(I), (C)-(II), (D)-(IV)

Sol. (d)

120. The number of geometrical isomers possible in triamminetrinitrocobalt (III) is X and in trioxalatochromate (III) is Y. Then the value of X + Y is ________. [27 July, 2021 (Shift-I)]

Sol. [2] $[Co(NH_3)_3(NO_2)_3] \rightarrow X = 2$, $[Cr(C_2O_4)]^{3-} \rightarrow Y = 0$

121. A reaction of cobalt(III)chloride and ethylenediamine in a 1 : 2 mole ratio generates two isomeric products A (violet coloured) and B (green coloured). A can show optical activity, but, B is optically inactive. What type of isomers does A and B represent? [10 Jan, 2019 (Shift-II)]

(a) Geometrical isomers
(b) Coordination isomers
(c) Linkage isomers
(d) Ionisation isomers

Sol. (a) $CoCl_3 + 2\ en \rightarrow [CoCl_2(en)_2]Cl$: Cis and trans isomerism

122. Which kind of isomerism is shown by $[Co(NH_3)_4Br_2]Cl$? (IIT JEE 2005)

(a) Geometrical and ionisation
(b) Optical and ionisation
(c) Geometrical and optical
(d) Geometrical only

Sol. (a)

123. The complex(es), which can exhibit the type of isomerism shown by $[Pt(NH_3)_2Br_2]$, is (are) (JEE Adv. 2023)
[en = $H_2NCH_2CH_2NH_2$]

(a) $[Pt(en)(SCN)_2]$
(b) $[Zn(NH_3)_2Cl_2]$
(c) $[Pt(NH_3)_2Cl_4]$
(d) $[Cr(en)_2(H_2O)(SO_4)]^+$

Sol. (c, d)

In $[Pt(NH_3)_2Br_2]$, the hybridisation of Pt is dsp^2 and geometry is square planar. It exhibits cis and trans isomerism:

(a) $[Pt(en)(SCN)_2]$: square planar and cis–trans not possible
(b) $[Zn(NH_3)_2Cl_2]$: tetrahedral and cis–trans not possible
(c) $[Pt(NH_3)_2Cl_4]$: octahedral and cis–trans possible
(d) $[Cr(en)_2(H_2O)SO_4]^+$: Octahedral → cis–trans

124. The correct option(s) regarding the complex $[Co(en)(NH_3)_3(H_2O)]^{3+}$ (en = $H_2NCH_2CH_2NH$ (are) (JEE Adv. 20

(a) It has two geometrical isomers

(b) It will have three geometrical isomers, if bidentate 'en' is replaced by two cyanide ligan

(c) It is paramagnetic

(d) It absorbs light at longer wavelength as compared to $[Co(en)(NH_3)_4]^{3+}$

Sol. (a, b, d)

(a) $[Co(en)(NH_3)_3(H_2O)]^{3+}$ complex is type of $[M(AA)b_3c]$ which will have two geometric isomers.

(b) If (en) is replaced by two cyanide ligands, complex will be type of $[Ma_2b_3c]$ and have geometrical isomers. $[Co(en)(NH_3)_3(H_2O)]^{3+} \xrightarrow[+\ 2\ CN^-]{-\ en} [Co(CN)_2(NH_3)_3(H_2O)]^{+}$

(c) $[Co(en)(NH_3)_3(H_2O)]^{3+}$ have d^6 configuration (t_{2g}^6) on central metal with strong fi ligands, therefore it is diamagnetic in nature.

(d) $[Co(en)(NH_3)_3(H_2O)]^{3+} < [Co(en)(NH_3)_4]^{3+}$: Δ_o value

$[Co(en)(NH_3)_3(H_2O)]^{3+} > [Co(en)(NH_3)_4]^{3+}$: λ absorbed

125. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is/are (JEE Adv. 201

(a) $[Cr(NH_3)_5Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2]Cl$ (b) $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$

(c) $[CoBr_2Cl_2]^{2-}$ and $[PtBr_2Cl_2]^{2-}$ (d) $[Pt(NH_3)_3(NO_2)]Cl$ and $[Pt(NH_3)_3Cl]Br$

Sol. (b, d)

☐ Octahedral $[Co(NH_3)_4Cl_2]^+$ and square planar $[Pt(NH_3)_2(H_2O)Cl]^+$ which shows geometric (cis–trans) isomerism

☐ Square planar $[Pt(NH_3)_3(NO_2)]Cl$ and square planar $[Pt(NH_3)_3\ Cl]$ Br shows ionizatio isomerism.

☐ $[Cr(NH_3)_5Cl]Cl_2$ neither shows structural nor stereoisomerism. $[Cr(NH_3)_4Cl_2]Cl$ shows geometrical (cis trans) isomerism.

☐ Tetrahedral $[CoBr_2Cl_2]^{2-}$ and square planar $[PtBr_2Cl_2]^{2-}$ do not show the same type o isomerism.

126. The compound(s) that exhibit(s) geometrical isomerism is/are (IIT JEE 200

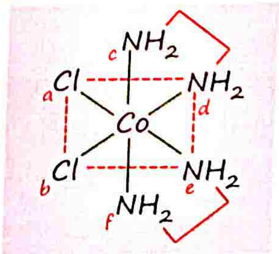
(a) $[Pt(en)Cl_2]$ (b) $[Pt(en)_2]Cl_2$ (c) $[Pt(en)_2Cl_2]Cl_2$ (d) $[Pt(NH_3)_2)Cl_2]$

Sol. (c, d)

127. Total number of cis N—Mn—Cl bond angles (that is Mn—N and Mn—Cl bonds in cis positions present in a molecule of cis $[Mn(en)_2Cl_2]$ complex is .... (en = $NH_2CH_2CH_2NH_2$) (JEE Adv. 201

Sol. [6] $\angle ClCoN = 90°$

1. $\angle_a ClCoN_c$
2. $\angle_a ClCoN_d$
3. $\angle_a ClCoN_f$
4. $\angle_b ClCoN_c$
5. $\angle_b ClCoN_e$
6. $\angle_b ClCoN_f$



128. The type of isom [illegible] the complex $[CoCl_2(en)_2]$ is: **[NEET 2018]**

(a) Geometrical isomerism (b) Coordination isomerism

(c) Linkage isomerism (d) Ionization isomerism

Sol. (a)

129. Number of possible isomers for the complex $[Co(en)_2Cl_2]$ Cl will be: (en = ethylenediamine) **[NEET 2015 Re]**

(a) 4 (b) 2 (c) 1 (d) 3

Sol. (d)

130. Which one of the following complexes is not expected to exhibit isomerism? **[NEET 2010 Mains]**

(a) $[Ni(NH_3)_4(H_2O)_2]^{2+}$ (b) $[Pt(NH_3)_2Cl_2]$

(c) $[Ni(NH_3)_2Cl_2]$ (d) $[Ni(en)_3]^{2+}$

Sol. (c)

131. The existence of two different coloured complexes with the composition of $[Co(NH_3)_4Cl_2]^+$ is due to: **[NEET 2010 Pre]**

(a) Ionization isomerism (b) Linkage isomerism

(c) Geometrical isomerism (d) Coodination isomerism

Sol. (c)

132. Which of the following does not show optical isomerism? **[NEET 2009]**

(a) $[Co(NH_3)_3Cl_3]^0$ (b) $[Co(en)Cl_2(NH_3)_2]^+$

(c) $[Co(en)_3]^{3+}$ (d) $[Co(en)_2Cl_2]^+$

(en = ethylenediamine)

Sol. (a)

133. $[Co(NH_3)_4(NO_2)_2]Cl$ exhibits: **[NEET 2006]**

(a) Linkage isomerism, ionization isomerism and optical isomerism

(b) Linkage isomerism, ionization isomerism and geometrical isomerism

(c) Ionization isomerism, geometrical isomerism and optical isomerism

(d) Linkage isomerism, geometrical isomerism and optical isomerism

Sol. (b)

134. Which one of the following is expected to exhibit optical isomerism? (en = ethylenediamine) **[NEET 2005]**

(a) cis-$[Pt(NH_3)_2Cl_2]$ (b) trans-$[Co(en)_2Cl_2]$

(c) trans-$[Pt(NH_3)_2Cl_2]$ (d) cis-$[Co(en)_2Cl_2]$

Sol. (d)

135. Which of the following coordination compounds would exhibit optical isomerism? **[NEET 2004]**

(a) Diamminedichloroplatinum (II)

(b) Trans-dicyanobis (ethylenediamine) chromium (III) chloride

(c) Tris-(ethylenediamine)cobalt (III) bromide

(d) Pentaamminenitrocobalt (III) iodide

Sol. (c)

Coordi

136. Which one of the following octahedral complexes will not show geometric isomerism? (A and monodentate ligands)? [NEET

(a) $[MA_2B_4]$ (b) $[MA_3B_3]$ (c) $[MA_4B_2]$ (d) $[MA_5B]$

Sol. (d)

137. The hypothetical complex chloro diaquatriammine cobalt (III) chloride can be represent [NEET

(a) $[CoCl(NH_3)_3(H_2O)_2]Cl_2$ (b) $[Co(NH_3)_3(H_2O)Cl_3]$

(c) $[Co(NH_2)_3(H_2O)_2Cl]$ (d) $[Co(NH_3)_3(H_2O)_3]Cl_2$

Sol. (a)

STABILITY OF COORDINATION COMPOUNDS

- ❒ The stability of complex in solution refers to the degree of association between the two species in the state of equilibrium.
- ❒ Equilibrium constant for the association expresses the stability

$$M + 4L \rightleftharpoons ML_4$$

- ❒ Value of equilibrium constant ↑ ⇒ Stability of $[ML_4]$ complex ↑
- ❒ **Stepwise stability constant** $(k_1, k_2 ...)$: The equilibrium constant of each step of a complex reac called stepwise stability constant.
- ❒ **Overall stability constant** (β_4): The equilibrium constant for net reaction

(a) $M + L \rightleftharpoons ML$ $k_1 : [ML] / [M][L]$

(b) $ML + L \rightleftharpoons ML_2$ $k_2 : [ML_2] / [ML][L]$

(c) $ML_2 + L \rightleftharpoons ML_3$ $k_3 : [ML_3] / [ML_2][L]$

(d) $ML_3 + L \rightleftharpoons ML_4$ $k_4 : [ML_4] / [ML_3][L]$

$M + 4L \rightleftharpoons ML_4$ $\beta_4 : [ML_4] / [M][L]^4$ Then → $\boxed{\beta_4 = k_1 \cdot k_2 \cdot k_3 \cdot k_4}$

138. Which of the following complexes formed by Cu^{2+} ions is most stable?

(a) $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)]^{2+}$, log K = 11.6

(b) $Cu^{2+} + 4CN^- \rightleftharpoons [Cu(CN_4)]^{2-}$, log K = 27.3

(c) $Cu^{2+} + 2en \rightleftharpoons [Cu(en_2)]^{2+}$, log K = 15.4

(d) $Cu^{2+} + 4H_2O \rightleftharpoons [Cu(H_2O_4)]^{2+}$, log K = 8.9

Sol. (b) The greater the value of log K, the greater will be stability of complex compound formed.

39. Calculate the [illegible] equilibrium constant for the $[Cu(NH_3)_4]^{2+}$ ions, given that stability constant (β_4) for this complex is 2.1×10^{13}.

(a) 8.27×10^{-13} (b) 4.76×10^{-14} (c) 2.39×10^{-7} (d) 1.83×10^{14}

Sol. (b) $$[Cu(NH_3)_4]^{2+} \xrightleftharpoons{k} Cu^{2+} + 4NH_3$$

Disscociation constant (k) is the reciprocal of the stability constant β_4 ($k = 1/\beta_4$).

$$k = \frac{1}{2.1 \times 10^{13}} \Rightarrow 4.76 \times 10^{-14}$$

40. The stepwise formation of $[Cu(NH_3)_4]^{2+}$ is given below:

$$Cu^{2+} + NH_3 \xrightleftharpoons{k_1} [Cu(NH_3)]^{2+}$$

$$[Cu(NH_3)]^{2+} + NH_3 \xrightleftharpoons{k_2} [Cu(NH_3)_2]^{2+}$$

$$[Cu(NH_3)_2]^{2+} + NH_3 \xrightleftharpoons{k_3} [Cu(NH_3)_3]^{2+}$$

$$[Cu(NH_3)_3]^{2+} + NH_3 \xrightleftharpoons{k_4} [Cu(NH_3)_4]^{2+}$$

The value of stability constants k_1, k_2, k_3 and k_4 are 10^4, 1.58×10^3, 5×10^2 and 10^2 respectively. The overall equilibrium constants for dissociation of $[Cu(NH_3)_4]^{2+}$ is $x \times 10^{-12}$. The value of x is ___ (Rounded off to the nearest integer)

[24 Feb, 2021 (Shift-I)]

Sol. [1] Overall stability constant K will be calculated as:

$K = K_1 \times K_2 \times K_3 \times K_4 = 7.9 \times 10^{1}$[illegible]

Now, calculate the overall equilibrium constant for dissociation of $[Cu(NH_3)_4]^{2+}$ as:

$$K' = \frac{1}{K} = \frac{1}{7.9 \times 10^{11}} = 0.126 \times 10^{-11} = 1.26 \times 10^{-12} \approx 1 \times 10^{-12}$$

INDUSTRY AND NATURAL USES

Coordination compounds play essential roles in analytical chemistry, metallurgy, biological systems, industry, and medicine, as described below:

Chemical Analysis–

- Coordination compounds are extensively used in both qualitative and quantitative chemical analysis. Common reagents include EDTA, DMG (dimethylglyoxime), α-nitroso-β-naphthol, and cupron.

  The characteristic color reactions that metal ions exhibit with various ligands, especially chelating ligands, are due to the formation of coordination entities.

  These color changes form the basis for the detection and estimation of metal ions using classical and instrumental methods.

Water Hardness Testing–

- ❐ The hardness of water can be measured by a simple titration with Na_2EDTA. Calcium (Ca^{2+}) magnesium (Mg^{2+}) ions form stable complexes with EDTA, allowing for their selective estimation to differences in the stability constants of their respective complexes.

Metal Extraction–

- ❐ Coordination compounds are also crucial in the extraction of metals, such as silver and gold instance, gold forms a coordination entity, $[Au(CN)_2]^-$, in the presence of cyanide, oxygen, and wa This allows gold to be separated from the solution in its metallic form by adding zinc.

Metal Purification–

- ❐ The purification of metals can be achieved by forming coordination compounds, which can later decomposed to isolate the pure metal.

$$\text{Metal} \longrightarrow \text{Volatile compound} \longrightarrow \text{Pure Metal}$$

For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

$$\underset{\text{Impure}}{Ni_{(s)}} + 4CO_{(g)} \xrightarrow{50°C} [Ni(CO)_4]_{(g)} \xrightarrow{230°C} \underset{\text{Pure}}{Ni_{(s)}} + 4CO\uparrow$$

Electroplating–

- ❐ Articles can be electroplated with silver and gold more smoothly and evenly using solutions of th complexes $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ compared to solutions containing simple metal ions.

Medicinal Applications–

- ❐ There is growing interest in using chelation therapy in medicine to treat metal toxicity in plants and animals.

For example, excess copper and iron can be removed by chelating ligands such as D-penicillamine and desferrioxamine B through the formation of coordination compounds.

Penicillamine → Chelating agent → Binds with Cu → Treatment of wilson's disease.

Desferrioxamine B → Chelator → Binds with Fe

Cis platin cis-$[Pt(NH_3)_2Cl_2]$ → To inhibit the growth of tumours.

In biological system–

Chlorophyll (Green Pigment Responsible for photosynthesis) → Co-ordination compound of Mg

Haemoglobin (Red pigment of blood : Acts as oxygen carrier) → Co-ordination compound of Fe

Vitamin B_{12} (Cyanocobalamine) → Co-ordination compound of Co.

Carboxy peptidase A (Removes the amino acid residue from the C-terminal of a peptide chain) → Coordination compound of Zn.

Carbonic Anhydrase (Catalyze the interconversion between CO_2 & H_2O and H_2CO_3) → coordination compound of Zn.

Photography–

- ☐ In black-and-white photography, the developed film is fixed by washing it with a hypo solution, which dissolves the undeveloped AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.

Industrial Catalysis–

- ☐ The rhodium complex, $[(Ph_3P)_3RhCl]$, known as Wilkinson's catalyst, is employed in the hydrogenation of alkenes.

141. $[Pd(F)(Cl)(Br)(I)]^{2-}$ has n number of geometrical isomers. Then, the spin-only magnetic moment and crystal field stabilisation energy [CFSE] of $[Fe(CN)_6]^{n-6}$, respectively, are: [Note : Ignore the pairing energy] [09 Jan, 2020 (Shift-I)]

(a) 5.92 BM and 0 (b) 0 BM and $-2.4\ \Delta_0$

(c) 1.73 BM and $-2.0\ \Delta_0$ (d) 2.84 BM and $-1.6\ \Delta_0$

Sol. (c) No. of Geometrical Isomers possible for square planar, $[Pd(F)(Cl)(Br)(I)]^{2-}$ are 3. Therefore, n = 3

- $[Fe(CN)_6]^{3-}$ $Fe^{3+} = 3d^5$, Acc. CFT configuration is $t_{2g}^5\ e_g^0$
- $M = \sqrt{n(n+2)} = 1.73$ B.M.
- $CFSE = -0.4\ \Delta_0 \times n_{t2g} + 0.6\ \Delta_0 \times n_{eg} = -0.4\ \Delta_0 \times 5 = -2.0\ \Delta_0$

142. Match List-I with List-II.

List-I (Substances)		List-II (Element Present)	
(A)	Ziegler catalyst	(I)	Rhodium
(B)	Blood Pigment	(II)	Cobalt
(C)	Wilkinson catalyst	(III)	Iron
(D)	Vitamin B_{12}	(IV)	Titanium

Choose the correct answer from the options given below: [29 Jan, 2024 (Shift-I)]

(a) A-II, B-IV, C-I, D-III (b) A-II, B-III, C-IV, D-I

(c) A-III, B-II, C-IV, D-I (d) A-IV, B-III, C-I, D-II

Sol. (d)

143. To inhibit the growth of tumours, identify the compounds used from the following: [30 Jan, 2023 (Shift-I)]

(A) EDTA (B) Coordination Compounds of Pt

(C) D - Penicillamine (D) Cis - Platin

Choose the correct answer from the option given below:

(a) B and D Only (b) C and D Only (c) A and B Only (d) A and C Only

Sol. (a)

144. Match List-I with List-II.

	List-I		List-II
(A)	Chlorophyll	(I)	Ruthenium
(B)	Vitamin-B_{12}	(II)	Platinum
(C)	Anticancer drug	(III)	Cobalt
(D)	Grubbs catalyst	(IV)	Magnesium

Choose the most appropriate answer from the options given below: [18 March, 2021 (Shift-

(a) (A) – (III), (B) – (II), (C) – (IV), D – (I)
(b) (A) – (IV), (B) – (III), (C) – (II), D – (I)
(c) (A) – (IV), (B) – (III), (C) – I; (D) – (II)
(d) (A) – (IV), (B) – (II), (C) – III; (D) – (I)

Sol. (b)

145. The compound used in the treatment of lead poisoning is: [12 April, 2019 (Shift-

(a) EDTA
(b) Cis-platin
(c) D-penicillamine
(d) desferrioxime B

Sol. (a)

146. Among the complex ions, $[Co(NH_2CH_2CH_2-NH_2)_2Cl_2]^+$, $[CrCl_2(C_2O_4)_2]^{3-}$, $[Fe(H_2O)_4(OH)_2]^+$, $[Fe(NH_3)_2(CN)_4]$, $[Co(NH_2-CH_2-CH_2-NH_2)_2(NH_3)Cl]^{2+}$ and $[Co(NH_3)_4(H_2O)Cl]^{2+}$ the number of complex ion(s) that show(s) cis–trans isomerism is (JEE Adv. 2015)

Sol. [6] Among given complexes, all six complexes will show cis–trans isomerism.

147. Among the following complexes (K – P), $K_3[Fe(CN)_6](K)$, $[Co(NH_3)_6]Cl_3(L)$, $Na_3[Co(Ox)_3](M)$, $[Ni(H_2O)_6]Cl_2(N)$, $K_2[Pt(CN)_4](O)$ and $[Zn(H_2O)_6](NO_3)_2(P)$ the diamagnetic complexes are (IIT JEE 2011)

(a) K, L, M, N
(b) K, M, O, P
(c) L, M, O, P
(d) L, M, N, O

Sol. (c) L & M → Co^{3+} (d^6) with NH_3/Ox^{2-} (Strong field ligand), O → $Pt^{+3}(d^8)$: Square planar : All electrons are paired, P → $Zn^{+2}(d^{10})$

148. The complex showing a spin only magnetic moment of 2.82BM is (IIT JEE 2010)

(a) $Ni(CO)_4$
(b) $[NiCl_4]^{2-}$
(c) $Ni(PPh_3)_4$
(d) $[Ni(CN)_4]^{2-}$

Sol. (b) $NiCl_4^{2-}$: Ni^{2+} (d^8) : Tetrahedral (sp^3) with 2 unpaired electrons

149. Spin only magnetic moment of the compound $Hg[Co(SCN)_4]$ is (IIT JEE 2004)

(a) $\sqrt{3}$
(b) $\sqrt{15}$
(c) $\sqrt{24}$
(d) $\sqrt{8}$

Sol. (b) In complex, $Hg[Co(SCN)_4]$, Co^{2+} has $3d^7$ electronic configuration. SCN^- weak ligand field, hence no pairing of electron occurs:

↑↓	↑↓	↑	↑	↑

$3d^7$

$$\mu = \sqrt{3(3+2)}BM = \sqrt{15}BM$$

150.The pair(s) of complexes wherein both exhibit tetrahedral geometry is(are)
(Note: py = pyridine
Given: Atomic numbers of Fe, Co, Ni and Cu are 26, 27, 28 and 29, respectively)
(JEE Adv. 2021)

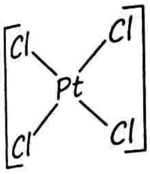
(a) $[FeCl_4]^-$ and $[Fe(CO)_4]^{2-}$
(b) $[Co(CO)_4]^-$ and $[CoCl_4]^{2-}$
(c) $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$
(d) $[Cu(py)_4]^+$ and $[Cu(CN)_4]^{3-}$

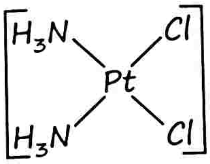
Sol. (a, b, d)

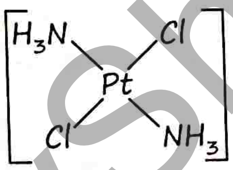
151.Which of the following complexes is used to be as an anticancer agent? [NEET 2014]
(a) cis-$[PtCl_2(NH_3)_2]$
(b) cis-$K_2[PtCl_2Br_2]$
(c) $Na_2[CoCl_4]$
(d) mer–$[Co(NH_3)_3Cl_3]$

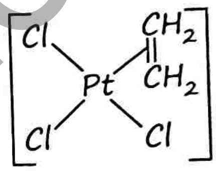
Sol. (a)

152.Which of the following is considered to be an anticancer species? [NEET 2004]

(a)


(b)


(c)


(d)


Sol. (b)

153.In the silver plating of copper, $K[Ag(CN)_2]$ is used instead of $AgNO_3$. The reason is: [NEET 2002]
(a) A thin layer of Ag is formed on Cu
(b) More voltage is required
(c) Ag^+ ions are completely removed from solution
(d) Less availability of Ag^+ ions, as Cu cannot displace Ag from $[Ag(CN)_2]^-$ ion

Sol. (d)

154.Which of the following pairs of ions will have same spin only magnetic moment values within the pair? [NEET 2024 Re]
A. Zn^{2+}, Ti^{2+}
B. Cr^{2+}, Fe^{2+}
C. Ti^{3+}, Cu^{2+}
D. V^{2+}, Cu^+

Choose the correct answer from the options given below:
(a) C and D only
(b) A and D only
(c) A and B only
(d) B and C only

Sol. (d)

155.'Spin only' magnetic moment is same for which of the following ions? [NEET 2024]
A. Ti^{3+}
B. Cr^{2+}
C. Mn^{2+}
D. Fe^{2+}
E. Sc^{3+}

Choose the most appropriate answer from the options given below:
(a) B and C only
(b) A and D only
(c) B and D only
(d) A and E only

Sol. (c)

156.The calculated spin only magnetic moment of Cr^{2+} ion is [NEET 2020]
(a) 4.90 BM
(b) 5.92 BM
(c) 2.84 BM
(d) 3.87 BM

Sol. (a)

157. Magnetic moment 2.84 B.M. is given by: (Atomic numbers, Ni = 28, Ti = 22, Cr = 24, Co = 27) [NEET 2015]

(a) Ti^{3+} (b) Cr^{2+} (c) Co^{2+} (d) Ni^{2+}

Sol. (d)

158. Magnetic moment 2.83 BM is given by which of the following ions? [NEET 2014]
(Atomic Number Ti = 22, Cr = 24, Mn = 25, Ni = 28)

(a) Ni^{2+} (b) Cr^{3+} (c) Mn^{2+} (d) Ti^{3+}

Sol. (a)

159. In which of the following pairs are both the ions coloured in aqueous solution?
(Atomic number : Sc = 21, Ti = 22, Ni = 28, Cu = 29, Co = 27) [NEET 2006]

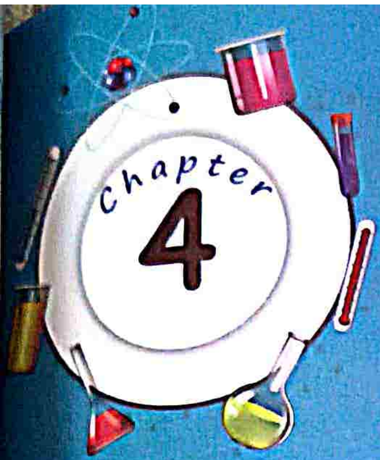
(a) Ni^{2+}, Ti^{3+} (b) Sc^{3+}, Ti^{3+} (c) Sc^{3+}, Co^{2+} (d) Ni^{2+}, Cu^{+}

Sol. (a)

160. The aqueous solution containing which one of the following ions will be colourless? (Atomic number. Sc = 21, Fe = 26, Ti = 22, Mn = 25) [NEET 2005]

(a) Sc^{3+} (b) Fe^{2+} (c) Ti^{3+} (d) Mn^{2+}

Sol. (a)



Chapter 4

The p- Block Elements (Group 13 to 18)

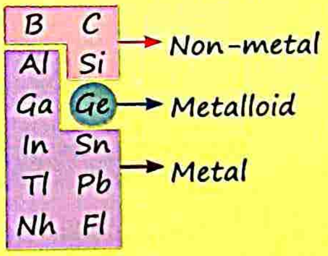
JEE Main & NEET

Syllabus

General Introduction: Electronic configuration and general trends in physical and chemical properties of elements across the periods and down the groups, unique behaviour of the first element in each group.

p-BLOCK ELEMENTS (GROUP 13 AND 14)

Electronic Configuration

Group-13 : [IG]ns^2np^1	Group-14 : [IG]ns^2np^2	Types of Element
B_5 : [He] $2s^2$ $2p^1$	C_6 : [He] $2s^2$ $2p^2$	 ☐ Nihonium (Nh) and Flerovium (Fl) are synthetically prepared radioactive element.
Al_{13} : [Ne] $3s^2$ $3p^1$	Si_{14} : [Ne] $3s^2$ $3p^2$	
Ga_{31} : [Ar] $4s^2$ $3d^{10}$ $4p^1$	Ge_{32} : [Ar] $4s^2$ $3d^{10}$ $4p^2$	
In_{49} : [Kr] $5s^2$ $4d^{10}$ $5p^1$	Sn_{50} : [Kr] $5s^2$ $4d^{10}$ $5p^2$	
Tl_{81} : [Xe] $6s^2 4f^{14}$ $5d^{10}$ $6p^1$	Pb_{82} : [Xe] $6s^2$ $4f^{14}$ $5d^{10}$ $6p^2$	
Nh_{113} : [Rn] $7s^2$ $5f^{14}$ $6d^{10}$ $7p^1$	Fl_{114} : [Rn] $7s^2$ $5f^{14}$ $6d^{10}$ $7p^2$	

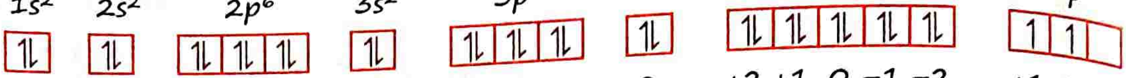
☐ Ga, Ge and Bi liquid expands when it forms the solid as water.

☐ Abundance in Earth Crust: O > Si > Al > Fe

GiGa Bite expand like water.
O Simran Aloo Feka kro
Jameen par.

1. Ge (Z = 32) in its ground state electronic configuration has x completely filled orbitals with $m_l = 0$. The value of x is-

Sol. Ge → $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$ $4p^2$

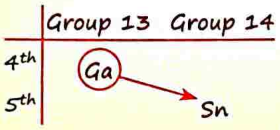


m_l → 0 | 0 | +1 0 −1 | 0 | +1 0 −1 | 0 | +2 +1 0 −1 −2 | +1 0 −1

Completely filled orbital with m_l =0 are 7

2. Outermost electronic configuration of group 13 element, E, is $4s^2$, $4p^1$. The electronic configuration of an element of p-block period-five placed diagonally to element, E is:
(a) [Kr] $4d^{10}$ $5s^2$ $5p^2$ (b) [Kr] $3d^{10}$ $4s^2$ $4p^2$ (c) [Xe] $5d^{10}$ $6s^2$ $6p^2$ (d) [Ar] $3d^{10}$ $4s^2$ $4p^2$

Sol. (a)



E is Gallium, so diagonally placed element is Tin ([Kr] $5s^2$ $4d^{10}$ $5p^2$).

Atomic Radius

Al_{13} : [Ne] $3s^2$ $3p^1$

Ga_{31} : [Ar] $4s^2$ $\boxed{3d^{10}}$ $4p^1$

poor shielding effect for outer electrons

B
∧
Al
∨
Ga
∧
In
∧
Tl

→ This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 d-electrons ($3d^{10}$) offer only poor screening effect for the outer electrons from the increased nuclear charge in Ga.

C
∧
Si
∧
Ge
∧
Sn
∧
Pb

	C	Si	Ge	Sn	Pb
Covalent radius/pm^a	77	118	122	140	146

- ☐ Considerable increase in covalent radius from C to Si.
- ☐ But from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled d and f orbitals in heavier members.

(JEE Adv. 2016)

3. The increasing order of atomic radii of the following Group 13 elements is
(a) Al < Ga < In < Tl (b) Ga < Al < In < Tl (c) Al < In < Ga < Tl (d) Al < Ga < Tl < In

Sol. (b) Atomic radii tends to increases down the group, However gallium has d electrons which fails to provide effective shielding and the outermost shell is strongly influenced by the nucleus making its radii less than that of aluminium

Ionic Radius

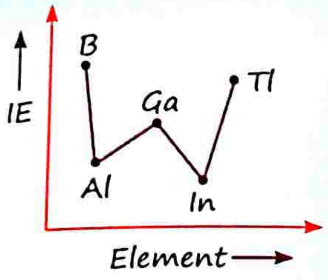
☐ $B^{3+} < Al^{3+} < Ga^{3+} < In^{3+} < Tl^{3+}$: Size

☐ $C^{4+} < Si^{4+} < Ge^{4+} < Sn^{4+} < Pb^{4+}$: Size

Ionisation Energy and Electronegativity

Ionisation Energy

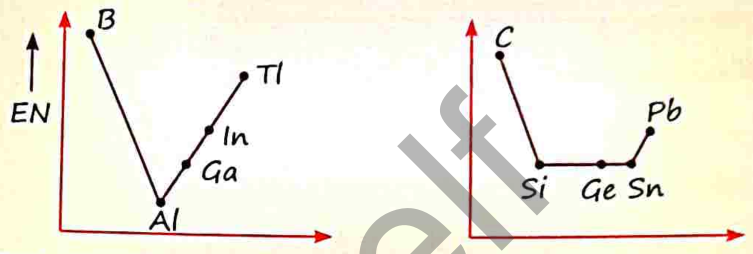
B > Tl > Ga > Al > In



C > Si > Ge > Pb < Sn

Observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of d-and f-electrons, which have low screening effect, to compensate the increase in nuclear charge.

Electronegativity



EN : B > Tl > In > Ga > Al

EN : C > Pb > Si = Ge = Sn

Small decrease in $\Delta_i H$ from Si to Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is the consequence of poor shielding effect of intervening d and f orbitals and increase in size of the atom.

4. Given below are two statements:
Statement-I: The electronegativity of group 14 elements from Si to Pb gradually decreases.
Statement-II: Group 14 contains non-metallic, metallic, as well as metalloid elements.
In the light of the above statements, choose the most appropriate from the options given below: **[29 Jan, 2024 (Shift-I)]**
(a) Statement-I is false but Statement-II is true
(b) Statement-I is true but Statement-II is false
(c) Both Statement-I and Statement-II are true
(d) Both Statement-I and Statement-II are false

Sol. (a) The electronegativity values for elements from silicon to lead are almost same. Hence, Statement I is false.

Group-14	Electronegative value
Carbon	2.5
Silicon	1.8
Germanium	1.8
Tin	1.8
Lead	1.9

Physical Properties

Generally in group-13 and 14 Density increases as we move down the group.

Density : $B < Al < Ga < In < Tl$

$C_{graphite} < Si < Ga < Sn < Pb$

$Si < C_{diamond} < Ga < Sn < Pb$

☐ Generally in group-13 and 14 Melting point (with some exception) and Boiling point (with no exception) decreases as we move down the group.

Melting point : B > Al > Tl > In > Ga

B → Due to very strong crystalline lattice, boron has unusually high melting point.

Ga → Gallium with unusually low melting point (303K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures.

: C > Si > Ge > $\boxed{Pb > Sn}$ [Same order in IE]

FIRST ATOM OF GROUP

1. 2nd period elements do not have d subshell, so possible hybridisations are sp, sp^2, sp^3.

   First atom of group/2nd Period element → **B C N O F**

   ◆ Maximum covalency of these elements is 4.

2. Small in size → Form multiple bond easily (P_π-P_π bond) [C = C, C ≡ C, C ≡ N, C = O]

   ◆ This type of π-bonding is not particularly strong for the heavier p-block elements. The heavier elements do form π bond but this involves d orbitals (dπ – pπ or dπ – dπ).

Note

Using d-orbitals the 3rd period elements (Al, S, Si, P, Cl) or more than 3rd period elements can expand covalency above four.

Existence: BF_4^- AlF_6^{3-} SiF_6^{2-} $[GeCl_6]^{2-}$ $[Sn(OH)_6]^{2-}$

☐ BF_4^- SiF_6^{2-} → Exist because F is small in size.

BCl_4^- $SiCl_6^{2-}$ → Does not exist because large chloride ions cannot be accommodated around central atom (B, Si) due to limitation of its size.

5. The element that shows greater ability to form pπ-pπ multiple bonds, is:

(a) Sn (b) C (c) Ge (d) Si

Sol. (b) The element that shows the greatest ability to form pπ-pπ multiple bonds is carbon (C).

INERT PAIR EFFECT

B	C	N
Al	Si	P
Ga	Ge	As
In	Sn	Sb
Tl	Pb	Bi

As we move from top to bottom → Stability of highest oxidation state decreases → Stability of lower oxidation state increases

- Tl^+ > Tl^{3+}
- Pb^{2+} > Pb^{4+}
- Bi^{3+} > Bi^{5+}

The oxidation state two unit less than the group oxidation state (group-13: +3, group- 14 : +4 group-15 : +5) becomes progressively more stable for the heavier elements in each group. The occurrence of oxidation states two unit less than the group oxidation states are sometime attributed to the 'inert pair effect'.

Reason: due to poor shielding of d and f e^- : 6s e^- pair does not take part in bonding.

Stability of Oxidation State

B^{+1}	C^{+2}	N^{+3}	B^{+3}	C^{+4}	N^{+5}
∧	∧	∧	∨	∨	∨
Al^{+1}	Si^{+2}	P^{+3}	Al^{+3}	Si^{+4}	P^{+5}
∧	∧	∧	∨	∨	∨
Ga^{+1}	Ge^{+2}	As^{+3}	Ga^{+3}	Ge^{+4}	As^{+5}
∧	∧	∧	∨	∨	∨
In^{+1}	Sn^{+2}	Sb^{+3}	In^{+3}	Sn^{+4}	Sb^{+5}
∧	∧	∧	∨	∨	∨
Tl^{+1}	Pb^{+2}	Bi^{+3}	Tl^{+3}	Pb^{+4}	Bi^{+5}

Applications

1. Stability of Compounds

(a) $\overset{+2}{PbO} > \overset{+4}{PbO_2}$ (b) $\overset{+2}{PbCl_2} > \overset{+4}{PbCl_4}$ (c) $\overset{+2}{SnCl_2} < \overset{+4}{SnCl_4}$ (d) $\overset{+2}{GeCl_2} < \overset{+4}{GeCl_4}$

2. Identification of oxidising agent and reducing agent

$Pb^{+4} \longrightarrow Pb^{+2}$

Oxidising agent

$PbCl_4 \longrightarrow PbCl_2 + Cl_2$

$SnCl_2 \xrightarrow{Cl_2} SnCl_4$

$Sn^{+2} \longrightarrow Sn^{+4}$

Reducing agent

$PbO_2 \xrightarrow{\Delta} PbO + 1/2\ O_2$

$SnO \xrightarrow{O_2} SnO_2$

3. Existence and Non-Existence

- $\overset{+3}{TlF_3}$ $\overset{+4}{PbF_4}$ $\overset{+5}{BiF_5}$ $\overset{+3}{Tl_2O_3}$ $\overset{+4}{PbO_2}$ → Exist in nature [high oxidation state of element is stable with F and O].
- TlI_3 exist as $Tl^+I_3^-$. $Tl^{3+} \xrightarrow{3I^-} Tl^+ + \boxed{I_2 + I^-} \longrightarrow Tl^+ I_3^-$
- PbI_4 does not exist because Pb^{+4} oxidises I^- into I_2 and convert itself in PbI_2.

$Pb^{+4} \xrightarrow[R.A.]{4I^-} I_2 + Pb^{+2} . 2I^- \rightarrow PbI_2$

$PbI_4 \xrightarrow{3I^-} I_2 + PbI_2$

'NCERT' → PbI_4 does not exist because Pb–I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom.

Note

The well characterised $\overset{(+5)}{Bi}$ compound is BiF_5 due to strong oxidising power of F_2.

4. Thermal Stability

$CCl_4 > SiCl_4 > GeCl_4 > SnCl_4 > PbCl_4$

$CCl_2 < SiCl_2 < GeCl_2 < SnCl_2 < PbCl_2$

Note

- In $GaCl_2$, Ga exist in +3 and +1 oxidation state. $2GaCl_2 \equiv GaCl_3 \cdot GaCl$

6. Given below are two statements: One is labelled as **[08 April, 2024 (Shift-I)]**
Assertion (A) and the other is labelled as Reason (R):
Assertion (A): The stability order of +1 oxidation state of Ga, In and Tl is Ga < In < Tl.
Reason (R): The inert pair effect stabilizes the lower oxidation state down the group.
In the light of the above statements, choose the correct answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) A is true but R is false.
(c) Both A and R are true but R is NOT the correct explanation of A.
(d) A is false but R is true.

Sol. (a)

7. Given below are two statements: One is labelled as Assertion (A) and the other is labelled as Reason (R).
Assertion (A): In TlI_3, isomorphous to CsI_3, the metal is present in +1 oxidation state.
Reason (R): Tl metal has fourteen f electrons in the electronic configuration.
In the light of the above statements, choose the most appropriate answer from the options given below: **[26 Feb, 2021 (Shift-II)]**
(a) (A) is correct but (R) is not correct
(b) Both (A) and (R) are correct but (R) is NOT the correct explanation of (A)
(c) (A) is not correct but (R) is correct
(d) Both (A) and (R) are correct and (R) is the correct explanation of (A)

Sol. (b) Both TlI_3 and CsI_3 has +1 oxidation state as well as have similar lattice structure.

(IIT JEE 2008)

8. Statement-I: Pb^{4+} compounds are stronger oxidising agents than Sn^{2+} compounds.
Statement-II: The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to the 'inert pair effect'.
(a) Statement-I is correct; Statement-II is correct Statement-II is the correct explanation of Statement-I
(b) Statement-I is correct; Statement-II is correct Statement-II is not the correct explanation of Statement I
(c) Statement-I is correct; Statement-II is incorrect
(d) Statement-I is incorrect; Statement-II is correct

Sol. (c)

9. Aluminium is usually found in +3 oxidation state. In contrast, thallium exists in +1 and +3 oxidation states. This is due to
(a) Inert pair effect
(b) Diagonal relationship
(c) Lattice effect
(d) Lanthanoid contraction

Sol. (a) Aluminium is usually found in +3 oxidation state. In contrast, thallium exists in +1 and +3 oxidation states. The reason for this is the inert pair effect, which refers to the tendency of the s-electrons (in this case, the 6s electrons of thallium) to remain non-reactive or "inert" and not participate in bonding.

10. The covalency and oxidation state respectively of boron in $[BF_4]^-$, are

(a) 4 and 3 (b) 4 and 4 (c) 3 and 4 (d) 3 and 5

Sol. (a) In $[BF_4]^-$, boron forms four bonds with fluorine, so its covalency is 4.
The oxidation state of boron can be calculated as: $x + 4 \times (-1) = -1, x = +3$

11. Assertion (A): Boron is unable to form BF_6^{3-}
Reason (R): Size of B is very small.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A)
(b) Both (A) and (R) are true and (R) is NOT the correct explanation of (A)
(c) (A) is true but (R) is false
(d) (A) is false but (R) is true

Sol. (b) Boron do not form $[BF_6]^{3-}$. Since Boron does not have vacant d orbitals, it can not expand its octet.

OXIDES

Group 13

- ☐ B is unreactive in crystalline form. Air (O_2, N_2), acids and alkalies do not react with boron.
- ☐ Al forms a very thin oxide layer on the surface which protects the metal from further attack.

Al → Al_2O_3 layer

B_2O_3 — Acidic Oxide

Al_2O_3 Ga_2O_3 — Amphoteric Oxide

In_2O_3 Tl_2O_3 — Basic Oxide

Group 14

CO Neutral
CO_2 Acidic

SiO exist only at High temp.
SiO_2 Acidic.

GeO Acidic
GeO_2 Acidic

Amphoteric Oxide
SnO, PbO, Pb_2O_3
SnO_2, PbO_2, Pb_3O_4

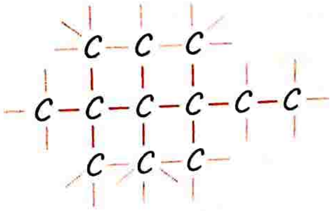
Red lead $Pb_3O_4 \equiv 2PbO.PbO_2$
$Pb_2O_3 \equiv PbO.PbO_2$

BOND ENERGY

Bond dissociation energy: $C-C > Si-Si > Ge-Ge > Sn-Sn$

CATENATION PROPERTY

- ☐ Self linking property of an element is known as catenation property.
- ☐ More single bond formation tendency with itself ⇒ More Self-linking property.



- ☐ The order of catenation is C >> Si > Ge ≈ Sn.
- ☐ Pb does not show catenation.

12. The element that does NOT show catenation is:

(a) Ge (b) Si (c) Sn (d) Pb

Sol. (d) Lead does not show catenation.

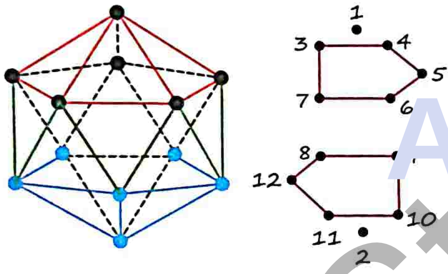
13. The correct order of bond enthalpy (kJ per mol) is:

(a) Si – Si > C – C > Sn – Sn > Ge – Ge
(b) Si – Si > C – C > Ge – Ge > Sn – Sn
(c) C – C > Si –Si > Sn – Sn > Ge – Ge
(d) C – C > Si – Si > Ge – Ge > Sn – Sn

Sol. (d) The correct order of bond enthalpy is C – C > Si – Si > Ge – Ge > Sn – Sn.

ABOUT BORON

B_{12} Unit Icosahedral



Boron is extremely hard and black coloured covalent solid with B_{12} icosahedral unit. Due to very strong crystalline lattice, boron has unusually high melting point.

Boron fibres are used in making bullet-proof vest and light composite material for aircraft.

Boron Isotopes: ^{10}B (19%)
^{11}B (81%)

^{10}B isotope: high ability to absorb neutrons

(metal borides are used in nuclear industry as protective shields and control rods.)

14. Statement-I : Boron is extremely hard indicating its high lattice energy.
Statement-II : Boron has highest melting and boiling point compared to its other group members.

[12 April, 2023 (Shift-I)]

(a) Statement-I is incorrect but Statement-II is correct
(b) Both Statement-I and statement-II is correct
(c) Statement-I is correct but statement-II is incorrect
(d) Both Statement-I and Statement-II is incorrect

Sol. (b)

15. The number of neutrons present in the more abundant isotope of boron is 'x'. Amorphous boron upon heating with air forms a product, in which the oxidation state of boron is 'y'. The value of x + y is ...

[05 April, 2024 (Shift-I)]

(a) 4 (b) 6 (c) 3 (d) 9

Sol. (d) More abundant isotope = B^{11}
The number of neutrons in this isotope is 6.
$x = 6$

$B + O_2 \rightarrow B_2O_3$
Oxidation state of B in B_2O_3 = +3
So, $y = 3$
$\therefore x + y = 6 + 3 = 9$

16. Taking stability as the factor, which one of the following represents correct relationship? [NEET 2023]

(a) $TlI > TlI_3$ (b) $TlCl_3 > TlCl$ (c) $InI_3 > InI$ (d) $AlCl > AlCl_3$

Sol. (a)

17. Select the element (M) whose trihalides cannot be hydrolysed to produce an ion of the form $[M(H_2O)_6]^{3+}$ [NEET 2023-Manipur]

(a) Ga (b) In (c) Al (d) B

Sol. (d)

18. The correct order of atomic radii in group 13 elements is [NEET 2018]

(a) $B < Al < In < Ga < Tl$ (b) $B < Al < Ga < In < Tl$

(c) $B < Ga < Al < In < Tl$ (d) $B < Ga < Al < Tl < In$

Sol. (c)

19. Which one of the following elements is unable to form MF_6^{3-} ion? [NEET 2018]

(a) Ga (b) Al (c) In (d) B

Sol. (d)

20. The stability of +1 oxidation state among Al, Ga, In and Tl increases in the sequence: [NEET 2015 Re]

(a) $In < Tl < Ga < Al$ (b) $Ga < In < Al < Tl$

(c) $Al < Ga < In < Tl$ (d) $Tl < In < Ga < Al$

Sol. (c)

21. Which of the following species is not stable? [NEET 2019]

(a) $[SiF_6]^{2-}$ (b) $[GeCl_6]^{2-}$ (c) $[Sn(OH)_6]^{2-}$ (d) $[SiCl_6]^{2-}$

Sol. (d)

22. It is because of inability of ns^2 electrons of the valence shell to participate in bonding that: [NEET 2017-Delhi]

(a) Sn^{4+} is reducing while Pb^{4+} is oxidising

(b) Sn^{2+} is reducing while Pb^{4+} is oxidising

(c) Sn^{2+} is oxidising while Pb^{4+} is reducing

(d) Sn^{2+} and Pb^{2+} are both oxidising and reducing

Sol. (b)

23. Which of the following oxidation states are the most characteristic for lead and tin respectively? [NEET 2007]

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

Sol. (a)

24. Carbon and silicon belong to (IV) group. The maximum coordination number of carbon in commonly occurring compounds is 4, whereas that of silicon is 6. This is due to: [NEET 1994]

(a) Availability of low lying d-orbitals in silicon

(b) Large size of silicon

(c) More electropositive nature of silicon

(d) Both (b) and (c)

Sol. (a)

p-BLOCK ELEMENTS (GROUP 15 TO 18)

Period No. / Group No.	Group 15	Group 16	Group 17	Group 18
1.				Helium ($_{2}$He) - Noble gas
2.	Nitrogen ($_{7}$N) - Non metal	Oxygen ($_{8}$O) - Non metal	Fluorine ($_{9}$F) - Non metal	Neon ($_{10}$Ne) - Noble gas
3.	Phosphorus ($_{15}$P) - Non metal	Sulphur ($_{16}$S) - Non metal	Chlorine ($_{17}$Cl) - Non metal	Argon ($_{18}$Ar) - Noble gas
4.	Arsenic ($_{33}$As) - Metalloid	Selenium ($_{34}$Se) - Metalloid	Bromine ($_{35}$Br) - Non metal	Krypton ($_{36}$Kr) - Noble gas
5.	Antimony ($_{51}$Sb) - Metalloid	Tellurium ($_{52}$Te) - Metalloid	Iodine ($_{53}$I) - Non metal	Xenon ($_{54}$Xe) - Noble gas
6.	Bismuth ($_{83}$Bi) - Metal	Polonium ($_{84}$Po) - Metal	Astatine ($_{85}$At) - Non metal	Radon ($_{86}$Rn) - Noble gas

☐ Polonium, Astatine, Radon are radioactive elements.

Electronic Configuration

Period No. / Group No.	Group 15 (Pnictogens)	Group 16 (Chalcogens)	Group 17 (Halogens)	Group 18 (Inert gas)
1.				He: $1s^2$
2.	N: [He] $2s^2\ 2p^3$	O: [He] $2s^2\ 2p^4$	F: [He] $2s^2\ 2p^5$	Ne: [He] $2s^2\ 2p^6$
3.	P: [Ne] $3s^2\ 3p^3$	S: [Ne] $3s^2\ 3p^4$	Cl: [Ne] $3s^2\ 3p^5$	Ar: [Ne] $3s^2\ 3p^6$
4.	As: [Ar] $4s^2\ 3d^{10}\ 4p^3$	Se: [Ar] $4s^2\ 3d^{10}\ 4p^4$	Br: [Ar] $4s^2\ 3d^{10}\ 4p^5$	Kr: [Ar] $4s^2\ 3d^{10}\ 4p^6$
5.	Sb: [Kr] $5s^2\ 4d^{10}\ 5p^3$	Te: [Kr] $5s^2\ 4d^{10}\ 5p^4$	I: [Kr] $5s^2\ 4d^{10}\ 5p^5$	Xe: [Kr] $5s^2\ 4d^{10}\ 5p^6$
6.	Bi: [Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^3$	Po: [Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^4$	At: [Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^5$	Rn: [Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^6$

☐ The elements present in Group 18 have their valence shell orbitals completely filled and, therefore, react with a few elements only under certain conditions. Therefore, they are now known as noble gases.

Atomic Radius

☐ As we move from top to bottom in a group, atomic size increases.

			He
			∧
N	O	F	Ne
∧	∧	∧	∧
P	S	Cl	Ar
∧	∧	∧	∧
As	Se	Br	Kr
∧	∧	∧	∧
Sb	Te	I	Xe
∧	∧		
Bi	Po		

Ionisation Energy

☐ As we move from top to bottom in a group, ionisation energy decreases.

			He
			∨
N	O	F	Ne
∨	∨	∨	∨
P	S	Cl	Ar
∨	∨	∨	∨
As	Se	Br	Kr
∨	∨	∨	∨
Sb	Te	I	Xe
∨	∨		
Bi	Po		

Note

☐ Ionisation energy: N > O

(Nitrogen has half filled subshell (p^3) which is stable, so removal of electron is tough with respect to oxygen having p^4 electronic configuration).

☐ Due to extra stable half-filled p orbitals electronic configurations of group 15 elements, larger amount of energy is required to remove electrons compared to group 16 elements.

Electron Gain Enthalpy

Group 16	$\Delta_{eg}H$	Group 17	$\Delta_{eg}H$	Group 0	$\Delta_{eg}H$
				He	+ 48
O	– 141	F	– 333	Ne	+ 116
S	– 200	Cl	– 349	Ar	+ 96
Se	– 195	Br	– 325	Kr	+ 96
Te	– 190	I	– 296	Xe	+ 77
Po	– 174	At	– 270	Rn	+ 68

☐ Order of (–)ve electron gain entahlpy:

S > Se > Te > Po > O
Cl > F > Br > I > At

[Chlorine has most (–)ve electron gain enthalpy in periodic table.]

☐ Order of (+)ve electron gain entahlpy:

Ne > Ar = Kr > Xe > Rn > He

[Noble gases have (+)ve electron gain enthalpy as they have completely filled valence shell orbitals.]

Electronegativity (Pauling Scale)

N 3.0	O 3.5	F 4.0
P 2.1	S 2.58	Cl 3.2
As 2.0	Se 2.55	Br 3.0
Sb 1.9	Te 2.01	I 2.7
Bi 1.9	Po 1.76	At 2.2

Group No.	Maximum oxidation state
13	+3 (B → In)
14	+4 (C → Sn)
15	+5 (N → Sb)
16	+6 (S → Te)*
17	+7 (Cl → I)*
18	+8 (Xe)

* O has +2 as maximum oxidation state (eg. OF_2).
* F always has −1 oxidation state.

Physical Properties

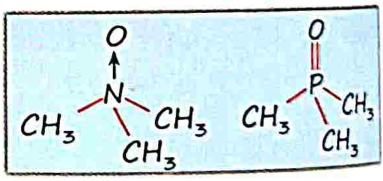
Generally Melting Point, Boiling Point and Density increases as we move down in the group-15, 16, 17 and 18.

Exception–

1. Boiling Point: Sb > Bi
2. Melting Point: N < P < As > Sb > Bi
3. Melting Point and Boiling Point: Te > Po

First Atom of Group

- ☐ First atom of the group has small size, so they can form π bond easily.
- ☐ First atom of the group (C, N, O) has 2^{nd} shell as valence shell which has one s orbital and three p orbitals but not any d orbital is available for hybridisation (for bonding purpose). So possible hybridisations are – sp, sp^2, sp^3.
- ☐ Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding.
- ☐ The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalence as in PF_6^-.



- ☐ Nitrogen cannot form dπ – pπ bond as the heavier elements can.
- ☐ Nitrogen has unique ability to form pπ–pπ multiple bonds with itself and with other elements having small size and high electronegativity (C, O).
- ☐ Heavier elements of this group do not form pπ–pπ bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.
- ☐ Phosphorus and arsenic can form d_π-d_π bond also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

25. Identify the incorrect statements about group 15 elements: [08 April, 2024 (Shift-II)]

(A) Dinitrogen is a diatomic gas which acts like an inert gas at room temperature.

(B) The common oxidation states of these elements are −3, +3 and +5.

(C) Nitrogen has unique ability to form $p\pi-p\pi$ multiple bonds.

(D) The stability of +5 oxidation states increases down the group.

(E) Nitrogen shows a maximum covalency of 6.

Choose the correct answer from the options given below.

(a) (A), (B), (D) only

(b) (A), (C), (E) only

(c) (B), (D), (E) only

(d) (D) and (E) only

Sol. (d) (D) Due to inert pair effect, lower oxidation state is more stable.

(E) Nitrogen belongs to 2nd period and cannot expands its octet.

26. PCl_5 is well known, but NCl_5 is not, Because [24 June, 2022 (Shift-II)]

(a) Nitrogen is less reactive than phosphorous

(b) Nitrogen doesn't have d-orbitals in its valence shell.

(c) catenation tendency is weaker in nitrogen than phosphorous

(d) size of phosphorous is larger than nitrogen

Sol. (b) Phosphorous has vacant 3d-orbital due to which it can expand its covalency beyond 4. Nitrogen can't expand its covalency beyond 4 as it does not have d-orbitals.

(IIT JEE 1994)

27. Statement-I: Although PF_5, PCl_5 and PBr_5 are known, the pentahalides of nitrogen have not been observed.

Statement-II: Phosphorus has lower electronegativity than nitrogen.

(a) Statement-I is correct; Statement-II is correct Statement-II is the correct explanation of Statement-I

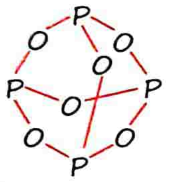
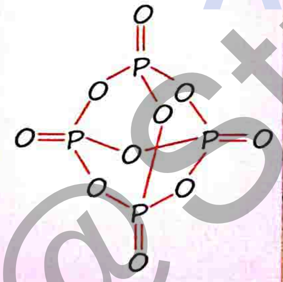
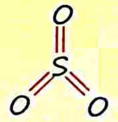
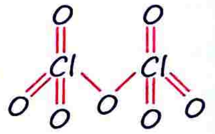
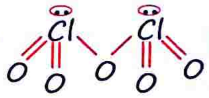
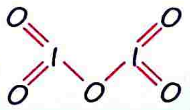
(b) Statement-I is correct; Statement-II is correct Statement-II is not the correct explanation of Statement-I

(c) Statement-I is correct; Statement-II is incorrect

(d) Statement-I is incorrect; Statement-II is correct

Sol. (b)

Oxides

Group 15	Group 16	Group 17	Group 18
NO, N_2O : Neutral oxide N_2O_3, N_2O_5, NO_2 N_2O_4 : Acidic oxide P_4O_6, P_4O_{10} : Acidic oxide As_2O_3, Sb_2O_3 : Amphoteric oxide As_2O_5, Sb_2O_5 : Acidic oxide Bi_2O_3 : Basic Oxide P_4O_6  P_4O_{10} 	SO_2 SeO_2 TeO_2 → Amphoteric oxide Acidic Oxide SO_3 SeO_3 TeO_3 PoO → Basic oxide ☐ O_3 and SO_2 → gas SeO_2 → solid ☐ Reducing nature → $SO_2 > SeO_2 > TeO_2$ Due to inert pair effect, stability of +6 oxidation state decreases as we go down the group. ☐ SO_2 is a reducing and TeO_2 is an oxidising agent. $\underset{\text{[Reducing Agent]}}{\overset{+4}{SO_2}} \longrightarrow \overset{+6}{SO_4^{2-}}$ or $\overset{+6}{SO_3}$ SO_2  SO_3 	Cl_2O_7, I_2O_7 Cl_2O_5, I_2O_5 ClO_2, Cl_2O_4, BrO_2, I_2O_4 Cl_2O_3, Cl_2O_6 Cl_2O, Br_2O ☐ Oxides of halogen are acidic in nature. Cl_2O_7  Cl_2O_5  ClO_2  I_2O_5 	XeO_3, XeO_4 XeO_4  XeO_3 

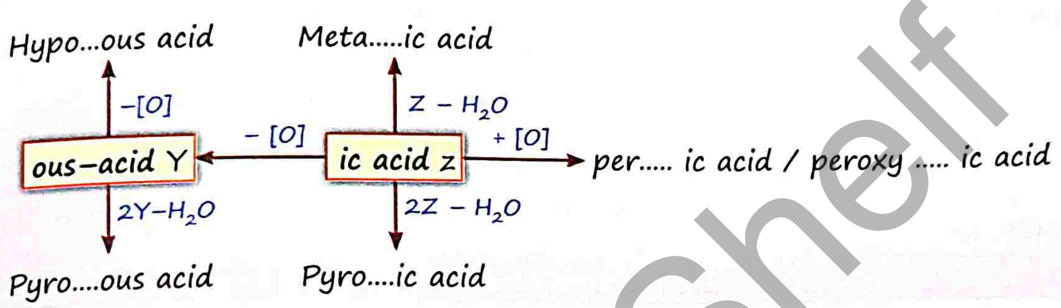
OXO-ACIDS

An oxyacid or oxoacid is a compound that contains hydrogen, oxygen, and at least one other element, with at least one hydrogen atom bonded to oxygen that can dissociate to produce the H^+ cation and the anion of the acid.

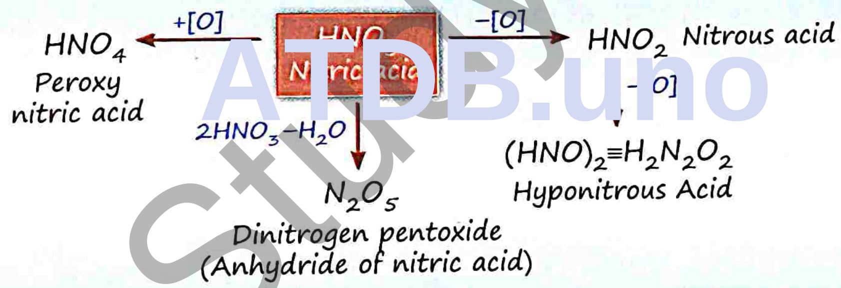
Group 15	Group 16	Group 17	Group 18
+5 (ic acid)	+6 (ic acid)	+7 (per.....ic acid)	+8 (per......ic acid)
+3 (ous acid)	+4 (ous acid)	+5 (ic acid)	+4 (ic acid)
+1 (Hypo....ous acisssd)		+3 (ous acid)	
		+1 (Hypo....ous acid)	

HNO_3 Nitric acid	H_3PO_4 Phosphoric acid	H_2SO_4 Sulphuric acid	$HClO_4$ Perchloric acid	H_4XeO_6 Perxenic acid
HNO_2 Nitrous acid	H_3PO_3 Phosphorous acid	H_2SO_3 Sulphurous acid	$HClO_3$ Chloric acid	H_4XeO_4 Xenic acid
$H_2N_2O_2$ Hypo nitrous acid	H_3PO_2 Hypo phosphorous acid		$HClO_2$ Chlorous acid	
			$HClO$ Hypo chlorous acid	

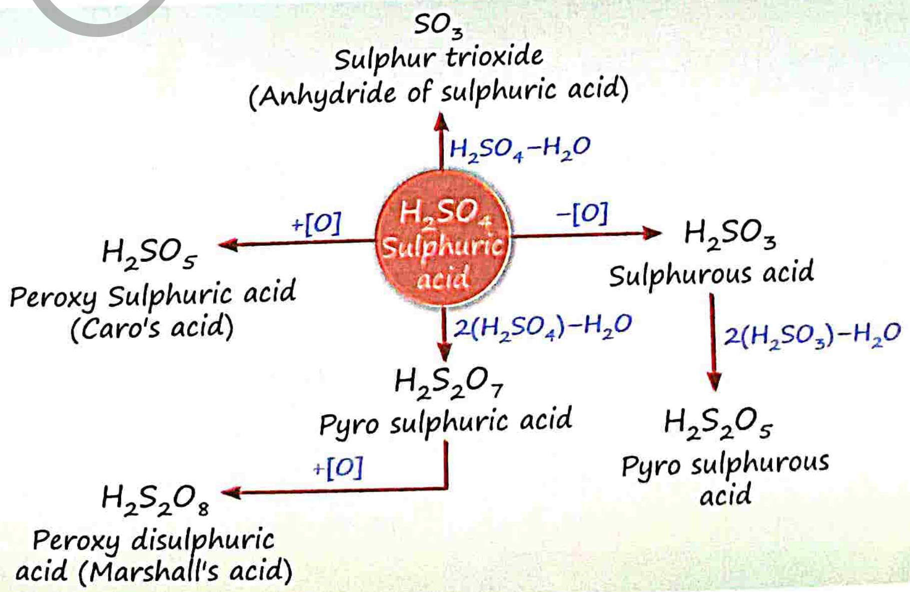
Meta, Pyro, Peroxy Acids



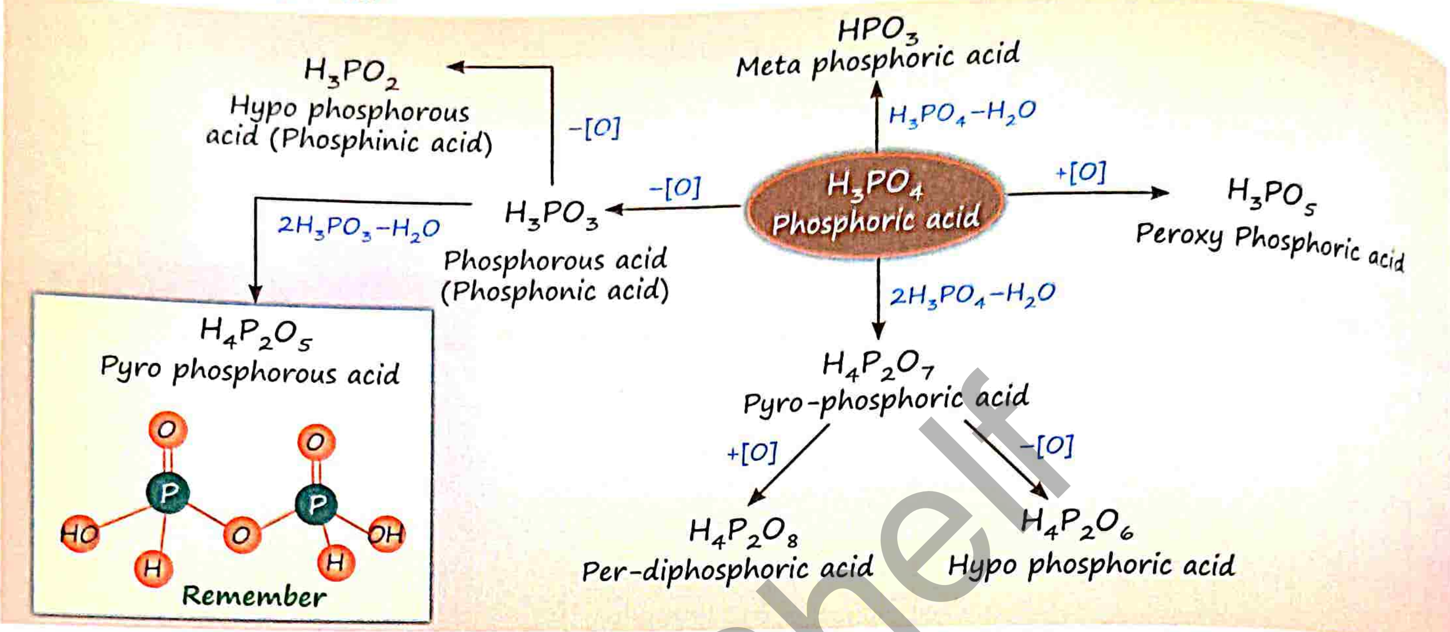
Oxo-Acids of Nitrogen



Oxo-Acids of Sulphur



Oxo-Acids of P

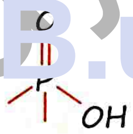


Structure of Acids having Single Central Atom

(i) Central atom from 2nd period (B, C, N) must be sp² hybridised.

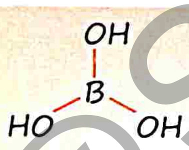
Central atom from 3rd period (Si, P, S) must be sp³ hybridised.

(ii) Oxo-acids of phosphorus always has

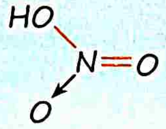


structure.

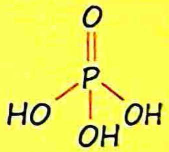
H_3BO_3



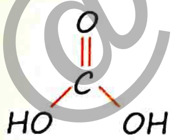
HNO_3



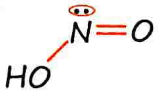
H_3PO_4



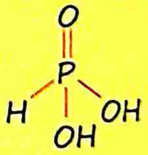
H_2CO_3



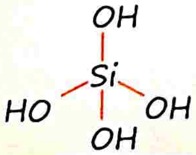
HNO_2



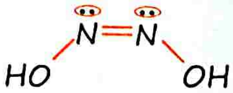
H_3PO_3



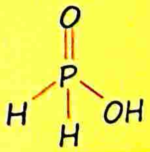
H_4SiO_4



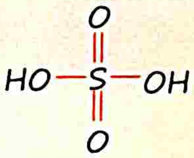
$H_2N_2O_2$



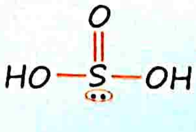
H_3PO_2



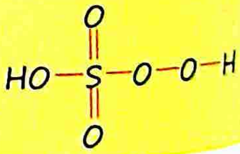
H_2SO_4



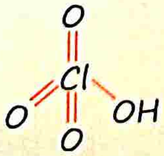
H_2SO_3



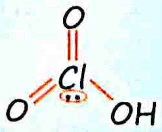
H_2SO_5



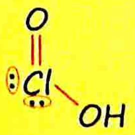
$HClO_4$



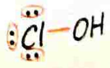
$HClO_3$



$HClO_2$



$HClO$



Structure of Acids having Two Central Atom (Z)

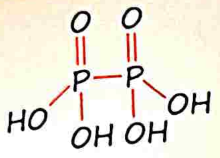
(i) Calculate theoretical oxidation state (TOS) of central atom z.

(ii) Compare it with maximum oxidation state (MOS) of central atom.

(iii) Then write type of bond between 2 central atoms.

Theoretical OS < Max. OS	Z—Z
Theoretical OS = Max. OS	Z—O—Z
Theoretical OS > Max. OS	Z—O—O—Z

$H_4P_2O_6$



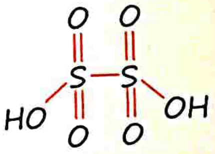
(i) $4 \times 1 + 2x + 6(-2) = 0$

$x = +4 = \text{T.O.S.}$

(ii) T.O.S. < M.O.S. $[\text{M.O.S.}]_P = +5$

(iii) P — P bond

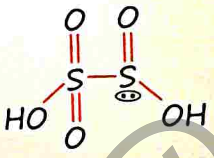
$H_2S_2O_6$



$[\text{M.O.S.}]_S = +6$

$[\text{T.O.S.}]_S = +5$

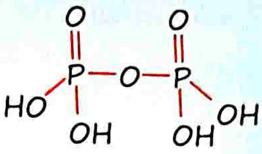
$H_2S_2O_5$



$[\text{M.O.S.}]_S = +6$

$[\text{T.O.S.}]_S = +4$

$H_4P_2O_7$



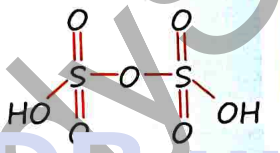
(i) $4 \times 1 + 2x + 7(-2) = 0$

$x = +5$

(ii) T.O.S. = M.O.S.

(iii) P — O — P bond

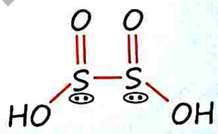
$H_2S_2O_7$



$[\text{M.O.S.}]_S = +6$

$[\text{T.O.S.}]_S = +6$

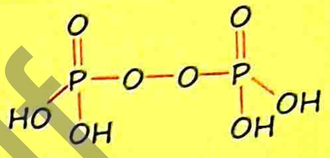
$H_2S_2O_4$



$[\text{M.O.S.}]_S = +6$

$[\text{T.O.S.}]_S = +3$

$H_4P_2O_8$



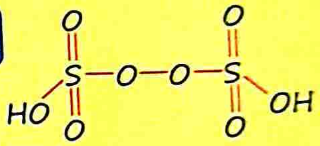
(i) $4 \times 1 + 2x + 8(-2) = 0$

$x = +6$

(ii) T.O.S. > M.O.S.

(iii) P — O — O — P bond

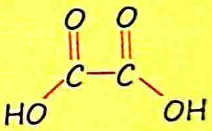
$H_2S_2O_8$



$[\text{M.O.S.}]_S = +6$

$[\text{T.O.S.}]_S = +7$

$H_2C_2O_4$



$[\text{M.O.S.}]_C = +4$

$[\text{T.O.S.}]_C = +3$

Meta Acids

These acids are polymeric in nature or have cyclic structures.

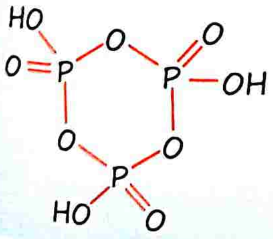
$H_3PO_4 \xrightarrow{-H_2O} HPO_3$

Ortho phosphoric acid → Meta phosphoric acid

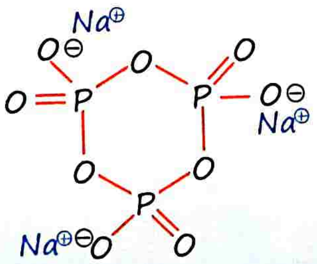
$H_3BO_3 \xrightarrow{-H_2O} HBO_2$

Ortho boric acid → Meta boric acid

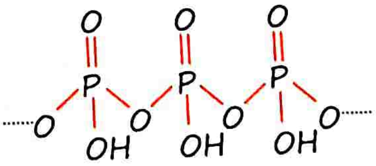
$(HPO_3)_3$: Tri-meta phosphoric acid



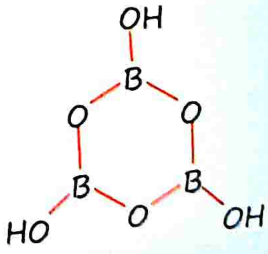
Sodium tri-meta phosphate $(NaPO_3)_3$



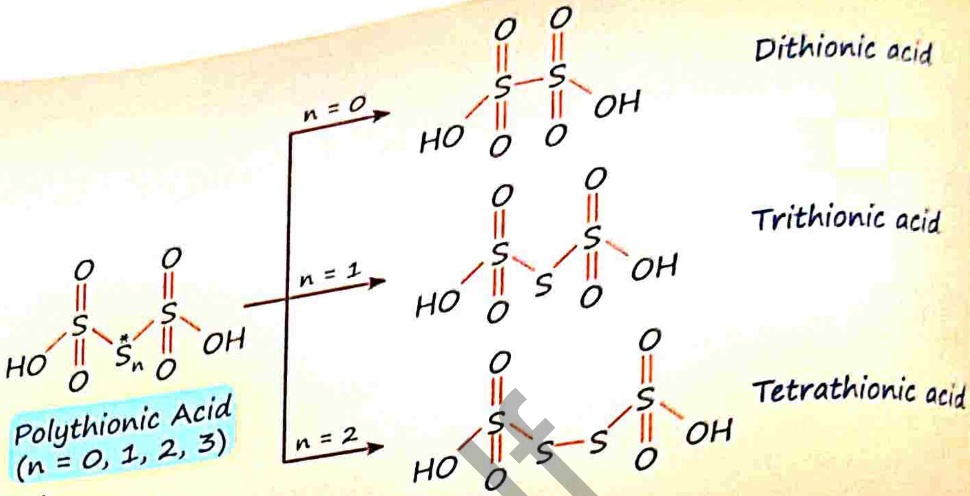
$(HPO_3)_n$: Poly-meta phosphoric acid



$(HBO_2)_3$: Tri-meta boric acid



Polythionic Acids

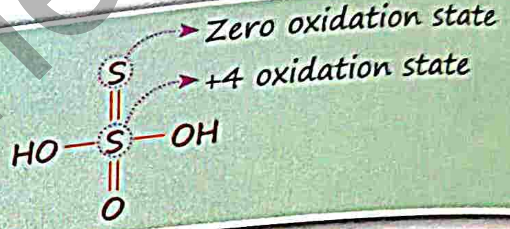


- Four $d\pi - p\pi$ bonds are present.
- * Marked sulphur has zero oxidation state and other 2 sulphur have +5 oxidation state.

Note

$$\text{Oxy Acid} \xrightarrow[\text{by 1 sulphur atom}]{\text{Exchange of 1 oxygen atom}} \text{Thio Acid}$$

$$\underset{\text{Sulphuric Acid}}{H_2SO_4} \longrightarrow \underset{\text{Thio-sulphuric acid}}{H_2S_2O_3}$$



Name of Anions

- ic acid → ate ion

$$\underset{\text{Perchloric acid}}{HClO_4} \xrightarrow{-H^+} \underset{\text{Perchlorate ion}}{ClO_4^-}$$

$$\underset{\text{Chloric acid}}{HClO_3} \xrightarrow{-H^+} \underset{\text{Chlorate ion}}{ClO_3^-}$$

$$\underset{\text{Chlorous acid}}{HClO_2} \xrightarrow{-H^+} \underset{\text{Chlorite ion}}{ClO_2^-}$$

$$\underset{\text{Hypochlorous acid}}{HClO} \xrightarrow{-H^+} \underset{\text{Hypochlorite ion}}{ClO^-}$$

- ous acid → ite ion

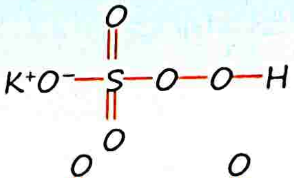
$$\underset{\text{Thio sulphuric acid}}{H_2S_2O_3} \xrightarrow{-2H^+} \underset{\text{Thiosulphate ion}}{S_2O_3^{2-}}$$

$$\underset{\text{Pyro sulphuric acid}}{H_2S_2O_7} \xrightarrow{-2H^+} \underset{\text{Pyrosulphate ion}}{S_2O_7^{2-}}$$

$$\underset{\text{Peroxodisulphuric acid}}{H_2S_2O_8} \xrightarrow{-2H^+} \underset{\text{Peroxodisulphate ion}}{S_2O_8^{2-}}$$

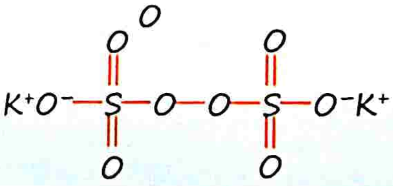
$$\underset{\text{Peroxy sulphuric acid}}{H_2SO_5} \xrightarrow{-H^+} \underset{\text{Peroxy monosulphate ion}}{HSO_5^-}$$

- Potassium peroxymonosulphate [$KHSO_5$]



$$K^+O^- - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - O - O - H$$

- Potassium peroxodisulphate [$K_2S_2O_8$]



$$K^+O^- - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - O - O - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - O^-K^+$$

Anhydride

To make anhydride (oxide) of any given acid remove all hydrogen from acid in the form of water (H_2O) molecule.

$2\ HNO_3 \xrightarrow[-H_2O]{} N_2O_5$

$2\ HNO_2 \xrightarrow[-H_2O]{} N_2O_3$

$H_2N_2O_2 \xrightarrow[-H_2O]{} N_2O$

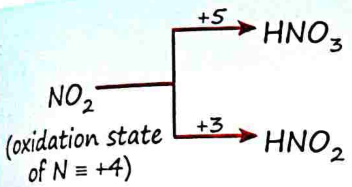
$2\ HClO_4 \xrightarrow[-H_2O]{} Cl_2O_7$

$2\ HClO_3 \xrightarrow[-H_2O]{} Cl_2O_5$

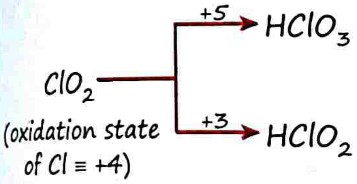
$2\ HClO_2 \xrightarrow[-H_2O]{} Cl_2O_3$

$2\ HClO \xrightarrow[-H_2O]{} Cl_2O$

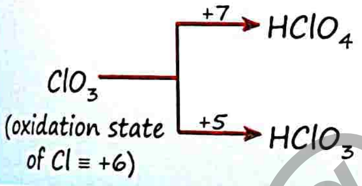
Mixed Anhydride



- ☐ NO_2 is a mixed anhydride of HNO_3 and HNO_2.
- ☐ $HNO_3 + HNO_2 \equiv H_2N_2O_5 - H_2O \equiv N_2O_4$ (Dimer of NO_2)



- ☐ ClO_2 is a mixed anhydride of $HClO_3$ and $HClO_2$.
- ☐ $HClO_3 + HClO_2 \equiv H_2Cl_2O_5 - H_2O \equiv Cl_2O_4$ (Dimer of ClO_2)



- ☐ ClO_3 is a mixed anhydride of $HClO_4$ and $HClO_3$.
- ☐ $HClO_4 + HClO_3 \equiv H_2Cl_2O_7 - H_2O \equiv Cl_2O_6$ (Dimer of ClO_3)

28. The number of P – O – P bonds in $H_4P_2O_7$, $(HPO_3)_3$ and P_4O_{10} are respectively. [15 April, 2023 (Shift-I)]

(a) 1, 3, 6 (b) 0, 3, 6 (c) 0, 3, 4 (d) 1, 2,4

Sol. (a)

29. The oxidation state of phosphorus in hypophosphoric acid is + ______ [31 Jan, 2023 (Shift-I)]

Sol. [4]

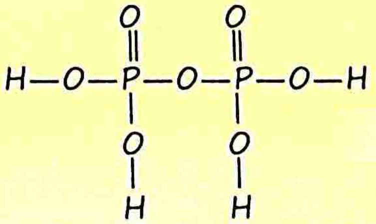
30. The ratio of sigma and π bonds present in pyrophosphoric acid is ______. [8 April, 2023 (Shift-II)]

Sol. [6] No. of σ bonds = 12

No. of π bonds = 2

$\therefore \frac{\sigma}{\pi} = \frac{12}{2} = 6$

Hence, ratio of σ and π bonds = 6



31. In polythionic acid, $H_2S_xO_6$($x = 3$ to 5) the oxidation state(s) of sulphur is/are: [27 Aug, 2021 (Shift-I)]

(a) + 3 and + 5 only (b) + 6 only

(c) 0 and + 5 only (d) + 5 only

Sol. (c)

(IIT JEE 2004)

32. Which of the following has –O – O – linkage?

(a) $H_2S_2O_6$ (b) $H_2S_2O_8$ (c) $H_2S_2O_3$ (d) $H_2S_4O_6$

Sol. (b)

HEATING EFFECT ON OXYACIDS

☐ Oxyacid having maximum oxidation state $\xrightarrow{\Delta}$ Anhydride

$$2\,HNO_3 \xrightarrow[-H_2O]{\Delta} N_2O_5$$

$$2\,HClO_4 \xrightarrow[-H_2O]{\Delta} Cl_2O_7$$

$$H_2SO_4 \xrightarrow[-H_2O]{\Delta} SO_3$$

$$2\,H_3PO_4 \xrightarrow[-3H_2O]{\Delta} P_2O_5$$

☐ Oxyacid having intermediate oxidation state $\xrightarrow{\Delta}$ ic acid + hydride/oxide (or lower oxidation state)

$$3HNO_2 \xrightarrow[\text{Reaction}]{\text{Disproportionation}} HNO_3 + 2NO + H_2O$$

$$2H_3PO_2 \xrightarrow{\Delta} H_3PO_4 + PH_3$$

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$$

$$3HClO \xrightarrow{\Delta} HClO_3 + 2HCl$$

HEATING OF AMMONIUM SALT

Type-1

☐ Heating of ammonium salt with oxidising anion $\xrightarrow{\Delta}$ N_2 or N_2O + Side Product

(i) $(\overset{-3}{N}H_4)_2\,\overset{+6}{Cr_2}O_7 \xrightarrow[-4H_2O]{\Delta} \overset{+3}{Cr_2}O_3 + \overset{\text{(zero)}}{N_2}\uparrow$

(ii) $\overset{-3}{N}H_4\overset{+3}{N}O_2 \xrightarrow[-4H_2O]{\Delta} N_2\uparrow$

$$\boxed{\overset{-3}{N}H_4\overset{+5}{N}O_3 \xrightarrow[-2H_2O]{\Delta} \overset{+1}{N_2}O}$$

Type-2

☐ Heating of ammonium salt with non-oxidising anion $\xrightarrow{\Delta}$ NH_3 + Side Product

(i) $NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$

(ii) $(NH_4)_2S \xrightarrow{\Delta} 2NH_3 + H_2S$

(iii) $(NH_4)_2CO_3 \xrightarrow[-H_2O]{\Delta} 2NH_3 + CO_2$

(iv) $NH_4CN \xrightarrow{\Delta} NH_3 + HCN$

HYDROLYSIS

1. Oxides

☐ Hydrolysis of oxide does not change the oxidation state of central atom.

- $\overset{+5}{N}_2O_5 \xrightarrow{H_2O} 2H\overset{+5}{N}O_3$
- $Na_2O \xrightarrow{H_2O} 2NaOH$

Hint: $2Na^+ O^{2-} \xrightarrow[OH^-]{H^+} 2NaOH$

☐ Hydrolysis helps to understand the mechanism behind the reactions.

- $Na_2O + N_2O_5 \longrightarrow 2NaNO_3$
- $\overset{+5}{P}_4O_{10} \xrightarrow{6H_2O} 4H_3\overset{+5}{P}O_4$
- $\overset{+3}{P}_4O_6 \xrightarrow{6H_2O} 4H_3\overset{+3}{P}O_3$

☐ Oxides $[O^{2-}]$

$CaO \xrightarrow{H_2O} Ca(OH)_2$

- $O^{2-} + H^+ \rightarrow \overset{\ominus}{O}-H$
- $Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2$

☐ Peroxides $[O_2^{2-}]$

$Na_2O_2 \xrightarrow{H_2O} H_2O_2 + 2NaOH$

- $Na_2O_2 \equiv 2Na^+ O_2^{2-}$
- $O_2^{2-} \xrightarrow[2H^+ + 2OH^-]{2H_2O} H_2O_2 + 2OH^-$

☐ Superoxides $[O_2^-]$

$2RbO_2 \xrightarrow{2H_2O} O_2\uparrow + H_2O_2 + 2RbOH$

- $RbO_2 \equiv Rb^+ O_2^-$
- $O_2^- + O_2^- \rightarrow O_2 + O_2^{2-}$

Oxidation

Reduction

- $O_2^{2-} \xrightarrow[2H^+ + 2OH^-]{2H_2O} H_2O_2 + 2OH^-$

2. Hydride (H^-)

$NaH \xrightarrow{H_2O} NaOH + H_2\uparrow$

$CaH_2 \xrightarrow{2H_2O} Ca(OH)_2 + 2H_2\uparrow$

(**Hint:** $Na^+H^- \xrightarrow{H^+OH^-} NaOH + H_2\uparrow$)

3. Silicide (Si^{4-})

$Ca_2Si \xrightarrow{4H_2O} 2Ca(OH)_2 + SiH_4 \xrightarrow{4H_2O} Si(OH)_4 + 4H_2\uparrow$ (**Hint:** $2Ca^{2+}Si^{4-} \xrightarrow{4H^+OH^-} 2Ca(OH)_2 + SiH_4$)

4. Borides (B^{3-})

$Ca_3B_2 \xrightarrow{6H_2O} 3Ca(OH)_2 + 2BH_3$ (**Hint:** $3Ca^{2+}.2B^{3-} \xrightarrow{6H^+OH^-} 3Ca(OH)_2 + 2BH_3$)

$Mg_3B_2 \xrightarrow{6H_2O} 3Mg(OH)_2 + 2BH_3$

5. Nitrides (N^{3-})

$Li_3N \xrightarrow{3H_2O} 3LiOH + NH_3$ (**Hint:** $3Li^+N^{3-} \xrightarrow{3H^+OH^-} 3LiOH + NH_3$)

$Mg_3N_2 \xrightarrow{6H_2O} 3Mg(OH)_2 + 2NH_3$

6. Phosphide (P^{3-})

$Ca_3P_2 \xrightarrow{6H_2O} 3Ca(OH)_2 + 2PH_3$

7. Carbide

$CaC_2 \xrightarrow{2H_2O} C_2H_2\uparrow + Ca(OH)_2$ (Hint: $Ca^{2+}C_2^{2-} \xrightarrow{2H^+OH^-} C_2H_2 + Ca(OH)_2$)

8. Hydrolysis of Halides

$\overset{+3}{P}Cl_3 + 3H_2O \longrightarrow H_3\overset{+3}{P}O_3 + 3HCl$

$\overset{+5}{P}Cl_5 + H_2O \xrightarrow[-2HCl]{} POCl_3 \xrightarrow[-3HCl]{3H_2O} H_3\overset{+5}{P}O_4$

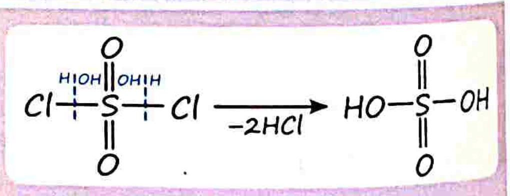
Phosphoryl Chloride
(Phosphorus Oxy Chloride)

Note

PCl_3 hydrolyses in the presence of moisture giving fumes of HCl.

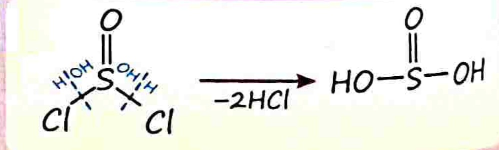
$\overset{+6}{S}O_2Cl_2 + 2H_2O \xrightarrow[-2HCl]{} H_2\overset{+6}{S}O_4$

Sulphuril Chloride



$\overset{+4}{S}OCl_2 + 2H_2O \xrightarrow[-2HCl]{} H_2\overset{+4}{S}O_3$

Thionyl Chloride



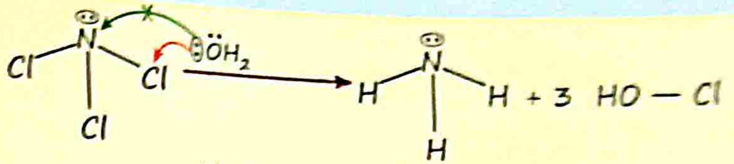
Hydrolysis of Group-15 Halides

$NCl_3 \xrightarrow{3H_2O} NH_3 + 3HOCl$

$PCl_3 \xrightarrow{3H_2O} H_3PO_3 + 3HCl$

$AsCl_3 \xrightarrow{3H_2O} As(OH)_3 + 3HCl$

$SbCl_3 \xrightarrow{H_2O} SbOCl + 2HCl$



H_2O attacks on Cl but not on N because Cl has vacant d orbital but N does not.

Partial Hydrolysis: $SbCl_3 \xrightarrow[-2HCl]{H_2O} Sb(OH)_2Cl \xrightarrow{-H_2O} SbOCl$ antimony(III) oxychloride

$BiCl_3 \xrightarrow{H_2O} BiOCl + 2HCl$

Partial Hydrolysis: $BiCl_3 \xrightarrow[-2HCl]{H_2O} Bi(OH)_2Cl \xrightarrow{-H_2O} BiOCl$ bismuth(III) oxychloride

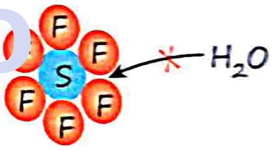
Hydrolysis of Group-16 Halides

$SCl_4 \xrightarrow{3H_2O} H_2SO_3 + 4HCl$

$SF_6 \longrightarrow$ No hydrolysis

$SeF_6 \xrightarrow{4H_2O} H_2SeO_4 + 6HF$
Selenic acid

$TeF_6 \xrightarrow{6H_2O} H_6TeO_6 + 6HF$
Telluric acid



SF_6 is exceptionally stable for steric reasons. So, water can not reach to the sulphur for hydrolysis.

9. Hydrolysis of Halogens

$\overset{\text{Zero}}{F_2} + H_2\overset{-2}{O} \longrightarrow \frac{1}{2}\overset{\text{Zero}}{O_2} + 2H\overset{-1}{F}$
(Oxidising agent)

$Br_2 + H_2O \longrightarrow HBr + HOBr$

$Cl_2 + H_2O \longrightarrow HCl + HOCl$

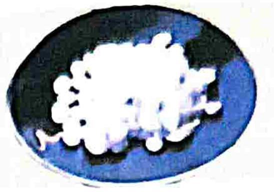
$2I^- + 2H^+ + \frac{1}{2}O_2 \longrightarrow I_2 + H_2O$
(Oxidising agent)

$X\overset{H|OH}{-}X \xrightarrow[X = Cl, Br]{} HX + HOX$

$NaOH_{(aq)}$

Chemical Name: Sodium Hydroxide.
Common name: Caustic Soda.

☐ NaOH is deliquescent in nature.


White translucent solid

$$H_2CO_3 \xrightarrow{2\ NaOH} Na_2CO_3 + 2H_2O$$

$$HNO_3 \xrightarrow{NaOH} NaNO_3 + H_2O$$

$$H_3PO_4 \xrightarrow{3NaOH} Na_3PO_4 + 3H_2O$$

$$H_3PO_2 \xrightarrow{NaOH} NaH_2PO_2 + H_2O$$

$$H_2S_2O_3 \xrightarrow{NaOH} Na_2S_2O_3 + 2H_2O$$

thio-sulphuric acid — Sodium thiosulphate

Deliquescent	Vs Hygroscopic
Ability to absorb so much water that it forms a liquid solution	Ability to absorb water.
NaOH $CaCl_2$ $MgCl_2$	Sugar Na_2CO_3

$$\text{Acidic Oxide} \longrightarrow \text{Acid} \xrightarrow{NaOH} \text{Salt}$$

☐ $CO_2 \xrightarrow{NaOH} Na_2CO_3$

☐ $N_2O_5 \xrightarrow{NaOH} NaNO_3 + H_2O$

☐ $P_2O_5 \xrightarrow{NaOH} Na_3PO_4 + H_2O$

☐ $Cl_2O_7 \xrightarrow{NaOH} NaClO_4$

☐ $SiO_2 \xrightarrow{NaOH} Na_2SiO_3$
Silica — Sodium Silicate

☐ $N_2O_3 \xrightarrow{NaOH} 2\ NaNO_2$

$$CO_2 \xrightarrow{H_2O} H_2CO_3 \xrightarrow{NaOH} Na_2CO_3$$

$$N_2O_5 \xrightarrow{H_2O} HNO_3 \xrightarrow{NaOH} NaNO_3$$

$$P_2O_5 \xrightarrow{H_2O} H_3PO_4 \xrightarrow{NaOH} Na_3PO_4$$

$$Cl_2O_7 \xrightarrow{H_2O} HClO_4 \xrightarrow{NaOH} NaClO_4$$

$$N_2O_3 \xrightarrow{H_2O} 2\ HNO_2 \xrightarrow{NaOH} 2\ NaNO_2$$

Reaction with mixed Anhydride

☐ $NO_2 \xrightarrow{H_2O} HNO_2 + HNO_3 \xrightarrow{NaOH} NaNO_2 + NaNO_3$

☐ $ClO_2 \xrightarrow{H_2O} HClO_2 + HClO_3 \xrightarrow{NaOH} NaClO_2 + CaClO_3$

N_2O is fairly soluble in water and N
is sparingly soluble in water. Both
produces neutral solution in water. S
they both do not react with NaOH

Reaction with amphoteric Oxides

☐ $ZnO + H_2O \longrightarrow$ Base alike formula $Zn(OH)_2$ or Acid alike formula H_2ZnO_2

$$Zn(OH)_2 \xrightarrow[\text{Acid}]{HCl} ZnCl_2$$

$$H_2ZnO_2 \xrightarrow[\text{Base}]{NaOH} Na_2ZnO_2$$

Amphoteric oxide $[MO_y] + H_2O \longrightarrow H_2MO_{y+1} \xrightarrow{NaOH} Na_2MO_{y+1}$

$\overset{+2}{Be}O \xrightarrow{NaOH} Be(OH)_2 \xrightarrow{2NaOH} Na_2[Be(OH)_4] \equiv Na_2BeO_2.2H_2O$ Sodium Beryllate

$\overset{+2}{Zn}O \xrightarrow{NaOH} Zn(OH)_2\downarrow \xrightarrow{NaOH} Na_2[Zn(OH)_4] \equiv Na_2ZnO_2.2H_2O$ Sodium Zincate

$\overset{+2}{Pb}O \xrightarrow{2NaOH} Na_2PbO_2$ Sodium Plumbite

$\overset{+4}{Pb}O_2 \xrightarrow{NaOH} Na_2PbO_3$ Sodium Plumbate

$\overset{+2}{Sn}O \xrightarrow{NaOH} Na_2SnO_2$ Sodium Stannite

$\overset{+4}{Sn}O_2 \xrightarrow{NaOH} Na_2SnO_3$ Sodium Stannate

$Al_2O_3 \xrightarrow{2NaOH} 2NaAlO_2$ Sodium meta-aluminate

$Na_2\,[Pb(OH)_4] \longrightarrow Na_2PbO_2 \cdot 2H_2O$

$Na_2\,[Zn(OH)_4] \longrightarrow Na_2ZnO_2\,.\,2H_2O$

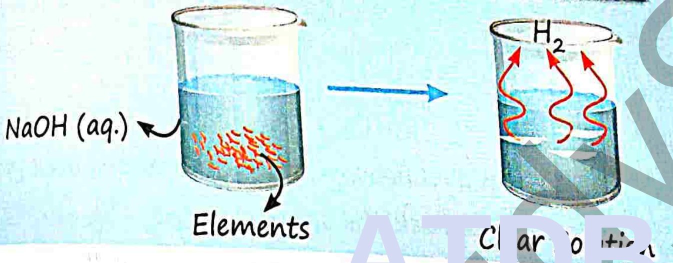
$Na\,[Al(OH)_4] \longrightarrow NaAlO_2\,.\,2H_2O$

$Na_2\,[Be(OH)_4] \longrightarrow Na_2BeO_2\,.\,2H_2O$

☐ Some elements $\xrightarrow{NaOH}$ Soluble complex + $H_2\uparrow$

$[M = Sn, Al, Pb, Zn, B, Si, Be] \xrightarrow{NaOH} Na_x\,M\,O_y + nH_2\uparrow$

$Sn^{4+}, Al^{+3}, Pb^{+2}, Zn^{2+}, B^{3+}, Si^{4+}, Be^{2+}$



Element (M)	Na_xMO_y
Be	Na_2BeO_2
Pb	Na_2PbO_2
Sn	Na_2SnO_2
Si	Na_2SiO_3
Zn	Na_2ZnO_2
B	Na_3BO_3
Al	$NaAlO_2$

देशी जुगाड़ :

Suno	Aliya	Pub	Zana	bhi	sikho	Be
↓	↓	↓	↓	↓	↓	↓
Sn	Al	Pb	Zn	B	Si	Be

Reaction of $NaOH_{(aq)}$ with metal salts

$Cr^{+3} \xrightarrow{3\overset{\ominus}{O}H} Cr(OH)_3\downarrow$ Green $\xrightarrow{OH^-} [Cr(OH)_4]^-$ Soluble

$Fe^{2+} \longrightarrow Fe(OH)_2\downarrow$ Green

$Ni^{2+} \longrightarrow Ni(OH)_2\downarrow$ Green

$Cr^{2+}/Cu^{2+} \longrightarrow Cr(OH)_2\downarrow / Cu(OH)_2\downarrow$ Blue

$Co^{2+}/Mn^{2+} \longrightarrow Co(OH)_2\downarrow / Mn(OH)_2\downarrow$ Pink

$Fe^{3+} \longrightarrow Fe(OH)_3\downarrow$ Brown

☐ Amphoteric hydroxides like $Cr(OH)_3$, $Pb(OH)_2$, $Al(OH)_3$, $Zn(OH)_2$ are soluble in base $NaOH_{(aq.)}$

☐ Basic hydroxides do not react with NaOH, so they are insoluble in $NaOH_{(aq.)}$

☐ Green Crow Fesa Nikalo
Blue CuCr se
Fer Brown munde ne Mn Co Kr diya pink.

☐ Hydroxides of d^{10} system & p-block element
↓
White in colour

$Zn^{+2} \longrightarrow Zn(OH)_2 \downarrow$ White $\xrightarrow{2OH^-} [Zn(OH)_4]^{2-}$ Soluble

$Pb^{2+} \longrightarrow Pb(OH)_2 \downarrow$ White $\xrightarrow{2OH^-} [Pb(OH)_4]^{2-}$ Soluble

$Al^{3+} \longrightarrow Al(OH)_3 \downarrow$ White gelatinous $\xrightarrow{OH^-} [Al(OH)_4]^-$ Soluble

Note

I_2, P_4 and S_8 do not react with water but they give disproportionation reaction with aq. NaOH.

$$\underset{\text{(Oxidising agent)}}{2F_2} \xrightarrow{4NaOH(aq)} O_2 + 4NaF + 2H_2O$$

Hint: $F_2 \xrightarrow{H_2O} \frac{1}{2}O_2 + 2HF \xrightarrow[-2H_2O]{2NaOH} 2NaF + \frac{1}{2}O_2$

$$Cl_2 \xrightarrow[\text{Room Temperature}]{NaOH(aq)} \underset{\text{Sodium Chloride}}{NaCl} + \underset{\text{Sodium hypochlorite}}{NaOCl}$$

$$Cl_2 \xrightarrow[\text{Hot}]{NaOH(aq)} \underset{\text{Sodium Chloride}}{NaCl} + \underset{\text{Sodium Chlorate}}{NaClO_3}$$

Hint:

$$\begin{tikzcd} Cl_2 \arrow[r, "H_2O"] & HCl + HOCl \arrow[r, "\Delta"] \arrow[d, "NaOH"] & HClO_3 + HCl \arrow[d, "NaOH"] \\ & NaCl + NaOCl & NaClO_3 + NaCl \end{tikzcd}$$

$$Br_2 \xrightarrow[\text{Room Temperature}]{NaOH(aq)} NaBr + NaOBr$$

$$Br_2 \xrightarrow[\text{Hot}]{NaOH(aq)} NaBr + NaBrO_3$$

☐ On acidification, the disproportionated product gives back the same element.

$$X^- + OX^- + 2H^+ \longrightarrow X_2 + H_2O$$

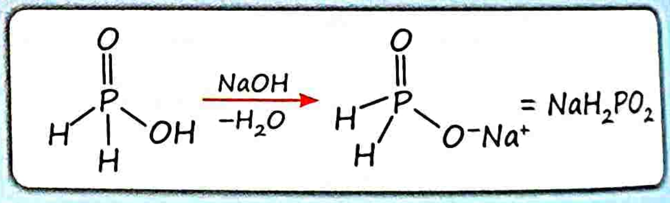
$$5X^- + XO_3^- + 6H^+ \longrightarrow 3X_2 + 3H_2O$$

$[X = Cl, Br, I]$

$$I_2 \xrightarrow[\text{Room Temperature}]{NaOH(aq)} NaI + NaOI$$

$$I_2 \xrightarrow[\text{Hot}]{NaOH(aq)} NaI + NaIO_3$$

$$\overset{\text{(zero)}}{P_4} + 3NaOH + 3H_2O \longrightarrow \underset{\text{Phosphine}}{\overset{(-3)}{PH_3}} + \underset{\text{Sodium hypophosphite}}{\overset{(+1)}{3NaH_2PO_2}}$$



$= NaH_2PO_2$

$$\overset{\text{(zero)}}{S_8} \xrightarrow{12NaOH} \overset{(-2)}{4Na_2S} + \underset{\text{Sodium thiosulphate}}{\overset{(+2)}{2Na_2S_2O_3}} + 6H_2O$$

Note

With dry slaked lime, it gives bleaching powder.

$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$

(IIT JEE 1999)

33. One mole of calcium phosphide on reaction with excess water gives
(a) one mole of phosphine
(b) two moles of phosphoric acid
(c) two moles of phosphine
(d) one mole of phosphorus pentoxide

Sol. (c) $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

34. Chlorine on reaction with hot and concentrated sodium hydroxide gives: [12 Jan, 2019 (Shift-II)]
(a) Cl^- and ClO_3^-
(b) Cl^- and ClO^-
(c) ClO_3^- and ClO_2^-
(d) Cl^- and ClO_2^-

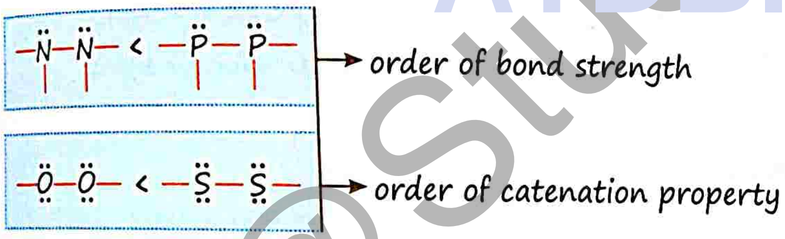
Sol. (a) $6NaOH + Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$

35. Among the following, the number of halide(s) which is / are inert to hydrolysis is ___. [25 Feb, 2021 (Shift-I)]
(a) BF_3
(b) $SiCl_4$
(c) PCl_5
(d) SF_6

Sol. [1] Due to presence of steric crowding, SF_6 does not undergo hydrolysis.

CATENATION PROPERTY

- ☐ Self linking property of an element is known as catenation property.
- ☐ Single bond formation tendency ∝ single bond strength.
- ☐ Single bond formation tendency : Catenation property ↑



The single N – N bond is weaker than the single P – P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result, the catenation tendency is weaker in nitrogen.

(a) H — F (b) H — Cl (c) H — Br (d) H — I

Bond length:	a < b < c < d
Bond strength:	a > b > c > d
Bond dissociation energy:	a > b > c > d
Acidic strength: (H⁺ ion donation tendency)	a < b < c < d
Boiling point:	b < c < d < a

(a) NH_3 (Ammonia) (b) PH_3 (Phosphine) (c) AsH_3 (Arsine) (d) SbH_3 (Stibine) (e) BiH_3 (Bismuthine)

Bond length: $a < b < c < d < e$

Bond strength: $a > b > c > d > e$

Bond dissociation energy: $a > b > c > d > e$

Basic strength: $a > b > c > d > e$ (lone pair donation from NH_3 is easy)

Reducing power: $a < b < c < d < e$ ($H^{\oplus}$ ion donation is easy with weak bond)

Boiling point: $b < c < a < d < e$

(a) H_2O (b) H_2S (c) H_2Se (d) H_2Te

Bond length: $a < b < c < d$

Bond strength: $a > b > c > d$

Bond dissociation energy: $a > b > c > d$

Acidic strength: $a < b < c < d$

Reducing power: $a < b < c < d$

Boiling point: $b < c < d < a$

36. Choose the correct statements about the hydrides of group 15 elements. [30 Jan, 2024 (Shift-II)]

A. The stability of the hydrides decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

B. The reducing ability of the hydride increases in the order $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

C. Among the hydrides, NH_3 is strong reducing agent while BiH_3 is mild reducing agent.

D. The basicity of the hydrides increases in the order $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

Choose the most appropriate from the option given below:

(a) B and C only (b) C and D only (c) A and B only (d) A and D only

Sol. (c)

REDOX REACTIONS IN THE p-BLOCK ELEMENTS

Oxidation

	Reactant	Oxidised Product		Reactant	Oxidised Product		Reactant	Oxidised Product
1.	Fe^{+2}	Fe^{+3}	7.	CO	CO_2	13.	HNO_2	HNO_3
2.	Cl^-	Cl_2	8.	H_3PO_3	H_3PO_4	14.	H_2O	O_2
3.	Br^-	Br_2	9.	H_2S	S	15.	NO	NO_2

4.	I^-	I_2	10.	Sn^{+2}	Sn^{+4}	16.	H_2SO_3	H_2SO_4
5.	NH_3	N_2	11.	$H_2C_2O_4$	CO_2	17.	S/S^{2-}	SO_2
6.	H_2O_2	O_2	12.	SO_2	SO_3/SO_4^{2-}	18.	$K_4[Fe(CN)_6]$	$K_3[Fe(CN)_6]$

Reduction

	Reactant	Reduced Product		Reactant	Reduced Product		Reactant	Reduced Product
1.	F_2	F^-	8.	Pb^{+4}	Pb^{+2}	15.	$K_2Cr_2O_7/H^+$	Cr^{+3}
2.	Br_2	Br^-	9.	Bi^{+5}	Bi^{+3}	16.	Fe^{+3}	Fe^{+2}
3.	Cl_2	Cl^-	10.	Cu^{+2}	Cu^{+1}	17.	HNO_3 (conc.)	NO_2
4.	I_2	I^-	11.	$CaOCl_2$	$CaCl_2$	18.	HNO_3 (dil.)	NO/N_2O
5.	O_3	O_2/O^{2-}	12.	Ag^+	Ag	19.	HNO_2	NO
6.	H_2O_2	H_2O	13.	Hg^{+2}	Hg_2^{+2}	20.	$KMnO_4$	$\xrightarrow{H^+} Mn^{2+}$ $\xrightarrow{\text{Neutral}} MnO_2$ $\xrightarrow{\text{Base}} MnO_4^{2-}$
7.	MnO_2	Mn^{2+}	14.	Hg_2^{+2}	Hg			

Sequential reduction: $\overset{+5}{HNO_3} \longrightarrow \overset{+4}{NO_2} \longrightarrow \overset{+2}{NO} \longrightarrow \overset{+1}{N_2O} \longrightarrow \overset{\text{Zero}}{N_2} \longrightarrow \overset{-3}{NH_3}$

$\overset{-2}{H_2S} \longrightarrow \overset{\text{Zero}}{S} \longrightarrow \overset{+4}{SO_2} \longrightarrow \overset{+6}{SO_4^{2-}}/\overset{+6}{SO_3}$

SRP Value and Oxidising Power

- ☐ Oxidising power: $F_2 > Cl_2 > Br_2 > I_2$

	F_2	Cl_2	Br_2	I_2
+ve E° value	2.87	1.36	1.09	0.54

- ☐ Three factors are responsible for E° order

(i) Bond dissociation energy

(ii) Electron gain enthalpy

(iii) Hydration energy

Oxidising & Reducing Agent

- ☐ $\underset{\text{(Strong oxidising agent)}}{F_2} + 2Cl^- \longrightarrow 2F^- + \underset{\text{(Weak oxidising agent)}}{Cl_2\uparrow}$

- ☐ Reactant having more oxidising power should be at reactant side and weak oxidising agent should be at product side.

$$\text{Strong oxidising agent} \xrightarrow{\text{Feasible}} \text{Weak oxidising agent}$$

F_2 as oxidising agent	Cl_2 as oxidising agent	Br_2 as oxidising agent
$F_2 + 2Cl^- \longrightarrow Cl_2 + 2F^-$	$Cl_2 + 2Br^- \longrightarrow Br_2 + 2Cl^-$	$Br_2 + 2I^- \longrightarrow I_2 + 2Br^-$
$F_2 + 2Br^- \longrightarrow Br_2 + 2F^-$	$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$	
$F_2 + 2I^- \longrightarrow I_2 + 2F^-$		

Oxidising Agent	Reducing Agent
☐ Elements with maximum oxidation state.	☐ Metals & Elements with lower or minimum oxidation state.
☐ Conc. H_2SO_4, Conc. HNO_3, Conc. HIO_3	☐ Na, Li, Al, Mg etc.
☐ Pb^{4+}, Fe^{3+}, Bi^{5+}, Cu^{2+}	☐ HI, SO_2, Fe^{2+}

Oxidising Power

Strong oxidising agent ⟶ F_2, O_3, $CaOCl_2$, $S_2O_8{}^{2-}$, $KMnO_4/H^+$, H_2O_2/H^+, MnO_2, $K_2Cr_2O_7/H^+$

Moderate oxidising agent ⟶ Cl_2, HIO_3, H_2SO_4

Weak oxidising agent ⟶ Br_2, HNO_2

Weakest oxidising agent ⟶ I_2

Note

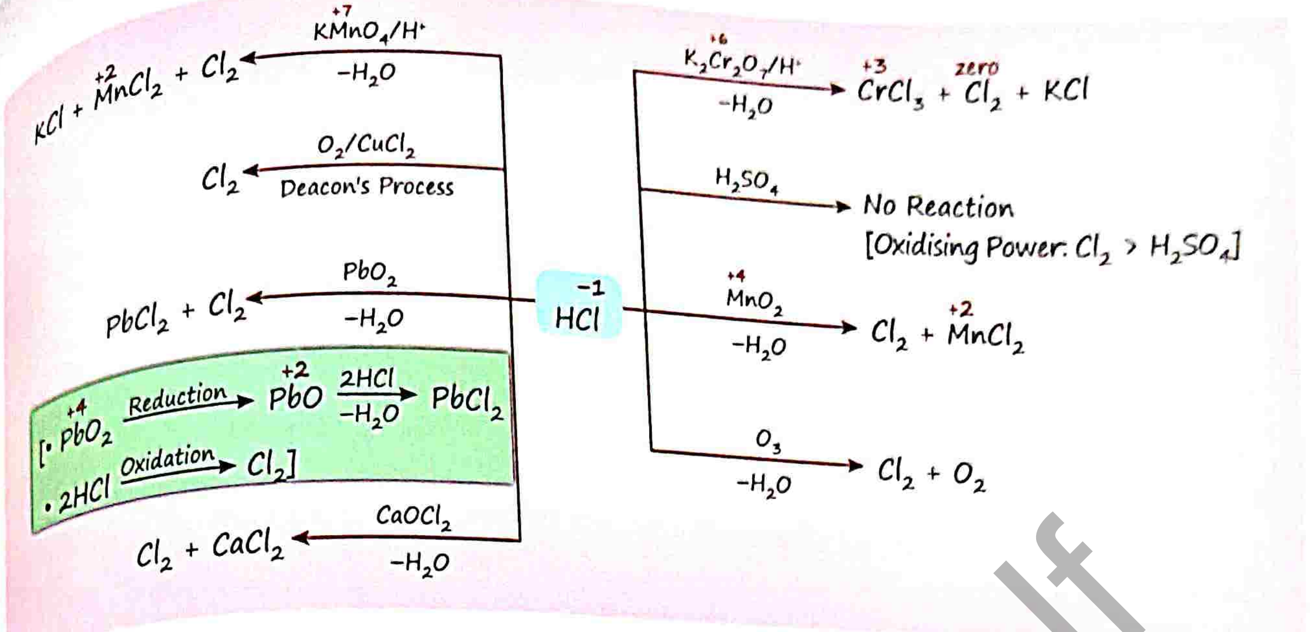
Some metal ions (Bi^{+5}, Pb^{+4}) are strong oxidising agent and some ions (Fe^{3+}, Cu^{2+}) are weak oxidising agent.

- ☐ $Mn^{2+} + PbO_2$ (excess) $\longrightarrow KMnO_4$
- ☐ $Mn^{2+} + BiO_3^-$ (excess) $\longrightarrow KMnO_4$
- ☐ $Mn^{2+} + S_2O_8^{2-}$ (excess) $\longrightarrow KMnO_4$
- ☐ $Pb^{+4} + 2I^- \longrightarrow I_2 + Pb^{+2}$
- ☐ $Fe^{+3} + 2I^- \longrightarrow I_2 + Fe^{+2}$
- ☐ $2Cu^{+2} + 2I^- \longrightarrow I_2 + 2Cu^{+1}$

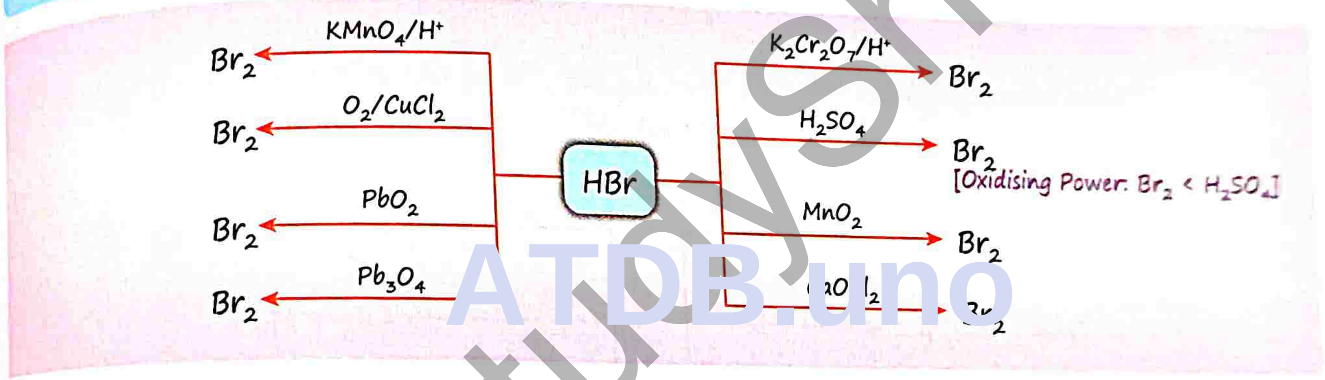
Due to oxidising nature of Pb^{4+}, Fe^{+3}, Cu^{2+} ions PbI_4, FeI_3 and CuI_2 do not exist.

Flow Chart Method for Reactions ⟶ Great Method for Product Prediction

$$\overset{-1}{HCl} \xrightarrow[\text{Agent}]{\text{Oxidising}} \overset{\text{Zero}}{Cl_2}$$ ⟶ Oxidising agents having more oxidising power than Cl_2, can oxidise HCl into Cl_2 gas.



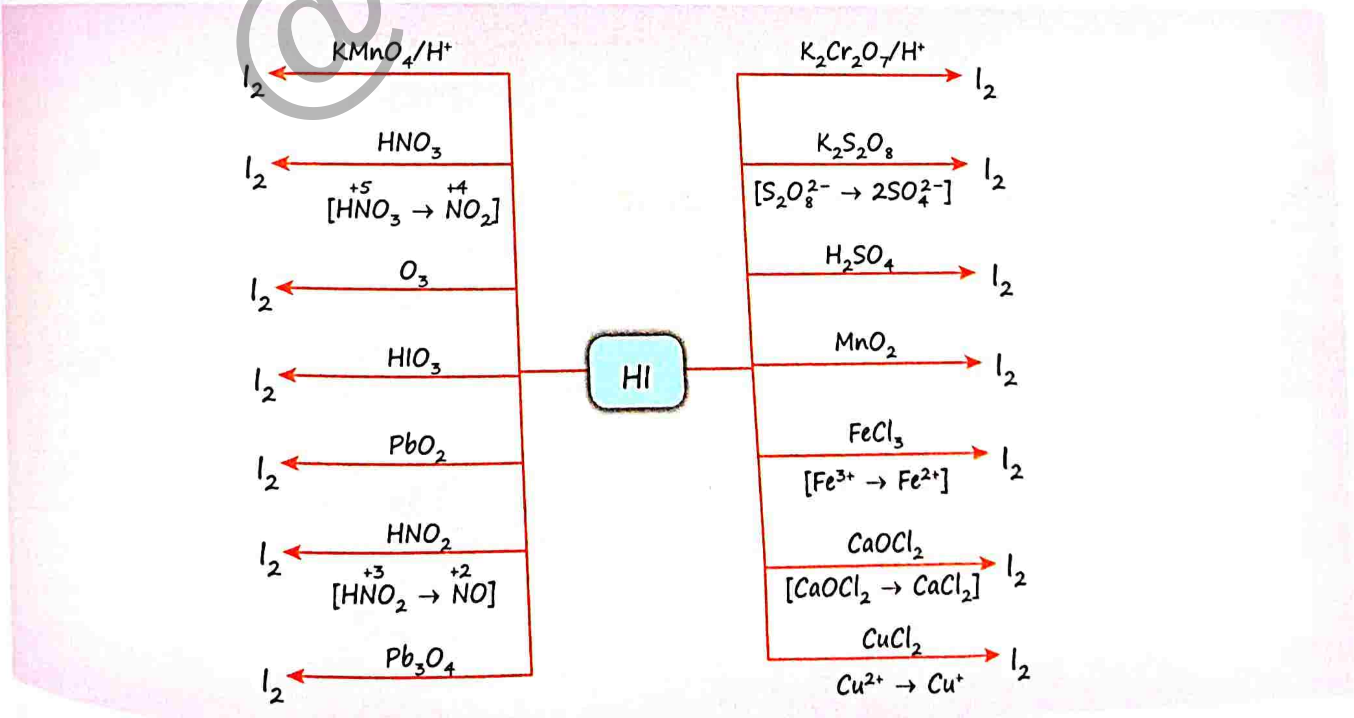
$\overset{-1}{HBr} \xrightarrow[\text{Agent}]{\text{Oxidising}} \overset{\text{Zero}}{Br_2}$ → Oxidising agents having more oxidising power than Br_2, can oxidise HBr into Br_2 (liquid).

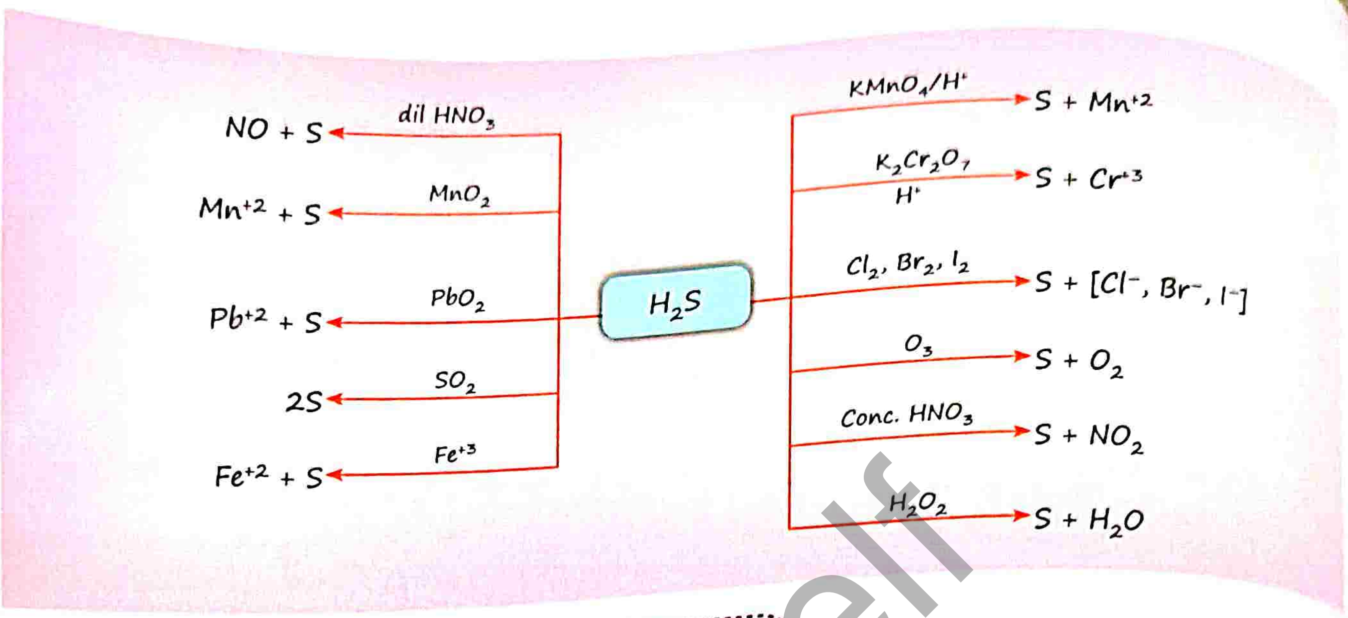


$\overset{-1}{HI} \xrightarrow[\text{Agent}]{\text{Oxidising}} \overset{\text{Zero}}{I_2}$

→ Oxidising agents having more oxidising power than I_2, can oxidise HI into I_2.

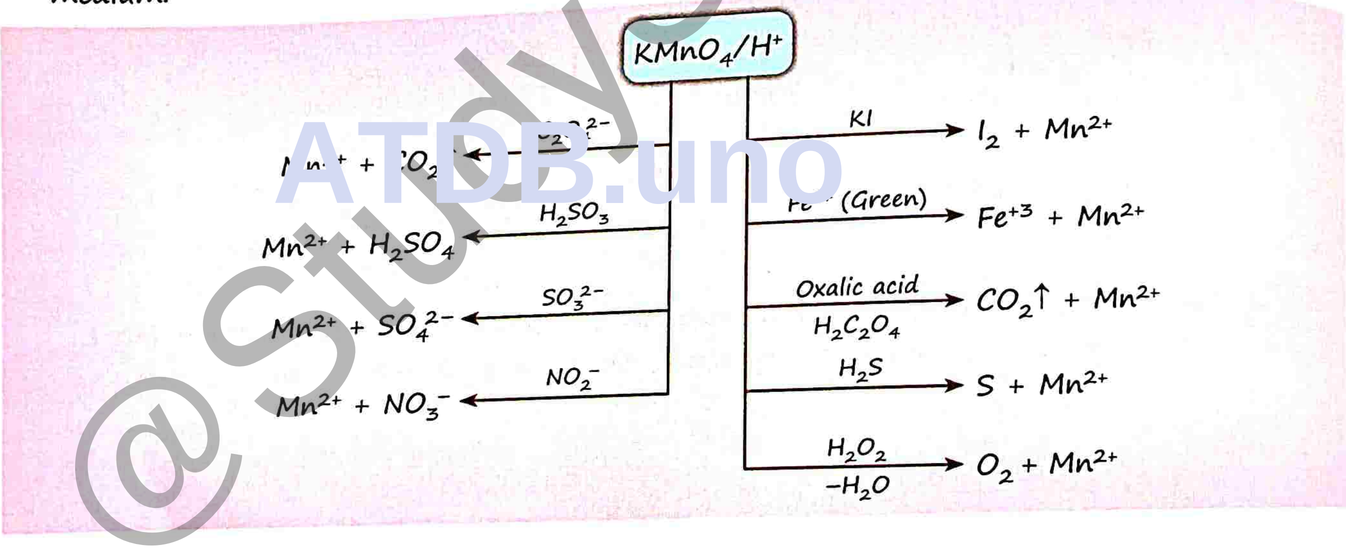
→ HI is a strong reducing agnet, can reduce maximum number of oxidising agent.





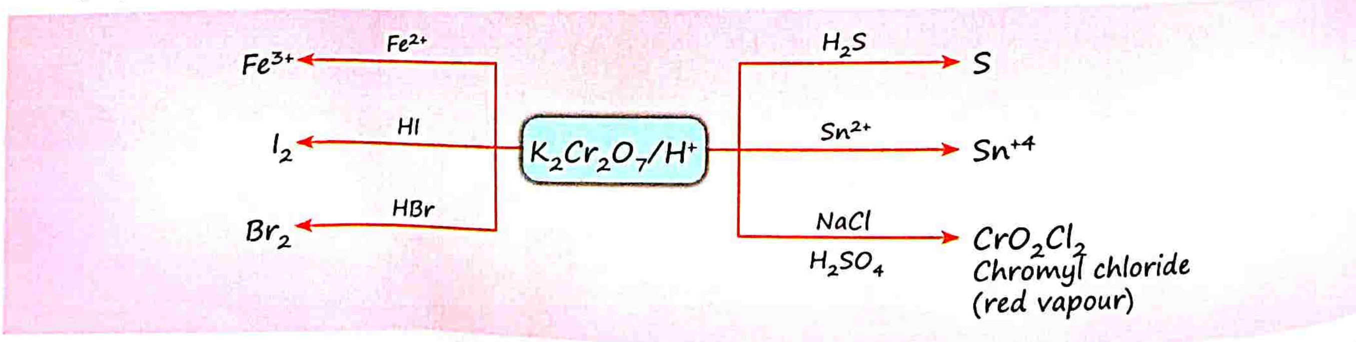
$KMnO_4$ with Acid as Oxidising Agent

- ☐ $KMnO_4$ is a strong oxidising agent, during reaction it reduces itself from Mn^{+7} to Mn^{+2} in acidic medium.



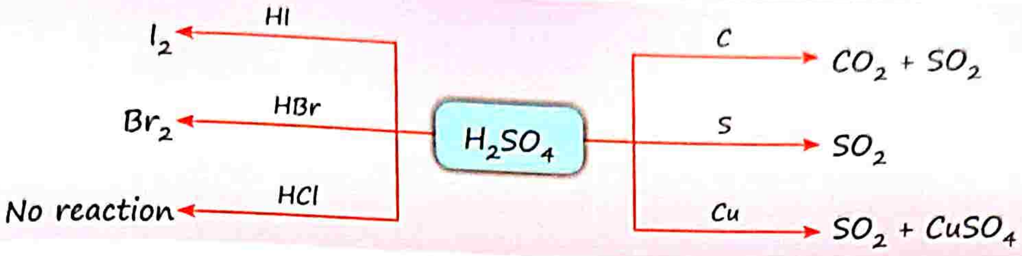
$K_2Cr_2O_7$ with Acid as Oxidising Agent

- ☐ $K_2Cr_2O_7$ with acid is a strong oxidising agent, during reaction it reduces itself from Cr^{+6} to Cr^{+3}.



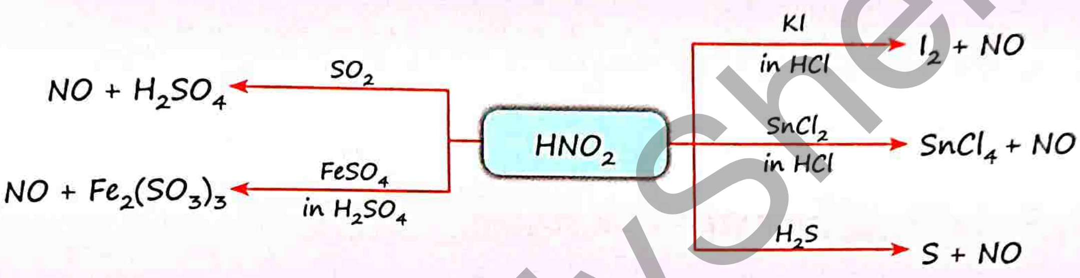
H_2SO_4 as Oxidising Agent

$$H_2SO_4 \xrightarrow[-H_2O]{} SO_2 + \frac{1}{2} O_2$$



HNO_2

- $2HNO_2 \xrightarrow[-H_2O]{} 2NO + \text{[O]} \longrightarrow$ Nascent oxygen is responsible for oxidising nature of HNO_2.



Chlorine as Oxidising Agent

- $2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow 2HCl + Fe_2(SO_4)_3$

  [Hint: $Fe^{2+} + Cl_2 \longrightarrow Fe^{3+} + 2Cl^-$]
- $Na_2SO_3 + Cl_2 + H_2O \longrightarrow 2HCl + Na_2SO_4$

  [Hint: $SO_3^{2-} + Cl_2 \longrightarrow SO_4^{2-} + 2Cl^-$]
- $SO_2 + 2H_2O + Cl_2 \longrightarrow 2HCl + H_2SO_4$

  [Hint: $SO_2 + H_2O \longrightarrow H_2SO_3$; $H_2SO_3 + Cl_2 \longrightarrow H_2SO_4 + 2Cl^-$]
- $I_2 + 6H_2O + 5Cl_2 \longrightarrow 10HCl + 2HIO_3$

GROUP-15 ELEMENTS

NITROGEN ($_7N$), PHOSPHORUS ($_{15}P$), ARSENIC ($_{33}As$), ANTIMONY ($_{51}Sb$), BISMUTH ($_{83}Bi$)

Oxidation States and Trends in Chemical Reactivity

- Group 15 elements commonly have oxidation states of −3, +3, and +5.
- The tendency to show a −3 oxidation state decreases as you move down the group because the atoms get larger and more metallic. For example, bismuth, the last element in the group, rarely forms compounds with a −3 oxidation state.

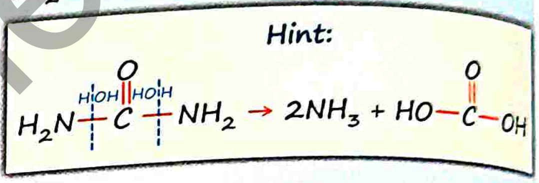
- ☐ The stability of the +5 oxidation state also decreases down the group. Bismuth's only well-known +5 compound is BiF_5.
- ☐ As you go down the group, the +5 oxidation state becomes less stable, while the +3 oxidation state becomes more stable due to the "inert pair effect."
- ☐ Nitrogen can also have +1, +2, and +4 oxidation states when it reacts with oxygen, and phosphorus can show +1 and +4 oxidation states in some oxoacids.

AMMONIA NH_3

Preparation Methods

- ☐ Urea + Water $\longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2\uparrow$

  $NH_2CONH_2 \xrightarrow{2H_2O} 2NH_3\uparrow + H_2O + CO_2\uparrow$


Hint:

$$H_2N \overset{H\,OH}{\vdots} \overset{O}{\overset{\|}{C}} \overset{HO\,H}{\vdots} NH_2 \rightarrow 2NH_3 + HO-\overset{O}{\overset{\|}{C}}-OH$$

- ☐ $2NH_4Cl + Ca(OH)_2 \xrightarrow[-2H_2O]{} 2NH_3\uparrow + CaCl_2$
- ☐ $(NH_4)_2SO_4 + 2NaOH \xrightarrow[-2H_2O]{Heat} 2NH_3\uparrow + Na_2SO_4$
- ☐ **Haber's process** $N_2 + 3H_2 \xrightarrow[Mo\ [Promoter]]{Fe\ [Catalyst]} 2NH_3\uparrow$

From nitrate and nitrite-

- ☐ $Na\overset{+3}{N}O_2$ or $Na\overset{+5}{N}O_3 \xrightarrow[H_2+Na_2ZnO_2]{\boxed{Zn/NaOH}} \overset{-3}{N}H_3$
- ☐ $Na\overset{+3}{N}O_2$ or $Na\overset{+5}{N}O_3 \xrightarrow[H_2+NaAlO_2]{\boxed{Al/NaOH}} \overset{-3}{N}H_3$

  → H_2 gas is responsible for reduction of NO_2^- or NO_3^- to NH_3.

Reactions of NH_3

NH_3 acts as base.

(i) $\ddot{N}H_3 + HCl \longrightarrow NH_4Cl$

(ii) $2\ddot{N}H_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

(iii) $\ddot{N}H_3 + H_2O \longrightarrow NH_4OH$ (Aq. Ammonia means ammonium hydroxide).

Aq. NH_3 forms ammonium salts with acids. As a weak base, it precipitates the hydroxides or hydrated oxides.

- ☐ $2NH_4OH + ZnSO_4 \longrightarrow \underset{\text{white ppt}}{Zn(OH)_2\downarrow} + (NH_4)_2SO_4$
- ☐ $3NH_4OH + FeCl_3 \longrightarrow Fe(OH)_3$ (Brown ppt, $Fe_2O_3.xH_2O$) + $3NH_4Cl$

Detection of d block metal ions

The presence of a lone pair of electrons on the nitrogen atom of the ammonia molecule makes it a Lewis base. It donates the electron pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of d block metal ions.

(i) $Cu^{2+}_{(aq.)} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$ Deep blue

(ii) $Ag^{+}_{(aq.)} + Cl^{-} \longrightarrow AgCl\downarrow$ white ppt

$AgCl_{(s)} + 2NH_3 \longrightarrow [Ag(NH_3)_2]Cl$ Soluble in water

37. Urea reacts with water to form A which will decompose to form B. B when passed through Cu^{2+} (aq), deep blue colour solution C is formed. What is the formula of C from the following? [NEET 2020]

(a) $[Cu(NH_3)_4]^{2+}$ (b) $Cu(OH)_2$

(c) $CuCO_3.Cu(OH)_2$ (d) $CuSO_4$

Sol. (a)

Conc. HNO_3 as a Oxidising Agent

☐ HNO_3 + Non metals $\xrightarrow[-H_2O]{}$ –ic acid + NO_2 (Brown colour)

$48\ HNO_3 + S_8 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$

$10\ HNO_3 + I_2 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

$20\ HNO_3 + P_4 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

$4\ HNO_3 + C \xrightarrow[-H_2O]{} 4NO_2 + H_2CO_3 \longrightarrow H_2O + CO_2$

☐ $\underset{\text{(Metal)}}{M} + \underset{(70\%)}{\text{Conc. } HNO_3} \xrightarrow[-H_2O]{} M(NO_3)_y + NO_2$ (Brown)

$Zn + 4HNO_3(conc.) \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$

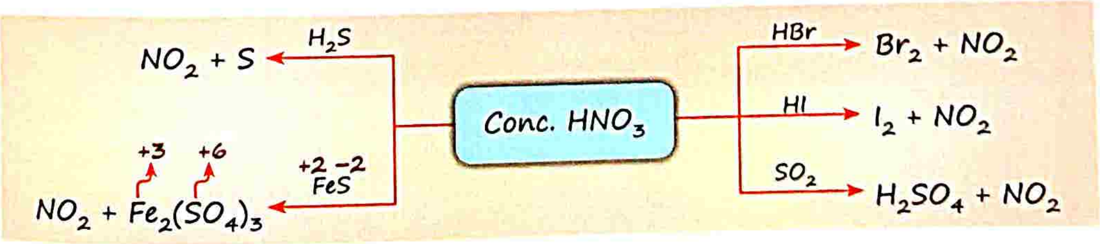
$Cu + 4HNO_3(conc.) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

☐ $\underset{\text{(Metal)}}{M} + \underset{(20\%)}{\text{dil. } HNO_3} \xrightarrow[-H_2O]{} M(NO_3)_y + N_2O/NO$

$4Zn + 10HNO_3(dil.) \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$ [Same type of reaction with Fe]

$3Cu + 8HNO_3(dil.) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$ [Same type of reaction with Pb, Cu, Ag, Hg]

☐ Noble Metals Au, Pt : Do not dissolve in HNO_3



☐ Some metals do not dissolve in concentrated HNO_3 because of the formation of a passive film of oxide on the surface.

For example → Fe, Cr, Co, Ni, Al, Be

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Aqua Regia

Au, Pt : Do not dissolve in HNO_3

$\overset{+3}{N}O\overset{-1}{Cl} \longrightarrow \overset{+2}{N}O \uparrow + \overset{Zero}{[Cl]}$

Aqua Regia → 3HCl + 1 HNO_3

$$H\overset{+5}{N}O_3 + 3H\overset{-1}{Cl} \xrightarrow[-2H_2O]{} \underset{\text{(nitrosyl chloride)}}{\overset{+3}{N}OCl} + \underbrace{\overset{\text{(zero)}}{2\,[Cl]}}_{} \rightarrow \text{Nascent chlorine}$$

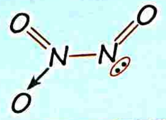
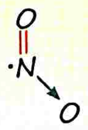
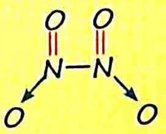
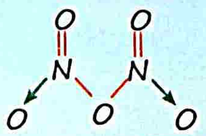
1. $Au + 3[Cl] \longrightarrow \overset{+3}{Au}Cl_3$

   $AuCl_3 + \overset{+}{H}Cl^-_{(aq.)} \longrightarrow \underset{\text{(Soluble)}}{H^+ AuCl_4^-}$ Chloro-auric acid

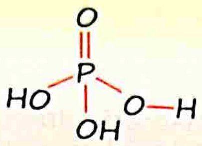
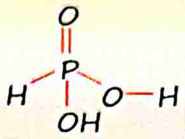
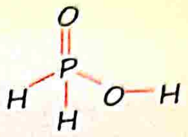
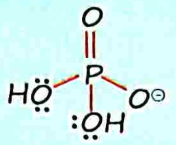
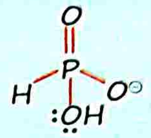
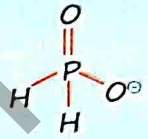
2. $Pt + 4[Cl] \longrightarrow PtCl_4$

   $PtCl_4 + 2HCl_{(aq.)} \longrightarrow \underset{\text{(Soluble)}}{H_2\,PtCl_6} \equiv 2H^+\,[PtCl_6]^{2-}$ Chloro-platinic acid

OXIDES OF NITROGEN

Formula	Oxidation State	Structure	Physical / Chemical Properties
N_2O **Nitrous oxide**	+1	$N \equiv N \rightarrow O$ $N \equiv \overset{+}{N}-\overset{-}{O} \leftrightarrow \overset{-}{N}=\overset{+}{N}=O$	• Gas • Neutral oxide
NO **Nitric oxide**	+2	$:N = \ddot{\underset{\cdot}{O}}: \leftrightarrow :\dot{N} = \ddot{O}:$	• Gas • Neutral oxide
N_2O_3 **Dinitrogen trioxide**	+3		Blue solid/liquid N_2O_3 (Solid) : $NO^+NO_2^-$
NO_2 **Nitrogen dioxide**	+4		Brown gas/paramagnetic nature
N_2O_4 **Dinitrogen Tetraoxide**	+4		Colorless/diamagnetic nature
N_2O_5 **Nitric Anhydride**	+5		• Gas (covalent molecule) • Solid (Ionic compound) N_2O_5(Solid) $\longrightarrow NO_2^+NO_3^-$

Reducing Properties of Oxoacids of Phosphorus

			
☐ No. of replacable H^+	$3H^+$ (Tribasic Acid)	$2H^+$ (Dibasic Acid)	$1H^+$ (Monobasic Acid)
☐ Stability of Conjugate Base (order is based on the effect of cross-conjugation)	 <	 <	
☐ Order of acidic nature	H_3PO_4 <	H_3PO_3 <	H_3PO_2
☐ No. of P—H bond	Zero	One	Two

☐ Reducing property is directly proportional to number of P—H bonds. So, H_3PO_2 is a better reducing agent than H_3PO_3.

38. The order of the oxidation state of the phosphorus atom in H_3PO_2, H_3PO_4, H_3PO_3 and $H_4P_2O_6$ is (JEE Adv. 2017)

(a) $H_3PO_4 > H_3PO_2 > H_3PO_3 > H_4P_2O_6$

(b) $H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$

(c) $H_3PO_2 > H_3PO_3 > H_4P_2O_6 > H_3PO_4$

(d) $H_3PO_3 > H_3PO_2 > H_3PO_4 > H_4P_2O_6$

Sol. (b) $H_3PO_2 \rightarrow +1$, $H_3PO_4 \rightarrow +5$, $H_3PO_3 \rightarrow +3$, $H_4P_2O_6 \rightarrow +4$

39. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen? (IIT JEE 2012)

(a) HNO_3, NO, NH_4Cl, N_2

(b) HNO_3, NO, N_2, NH_4Cl

(c) HNO_3, NH_4Cl, NO, N_2

(d) NO, HNO_3, NH_4Cl, N_2

Sol. (b) $HNO_3 \rightarrow +5$, $NO \rightarrow +2$, $N_2 \rightarrow 0$, $NH_4Cl \rightarrow -3$

40. For H_3PO_3 and H_3PO_4, the correct choice is (IIT JEE 2003)

(a) H_3PO_3 is dibasic and reducing

(b) H_3PO_3 is dibasic and non-reducing

(c) H_3PO_4 is tribasic and reducing

(d) H_3PO_3 is tribasic and non-reducing

Sol. (a)

GROUP-16 ELEMENTS

OXYGEN ($_8O$), SULPHUR ($_{16}S$), SELENIUM ($_{34}Se$), TELLURIUM ($_{52}Te$), POLONIUM ($_{84}Po$)

Oxidation States and Trends in Chemical Reactivity

- The stability of the –2 oxidation state decreases as you go down the group in the periodic table. For example, polonium rarely shows a –2 oxidation state.
- Oxygen, due to its high electronegativity, usually has a –2 oxidation state, except in the compound OF_2, where it has a +2 oxidation state.
- The other elements in the group like S, Se and Te can have oxidation states of +2, +4, and +6, but +4 and +6 are more common.
- In compounds with oxygen, these elements typically have a +4 oxidation state, and in compounds with fluorine, they usually have a +6 oxidation state.
- As you move down the group, the +6 oxidation state becomes less stable, while the +4 oxidation state becomes more stable. This is due to the "inert pair effect," which makes the lower oxidation states more stable in heavier elements.
- The bonding in the +4 and +6 oxidation states is mainly covalent.

DIOXYGEN O_2

Preparation

- By Heating:

$$K\overset{+7}{Cl}O_4 \xrightarrow{\Delta} K\overset{-1}{Cl} + 2O_2\uparrow$$

$$2K\overset{+5}{Cl}O_3 \xrightarrow[\Delta]{MnO_2} 2K\overset{-1}{Cl} + 3O_2\uparrow$$

$$2K\overset{+7}{Mn}O_4 \xrightarrow{\Delta} K_2\overset{+6}{Mn}O_4 + \overset{+4}{Mn}O_2 + O_2\uparrow$$

$$2K_2\overset{+6}{Cr_2}O_7 \xrightarrow{\Delta} 2K_2\overset{+6}{Cr}O_4 + \overset{+3}{Cr_2}O_3 + \frac{3}{2}O_2\uparrow$$

- Decomposition of H_2O_2

$$2H_2O_{2(aq.)} \xrightarrow{Catalyst} 2H_2O + O_2\uparrow$$

- By the thermal decomposition of the oxides of metals:

$$Ag_2O_{(s)} \xrightarrow{\Delta} 2\ Ag + \frac{1}{2}O_2\uparrow$$

$$HgO_{(s)} \xrightarrow{\Delta} Hg + \frac{1}{2}O_2\uparrow$$

$$\overset{+4}{Pb}O_{2(s)} \xrightarrow{\Delta} \overset{+2}{Pb}O + \frac{1}{2}O_2\uparrow$$

GROUP-17 ELEMENTS

FLUORINE ($_9F$), CHLORINE ($_{17}Cl$), BROMINE ($_{35}Br$), IODINE ($_{53}I$), ASTATINE ($_{85}At$)

Oxidation States

- All the halogens exhibit −1 oxidation state. However, chlorine, bromine and iodine exhibit +1, +3, +5 and +7 oxidation states.
- It can be explained as below for halogen atoms other than fluorine:

	ns	np	nd	
Halogen atom in ground state	↑↓	↑↓ ↑↓ ↑	☐ ☐ ☐ ☐ ☐	1 unpaired electron accounts for −1 or +1 oxidation states
First excited state	↑↓	↑↓ ↑ ↑	↑ ☐ ☐ ☐ ☐	3 unpaired electron accounts for +3 oxidation states
Second excited state	↑↓	↑ ↑ ↑	↑ ↑ ☐ ☐ ☐	5 unpaired electron accounts for +5 oxidation states
Third excited state	↑	↑ ↑ ↑	↑ ↑ ↑ ☐ ☐	7 unpaired electron accounts for +7 oxidation states

- The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only -1 oxidation state.

INTERHALOGEN COMPOUNDS

Compounds having 2 different halogens are called interhalogen compounds.

Hydrolysis of Interhalogen Compounds

$$\overset{+1\,-1}{ICl} \xrightarrow{H_2O} \overset{-1}{HCl} + \overset{+1}{HOI}$$

$$\overset{+3\,-1}{ClF_3} \xrightarrow{2H_2O} \overset{+3}{HClO_2} + \overset{-1}{3HF}$$

$$\overset{+5\,-1}{IF_5} \xrightarrow{3H_2O} \overset{+5}{HIO_3} + \overset{-1}{5HF}$$

$$\overset{+7\,-1}{IF_7} \xrightarrow{4H_2O} \overset{+7}{HIO_4} + \overset{-1}{7HF}$$

These compounds undergo hydrolysis giving halide ion derived from the smaller halogen and an anion derived from larger halogen such as−

(i) hypohalite (when AB)

(ii) halite (when AB_3)

(iii) halate (when AB_5)

(iv) perhalate (when AB_7)

GROUP-18 ELEMENTS

HELIUM ($_2$He), NEON ($_{10}$Ne), ARGON ($_{18}$Ar), KRYPTON ($_{36}$Kr), XENON ($_{54}$Xe), RADON ($_{86}$Rn)

- ☐ Group 18 consists of six elements: helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn).
- ☐ All these are gases and chemically unreactive. Because of this, they are termed noble gases.
- ☐ All the noble gases except radon occur in atmosphere.
- ☐ Most abundant element from group 18 in air is Ar.

Physical Properties

- ☐ All the noble gases are monoatomic.
- ☐ They are colourless, odourless and tasteless.
- ☐ They are sparingly soluble in water.
- ☐ They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces.
- ☐ Helium has the lowest boiling point (4.2 K) of any known substance.
- ☐ Helium has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

Chemical Properties

Noble gases are least reactive because–

(i) The noble gases except helium ($1s^2$) have completely filled $ns^2\ np^6$ electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

Interesting discovery of the reactivity of noble gases–

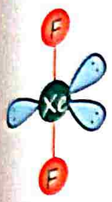
Neil Bartlett at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as $O_2^+\ PtF_6^-$. He, then realised that the first ionisation enthalpy of molecular oxygen (1175 kJmol^{-1}) was almost identical with that of xenon (1170 kJ mol^{-1}). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour compound $Xe^+\ PtF_6^-$ by mixing PtF_6 and xenon.

$$O_2 \xrightarrow[\text{Energy of } O_2]{\text{Ionisation}} O_2^+ + e^- \xrightarrow{PtF_6} O_2^+PtF_6^-$$

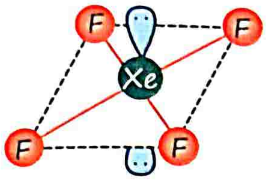
$$Xe \xrightarrow[\text{Energy of Xe}]{\text{Ionisation}} Xe^+ + e^- \xrightarrow{PtF_6} Xe^+PtF_6^-$$

First ionisation enthalpy of molecular oxygen : 1175 kJmol^{-1}
First ionisation enthalpy of Xenon : 1170 kJmol^{-1}

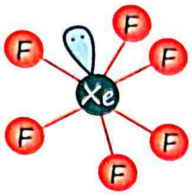
- No true compounds of Ar, Ne or He are yet known.
- In all noble gases, only Xe and Kr form very few compounds (fluorides and oxides like KrF_2, XeF_2, XeF_4, XeF_6, $XeOF_4$, XeO_2F_2, XeO_4, XeO_3).
- Compounds of Rn have not been isolated but only identified (e.g. RnF_2) by radiotracer technique.



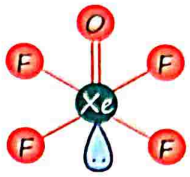
(a) Linear



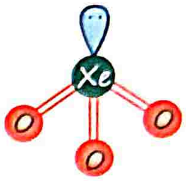
(b) Square planar



(c) Distorted octahedral



(d) Square pyramidal (Colourless volatile liquid)



(e) Pyramidal (Explosive solid)

USES

- **Helium:** It is a non-flammable and lightweight gas, which is why it's used to fill balloons for weather observations.
  - It is also important in gas-cooled nuclear reactors. Liquid helium, which has a very low boiling point of 4.2 K, is used as a cooling agent for experiments at extremely low temperatures.
  - It helps to create and maintain powerful superconducting magnets, which are crucial for modern NMR spectrometers and MRI machines used in medical diagnoses.
  - Helium is also mixed with oxygen in modern diving equipment because it doesn't dissolve much in blood.
- **Neon** is used in neon signs and fluorescent bulbs for advertising displays. These bulbs are also found in botanical gardens and greenhouses.
- **Argon** is mostly used to create an inert atmosphere in high-temperature metalworking processes, like arc welding, and for filling electric light bulbs. In laboratories, it is used to handle materials that react with air.
- **Xenon and Krypton** don't have many significant uses but are used in special light bulbs.

OCCURRENCE OF p-BLOCK ELEMENTS

GROUP-15 ELEMENTS

Nitrogen

- Makes up 78% of the atmosphere by volume.
- Found in the Earth's crust as sodium nitrate ($NaNO_3$, known as Chile saltpetre) and potassium nitrate (KNO_3, known as Indian saltpetre).
- Present in proteins in plants and animals.

Phosphorus

- ☐ Found in minerals of the apatite family, such as fluorapatite ($Ca_9(PO_4)_6 \cdot CaF_2$), which are major components of phosphate rocks.
- ☐ Essential for life, present in bones and living cells.
- ☐ Found in phosphoproteins in milk and eggs.

Arsenic, Antimony, and Bismuth

- ☐ Mainly found as sulphide minerals.

GROUP-16 ELEMENTS

Oxygen

- ☐ Oxygen is the most abundant element on Earth, making up about 46.6% of the Earth's crust by mass. In the air we breathe, dry air contains about 20.946% oxygen by volume.

Sulphur

- ☐ Sulphur is much less abundant in the Earth's crust, making up only about 0.03–0.1%. Sulphur is mainly found in the form of–

(i) Sulphates : Gypsum – $CaSO_4 \cdot 2H_2O$ Epsom salt – $MgSO_4 \cdot 7H_2O$ Baryte – $BaSO_4$	**(ii) Sulphides :** Galena – PbS Zinc blende – ZnS Copper pyrites – $CuFeS_2$

Small amounts of Sulphur can also be found as hydrogen sulphide in volcanic gases. Additionally, Sulphur is present in organic materials like eggs, proteins, garlic, onions, mustard, hair, and wool.

Selenium and Tellurium

- ☐ Selenium and tellurium are also found as metal selenides and tellurides in sulphide ores.

Polonium

- ☐ Polonium occurs in nature as a decay product of thorium and uranium minerals.

GROUP-17 ELEMENTS

Fluorine and chlorine are fairly abundant while bromine and iodine less so.

Fluorine

- Found mainly in insoluble fluorides like fluorspar (CaF_2), cryolite (Na_3AlF_6), and fluoroapatite ($3Ca_3(PO_4)_2 \cdot CaF_2$).
- Also present in small amounts in soil, river water, plants, and in the bones and teeth of animals.

Chlorine, Bromine, and Iodine

- They are found in sea water as chlorides, bromides, and iodides of sodium, potassium, magnesium, and calcium.
- Sea water is primarily a sodium chloride solution (2.5% by mass).
- Dried-up sea deposits contain compounds like sodium chloride and carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$).
- **Iodine** is found in certain marine life, such as seaweeds, which can contain up to 0.5% iodine. Chile saltpetre contains up to 0.2% sodium iodate.

GROUP-18 ELEMENTS

- All noble gases, except radon, are present in the atmosphere.
- They make up about 1% of the volume of dry air, with argon being the most abundant.

Helium, Neon, Xenon and Radon

Helium and Neon are found in minerals of radioactive origin, such as pitchblende, monazite, and cleveite. The main commercial source of helium is natural gas.

Xenon and Radon are the rarest noble gases.

Radon is obtained as a decay product of the radioactive element radium-226 (^{226}Ra).

$$^{226}_{88}Ra \longrightarrow ^{222}_{86}Rn + ^{4}_{2}He$$

41. Identify the incorrect pair from the following: [29 Jan, 2024 (Shift-I)]

(a) Fluorspar- BF_3
(b) Cryolite-Na_3AlF_6
(c) Fluoroapatite-$3Ca_3(PO_4)_2.CaF_2$
(d) Carnallite-$KCl.MgCl_2.6H_2O$

Sol. (a)

42. The F- ions make the enamel on teeth much harder by converting hydroxyapatite (the enamel on the surface of teeth) into much harder fluoroapatite having the formula. [09 April, 2024 (Shift-I)]

(a) $[3(Ca_3(PO_4)_2).CaF_2]$
(b) $[3(Ca_2(PO_4)_2).Ca(OH)_2]$
(c) $[3(Ca_3(PO_4)_3).CaF_2]$
(d) $[3(Ca_3(PO_4)_2).Ca(OH)_2]$

Sol. (a)

43. Given below are two statements: [NEET 2025]

Statement I: Like nitrogen that can form ammonia, arsenic can form arsine.

Statement II: Antimony cannot form antimony pentoxide

In the light of the above statements, choose the most appropriate answer from the options given below:

(a) Both Statement I and Statement II are correct

(b) Both Statement I and Statement II are incorrect

(c) Statement I is correct but Statement II is incorrect

(d) Statement I is incorrect but Statement II is correct

Sol. (c)

44. Identify the incorrect statement. [NEET 2024 Re]

(a) PEt_3 and $AsPh_3$ as ligands can form $d\pi - d\pi$ bond with transition metals

(b) The N – N single bond is as strong as the P – P single bond

(c) Nitrogen has unique ability to form $p\pi - p\pi$ multiple bonds with nitrogen, carbon and oxygen

(d) Nitrogen cannot form $d\pi - p\pi$ bond as other heavier elements of its group

Sol. (b)

45. The correct order of N-compounds in its decreasing order of oxidation states is [NEET 2018]

(a) HNO_3, NO, N_2, NH_4Cl

(b) HNO_3, NO, NH_4Cl, N_2

(c) NH_4Cl, N_2, NO, HNO_3

(d) HNO_3, NH_4Cl, NO, N_2

Sol. (a)

46. Strong reducing behaviour of H_3PO_2 is due to [NEET 2015 Re]

(a) Presence of two –OH groups and one P – H bond

(b) Presence of one –OH group and two P – H bonds

(c) High electron gain enthalpy of phosphorus

(d) High oxidation state of phosphorus

Sol. (b)

47. When copper is heated with conc. HNO_3 it produces: [NEET 2016-I]

(a) $Cu(NO_3)_2$ and N_2O

(b) $Cu(NO_3)_2$ and NO_2

(c) $Cu(NO_3)_2$ and NO

(d) $Cu(NO_3)_2$, NO and NO_2

Sol. (b)

48. Given below are two statements: [NEET 2022]

Statement-I: The boiling points of the following hydrides of group 16 elements increases in the order- $H_2O < H_2S < H_2Se < H_2Te$.

Statement-II: The boiling points of these hydrides increase with increase in molar mass.

In the light of the above statements, choose the most appropriate answer from the options given below:

(a) Statement-I is incorrect but Statement-II is correct.

(b) Both Statement-I and Statement-II are correct

(c) Both Statement-I and Statement-II are incorrect

(d) Statement-I is correct but Statement-II is incorrect

Sol. (c)

49. In which one of the following arrangements the given sequence is not strictly according to the properties indicated against it? [NEET 2021]

(a) $H_2O < H_2S < H_2Se < H_2Te$: Increasing pK_a values

(b) $NH_3 < PH_3 < AsH_3 < SbH_3$: Increasing acidic character

(c) $CO_2 < SiO_2 < SnO_2 < PbO_2$: Increasing oxidizing power

(d) $HF < HCl < HBr < HI$: Increasing acidic strength

Sol. (a)

50. Which of the following is the most basic oxide? [NEET 2006]

(a) Al_2O_3 (b) Sb_2O_3 (c) Bi_2O_3 (d) SeO_2

Sol. (c)

51. Given below are two statements: [NEET 2024]

Statement I: The boiling point of hydrides of Group 16 elements follow the order $H_2O > H_2Te > H_2Se > H_2S$.

Statement II: On the basis of molecular mass, H_2O is expected to have lower boiling point than the other members of the group but due to the presence of extensive H-bonding in H_2O, it has higher boiling point.

In the light of the above statements, choose the correct answer from the options given below:

(a) Statement I is true but Statement II is false.

(b) Statement I is false but Statement II is true

(c) Both Statement I and Statement II are true

(d) Both Statement I and Statement II are false.

Sol. (c)

52. Among Group 16 elements, which one does NOT show −2 oxidation state? [NEET 2024]

(a) Te (b) Po (c) O (d) Se

Sol. (b)

53. Amongst the given options, which of the following molecules/ion acts as a Lewis acid? [NEET 2023]

(a) OH^- (b) NH_3 (c) H_2O (d) BF_3

Sol. (d)

54. Which is the correct thermal stability order for H_2E (E = O, S, Se, Te and Po)? [NEET 2019]

(a) $H_2S < H_2O < H_2Se < H_2Te < H_2Po$ (b) $H_2O < H_2S < H_2Se < H_2Te < H_2Po$

(c) $H_2Po < H_2Te < H_2Se < H_2S < H_2O$ (d) $H_2Se < H_2Te < H_2Po < H_2O < H_2S$

Sol. (c)

55. Which of the statements given below is incorrect? [NEET 2015 Re]

(a) O_3 molecule is bent (b) ONF is isoelectronic with O_2N^-

(c) OF_2 is an oxide of fluorine (d) Cl_2O_7 is an anhydride of perchloric acid

Sol. (c)

56. Acidity of diprotic acids in aqueous solutions increases in the order: **[NEET 2014]**

(a) $H_2Se < H_2S < H_2Te$ (b) $H_2Te < H_2S < H_2Se$

(c) $H_2Se < H_2Te < H_2S$ (d) $H_2S < H_2Se < H_2Te$

Sol. (d)

57. Which one of the following reactions does not come under hydrolysis type reaction? **[NEET 2020-Covid]**

(a) $Li_3N(s) + 3H_2O(l) \rightarrow NH_3(s) + 3LiOH(aq)$ (b) $2F_2(g) + 2H_2O(l) \rightarrow 4HF(aq) + O_2(g)$

(c) $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$ (d) $SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$

Sol. (b)

58. In which pair of ions both the species contain S – S bond? **[NEET 2017-Delhi]**

(a) $S_4O_6^{2-}, S_2O_7^{2-}$ (b) $S_2O_7^{2-}, S_2O_3^{2-}$ (c) $S_4O_6^{2-}, S_2O_3^{2-}$ (d) $S_2O_7^{2-}, S_2O_8^{2-}$

Sol. (c)

59. The oxidation states of sulphur in the anions SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_6^{2-}$ follow the order: **[NEET 2003]**

(a) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$ (b) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$

(c) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$ (d) $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$

Sol. (a)

60. Fluorine is a stronger oxidising agent than chlorine because:

(A) F–F bond has a low enthalpy of dissociation.

(B) Fluoride ion (F^-) has high hydration enthalpy.

(C) Electron gain enthalpy of fluorine is less negative than chlorine.

(D) Fluorine has a very small size. **[NEET 2022 Re]**

Choose the most appropriate answer from the options given:

(a) (B) and (C) only (b) (A) and (B) only

(c) (A) and (C) only (d) (A) and (D) only

Sol. (b)

61. Identify the incorrect statement from the following: **[NEET 2024 Re]**

(a) The acidic strength of HX(X = F, Cl, Br and I) follows the order: HF > HCl > HBr > HI.

(b) Fluorine exhibits –1 oxidation state whereas other halogens exhibit +1, +3, +5 and +7 oxidation states also.

(c) The enthalpy of dissociation of F_2 is smaller than that of Cl_2.

(d) Fluorine is stronger oxidising agent than chlorine.

Sol. (a)

62. When Cl_2 gas reacts with hot and concentrated sodium hydroxide solution, the oxidation number of chlorine changes from: **[NEET 2012 Re]**

(a) Zero to + 1 and zero to –3 (b) Zero to +1 and zero to –5

(c) Zero to –1 and zero to + 5 (d) Zero to –1 and zero to + 3

Sol. (c)

63. Which one of the following arrangements does not give the correct picture of the trends indicated against it? [NEET 2008]

(a) $F_2 > Cl_2 > Br_2 > I_2$: Electronegativity

(b) $F_2 > Cl_2 > Br_2 > I_2$: Oxidizing power

(c) $F_2 > Cl_2 > Br_2 > I_2$: Electron gain enthalpy

(d) $F_2 > Cl_2 > Br_2 > I_2$: Bond dissociation energy

Sol. (d)

64. Match List-I with List-II [NEET 2025]

List-I		List-II	
A.	XeO_3	I.	sp^3d; linear
B.	XeF_2	II.	sp^3; pyramidal
C.	$XeOF_4$	III.	sp^3d^3; distorted octahedral
D.	XeF_6	IV.	sp^3d^2; square pyramidal

Choose the correct answer from the options given below:

(a) A-II, B-I, C-IV, D-III
(b) A-II, B-I, C-III, D-IV
(c) A-IV, B-II, C-III, D-I
(d) A-IV, B-II, C-I, D-III

Sol. (a)

65. Match List-I with List-II : [NEET 2024 Re]

List-I (Atom/Molecule)		List-II (Property)	
A.	Nitrogen atom	I.	Paramagnetic
B.	Fluorine molecule	II.	Most reactive element in group 18
C.	Oxygen molecule	III.	Element with highest ionisation enthalpy in group 15
D.	Xenon atom	IV.	Strongest oxidising agent

Identify the correct answer from the options given below:

(a) A-III, B-I, C-IV, D-II
(b) A-I, B-IV, C-III, D-II
(c) A-II, B-IV, C-I, D-III
(d) A-III, B-IV, C-I, D-II

Sol. (d)

66. Noble gases are named because of their inertness towards reactivity. Identify an incorrect statement about them. [NEET 2021]

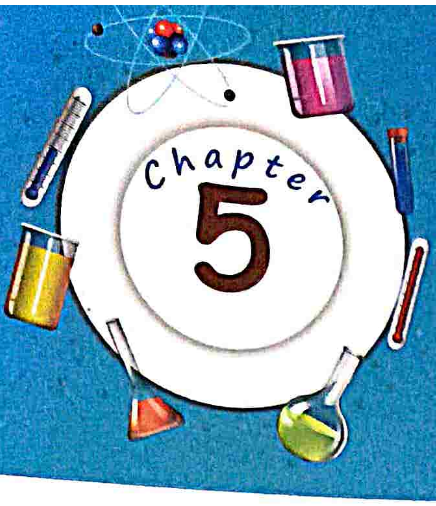
(a) Noble gases have very high melting and boiling points

(b) Noble gases have weak dispersion forces

(c) Noble gases have large positive values of electron gain enthalpy

(d) Noble gases are sparingly soluble in water

Sol. (a)



Chapter 5

The d- and f- Block Elements

JEE Main & NEET

Syllabus

Transition Elements: General introduction, electronic configuration, occurrence and characteristics, general trends in properties of the first-row transition elements- physical properties, ionization enthalpy, oxidation states, atomic radii, colour, catalytic behaviour, magnetic properties, complex formation, interstitial compounds, alloy formation, preparation, properties and uses of $K_2Cr_2O_7$ and $KMnO_4$.

Inner Transition Elements:

Lanthanoids- Electronic configuration, oxidation states and Lanthanoid contraction.

Actinoids- Electronic configuration and oxidation states

d-BLOCK ELEMENTS

Series name ↓ | Group →	3		4	5	6	7	8	9	10	11	12
3d-series	Sc_{21}		Ti_{22}	V	Cr	Mn	Fe	Co	Ni	Cu	Zn_{30}
4d-series	Y_{39}		Zr_{40}	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd_{48}
5d-series	La_{57}	4f Series	Hf_{72}	Ta	W	Re	Os	Ir	Pt	Au	Hg_{80}
6d-series	Ac_{89}	5f Series	Rf_{104}	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn_{112}

Electronic Configuration

3d series: [Ar] 4s 3d

4d series: [Kr] 5s 4d

5d series: [Xe] 6s 5d : for La
[Xe] 6s 5d $4f^{14}$: from Hf → Hg

6d series: [Rn] 7s 6d : for Ac
[Rn] 7s 6d $5f^{14}$: from Rf → Cn

देशी जुगाड़ For Electronic Configuration of 11 Elements

Rahgir(Rg) Kyu(Cu) Aage(Ag) Aau(Au) Pitayi(Pt) Croge(Cr), Nabab(Nb) Mout(Mo) Rukawat(Ru) Rah(Rh) Padegi(Pd)

Rg	Cu	Ag	Au	Pt	Cr	Nb	Mo	Ru	Rh

↓ ns^1

Pd

↓ ns^0

Sc $4s^2\ 3d^1$	Ti $4s^2\ 3d^2$	V $4s^2\ 3d^3$	Cr $4s^1\ 3d^5$	Mn $4s^2\ 3d^5$	Fe $4s^2\ 3d^6$	Co $4s^2\ 3d^7$	Ni $4s^2\ 3d^8$	Cu $4s^1\ 3d^{10}$	Zn $4s^2\ 3d^{10}$
Y $5s^2\ 4d^1$	Zr $5s^2\ 4d^2$	Nb $5s^1\ 4d^4$	Mo $5s^1\ 4d^5$	Tc $5s^2\ 4d^5$	Ru $5s^1\ 4d^7$	Rh $5s^1\ 4d^8$	Pd $5s^0\ 4d^{10}$	Ag $5s^1\ 4d^{10}$	Cd $5s^2\ 4d^{10}$
La $6s^2\ 5d^1$	Hf $6s^2\ 5d^2$ $4f^{14}$	Ta $6s^2\ 5d^3$ $4f^{14}$	W $6s^2\ 5d^4$ $4f^{14}$	Re $6s^2\ 5d^5$ $4f^{14}$	Os $6s^2\ 5d^6$ $4f^{14}$	Ir $6s^2\ 5d^7$ $4f^{14}$	Pt $6s^1\ 5d^9$ $4f^{14}$	Au $6s^1\ 5d^{10}$ $4f^{14}$	Hg $6s^2\ 5d^{10}$ $4f^{14}$
Ac $7s^2\ 6d^1$	Rf $7s^2\ 6d^2$ $5f^{14}$	Db $7s^2\ 6d^3$ $5f^{14}$	Sg $7s^2\ 6d^4$ $5f^{14}$	Bh $7s^2\ 6d^5$ $5f^{14}$	Hs $7s^2\ 6d^6$ $5f^{14}$	Mt $7s^2\ 6d^7$ $5f^{14}$	Ds $7s^2\ 6d^8$ $5f^{14}$	Rg $7s^1\ 6d^{10}$ $5f^{14}$	Cn $7s^2\ 6d^{10}$ $5f^{14}$

1. Choose the correct option having all the elements with d^{10} electronic configuration from the following: **[27 Jan, 2024 (Shift-II)]**

(a) $^{27}Co, ^{28}Ni, ^{26}Fe, ^{24}Cr$ (b) $^{29}Cu, ^{30}Zn, ^{48}Cd, ^{47}Ag$

(c) $^{46}Pd, ^{28}Ni, ^{26}Fe, ^{24}Cr$ (d) $^{28}Ni, ^{24}Cr, ^{26}Fe, ^{29}Cu$

Sol. (b)

$[Cd] = [Kr]5s^24d^{10}$, $[Cu] = [Ar]4s^13d^{10}$, $[Ag] = [Kr]5s^14d^{10}$, $[Zn] = [Ar]4s^23d^{10}$

2. Match List-I with List-II.

List-I (Species)		List-II (Electronic distribution)	
(A)	Cr^{+2}	(I)	$3d^8$
(B)	Mn^+	(II)	$3d^34s^1$
(C)	Ni^{+2}	(III)	$3d^4$
(D)	V^+	(IV)	$3d^5\ 4s^1$

Choose the correct answer from the options given below: **[30 Jan, 2024 (Shift-I)]**

(a) (A)-I, (B)-II, (C)-III, (D)-IV (b) (A)-III, (B)-IV, (C)-I, (D)-II

(c) (A)-IV, (B)-III, (C)-I, (D)-II (d) (A)-II, (B)-I, (C)-IV, (D)-III

Sol. (b) $_{24}Cr \rightarrow [Ar]\ 3d^54s^1$; $Cr^{2+} \rightarrow [Ar]3d^4$

$_{25}Mn \rightarrow [Ar]\ 3d^54s^2$; $Mn^+ \rightarrow [Ar]3d^5\ 4s^1$

$_{28}Ni \rightarrow [Ar]\ 3d^84s^2$; $Ni^{2+} \rightarrow [Ar]3d^8$

$_{23}V \rightarrow [Ar]\ 3d^34s^2$; $V^+ \rightarrow [Ar]3d^34s^1$

3. Which one of the following ions has electronic configuration $[Ar]3d^6$? [NEET 2010 Pre]
(a) Co^{3+} (b) Ni^{3+} (c) Mn^{3+} (d) Fe^{3+}

Sol. (a)

4. Among the following series of transition metal ions, the one where all metal ions have $3d^2$ electronic configuration is: [NEET 2004]
Atomic numbers of Ti = 22; V = 23; Cr = 24; Mn = 25
(a) $Ti^{+}, V^{4+}, Cr^{6+}, Mn^{7+}$ (b) $Ti^{4+}, V^{3+}, Cr^{2+}, Mn^{3+}$
(c) $Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}$ (d) $Ti^{3+}, V^{2+}, Cr^{3+}, Mn^{4+}$

Sol. (c)

TRANSITION METALS

The elements whose atoms or simple ions contain partially filled d-orbitals are called transition metals.

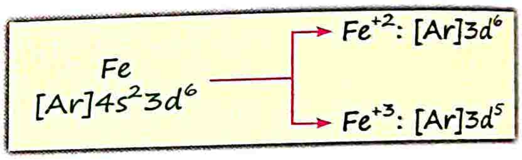
1. Sc is a transition metal because Sc has partially filled d-orbitals.
   Sc : $[Ar]\ 4s^2\ 3d^1$
2. Zn is not a transition metal because Zn and Zn^{2+} both have filled d-orbitals.
   Zn : $[Ar]\ 4s^2\ 3d^{10}$ Zn^{2+} : $[Ar]\ 3d^{10}$
3. Cu is a transition metal because Cu^{2+} has partially filled d-orbitals.
   Cu : $[Ar]\ 4s^1\ 3d^{10}$ Cu^{2+} : $[Ar]\ 3d^9$

Note

- ☐ Zn, Cd, Hg are not considered as transition elements because they have filled 'd^{10} configuration' in atomic (M) and ionic (M^{2+}) form.
- ☐ All transition elements are d-block elements but not all d-block elements are transition elements.

OXIDATION STATE

- ☐ Generally transition metals show more than one oxidation state (**variable oxidation state**).
  - ◆ Due to similar energies of ns and (n − 1)d orbitals both can participate to show variable oxidation state.
  - ◆ For example, Fe shows variable oxidation state (+2 and +3). Fe^{+3} is more stable then Fe^{+2} due to half filled electronic configuration.



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+1	+2
+3	+3	+3	+3	+3	+3	+3	+3	+2	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

- Sc and Zn shows ONLY one oxidation state +3 and +2 respectively.
- Highest Oxidation State in 3d series : Mn (+7) [Mn_2O_7]
- Most Common Oxidation State in 3d series : +2
- Highest Oxidation state in d block → Ru and Os : +8 [RuO_4, OsO_4]
- Sc^{2+} is not known (Sc exist as only Sc^{+3} ion because of stable inert gas configuration in Sc^{+3} ion).

  Sc : [Ar]$4s^2$ $3d^1$

  Sc^{+3} : [Ar] $4s^\circ$: Inert gas configuration
- Ti^{+4} is more stable than Ti^{2+} or Ti^{3+} because Ti^{4+} has inert gas configuration.

  Ti : [Ar] $4s^2$ $3d^2$ Ti^{2+} : [Ar] $4s^\circ$ $3d^2$ Ti^{3+} : [Ar] $4s^\circ$ $3d^1$

  Ti^{+4} : [Ar] $4s^\circ$ $3d^\circ$: Inert gas configuration
- Zn shows only one oxidation state +2 because Zn^{+2} has [Ar]$3d^{10}$ configuration which is stable.

  Zn : [Ar] $4s^2$ $3d^{10}$

  Zn^{+2} : [Ar] $3d^{10}$: Completely filled orbitals
- From Sc to Mn, maximum oxidation state is the sum of no. of electrons in 's' and 'd' subshell.

	Sc	Ti	V	Cr	Mn
	$4s^2$ $3d^1$	$4s^2$ $3d^2$	$4s^2$ $3d^3$	$4s^1$ $3d^5$	$4s^2$ $3d^5$
Maximum oxidation state [sum of s and d electrons]	3	4	5	6	7

- Highest oxidation state in 3d series is +7 shows by Mn because it has 7 electrons in 's' and 'd' subshell.
- Oxidation state of transition elements differ from each other by unity (V^{2+}, V^{3+}, V^{4+}, V^{5+}) but in non-transition elements oxidation state differ by a unit of two (Pb^{2+}, Pb^{4+}).
- In p block, due to inert pair effect lower oxidation states are more stable than higher oxidation state in heavier element (Tl, Pb, Bi). But in d block opposite is true.

  p block – $Tl^+ > Tl^{3+}$, $Pb^{2+} > Pb^{4+}$, $Bi^{3+} > Bi^{5+}$

  d block – $Cr^{+6} < Cr^{+3}$, $W^{+6} >> W^{+3}$
- Mo(+6) and W(+6) are more stable than Cr (+6).

  Stability : Cr (+6) < Mo (+6) / W(+6)
- Among MoO_3, WO_3 and $K_2Cr_2O_7$ /H^+ only $K_2Cr_2O_7$ with $H^+$is an oxidizing agent because Cr(+6) reduces itself to Cr(+3).

○ $K_2 \overset{(+6)}{Cr_2}O_7/H^+ \longrightarrow Cr^{+3}$

○ $\overset{(+6)}{Mo}O_3 \xrightarrow{\times} Mo^{+3}$

○ $\overset{(+6)}{W}O_3 \xrightarrow{\times} W^{+3}$

- Low or zero oxidation states of metal (Ni, Fe) are found when a complex compound has σ donor and π acceptor ligands (such as CO).

For Example: In $Ni(CO)_4$ and $Fe(CO)_5$, oxidation states of Ni and Fe is zero.

(IIT JEE 1994)

5. The compound $YBa_2Cu_3O_7$ which shows the superconductivity, has copper in an oxidation state ...... assuming that the rare earth element Yttrium in its usual + 3 oxidation state

Sol. $YBa_2Cu_3O_7$

Let oxidation state of copper be x $\Rightarrow 3 + 2 \times 2 + 3 \times x - 2 \times 7 = 0$

$\Rightarrow x = +\frac{7}{3}$

6. Match the properties given in Column-I with the metals given in Column-II.

	Column-I (Property)		Column-II (Metal)
(i)	An element which can show +8 oxidation state	(a)	Mn
(ii)	3d block element that can show upto + 7 oxidation state	(b)	Cr
(iii)	3d block element with highest melting point	(c)	Os
		(d)	Fe

Sol. (i) → (c), (ii) → (a), (iii) → (b)

7. Which of the following will not act as oxidising agents?

(a) CrO_3 (b) MoO_3 (c) WO_3 (d) CrO_4^{2-}

Sol. Higher oxidation states of Mo and W are more stable, they will not act as oxidising agent.

8. The element that usually does NOT show variable oxidation states is: (2019/12th Jan/Shift-1)

(a) Cu (b) Ti (c) Sc (d) V

Sol. (c) Scandium (Sc) typically shows only a +3 oxidation state.

9. Generally transition elements form coloured salt due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state?

(a) Ag_2SO_4 (b) CuF_2 (c) ZnF_2 (d) Cu_2Cl_2

Sol. (b) $CuF_2 \rightarrow Cu^{2+} : d^9$ [Unpaired electron – coloured compound]

(a) $Ag_2SO_4 \rightarrow Ag^+ : d^{10}$ (b) $CuF_2 \rightarrow Cu^{2+} : d^9$

(c) $ZnF_2 \rightarrow Zn^{+2} : d^{10}$ (d) $Cu_2Cl_2 \rightarrow Cu^+ : d^{10}$

10. The set of correct statements is: (2023/29 Jan/Shift-2)

(a) Manganese exhibits +7 oxidation state in its oxide.

(b) Ruthenium and Osmium exhibit +8 oxidation in their oxides.

(c) Sc shows +4 oxidation state which is oxidising in nature.

(d) Cr shows oxidising nature in +6 oxidation state.

Sol. (a), (b) and (d)

11. Which one of the elements with the following outer orbital configurations may exhibit the largest number of oxidation states? [NEET 2009]

(a) $3d^5 4s^1$ (b) $3d^5 4s^2$ (c) $3d^2 4s^2$ (d) $3d^3 4s^2$

Sol. (b)

12. Which of the following shows maximum number of oxidation states? [NEET 2002]

(a) Cr (b) Fe (c) Mn (d) V

Sol. (c)

PHYSICAL PROPERTIES

d-block elements contains metals so they are

1. **Malleable :** Able to be pressed into shape without breaking or cracking.
2. **Sonorous :** Able to resonate sound.
3. **Ductile :** Able to be deformed without losing toughness.
4. **Lustrous :** Majority lose lustre on exposure to air (moist).

ALLOY

- Mixture of element
- (i) Brass → Cu + Zn
- (ii) Bronze → Cu + Sn
- (iii) Gun metal/Bell metal → Cu + Zn + Sn
- (iv) Stainless steel → C + Fe + Cr + Ni
- (v) German silver → Cu + Zn + Ni
- UK 'copper' coins are copper-coated steel.
- The 'silver' UK coins are a Cu/Ni alloy.

13. The major components in "Gun Metal" are: [24 Feb, 2021 (Shift-I)]

(a) Cu, Ni and Fe (b) Al, Cu, Mg and Mn (c) Cu, Sn and Zn (d) Cu, Zn and Ni

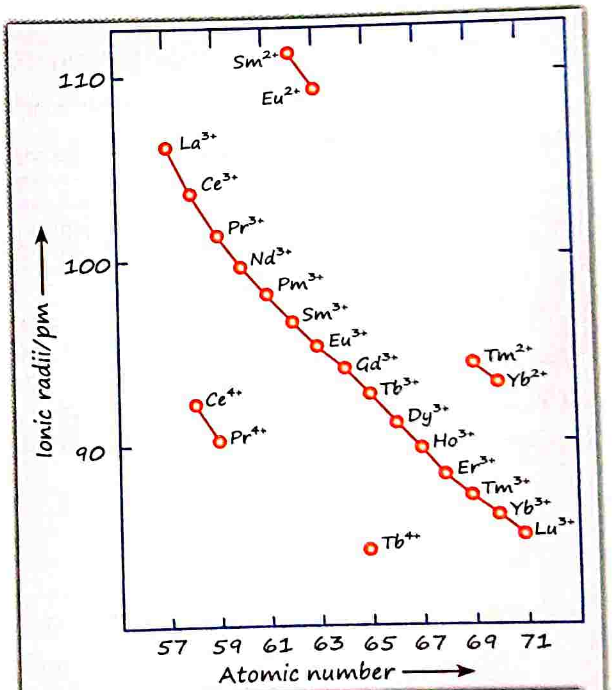
Sol. (c) Major components of gun metal = Cu, Sn and Zn

ATOMIC SIZE

- Lanthanoid contraction – atomic or ionic size contraction in lanthanoid series.
- The decrease in atomic or ionic radii from Ce to Lu due to imperfect shielding of 4f e^- from nuclear charge is known as lanthanoid contraction.

- Lanthanoid contraction is similar to that observed in an ordinary transition series and is attributed to the same cause, the imperfect shielding of one electron by another in the same sub-shell.
- The shielding of one 4 f electron by another is less than one d electron by another with the increase in nuclear charge along the series. There is fairly regular decrease in the sizes with increasing atomic number.
- Lanthanoid contraction is applicable on both Ln and Ln^{3+} size orders. **Remember, Atomic size : Eu > Ce**

Ce → Lu
Ce^{3+} → Lu^{3+}
→ size decreases



Trends in ionic radii of lanthanoids

14. The effect of lanthanoid contraction in the lanthanoid series of elements by the large means [10 Jan, 2019 (Shift-I)]

(a) Increase in both atomic and ionic radii
(b) Decrease in atomic radii and increase in ionic radii
(c) Decrease in both atomic and ionic radii
(d) Increase in atomic radii and decrease in ionic radii

Sol. (c)

Effect of Lanthanide Contraction on Size of d-Block Elements

- ☐ Due to lanthanoid contraction, radii of the members of 5d series are found to be very similar to those of corresponding members of the 4d series.
- ☐ Due to similar size of element of 4d series (Zr) and 5d series (Hf), they have similar chemical and physical properties, that's why separation of these elements is tough.

15. Assertion: Separation of Zr and Hf is difficult.
Reason: Because Zr and Hf lie in the same group of the periodic table.

(a) Both assertion and reason are true and reason is the correct explanation of the assertion.
(b) Both assertion and reason are true but reason is the not correct explanation of the assertion.
(c) Assertion is not true but the reason is true.
(d) Both assertion and reason are false.

Sol. (b) Zr and Hf have nearly the same size.

16. Zr (Z = 40) and Hf (Z = 72) have similar atomic and ionic radii because of: [NEET 2021]

(a) Diagonal relationship
(b) Lanthanoid contraction
(c) Having similar chemical properties
(d) Belonging to same group

Sol. (b)

17. Because of lanthanoid contraction, which of the following pairs of elements have nearly same atomic radii? (Numbers in the parenthesis are atomic numbers) [NEET 2015]

(a) Zr (40) and Nb (41)
(b) Zr (40) and Hf (72)
(c) Zr (40) and Ta (73)
(d) Ti (22) and Zr (40)

Sol. (b)

18. Which of the following pairs has the same size? [NEET 2010 Pre]

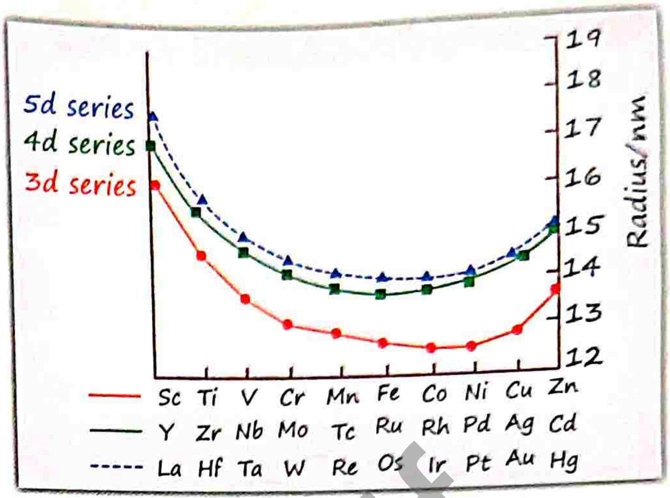
(a) Zn^{2+}, Hf^{4+}
(b) Fe^{2+}, Ni^{2+}
(c) Zr^{4+}, Ti^{4+}
(d) Zr^{4+}, Hf^{4+}

Sol. (d)

Atomic Size of 3d Series

here are two factors in order to decide atomic radius f an element.

1. Nuclear charge [Nuclear charge↑ : size↓]
2. Inter electronic repulsion (IER) [IER↑ : size↑]



Elements	Sc → Ti → V → Cr	Mn → Fe → Co → Ni	Cu → Zn
Size	Decreases	Nearly constant	Slightly increases
Reason	Nuclear charge dominates over IER	Nuclear charge ≈ IER	IER dominates over nuclear charge

DENSITY

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Density (g/cm^{+3})	3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

- The decrease in Metallic radius coupled with increase in atomic mass results in a general increase in density, as we go left (Sc) to right (Cu).

$$\boxed{\text{Density} = \frac{\text{Mass}}{\text{Volume}}}$$

- Metallic radius of Zn is more than radius of Cu ⇒ [$(\text{Volume})_{Zn} > (\text{Volume})_{Cu}$].
  So, density : Cu > Zn
- Highest Density in d block–
  Osmium (Os) = 22.51 g/cm^3, Iridium (Ir) = 22.61 g/cm^3

19. What is the correct order of the following elements with respect to their density? [24 Feb, 2021 (Shift-II)]

(a) Zn < Cr < Fe < Co < Cu
(b) Zn < Cu < Co < Fe < Cr
(c) Cr < Fe < Co < Cu < Zn
(d) Cr < Zn < Co < Cu < Fe

Sol. (a)

(2020/07 Jan/Shift-1)

20. The atomic radius of Ag is closest to:

(a) Au (b) Ni (c) Cu (d) Hg

Sol. (a) Atomic radius of Ag and Au is nearly same.

(2019/12th April/Shift-2)

21. The pair that has similar atomic radii is:

(a) Mn and Re (b) Ti and Hf (c) Sc and Ni (d) Mo and W

Sol. (d) Molybdenum (Mo) and Tungsten (W) have similar atomic radii due to the lanthanide contraction.

IONISATION ENERGY

- ☐ Generally ionisation energy increases from left to right due to increase in atomic number.
- ☐ Sc has lowest and Zn has highest value for first enthalpy of ionisation.
- ☐ Zn, Cd and Hg have very high $I.E_1$ due to their fully filled electronic configuration.
- ☐ **2nd Ionisation Energy :** Cr > Mn [Removal of electron from Cr^+ is tough (due to half filled stable electronic configuration) with respect to Mn^+.]

$$Cr : [Ar]4s^1\,3d^5 \xrightarrow{I.E_1} Cr^+ : [Ar]3d^5 \xrightarrow{I.E_2} Cr^{+2} : [Ar]\,3d^4$$

$$Mn : [Ar]4s^2 3d^5 \xrightarrow{I.E_1} Mn^+ : [Ar]4s^1 3d^5 \xrightarrow{I.E_2} Mn^{+2} : [Ar]3d^5$$

- ☐ For an element : $IE_1 < IE_2 < IE_3$
- ☐ The trend in steady increase in 2nd and 3rd ionisation enthalpy breaks for the formation of Mn^{2+} and Fe^{+3} respectively.

Explanation:

$$\underset{[Ar]4s^1 3d^5}{Mn^+} \xrightarrow{2^{nd}\text{ IE of Mn}} \underset{[Ar]3d^5}{Mn^{2+}}$$

$$\underset{[Ar]3d^6}{Fe^{2+}} \xrightarrow{3^{rd}\text{ IE of Fe}} \underset{[Ar]3d^5}{Fe^{+3}}$$

Mn^{2+} and Fe^{+3} have d^5 configuration which is relatively more stable due to higher exchange energy.

- ☐ **3rd Ionisation Energy :** Mn > Fe

$$\underset{[Ar]3d^5}{Mn^{2+}} \longrightarrow \underset{[Ar]3d^4}{Mn^{3+}}$$

$$\underset{[Ar]3d^6}{Fe^{2+}} \longrightarrow \underset{[Ar]3d^5}{Fe^{3+}}$$

Removal of electron from Mn^{2+} is tough (due to half filled d^5 stable configuration) with respect to Fe^{+2}.

- ☐ Second ionisation enthalpy for Cr and Cu is high because removal of electron from ions Cr^+ and Cu^+ ions (d^5 and d^{10} configuration respectively) is relatively tough.

$$\underset{[Ar]3d^5}{Cr^+} \longrightarrow \underset{[Ar]3d^4}{Cr^{2+}}$$

$$\underset{[Ar]3d^{10}}{Cu^+} \longrightarrow \underset{[Ar]3d^9}{Cu^{2+}}$$

- ☐ 2nd ionisation energy of Zn is low but 3rd ionisation energy is high with respect to Cu.

$$\underset{[Ar]3d^{10}}{Cu^+} \longrightarrow \underset{[Ar]3d^9}{Cu^{2+}} \longrightarrow \underset{[Ar]3d^8}{Cu^{3+}}$$

$$\underset{[Ar]4s^1 3d^{10}}{Zn^+} \longrightarrow \underset{[Ar]3d^{10}}{Zn^{2+}} \longrightarrow \underset{[Ar]3d^9}{Zn^{3+}}$$

Removal of e^- from $3d^{10}$ (fully filled) subshell is tough with respect to $3d^9$. So, IE : $Zn^{2+} > Cu^{2+}$

- ☐ The trend in the third ionisation enthalpies is not complicated by the 4s orbital factor because 4s orbital is empty before 3rd ionisation and shows the greater difficulty of removing an electron from the $d^5(Mn^{2+})$ and d^{10} (Zn^{2+}) ions.
- ☐ In general, the third ionisation enthalpies are "quite high." Also the high values for third ionisation enthalpies of copper, nickel and zinc indicate why it is difficult to obtain oxidation state greater than two for these element.

22. The third ionization enthalpy is minimum for: (2020/08th Jan/Shift-1)

(a) Co (b) Fe (c) Ni (d) Mn

Sol. (b) $Fe^{2+} \longrightarrow Fe^{3+}$

$3d^6 \longrightarrow 3d^5$ [half filled]

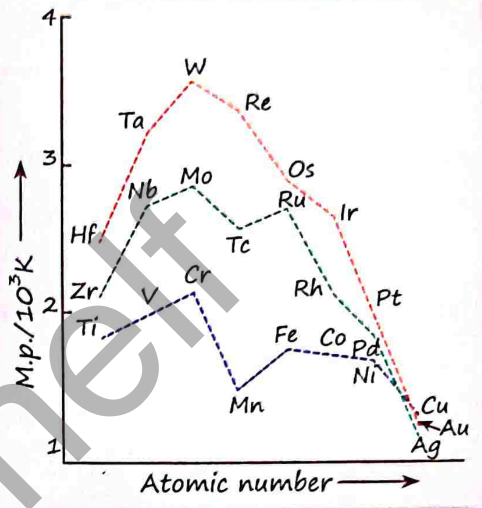
23. The correct order of decreasing second ionisation enthalpy of Ti (22), V (23), Cr (24) and Mn (25) is: **[NEET 2008]**

(a) Ti > V > Cr > Mn
(b) Cr > Mn > V > Ti
(c) V > Mn > Cr > Ti
(d) Mn > Cr > Ti > V

Sol. (b)

MELTING POINT & BOILING POINT

- Transition elements have high melting and boiling point because of stronger interatomic metallic bonding.
- This strong bonding is due to involvement of greater number of electrons from (n − 1)d in addition to ns electrons in the interatomic metallic bonding.



Trends in melting points of transition elements

No. of unpaired electrons ↑ : Metallic bonding ↑ : MP / B.P. ↑

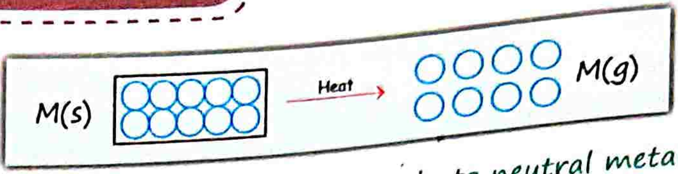
Metals	No. of unpaired electrons	Metals	No. of unpaired electrons
Sc → $4s^2\ 3d^1$	1	Fe → $4s^2\ 3d^6$	4
Ti → $4s^2\ 3d^2$	2	Co → $4s^2\ 3d^7$	3
V → $4s^2\ 3d^3$	3	Ni → $4s^2\ 3d^8$	2
Cr → $4s^1\ 3d^5$	6	Cu → $4s^1\ 3d^{10}$	1
Mn → $4s^2\ 3d^5$	5	Zn → $4s^2\ 3d^{10}$	0

- Chromium has highest M.P. among 3d-series.
- Group 6 elements have highest melting point with respect to other group in d block.
- Due to high melting point, Tungsten W is used in bulb filament.

Metallic Bonding : Cr < Mo < W
Melting Point : Cr < Mo < W

- As Mn and Zn has stable configuration, so they won't like to lose electron for delocalization leads to weak metallic bonding hence low M.P.
- Zn, Cd and Hg are more volatile than other d block elements because they do not have any unpaired electron.

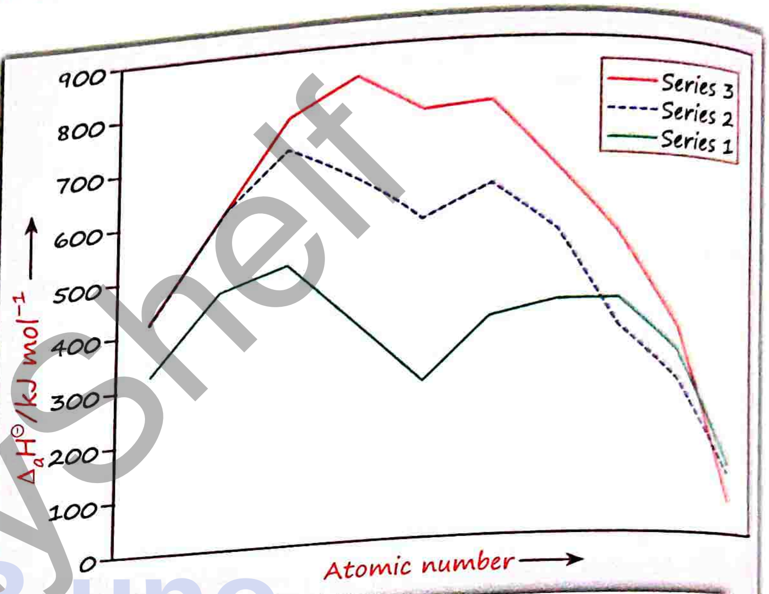
HEAT OF ATOMISATION



- ☐ The energy required to break 1 mole of metal lattice in to neutral metal atom is known as heat of atomization.
- ☐ No. of unpaired electrons ↑ : Metallic bonding ↑ : Heat of atomization ↑.
- ☐ Metallic Bonding: 3d series < 4d series < 5d series

  Heat of atomization: 3d series < 4d series < 5d series
- ☐ VANADIUM has highest heat of atomization among 3d-series.
- ☐ Mn and Zn has low enthalpy of atomization.

  Mn ($3d^5$: half filled) and Zn ($3d^{10}$: fully filled) has stable configuration so they have weak metallic bonding hence low enthalpy of atomization.



Trends in enthalpies of atomisation of transition elements

24. The transition element that has lowest enthalpy of atomisation is: (2019/09th Jan/Shift-II)

(a) Fe (b) Cu (c) V (d) Zn

Sol. (b) Among Fe, Cu, V and Zn → Zn has lowest enthalpy of atomisation but zinc is not considered a transition element. Among the other transition elements—Cu, V, and Fe—copper (Cu) has the lowest enthalpy of atomisation.

25. Which of the following statements are correct about Zn, Cd and Hg?

A. They exhibit high enthalpy of atomisation as the d-subshell is full.

B. Zn and Cd do not show variable oxidation state while Hg shows +I and +II.

C. Compounds of Zn, Cd and Hg are paramagnetic in nature.

D. Zn, Cd and Hg are called soft metals.

Choose the most appropriate from the options given below: [29 Jan, 2024 (Shift-II)]

(a) B, D only (b) B, C only (c) A, D only (d) C, D only

Sol. (a) (A) Zn, Cd, Hg exhibit lowest enthalpy of atomisation in respective transition series.

(C) Compounds of Zn, Cd and Hg are diamagnetic in nature.

REDUCTION POTENTIAL

Reduction Potential $E^o_{M^{2+}/M}$

Reduction Potential depends on 3 following factors.

(a) $M_{(s)} \longrightarrow M_{(g)}$ Atomisation enthalpy

(b) $M_{(g)} \longrightarrow M^{2+}_{(g)} + 2e^-$ Ionisation enthalpy $[IE_1 + IE_2]$

(c) $M^{2+}_{(g)} + H_2O \longrightarrow M^{2+}_{(aq)}$ Hydration enthalpy

$M_{(s)} \longrightarrow M^{2+}_{(aq)}$

Element	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E^o_{M^{2+}/M}$	–1.18	–0.91	–1.18	–0.44	–0.28	–0.25	+0.34	–0.76

- ☐ E^o = high (+) value means M^{2+} has great tendency to get reduced in Metal.
- ☐ E^o = high (–) value means M^{2+} has low tendency to get reduced in Metal.

- ☐ $M_{(s)} \longrightarrow M^{2+}_{(aq.)}$ becomes very spontaneous when
  1. Atomisation enthalpy of metal $M_{(s)}$ is low.
  2. Sum of 1st and 2nd ionisation enthalpy of $M_{(s)}$ is low.
  3. Hydration enthalpy of $M^{2+}_{(g)}$ is high.

- ☐ All 3d metals have –ve reduction potential except Cu. Cu has +ve reduction potential, so Cu^{2+} has great tendency to get reduced in Cu metal.
- ☐ Cu cannot liberate H_2 from acids.

$[Cu + dil\ HCl \xrightarrow{\times} H_2\uparrow]$

	Heat of atomisation of metal	1st ionisation energy	2nd ionisation energy	Hydration Energy of M^{2+}	
Element (M)	$\Delta H^\ominus$ (M)	$\Delta_i H_1^\ominus$	$\Delta_i H_2^\ominus$	$\Delta_{hyd} H^\ominus (M^{2+})$	$E^\ominus$ /V
Ti	469	656	1309 (min)	-1866	-1.63
V	515 (max)	650 (min)	1414	-1895	-1.18
Cr	398	653	1592	-1925	-0.90
Mn	279	717	1509	-1862 (min)	-1.18
Fe	418	762	1561	-1998	-0.44
Co	427	758	1644	-2079	-0.28
Ni	431	736	1752	-2121 (max)	-0.25
Cu	339	745	1958 (max)	-2121 (max)	0.34
Zn	130 (min)	906 (max)	1734	-2059	-0.76

- ☐ $E°$ values of Mn and Zn are more -ve than expected from the general trend.

Less ΔH_{atom} : More $\ominus E°_{RP}$

This is due to low enthalpy of atomisation in Mn and Zn.

(stability of half-filled d subshell in Mn and configuration in Zn, is the reason for low enthalpy of atomisation)

- ☐ $E°$ value of Ni is more -ve than expected from the general trend.

$E°$ for Ni is related to the highest negative hydration enthalpy →

More ΔH_{hyd} : More $\ominus E°_{RP}$

- ☐ $E°_{Cu^{2+}/Cu}$ = +ve because-

The high energy to transform $Cu_{(s)}$ to $Cu^{2+}_{(aq)}$ is not balanced by its hydration enthalpy.

$$Cu_{(s)} \xrightarrow{\text{Heat of atomisation}} Cu_{(g)} \xrightarrow{IE_1 + IE_2} Cu^{2+}_{(g)} \xrightarrow[\text{Hydration Energy}]{H_2O} Cu^{2+}_{(aq)}$$

26. Which of the following 3d-metal ion will give the lowest enthalpy of hydration ($\Delta_{hyd}H$) when dissolved in water? [29 July, 2022 (Shift-II)]

(a) Cr^{2+} (b) Mn^{2+} (c) Fe^{2+} (d) Co^{2+}

Sol. (b)

27. Assertion : Cu cannot liberate hydrogen from acids.

Reason: Value of $E°_{Cu^{2+}/Cu}$ is positive.

(a) Both assertion and reason are true and reason is the correct explanation of the assertion

(b) Both assertion and reason are true but reason is the not correct explanation of the assertion

(c) Assertion is not true but the reason is true.

(d) Both assertion and reason are false.

Sol. (a) Cu has +ve reduction potential, so Cu^{2+} has great tendency to get reduced in Cu metal. Cu cannot liberate H_2 from acids.

28. The colour of light absorbed by an aqueous solution of $CuSO_4$ is (JEE Adv. 2012)

(a) Orange - red (b) Blue - green

(c) yellow (d) violet

Sol. (a) Aqueous solution of copper sulphate absorbs orange-red light and appears blue (complementary colour).

29. Which of the following pair is expected to exhibit same colour in solution? (JEE Adv. 2005)

(a) $VOCl_2$; $FeCl_2$ (b) $CuCl_2$; $VOCl_2$

(c) $MnCl_2$; $FeCl_2$ (d) $FeCl_2$; $CuCl_2$

Sol. (b) Since both Cu^{2+} in $CuCl_2$ and V^{4+} in $VOCl_2$ have one unpaired electron in their d-orbitals, their colours are likely to be similar .

30. The pair of compounds having metals in their highest oxidation state is (JEE Adv. 2004)

(a) MnO_2 , $FeCl_3$ (b) $[MnO_4]^-$, CrO_2Cl_2

(c) $[Fe(CN)_6]^{3-}$, $[Co(CN)_3]$ (d) $[NiCl_4]^{2-}$, $[CoCl_4]^-$

Sol. (b) $[MnO_4]^-$ contains Mn in the +7 oxidation state, and CrO_2Cl_2 contains Cr in the +6 oxidation state, both representing the highest oxidation states of manganese and chromium.

31. Amongst the following, identify the species with an atom in +6 oxidation state (JEE Adv. 2000)
(a) MnO^{-}_{4} (b) $Cr(CN)_6^{3-}$ (c) NiF_6^{2-} (d) CrO_2Cl_2

Sol. (d) Chromium in CrO_2Cl_2 is in the +6 oxidation state, which is the highest oxidation state for chromium in most compounds.

Reduction Potential M^{3+}/M^{2+}

$$M^{3+}/M^{2+}:\ \underbrace{\begin{array}{ccc}Ti & V & Cr\\ -0.37 & -0.26 & -0.41\end{array}}_{\boxed{-ve}} \qquad \underbrace{\begin{array}{ccc}Mn & Fe & Co\\ 1.57 & 0.77 & 1.97\end{array}}_{\boxed{+ve}}$$

(1) $Ti^{2+} + H^+ \longrightarrow Ti^{3+} + \frac{1}{2}H_2\uparrow$

(2) $V^{2+} + H^+ \longrightarrow V^{3+} + \frac{1}{2}H_2\uparrow$

(3) $Cr^{2+} + H^+ \longrightarrow Cr^{3+} + \frac{1}{2}H_2\uparrow$

(1) $Mn^{2+} + H^+ \xrightarrow{\times} Mn^{3+} + \frac{1}{2}H_2\uparrow$

(2) $Fe^{2+} + H^+ \xrightarrow{\times} Fe^{3+} + \frac{1}{2}H_2\uparrow$

Note

Aq. solution of Ti^{2+}, V^{2+}, Cr^{2+} ions are strong reducing agents, can evolve H_2 from dil. acid.

☐ High Value for Mn and Zn: $\underset{[Ar]3d^5}{Mn^{2+}} \longrightarrow \underset{[Ar]3d^4}{Mn^{3+}}$ $\quad \underset{[Ar]3d^{10}}{Zn^{2+}} \longrightarrow \underset{[Ar]3d^9}{Zn^{3+}}$

- The highest value for Zn is due to the removal of an electron from the stable d^{10} configuration of Zn^{2+} is tough.
- The comparatively high value for Mn shows that Mn^{2+} (d^5) is particularly stable.

☐ Low Value for Sc: $\underset{[Ar]3d^1}{Sc^{2+}} \longrightarrow \underset{[Ar]3d^0}{Sc^{+3}}$

The low value for Sc reflects the stability of Sc^{3+} which has a noble gas configuration.

☐ Comparatively Low value (less +ve value) for Fe, with respect to Co and Mn

$Fe^{3+}[3d^5] \longrightarrow Fe^{2+}[3d^6] + e^-$

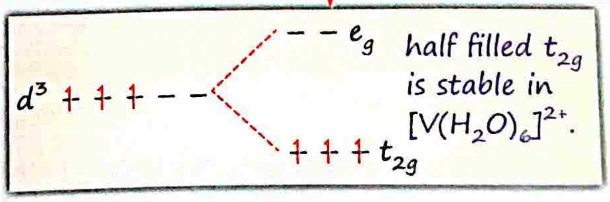
$\downarrow$ half filled d subshell is stable in $[Fe(H_2O)_6]^{3+}$.

$$\underbrace{\begin{array}{ccc}Mn & Fe & Co\\ 1.57 & 0.77 & 1.97\end{array}}_{\boxed{+ve}}$$

☐ Comparatively Low value (less –ve value) for V, with respect to Ti and Cr

$V^{3+}[3d^2] \xrightarrow{e^-} V^{+2}[3d^3]$

$$\underbrace{\begin{array}{ccc}Ti & V & Cr\\ -0.37 & -0.26 & -0.41\end{array}}_{\boxed{-ve}}$$



half filled t_{2g} is stable in $[V(H_2O)_6]^{2+}$.

32. Among Co^{3+}, Ti^{2+}, V^{2+} and Cr^{2+} ions, one if used as a reagent cannot liberate H_2 from dilute mineral acid solution, its spin-only magnetic moment in gaseous state is ____ B.M. (Nearest integer) [25 July, 2022 (Shift-1)]

Sol. [5] Among the given, Co^{3+} can't liberate H_2.

Co^{3+} : $[Ar]\ 3d^6\ 4s^0\ 4p^0$

Number of unpaired electrons = 4

$\mu = \sqrt{4 \times 6} = 4.89$ B.M. ≈ 5 B.M.

33. The spin-only magnetic moment value of M^{3+} ion (in gaseous state) from the pairs Cr^{3+}/Cr^{2+}, Mn^{3+}/Mn^{2+}, Fe^{3+}/Fe^{2+} and Co^{3+}/Co^{2+} that has negative standard electrode potential, is ____ B.M [Nearest integer] [25 July, 2022 (Shift-2)]

Sol. [4] In given electrodes, only $E^o_{Cr^{3+}/Cr^{2+}}$ is negative

Electronic configuration of Cr in +3 o.s. is $[Ar]3d^3\ 4s^0\ 4p^0$

Number of unpaired electrons = 3

$\mu = \sqrt{n(n+2)}BM = \sqrt{3(3+2)}BM = 3.87BM \approx 4BM$

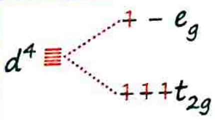
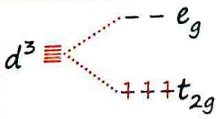
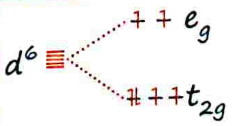
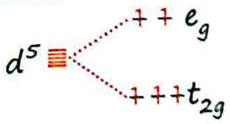
34. Which of the following ions does not liberate hydrogen gas on reaction with dilute acids? (JEE Main 2017)

(a) Ti^{2+} (b) V^{2+} (c) Cr^{2+} (d) Mn^{2+}

Sol. (d) Mn^{2+} does not liberate hydrogen gas on reaction with dilute acids.

35. Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why?

Sol. Cr^{2+} is stronger reducing agent than Fe^{2+} in aqueous solution because $[Cr(H_2O)_6]^{2+}$ with d^4 configuration converts easily into $[Cr(H_2O)_6]^{3+}$ with d^3 configuration because in water $[Cr(H_2O)_6]^{3+}$ (d^3) is more stable as compared to $[Cr(H_2O)_6]^{2+}$ (d^4) due to more CFSE in d^3 configuration.

$[Cr(H_2O)_6]^{2+} \longrightarrow [Cr(H_2O)_6]^{3+}$		$[Fe(H_2O)_6]^{2+} \xrightarrow{\times} [Fe(H_2O)_6]^{3+}$	
 CFSE = $-3 \times 0.4\ \Delta_o + 1 \times 0.6\ \Delta_o$ $= -0.6\ \Delta_o$	 CFSE = $-3 \times 0.4\ \Delta_o$ $= -1.2\Delta_o$	 CFSE = $-4 \times 0.4\ \Delta_o + 2 \times 0.6\Delta_o$ $= -0.4\Delta_o$	 CFSE = $-3 \times 0.4\ \Delta_o + 2 \times 0.6\ \Delta_o$ $= 0$

Note

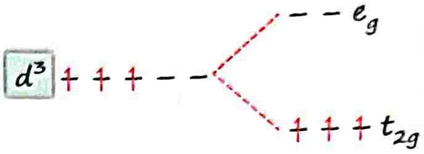
Fe^{2+} (d^6) does not convert into $Fe^{3+}(d^5)$ because d^5 has zero CFSE.

36. Why is Cr^{2+} reducing agent and Mn^{3+} oxidising agent when both have d^4 configuration

Sol. • $Cr^{2+}(d^4) \longrightarrow Cr^{+3}(d^3)$

t_{2g} is half filled so, more stable

• $Mn^{2+}(d^5) \longrightarrow Mn^{3+}(d^4)$ is not possible because ionisation of Mn^{2+} to Mn^{3+} is not easy due to stability of d^5 configuration. So Mn^{2+} is not a reducing agent but Mn^{3+} is an oxidizing agent.



$Mn^{3+}(d^4) \longrightarrow Mn^{2+}(d^5)$ (stable configuration)

37. Why is the E° value for the Mn^{3+}/Mn^{2+} couple much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+} ? Explain.

Sol. $Mn^{3+}(d^4) \longrightarrow \underset{\text{(half filled)}}{Mn^{2+}(d^5)}$ E° = more +ve

• 3^{rd} Ionisation energy of Mn^{2+} is more than Fe^{+2} and Cr^{+2}.

38. Which of the following statements is not correct?

(a) Copper liberates hydrogen from acids

(b) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine

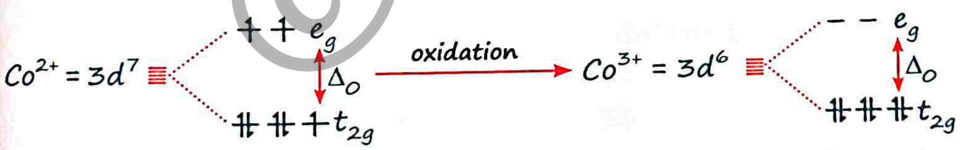
(c) Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution

(d) Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution

Sol. (a) Copper does not liberate hydrogen gas from acids.

39. How would you account for the following:
Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidized.

Sol. $[Co(H_2O)_6]^{2+} \xrightarrow[\text{oxidation}]{+3\text{ en}} [Co(en)_3]^{3+} + 6H_2O + e^-$



high CFSE favours the formation of Co^{+3}.

CFSE = $-0.4\ \Delta_o \times 5 + 2 \times 0.6\ \Delta_o$
= $-0.8\Delta_o$

CFSE = $-0.4\ \Delta_o \times 6$
= $-2.4\ \Delta_o$

40. The E° value for the Mn^{3+}/Mn^{2+} couple is more positive than that of Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+} due to change of [NEET 2024]

(a) d^4 to d^5 configuration
(b) d^3 to d^5 configuration
(c) d^5 to d^4 configuration
(d) d^5 to d^2 configuration

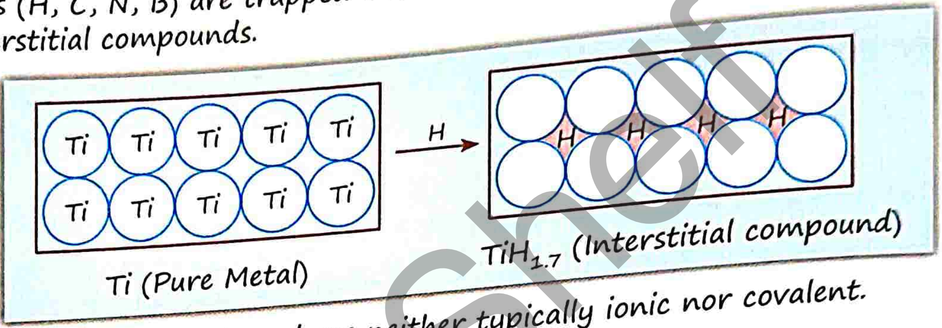
Sol. (a)

41. Which one of the following ions is the most stable in aqueous solution? [NEET 2007]
(a) V^{3+} (b) Ti^{3+} (c) Mn^{3+} (d) Cr^{3+}
(Atomic Number Ti = 22, V = 23, Cr = 24, Mn = 25)

Sol. (d)

INTERSTITIAL COMPOUNDS

When small atoms (H, C, N, B) are trapped inside the crystal lattices of metals. Then these compounds are known as interstitial compounds.



Ti (Pure Metal)

$TiH_{1.7}$ (Interstitial compound)

They are usually non-stoichiometric and are neither typically ionic nor covalent.

Example : TiC, Mn_4N, Fe_3H, $VH_{0.56}$ and $TiH_{1.7}$

☐ The formulas quoted do not, of course, correspond to any normal oxidation state of the metal.

Physical and Chemical Characteristics

[MP : Ti < TiC]

(i) They have high melting points, higher than those of pure metals.
(ii) They are very hard (some borides approach diamond in hardness)
(iii) They retain metallic conductivity.
(iv) They are chemically inert.

42. Interstitial compounds are not formed by:
(a) Co (b) Ni (c) Fe (d) Ca

Sol. (d) Ca is not a d block element.

43. The statement that is INCORRECT about the interstitial compounds is: (2019/08th April/Shift-II)
(a) They are chemically reactive. (b) They are very hard.
(c) They have metallic conductivity. (d) They have high melting points.

Sol. (a) Interstitial compounds are chemically inert.

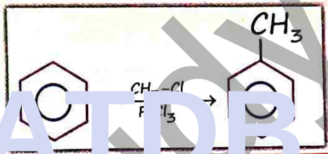
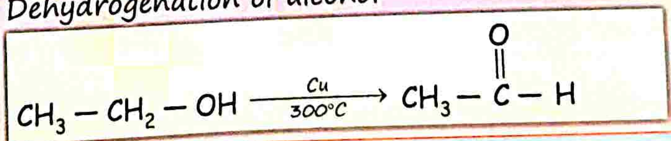
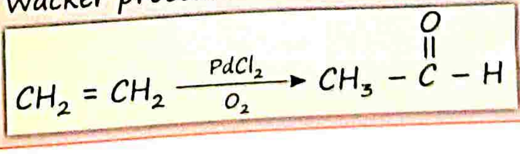
44. Which of the following statements about the interstitial compounds is incorrect? [NEET 2013]
(a) They retain metallic conductivity
(b) They are chemically reactive
(c) They are much harder than the pure metal
(d) They have higher melting points than the pure metal

Sol. (b)

CATALYTIC ACTIVITY

Factors responsible for catalytic activity of transition metals-

- ☐ Large surface area.
- ☐ Ability to form complexes.
- ☐ Variable oxidation state.
- ☐ Presence of empty d-orbital.

Metal	Catalyst	Process/Reaction
Ti	$TiCl_4 + Et_3Al$	Ziegler Natta Catalyst : Preparation of polythene from ethene $nCH_2=CH_2 \xrightarrow{TiCl_4+Et_3Al} \left(CH_2-CH_2\right)_n$
V	V_2O_5	V_2O_5 is used in contact process $SO_2 \xrightarrow[O_2]{V_2O_5} SO_3$
Cr	$Al_2O_3 + Cr_2O_3$	Used for aromatization 
Mn	MnO_2	Used as catalyst in producing oxygen $2KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$
Fe	Anhydrous $FeCl_3$	Friedel Craft Reaction 
	Fe tube/Δ	Used for preparation of benzene from acetylene $3HC\equiv CH \longrightarrow$ 
		Haber's Process $N_2 + 3H_2 \xrightarrow[\text{Mo: As promoter}]{\text{Fe: As catalyst}} 2NH_3$
Ni Pd Pt		Hydrogenation of alkene and alkyne $CH_2=CH_2 \xrightarrow[Pt]{H_2} CH_3-CH_3$ $CH\equiv CH \xrightarrow[Pt]{H_2} CH_3-CH_3$
Cu		Dehydrogenation of alcohol  $CH_3-CH_2-OH \xrightarrow[300^\circ C]{Cu} CH_3-\overset{\overset{O}{\parallel}}{C}-H$
Ag	AgBr	The photographic industry relies on the special light-sensitive properties of AgBr
Pd		Wacker process  $CH_2=CH_2 \xrightarrow[O_2]{PdCl_2} CH_3-\overset{\overset{O}{\parallel}}{C}-H$

Note

Transition metal ions can change their oxidation states, so they become more effective as catalyst.

☐ Fe^{+3} catalyses the reaction between I^- and persulphate ion ($S_2O_8^{2-}$).

Reaction - $S_2O_8^{2-} + 2I^- \xrightarrow{Fe^{+3}} I_2 + 2SO_4^{2-}$

Mechanism:

(i) $2Fe^{+3} + 2I^- \longrightarrow 2Fe^{+2} + I_2$

(ii) $2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{+3} + 2SO_4^{2-}$

Note

Some compounds are manufactured for special purposes such as TiO for the pigment industry and MnO_2 for use in dry battery cells. The battery industry also requires Zn and Ni/Cd. The elements of Group 11 [Cu, Ag, Au] are still worthy of being called the coinage metals.

45. Match the catalysts (Column-I) with products (Column-II). (2019/09th April/Shift-I)

Column-I (Catalyst)		Column-II (Product)	
(A)	V_2O_5	(i)	Polyethylene
(B)	$TiCl_4/Al(Me)_3$	(ii)	ethanal
(C)	$PdCl_2$	(iii)	H_2SO_4
(D)	Iron Oxide	(iv)	NH_3

(a) (A) – (iii), (B) – (iv), (C) – (i), (D) –(ii)

(b) (A) – (ii), (B) – (iii), (C) – (i), (D) –(iv)

(c) (A) – (iii), (B) – (i), (C) – (ii), (D) –(iv)

(d) (A) – (iv), (B) – (iii), (C) – (ii), (D) –(i)

Sol. (c) (A) – (iii), (B) – (i), (C) – (ii), (D) – (iv)

46. Match the catalysts given in Column-I with the processes given in Column-II.

Column-I (Catalyst)		Column-II (Process)	
(i)	Ni in the presence of hydrogen	(a)	Zieglar Natta catalyst
(ii)	Cu_2Cl_2	(b)	Contact process
(iii)	V_2O_5	(c)	Vegetable oil to ghee
(iv)	Finely divided iron	(d)	Sandmeyer reaction
(v)	$TiCl_4 + Al(CH_3)_3$	(e)	Haber's Process
		(f)	Decomposition of $KClO_3$

Sol. (i) → (c), (ii) → (d), (iii) → (b), (iv) → (e), (v) → (a)

47. In the context with the first transition series which of the following statement is incorrect?
(a) In the highest oxidation state of first five elements all the 4s and 3d are used for bonding.
(b) Once the d^5 configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.
(c) Zero oxidation state is also shown by these elements in complexes.
(d) In the highest oxidation state, the transition metals show basic character and form cationic complexes.

Sol. (d) In their highest oxidation states, first series transition metals are electron deficient, making them strongly acidic rather than basic.

48. Among the following, which is the strongest oxidising agent? (2022/25 June/Shift-I)
(a) Mn^{3+} (b) Fe^{3+} (c) Ti^{3+} (d) Cr^{3+}

Sol. (a) The strength of an oxidising agent is reflected in its tendency to accept electrons, which is quantitatively given by its reduction potential. Mn^{3+} has a high reduction potential ($Mn^{3+} + e^- \rightarrow Mn^{2+}$ is approximately +1.57 V), indicating that it readily gains an electron.

(JEE Adv. 2015)

49. The correct statement(s) about Cr^{2+} and Mn^{3+} is/are [atomic number of Cr = 24 and Mn = 25]
(a) Cr^{2+} is a reducing agent
(b) Mn^{3+} is an oxidising agent
(c) Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration
(d) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration

Sol. (a), (b), (c)

- $Cr^{+2} \rightarrow Cr^{+3}$
  d^4 d^3 (stable) → So, Cr^{+2} act as a reducing agent
- $Mn^{+3} \rightarrow Mn^{+2}$
  d^4 d^5 (stable) → So, Mn^{3+} act as a oxidising agent

50. Match List-I with List-II. [NEET 2025]

List-I		List-II	
A.	Haber process	I.	Fe catalyst
B.	Wacker oxidation	II.	$PdCl_2$
C.	Wilkinson catalyst	III.	$[(PPh_3)_3RhCl]$
D.	Ziegler catalyst	IV.	$TiCl_4$ with $Al(CH_3)_3$

Choose the correct answer from the options given below:
(a) A-I, B-II, C-IV, D-III
(b) A-II, B-III, C-I, D-IV
(c) A-I, B-II, C-III, D-IV
(d) A-I, B-IV, C-III, D-II

Sol. (c)

[NEET 2022 Re]

51. Given below are two statements:

Statement I: Cr^{2+} is oxidising and Mn^{3+} is reducing in nature.

Statement II: Sc^{3+} compounds are repelled by the applied magnetic field.

In the light of the above statements, choose the most appropriate answer from the options given below:

(a) Statement I is incorrect but Statement II is correct

(b) Both Statement I and Statement II are correct

(c) Both Statement I and Statement II are incorrect

(d) Statement I is correct but Statement II is incorrect

Sol. (a)

52. The catalytic activity of transition metals and their compounds is ascribed mainly to: [NEET 2012 Mains]

(a) Their chemical reactivity

(b) Their magnetic behaviour

(c) Their unfilled d-orbitals

(d) Their ability to adopt variable oxidation states

Sol. (d)

53. Four successive members of the first series of the transition metals are listed below. For which one of them the standard potential $E^{o}_{M^{2+}/M}$ value has a positive sign? [NEET 2012 Mains]

(a) Fe (Z = 26) (b) Co (Z = 27) (c) Ni (Z = 28) (d) Cu (Z = 29)

Sol. (d)

54. Identify the alloy contaning a non-metal as a constituent in it. [NEET 2012 Pre]

(a) Invar (b) Steel (c) Bell metal (d) Bronze

Sol. (b)

55. From the four successive transition elements (Cr, Mn, Fe and Co), the stability of +2 oxidation state will be there in which of the following order? [NEET 2011 Pre]

(Atomic Number Cr = 24, Mn = 25, Fe = 26, Co = 27)

(a) Cr > Mn > Co > Fe (b) Mn > Fe > Cr > Co

(c) Fe > Mn > Co > Cr (d) Co > Mn > Fe > Cr

Sol. (b) Mn^{2+} being the most stable because after losing 2 electron it has now half filled stable configuration. Hence, stability of +2 oxidation state becomes:

Mn > Fe > Cr > Co

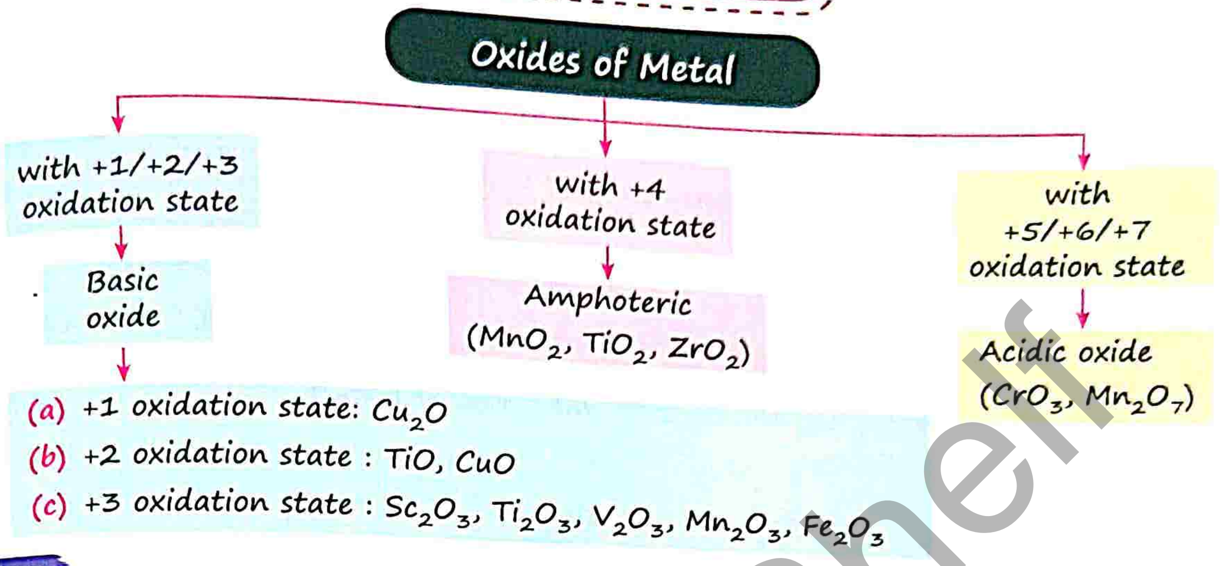
56. Which one of the following characteristics of the transition metals is associated with their catalytic activity? [NEET 2003]

(a) High enthalpy of atomization (b) Paramagnetic behaviour

(c) Colour of hydrated ions (d) Variable oxidation states

Sol. (d)

OXIDES OF TRANSITION ELEMENTS



Oxides of Metal

with +1/+2/+3 oxidation state → Basic oxide

(a) +1 oxidation state: Cu_2O

(b) +2 oxidation state : TiO, CuO

(c) +3 oxidation state : Sc_2O_3, Ti_2O_3, V_2O_3, Mn_2O_3, Fe_2O_3

with +4 oxidation state → Amphoteric (MnO_2, TiO_2, ZrO_2)

with +5/+6/+7 oxidation state → Acidic oxide (CrO_3, Mn_2O_7)

Note

ZnO, Cr_2O_3, TiO_2, V_2O_5 are amphoteric in nature. Remember V_2O_4 is basic (less) in nature.

Oxidation Number	Groups									
	3	4	5	6	7	8	9	10	11	12
+7					Mn_2O_7					
+6				CrO_3						
+5			V_2O_5							
+4		TiO_2	V_2O_4							
+3	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3				
+2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+1									Cu_2O	

Oxides, Oxo-anion and Oxo-cation

1. As oxidation number of a metal increases, acidic character and covalent character increases.

For V : V_2O_3 (basic) ⟶ V_2O_4 (less basic) ⟶ V_2O_5 (amphoteric)

For Cr : CrO (basic) ⟶ Cr_2O_3 (amphoteric) ⟶ CrO_3 (acidic)

2. All metal except Sc form MO oxides which are ionic. Example : ZnO, CuO, TiO

3. Mn_2O_7, CrO_3, V_2O_5 are covalent molecule.

4. Generally covalent compounds (CrO_3, V_2O_5) have low melting point.

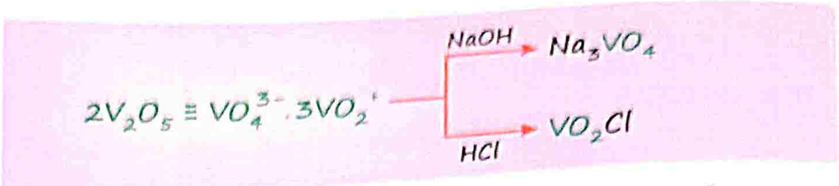
5. V_2O_5 is amphoteric (predominantly acidic) because it reacts with alkalies (NaOH) as well as acids (HCl) to give VO_4^{3-} and VO_2^+ respectively.

According to Fajan's rule-

☐ Charge on cation ↑ ≡ covalent character ↑

☐ MnO : Ionic compound

Mn_2O_7 : Covalent compound



6. Remember V_2O_4 is less basic in nature. It dissolves in acids to give VO^{2+} salts.

❑ CrO_3 gives chromic acid H_2CrO_4 and dichromic acid $H_2Cr_2O_7$.

$$CrO_3 \xrightarrow{H_2O} \underset{\text{Chromic acid}}{H_2CrO_4} \xrightarrow{-2H^+} \underset{\text{Chromate ion}}{CrO_4^{2-}} \qquad \underset{\text{Chromic acid}}{2H_2CrO_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{Dichromic acid}}{H_2Cr_2O_7} \xrightarrow{-2H^+} \underset{\text{Dichromate ion}}{Cr_2O_7^{2-}}$$

❑ Mn_2O_7 gives $HMnO_4$ or we can say Mn_2O_7 is an anhydride of $HMnO_4$.

$$\underset{\text{Acidic oxide}}{Mn_2O_7} \xrightleftharpoons{H_2O} \underset{\text{Permanganic Acid}}{HMnO_4} \xrightarrow{-H^+} \underset{\text{Permangnate ion}}{MnO_4^-} \qquad \underset{\text{Manganic Acid}}{H_2MnO_4} \xrightleftharpoons{-2H^+} \underset{\text{Mangante ion}}{MnO_4^{2-}}$$

57. A first row transition metal with highest enthalpy of atomisation, upon reaction with oxygen at high temperature forms oxides of formula M_2O_n (where n = 3, 4, 5). The 'spin-only' magnetic moment value of the amphoteric oxide from the above oxides is ___ BM (near integer) (Given atomic number : Sc : 21, Ti : 22, V : 23, Cr : 24, Mn : 25, Fe : 26, Co : 27, Ni : 28, Cu : 29, Zn : 30) [04 April, 2024 (Shift-II)]

Sol. [0]

'V' has highest enthalpy of atomisation among first row transition elements.

In V_2O_5, 'V' is in +5 oxidation state.

Its electronic configuration is $V^{5+} \Rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ (no unpaired electrons)

Hence, 'spin only' magnetic moment = 0

58. Which of the following is correctly matched? [NEET 2023]

(a) Basic oxides $\Rightarrow In_2O_3, K_2O, SnO_2$

(b) Neutral oxides $\Rightarrow CO, NO_2, N_2O$

(c) Acidic oxides $\Rightarrow Mn_2O_7, SO_2, TeO_3$

(d) Amphoteric oxides $\Rightarrow BeO, Ga_2O_3, GeO$

Sol. (c)

59. The basic character of the transition metal monoxides follows the order: [NEET 2003]
(Atomic numbers Ti = 22, V = 23, Cr = 24, Fe = 26)

(a) VO > CrO > TiO > FeO
(b) CrO > VO > FeO > TiO
(c) TiO > FeO > VO > CrO
(d) TiO > VO > CrO > FeO

Sol. (d)

SO_3 Vs CrO_3

xavalent chromium shows similarities in properties with hexavalent sulphur compounds because both e elements have the same number of valence shell electrons.

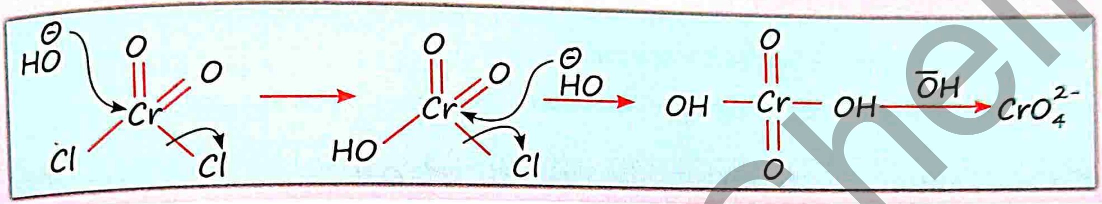
SO_3 and CrO_3 are both acidic.

S forms SO_4^{2-}, $S_2O_7^{2-}$ and similarly Cr forms CrO_4^{2-} (chromate), $Cr_2O_7^{2-}$ (dichromate)

K_2CrO_4 $[2K^+ . CrO_4{}^{2-}]$ and K_2SO_4 $[2K^+ . SO_4{}^{2-}]$ are isomorphous (same crystal type)

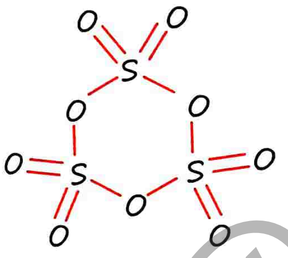
$SO_2Cl_2 \xrightarrow{OH^-} SO_4^{2-}$ and $CrO_2Cl_2 \xrightarrow{OH^-} CrO_4^{2-}$

Sulphuryl chloride   Chromyl chloride

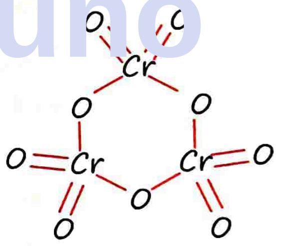


5. CrO_3 and $\beta(SO_3)$ have the same structures.

$\beta(SO_3) \equiv (SO_3)_3 \equiv S_3O_9$ $\equiv$ Trimer of SO_3 $\equiv$ Cyclic Structure	$(CrO_3)_3$: Cr_3O_9



- S – O – S bond : 3
- Type of p bond : 6 Pπ – dπ
- Each sulphur is sp^3 hybridised.



- Cr – O – Cr bond : 3
- Type of π bond : 6 pπ – dπ
- Each chromium is sp^3 hybridised.

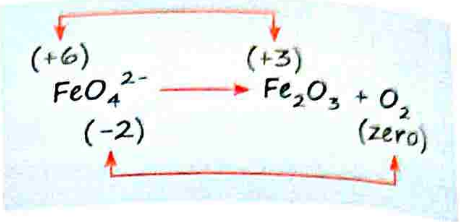
Oxo-anions

Tetrahedral $[MO_4]^{n-}$ ions are known for V^{+5}, Cr^{+6}, Fe^{+6}, Mn^{+6}.

$VO_4{}^{3-}$ Vanadate	$CrO_4{}^{2-}$ Chromate ion $MoO_4{}^{2-}$ Molybdate ion $WO_4{}^{2-}$ Tungstate ion	$MnO_4{}^{2-}$ Manganate ion	$FeO_4{}^{2-}$ Ferrate ion

☐ These ions are stable in alkaline medium.

- ☐ FeO_4^{2-} (ferrate ion has +6 oxidation state of Fe) are formed in alkaline media but it readily decompose to Fe_2O_3 and O_2.

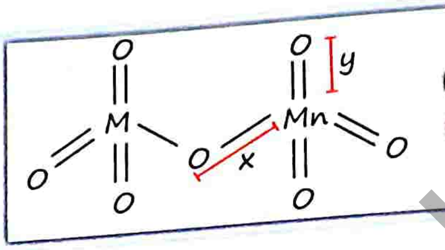


$$\overset{(+6)}{FeO_4^{2-}} \longrightarrow \overset{(+3)}{Fe_2O_3} + O_2$$
(−2) (zero)

- ☐ V and Ti form oxo-cations $\overset{(+5)}{VO_2^+}$, $\overset{(+4)}{VO^{2+}}$, and $\overset{(+4)}{TiO^{2+}}$.

Mn_2O_7

$$2\ HMnO_4 \xrightarrow[\text{(Dehydrating agent)}]{Conc.\ H_2SO_4} Mn_2O_7$$



Bond length : y < x
π bond : pπ − dπ

- ☐ Non-linear and symmetrical covalent molecule.
- ☐ Each Mn is tetrahedrally surrounded by O's including a Mn–O–Mn bridge.
- ☐ Highly explosive in nature. $[Mn_2O_7 \xrightarrow{\Delta} 2MnO_2 + \frac{3}{2}O_2]$
- ☐ Green oily compound.

60. On addition of small amount of $KMnO_4$ to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following:

(a) Mn_2O_7 (b) MnO_2 (c) $MnSO_4$ (d) Mn_2O_3

Sol. (a) $KMnO_4 \xrightarrow{H_2SO_4} HMnO_4 \xrightarrow[H_2SO_4]{Con} Mn_2O_7$

61. Highest oxidation state of Mn is exhibited in Mn_2O_7. The correct statements about Mn_2O_7 are-

(a) Mn is tetrahedrally surrounded by oxygen atoms.

(b) Mn is octahedrally surrounded by oxygen atoms.

(c) Contains Mn–O–Mn bridge.

(d) Contains Mn–Mn bond.

Sol. (a, c)

62. The correct order of following 3d metal oxides, according to their oxidation numbers is: (2021/31 Aug)

(a) CrO_3 (b) Fe_2O_3 (c) MnO_2 (d) V_2O_5 (e) Cu_2O

Sol The oxidation state of the metal in each oxide:

(a) $\underset{+6}{\underset{\downarrow}{CrO_3}}$ (b) $\underset{+3}{\underset{\downarrow}{Fe_2O_3}}$ (c) $\underset{+4}{\underset{\downarrow}{MnO_2}}$ (d) $\underset{+5}{\underset{\downarrow}{V_2O_5}}$ (e) $\underset{+1}{\underset{\downarrow}{Cu_2O}}$

Thus, the increasing order of oxidation numbers is: $Cu_2O < Fe_2O_3 < MnO_2 < V_2O_5 < CrO_3$.

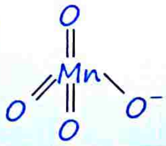
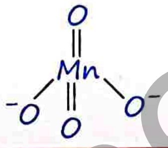
63. The correct order of basicity of oxides of vanadium is- (2023/31 Jan/Shift-I

(a) $V_2O_3 > V_2O_4 > V_2O_5$ (b) $V_2O_3 > V_2O_5 > V_2O_4$

(c) $V_2O_4 > V_2O_3 > V_2O_5$ (d) $V_2O_5 > V_2O_4 > V_2O_3$

Sol. (a) The oxides in the lower oxidation states of the metals are basic and in their higher oxidatio states they are acidic.

PERMANGANATE AND MANGANATE ION

Permanganate ion : MnO_4^-	Manganate ion: MnO_4^{2-}
☐ Mn^{+7} : $3d^0$	☐ Mn^{+6} : $3d^1$
☐ Colour : Purple	☐ Colour : Green
☐ Colour is due to charge transfer from O^{2-} to Mn^{+7}.	☐ Colour is due to charge transfer from O^{2-} to Mn^{+6}.
☐ Magnetic property → Diamagnetic due to absence of unpaired electron.	☐ Magnetic property → Paramagnetic due to presence of 1 unpaired electron.
	☐ $MnO_4^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} MnO_4^{2-}$
☐ Structure : 	☐ Structure : 

☐ All 4 Mn – O bonds are same in MnO_4^- and MnO_4^{2-}.

☐ In both ion, π bond is a pπ – dπ bond because π bonding takes place by overlap of p orbital of O and d orbital of Mn.

Preparation of $KMnO_4$

From $S_2O_8^{2-}$ or PbO_2

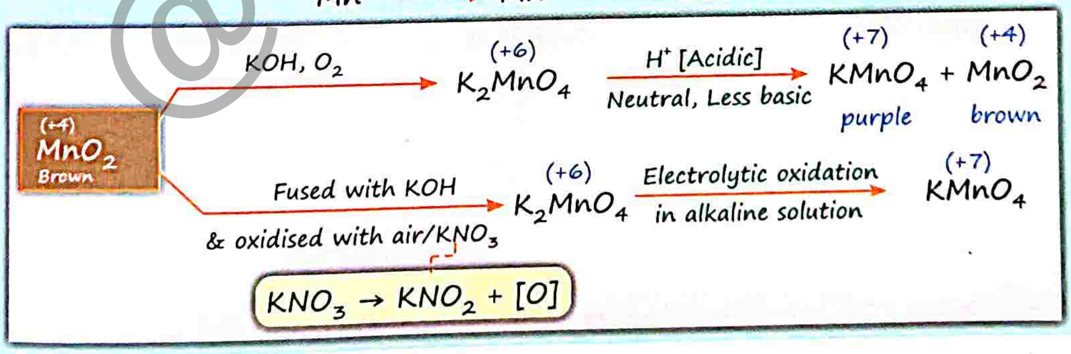
$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

Manganese (II) ion salt is oxidised by peroxodisulphate ($S_2O_8^{2-}$) to permanganate (MnO_4^-).

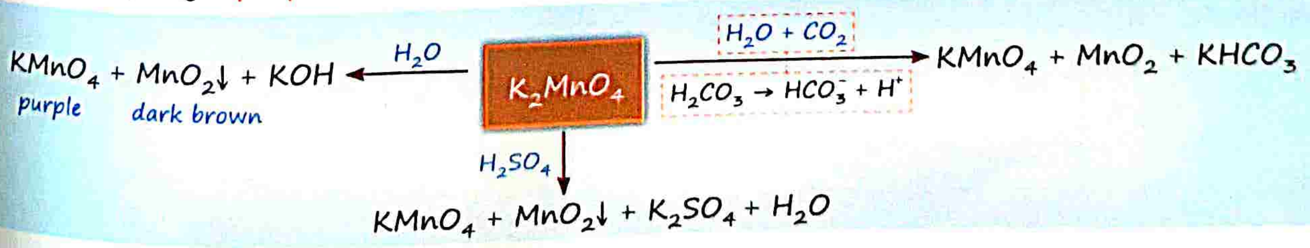
$$2Mn^{2+} + 5PbO_2 + 4H_2O \longrightarrow 2MnO_4^- + 5\,Pb^{2+} + 8H^+$$

From MnO_2 (Pyrolusite)

$$Mn^{+4} \longrightarrow Mn^{+6} \longrightarrow Mn^{+7}$$



☐ Green solution (K_2MnO_4) is quite stable in alkali, but in pure water and in presence of acids, depositing MnO_2 and giving a purple solution of permanganate.



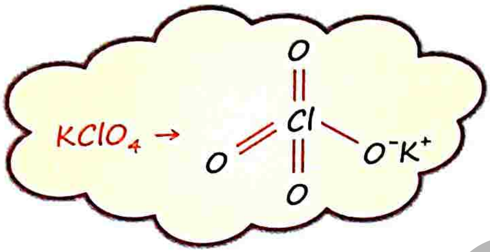
Properties of $KMnO_4$

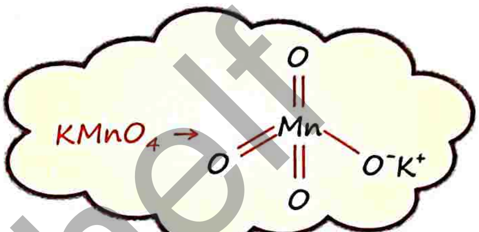
☐ Permanganate at $[H^+] = 1$ should oxidise water but in practice the reaction is extremely slow unless either manganese(II) ions are present or the temperature is raised.

$$H_2O \xrightarrow{MnO_4^- / H^+} O_2 \text{ [Slow]}$$

$$H_2O \xrightarrow[\text{Mn}^{2+} \text{ [Catalyst] or high temperature}]{MnO_4^- / H^+} O_2 \text{ [Fast]}$$

☐ Potassium permanganate forms dark purple (almost black) crystals which are isostructural with those of $KClO_4$.





☐ The salt is not very soluble in water (6.4 g/100 g of water at 293 K), but when heated it decomposes at 513 K.

$$2KMnO_4 \xrightarrow{513 K} K_2MnO_4 + MnO_2 + O_2$$

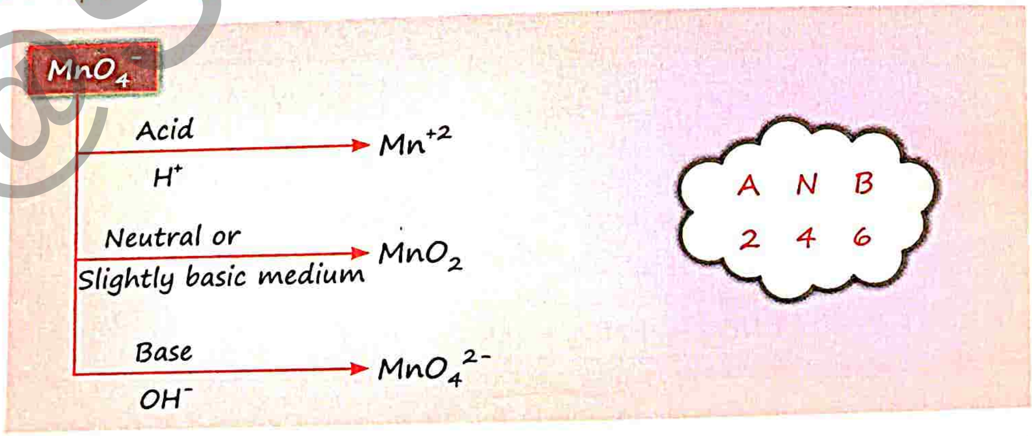
$2KMnO_4$ → Diamagnetic

K_2MnO_4 → Paramagnetic

☐ $KMnO_4$ has 2 physical properties of considerable interest

(i) Its intense colour and

(ii) Its diamagnetism along with temperature-dependent weak paramagnetism [As temperature increases $KMnO_4$ (diamagnetic) converts into K_2MnO_4 (weak paramagnetic)].



☐ The reduction of permanganate to manganate, manganese dioxide and manganese(II) salt by half - reactions,

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-} \qquad (E^\ominus = +0.56 \text{ V})$$

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O \qquad (E^\ominus = +1.69 \text{ V})$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \qquad (E^\ominus = +1.52 \text{ V})$$

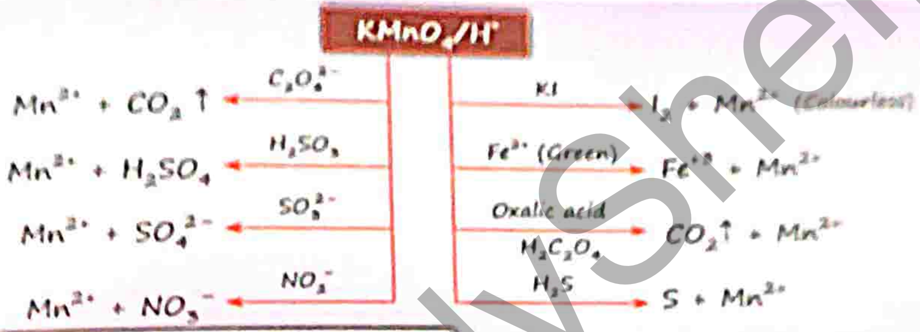
Note

Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine

$$2HCl \xrightarrow{KMnO_4} Cl_2 \uparrow$$

- We can not use HCl to create acidic medium for $KMnO_4$ because HCl get oxidised to Cl_2 by $KMnO_4$, so we use H_2SO_4 to create acidic medium because $KMnO_4$ cannot oxidise H_2SO_4 as sulphur is in higher (+6) oxidation state

Reactions of $KMnO_4$ in Acidic Medium



$$\boxed{MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O}$$ —(i)

(1) Iodine is liberated from potassium iodide (KI)- —(ii)

$2I^- \longrightarrow I_2 + 2e^-$

For balanced equation multiply equation (i) by 2 and (ii) by 5-

$10I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$

(2) Fe^{2+} ion (green) is converted to Fe^{3+} (yellow): —(iii)

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

For balanced equation multiply equation (i) by 1 and (iii) by 5 -

$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

(3) Oxalate ion or oxalic acid is oxidised at 333 K: —(iv)

$$\begin{array}{l} COO^- \\ | \\ COO^- \end{array} \longrightarrow 2CO_2 + 2e^-$$

For balanced equation multiply equation (i) by 2 and (iv) by 5-

$5C_2O_4^{-2} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

(4) Hydrogen sulphide is oxidised, sulphur being precipitated:

$H_2S \longrightarrow 2H^+ + S^{2-}$

$5S^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5S\downarrow$

(5) Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:

$5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$

(6) Nitrite is oxidised to nitrate:

$5NO_2^- + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

Reactions of $KMnO_4$ in Neutral or Slightly Basic Medium

(1) A notable reaction is the oxidation of iodide to iodate:

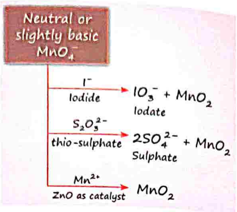
$$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$$

(2) Thiosulphate is oxidised almost quantitatively to sulphate:

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

(3) Manganous salt is oxidised to MnO_2; the presence of zinc sulphate or zinc oxide catalyses the oxidation:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$



64. H_2S (5 moles) reacts completely with acidified aqueous potassium permanganate solution. In this reaction, the number of moles of water produced is x, and the number of moles of electrons involved is y. The value of (x + y) is ___. (JEE Adv. 2023)

Sol. (18)

- $H_2S \rightarrow S^{2-} + 2H^+$

  $\overset{-2}{S} \rightarrow \overset{(zero)}{S} + 2e^-$

- $\overset{(+7)}{KMnO_4} + 8H^+ + 5e^- \longrightarrow \overset{(+2)}{Mn^{2+}} + 4H_2O$

  for balanced equation multipy (i) by 5 and (ii) by 2–

  $2\ KMnO_4 + 16\ H^+ + 5S^{2-} \longrightarrow 5\ S + 2\ Mn^{2+} + \underline{8}\ H_2O$ $\boxed{x = 8}$

  moles of electron involved in reaction = 10 = y

  x+y ⇒ 8 + 10 = 18

65. In the chemical reaction between stoichiometric quantities of $KMnO_4$ and KI in weakly basic solution, what is the number of moles of I_2 released for 4 moles of $KMnO_4$ consumed? (JEE Adv. 2020)

Sol. (6)

- $\overset{(+7)}{MnO_4^-} + H_2O + 3e^- \xrightarrow[\text{Weakly basic solution}]{\text{Neutral or}} \overset{(+4)}{MnO_2} + 2OH^-$ ...(i)

- $\overset{(-1)}{2I^-} \longrightarrow \overset{(Zero)}{I_2} + 2e^-$ ...(ii)

  for balanced equation multipy equation (i) by 2 and (ii) by 3 and add them–

  $2MnO_4^- + 2H_2O + 6I^- \longrightarrow 2MnO_2 + 4OH^- + 3I_2$

- 2 moles $KMnO_4$ give 3 moles of I_2.

  then, 4 moles $KMnO_4$ given 6 moles of I_2.

66. In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitatively oxidise thiosulphate anions to produce X moles of a sulphur containing product. The magnitude of X is .... (JEE Adv. 2016)

Sol. (6)

- $\overset{(+7)}{MnO_4^-} + H_2O + 3e^- \longrightarrow \overset{(+4)}{MnO_2} + 2OH^-$ ...(i)
- $\overset{(+2)}{S_2O_3^{2-}} \longrightarrow \overset{(+6)}{2SO_4^{2-}} + 8e^-$ ...(ii)

(i) × 8 + (ii) × 3 →

$$8\ MnO_4^- + 8H_2O + 3S_2O_3^{2-} \longrightarrow 6SO_4^{2-} + 16OH^- + 8MnO_2$$

↓ 8 moles of permanganate anion ↓ 6 moles of sulphur containing product

67. In dilute aqueous H_2SO_4 the complex diaquadioxalatoferrate (II) is oxidised by MnO_4^-. For this reaction, the ratio of the rate of change of $[H^+]$ to the rate of change of $[MnO_4^-]$ is (JEE Adv. 2015)

Sol. (8)

- $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
- $[Fe(H_2O)_2\ (C_2O_4)_2]^{2-} \longrightarrow Fe^{3+} + 4CO_2 + 2H_2O + 5e^-$

$$\left[\begin{array}{l} Fe^{2+} \xrightarrow{MnO_4} Fe^{3+} + e^- \\ 2C_2O_4^{2-} \longrightarrow 4CO_2 + 4e^- \end{array}\right]$$

$$MnO_4^- + [Fe(H_2O)_2(C_2O_4)_2]^{2-} + 8H^+ \longrightarrow Mn^{2+} + Fe^{3+} + 6H_2O + 4CO_2$$

Rate of reaction ⇒ $-\frac{d}{dt}[MnO_4^-] = -\frac{1}{8}\cdot\frac{d}{dt}[H^+]$

Rate of change of $[H^+]$ to the rate of change of $[MnO_4^-]$ ⇒ $\dfrac{-\frac{d}{dt}[H^+]}{\frac{d}{dt}[MnO_4^-]} = 8$

68. Potassium permanganate on heating at 513 K gives a product which is: [27 Aug, 2021 (Shift-II)]

(a) paramagnetic and colourless (b) diamagnetic and colourless

(c) diamagnetic and green (d) paramagnetic and green

Sol. (d) $K_2\overset{+6}{Mn}O_4$ (green), Mn^{6+} contains one unpaired electron, thus paramagnetic, and green in colour.

69. $KMnO_4$ oxidises I^- in acidic and neutral/faintly alkaline solution, respectively, to

(a) I_2 and IO_3^- (b) I_2 and I_2 (c) IO_3^- and I_2 (d) IO_3^- and IO_3^-

Sol. (a)

70. Incorrect statement about K_2MnO_4:

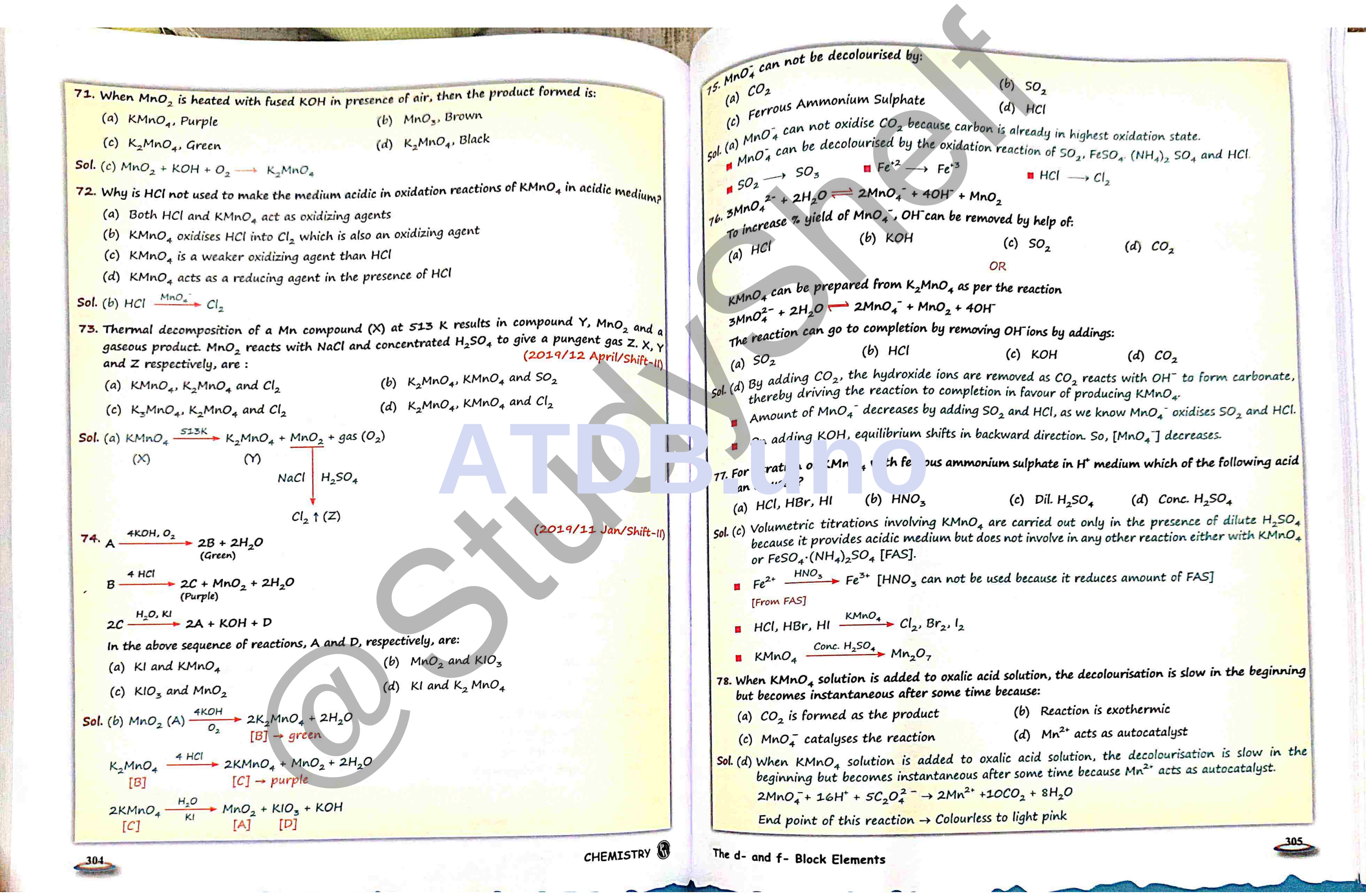
(a) It's prepared by reaction of pyrolusite with KOH and air.

(b) It is tetrahedral, paramagnetic and green compound

(c) 2pπ – 3pπ bonding is present

(d) In acidic medium, it is disproportionate to produce compound with Mn(VII) and Mn(IV).

Sol. (c) The manganate ion is tetrahedral; the π bonding takes place by overlap of p orbitals of oxygen with d orbitals of manganese.



71. When MnO_2 is heated with fused KOH in presence of air, then the product formed is:

(a) $KMnO_4$, Purple (b) MnO_3, Brown

(c) K_2MnO_4, Green (d) K_2MnO_4, Black

Sol. (c) $MnO_2 + KOH + O_2 \longrightarrow K_2MnO_4$

72. Why is HCl not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium?

(a) Both HCl and $KMnO_4$ act as oxidizing agents

(b) $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidizing agent

(c) $KMnO_4$ is a weaker oxidizing agent than HCl

(d) $KMnO_4$ acts as a reducing agent in the presence of HCl

Sol. (b) $HCl \xrightarrow{MnO_4^-} Cl_2$

73. Thermal decomposition of a Mn compound (X) at 513 K results in compound Y, MnO_2 and a gaseous product. MnO_2 reacts with NaCl and concentrated H_2SO_4 to give a pungent gas Z. X, Y and Z respectively, are : (2019/12 April/Shift-II)

(a) $KMnO_4$, K_2MnO_4 and Cl_2 (b) K_2MnO_4, $KMnO_4$ and SO_2

(c) K_3MnO_4, K_2MnO_4 and Cl_2 (d) K_2MnO_4, $KMnO_4$ and Cl_2

Sol. (a) $\underset{(X)}{KMnO_4} \xrightarrow{513K} \underset{(Y)}{K_2MnO_4} + \underline{MnO_2} + gas\ (O_2)$

$$MnO_2 \xrightarrow{NaCl \mid H_2SO_4} Cl_2 \uparrow (Z)$$

74. $A \xrightarrow{4KOH,\ O_2} \underset{(Green)}{2B} + 2H_2O$ (2019/11 Jan/Shift-II)

$B \xrightarrow{4\ HCl} \underset{(Purple)}{2C} + MnO_2 + 2H_2O$

$2C \xrightarrow{H_2O,\ KI} 2A + KOH + D$

In the above sequence of reactions, A and D, respectively, are:

(a) KI and $KMnO_4$ (b) MnO_2 and KIO_3

(c) KIO_3 and MnO_2 (d) KI and K_2MnO_4

Sol. (b) $MnO_2\ (A) \xrightarrow[O_2]{4KOH} \underset{[B] \rightarrow green}{2K_2MnO_4} + 2H_2O$

$\underset{[B]}{K_2MnO_4} \xrightarrow{4\ HCl} \underset{[C] \rightarrow purple}{2KMnO_4} + MnO_2 + 2H_2O$

$\underset{[C]}{2KMnO_4} \xrightarrow[KI]{H_2O} \underset{[A]}{MnO_2} + \underset{[D]}{KIO_3} + KOH$

75. MnO_4^- can not be decolourised by:

(a) CO_2 (b) SO_2

(c) Ferrous Ammonium Sulphate (d) HCl

Sol. (a) MnO_4^- can not oxidise CO_2 because carbon is already in highest oxidation state.

- MnO_4^- can be decolourised by the oxidation reaction of SO_2, $FeSO_4 \cdot (NH_4)_2SO_4$ and HCl.
- $SO_2 \longrightarrow SO_3$ ■ $Fe^{+2} \longrightarrow Fe^{+3}$ ■ $HCl \longrightarrow Cl_2$

76. $3MnO_4^{2-} + 2H_2O \rightleftharpoons 2MnO_4^- + 4OH^- + MnO_2$

To increase % yield of MnO_4^-, OH^- can be removed by help of:

(a) HCl (b) KOH (c) SO_2 (d) CO_2

OR

$KMnO_4$ can be prepared from K_2MnO_4 as per the reaction

$3MnO_4^{2-} + 2H_2O \rightleftharpoons 2MnO_4^- + MnO_2 + 4OH^-$

The reaction can go to completion by removing OH^- ions by addings:

(a) SO_2 (b) HCl (c) KOH (d) CO_2

Sol. (d) By adding CO_2, the hydroxide ions are removed as CO_2 reacts with OH^- to form carbonate, thereby driving the reaction to completion in favour of producing $KMnO_4$.

- Amount of MnO_4^- decreases by adding SO_2 and HCl, as we know MnO_4^- oxidises SO_2 and HCl.
- On adding KOH, equilibrium shifts in backward direction. So, $[MnO_4^-]$ decreases.

77. For titration of $KMnO_4$ with ferrous ammonium sulphate in H^+ medium which of the following acid can be used?

(a) HCl, HBr, HI (b) HNO_3 (c) Dil. H_2SO_4 (d) Conc. H_2SO_4

Sol. (c) Volumetric titrations involving $KMnO_4$ are carried out only in the presence of dilute H_2SO_4 because it provides acidic medium but does not involve in any other reaction either with $KMnO_4$ or $FeSO_4 \cdot (NH_4)_2SO_4$ [FAS].

- $\underset{[From\ FAS]}{Fe^{2+}} \xrightarrow{HNO_3} Fe^{3+}$ [HNO_3 can not be used because it reduces amount of FAS]
- $HCl, HBr, HI \xrightarrow{KMnO_4} Cl_2, Br_2, I_2$
- $KMnO_4 \xrightarrow{Conc.\ H_2SO_4} Mn_2O_7$

78. When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because:

(a) CO_2 is formed as the product (b) Reaction is exothermic

(c) MnO_4^- catalyses the reaction (d) Mn^{2+} acts as autocatalyst

Sol. (d) When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because Mn^{2+} acts as autocatalyst.

$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

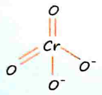
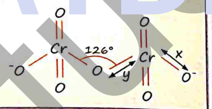
End point of this reaction → Colourless to light pink

79. E°_{cell} of reaction of $KMnO_4$ with H_2O is +ve, even $KMnO_4$ can be used as analytical reagent with H_2O. How can you explain it?

Sol. Because the reaction rate is extremely slow under normal conditions; essentially, the reaction is kinetically inhibited despite its positive E°cell, meaning it takes a very long time to occur at room temperature, allowing for practical use in analysis. This slow reaction rate allows $KMnO_4$ to be used in analytical chemistry as a titrant, where the colour change upon reduction is readily observed when reacting with a suitable reducing agent.

OXI-ANIONS OF Cr

$$CrO_4^{2-} \underset{^-OH}{\overset{H^+}{\rightleftharpoons}} Cr_2O_7^{2-}$$

☐ Chromate ion ☐ Yellow Colour ☐ Cr^{+6} : d° ☐ Diamagnetic ☐ d^3s (Tetrahedral) ☐ All Cr – O bonds are same due to resonance	☐ Dichromate ion ☐ Orange colour ☐ Cr^{+6} : d° ☐ Diamagnetic ☐ d^3 s (tetrahedral) Terminal Cr–O bond length (x) < Bridged Cr–O bond length (y) small due to resonance
	

K₂Cr₂O₇ [ORANGE, SOLID]

Preparation of Potassium Dichromate

☐ From Chromite Ore: $FeCr_2O_4$ $[FeO.Cr_2O_3]$

- $FeCr_2O_4 + Na_2CO_3 + O_2 \longrightarrow Na_2CrO_4 + CO_2\uparrow + Fe_2O_3$

$$\left.\begin{array}{l} Na_2CO_3 \equiv \underset{\text{(Basic oxide)}}{Na_2O} \cdot \underset{\text{(Acidic oxide)}}{CO_2} \\ FeCr_2O_4 \equiv FeO \cdot Cr_2O_3 \xrightarrow{O_2} \underset{\text{(Basic oxide)}}{Fe_2O_3} + \underset{\text{(Acidic oxide)}}{CrO_3} \end{array}\right] \rightarrow \boxed{Na_2O + CrO_3 \longrightarrow Na_2CrO_4}$$

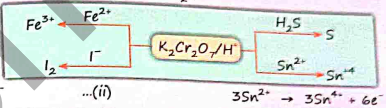
- $\underset{\text{(yellow solution)}}{Na_2CrO_4} \xrightarrow[H^+]{H_2SO_4} Na_2Cr_2O_7 \xrightarrow[KCl]{} K_2Cr_2O_7$ (Orange crystals) + NaCl

$K_2Cr_2O_7$ and NaCl both are water soluble and hence fractional crystallization is carried out. NaCl crystallizes out first and is filtered off. Then $K_2Cr_2O_7$ is crystallized out further.

Reactions of K₂Cr₂O₇

1. $K_2Cr_2O_7$ is a very important chemical in leather industry and in the preparation of azo compounds.
2. $K_2Cr_2O_7$ is used as a primary standard in volumetric analysis.
3. In acidic medium, $Cr_2O_7^{2-}$ acts as oxidising agent.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{+3} + 7H_2O \quad \text{...(i)}$$



$6I^- \rightarrow 3I_2 + 6e^-$ ...(ii)

$3Sn^{2+} \rightarrow 3Sn^{4+} + 6e^-$ ...(iii)

$3H_2S \rightarrow 6H^+ + 3S + 6e^-$ ...(iv)

$6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$ ...(v)

The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent–

By equation (i) & (ii) → $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$

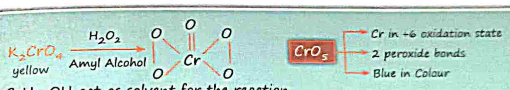
By equation (i) & (iii) → $Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \rightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$

By equation (i) & (v) → $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

Sodium and potassium dichromates are strong oxidising agents, the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry.

Heating effect $\overset{+6}{K_2Cr_2O_7} \xrightarrow{\Delta} \overset{+3}{Cr_2O_3} + \overset{+6}{K_2CrO_4} + \overset{\text{Zero}}{O_2}$

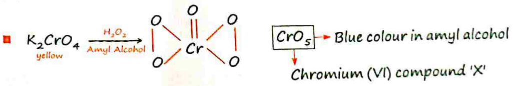
Note



Amyl alcohol $C_5H_{11}OH$ act as solvent for the reaction.

80. An acidified solution of potassium chromate was layered with an equal volume of amyl alcohol. When it was shaken after the addition of 1 mL of 3% H_2O_2, a blue alcohol layer was obtained. The blue color is due to the formation of a chromium (VI) compound 'X'. What is the number of oxygen atoms bonded to chromium through only single bonds in a molecule of X? (JEE Adv. 2020)

Sol. (4)



- No. of oxygen atoms bonded to Cr through only single bonds ≡ 4

81. Mn^{2+} can be oxidised to MnO_4^- by ... (IIT JEE 1981)
(SnO_2, PbO_2, BaO_2)

Sol. [Only PbO_2]

- $2Mn^{2+} + 5PbO_2 + 4H^+ \rightarrow 2MnO_4^- + 5Pb^{2+} + 2H_2O$
- SnO_2 can not act as oxidising agent because Sn^{4+} is more stable [SnO_2] than Sn^{+2} [SnO].
- $BaO_2 \equiv Ba^{2+} . O_2^{2-} \rightarrow$ Peroxide can act as an oxidising agent but not strong enough to oxidise Mn^{+2} to MnO_4^-.

82. Acidified $K_2Cr_2O_7$ can not oxidise:

(a) Green vitriol $FeSO_4 . 7H_2O$
(b) Mohr's salt $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$
(c) Ferric oxalate $Fe_2(C_2O_4)_3$
(d) Ferric sulphate $Fe_2(SO_4)_3$

Sol. (d)

$$Fe^{2+} \xrightarrow{K_2Cr_2O_7/H^+} Fe^{+3}$$
↓
[Green vitriol and Mohr's salt]

$$C_2O_4^{2-} \xrightarrow{K_2Cr_2O_7/H^+} 2CO_2\uparrow$$

$$2Fe^{3+} . 3SO_4^{2-} \xrightarrow{K_2Cr_2O_7/H^+} \text{No reaction}$$

83. Consider the following reactions:

$$NaCl + K_2Cr_2O_7 + \underset{\text{(conc.)}}{H_2SO_4} \rightarrow (A) + \text{side products}$$

$$(A) + NaOH \rightarrow (B) + \text{Side products}$$

$$(B) + \underset{\text{(dilute)}}{H_2SO_4} + H_2O_2 \rightarrow (C) + \text{Side products}$$

The sum of the total number of atoms in one molecule each of (A), (B) and (C) is ______. [7 Jan, 2020 (Shift-II)]

Sol. [18.00] $4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 2KHSO_4 + 4NaHSO_4 + 3H_2O$

$$\underset{(A)}{CrO_2Cl_2} + 4NaOH \rightarrow \underset{(B)}{Na_2CrO_4} + 2NaCl + 2H_2O$$

$$\underset{(B)}{Na_2CrO_4} + H_2SO_4 + 2H_2O_2 \rightarrow \underset{(C)}{CrO_5} + Na_2SO_4 + 3H_2O$$

Total no. of atoms in A, B and C = 5 + 7 + 6 = 18

(A) = CrO_2Cl_2, (B) = Na_2CrO_4, (C) = CrO_5

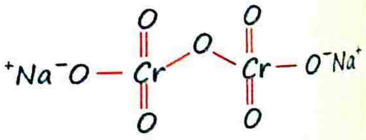
84. The number of terminal oxygen atoms present in the product B obtained from the following reaction is________. [29 June, 2022 (Shift-1)]

$$FeCr_2O_4 + Na_2CO_3 + O_2 \longrightarrow A + Fe_2O_3 + CO_2$$

$$A + H^+ \longrightarrow B + H_2O + Na^+$$

Sol. [6] $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow \underset{(A)}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$

$$\underset{(A)}{2Na_2CrO_4} + 2H^+ \longrightarrow \underbrace{Na_2Cr_2O_7}_{(B)} + 2Na + H_2O$$



Hence, there are 6 terminal oxygen atoms present in the product B.

85. Given below are two statements

Statement-I: Aqueous solution of $K_2Cr_2O_7$ is preferred as a primary standard in volumetric analysis over $Na_2Cr_2O_7$ aqueous solution.

Statement-II: $K_2Cr_2O_7$ has a higher solubility in water than $Na_2Cr_2O_7$ [10 April, 2023 (Shift-I)]

(a) Both Statement-I and Statement-II are true
(b) Both Statement-I and Statement-II are false
(c) Statement-I is true but Statement-II is false
(d) Statement-I is false but Statement-II is true

Sol. (c) (1) Since, $Na_2Cr_2O_7$ is hygroscopic in nature and $K_2Cr_2O_7$ is not, hence $K_2Cr_2O_7$ is generally preferred over $Na_2Cr_2O_7$ in volumetric analysis.

(2) It is less soluble than $Na_2Cr_2O_7$ as sodium salts has greater solubility in water.

86. A solution of CrO_5 in amyl alcohol has a..... colour (2023/29 Jan/Shift-II)

(a) Green (b) Orange-Red (c) Yellow (d) Blue

Sol. (d) A solution of CrO_5 in amyl alcohol has a blue colour.

87. $Cr_2O_7^{2-} \xrightleftharpoons[Y]{X} 2CrO_4^{2-}$, X and Y are respectively

(a) $X = OH^-, Y = H^+$ (b) $X = H^+, Y = OH^-$
(c) $X = OH^-, Y = H_2O_2$ (d) $X = H_2O_2, Y = OH^-$

Sol. (a) $Cr_2O_7^{2-} \xrightleftharpoons[H^+]{^-OH} CrO_4^{-}$

88. In which of the following oxo anion, all Cr – O bond lengths are not identical?

(a) MnO_4^- (b) CrO_4^{2-} (c) MnO_4^{2-} (d) $Cr_2O_7^{2-}$

Sol. (d) In $Cr_2O_7^{2-}$ ion, the two Cr–O bonds which share an oxygen atom at the common vertex of two tetrahedral units are longer than the other six equivalent Cr–O bonds.

(JEE Adv. 2019)

89. Fusion of MnO_2 with KOH in presence of O_2 produces a salt W. Alkaline solution of W upon electrolytic oxidation yields another salt X. The manganese containing ions present in W and X, respectively, are Y and Z. Correct statement(s) is (are)

(a) Both Y and Z are coloured and have tetrahedral shape
(b) Y is diamagnetic in nature while Z is paramagnetic
(c) In both Y and Z, π-bonding occurs between p-orbitals of oxygen and d-orbitals of manganese
(d) In aqueous acidic solution, Y undergoes disproportionation reaction to give Z and MnO_2

Sol. (a), (c) and (d)

$$\underset{}{MnO_2 + KOH + O_2} \longrightarrow \underset{[W]}{K_2MnO_4} \xrightarrow[\text{Oxidation}]{\text{Electrolytic}} \underset{[X]}{KMnO_4}$$

$Y \rightarrow MnO_4^{-2}$
$Z \rightarrow MnO_4^{-}$

HALIDES OF d-BLOCK ELEMENTS

- ☐ The ability of F to stabilise the highest oxidation state is due to 2 factors-
  - (i) High lattice energy [in ionic compound – CoF_3]
  - (ii) High bond enthalpy [in covalent compound –VF_5, CrF_6]
- ☐ The +7 state for Mn is not represented in simple halides (MnF_7 does not exist but oxohalide of Mn, MnO_3F has +7 oxidation state.)
- ☐ Highest Mn fluoride is MnF_4 whereas the highest oxide is Mn_2O_7.
  The ability of oxygen to form multiple bonds with metals explains its superiority (means fluorine forms single bond with metal but oxygen forms double bond with metal).

Oxidation Number	Formulas of Halides of 3d Metals								
+6			CrF_6						
+5		VF_5	CrF_5						
+4	TiX_4	VX'_4	CrX_4	MnF_4					
+3	TiX_3	VX_3	CrX_3	MnF_3	FeX'_3	CoF_3			
+2	TiX'''_2	VX_2	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX''_2	ZnX_2
+1								CuX'''	

Key: $X = F \to I$; $X' = F \to Br$; $X'' = F, Cl$; $X''' = Cl \to$

- ☐ V^{+5} is represented only by VF_5. The other halides, however, undergo hydrolysis to give oxohalides VOY_3. (Y = Cl, Br, I).

$$VCl_5\text{ (unstable)} \xrightarrow{\text{moist}} VOCl_3 + 2HCl$$

- ☐ Another feature of fluorides is their instability in the low oxidation states VY_2 (Y = Cl, Br, or I).
- ☐ All Cu(II) halides are known except the iodide because Cu^{2+} oxidises I^- to I_2. CuF_2, $CuCl_2$ & $CuBr_2$ exist but CuI_2 does not exist because-

$$\text{(a) } Cu^{2+} + 2I^- \longrightarrow I_2 + Cu^+$$
$$\text{(b) } 2Cu^+ + 2I^- \longrightarrow Cu_2I_2$$

- ☐ Many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

$$\underset{(aq.)}{2Cu^+} \longrightarrow \underset{(aq.)}{Cu^{2+}} + Cu$$

- ◆ Hydration Energy : Cu^{2+} > Cu^+
- ◆ $[\text{Hydration Energy}]_{Cu^{2+}} >> [\text{Second ionisation energy}]_{Cu}$

The stability of $Cu^{2+}_{(aq)}$ rather than $Cu^+_{(aq)}$ is due to the much more negative ΔH_{hyd} of $Cu^{2+}_{(aq)}$ than Cu^+, which more than compensates for the second ionisation enthalpy of Cu.

90. When Cu^{2+} ion is treated with KI, a white precipitate is formed. Explain the reaction with the help of a chemical equation.

Sol. Reduction of Cu^{2+} to Cu^{+} takes place due to reaction with I^{-} ion.

$$2Cu^{2+} + 4I^{-} \longrightarrow \underset{\text{White ppt.}}{Cu_2I_2} + I_2$$

91. Out of Cu_2Cl_2 and $CuCl_2$, which is more stable and why?

Sol. $CuCl_2$ is more stable than Cu_2Cl_2. The stability of $CuCl_2$ is because of higher enthalpy of hydration of $Cu^{2+}(aq)$ than that of $Cu^{+}(aq)$.

92. Cu^{2+} salt reacts with potassium iodide to give (2021/20 July)

(a) Cu_2I_2 (b) Cu_2I_3 (c) CuI (d) $Cu(I_3)_2$

Sol. (a) $Cu^{2+} + 2KI \longrightarrow \underset{\text{Unstable}}{CuI_2\downarrow} + 2K^{+}$

I^{-} is strong R.A. It reduces Cu^{2+} to Cu^{+}

$2CuI_2 \longrightarrow Cu_2I_2\downarrow + I_2$

93. The stability of Cu^{2+} is more than Cu^{+} salts in aqueous solutions due to: [NEET 2023]

(a) second ionisation enthalpy (b) first ionisation enthalpy

(c) enthalpy of atomisation (d) hydration energy

Sol. (d)

94. Which of the following statements are INCORRECT? [NEET 2023]

A. All the transition metals except scandium form MO oxides which are ionic.

B. The highest oxidation number corresponding to group number in transition metal oxides is attained in Sc_2O_3 to Mn_2O_7.

C. Basic character increases from V_2O_3 to V_2O_4 to V_2O_5.

D. V_2O_4 dissolves in acids to give VO_4^{3-} salts.

E. CrO is basic but Cr_2O_3 is amphoteric.

Choose the correct answer from the options given below:

(a) B and C only (b) A and E only (c) B and D only (d) C and D only

Sol. (d)

95. In the neutral or faintly alkaline medium, $KMnO_4$ oxidises iodide into iodate. The change in oxidation state of manganese in this reaction is from [NEET 2022]

(a) + 6 to + 5 (b) + 7 to + 4 (c) + 6 to + 4 (d) + 7 to + 3

Sol. (b)

96. Identify the incorrect statement. [NEET 2020]

(a) The transition metals and their compounds are known for their catalytic activity due to their ability to adopt multiple oxidation states and to form complexes.

(b) Interstitial compounds are those that are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals.

(c) The oxidation states of chromium in CrO_4^{2-} and $Cr_2O_7^{2-}$ are not the same.

(d) $Cr^{2+}(d^4)$ is a stronger reducing agent than $Fe^{2+}(d^6)$ in water.

Sol. (c)

97. The manganate and permanganate ions are tetrahedral, due to: [NEET 2019]

(a) The p-bonding involves overlap of p-orbitals of oxygen with d-orbitals of manganese

(b) There is no p-bonding

(c) The p-bonding involves overlap of p-orbitals of oxygen with p-orbitals of manganese

(d) The p-bonding involves overlap of d-orbitals of oxygen with d-orbitals of manganese

Sol. (a)

98. Which one of the following ions exhibits d-d transition and paramagnetism as well? [NEET 2018]

(a) CrO_4^{2-} (b) $Cr_2O_7^{2-}$ (c) MnO_4^{2-} (d) MnO_4^-

Sol. (c)

99. Name the gas that can readily decolourise acidified $KMnO_4$ solution: [NEET 2017-Delhi]

(a) P_2O_5 (b) CO_2 (c) SO_2 (d) NO_2

Sol. (c)

100. Which one of the following statements is correct when SO_2 is passed through acidified $K_2Cr_2O_7$ solution? [NEET 2016-I]

(a) SO_2 is reduced (b) Green $Cr_2(SO_4)_3$ is formed

(c) The solution turns blue (d) The solution is decolourised

Sol. (b)

101. Assuming complete ionisation, same moles of which of the following compounds will require the least amount of acidified $KMnO_4$ for complete oxidation? [NEET 2015 Re]

(a) $Fe(NO_2)_2$ (b) $FeSO_4$ (c) $FeSO_3$ (d) FeC_2O_4

Sol. (b)

102. Which of the statements is not true? [NEET 2012 Re]

(a) $K_2Cr_2O_7$ solution becomes yellow on increasing the pH beyond 7

(b) On passing H_2S through acidified $K_2Cr_2O_7$ solution, a milky colour is observed

(c) $Na_2Cr_2O_7$ is preferred over $K_2Cr_2O_7$ in volumetric analysis

(d) $K_2Cr_2O_7$ solution in acidic medium is orange

Sol. (c)

103. Acidified $K_2Cr_2O_7$ solution turns green when Na_2SO_3 is added to it. This is due to the formation of: [NEET 2011 Pre]

(a) $CrSO_4$ (b) $Cr_2(SO_4)_3$ (c) CrO_4^{2-} (d) $Cr_2(SO_3)_3$

Sol. (b)

104. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is: [NEET 2007]

(a) 4/5 (b) 2/5 (c) 1 (d) 3/5

Sol. (b)

105. The number of moles of $KMnO_4$ reduced by one mole of KI in alkaline medium is: [NEET 2005]

(a) 2/5 (b) 5 (c) 1 (d) 2

Sol. (d)

f-BLOCK ELEMENT

The f-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium).

Lanthanoids	Ce$_{58}$	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu$_{71}$
Actinoids	Th$_{90}$	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr$_{103}$

- ☐ All elements are radioactive in actinoid series.
- ☐ Promethium is the only synthetic radioactive in Lanthanides.
- ☐ Elements of f-block are soft in nature and on expose to air get oxidized.

LANTHANIDE SERIES

Electronic Configuration

La$_{57}$ → [Xe]$6s^2 5d^1$

Ce$_{58}$ → Lu$_{71}$

Ce$_{58}$ → [Xe]$6s^2 5d^1 4f^1$

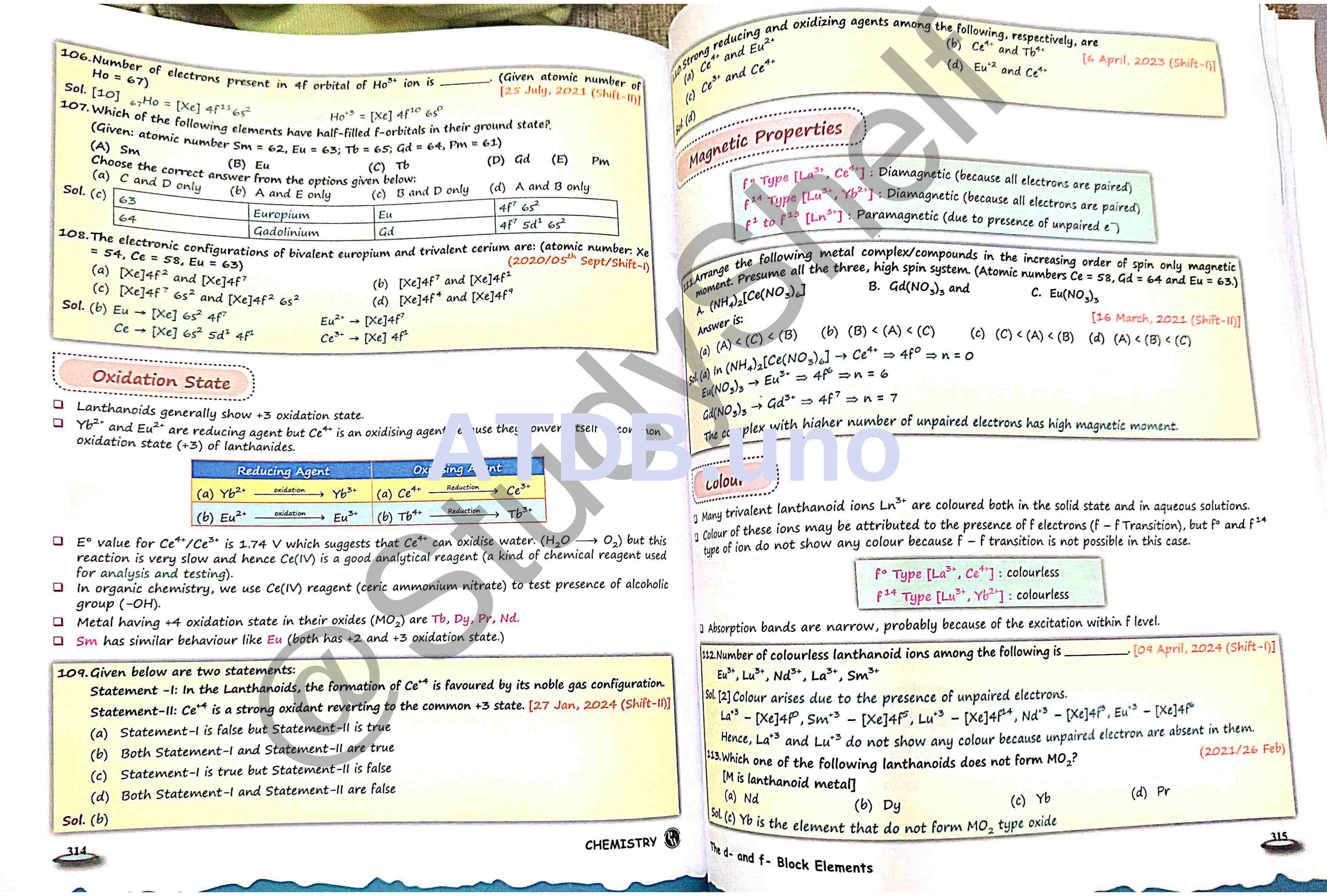
Lu$_{71}$ → [Xe]$6s^2 5d^1 4f^{14}$

Hf$_{72}$ → [Xe]$6s^2 5d^2 4f^{14}$

Atomic Number	Name	Symbol (Ln)	Electronic Configuration
58	Cerium	Ce	$4f^1\ 5d^1\ 6s^2$
59	Praseodymium	Pr	$4f^3\ 6s^2$
60	Neodymium	Nd	$4f^4 6s^2$
61	Promethium	Pm	$4f^5\ 6s^2$
62	Samarium	Sm	$4f^6 6s^2$
63	Europium	Eu	$4f^7 6s^2$
64	Gadolinium	Gd	$4f^7\ 5d^1\ 6s^2$
65	Terbium	Tb	$4f^9\ 6s^2$
66	Dysprosium	Dy	$4f^{10} 6s^2$
67	Holmium	Ho	$4f^{11} 6s^2$
68	Erbium	Er	$4f^{12} 6s^2$
69	Thulium	Tm	$4f^{13} 6s^2$
70	Ytterbium	Yb	$4f^{14} 6s^2$
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$

Important configuration
1st element → Ce: [Xe] $4f^1\ 5d^1\ 6s^2$
7th element → Gd: [Xe] $4f^7\ 5d^1\ 6s^2$
14th element → Lu: [Xe] $4f^{14}\ 5d^1\ 6s^2$

- ☐ The irregularities in the electronic configurations of the lanthanoids are related to the stabilities of the f^0, f^7 and f^{14} occupancies of the 4f orbitals.



106. Number of electrons present in 4f orbital of Ho^{3+} ion is ________. (Given atomic number of Ho = 67) [25 July, 2021 (Shift-II)]

Sol. [10] $_{67}Ho = [Xe]\ 4f^{11} 6s^2$ $\quad Ho^{+3} = [Xe]\ 4f^{10}\ 6s^0$

107. Which of the following elements have half-filled f-orbitals in their ground state?
(Given: atomic number Sm = 62, Eu = 63; Tb = 65; Gd = 64, Pm = 61)

(A) Sm (B) Eu (C) Tb (D) Gd (E) Pm

Choose the correct answer from the options given below:

(a) C and D only (b) A and E only (c) B and D only (d) A and B only

Sol. (c)

63	Europium	Eu	$4f^7\ 6s^2$
64	Gadolinium	Gd	$4f^7\ 5d^1\ 6s^2$

108. The electronic configurations of bivalent europium and trivalent cerium are: (atomic number: Xe = 54, Ce = 58, Eu = 63) (2020/05th Sept/Shift-I)

(a) $[Xe]4f^2$ and $[Xe]4f^7$
(b) $[Xe]4f^7$ and $[Xe]4f^1$
(c) $[Xe]4f^7\ 6s^2$ and $[Xe]4f^2\ 6s^2$
(d) $[Xe]4f^4$ and $[Xe]4f^9$

Sol. (b) $Eu \rightarrow [Xe]\ 6s^2\ 4f^7$ $\quad Eu^{2+} \rightarrow [Xe]4f^7$
$Ce \rightarrow [Xe]\ 6s^2\ 5d^1\ 4f^1$ $\quad Ce^{3+} \rightarrow [Xe]\ 4f^1$

Oxidation State

- Lanthanoids generally show +3 oxidation state.
- Yb^{2+} and Eu^{2+} are reducing agent but Ce^{4+} is an oxidising agent because they convert itself to common oxidation state (+3) of lanthanides.

Reducing Agent	Oxidising Agent
(a) $Yb^{2+} \xrightarrow{\text{oxidation}} Yb^{3+}$	(a) $Ce^{4+} \xrightarrow{\text{Reduction}} Ce^{3+}$
(b) $Eu^{2+} \xrightarrow{\text{oxidation}} Eu^{3+}$	(b) $Tb^{4+} \xrightarrow{\text{Reduction}} Tb^{3+}$

- E° value for Ce^{4+}/Ce^{3+} is 1.74 V which suggests that Ce^{4+} can oxidise water. ($H_2O \longrightarrow O_2$) but this reaction is very slow and hence Ce(IV) is a good analytical reagent (a kind of chemical reagent used for analysis and testing).
- In organic chemistry, we use Ce(IV) reagent (ceric ammonium nitrate) to test presence of alcoholic group (–OH).
- Metal having +4 oxidation state in their oxides (MO_2) are Tb, Dy, Pr, Nd.
- Sm has similar behaviour like Eu (both has +2 and +3 oxidation state.)

109. Given below are two statements:
Statement –I: In the Lanthanoids, the formation of Ce^{+4} is favoured by its noble gas configuration.
Statement–II: Ce^{+4} is a strong oxidant reverting to the common +3 state. [27 Jan, 2024 (Shift-II)]

(a) Statement–I is false but Statement–II is true
(b) Both Statement–I and Statement–II are true
(c) Statement–I is true but Statement–II is false
(d) Both Statement–I and Statement–II are false

Sol. (b)

110. Strong reducing and oxidizing agents among the following, respectively, are [6 April, 2023 (Shift-I)]

(a) Ce^{4+} and Eu^{2+}
(b) Ce^{4+} and Tb^{4+}
(c) Ce^{3+} and Ce^{4+}
(d) Eu^{+2} and Ce^{4+}

Sol. (d)

Magnetic Properties

f^0 Type [La^{3+}, Ce^{4+}] : Diamagnetic (because all electrons are paired)
f^{14} Type [Lu^{3+}, Yb^{2+}] : Diamagnetic (because all electrons are paired)
f^1 to f^{13} [Ln^{3+}] : Paramagnetic (due to presence of unpaired e^-)

111. Arrange the following metal complex/compounds in the increasing order of spin only magnetic moment. Presume all the three, high spin system. (Atomic numbers Ce = 58, Gd = 64 and Eu = 63.)

A. $(NH_4)_2[Ce(NO_3)_6]$ B. $Gd(NO_3)_3$ and C. $Eu(NO_3)_3$

Answer is: [16 March, 2021 (Shift-II)]

(a) (A) < (C) < (B) (b) (B) < (A) < (C) (c) (C) < (A) < (B) (d) (A) < (B) < (C)

Sol. (a) In $(NH_4)_2[Ce(NO_3)_6] \rightarrow Ce^{4+} \Rightarrow 4f^0 \Rightarrow n = 0$
$Eu(NO_3)_3 \rightarrow Eu^{3+} \Rightarrow 4f^6 \Rightarrow n = 6$
$Gd(NO_3)_3 \rightarrow Gd^{3+} \Rightarrow 4f^7 \Rightarrow n = 7$
The complex with higher number of unpaired electrons has high magnetic moment.

Colour

- Many trivalent lanthanoid ions Ln^{3+} are coloured both in the solid state and in aqueous solutions.
- Colour of these ions may be attributed to the presence of f electrons (f – f Transition), but f° and f^{14} type of ion do not show any colour because f – f transition is not possible in this case.

f° Type [La^{3+}, Ce^{4+}] : colourless
f^{14} Type [Lu^{3+}, Yb^{2+}] : colourless

- Absorption bands are narrow, probably because of the excitation within f level.

112. Number of colourless lanthanoid ions among the following is ________. [09 April, 2024 (Shift-I)]

Eu^{3+}, Lu^{3+}, Nd^{3+}, La^{3+}, Sm^{3+}

Sol. [2] Colour arises due to the presence of unpaired electrons.
La^{+3} – $[Xe]4f^0$, Sm^{+3} – $[Xe]4f^5$, Lu^{+3} – $[Xe]4f^{14}$, Nd^{+3} – $[Xe]4f^3$, Eu^{+3} – $[Xe]4f^6$
Hence, La^{+3} and Lu^{+3} do not show any colour because unpaired electron are absent in them.

113. Which one of the following lanthanoids does not form MO_2? (2021/26 Feb)
[M is lanthanoid metal]

(a) Nd (b) Dy (c) Yb (d) Pr

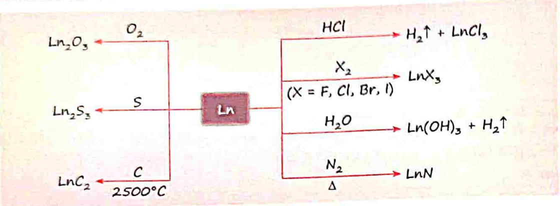
Sol. (c) Yb is the element that do not form MO_2 type oxide

114. The lanthanoid that does NOT show +4 oxidation state is: (2020/06 Sept/Shift-I)

(a) Dy (b) Ce (c) Eu (d) Tb

Sol. (c) Eu does not exhibit the +4 oxidation state.

Reactions of Lanthanides



- ☐ Ln forms oxide Ln_2O_3 and hydroxide $Ln(OH)_3$ and both are basic like alkaline earth metal (such as Ca) oxides and hydroxides.
- ☐ On moving from left to right, basicity of lanthanoid hydroxide decrea

Basicity : $La(OH)_3$ > $Ce(OH)_3$ > ………… > Lu(OH)

Size : La^{3+} > Ce^{3+} > ………… > 3+

Bigger cation has less polarising power so it has more ionic character in La—OH bond. Hence more basic.

Smaller cation has more polarising power so it has more covalent character in Lu—OH bond. Hence least basic.

- ☐ Basic nature gradually decreases from $Ce(OH)_3$ to $Lu(OH)_3$, due to high polarisation caused by gradual decrease in size M^{3+} ion. The hydroxides of lanthanoids $Ln(OH)_3$ are less basic than $Ca(OH)_2$ and more basic than $Al(OH)_3$.
- ☐ The first ionisation enthalpies of the lanthanoids are around 600 kJ mol^{-1}, the second about 1200 kJ mol^{-1} comparable with those of calcium.
- ☐ 3^{rd} Ionisation enthalpy of La, Gd , Lu is low.

  Because La^{3+} , Gd^{3+} and Lu^{3+} have stable electronic configuration $4f^0$, $4f^7$ and $4f^{14}$ respectively.

$La^{2+} \xrightarrow{IE_3} La^{3+}$: $[Xe]\ 4f^0$

$Gd^{2+} \xrightarrow{IE_3} Gd^{3+}$: $[Xe]\ 4f^7$

$Lu^{2+} \xrightarrow{IE_3} Lu^{3+}$: $[Xe]\ 4f^{14}$

- ☐ I^{st} and II^{nd} ionisation enthalpies of lanthanoids are comparable with Ca.
- ☐ In general, initial members of lanthanoid series have reactivity similar to Ca, but with increasing atomic number elements behave more like Al.
- ☐ $E^\circ_{Ln^{3+}/Ln}$ values are in range of -2.2 to -2.4 V except for Eu ($E^\circ_{Eu^{3+}/Eu^{2+}}$ = 2.0 V)

$Ln + 3H^{+} \rightarrow Ln$ 2

♦ Lanthanoids are good reducing agents because they have -ve reduction potential.

- ☐ Hardness increases as atomic number increases in lanthanides (Sm is a steel hard material and has highest melting point).
- ☐ Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.

Uses of Lanthanides

- ☐ The best single use of the lanthanoids is for the production of alloy steels for plates and pipes.
- ☐ A well known alloy is mischmetal which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al.
- ☐ An unseparated mixture of La and the lanthanoids called Misch metal is added to steel to improve its strength and workability. It is pyrophoric and also used in gas lighters.

- ☐ A good deal of mischmetal is used in Mg-based alloy to produce bullets, shell and lighter flint.
- ☐ Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking.
- ☐ Some individual Ln oxides are used as phosphors (materials that emit light when exposed to radiation) in television screens and similar fluorescing surfaces.
- ☐ In the context of a lighter, "flint" refers to the small piece of metal, typically an iron alloy, that is rubbed against a wheel to produce sparks and ignite the fuel.
- ☐ Pyrophoric materials are known for their tendency to ignite spontaneously when exposed to air, meaning they don't require an external ignition source like a flame or spark to start burning.

115. The incorrect statement(s) among (A) - (C) is (are) [4 Sept. 2020 (Shift-II)]

A. W(VI) is more stable than Cr (VI).

B. In the presence of HCl, permanganate titrations provide satisfactory results.

C. Some lanthanoid oxides can be used as phosphors.

(a) (A) and (B) only (b) (A) only

(c) (B) and (C) only (d) (B) only

Sol. (d)

116. Match the compounds/elements given in Column-I with uses given in Column-II

	Column-I (Compound / element)		Column-II (Uses)
(i)	Lanthanoid oxide	(a)	Production of iron alloy
(ii)	Lanthanoid	(b)	Television screen
(iii)	Misch metal	(c)	Petroleum cracking
(iv)	Magnesium based alloy is constituent of	(d)	Lanthanoid metal + iron
(v)	Mixed oxides of lanthanoids are employed	(e)	Bullets
		(f)	In X-ray screen

Sol. (i) → (b), (ii) → (a), (iii) → (d), (iv) → (e), (v) → (c)

117. Which one amongst the following are good oxidising agents?

(A) Sm^{2+} (B) Ce^{2+} (C) Ce^{4+} (D) Tb^{4+}

Choose the most appropriate answer from the options given below:

(a) A and B only (b) C and D only (c) D only (d) C only

Sol. (b) Ce^{4+} and Tb^{4+} ions are good oxidising agents.

118. Select reducing agent from Eu^{+2}, Yb^{+2}, Ce^{+4}, Mn^{+2}, Cr^{+2}, M[illegible].

(a) Mn^{2+}, Cr^{2+}, Eu^{2+} (b) Eu^{+2}, [illegible]$^{2+}$, [illegible]$^{2+}$

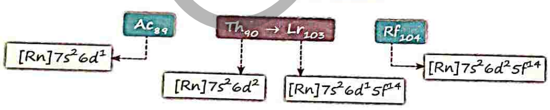
(c) Cr^{3+}, Eu^{2+}, Yb^{2+} (d) Cu^{+4}, [illegible]b^{2+}, [illegible]$^{3+}$

Sol. (b) Reducing agents are species that readily donate electrons. In the given list, Eu^{2+} and Yb^{2+} are well-known strong reducing agents because they easily oxidize to their +3 states. Similarly, Cr^{2+} is a strong reducing agent, as it tends to be oxidized to Cr^{3+}.

ACTINIDES

- The chemistry of the actinoids is much more complicated due to mainly 2 reasons–
  - (i) Due to the occurrence of a wide range of oxidation states in these elements.
  - (ii) Due to their radioactivity creates special problems in their study.

Actinide Series



Atomic Number	Name	Symbol	Electronic Configuration
90	Thorium	Th	$6d^27s^2$
91	Protactinium	Pa	$5f^26d^17s^2$
92	Uranium	U	$5f^36d^17s^2$
93	Neptunium	Np	$5f^46d^17s^2$
94	Plutonium	Pu	$5f^67s^2$
95	Americium	Am	$5f^77s^2$
96	Curium	Cm	$5f^76d^17s^2$
97	Berkelium	Bk	$5f^97s^2$
98	Californium	Cf	$5f^{10}7s^2$
99	Einstenium	Es	$5f^{11}7s^2$
100	Fermium	Fm	$5f^{12}7s^2$
101	Mendelevium	Md	$5f^{13}7s^2$
102	Nobelium	No	$5f^{14}7s^2$
103	Lawrencium	Lr	$5f^{14}6d^17s^2$

- Ur[illegible]ium [illegible] the heaviest naturally occurring element.
- Aft[illegible] [illegible]iu[illegible] 12 mo[illegible] elements have been artificially synthesized (having atomic number more than 92) and are someti[illegible] called the transuranium elements. (Z > 92)
- The actinoids are radioactive elements and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium (Z = 103). The latter members could be prepared only in nanogram quantities.
- The 5f orbitals resemble the 4f orbitals in their angular part of the wave-function, they are not as buried as 4f orbitals and hence 5f electrons can participate in bonding to a far greater extent.

Atomic Radius

- Actinides also shows contraction in radius similar to lanthanides due to poor shielding of f-electrons.

There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the actinoid contraction (like lanthanoid contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5f electrons.

Radii contraction is more for Actinides than the Lanthanides.

119. Actinoid contraction is greater than lanthanoid contraction. Why ?

Sol. In actinoids, 5f orbitals are filled. These 5f orbitals have a poorer shielding effect than 4f orbitals (in lanthanoids). Thus, the effective nuclear charge experienced by electrons in valence shells in case of actinoids is much more than experienced by lanthanoids. Hence, the size contraction in actinoids is greater as compared to that in lanthanoids.

Oxidation State of Actinides

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3		3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

- ☐ There is a greater range of oxidation states because the 5f, 6d and 7s levels are of comparable energies.
- ☐ The elements, in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements.
- ☐ The actinoids show in general +3 oxidation state.
- ☐ The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state.

Lanthanoids	Actinoids
1. Apart from +3 oxidation state, +2 and +4 are available for some of the elements.	1. Apart from +3 oxidation state, +4, +5, +6 and +7 available for some of the elements.
2. All elements are non-radioactive except Pm.	2. All elements are radioactive.
3. Lanthanoid contraction is less than actinoid contraction.	3. Actinoid contraction is more than lanthanoid contraction.
4. Lanthanoids have lesser tendency towards complex formation.	4. Actinoids have relatively stronger tendency towards complex formation.
5. Oxides and hydroxides are relatively less basic.	5. Oxides and hydroxides are more basic.
6. Elements have less density.	6. Elements have relatively more density.

120. The highest possible oxidation states of uranium and plutonium respectively, are:

(10th April 2019, Shift-II)

(a) 6 and 7 (b) 6 and 4 (c) 7 and 6 (d) 4 and 6

Sol. (a) Uranium typically exhibits a maximum oxidation state of +6. Plutonium, on the other hand, can attain a higher oxidation state of +7.

121. Which of the following property decreases on moving from Ce to Lu?

(a) Basic nature of oxides
(b) Covalent character of halides
(c) Paramagnetism of trivalent ions
(d) Complex forming tendency

Sol. (a)

122. The maximum number of possible oxidation states of actinoids are shown by:

(09th April 2019, Shift - II)

(a) Nobelium (No) and lawrencium (Lr)
(b) Actinium (Ac) and thorium (Th)
(c) Berkelium (Bk) and californium (Cf)
(d) Neptunium (Np) and plutonium (Pu)

Sol. (d)

123. Which one of the following statements related to lanthanons is incorrect?

(a) All the lanthanoids are much more reactive than aluminium
(b) Ce(+4) solutions are widely used as oxidizing agent in volumetric analysis
(c) Europium shows +2 oxidation state
(d) The basicity decrease as the ionic radius decreases from Pr to Lu

Sol. (a)

124. Which of the following statement is not correct?

(a) Lu^{3+} has the strongest tendency toward complex formation among trivalent lanthanoid ions.
(b) Ce has maximum composition in misch metal.
(c) f-Block elements can have electrons from f^0 to f^{14}.
(d) Nd, Np and Nb all are f-block elements.

Sol. (d) Nd is a lanthanide (f-block) and Np is an actinide (f-block), but Nb (niobium) is a d-block element, making option (d) incorrect.

(JEE Adv. 2014)

125. Consider the following list of reagents, acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$, HNO_3 and $Na_2S_2O_3$. The total number of reagents that can oxidise aqueous iodide to iodine is

Sol. (7)

- Acidified $K_2Cr_2O_7$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$ and HNO_3 oxidise aq. iodide to iodine.
- Alkaline $KMnO_4$ oxidise aq. iodide to IO_3^-.
- $Na_2S_2O_3$ is a strong reducing agent which on reaction with I_2 produces I^-

  $Na_2S_2O_3 + I_2 \rightarrow 2I^- + Na_2S_4O_6$

  Therefore, no reaction takes place between $Na_2S_2O_3$ and iodide ion.

[16 March, 2021 (Shift-II)]

126. Fex_2 and Fey_3 are known when x and y are

(a) x = F, Cl, Br, I and y = F, Cl, Br
(b) x = Cl, Br, I and y = F, Cl, Br, I
(c) x = F, Cl, Br, I and y = F, Cl, Br, I
(d) x = F, Cl, Br and y = F, Cl, Br, I

Sol. (a)

$$\underset{\text{(Unstable)}}{2FeI_3} \longrightarrow \underset{\text{(Stable)}}{2FeI_2} + I_2$$

Due to strong reducing nature of I^-

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

Remaining halides of Fe^{2+} and Fe^{3+} are stable.

127. Match the following aspects with the respective metal. [NEET 2020-Covid]

Aspects		Metal	
A.	The metal which reveals a maximum number of oxidation states	i.	Scandium
B.	The metal although placed in 3d block is considered not as a transition element	ii.	Copper
C.	The metal which does not exhibit variable oxidation states	iii.	Manganese
D.	The metal which in +1 oxidation state in aqueous solution undergoes disproportionation	iv.	Zinc

Select the correct option:

(a)	A–iii	B–iv	C–i	D–ii
(b)	A–iii	B–i	C–iv	D–ii
(c)	A–ii	B–iv	C–i	D–iii
(d)	A–i	B–iv	C–ii	D–iii

Sol. (a)

128. Match the metal ions given in Column-I with the spin magnetic moments of the ions given in Column-II and assign the correct code: [NEET 2018]

Column-I		Column-II	
A.	Co^{3+}	i.	$\sqrt{8}$ B.M
B.	Cr^{3+}	ii.	$\sqrt{35}$ B.M
C.	Fe^{3+}	iii.	$\sqrt{3}$ B.M
D.	Ni^{2+}	iv.	$\sqrt{24}$ B.M
		v.	$\sqrt{15}$ B.M

(a)	A–iv	B–v	C–ii	D–i
(b)	A–i	B–ii	C–iii	D–iv
(c)	A–iii	B–v	C–i	D–ii
(d)	A–iv	B–i	C–ii	D–iii

Sol. (a)

129. Which of the following processes does not involve oxidation of iron? [NEET 2015]

(a) Decolourisation of blue $CuSO_4$ solution by iron

(b) Formation of $Fe(CO)_5$ from Fe

(c) Liberation of H_2 from steam by iron at high temperature

(d) Rusting of iron sheets

Sol. (b)

130. Which one of the following does not correctly represent the correct order of the property indicated against it? [NEET 2012 Mains]

(a) Ti < V < Mn < Cr : increasing 2nd ionization enthalpy

(b) Ti < V < Cr < Mn : increasing number of oxidation states

(c) $Ti^{3+} < V^{3+} < Cr^{3+} < Mn^{3+}$: increasing magnetic moment

(d) Ti < V < Cr < Mn : increasing melting points

Sol. (d)

131. Which of the following ions will exhibit colour in aqueous solutions? [NEET 2010 Pre]

(a) Sc^{3+} (Z = 21) (b) La^{3+} (Z = 57) (c) Ti^{3+} (Z = 22) (d) Lu^{3+} (Z = 71)

Sol. (c)

132. Among K, Ca, Fe and Zn, the element which can form more than one binary compound with chlorine is [NEET 2004]

(a) Zn (b) K (c) Ca (d) Fe

Sol. (d)

133. Given below are two statements: [NEET 2025]

Statement I: Ferromagnetism is considered as an extreme form of paramagnetism.

Statement II: The number of unpaired electrons in a Cr^{2+} ion (Z = 24) is the same as that of a Nd^{3+} ion (Z = 60).

In the light of the above statements, choose the correct answer from the options given below:

(a) Both Statement I and Statement II are true (b) Both Statement I and Statement II are false

(c) Statement I is true but Statement II is false (d) Statement I is false but Statement II is true

Sol. (c)

134. Which of the following set of ions act as oxidising agents? [NEET 2024 Re]

(a) Ce^{4+} and Tb^{4+} (b) La^{3+} and Lu^{3+} (c) Eu^{2+} and Yb^{2+} (d) Eu^{2+} and Tb^{4+}

Sol. (a)

135. The UV-visible absorption bands in the spectra of lanthanoid ions are 'X', probably because of the excitation of electrons involving 'Y'. The 'X' and 'Y', respectively, are: [NEET 2024 Re]

(a) Broad and f orbitals (b) Narrow and f orbitals

(c) Broad and d and f orbitals (d) Narrow and d and f orbitals

Sol. (b)

136. The pair of lanthanoid ions which are diamagnetic is [NEET 2024]

(a) Gd^{3+} and Eu^{3+} (b) Pm^{3+} and Sm^{3+} (c) Ce^{4+} and Yb^{2+} (d) Ce^{3+} and Eu^{2+}

Sol. (c)

137. Match List-I with List-II: [NEET 2024 Re]

List-I (Block/group in periodic table)		List-II (Element)	
A.	Lanthanoid	I.	Ce
B.	d-block element	II.	As
C.	p-block element	III.	Cs
D.	s-block element	IV.	Mn

Choose the correct answer from the options given below:

(a) A-I, B-II, C-IV, D-III
(b) A-I, B-IV, C-III, D-II
(c) A-I, B-IV, C-II, D-III
(d) A-IV, B-I, C-II, D-III

Sol. (c)

138. Given below are two statements : one is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A): Ionisation enthalpies of early actinoids are lower than for early lanthanoids.

Reason (R): Electrons are entering 5f orbitals in actinoids which experience greater shielding from nuclear charge.

In the light of the above statements, choose the correct answer from the options given below: [NEET 2023-Manipur]

(a) (A) is true but (R) is false.
(b) (A) is false but (R) is true.
(c) Both (A) and (R) are true and (R) is the correct explanation of (A).
(d) Both (A) and (R) are true but (R) is not the correct explanation of (A).

Sol. (c)

139. Decrease in size from left to right in actinoid series is greater and gradual than that in lanthanoid series due to: [NEET 2022 Re]

(a) 5f orbitals have greater shielding effect
(b) 4f orbitals are penultimate
(c) 4f orbitals have greater shielding effect
(d) 5f orbitals have poor shielding effect

Sol. (d)

140. Gadolinium has a low value of third ionisation enthalpy because of [NEET 2022]

(a) high basic character
(b) small size
(c) high exchange enthalpy
(d) high electronegativity

Sol. (c)

141. The incorrect statement among the following is: [NEET 2021]

(a) Most of the trivalent Lanthanoid ions are colorless in the solid state
(b) Lanthanoids are good conductors of heat and electricity
(c) Actinoids are highly reactive metals, especially when finely divided
(d) Actinoid contraction is greater for element to element than Lanthanoid contraction

Sol. (a)

142. Identify the incorrect statement from the following: [NEET 2020-Covid]

(a) Lanthanoids reveal only +3 oxidation state.
(b) The lanthanoid ions other than the f^0 type and the f^{14} type are all paramagnetic.
(c) The overall decreases in atomic and ionic radii from lanthanum to lutetium is called lanthanoid contraction.
(d) Zirconium and Hafnium have identical radii of 160 pm and 159 pm, respectively as a consequence of lanthanoid contraction.

Sol. (a)

143. Match the element in Column-I with that in Column-II. [NEET 2020-Covid]

Column-I		Column-II	
A.	Copper	i.	Non-metal
B.	Fluorine	ii.	Transition metal
C.	Silicon	iii.	Lanthanoid
D.	Cerium	iv.	Metalloid

Select the correct option:

(a)	A-i	B-ii	C-iii	D-iv
(b)	A-ii	B-iv	C-i	D-iii
(c)	A-ii	B-i	C-iv	D-iii
(d)	A-iv	B-iii	C-i	D-ii

Sol. (c)

144. The reason for greater range of oxidation states in actinoids is attributed to: [NEET 2017-Delhi]

(a) 4f and 5d levels being close in energies

(b) The radioactive nature of actinoids

(c) Actinoid contraction

(d) 5f, 6d and 7s levels having comparable energies

Sol. (d)

145. Which one of the following statements related to lanthanons is incorrect? [NEET 2016-II]

(a) All the lanthanons are much more reactive than aluminium

(b) Ce(+4) solutions are widely used as oxidizing agent in volumetric analysis

(c) Europium shows +2 oxidation state.

(d) The basicity decreases as the ionic radius decreases from Pr to Lu.

Sol. (a)

146. The electronic configurations of Eu (Atomic Number 63) Gd (Atomic Number 64) and Tb (Atomic Number 65) are: [NEET 2016-I]

(a) $[Xe]4f^7 6s^2$, $[Xe]4f^7 5d^1 6s^2$ and $[Xe]4f^9 6s^2$

(b) $[Xe]4f^7 6s^2$, $[Xe]4f^8\ 6s^2$ and $[Xe]4f^8\ 5d^1 6s^2$

(c) $[Xe]4f^6\ 5d^1 6s^2$, $[Xe]4f^7\ 5d^1 6s^2$ and $[Xe]4f^9\ 5d^1 6s^2$

(d) $[Xe]4f^6\ 5d^1 6s^2$, $[Xe]4f^7\ 5d^1 6s^2$ and $[Xe]4f^8\ 5d^1 6s^2$

Sol. (a)

147. Gadolinium belongs to 4f series. Its atomic number is 64. Which of the following is the correct electronic configuration of gadolinium? [NEET 2015-Re]

(a) $[Xe]4f^6 5d^2 6s^2$ (b) $[Xe]4f^8 6d^2$ (c) $[Xe]4f^9 5s^1$ (d) $[Xe]4f^7 5d^1 6s^2$

Sol. (d)

148. Reason of lanthanoid contraction is: [NEET 2014]

(a) Increasing nuclear charge (b) Decreasing nuclear charge

(c) Decreasing screening effect (d) Negligible screening effect of 'f' orbitals

Sol. (d)

149. Which of the following lanthanoid ions is diamagnetic? (Atomic Number Ce = 58, Sm = 62, Eu = 63, Yb = 70) [NEET 2013]

(a) Ce^{2+} (b) Sm^{2+} (c) Eu^{2+} (d) Yb^{2+}

Sol. (d)

150. Which of the following exhibits only + 3 oxidation state? [NEET 2012 Mains]

(a) U (b) Th (c) Ac (d) Pa

Sol. (c)

151. Which of the following oxidation states is the most common among the lanthanoids? [NEET 2010 Mains]

(a) 4 (b) 2 (c) 5 (d) 3

Sol. (d)

152. Identify the incorrect statement among the following: [NEET 2007]

(a) Lanthanoid contraction is the accumulation of successive shrinkages.

(b) As a result of lanthanoid contraction, the properties of 4d series of the transition elements have no similarities with the 5d series of elements.

(c) Shielding power of 4f electrons is quite weak.

(d) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.

Sol. (b)

153. More number of oxidation states are exhibited by the actinoids than by the lanthanoids. The main reason for this is: [NEET 2006]

(a) More energy difference between 5f and 6d orbitals than that between 4f and 5d orbitals

(b) Lesser energy difference between 5f and 6d orbitals than that between 4f and 5d orbitals

(c) Greater metallic character of the lanthanoids than that of the corresponding actinoids

(d) More active nature of the actinoids

Sol. (b)

154. The main reason for larger number of oxidation states exhibited by the actinides than the corresponding lanthanides, is: [NEET 2005]

(a) Lesser energy difference between 5f and 6d orbitals than between 4f and 5d orbitals

(b) Larger atomic size of actinides than the lanthanides

(c) More energy difference between 5f and 6d orbitals than between 4f and 5d orbitals

(d) Greater reactive nature of the actinides than the lanthanides

Sol. (a)

155. Lanthanoids are: [NEET 2004]

(a) 14 elements in the seventh period
(atomic number = 90 to 103) that are filling 5f sublevel.

(b) 14 elements in the sixth period
(atomic number = 58 to 71) that are filling 4f sublevel

(c) 14 elements in the seventh period
(atomic number = 58 to 71) that are filling 4f sublevel

(d) 14 elements in the sixth period
(atomic number = 90 to 103) that are filling 4f sublevel

Sol. (b)

156. The correct order of ionic radii of Y^{3+}, La^{3+}, Eu^{3+} and Lu^{3+} is: [NEET 2003]
(Atomic numbers Y = 39, La = 57, Eu = 63, Lu = 71)

(a) $Y^{3+} < La^{3+} < Eu^{3+} < Lu^{3+}$ (b) $Y^{3+} < Lu^{3+} < Eu^{3+} < La^{3+}$

(c) $Lu^{3+} < Eu^{3+} < La^{3+} < Y^{3+}$ (d) $La^{3+} < Eu^{3+} < Lu^{3+} < Y^{3+}$

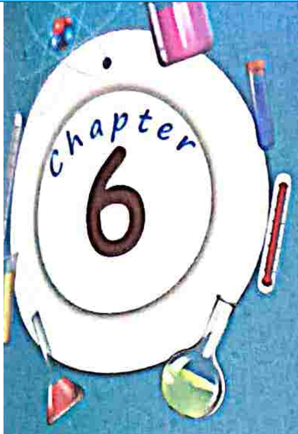
Sol. (b)

157. General electronic configuration of lanthanides is: [NEET 2002]

(a) $(n-2)\,f^{1-14}\,(n-1)\,s^2p^6d^{0-1}\,ns^2$ (b) $(n-2)\,f^{10-14}\,(n-1)\,d^{0-1}\,ns^2$

(c) $(n-2)\,f^{10-4}\,(n-1)\,d^{10}\,ns^2$ (d) $(n-2)\,d^{0-1}\,(n-1)\,f^{1-14}\,ns^2$

Sol. (a)



Chapter 6

Salt Analysis

JEE Main & NEET

Syllabus

Chemical principles involved in the qualitative salt analysis:

Cations– Pb^{2+}, Cu^{2+}, Al^{3+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, NH_4^+

Anions- CO_3^{2-}, S^{2-}, SO_4^{2-}, NO_3^-, NO_2^-, Cl^-, Br^-, I^- (Insoluble salts excluded).

ACIDIC AND BASIC RADICAL

NaCl

Basic radical Na^+ ← → Cl^- Acidic radical

(Cations) (Anions)

$NaOH + HCl \xrightarrow[-H_2O]{} NaCl$

Cations

Pb^{2+}	Cu^{2+}	Zn^{2+}	Fe^{3+}	Ni^{2+}
Al^{3+}	Ca^{2+}	Mg^{2+}	Ba^{2+}	NH_4^+

Anions

CH_3COO^-	CO_3^{2-}	S^{2-}	SO_3^{2-}	NO_2^-	NO_3^-	Cl^-	Br^-	I^-

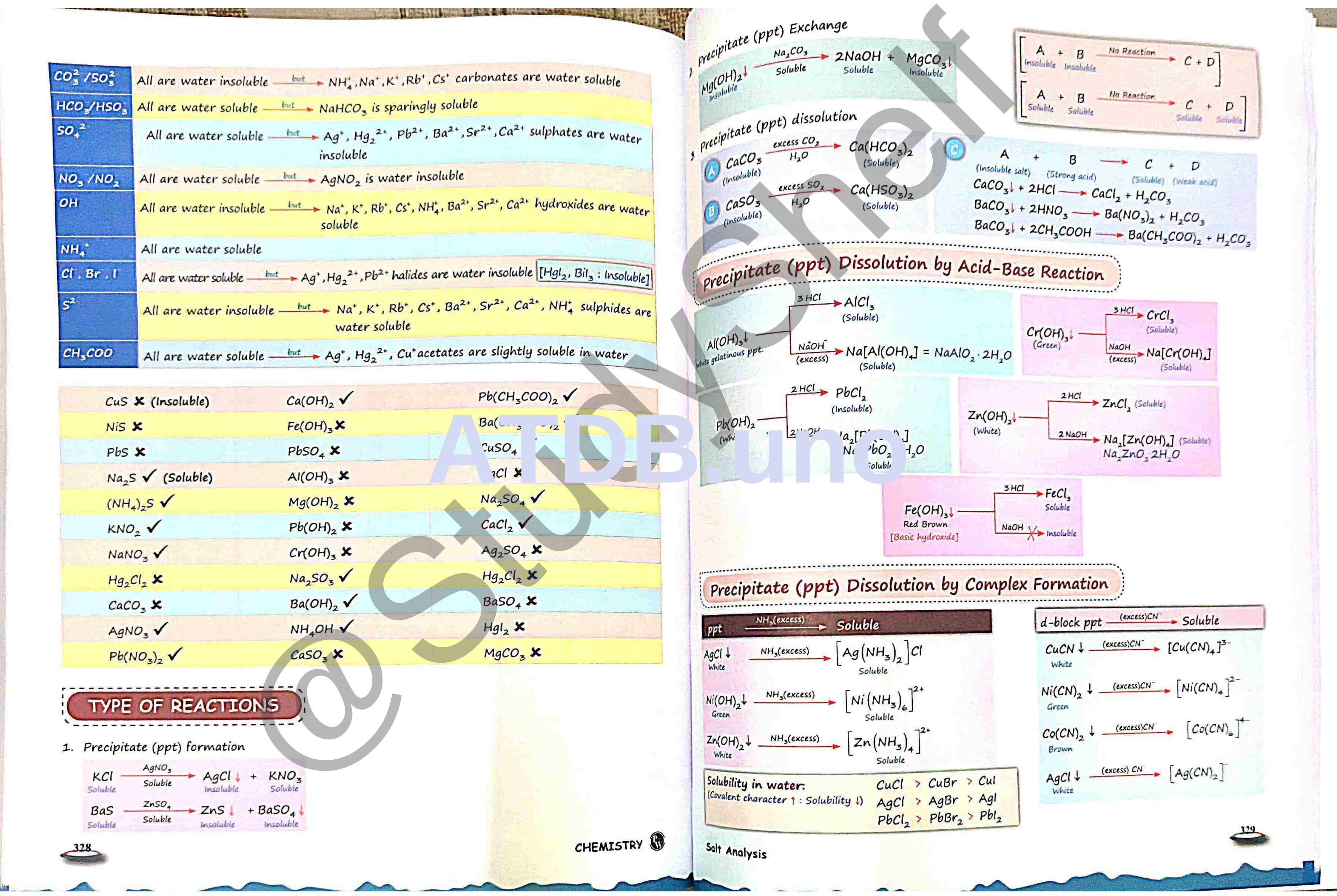
SOLUBILITY IN WATER

Low K_{sp} : Low solubility : ppt formation tendency↑

$$\underset{}{A} + \underset{\text{(Soluble)}}{B} \rightleftharpoons C + \underset{\text{(Soluble)}}{D}$$

☐ K_{sp} of A > K_{sp} of C ⟶ Then equilibrium shifts in forward direction.

☐ K_{sp} of C > K_{sp} of A ⟶ Backward reaction is favourable.



CO_3^{2-}/SO_3^{2-}	All are water insoluble $\xrightarrow{but}$ $NH_4^+, Na^+, K^+, Rb^+, Cs^+$ carbonates are water soluble
HCO_3^-/HSO_3^-	All are water soluble $\xrightarrow{but}$ $NaHCO_3$ is sparingly soluble
SO_4^{2-}	All are water soluble $\xrightarrow{but}$ $Ag^+, Hg_2^{2+}, Pb^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}$ sulphates are water insoluble
NO_3^-/NO_2^-	All are water soluble $\xrightarrow{but}$ $AgNO_2$ is water insoluble
OH^-	All are water insoluble $\xrightarrow{but}$ $Na^+, K^+, Rb^+, Cs^+, NH_4^+, Ba^{2+}, Sr^{2+}, Ca^{2+}$ hydroxides are water soluble
NH_4^+	All are water soluble
Cl^-, Br^-, I^-	All are water soluble $\xrightarrow{but}$ Ag^+, Hg_2^{2+}, Pb^{2+} halides are water insoluble [HgI_2, BiI_3 : Insoluble]
S^{2-}	All are water insoluble $\xrightarrow{but}$ $Na^+, K^+, Rb^+, Cs^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, NH_4^+$ sulphides are water soluble
CH_3COO^-	All are water soluble $\xrightarrow{but}$ Ag^+, Hg_2^{2+}, Cu^+ acetates are slightly soluble in water

CuS ✗ (Insoluble)	$Ca(OH)_2$ ✓	$Pb(CH_3COO)_2$ ✓
NiS ✗	$Fe(OH)_3$ ✗	Ba([illegible]
PbS ✗	$PbSO_4$ ✗	$CuSO_4$ [illegible]
Na_2S ✓ (Soluble)	$Al(OH)_3$ ✗	[illegible]Cl ✗
$(NH_4)_2S$ ✓	$Mg(OH)_2$ ✗	Na_2SO_4 ✓
KNO_2 ✓	$Pb(OH)_2$ ✗	$CaCl_2$ ✓
$NaNO_3$ ✓	$Cr(OH)_3$ ✗	Ag_2SO_4 ✗
Hg_2Cl_2 ✗	Na_2SO_3 ✓	Hg_2Cl_2 ✗
$CaCO_3$ ✗	$Ba(OH)_2$ ✓	$BaSO_4$ ✗
$AgNO_3$ ✓	NH_4OH ✓	HgI_2 ✗
$Pb(NO_3)_2$ ✓	$CaSO_3$ ✗	$MgCO_3$ ✗

TYPE OF REACTIONS

1. Precipitate (ppt) formation

$$\underset{Soluble}{KCl} \xrightarrow[Soluble]{AgNO_3} \underset{Insoluble}{AgCl\downarrow} + \underset{Soluble}{KNO_3}$$

$$\underset{Soluble}{BaS} \xrightarrow[Soluble]{ZnSO_4} \underset{Insoluble}{ZnS\downarrow} + \underset{Insoluble}{BaSO_4\downarrow}$$

Precipitate (ppt) Exchange

$$\underset{Insoluble}{Mg(OH)_2\downarrow} \xrightarrow[Soluble]{Na_2CO_3} \underset{Soluble}{2NaOH} + \underset{Insoluble}{MgCO_3\downarrow}$$

$$\left[\underset{Insoluble}{A} + \underset{Insoluble}{B} \xrightarrow{No\ Reaction} C + D\right]$$

$$\left[\underset{Soluble}{A} + \underset{Soluble}{B} \xrightarrow{No\ Reaction} \underset{Soluble}{C} + \underset{Soluble}{D}\right]$$

3. Precipitate (ppt) dissolution

Ⓐ $\underset{(Insoluble)}{CaCO_3} \xrightarrow[H_2O]{excess\ CO_2} \underset{(Soluble)}{Ca(HCO_3)_2}$

Ⓑ $\underset{(Insoluble)}{CaSO_3} \xrightarrow[H_2O]{excess\ SO_2} \underset{(Soluble)}{Ca(HSO_3)_2}$

Ⓒ $\underset{(Insoluble\ salt)}{A} + \underset{(Strong\ acid)}{B} \longrightarrow \underset{(Soluble)}{C} + \underset{(Weak\ acid)}{D}$

$CaCO_3\downarrow + 2HCl \longrightarrow CaCl_2 + H_2CO_3$

$BaCO_3\downarrow + 2HNO_3 \longrightarrow Ba(NO_3)_2 + H_2CO_3$

$BaCO_3\downarrow + 2CH_3COOH \longrightarrow Ba(CH_3COO)_2 + H_2CO_3$

Precipitate (ppt) Dissolution by Acid-Base Reaction

$Al(OH)_3\downarrow$ (White gelatinous ppt.) $\xrightarrow{3\,HCl}$ $AlCl_3$ (Soluble)

$Al(OH)_3\downarrow$ $\xrightarrow[(excess)]{NaOH}$ $Na[Al(OH)_4] = NaAlO_2 \cdot 2H_2O$ (Soluble)

$Cr(OH)_3\downarrow$ (Green) $\xrightarrow{3\,HCl}$ $CrCl_3$ (Soluble)

$Cr(OH)_3\downarrow$ $\xrightarrow[(excess)]{NaOH}$ $Na[Cr(OH)_4]$ (Soluble)

$Pb(OH)_2$ (Whi[illegible] $\xrightarrow{2\,HCl}$ $PbCl_2$ (Insoluble)

$Pb(OH)_2$ $\xrightarrow{2[illegible]}$ [illegible]a$_2$[illegible]] / N[illegible]PbO_2[illegible]H_2O [illegible]oluble

$Zn(OH)_2\downarrow$ (White) $\xrightarrow{2\,HCl}$ $ZnCl_2$ (Soluble)

$Zn(OH)_2\downarrow$ $\xrightarrow{2\,NaOH}$ $Na_2[Zn(OH)_4]$ (Soluble) $Na_2ZnO_2.2H_2O$

$Fe(OH)_3\downarrow$ Red Brown [Basic hydroxide] $\xrightarrow{3\,HCl}$ $FeCl_3$ Soluble

$Fe(OH)_3\downarrow$ $\xrightarrow{NaOH}$ ✗ Insoluble

Precipitate (ppt) Dissolution by Complex Formation

$ppt \xrightarrow{NH_3(excess)}$ Soluble

$\underset{White}{AgCl\downarrow} \xrightarrow{NH_3(excess)} \underset{Soluble}{\left[Ag(NH_3)_2\right]Cl}$

$\underset{Green}{Ni(OH)_2\downarrow} \xrightarrow{NH_3(excess)} \underset{Soluble}{\left[Ni(NH_3)_6\right]^{2+}}$

$\underset{White}{Zn(OH)_2\downarrow} \xrightarrow{NH_3(excess)} \underset{Soluble}{\left[Zn(NH_3)_4\right]^{2+}}$

Solubility in water:
(Covalent character ↑ : Solubility ↓)

$CuCl > CuBr > CuI$
$AgCl > AgBr > AgI$
$PbCl_2 > PbBr_2 > PbI_2$

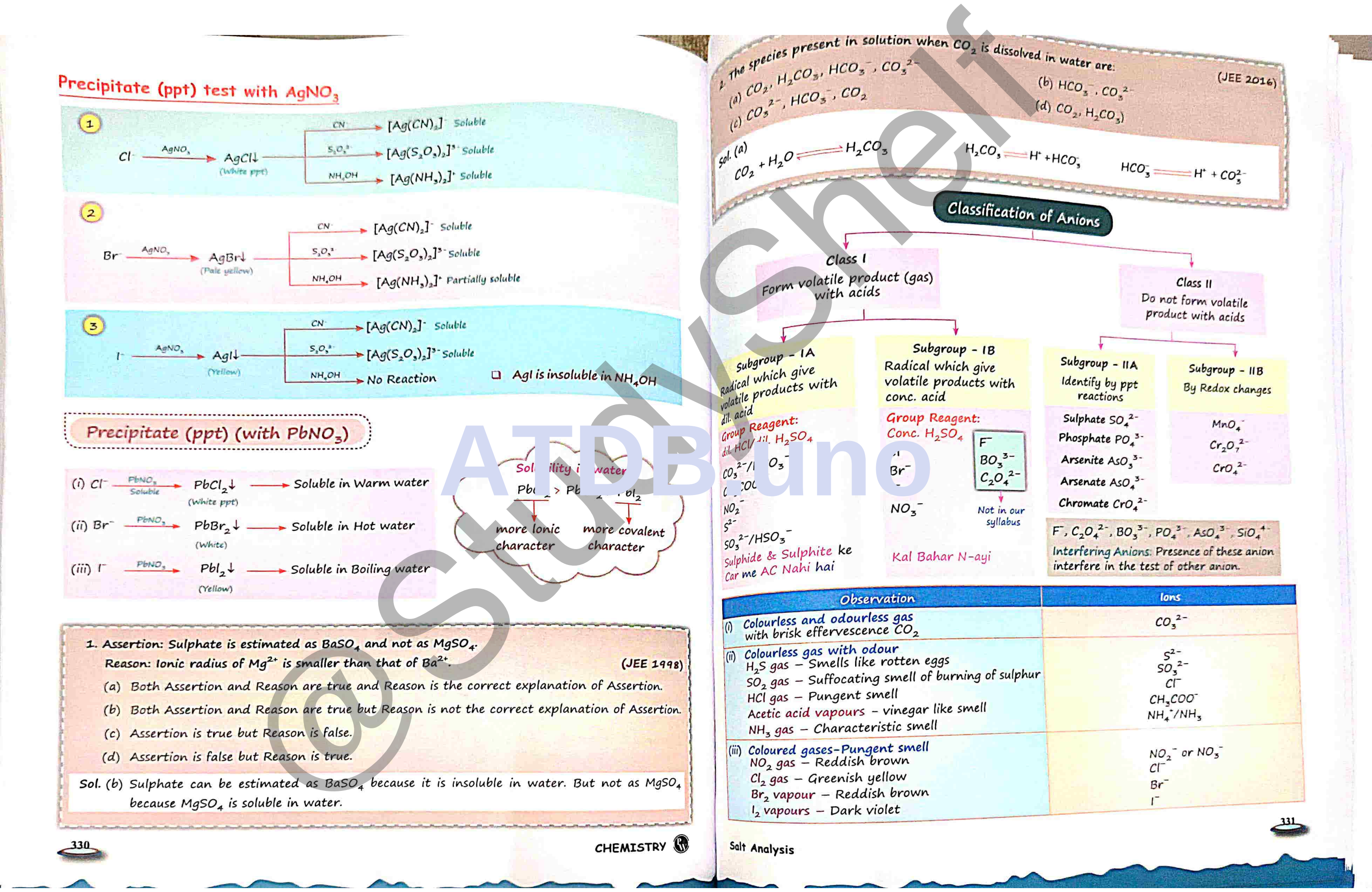
d-block ppt $\xrightarrow{(excess)CN^-}$ Soluble

$\underset{White}{CuCN\downarrow} \xrightarrow{(excess)CN^-} [Cu(CN)_4]^{3-}$

$\underset{Green}{Ni(CN)_2\downarrow} \xrightarrow{(excess)CN^-} \left[Ni(CN)_4\right]^{2-}$

$\underset{Brown}{Co(CN)_2\downarrow} \xrightarrow{(excess)CN^-} \left[Co(CN)_6\right]^{4-}$

$\underset{White}{AgCl\downarrow} \xrightarrow{(excess)\ CN^-} \left[Ag(CN)_2\right]^-$



Precipitate (ppt) test with $AgNO_3$

①
$Cl^- \xrightarrow{AgNO_3} AgCl\downarrow$ (White ppt)
$\xrightarrow{CN^-} [Ag(CN)_2]^-$ Soluble
$\xrightarrow{S_2O_3^{2-}} [Ag(S_2O_3)_2]^{3-}$ Soluble
$\xrightarrow{NH_4OH} [Ag(NH_3)_2]^+$ Soluble

②
$Br^- \xrightarrow{AgNO_3} AgBr\downarrow$ (Pale yellow)
$\xrightarrow{CN^-} [Ag(CN)_2]^-$ Soluble
$\xrightarrow{S_2O_3^{2-}} [Ag(S_2O_3)_2]^{3-}$ Soluble
$\xrightarrow{NH_4OH} [Ag(NH_3)_2]^+$ Partially soluble

③
$I^- \xrightarrow{AgNO_3} AgI\downarrow$ (Yellow)
$\xrightarrow{CN^-} [Ag(CN)_2]^-$ Soluble
$\xrightarrow{S_2O_3^{2-}} [Ag(S_2O_3)_2]^{3-}$ Soluble
$\xrightarrow{NH_4OH}$ No Reaction

☐ AgI is insoluble in NH_4OH

Precipitate (ppt) (with $PbNO_3$)

(i) $Cl^- \xrightarrow[\text{Soluble}]{PbNO_3} PbCl_2\downarrow$ (White ppt) $\longrightarrow$ Soluble in Warm water

(ii) $Br^- \xrightarrow{PbNO_3} PbBr_2\downarrow$ (White) $\longrightarrow$ Soluble in Hot water

(iii) $I^- \xrightarrow{PbNO_3} PbI_2\downarrow$ (Yellow) $\longrightarrow$ Soluble in Boiling water

Solubility in water
$PbCl_2 > PbBr_2 > PbI_2$
more Ionic character
more covalent character

1. **Assertion: Sulphate is estimated as $BaSO_4$ and not as $MgSO_4$.**
Reason: Ionic radius of Mg^{2+} is smaller than that of Ba^{2+}. **(JEE 1998)**
(a) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.
(b) Both Assertion and Reason are true but Reason is not the correct explanation of Assertion.
(c) Assertion is true but Reason is false.
(d) Assertion is false but Reason is true.

Sol. (b) Sulphate can be estimated as $BaSO_4$ because it is insoluble in water. But not as $MgSO_4$ because $MgSO_4$ is soluble in water.

2. The species present in solution when CO_2 is dissolved in water are: (JEE 2016)
(a) $CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}$
(b) HCO_3^-, CO_3^{2-}
(c) CO_3^{2-}, HCO_3^-, CO_2
(d) $CO_2, H_2CO_3)$

Sol. (a)
$CO_2 + H_2O \rightleftharpoons H_2CO_3$ $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

Classification of Anions

Class I
Form volatile product (gas) with acids

Subgroup - IA
Radical which give volatile products with dil. acid
Group Reagent: dil. HCl/ dil. H_2SO_4
CO_3^{2-}/HCO_3^-
CH_3COO^-
NO_2^-
S^{2-}
SO_3^{2-}/HSO_3^-
Sulphide & Sulphite ke Car me AC Nahi hai

Subgroup - IB
Radical which give volatile products with conc. acid
Group Reagent: Conc. H_2SO_4
Cl^-
Br^-
I^-
NO_3^-
Kal Bahar N-ayi

F^-
BO_3^{3-}
$C_2O_4^{2-}$
Not in our syllabus

Class II
Do not form volatile product with acids

Subgroup - IIA
Identify by ppt reactions
Sulphate SO_4^{2-}
Phosphate PO_4^{3-}
Arsenite AsO_3^{3-}
Arsenate AsO_4^{3-}
Chromate CrO_4^{2-}

Subgroup - IIB
By Redox changes
MnO_4^-
$Cr_2O_7^{2-}$
CrO_4^{2-}

$F^-, C_2O_4^{2-}, BO_3^{3-}, PO_4^{3-}, AsO_4^{3-}, SiO_4^{4-}$
Interfering Anions: Presence of these anion interfere in the test of other anion.

Observation	Ions
(i) Colourless and odourless gas with brisk effervescence CO_2	CO_3^{2-}
(ii) Colourless gas with odour H_2S gas – Smells like rotten eggs SO_2 gas – Suffocating smell of burning of sulphur HCl gas – Pungent smell Acetic acid vapours – vinegar like smell NH_3 gas – Characteristic smell	S^{2-} SO_3^{2-} Cl^- CH_3COO^- NH_4^+/NH_3
(iii) Coloured gases–Pungent smell NO_2 gas – Reddish brown Cl_2 gas – Greenish yellow Br_2 vapour – Reddish brown I_2 vapours – Dark violet	NO_2^- or NO_3^- Cl^- Br^- I^-

SODIUM CARBONATE EXTRACT

MX (1 part) + Na_2CO_3 (3 part) → NaX / Na_2X

Salt → insoluble

Sodium carbonate extract (Soda extract)

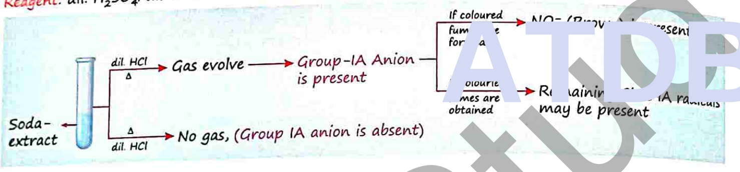
Note

- ☐ If the given salt is insoluble in H_2O, we add Na_2CO_3 in the salt to get soda extract.
- ☐ Almost all sodium salts are water soluble. Na^+ displaces the cation of the salt to obtain soluble salt solution.
- ☐ Soda extract → Basic in nature (neutralise by small amount of acid like CH_3COOH)
- ☐ We cannot use soda extract to identify CO_3^{2-} and HCO_3^- ion because CO_3^{2-} ion is already present in soda extract.

TEST FOR GROUP-1A ANION

$CO_3^{2-}, S^{2-}, SO_3^{2-}, CH_3COO^-, NO_2^-$

Reagent: dil. H_2SO_4/dil. HCl



TEST FOR CO_3^{2-}

$$\underset{\text{(given salt)}}{CO_3^{2-}} + dil.HCl \xrightarrow{\Delta} H_2CO_3 \longrightarrow H_2O + CO_2\uparrow$$ [Brisk effervescence of CO_2 gas]

→ Rapid, vigorous release of gas bubbles from liquid solution

Confirmatory Test

1. LIME WATER [$Ca(OH)_2$] TEST

$$CO_2 + \underset{\text{Clear solution}}{Ca(OH)_2} \longrightarrow CaCO_3\downarrow$$ [milky solution]

$$CaCO_3 + H_2O + \underset{\text{(Excess)}}{CO_2} \longrightarrow Ca(HCO_3)_2$$ Soluble [Clear solution]

CO_2 turns Lime water milky but when excess of CO_2 is passed, milkiness disappears.

2. BARYTA WATER [$Ba(OH)_2$] TEST

$$CO_2 + Ba(OH)_2 \longrightarrow BaCO_3\downarrow \xrightarrow[H_2O]{CO_2} Ba(HCO_3)_2$$ Clear solution

$$\underset{\text{[Soluble]}}{Na_2CO_3} + \underset{\text{[Soluble]}}{BaCl_2} \longrightarrow \underset{\text{White ppt}}{BaCO_3\downarrow} \xrightarrow{HCl} BaCl_2$$ (Soluble)

$$BaCO_3 \xrightarrow{HNO_3} Ba(NO_3)_2$$ (Soluble)

- ☐ CO_2 does not show redox reaction as it has maximum oxidation state (+4) of carbon but can provide acidic medium for many reactions:

$$K_2\overset{+6}{Mn}O_{4\,(aq)} \xrightarrow{CO_2} K\overset{+7}{Mn}O_4 + \overset{+4}{Mn}O_2$$

$$CaOCl_{2\,(aq)} \xrightarrow{CO_2} Cl_2 + CaCO_3$$

$$\underset{\text{Yellow}}{Na_2CrO_{4\,(aq)}} \xrightarrow[\text{Acidic medium}]{CO_2} \underset{\text{Orange}}{Na_2Cr_2O_{7\,(aq)}}$$

$$\boxed{Cl_2 \underset{\text{Acid }[H^+\text{ or }CO_2]}{\overset{\text{Base }[Ca(OH)_2]}{\rightleftharpoons}} CaCl_2 + Ca(OCl)_2}$$

TEST FOR SO_3^{2-}

$$Na_2SO_3 + dil.\,HCl \xrightarrow{\Delta} H_2SO_3 \xrightarrow{\Delta} H_2O + SO_2\uparrow$$

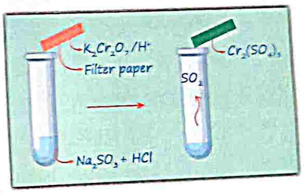
$$SO_2 \xrightarrow{Ca(OH)_2} CaSO_3\downarrow \xrightarrow[SO_2 + H_2O]{\text{Excess}} Ca(HSO_3)_2$$ Clear solution

Confirmatory Test:

1. The filter paper dipped in acidified $K_2Cr_2O_7$ turns green

$$\overset{+4}{SO_2} + \underset{\text{Orange}}{K_2Cr_2O_7/H^+} \longrightarrow \underset{\text{Green}}{\overset{+3}{Cr_2}(\overset{+6}{S}O_4)_3}$$

$$\overset{+4}{CO_2} + \underset{\text{Orange}}{K_2Cr_2O_7/H^+} \longrightarrow \text{No reaction}$$



2. Sodium carbonate extract of the salt produces a white precipitate of barium sulphite on addition of barium chloride solution

$$\underset{\text{[soluble]}}{Na_2SO_3} + \underset{\text{[soluble]}}{BaCl_2} \longrightarrow BaSO_3\downarrow$$ (white ppt)

(i) This precipitate on treatment with dilute HCl, dissolves due to decomposition of sulphite by dilute HCl.

$$BaSO_3\downarrow + 2HCl \longrightarrow \underset{[soluble]}{BaCl_2} + H_2SO_3 \longrightarrow H_2O + SO_2\uparrow$$

(ii) Precipitate of sulphite decolourises acidified $KMnO_4$ solution (purple).

$$BaSO_3\downarrow \xrightarrow[Mn^{2+}\ :\ Colourless]{KMnO_4/H^+} BaSO_4\downarrow$$

3. On treating a compound with warm dil. H_2SO_4, gas X is evolved which turns $K_2Cr_2O_7$ paper acidified with dil. H_2SO_4 to a green compound Y. X and Y respectively are: (JEE Mains 2021)
   (a) $X = SO_2, Y = Cr_2O_3$
   (b) $X = SO_3, Y = Cr_2O_3$
   (c) $X = SO_2, Y = Cr_2(SO_4)_3$
   (d) $X = SO_3, Y = Cr_2(SO_4)_3$

Sol. (c)

4. $K_2Cr_2O_7$ paper acidified with dilute H_2SO_4 turns green when exposed to (JEE Mains 2023)
   (a) Hydrogen sulphide
   (b) Carbon dioxide
   (c) Sulphur dioxide
   (d) Sulphur trioxide

Sol. (c)

5. A white precipitate was formed when $BaCl_2$ was added to water extract of an inorganic salt. Further, a gas 'X' with characteristic odour was released when the formed white precipitate was dissolved in dilute HCl. The anion present in the inorganic salt is [24 Jan, 2[illegible] (Shift-I)]
   (a) I^-
   (b) SO_3^{2-}
   (c) S^{2-}
   (d) NO_2^-

Sol. (b)

$$BaCl_2 + SO_3^{2-} \longrightarrow \underset{white}{BaSO_3\downarrow} \xrightarrow{dil.HCl} SO_2\uparrow \quad \text{(Burning sulphur like smell)}$$

6. $[X] + H_2SO_4 \rightarrow [Y]$ a colourless gas with irritating smell
   $[Y] + K_2Cr_2O_7 + H_2SO_4 \rightarrow$ green solution ; [X] and [Y] are (JEE Adv. 2003)
   (a) SO_3^{2-}, SO_2
   (b) Cl^-, HCl
   (c) S^{2-}, H_2S
   (d) CO_3^{2-}, CO_2

Sol. (a)

$$\underset{(X)}{SO_3^{2-}} + H_2SO_4 \longrightarrow \underset{(Y)}{SO_2} + H_2O + SO_4^{2-}$$

$$\underset{(Y)}{3SO_2} + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + \underset{\text{(Green colour solution)}}{Cr_2(SO_4)_3} + H_2O$$

TEST FOR SULPHIDE (S^{2-}) ION

(i) $Na_2S + dil.\ H_2SO_4 \xrightarrow{\Delta} H_2S\uparrow$ Rotten egg like smell

(a) $\underset{\text{Filter Paper}}{(CH_3COO)_2Pb} + H_2S \longrightarrow \underset{Black}{PbS}$

(b) $\underset{\text{Filter Paper}}{(CH_3COO)_2Cd} + H_2S \longrightarrow \underset{Yellow}{CdS}$

(ii) $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5(NOS)]$

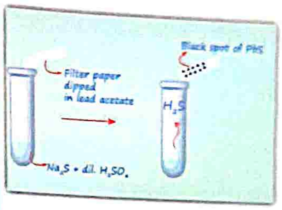
Sodium nitroprusside
Brown red [Fe^{+2} with NO^+]

Sodium thio-nitroprusside
Violet [Fe^{+2} with NOS^-]

$\underset{\text{[ionic sulphide]}}{NO^+ + S^{2-}} \longrightarrow NOS^-$

$NO^+ + H_2S \longrightarrow$ No reaction

Sodium Nitroprusside Test



Note

H_2S does not provide sufficient concentration of S^{2-} ions so that it does not give sodium nitroprusside test.

7. Which one of the following complexes is violet in colour? [26 Aug. 2021(Shift-I)]
   (a) $[Fe(CN)_5NOS]^{4-}$
   (b) $[Fe(SCN)_6]^{4-}$
   (c) $Fe_4[Fe(CN)_6]_3 . H_2O$
   (d) $[Fe(CN)_6]^{4-}$

Sol. (a) $[Fe(CN)_5NOS]^{4-} \rightarrow$ Violet Colour

8. In which reaction no colour change will be observed?
   (a) $K_2Cr_2O_7 \xrightarrow{CO_2}$
   (b) $K_2Cr_2O_7 \xrightarrow{SO_2}$
   (c) $Na_2CrO_4 \xrightarrow{CO_2}$
   (d) $Na_2S \xrightarrow{Na_2[Fe(CN)_5 NO]}$

Sol. (a)

9. In nitroprusside ion, the iron and NO exist. They exist as Fe^{II} and NO^+ rather than Fe^{III} and NO. These forms can be differentiated by (JEE 1998)
   (a) estimating the concentration of Iron.
   (b) measuring the concentration of CN^-.
   (c) measuring the solid state magnetic moment.
   (d) thermally decomposing the compound.

Sol. (c)

10. Which statements is/are correct about sodium nitroprusside test?
   (a) This test is used for detection of S^{2-} anion.
   (b) H_2S also gives positive test.
   (c) Formation of $Na_2[Fe(H_2O)_5NOS]$ complex confirm the presence of S^{2-} anion.
   (d) Iron has +2 oxidation state in sodiumthionitroprusside complex.

Sol. (a) and (d)

TEST FOR NO_2^- ION

Preliminary Test

$NaNO_2 + dil.\ H_2SO_4 \xrightarrow{\Delta} HNO_2$ (Unstable)

$2\overset{+3}{HNO_2} \xrightarrow{\Delta} \overset{+5}{HNO_3} + \overset{+2}{NO}$

$NO + \frac{1}{2}O_2 \longrightarrow NO_2$ [Reddish brown vapours]

☐ $NO_2^- \xrightarrow{CH_3COOH} \overset{+3}{HNO_2} \xrightarrow{KI} \overset{+2}{NO} + I_2 \xrightarrow{Starch}$ Blue complex

☐ $\overset{+5}{NO_3^-} / \overset{+3}{NO_2^-} \xrightarrow[NaOH]{Al + Zn + Cu\ [Devarda's\ alloy]} \overset{-3}{NH_3} \xrightarrow{HCl} NH_4Cl$ (white fume)

$NH_3 \xrightarrow{CuSO_4} [Cu(NH_3)_4]SO_4$ Blue

$NH_3 \xrightarrow{AgCl \downarrow} [Ag(NH_3)_2]Cl$ Clear Solution

$NH_3 \xrightarrow{Red\ Litmus}$ Blue

$Al/Zn \xrightarrow{NaOH} H_2 \uparrow + NaAlO_2/Na_2ZnO_2$

Brown Ring Test ⇒ Test for Nitrates

$NO_2^- \xrightarrow[from\ dil.\ H_2SO_4]{H^+} HNO_2 \rightarrow HNO_3$

$HNO_2 \rightarrow NO$

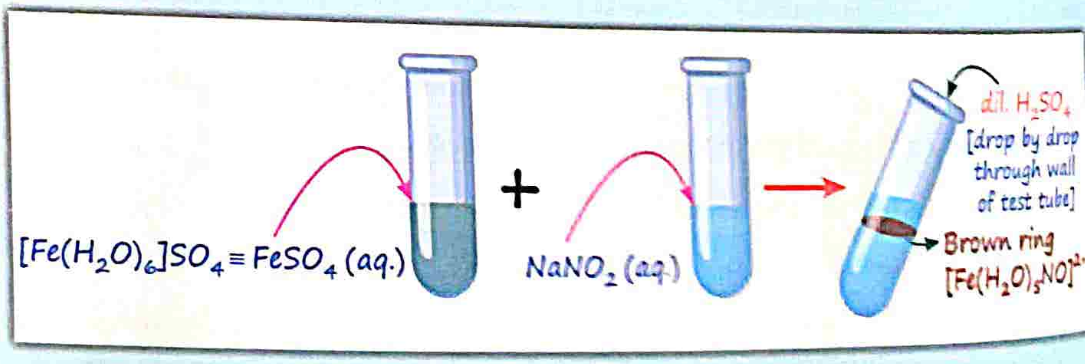
$NO_3^- + Fe^{2+} \xrightarrow[H_2SO_4]{dilute} NO + Fe^{+3}$
(from HNO_3)

Fe^{2+} $\ominus\ddot{N}=O \longrightarrow Fe^{+} \leftarrow \ominus\dot{N}=O$
Ligand to metal charge transfer
(Metal–Ligand bond)

$[Fe(H_2O)_6]^{2+} + NO \longrightarrow [Fe(H_2O)_5NO]^{2+}$

☐ Reason for brown colour → Ligand to metal charge transfer spectra

A brown ring at the interface between the solution and sulphuric acid layers indicates the presence of nitrate ion in solution.

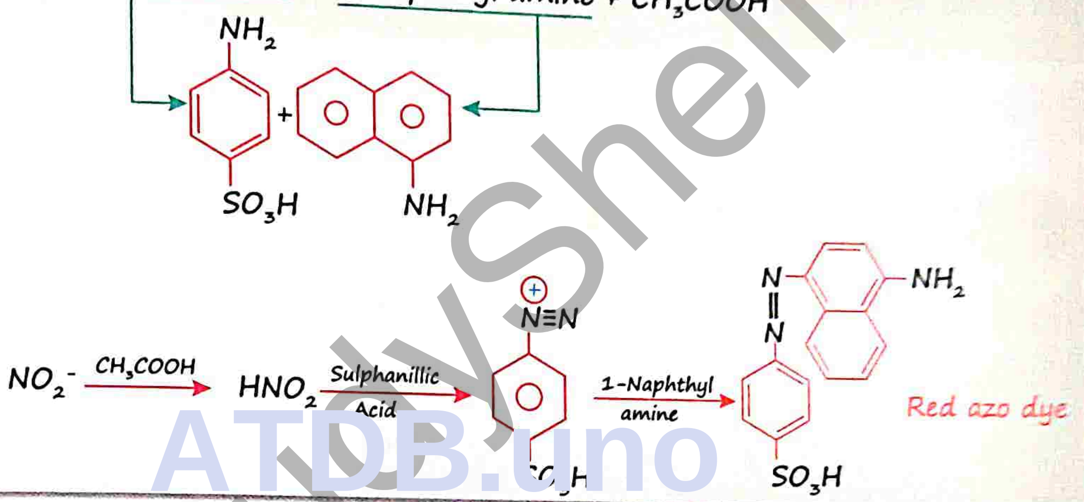


Note

- $FeSO_4$ solution must be freshly prepared because Fe^{2+} ion is very prone to aerial oxidation and gets converted to Fe^{3+}, which does not give this test.
- Concentrated H_2SO_4 cannot be used in this test instead of dil. H_2SO_4 because it produces intense brown fumes with NO_2^- and under these conditions no ring can be observed.
- Shaking and warming are not allowed for this test because $[Fe(H_2O)_5NO]^{2+}$ formed is unstable and liberates NO easily.

Confirmatory Test for NO_2^-

Griss – Hosray Test → Sulphanillic Acid + 1-Naphthyl amine + CH_3COOH



11. Reagent 1-naphthylamine and sulphanilic acid in acetic acid is used for the detection of: (JEE Mains 2021)

(a) N_2O (b) NO_2^- (c) NO_3^- (d) NO

Sol. (b)

12. Which statement(s) is/are correct about Brown ring test?
   (a) The test is given by NO_2^-, NO_3^- anions.
   (b) Brown ring test depend upon the reduction of NO_2^- and NO_3^- to Nitric oxide.
   (c) Brown ring is formed due to formation of $[Fe(H_2O)_5NO]_2(SO_4)_3$
   (d) Charge on NO in brown ring complex is +1.

Sol. (a, b, d)

TEST FOR ACETATE (CH_3COO^-) ION

$$\underset{\text{(given salt)}}{CH_3COO^-} + \text{dil. } H_2SO_4 \xrightarrow{\Delta} CH_3COOH\uparrow \quad \text{Vinegar like smell}$$

$$CH_3COOH + C_2H_5OH \xrightarrow[\text{Conc. } H_2SO_4]{\Delta} \underset{\text{(Fruity odour)}}{CH_3COOC_2H_5} \text{ [Ester]}$$

Note

Acetate gives deep red colour on reaction with neutral ferric chloride solution due to the formation of complex ion which decomposes on heating to give Iron (III) dihydroxyacetate as brown red precipitate

$$CH_3COO^- \xrightarrow[FeCl_3]{Neutral} \text{Red Colour} \xrightarrow{\Delta} \text{Brown Red}\downarrow$$

$$6CH_3COO^- + 3Fe^{3+} + 2H_2O \longrightarrow [Fe_3(OH)_2(CH_3COO)_6]^+ + 2H^+$$

$$\underset{\text{(Red colour)}}{[Fe_3(OH)_2(CH_3COO)_6]^+} + 4H_2O \longrightarrow \underset{\substack{\text{Iron (III) dihydroxyacetate}\\ \text{(Brown-red precipitate)}}}{3[Fe\ (OH)_2(CH_3COO)]\downarrow} + 3CH_3COOH + H^+$$

TEST FOR GROUP 1B (Cl^-, Br^-, I^-, NO_3^-)

Reagent: Conc. H_2SO_4

TEST FOR NO_3^- ION

Preliminary Test

$$NaNO_3 + \text{Conc. } H_2SO_4 \longrightarrow HNO_3$$

$$\overset{+5}{HNO_3} \xrightarrow{\Delta} \underset{\substack{\text{[Reddish}\\ \text{brown vapours]}}}{\overset{+4}{NO_2}\uparrow} + O$$

☐ If on heating the salt with conc. H_2SO_4 light brown fumes are evolved then heat a small quantity of the given salt with few copper turnings or chips and conc. H_2SO_4, intensity of brown fume increases.

$$H_2SO_4 + HNO_3 + Cu \longrightarrow \underset{\text{[Blue solution]}}{CuSO_4} + NO \xrightarrow{O_2} NO_2\uparrow$$

Brown Ring Test → Test for Nitrates

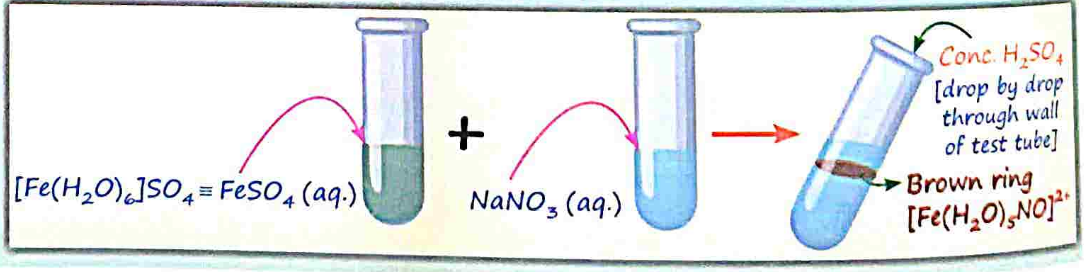
$$NO_3^- + Fe^{2+} \xrightarrow[H_2SO_4]{Conc.} NO + Fe^{+3}$$

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow [Fe(H_2O)_5NO]^{2+}$$

$$\underset{\substack{\text{Ligand to metal}\\ \text{charge transfer}}}{Fe^{2+}\ \ \ominus\dot{N}=O} \longrightarrow \underset{\text{(Metal-Ligand bond)}}{Fe^{+} \longleftarrow \ominus\overset{+}{N}=O}$$

☐ Reason for brown colour → Ligand to metal charge transfer spectra

A brown ring at the interface between the solution and sulphuric acid layers indicates the presence of nitrate ion in solution.



Note

☐ On shaking or warming, the brown colour disappears and NO gas in evolved.

$$\text{Brown ring complex } [Fe(H_2O)_5NO]^{2+} + H_2O \longrightarrow [Fe(H_2O)_6]^{2+} + NO\uparrow$$

☐ Radicals such as Br^-, I^- and NO_2^- must be absent because these produce coloured gases with conc. H_2SO_4 like Br_2, I_2 and NO_2 respectively and no ring is observed.

☐ $Ca(NO_3)_2$, $Ba(NO_3)_2$, $Pb(NO_3)_2$ do not respond to the test due to precipitation of their corresponding metal sulphates.

$$\underset{\text{Soluble in water}}{Ca(NO_3)_2,\ Ba(NO_3)_2,\ Pb(NO_3)_2} \xrightarrow{\text{Conc. } H_2SO_4} CaSO_4\downarrow,\ BaSO_4\downarrow,\ PbSO_4\downarrow$$

TEST FOR Cl^- ION

1. **Preliminary Test:**

$$NaCl_{(aq)} + \text{Conc } H_2SO_4 \xrightarrow{\Delta} HCl\uparrow$$

Oxidising power: $F_2 > Cl_2 > H_2SO_4 > Br_2 > I_2$

☐ A colourless gas with pungent smell, which gives dense white fumes when a rod dipped in ammonium hydroxide is brought near the mouth of the test tube.

$$NH_4OH + HCl \longrightarrow NH_4Cl \text{ (white fumes)}$$

2. If a salt gives effervescence on heating with conc. H_2SO_4 and MnO_2 and a light greenish yellow pungent gas is evolved, this indicates the presence of Cl^- ions.

$$\underset{\text{(OA)}}{MnO_2} + \underset{\text{(Salt)}}{Cl^-} + H_2SO_4 \longrightarrow Cl_2\uparrow \text{ (greenish yellow gas)}$$

3. **Aq. $AgNO_3$ Test:** Salt solution acidified with dilute HNO_3 on addition of silver nitrate solution gives a curdy white precipitate soluble in ammonium hydroxide solution. This indicates the presence of Cl^- ions in the salt.

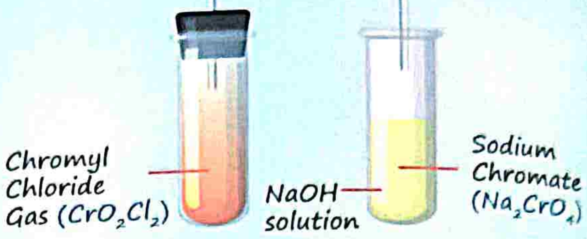
$$NaCl + AgNO_3 \longrightarrow NaNO_3 + \underset{\text{Silver chloride}}{AgCl\downarrow} \text{ (Curdy white ppt)}$$

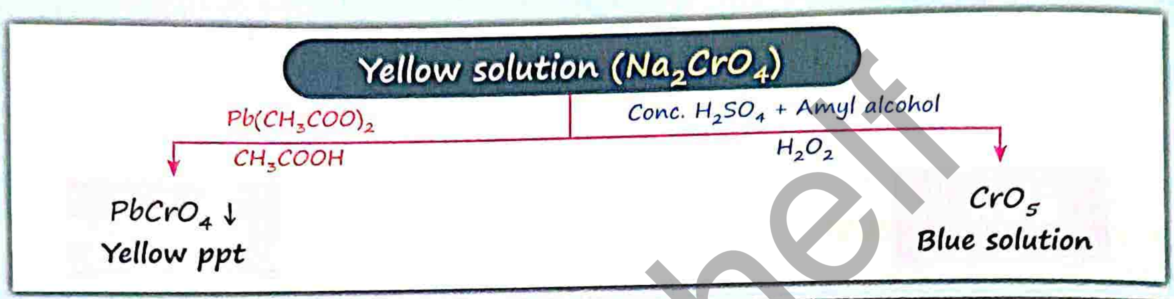
$$\underset{\text{(ppt)}}{AgCl} + 2NH_4OH \longrightarrow \underset{\text{(Soluble)}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

4. **Chromyl Chloride Test:**

$$\underset{\text{Solid}}{Cl^-} + \underset{\text{Solid}}{K_2\overset{+6}{Cr_2}O_7} + \text{Conc. } H_2SO_4 \longrightarrow \underset{\substack{\text{Chromyl chloride}\\ \text{(Red vapours)}}}{\overset{+6}{Cr_2}O_2Cl_2\uparrow}$$

$$\underset{\text{Solid}}{Cl^-} \xrightarrow[\text{Solid } K_2Cr_2O_7]{\text{Conc } H_2SO_4} \underset{[\text{Red}]}{CrO_2Cl_2} \xrightarrow{NaOH} \underset{[\text{Yellow Solution}]}{Na_2CrO_4}$$





Note

- ☐ Ionic chlorides can give this test (NaCl, KCl, $SnCl_2$).
- ☐ Insoluble and covalent chlorides do not give this test (AgCl, $HgCl_2$, Hg_2Cl_2, $PbCl_2$, $SnCl_4$ & CCl_4).
- ☐ Br^- and I^- must be absent for this test because they are oxidized by $Cr_2O_7^{2-}$ into Br_2 (red vapours) and I_2 (violet vapours) respectively.

$$Br^- + Cr_2O_7^{2-} + H^+ \longrightarrow Br_2\uparrow + Cr^{3+} + H_2O$$

$$I^- + Cr_2O_7^{2-} + H^+ \longrightarrow I_2\uparrow + Cr^{3+} + H_2O$$

13. Consider the following reactions

$$A + \underset{\substack{\text{Little}\\ \text{amount}}}{NaCl} + H_2SO_4 \rightarrow CrO_2Cl_2 + \text{ Side Products}$$

$$CrO_2Cl_{2(Vapour)} + NaOH \rightarrow B + NaCl + H_2O$$

$$B + H^+ \rightarrow C + H_2\,O$$

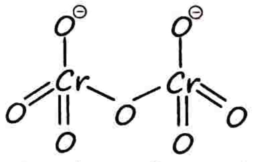
The number of terminal 'O' present in the compound 'C' is ____. **[03 April, 2025 (Shift-I)]**

Sol. [6] $Cr_2O_7{}^{2-} + NaCl + H_2SO_4 \rightarrow CrO_2Cl_2$

$$\underset{(\text{Vapour})}{CrO_2Cl_2} + NaOH \rightarrow Na_2CrO_4 + NaCl + H_2O$$

$$Na_2CrO_4 + H^{\oplus} \rightarrow \underset{(C)}{Na_2Cr_2O_7} + H_2O$$

$$Na_2Cr_2O_7 \rightarrow 2Na^{\oplus} + Cr_2O_7{}^{2-}$$



Number of terminal "O" = 6

14. A solution of CrO_5

[JEE Mains 2023]

(a) Blue (b) Yellow (c) Green (d) Orange-Red

Sol. (a)

15. When a mixture of solid NaCl, solid $K_2Cr_2O_7$ is heated with conc. H_2SO_4, orange red vapours are obtained. The compound formed is

(a) Chromous chloride (b) Chromyl chloride
(c) Chromic chloride (d) Chromic sulphate

Sol. (b)

16. Choose the following reactions

[07 Jan, 2020 (shift-II)]

$NaCl + K_2Cr_2O_7 + H_2SO_4 \rightarrow (A) + \text{side products}$

$(A) + NaOH \rightarrow (B) + \text{side products}$

$(B) + \underset{\text{(dilute)}}{H_2SO_4} + H_2O_2 \rightarrow (C) + \text{Side products}$

The sum of the total number of atoms in one molecule each of (A), (B) and (C) is____.

Sol. [18]

$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \longrightarrow \underset{(A)}{2CrO_2Cl_2} + 4NaHSO_4 + 2KHSO_4 + 3H_2O$$

$$CrO_2Cl_2 + 4NaOH \longrightarrow \underset{(B)}{Na_2CrO_4} + 2NaCl + 2H_2O$$

$$Na_2CrO_4 + 2H_2SO_4 + 2H_2O_2 \longrightarrow \underset{(C)}{CrO_5} + 2NaHSO_4 + 3H_2O$$

Total number of atom in A + B + C = 18

TEST FOR Br^- ION

$$NaBr_{(aq)} + \text{Conc. } H_2SO_4 \xrightarrow{\Delta} Br_2\uparrow \text{ [Reddish Brown fumes]}$$

$$NaBr_{(aq)} + \underset{\text{[OA]}}{\text{Conc. } H_2SO_4} + \underset{\text{[Supportive OA]}}{MnO_2} \xrightarrow{\Delta} Br_2\uparrow \text{ [Reddish Brown Colour with intensity]}$$

☐ **Aq. $AgNO_3$ Test:** Acidify the sodium carbonate extract of the salt with dil. HNO_3. Add silver nitrate ($AgNO_3$) solution and shake the test tube. A pale yellow precipitate is obtained which dissolves in ammonium hydroxide with difficulty.

$$NaBr + AgNO_3 \longrightarrow NaNO_3 + \underset{\text{(pale yellow ppt)}}{AgBr} \xrightarrow{NH_4OH} \underset{\text{(partially Soluble)}}{[Ag(NH_3)_2]Br}$$

TEST FOR I⁻ ION

- ❑ If on heating the salt with conc. H_2SO_4, deep violet vapours with a pungent smell are evolved. These turns starch paper blue, a violet sublimate is formed on the sides of the test tube, it indicates the presence of I^- ions.

$$Na^+I^-_{(aq)} + conc.\ H_2\overset{+6}{S}O_4 \xrightarrow{\Delta} I_2 + \overset{+4}{S}O_2$$

[Violet vapours]

$$I_2 + \text{Starch Solution} \longrightarrow \text{Blue Colour}$$

Some HI, sulphur dioxide, hydrogen sulphide, and sulphur are also formed due to the following reactions.

$$NaI + H_2SO_4 \xrightarrow[-NaHSO_4]{} \underset{(R.A.)}{HI} \xrightarrow[(O.A.)]{H_2SO_4} I_2 + \overset{+4}{S}O_2 \xrightarrow{HI} \overset{0}{S} \xrightarrow{HI} H_2\overset{-2}{S}$$

- ❑ On adding MnO_2 to the reaction mixture, the violet vapours become dense.

$$NaI_{(aq)} + Conc.\ H_2SO_4 + MnO_2 \xrightarrow{\Delta} I_2\uparrow$$

- ❑ **Aq. $AgNO_3$ Test:** Acidify sodium carbonate extract of the salt with dil.HNO_3 and add $AgNO_3$ solution. Appearance of a yellow precipitate insoluble in excess of NH_4OH confirms the presence of iodide ions.

$$NaI + AgNO_3 \longrightarrow \underset{[\text{yellow ppt}]}{AgI\downarrow} + NaNO_3$$

$$AgI \xrightarrow{NH_4OH_{(aq)}} \text{No reaction}$$

- ❑ **From $HgCl_2$**

$$2I^- + HgCl_2 \longrightarrow \underset{\text{Scarlet red}}{HgI_2\downarrow} \xrightarrow[\text{Excess}]{2KI} K_2[HgI_4]\ \text{(Soluble)}$$

- ❑ **From $CuSO_4$**

$$\underset{[R.A.]}{I^-} + \underset{[O.A.]}{Cu^{2+}} \longrightarrow \underset{\text{White ppt}}{Cu_2I_2} + I_2 \xrightarrow[\text{Hypo Solution}]{2Na_2S_2O_3} Na_2S_4O_6\ \text{(white)} + 2NaI$$

- ❑ **Layer Test**

$$\underset{\text{Soda extract}}{NaX} \xrightarrow[\text{chlorine water}]{\text{Add few drop of}} \text{Shake the mixture} \xrightarrow{\text{Add } CS_2 \text{ or } CHCl_3} \text{Observe the colour of organic layer (bottom layer)}$$

◆ $2\ NaBr + \underset{[O.A.]}{Cl_2\ Water} \longrightarrow Br_2\ \text{(Non-polar)} + \underset{\text{(Soluble in water)}}{2\ NaCl}$

Br_2 ↓ Soluble in organic solvent

A brown colouration in the organic layer confirms the presence of bromide ion.

◆ $2\ NaI + \underset{\text{(limited)}}{Cl_2\ water} \longrightarrow I_2 + 2NaCl$

A violet colour appears in the organic layer

Note

- $NaI + \underset{[Excess]}{\text{Chlorine water}} \longrightarrow \underset{\text{(Violet)}}{I_2} \longrightarrow IO_3^-$ (Colourless)
- When chlorine water is added to a solution containing both Br^- and I^- ions, the iodide is first oxidized to iodine, which forms a violet colored layer in the organic solvent. Then Br^- oxidises to bromine, which forms an orange-yellow layer in the organic solvent.

17. When Cu^{2+} ion is treated with KI a white precipitate, X appears in solution. The solution is titrated with sodium thiosulphate, the compound Y is formed. X and Y respectively are (JEE Mains 2023)

(a) $X = CuI_2$ $Y = Na_2S_2O_3$
(b) $X = CuI_2$ $Y = Na_2S_4O_6$
(c) $X = Cu_2I_2$ $Y = Na_2S_4O_5$
(d) $X = Cu_2I_2$ $Y = Na_2S_4O_6$

Sol. (d) $Cu^{2+} + K^+I^- \longrightarrow Cu_2I_2\ (X) \xrightarrow{Na_2S_2O_3} Na_2S_4O_6\ (Y)$

18. Match List-I with List-II.

List – I (Anion)		List – II (Gas evolved on reaction with dil. H_2SO_4	
(A)	CO_3^{2-}	(I)	Colourless gas which turns lead acetate paper black.
(B)	S^{2-}	(II)	Colourless gas which turns acidified potassium dichromate solution green.
(C)	SO_3^{2-}	(III)	Brown fumes which turns acidified KI solution containing starch blue.
(D)	NO	(IV)	Colourless gas evolved with brisk effervescence, which turns lime water milky.

Choose the correct answer from the options given below: (JEE Mains 2022)

(a) A – III, B – I, C – II, D – IV
(b) A – III, B – I, C – IV, D – III
(c) A – IV, B – I, C – III, D – II
(d) A – IV, B – I, C – II, D – III

Sol. (d) A – IV, B – I, C – II, D – III

Note

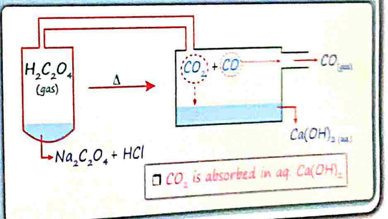
$C_2O_4^{2-}$

Colorless, odourless gas is evolved which turns lime water milky and the gas coming out of lime water burns with a blue flame, if ignited.

$$C_2O_4^{2-} \xrightarrow[dil]{H^+} \underset{\text{Oxalic acid}}{H_2C_2O_4}$$

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow[-H_2O]{\Delta} CO\uparrow + CO_2\uparrow$$

$$CO_2 \xrightarrow{Ca(OH)_2} \underset{\text{[Burn with blue flame]}}{CO_{(g)}}$$



❑ CO_2 is absorbed in aq. $Ca(OH)_2$

TEST FOR CATIONS

Cations

Dry Test (Solid Form)

- Colour Test
- Dry Heating Test
- Flame Test
- Borax Bead Test
- Phosphate Bead test (Microcosmic salt)
- Charcoal cavity and cobalt nitrate test

Wet Test (aq. Reaction) Group -test

DRY TEST

Colour Test

- Observe the colour of the salt, which may provide useful information.

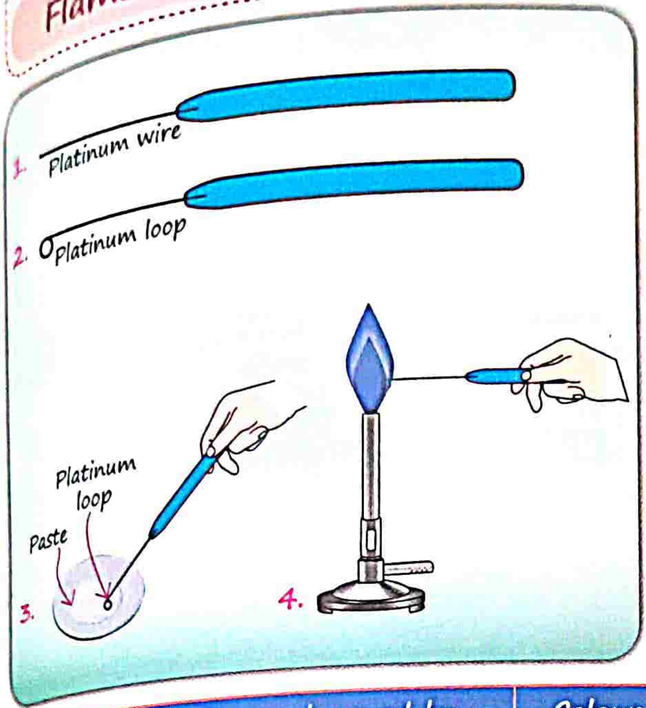
Colour	Cations Indicated
Light green, Yellow, Brown	Fe^{2+}, Fe^{3+}
Blue	Cu^{2+}
Bright green	Ni^{2+}
Blue, Red, Violet, Pink	Co^{2+}
Light pink	Mn^{2+}

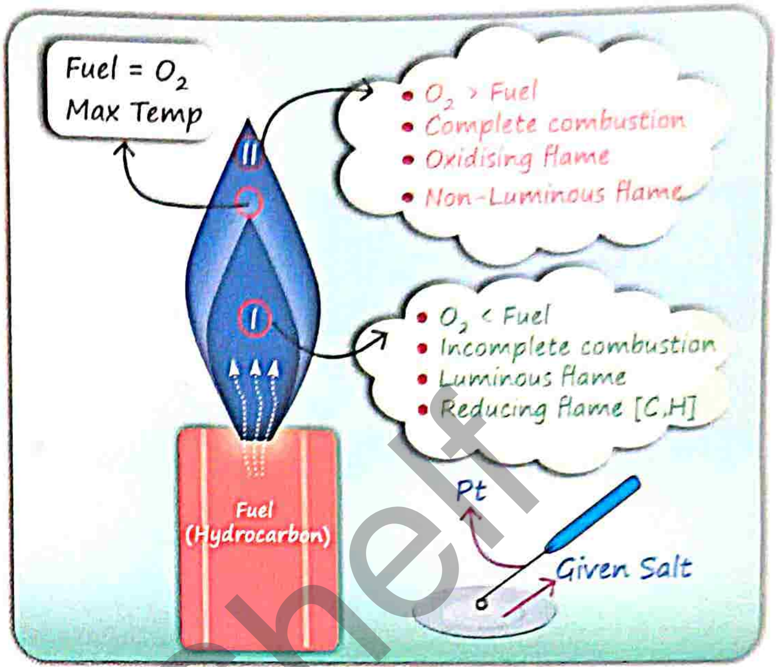
Dry Heating Test

- Heat the given salt in a dry test tube for about 1 minute and observe the colour of residue.

Colour when cold	Colour when hot	Inference
Blue	White	Cu^{2+}
Green	Dirty white or yellow	Fe^{2+}
White	Yellow	Zn^{2+}
Pink	Blue	Co^{2+}

Flame Test





Colour of the flame observed by naked eye	Colour of the flame observed through blue glass	Inference
Green flame with blue centre	Same colour as observed without glass	Cu^{2+}
Crimson red	Purple	Sr^{2+}
Apple green	Bluish green	Ba^{2+}
Brick red	Green	Ca^{2+}

19. In the flame test of a mixture of salts, a green flame with blue centre was observed. Which one of the following cations may be present? [24 Jan, 2022 (Shift-II)]

(a) Cu^{2+} (b) Sr^{2+} (c) Ba^{2+} (d) Ca^{2+}

Sol. (a)

Borax Bead Test → Identification of d block metals (like Cr, Co, Cu)

- ❑ On Heating borax, first loses water and swells up.
- ❑ On further heating it turns into transparent liquid which solidifies in glass like material (borax bead).

$$Na_2B_4O_7.10H_2O \xrightarrow[-10\,H_2O]{\Delta} Na_2B_4O_7 \equiv Na_2O.2B_2O_3 \longrightarrow \underset{\substack{\downarrow \\ 2NaBO_2 \text{ Sodium Metaborate}}}{\underline{Na_2O.B_2O_3}} + B_2O_3 \text{ Boric Anhydride}$$

❑ $$CuSO_4 \xrightarrow[\text{Non-luminous flame}]{B_2O_3} \underset{\text{Cupric metaborate}}{Cu(BO_2)_2} \begin{cases} \xrightarrow{\text{Cold}} \text{Blue} \\ \xrightarrow{\text{hot}} \text{Green} \end{cases}$$

When borax is heated in a Bunsen burner flame with CuO on a loop of platinum wire, a blue coloured $Cu(BO_2)_2$ bead is formed.

☐ $\overset{+2}{2Cu(BO_2)_2} + 2NaBO_2 \xrightarrow[\text{Luminous flame}]{C} \overset{+1}{2CuBO_2} + Na_2B_4O_7 + CO\uparrow$

Cupric metaborate (Colourless when hot)

$\xrightarrow[\text{When cold}]{C} 2Cu + CO\uparrow$

(red and opaque)

Heating in oxidising (non-luminous) flame Colour of the salt bead		Heating in reducing (luminous) flame Colour of the salt bead		Inference
In cold	In hot	In cold	In hot	
Blue	Green	Red opaque	Colourless	Cu^{2+}
Reddish brown	Violet	Grey	Grey	Ni^{2+}
Light violet	Light violet	Colourless	Colourless	Mn^{2+}
Yellow	Yellowish brown	Green	Green	Fe^{3+}

Phosphate Bead Test

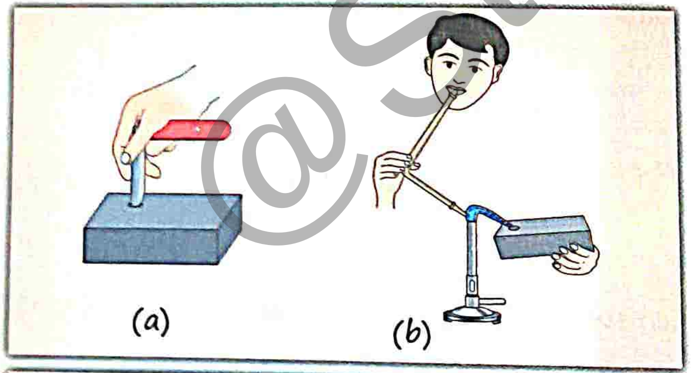
$NaNH_4HPO_4 \cdot 4H_2O \xrightarrow{\Delta} NH_3\uparrow + 5H_2O\uparrow + \boxed{NaPO_3}$ Sodium metaphosphate

Microcosmic salt Phosphate bead

$CuO + NaPO_3 \longrightarrow NaCuPO_4$ (Blue)

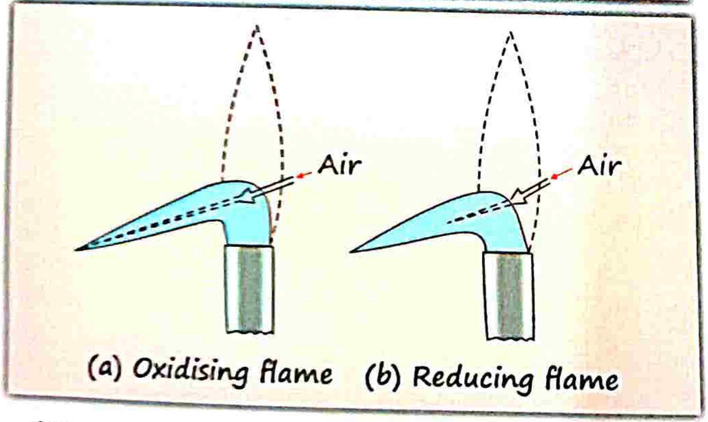
$\xrightarrow[NaBO_2]{B_2O_3} Cu(BO_2)_2$ (Blue)

Charcoal Cavity Test



Salt + $Na_2CO_3 \xrightarrow{\Delta}$ Coloured Metal oxides

$CaCO_3 \xrightarrow{\Delta} CO\uparrow + \boxed{CuO} \xrightarrow{C} Cu$ (Red)



Colour of oxides (cold)	
Pb^{2+}	Grey
Cd^{2+}	Brown
As^{3+}	White (garlic odour)
Zn^{2+}	White

☐ When test is performed with $CuSO_4$, the following change occurs:

$$CuSO_4 + Na_2CO_3 \xrightarrow{Heat} CuCO_3 + Na_2SO_4$$

$$CuCO_3 \xrightarrow{Heat} CuO + CO_2$$

$$CuO + C \xrightarrow{Heat} \underset{\text{Red colour}}{Cu} + CO\uparrow$$

☐ In case of $ZnSO_4$:

$$ZnSO_4 + Na_2CO_3 \xrightarrow{Heat} ZnCO_3 + Na_2SO_4$$

$$ZnCO_3 \xrightarrow{Heat} \underset{\text{Yellow when hot, white when cold}}{ZnO} + CO_2$$

Observations	Inference
Yellow residue when hot and grey metal when cold	Pb^{2+}
White residue with the odour of garlic	As^{3+}
Brown residue	Cd^{2+}
Yellow residue when hot and white when cold	Zn^{2+}

Cobalt Nitrate Test

If the residue in the charcoal cavity is white, cobalt nitrate test is performed.

(i) Treat the residue with two or three drops of cobalt nitrate solution.

(ii) Heat it strongly in non-luminous flame with the help of a blow pipe and observe the colour of the residue.

On heating, cobalt nitrate decomposes into cobalt (II) oxide, which gives a characteristic colour with metal oxide present in the cavity.

☐ $$2Co(NO_3)_2 \xrightarrow{Heat} 2CoO + 4NO_2 + O_2$$

$$CoO + ZnO \longrightarrow CoO.ZnO \text{ Green}$$

$$CoO + MgO \longrightarrow CoO.MgO \text{ Pink}$$

$$CoO + Al_2O_3 \longrightarrow CoO.Al_2O_3 \text{ Blue}$$

WET TESTS FOR IDENTIFICATION OF CATIONS

Preparation of Original Solutions

1. Take a little amount of the salt in a clean boiling tube and add a few mL of distilled water and shake it. If the salt does not dissolved, heat the content of the boiling tube till the salt completely dissolves.
2. If the salt is insoluble in water as detailed above, take fresh salt in a clean boiling tube and add a few mL of dil. HCl to it. If the salt is insoluble in cold, heat the boiling tube till the salt is completely dissolved.
3. If the salt does not dissolve either in water or in dilute HCl even on heating, try to dissolve it in a few mL of conc. HCl by heating.
4. If salt does not dissolve in conc. HCl , then dissolve it in dilute nitric acid.
5. If salt does not dissolve even in nitric acid then a mixture of conc. HCl and conc. HNO_3 in the ratio 3 : 1 is tried. This mixture is called aqua regia. A salt not soluble in aqua regia is considered to be an insoluble salt.

GROUP TEST

Group	Cations		Group Reagent
I.	Pb^{+2} Hg_2^{+2} Ag^+ Aaj ka Hoga Prabhu		dil HCl
II.	IIA	Pb^{+2} Cu^{+2} Hg^{+2} Cd^{+2} Bi^{+3} [Cu group] Prabhu Cadbury Kyu Bimar Hogayi	H_2S gas + HCl $\longrightarrow$ less $[S^{2-}]$
	IIB	As^{+3} As^{+5} Sb^{+3} Sb^{+5} Sn^{+2} Sn^{+4} [As group] Aas Sab Suno	
III.	Al^{+3} Cr^{+3} Fe^{+3} Aloo Feka Kro		$NH_4OH + NH_4Cl \longrightarrow$ less $[OH^-]$
IV.	Ni^{+2} Co^{+2} Mn^{+2} Zn^{+2} Coi nahi Man Zinda		H_2S gas + $NH_4OH \longrightarrow$ more $[S^{2-}]$
V.	Ba^{+2} Sr^{+2} Ca^{+2} Bharat Sar-kar		$(NH_4)_2CO_3 + NH_4OH$
VI.	Na^+ K^+ Mg^{+2}		$Na_2HPO_4 + NH_4OH$

This table is based on K_{sp} values –
K_{sp} : I < II < III < IV < V < VI

For example → K_{sp} : $Na_2S > ZnS > CuS$
: $CdS < NiS$

TEST FOR GROUP-0 CATION : NH_4^+

Group Reagent: Aq. NaOH, KOH

☐ Zero group test is performed before group analysis begins.

☐ Reasons Why NH_4^+ Is Not in the Table of Cations in Salt Analysis:

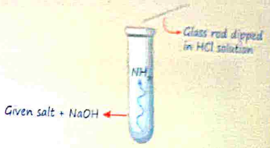
- NH_4^+ doesn't form characteristic precipitates with group reagents like HCl, H_2S, NH_4OH.
- NH_4^+ is already present in the form of group reagent, so group reagent can not be used for identification of NH_4^+.
- NH_4^+ cation is the only cation which is identified by it's volatile product.

$$NH_4^+ + \underset{\text{(base)}}{OH^-} \longrightarrow \boxed{NH_3\uparrow} + H_2O$$

→ NH_4^+ is detected by characteristic smell of ammonia.

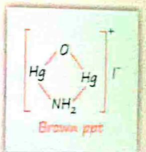
Detection of NH_3 & NH_4^+

It is characterised by
(i) Its smell
(ii) Turns red litmus blue.
(iii) When a glass rod dipped in HCl solution is brought near the gas white dense fumes form
$NH_3 + HCl \longrightarrow NH_4Cl\uparrow$



$$\underset{\text{(Given salt)}}{NH_4^+} + KOH + \underbrace{K_2HgI_4}_{\text{Nessler's Reagent}} \longrightarrow HgO{\cdot}Hg(NH_2)I\downarrow$$

Brown ppt
Iodide of Melon's base
(Basic mercury (II) amido-iodine)



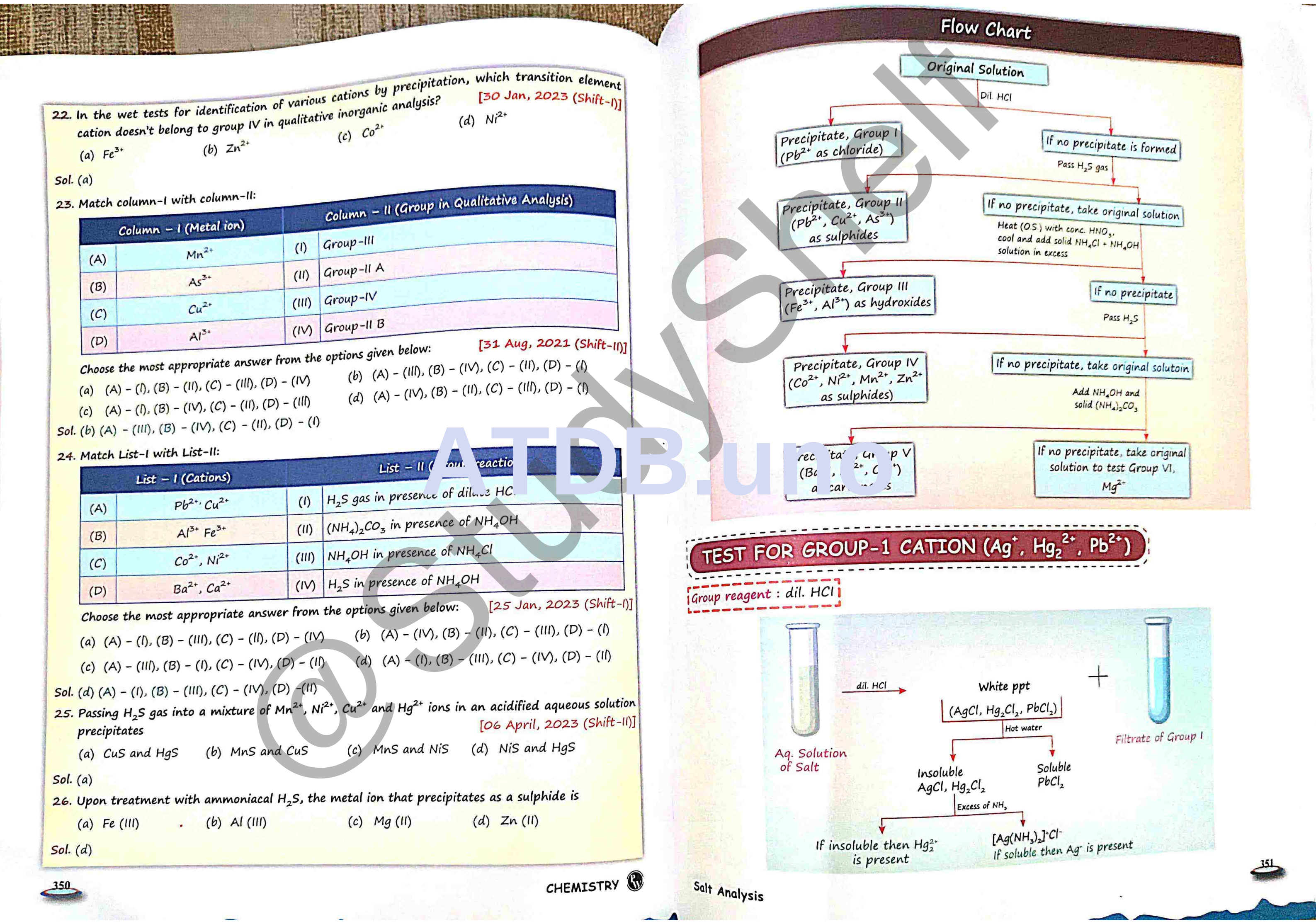
Brown ppt

20. When a salt is treated with sodium hydroxide solution it gives gas X. On passing gas X through reagent Y a brown coloured precipitate is formed. X and Y respectively, are [07 April, 2025 (Shift-I)]
(a) X = NH_3 and Y = HgO
(b) X = NH_3 and Y = K_2HgI_4 + KOH
(c) X = NH_4Cl and Y = KOH
(d) X = HCl and Y = NH_4Cl

Sol. (b)

21. Formulae of Nessler's Reagent is (JEE Mains 2023)
(a) KHg_2I_2
(b) $KHgI_3$
(c) K_2HgI_4
(d) HgI_2

Sol. (c)



22. In the wet tests for identification of various cations by precipitation, which transition element cation doesn't belong to group IV in qualitative inorganic analysis? [30 Jan, 2023 (Shift-I)]

(a) Fe^{3+} (b) Zn^{2+} (c) Co^{2+} (d) Ni^{2+}

Sol. (a)

23. Match column-I with column-II:

Column – I (Metal ion)		Column – II (Group in Qualitative Analysis)	
(A)	Mn^{2+}	(I)	Group-III
(B)	As^{3+}	(II)	Group-II A
(C)	Cu^{2+}	(III)	Group-IV
(D)	Al^{3+}	(IV)	Group-II B

Choose the most appropriate answer from the options given below: [31 Aug, 2021 (Shift-II)]

(a) (A) – (I), (B) – (II), (C) – (III), (D) – (IV)
(b) (A) – (III), (B) – (IV), (C) – (II), (D) – (I)
(c) (A) – (I), (B) – (IV), (C) – (II), (D) – (III)
(d) (A) – (IV), (B) – (II), (C) – (III), (D) – (I)

Sol. (b) (A) – (III), (B) – (IV), (C) – (II), (D) – (I)

24. Match List-I with List-II:

List – I (Cations)		List – II ([illegible]reactio[illegible]	
(A)	Pb^{2+}, Cu^{2+}	(I)	H_2S gas in presence of dilute HC[illegible]
(B)	Al^{3+} Fe^{3+}	(II)	$(NH_4)_2CO_3$ in presence of NH_4OH
(C)	Co^{2+}, Ni^{2+}	(III)	NH_4OH in presence of NH_4Cl
(D)	Ba^{2+}, Ca^{2+}	(IV)	H_2S in presence of NH_4OH

Choose the most appropriate answer from the options given below: [25 Jan, 2023 (Shift-I)]

(a) (A) – (I), (B) – (III), (C) – (II), (D) – (IV)
(b) (A) – (IV), (B) – (II), (C) – (III), (D) – (I)
(c) (A) – (III), (B) – (I), (C) – (IV), (D) – (II)
(d) (A) – (I), (B) – (III), (C) – (IV), (D) – (II)

Sol. (d) (A) – (I), (B) – (III), (C) – (IV), (D) –(II)

25. Passing H_2S gas into a mixture of Mn^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates [06 April, 2023 (Shift-II)]

(a) CuS and HgS (b) MnS and CuS (c) MnS and NiS (d) NiS and HgS

Sol. (a)

26. Upon treatment with ammoniacal H_2S, the metal ion that precipitates as a sulphide is

(a) Fe (III) (b) Al (III) (c) Mg (II) (d) Zn (II)

Sol. (d)

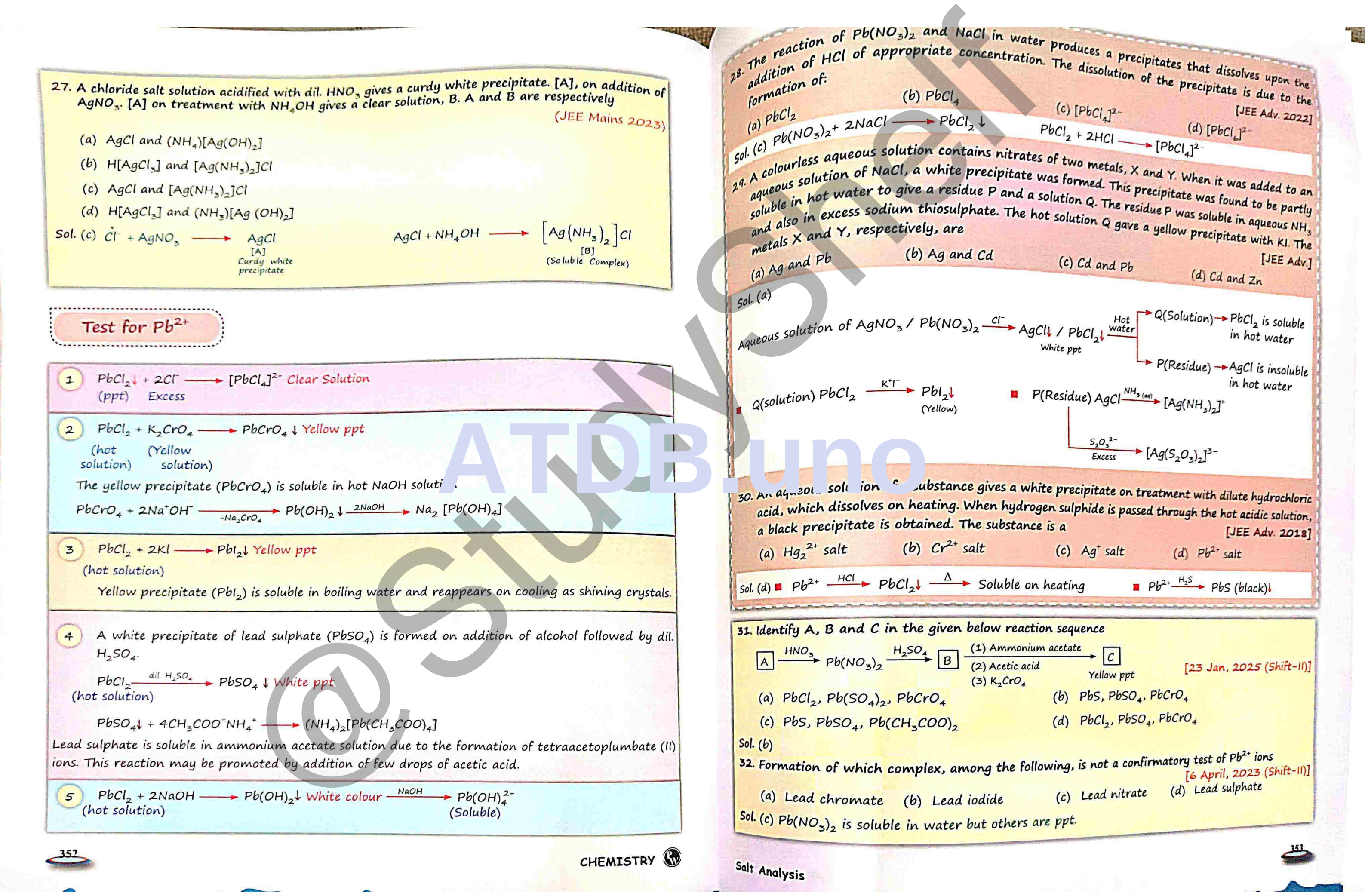
Flow Chart

Original Solution
Dil. HCl
Precipitate, Group I (Pb^{2+} as chloride)
If no precipitate is formed
Pass H_2S gas
Precipitate, Group II (Pb^{2+}, Cu^{2+}, As^{3+}) as sulphides
If no precipitate, take original solution
Heat (O.S) with conc. HNO_3, cool and add solid NH_4Cl + NH_4OH solution in excess
Precipitate, Group III (Fe^{3+}, Al^{3+}) as hydroxides
If no precipitate
Pass H_2S
Precipitate, Group IV (Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+} as sulphides)
If no precipitate, take original solutoin
Add NH_4OH and solid $(NH_4)_2CO_3$
[illegible]rec[illegible]ta[illegible], G[illegible]p V (B[illegible], [illegible]$^{2+}$, C[illegible]) a[illegible]car[illegible]s
If no precipitate, take original solution to test Group VI, Mg^{2+}

TEST FOR GROUP-1 CATION (Ag^+, Hg_2^{2+}, Pb^{2+})

Group reagent : dil. HCl

Aq. Solution of Salt
dil. HCl
White ppt ($AgCl$, Hg_2Cl_2, $PbCl_2$)
+
Filtrate of Group I
Hot water
Insoluble $AgCl$, Hg_2Cl_2
Soluble $PbCl_2$
Excess of NH_3
If insoluble then Hg_2^{2+} is present
$[Ag(NH_3)_2]^+Cl^-$ If soluble then Ag^+ is present



27. A chloride salt solution acidified with dil. HNO_3 gives a curdy white precipitate. [A], on addition of $AgNO_3$. [A] on treatment with NH_4OH gives a clear solution, B. A and B are respectively (JEE Mains 2023)

(a) AgCl and $(NH_4)[Ag(OH)_2]$

(b) $H[AgCl_3]$ and $[Ag(NH_3)_2]Cl$

(c) AgCl and $[Ag(NH_3)_2]Cl$

(d) $H[AgCl_3]$ and $(NH_3)[Ag(OH)_2]$

Sol. (c) $Cl^- + AgNO_3 \longrightarrow \underset{\substack{[A] \\ \text{Curdy white} \\ \text{precipitate}}}{AgCl}$ $\quad AgCl + NH_4OH \longrightarrow \underset{\substack{[B] \\ \text{(Soluble Complex)}}}{[Ag(NH_3)_2]Cl}$

Test for Pb^{2+}

① $\underset{\text{(ppt)}}{PbCl_2\downarrow} + \underset{\text{Excess}}{2Cl^-} \longrightarrow [PbCl_4]^{2-}$ Clear Solution

② $\underset{\text{(hot solution)}}{PbCl_2} + \underset{\text{(Yellow solution)}}{K_2CrO_4} \longrightarrow PbCrO_4\downarrow$ Yellow ppt

The yellow precipitate ($PbCrO_4$) is soluble in hot NaOH solution.

$$PbCrO_4 + 2Na^+OH^- \xrightarrow[-Na_2CrO_4]{} Pb(OH)_2\downarrow \xrightarrow{2NaOH} Na_2\,[Pb(OH)_4]$$

③ $\underset{\text{(hot solution)}}{PbCl_2} + 2KI \longrightarrow PbI_2\downarrow$ Yellow ppt

Yellow precipitate (PbI_2) is soluble in boiling water and reappears on cooling as shining crystals.

④ A white precipitate of lead sulphate ($PbSO_4$) is formed on addition of alcohol followed by dil. H_2SO_4.

$\underset{\text{(hot solution)}}{PbCl_2} \xrightarrow{\text{dil } H_2SO_4} PbSO_4\downarrow$ White ppt

$$PbSO_4\downarrow + 4CH_3COO^-NH_4^+ \longrightarrow (NH_4)_2[Pb(CH_3COO)_4]$$

Lead sulphate is soluble in ammonium acetate solution due to the formation of tetraacetoplumbate (II) ions. This reaction may be promoted by addition of few drops of acetic acid.

⑤ $\underset{\text{(hot solution)}}{PbCl_2} + 2NaOH \longrightarrow Pb(OH)_2\downarrow$ White colour $\xrightarrow{NaOH} \underset{\text{(Soluble)}}{Pb(OH)_4^{2-}}$

28. The reaction of $Pb(NO_3)_2$ and NaCl in water produces a precipitates that dissolves upon the addition of HCl of appropriate concentration. The dissolution of the precipitate is due to the formation of: [JEE Adv. 2022]

(a) $PbCl_2$ (b) $PbCl_4$ (c) $[PbCl_4]^{2-}$ (d) $[PbCl_6]^{2-}$

Sol. (c) $Pb(NO_3)_2 + 2NaCl \longrightarrow PbCl_2\downarrow$ $\quad PbCl_2 + 2HCl \longrightarrow [PbCl_4]^{2-}$

29. A colourless aqueous solution contains nitrates of two metals, X and Y. When it was added to an aqueous solution of NaCl, a white precipitate was formed. This precipitate was found to be partly soluble in hot water to give a residue P and a solution Q. The residue P was soluble in aqueous NH_3 and also in excess sodium thiosulphate. The hot solution Q gave a yellow precipitate with KI. The metals X and Y, respectively, are [JEE Adv.]

(a) Ag and Pb (b) Ag and Cd (c) Cd and Pb (d) Cd and Zn

Sol. (a)

Aqueous solution of $AgNO_3 / Pb(NO_3)_2 \xrightarrow{Cl^-} \underset{\text{White ppt}}{AgCl\downarrow / PbCl_2\downarrow} \xrightarrow{\text{Hot water}}$

→ Q(Solution) → $PbCl_2$ is soluble in hot water

→ P(Residue) → AgCl is insoluble in hot water

- Q(solution) $PbCl_2 \xrightarrow{K^+I^-} \underset{\text{(Yellow)}}{PbI_2\downarrow}$
- P(Residue) $AgCl \xrightarrow{NH_{3\,(aq)}} [Ag(NH_3)_2]^+$
  $AgCl \xrightarrow[\text{Excess}]{S_2O_3^{2-}} [Ag(S_2O_3)_2]^{3-}$

30. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a [JEE Adv. 2018]

(a) Hg_2^{2+} salt (b) Cr^{2+} salt (c) Ag^+ salt (d) Pb^{2+} salt

Sol. (d) ■ $Pb^{2+} \xrightarrow{HCl} PbCl_2\downarrow \xrightarrow{\Delta}$ Soluble on heating ■ $Pb^{2+} \xrightarrow{H_2S} PbS\text{ (black)}\downarrow$

31. Identify A, B and C in the given below reaction sequence [23 Jan, 2025 (Shift-II)]

$$\boxed{A} \xrightarrow{HNO_3} Pb(NO_3)_2 \xrightarrow{H_2SO_4} \boxed{B} \xrightarrow[\substack{\text{(2) Acetic acid} \\ \text{(3) } K_2CrO_4}]{\text{(1) Ammonium acetate}} \underset{\text{Yellow ppt}}{\boxed{C}}$$

(a) $PbCl_2$, $Pb(SO_4)_2$, $PbCrO_4$ (b) PbS, $PbSO_4$, $PbCrO_4$

(c) PbS, $PbSO_4$, $Pb(CH_3COO)_2$ (d) $PbCl_2$, $PbSO_4$, $PbCrO_4$

Sol. (b)

32. Formation of which complex, among the following, is not a confirmatory test of Pb^{2+} ions [6 April, 2023 (Shift-II)]

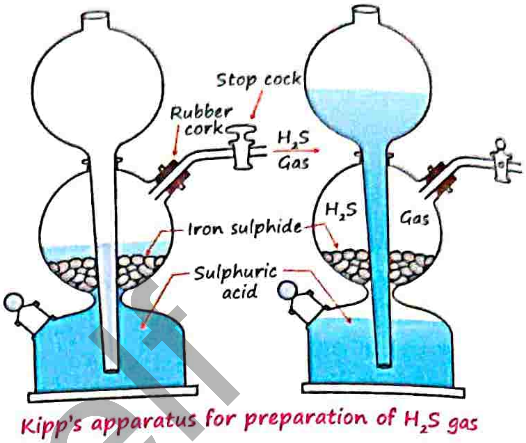
(a) Lead chromate (b) Lead iodide (c) Lead nitrate (d) Lead sulphate

Sol. (c) $Pb(NO_3)_2$ is soluble in water but others are ppt.

TEST FOR GROUP-II A (Pb^{+2}, Cu^{+2}, Hg^{+2}, Cd^{+2}, Bi^{+3})

Group reagent : H_2S gas + HCl

$$Pb^{2+} / Cu^{2+} / Hg^{2+} / Cd^{2+} \xrightarrow[HCl]{H_2S} \underset{\text{Black}}{\underset{\downarrow}{PbS, CuS, HgS}} \quad \underset{\text{Yellow}}{\underset{\downarrow}{CdS}}$$



Kipp's apparatus for preparation of H_2S gas

Test for Pb^{2+}

$$Pb^{+2} + H_2S \longrightarrow \underset{[\text{Black}]}{\overset{+2\,-2}{PbS}} \xrightarrow[\overset{+2}{NO}\uparrow]{\overset{+5}{HNO_3}} \underset{+\ S}{Pb(NO_3)_2} \xrightarrow{H_2SO_4} \underset{\text{White ppt}}{PbSO_4\downarrow}$$

☐ $\underset{\text{White}}{PbSO_4\downarrow} \xrightarrow[\text{Boiling}]{CH_3COONH_4} (NH_4)_2[Pb(CH_3COO)_4]$ Clear solution

$\xrightarrow{K_2CrO_4}$ $PbCrO_4\downarrow$ Yellow ppt

$\xrightarrow{KI}$ $PbI_2\downarrow$ Yellow ppt

Test for Cu^{2+}

$$Cu^{+2} + H_2S \longrightarrow \underset{\text{Black ppt}}{\overset{+2\ -2}{CuS}} \xrightarrow[NO\uparrow]{\text{Excess } HNO_3} Cu(NO_3)_2 + S$$

① $S \xrightarrow{\text{Conc. } HNO_3} H_2SO_4$

② $Cu(NO_3)_2 \xrightarrow{H_2SO_4} \underset{\text{(Light blue)}}{CuSO_4}$

$$\underset{\text{(Light Blue)}}{CuSO_4} + NH_4OH \longrightarrow \underset{\substack{\text{Light Blue ppt} \\ \text{[Basic Copper sulphate]}}}{Cu(OH)_2 \cdot CuSO_4\downarrow} \xrightarrow[\text{excess}]{NH_4OH} [Cu(NH_3)_4]SO_4 \quad \underset{\text{(Deep blue)}}{\text{Soluble}}$$

The blue solution on acidification with acetic acid and then adding $K_4[Fe(CN)_6]$ solution gives a chocolate colouration due to the formation of copper ferrocyanide.

$[Cu(NH_3)_4]SO_4 \xrightarrow{CH_3COOH} CuSO_4$

$Cu^{+2} + K_4[Fe(CN)_6] \longrightarrow Cu_2[Fe(CN)_6]\downarrow$ Chocolate Brown ppt

☐ $Cu^{+2} + K_3[Fe(CN)_6] \longrightarrow \underset{\text{Green ppt}}{Cu_3[Fe(CN)_6]_2}$

☐ $2Cu^{+2} + 4KI \longrightarrow \underset{\text{(Yellow coloured solution)}}{2CuI_2} \longrightarrow \underset{\text{(White ppt)}}{Cu_2I_2} + I_2$

$I_2 \xrightarrow[\text{excess}]{I^-} \underset{\text{(Dark brown appearance)}}{I_3^-} \xrightarrow[\text{hypo solution}]{2S_2O_3^{2-}} 3I^- + \underset{\text{(Colourless)}}{S_4O_6^{2-}}$

☐ $CuSO_4$ decolourises on addition of KCN.

$Cu^{+2} + 2KCN \longrightarrow \underset{\text{Yellow}}{Cu(CN)_2} \longrightarrow CuCN + (CN)_2\uparrow$ Cyanogen gas

$CuCN \xrightarrow{3\ KCN} K_3[Cu(CN)_4]$ Soluble

33. The pair(s) of ions where both the ions are precipitated upon passing H_2S gas in presence of dilute HCl, is (are) **[JEE Adv. 2015]**

(a) Ba^{2+}, Zn^{2+} (b) Bi^{3+}, Fe^{3+} (c) Cu^{2+}, Pb^{2+} (d) Hg^{2+}, Bi^{3+}

Sol. (c) and (d)

34. $CuSO_4$ decolourises on addition of KCN, the product is **[JEE Adv. 2006]**

(a) $[Cu(CN)_4]^{2-}$
(b) Cu^{2+} get reduced to form $[Cu(CN)_4]^{3-}$
(c) $Cu(CN)_2$
(d) CuCN

Sol. (b) $Cu^{2+} \xrightarrow{\text{Excess } CN^-} (CN)_2\uparrow + \boxed{[Cu(CN)_4]^{3-}} \longrightarrow$ Oxidation state of Cu is +1.

35. An aqueous blue coloured solution of a transition metal sulphate reacts with H_2S in acidic medium to give a black precipitate A, which is insoluble in warm aqueous solution of KOH. The blue solution on treatment with KI in weakly acidic medium, turns yellow and produces a white precipitate B. Identify the transition metal ion. Write the chemical reactions involved in the formation of A and B. **[JEE Adv. 2000]**

Sol. The transition metal involved is Cu^{2+}, and the compound $CuSO_4 \cdot 5H_2O$. It dissolves in water producing a blue-colored solution. When H_2S is passed into the acidic solution, a black precipitate of CuS is formed.

$$CuSO_4 + H_2S \xrightarrow[\text{medium}]{\text{Acidic}} \underset{\substack{\text{(black ppt.)} \\ \text{(insoluble in aq. KOH)}}}{CuS\downarrow} + H_2SO_4$$

When KI solution is added to the aqueous $CuSO_4$ solution, a yellow-coloured solution of CuI_2 is formed. This solution decomposes to form a white precipitate of Cu_2I_2 and liberates I_2.

$CuSO_4 + 2KI \longrightarrow \underset{\text{Yellow solution}}{CuI_2 + K_2SO_4}$ $2CuI_2 \longrightarrow \underset{\text{white ppt.}}{Cu_2I_2} + I_2$

II^{nd} GROUP (Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+} As^{3+}, Sb^{3+}, Sn^{2+})

On the basis of the solubility of the precipitates of the sulphides of II group cations in yellow ammonium sulphide, they have been classified into two subgroups as given below:

IIA	IIB
HgS, PbS, CuS, Bi_2S_3, all black but CdS is yellow. All insoluble in yellow ammonium sulphide.	SnS_2, As_2S_3 are yellow, Sb_2S_5 is orange & SnS is dark brown. All soluble in yellow ammonium sulphide.

TEST FOR GROUP-II B (As^{3+})

$$As_2S_3 \xrightarrow[\text{Yellow ammonium sulphide}]{\text{1. }(NH_4)_2S_2} \underset{\text{Ammonium thioarsenide}}{(NH_4)_3AsS_4} \xrightarrow{\text{2. HCl}} \underset{\text{Arsenic (V) sulphide}}{As_2S_5} \xrightarrow[\Delta]{\text{3. Conc. }HNO_3} \underset{\text{Arsenic acid (Clear solution)}}{H_3AsO_4}$$

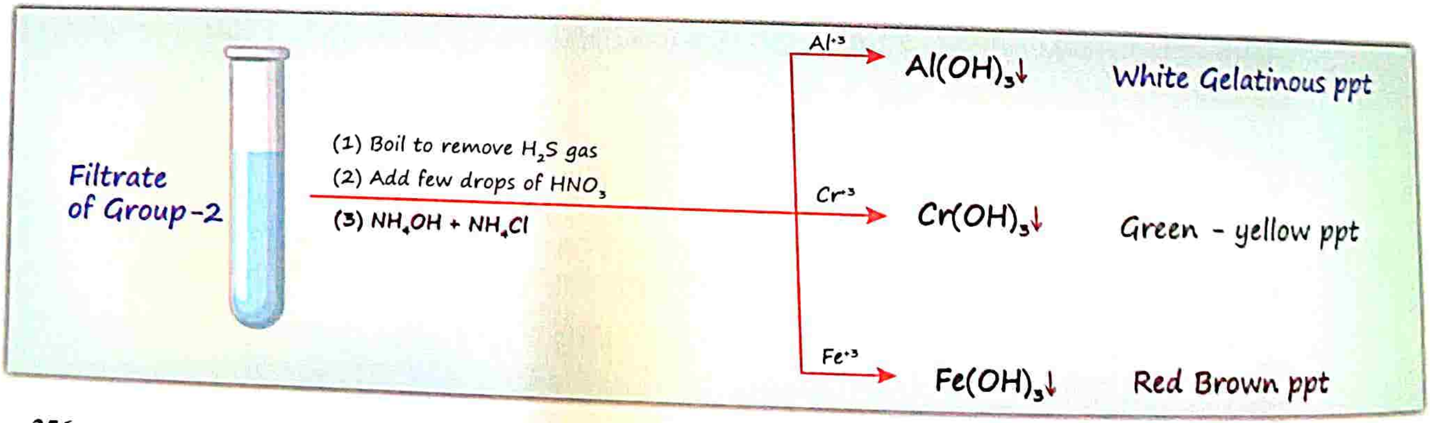
$$H_3AsO_4 \xrightarrow[HNO_3]{\text{4. }(NH_4)_2MoO_4 \text{ Ammonium molybdate}} \underset{\text{Ammonium arsinomolybdate (Canary yellow ppt)}}{(NH_4)_3[As(Mo_3O_{10})_4]}$$

TEST FOR GROUP-III (Fe^{+3}, Cr^{+3}, Al^{+3})

Group reagent ⟶ $NH_4OH + NH_4Cl$: Less $[OH^-]$

☐ $\underset{(O.A)}{Fe^{3+}} + \underset{(R.A)}{H_2S} \longrightarrow Fe^{+2} \xrightarrow{HNO_3} Fe^{+3}$

Before performing the test of III^{rd} group cation, boil II^{nd} group filtrate to remove H_2S gas. After this add few drops of conc. HNO_3 to oxidise Fe^{+2} ion (which was obtain after reduction of Fe^{+3} ion) into Fe^{+3}.



Test for Al^{+3}

$$\underset{\text{White ppt}}{Al(OH)_3\downarrow} + \underset{(excess)}{NaOH} \longrightarrow Na[Al(OH)_4] \quad \text{Soluble}$$

Lake Test

☐ The lake test is confirmatory test used to detect the presence of Al^{3+} in a solution.

$$\begin{tikzcd}
\text{Aq. solution of given mixture} \arrow[r, "NH_4Cl", "NH_4OH"'] & \text{White gelatinous ppt } Al(OH)_3 \arrow[r, "\text{Add HCl}"] & AlCl_3 \text{ (Soluble)} \arrow[d, "\text{Add 2 drops of blue litmus solution}"] \\
\text{Blue floating ppt} & & \text{Red Colour [acidic nature due to presence of HCl]} \arrow[ll, "\text{Add } NH_4OH \text{ to make}"', "\text{solution alkaline}"]
\end{tikzcd}$$

☐ **Principle for this test:**
$Al(OH)_3$ is a good adsorbent, and therefore it adsorbs the blue litmus solution and gives this blue lake test.

Test for Fe^{+3}

$$\begin{tikzcd}
\underset{\text{Reddish brown}}{Fe(OH)_3\downarrow} + HCl \arrow[r] \arrow[d, "NaOH"] & \underset{\text{Soluble (Yellow)}}{FeCl_3} \\
\text{Not Soluble} &
\end{tikzcd}$$

☐ $\underset{\text{(Yellow solution)}}{Fe^{+3}} + \underset{\text{(Light yellow)}}{K_4[Fe(CN)_6]} \longrightarrow Fe_4[Fe(CN)_6]_3\downarrow$ Prussian Blue (ppt)

☐ $Fe^{+3} + \underset{\text{(Excess)}}{K_4[Fe(CN)_6]} \longrightarrow KFe[Fe(CN)_6]$ Soluble Prussian Blue (Colloidal Solution) [can not be filtered.]

☐ $Fe^{+3} + SCN^- \longrightarrow Fe(SCN)^{2+}/Fe(SCN)_3$ Blood Red (Ferric thiocyanate) $[Fe(H_2O)_5(SCN)]^{2+}$ – sp^3d^2

36. When metal 'M' is treated with NaOH a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal M is **[JEE Mains 2019, 2018]**

(a) Zn (b) Ca (c) Al (d) Fe

Sol. (c)

$$\begin{tikzcd}
Al + NaOH \arrow[r] & Al(OH)_3 + H_2\uparrow \arrow[dl, "\Delta"'] \arrow[d, "NaOH"] \\
H_2O + Al_2O_3 & Na[Al(OH)_4]
\end{tikzcd}$$

37. Acidic ferric chloride solution on treatment with excess of potassium ferrocyanide gives a Prussian blue coloured colloidal species. It is [27 Aug, 2021 (Shift-I)]

(a) $KFe[Fe(CN)_6]$ (b) $K_5Fe[Fe(CN)_6]_2$ (c) $Fe_4[Fe(CN)_6]_3$ (d) $HFe[Fe(CN)_6]$

Sol. (a)

38. A solution of $FeCl_3$ when treated with $K_4[Fe(CN)_6]$ gives a prussiun blue precipitate due to the formation of [01 Feb, 2023 (Shift-I)]

(a) $K[Fe_2(CN)_6]$ (b) $Fe[Fe(CN)_6]$ (c) $Fe_3[Fe(CN)_6]_2$ (d) $Fe_4[Fe(CN)_6]_3$

Sol. (d)

Note

$$\underset{\text{Green yellow ppt}}{Cr(OH)_3\downarrow} \xrightarrow[\text{basic medium}]{OH^-} \underset{\text{Clear solution (green)}}{\overset{+3}{Cr}(OH)_4^-}$$

$$\overset{+3}{Cr}(OH)_4^- \xrightarrow{H_2O_2} \overset{+6}{Cr}O_4^{2-} \text{ (yellow coloured solution)}$$

$$\overset{+3}{Cr}(OH)_4^- \xrightarrow{IO_3^-} \overset{+6}{Cr}O_4^{2-} \text{ (yellow coloured solution)}$$

TEST FOR GROUP -IV (Ni^{+2}, Co^{+2}, Mn^{+2}, Zn^{+2})

Group Reagent: $NH_4OH + H_2S$ High $[S^{2-}]$

☐ $Ni^{+2}, Co^{+2}, Mn^{+2}, Zn^{+2} \xrightarrow{\text{high } [S^{2-}]} \underset{\text{Black ppt}}{NiS, CoS}, \underset{\text{Buff pink}}{MnS}, \underset{\text{White}}{ZnS}$

$$MnS, ZnS \xrightarrow[\text{boil}]{HCl} MnCl_2 / ZnCl_2 \text{ (Soluble)}$$

$$CoS, NiS \xrightarrow[HNO_3]{HCl} Co^{2+} \text{ (pink)} / Ni^{2+} \text{ (green)}$$

$$CoS, NiS \xrightarrow{HCl} \text{No reaction}$$

$Zn_2[Fe(CN)_6]$	Bluish white ppt
$Cu_2[Fe(CN)_6]$	Chocolate brown ppt
$Fe_4[Fe(CN)_6]_3$	Prussian blue ppt
$K_4[Fe(CN)_6]$	Light yellow solution
$K_3[Fe(CN)_6]$	Orange-red

Test for Zn^{+2}

$$ZnS \xrightarrow[\text{boil}]{HCl} ZnCl_2 \text{ (Soluble)}$$

☐ $ZnCl_2 + NaOH \longrightarrow \underset{\text{(White)}}{Zn(OH)_2\downarrow}$

$$Zn(OH)_2 \xrightarrow{\text{Excess NaOH}} \underset{\text{(soluble)}}{Na_2[Zn(OH)_4]} \xrightarrow{H_2S} \underset{\text{(Black)}}{ZnS\downarrow}$$

$$Zn(OH)_2 \xrightarrow[NH_4OH]{\text{Excess}} \underset{\text{(soluble)}}{[Zn(NH_3)_4]^{2+}}$$

☐ $ZnCl_2 + K_4[Fe(CN)_6] \xrightarrow[\text{small amount}]{NH_4OH} Zn_2[Fe(CN)_6]\downarrow / K_2Zn_3[Fe(CN)_6]_2\downarrow$ (Bluish White)

Test for Ni^{+2}

$$\underset{(Black)}{NiS} + 2HNO_3 + 6HCl \longrightarrow S + \underset{Soluble}{NiCl_2} + NO\uparrow$$

☐ When dimethyl glyoxime is added to the aqueous solution of nickel chloride, made alkaline, by adding NH_4OH solution, a brilliant red precipitate is obtained.

$$\underset{(Soluble\ in\ water)}{NiCl_2} + dmg^- \longrightarrow \underset{(Rosy\ red\ ppt)}{Ni(dmg)_2\downarrow}$$

Test for Mn^{2+}

$$MnS \xrightarrow[boiling]{2HCl} \underset{(Clear\ solution)}{MnCl_2} \xrightarrow{NaOH} \underset{(White)}{Mn(OH)_2\downarrow} \xrightarrow[oxidation]{Atmospheric} \underset{(Hydrated\ Manganese\ dioxide)}{MnO(OH)_2 \equiv MnO_2 . H_2O} \text{ (Brown Colour)}$$

Test for Co^{2+}

$$CoS \xrightarrow[aqua\ regia]{HNO_3 + 3HCl} \overset{+2}{CoCl_2} + NOCl + S \xrightarrow[CH_3COOH]{\overset{+3}{KNO_2}} \underset{(Yellow\ ppt)}{K_3[\overset{+3}{Co}(NO_2)_6]} + \overset{+2}{NO}$$

39. A solution when diluted with H_2O and boiled, it gives a white precipitate. On addition of excess NH_4Cl / NH_4OH, the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in NH_4Cl / NH_4OH : [JEE Adv. 2006]

(a) $Zn(OH)_2$ (b) $Al(OH)_3$ (c) $Mg(OH)_2$ (d) $Ca(OH)_2$

Sol. (a) $Zn^{2+} + 2H_2O \longrightarrow \underset{White\ ppt.}{Zn(OH)_2\downarrow} + 2H^+$

$$Zn(OH)_2 + 4NH_4OH \xrightarrow{NH_4Cl} \underset{\substack{complex\ ion\\(soluble)}}{[Zn(NH_3)_4]^{2+}} + 4H_2O + 2OH^-$$

40. An ammoniacal metal salt solution gives a brilliant red precipitate on addition of dimethylglyoxime. The metal ion is [JEE Mains 2023]

(a) Ni^{2+} (b) Cu^{2+} (c) Fe^{2+} (d) Co^{2+}

Sol. (a)

41. During the qualitative analysis of salt with cation (Y^{2+}), addition of a reagent (X) to alkaline solution of the salt gives a bright red precipitate. The reagent (X) and the cation (Y^{2+}) present respectively are: [24 Jan 2022, (Shift-I)]

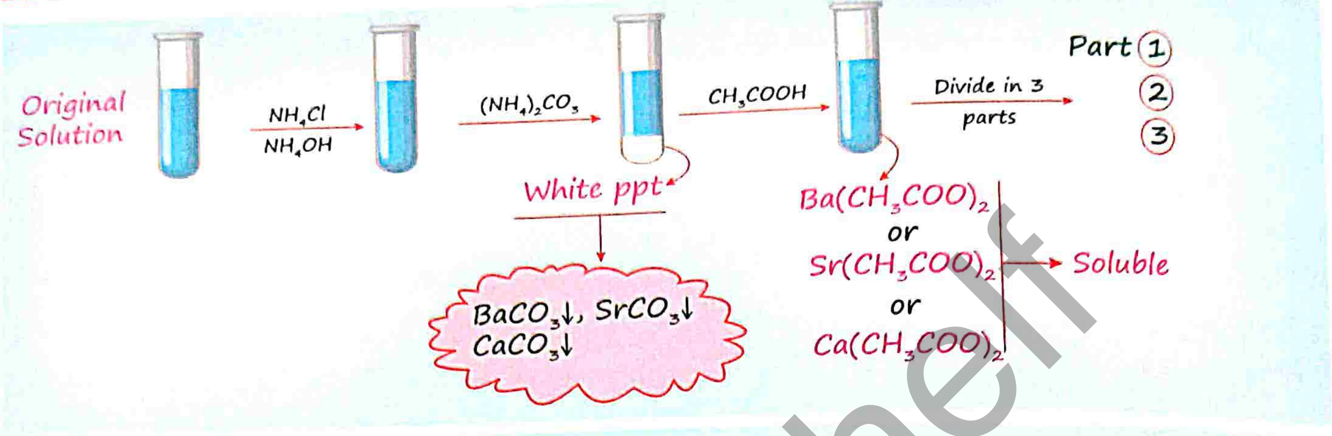
(a) Dimethylglyoxime and Ni^{2+} (b) Dimethylglyoxime and Co^{2+}

(c) Nessler's reagent and Hg^{2+} (d) Nessler's reagent and Ni^{2+}

Sol. (a)

TEST FOR GROUP-V (Ba^{+2}, Sr^{2+}, Ca^{2+})

Group Reagent: $(NH_4)_2CO_3$ in presence of NH_4OH



☐ Preserve a small amount of the precipitate for flame test.

Part (1) $\xrightarrow{K_2CrO_4}$ Yellow ppt of $BaCrO_4$

Part (2) $\xrightarrow{(NH_4)_2SO_4}$ White ppt of $SrSO_4$

Part (3) $\xrightarrow{(NH_4)_2C_2O_4}$ White ppt of CaC_2O_4

$Ba^{2+} \longrightarrow CrO_4^{2-} / SO_4^{2-} / C_2O_4^{2-}$ Insoluble

$Sr^{2+} \longrightarrow SO_4^{2-} / C_2O_4^{2-}$ Insoluble

$Ca^{2+} \longrightarrow C_2O_4^{2-}$ Insoluble

- $\underset{\text{(soluble)}}{Ba(CH_3COO)_2} + \underset{\text{(soluble)}}{K_2CrO_4} \longrightarrow BaCrO_4\downarrow$ Yellow ppt
- $Sr(CH_3COO)_2 + (NH_4)_2SO_4 \longrightarrow SrSO_4\downarrow$ White
- $Ca(CH_3COO)_2 + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4\downarrow$ White

Ba^{2+} ions	Sr^{2+} ions	Ca^{2+} ions
(a) To the first part add potassium chromate solution. A yellow precipitate appears. (b) Perform the flame test with the preserved precipitate. A grassy green flame is obtained.	(a) If barium is absent, take second part of the solution and add ammonium sulphate solution. Heat and scratch the sides of the test tube with a glass rod and cool. A white precipitate is formed. (b) Perform the flame test with the preserved precipitate. A **crimson-red** flame confirms the presence of Sr^{2+} ions.	(a) If both barium and strontium are absent, take the third part of the solution. Add ammonium oxalate solution and shake well. A white precipitate of calcium oxalate is obtained. (b) Perform the flame test with the preserved precipitate. A brick red flame, which looks greenish-yellow through blue glass, confirms the presence of Ca^{2+} ions.

TEST FOR GROUP - VI (Mg^{+2}, K^+, Na^+)

Reagent: Na_2HPO_4

If group- V is absent, the solution may contain $MgCO_3$, which is soluble in water in the presence of ammonium salts (NH_4^+) because the equilibrium is shifted towards the right hand side and hence concentration of carbonate ions (CO_3^{2-}) required to produce a ppt is not attained.

$$NH_4^+ + CO_3^{2-} \rightleftharpoons NH_3 + HCO_3^-$$

$$Mg^{+2} + \underset{\text{[Disodium hydrogen phosphate]}}{Na_2HPO_{4(aq.)}} \xrightarrow{NH_4OH} MgNH_4PO_4 \downarrow \text{ [White crystalline ppt]}$$

42. $MgSO_4$ on reaction with NH_4OH and Na_2HPO_4 forms a white crystalline precipitate. What is its formula? [JEE Adv. 2018]
(a) $Mg(NH_4)PO_4$ (b) $Mg_3(PO_4)_2$ (c) $MgCl_2 \cdot MgSO_4$ (d) $MgSO_4$

Sol. (a)

43. A sodium salt of an unknown anion when treated with $MgCl_2$ gives white precipitate only on boiling. The anion is [JEE Adv. 2004]
(a) SO_4^{2-} (b) HCO_3^- (c) CO_3^{2-} (d) NO_3^-

Sol. (b) $MgCl_2 + 2NaHCO_3 \longrightarrow \underset{\text{(Soluble)}}{Mg(HCO_3)_2} + 2NaCl$

$$Mg(HCO_3)_2 \xrightarrow{Boiling} \underset{\text{(white ppt.)}}{MgCO_3.Mg(OH)_2} \downarrow + H_2O + CO_2$$

44. When a solution of mixture having two inorganic salts was treated with freshly prepared sulphate in acidic medium, a dark brown ring was formed whereas on treatment with neutral $FeCl_3$, it gave deep red colour which disappeared on boiling and a brown red ppt was formed. The mixture contains [11 April, 2023 (Shift-I)]
(a) CH_3COO^- and NO_3^- (b) $C_2O_4^{2-}$ and NO_3^-
(c) SO_3^{2-} and CH_3COO^- (d) SO_3^{2-} and $C_2O_4^{2-}$

Sol. (a) NO_3^- : a dark brown ring CH_3COO^- : deep red colour with neutral $FeCl_3$

45. To an aqueous solution containing ions such as Al^{3+}, Zn^{2+}, Ca^{2+}, Fe^{3+}, Ni^{2+}, Ba^{2+} and Cu^{2+} was added conc. HCl, followed by H_2S. The total number of cation precipitated during this reaction is/are: [27 July, 2021 (Shift-II)]
(a) 1 (b) 3 (c) 4 (d) 2

Sol. (a) Only Cu^{2+}.

46. The complex that dissolves in water is [11 April, 2023 (Shift-I)]
(a) $Fe_4[Fe(CN)_6]_3$ (b) $[Fe_3(OH)_2(OAc)_6]Cl$
(c) $K_3[Co(NO_2)_6]$ (d) $(NH_4)_3[As(Mo_3O_{10})_4]$

Sol. (b) [Complex a, c, d are precipitates].

47. The reaction of zinc with excess of aqueous alkali, evolves hydrogen gas and gives: [29 July, 2022 (Shift-I)]

(a) $Zn(OH)_2$ (b) ZnO (c) $[Zn(OH)_4]^{2-}$ (d) $[ZnO_2]^{2-}$

Sol. (c)

48. 25 mL of silver nitrate solution (1 M) is added dropwise to 25 mL of potassium iodide (1.05 M) solution. The ion(s) present in very small quantity in the solution is / are [11 April, 2023 (Shift-I)]

(a) NO_3^- only (b) K^+ only (c) Ag^+ and I^- both (d) I^- only

Sol. (c) Major quantity of Ag^+ and I^- precipitate down as AgI. So very small quantity of Ag^+ and I^- will be there in solution.

49. Choose the correct tests with respective observations.

(A) $CuSO_4$ (acidified with acetic acid) + $K_4[Fe(CN)_6]$ → Chocolate brown precipitate.

(B) $FeCl_3$ + $K_4[Fe(CN)_6]$ → Prussian blue precipitate.

(C) $ZnCl_2$ + $K_4[Fe(CN)_6]$, neutralised with NH_4OH → White or bluish white precipitate.

(D) $MgCl_2$ + $K_4[Fe(CN)_6]$ → Blue precipitate.

(E) $BaCl_2$ + $K_4[Fe(CN)_6]$, neutralised with NaOH → White precipitate.

Choose the correct answer from the options given below: [02 April, 2025 (Shift-I)]

(a) A, D and E only (b) B, D and E only (c) A, B and C only (d) C, D and E only

Sol. (c)

$$2CuSO_4 + K_4[Fe(CN)_6] \xrightarrow{CH_3COOH} \underset{\text{(Chocolate brown Precipitate)}}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$$

$$4FeCl_3 + 3K_4[Fe(CN_6)] \longrightarrow \underset{\text{(Prussian Blue Precipitate)}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

$$3ZnCl_2 + 2K_4[Fe(CN_6)] \xrightarrow{NH_4OH} \underset{\text{(White or bluish white precipitate)}}{K_2Zn_3[Fe(CN)_6]_2} + 6KCl$$

50. Among the following cations, the number of cations which will give characteristic precipitate in their identification tests with $K_4[Fe(CN)_6]$ is ______. [24 Jan, 2025 (Shift-I)]

Cu^{2+} , Fe^{3+} , Ba^{2+} , Ca^{2+} , NH_4^+ , Mg^{2+} , Zn^{2+}

Sol. [4]

Cu^{2+} + $K_4[Fe(CN)_6]$ → Brown precipitate of $Cu_2[Fe(CN)_6]$

Fe^{3+} + $K_4[Fe(CN)_6]$ → Prussian blue precipitate of $Fe_4[Fe(CN)_6]_3$

Zn^{2+} + $K_4[Fe(CN)_6]$ → White precipitate of $Zn_2[Fe(CN)_6]$

→ NTA Ans key : 3

Ca^{2+} + $K_4[Fe(CN)_6]$ → White precipitate of $Ca_2[Fe(CN)_6]$

51. Find the compound 'A' from the following reaction sequences. [24 Jan, 2025 (Shift-II)]

$$A \xrightarrow{\text{aqua-regia}} B \xrightarrow[(2)\ AcOH]{(1)\ KNO_2 | NH_4OH} \text{yellow ppt}$$

(a) NiS (b) MnS (c) CoS (d) ZnS

Sol. (c)

52. Identify the inorganic sulphides that are yellow in colour:

(A) $(NH_4)_2S$ (B) PbS (C) CuS (D) As_2S_3 (E) As_2S_5

Choose the correct answer from the options given below: [28 Jan, 2025 (Shift-II)]

(a) (D) and (E) only (b) (A) and (B) only

(c) (A), (D) and (E) only (d) (A) and (C) only

Sol. (c) PbS and CuS are black while other three sulphides that is $(NH_4)_2S$, As_2S_3 and As_2S_5 are yellow in color.

53. The number of white coloured salts among the following is .... [01 Feb, 2024 (Shift-I)]

(A) $SrSO_4$ (B) $Mg(NH_4)PO_4$ (C) $BaCrO_4$ (D) $Mn(OH)_2$

(E) $PbSO_4$ (F) $PbCrO_4$ (G) AgBr (H) PbI_2

(I) CaC_2O_4 (J) $[Fe(OH)_2(CH_3COO)]$

Sol. [5] $SrSO_4$ – white, $Mg(NH_4)PO_4$ – white, $BaCrO_4$ – yellow, $Mn(OH)_2$ – white, $PbSO_4$ – white, $PbCrO_4$ – yellow, AgBr – pale yellow, PbI_2 – yellow, CaC_2O_4 – white, $[Fe(OH)_2(CH_3COO)]$ – Brown Red

54. Match List-I with List-II

	List-I (Name of the test)		List-II (Reaction sequence involved)
A.	Borax bead test	I.	$MCO_3 \rightarrow MO \xrightarrow[+\Delta]{Co(NO_3)_2} CoO.MO$
B.	Charcoal cavity test	II.	$MCO_3 \rightarrow MCl_2 \rightarrow M^{2+}$
C.	Cobalt nitrate test	III.	$MSO_4 \xrightarrow[\Delta]{Na_2B_4O_7} M(BO_2)_2 \rightarrow MBO_2 \rightarrow M$
D.	Flame test	IV.	$MSO_4 \xrightarrow[\Delta]{Na_2CO_3} MCO_3 \rightarrow MO \rightarrow M$

Choose the correct answer from the option below: [08 April, 2024 (Shift-I)]

(a) A-III, B-I, C-IV, D-II (b) A-III, B-II, C-IV, D-I

(c) A-III, B-I, C-II, D-IV (d) A-III, B-IV, C-I, D-II

Sol. (d)

55. Consider the following test for a group-IV cation.

$M^{2+} + H_2S \rightarrow A$ (Black precipitate) + byproduct

A + aqua regia $\rightarrow B + NOCl + S + H_2O$

$B + KNO_2 + CH_3COOH \rightarrow C$ + byproduct

The spin only magnetic moment value of the metal complex C is _____BM. (Nearest integer) [09 April, 2024 (Shift-II)]

Sol. [0]

$Co^{2+} + H_2S \rightarrow \underset{(A)}{CoS}\downarrow$ (Black)

$\underset{(A)}{CoS} + \text{Aqua-regia} \rightarrow \underset{(B)}{Co^{2+}(aq)} + NOCl + S + H_2O$

$Co^{2+}(aq) + KNO_2 + CH_3COOH \rightarrow \underset{(C)}{K_3[Co(NO_2)_6]} + NO + S + H_2O$

In $K_3[Co(NO_2)_6]$, Co is in Co^{3+} oxidation state.

Co^{3+} : $3d^6 4s^0$

Hence, it has d^2sp^3 hybridisation. Number of unpaired e^- = 0

Hence, Magnetic moment, $\mu = \sqrt{n(n+2)} = 0$ B.M

56. Consider the sulphides HgS, PbS, CuS, Sb_2S_3, As_2S_3 and CdS. Number of these sulphides soluble in 50% HNO_3 is ______. [31 Aug, 2021 (Shift-I)]

Sol. [4] Out of the given sulphides, only CdS, PbS, As_2S_3 & CuS are soluble in 50% HNO_3 but Sb_2S_3 & HgS are not soluble.

57. Upon treatment with ammoniacal H_2S, the metal ion that precipitates as a sulphide is (JEE Adv. 2013)

(a) Fe (III) (b) Al (III) (c) Mg (II) (d) Zn(II)

Sol. (d)

58. Passage: When potassium iodide is added to an aqueous solution of potassium ferricyanide, a reversible reaction is observed in which a complex P is formed. In a strong acidic medium, the equilibrium shifts completely towards P. Addition of zinc chloride to P in a slightly acidic medium results in a sparingly soluble complex Q.

(i) The number of moles of potassium iodide required to produce two moles of P is ______. (JEE Adv. 2024)

Sol. [2] We require 2 mol of KI.

$2KI + 2\ K_3[Fe(CN)_6] \rightarrow I_2 + 2\ \underset{P}{K_4[Fe(CN)_6]}$

(ii) The number of zinc ions present in the molecular formula of Q is ______. (JEE Adv. 2024)

Sol. [3 or 2]

$2\underset{\boxed{P}}{K_4[Fe(CN)_6]} + \underset{\text{(Zinc chloride)}}{3ZnCl_2} \rightarrow \underset{Ⓠ}{K_2Zn_3[Fe(CN)_6]_2} + 6KCl$

→ 3 zinc ions are present

OR

$\underset{\boxed{P}}{K_4[Fe(CN)_6]} + \underset{\text{(Zinc chloride)}}{ZnCl_2} \rightarrow \underset{Ⓠ}{Zn_2[Fe(CN)_6]} + KCl$

→ 2 zinc ions are present

59. **Passage:** The reaction of $K_3[Fe(CN)_6]$ with freshly prepared $FeSO_4$ solution produces a dark blue precipitate called Turnbull's blue. Reaction of $K_4[Fe(CN)_6]$ with the $FeSO_4$ solution in complete absence of air produces a white precipitate X, which turns blue in air. Mixing the $FeSO_4$ solution with $NaNO_3$, followed by a slow addition of concentrated H_2SO_4 through the side of the test tube produces a brown ring.

(JEE Adv. 2021)

(i) Precipitate X is

(a) $Fe_4[Fe(CN)_6]_3$ (b) $Fe[Fe(CN)_6]$ (c) $K_2Fe[Fe(CN)_6]$ (d) $KFe[Fe(CN)_6]$

Sol. (c) $K_3[\overset{+3}{Fe}(CN)_6] + Fe^{2+} \longrightarrow \overset{+2}{Fe_3}[\overset{+3}{Fe}(CN)_6]_2$ Dark blue ppt (Turnbull's blue)

$K_4[\overset{+2}{Fe}(CN)_6] + Fe^{2+} \longrightarrow \underset{\text{white ppt. [X]}}{K_2\overset{+2}{Fe}[\overset{+3}{Fe}(CN)_6]} \xrightarrow[\text{Oxidation of } Fe^{+2}]{\text{Air } [O_2]} \underset{\text{blue (Prussian blue)}}{K\overset{+3}{Fe}[\overset{+3}{Fe}(CN)_6]}$

(ii) Among the following, the brown ring is due to the formation of (JEE Adv. 2021)

(a) $[Fe(NO)_2(SO_4)_2]^{2-}$ (b) $[Fe(NO)_2(H_2O)_4]^{3+}$ (c) $[Fe(NO)_4(SO_4)_2]$ (d) $[Fe(NO)(H_2O)_5]^{2+}$

Sol. (d)

60. **Statement-I:** A very dilute acidic solution of Cd^{2+} and Ni^{2+} gives yellow precipitate of CdS on passing H_2S (IIT JEE 1989)

Statement-II: Solubility product of CdS is more than that of NiS.

(a) Statement-I is correct; Statement-II is correct Statement-II is the correct explanation of Statement-I

(b) Statement-I is correct; Statement-II is correct Statement-II is not the correct explanation of Statement-I

(c) Statement-I is correct; Statement-II is incorrect

(d) Statement-I is incorrect; Statement-II is correct

Sol. (c) Cd^{2+} and $Ni^{2+} \xrightarrow[\text{Very dilute acidic medium}]{H_2S} CdS \downarrow$ (Yellow ppt) ■ K_{sp} : CdS < NiS

Cd^{2+} belongs to group II while Ni^{2+} belongs to group III of analytical group. Group II radicals are precipitated by passing H_2S gas through acidic solution of salt whereas group III radicals are precipitated by passing H_2S gas in NH_3 / NH_4Cl buffer solution of salt due to greater solubility products of later salt.

61. Among PbS, CuS, HgS, MnS, Ag_2S, NiS, CoS, Bi_2S_3 and SnS_2 the total number of black coloured sulphides is (JEE Adv. 2014)

Sol. [6 or 7]

From qualitative analysis of the different metal ions it is found that PbS, CuS, HgS, Ag_2S, NiS, CoS are black coloured. MnS — dirty pink/buff coloured, SnS_2 — yellow coloured. Bi_2S_3 — brown/black (brownish black) coloured. Hence, the correct integer is (6 or 7)

2. $HgCl_2$ and I_2 both when dissolved in water containing I^- ions, the pair of species formed is: [NEET 2017-Delhi]

(a) Hg_2I_2, I^- (b) HgI_2, I_3^- (c) HgI_2, I^- (d) HgI_4^{2-}, I_3^-

ol. (d)

3. Match List-I with List-II: [NEET 2024 Re]

List-I: Solid salt treated with dil. H_2SO_4		List-II: Anion detected	
A.	effervescence of colourless gas	I.	NO_2^-
B.	gas with smell of rotten egg	II.	CO_3^{2-}
C.	gas with pungent smell	III.	S^{2-}
D.	brown fumes	IV.	SO_3^{2-}

Choose the correct answer from the options given below:

(a) A-II, B-III, C-IV, D-I
(b) A-IV, B-III, C-II, D-I
(c) A-I, B-II, C-III, D-IV
(d) A-II, B-III, C-I, D-IV

Sol. (a)

64. Match List-I with List-II [NEET 2025]

List-I: Ion		List-II: Group Number in Cation Analysis	
A.	Co^{2+}	I.	Group-I
B.	Mg^{2+}	II.	Group-III
C.	Pb^{2+}	III.	Group-IV
D.	Al^{3+}	IV.	Group-VI

Choose the correct answer from the options given below :

(a) A-III, B-IV, C-II, D-I
(b) A-III, B-IV, C-I, D-II
(c) A-III, B-II, C-IV, D-I
(d) A-III, B-II, C-I, D-IV

Sol. (b)

65. Match List-I with List-II : [NEET 2024 Re]

List-I: Test/reagent		List-II: Radical identified	
A.	Lake Test	I.	NO_3^-
B.	Nessler's Reagent	II.	Fe^{3+}
C.	Potassium sulphocyanide	III.	Al^{3+}
D.	Brown Ring Test	IV.	NH_4^+

Choose the correct answer from the options given below :

(a) A-IV, B-II, C-III, D-I
(b) A-II, B-IV, C-III, D-I
(c) A-II, B-III, C-IV, D-I
(d) A-III, B-IV, C-II, D-I

ol. (d)

6. Given below are certain cations. Using inorganic qualitative analysis, arrange them in increasing group number from 0 to VI. [NEET 2024]

A. Al^{3+} B. Cu^{2+} C. Ba^{2+} D. Co^{2+} E. Mg^{2+}

Choose the correct answer from the options given below:

(a) E, C, D, B, A (b) E, A, B, C, D (c) B, A, D, C, E (d) B, C, A, D, E

l. (c)