

# Inorganic Chemistry

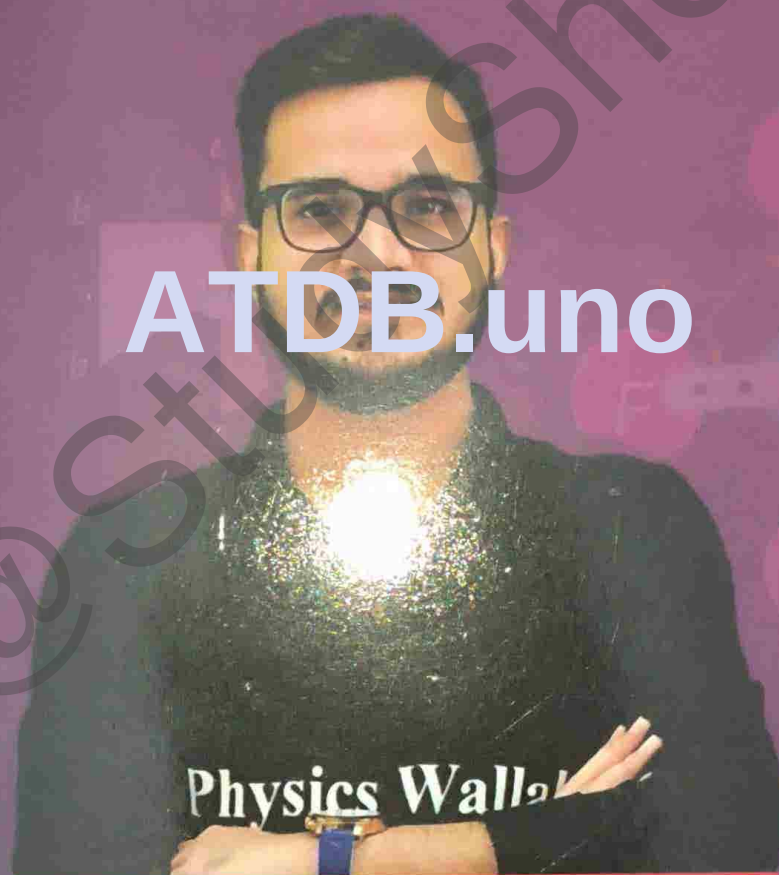
## Easy Notes



Class Notes in Handwritten Format

Class 11 + 12

NEET + JEE Main



Physics Wallah

Om Pandey  
(IIT - Delhi)

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मैं कर्म के साथ हूँ  
किस्मत के हाथ नहीं।

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# Classification of Elements and Periodicity in Properties

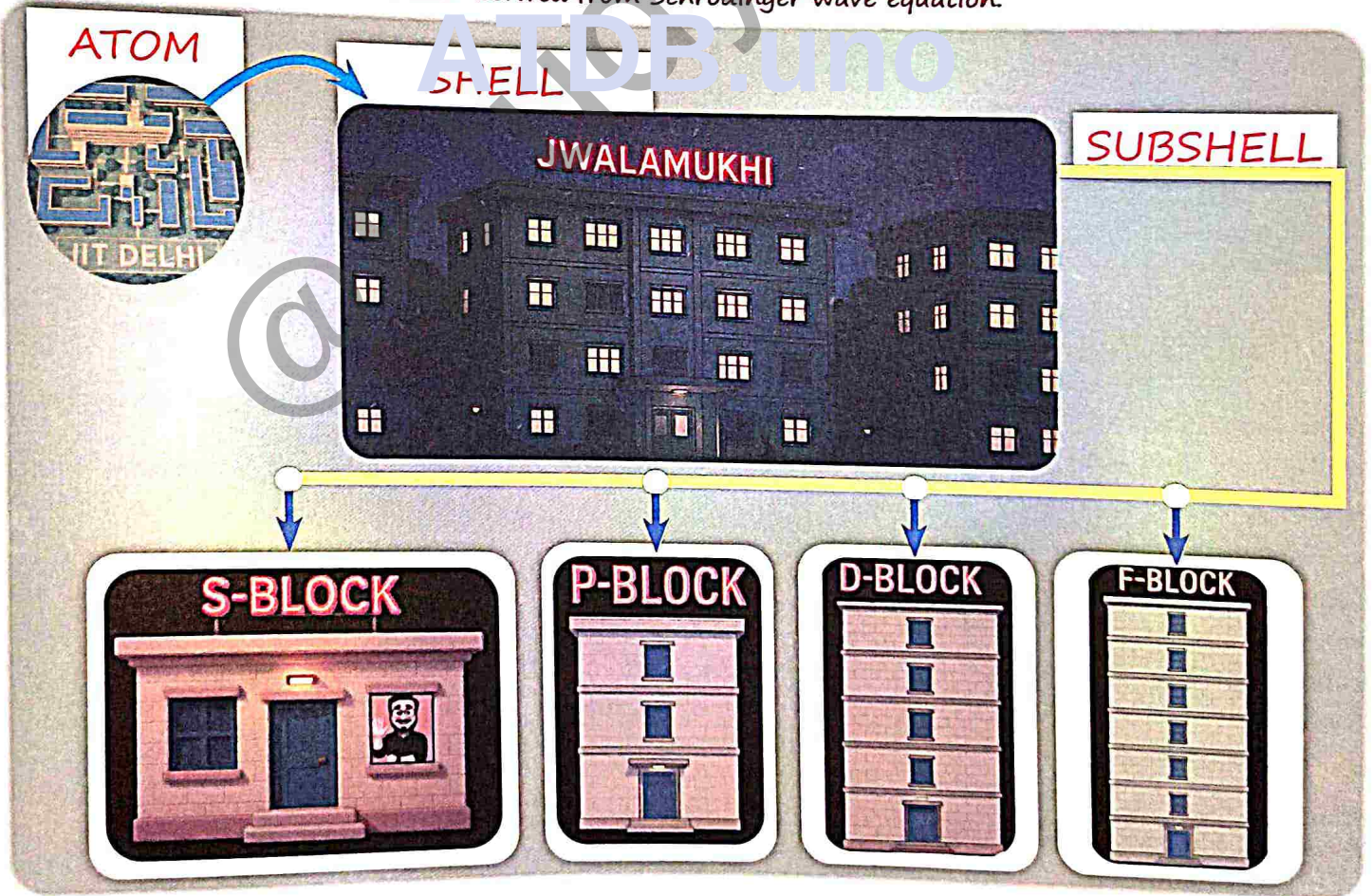
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Syllabus

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.



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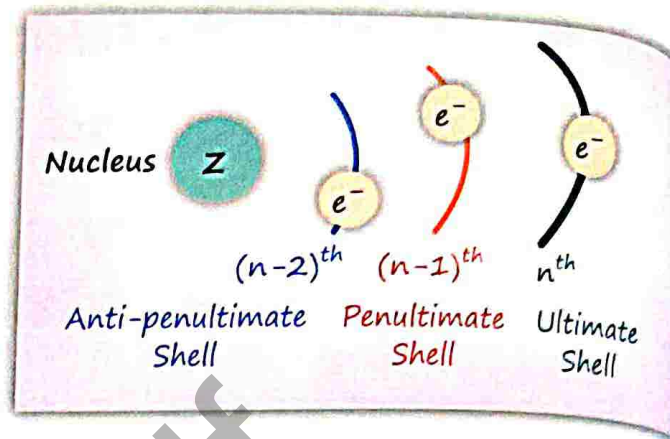


## [I] Principal Quantum Number (n)

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  $n^{\text{th}}$  shell = n

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



❑ Number of orbitals present in  $n^{\text{th}}$  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 terms that were used to describe the atomic spectra and have the following full form:

|   |           |   |             |
|---|-----------|---|-------------|
| s | sharp     | f | fundamental |
| p | principal | g | generalized |
| d | diffused  |   |             |

## [III] Magnetic Quantum Number (m)

It describes the orientation of an orbital within a subshell.

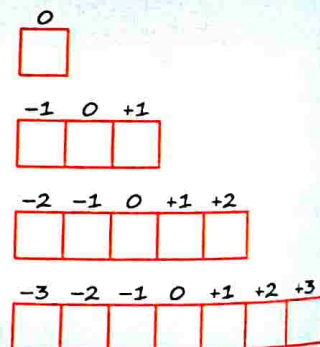
It can have values from  $-l$  to  $+l$  including zero, i.e., total  $(2l + 1)$  values. Each value corresponds to an orbital, s-subshell has one orbital, p-subshell three orbitals ( $p_x, p_y$  and  $p_z$ ), d-subshell five orbitals ( $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$ ) and f-subshell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

$$s \rightarrow l = 0, m = 0$$

$$p \rightarrow l = 1, m = -1, 0, +1$$

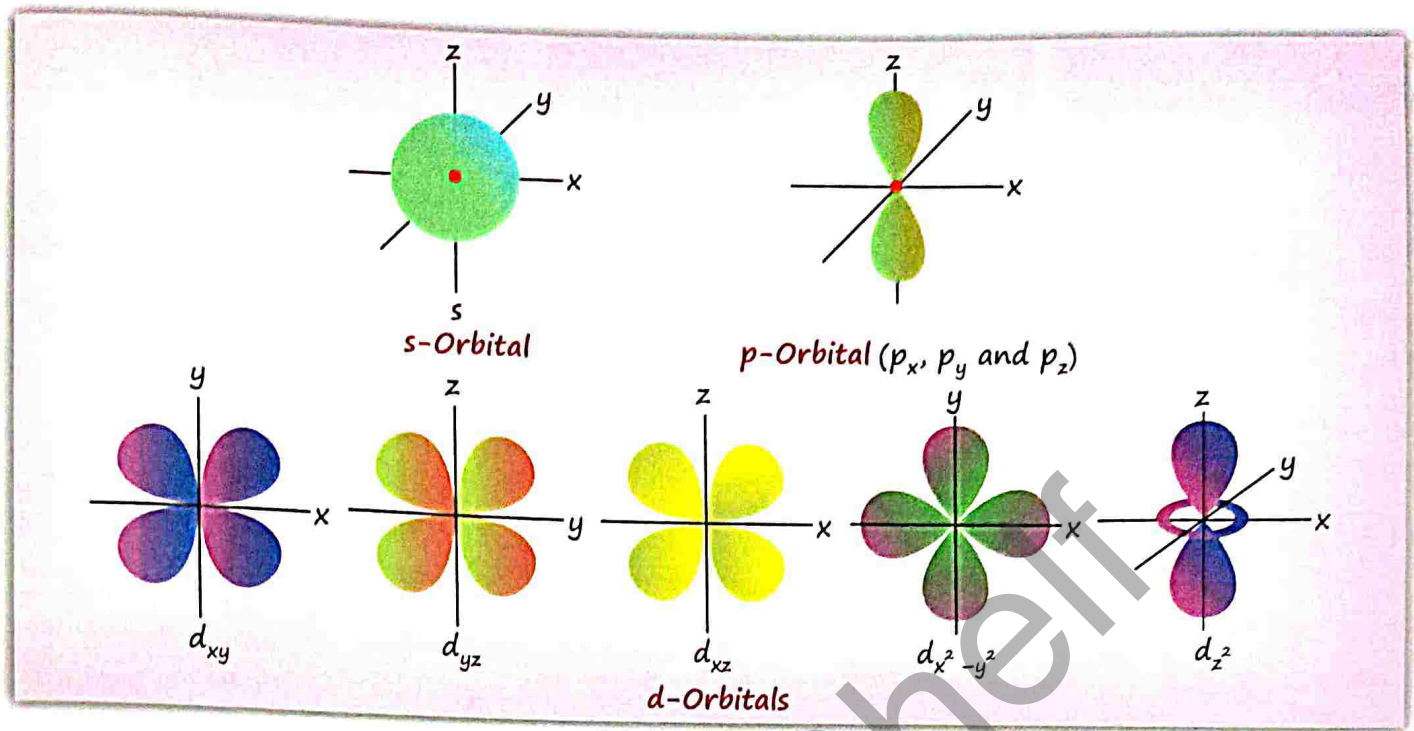
$$d \rightarrow l = 2, m = -2, -1, 0, +1, +2$$

$$f \rightarrow l = 3, m = -3, -2, -1, 0, +1, +2, +3$$



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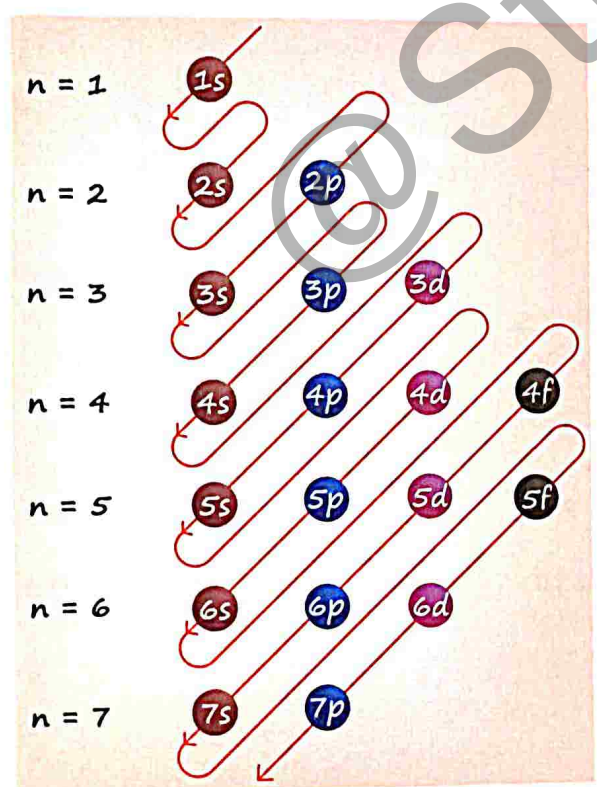




[IV] Spin Quantum Number (s)

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

The diagram illustrates the periodic table with the following orbital filling order:

- Period 1:** 1s<sup>1</sup>
- Period 2:** 2s<sup>1</sup>, 2s<sup>2</sup>
- Period 3:** 3s, 3d, 3p
- Period 4:** 4s, 4p, 4d, 4f
- Period 5:** 5s, 5p, 5d, 5f
- Period 6:** 6s, 6p, 6d, 6f
- Period 7:** 7s, 7p, 7d, 7f

Arrows indicate the sequence of filling, showing that orbitals are filled in order of increasing energy, with some exceptions (e.g., 4s fills before 3d).

## ATOMIC NUMBER DISTRIBUTION

The diagram illustrates the periodic table with various series highlighted in different colors. Callouts provide specific information about elements and their positions:

- Top Left:** A small table showing the first 10 elements: 1, 3, 4, 11, 12, 19, 20, 37, 38, 55, 56, 87, 88.
- Top Center:** A callout for  $Z = 29$  (Copper) with properties:
  - 1 position left from Group 12 ( $Z = 30$ )
  - Group-11
  - Period-4
- Top Right:** A callout for  $Z = 34$  (Selenium) with properties:
  - 2 position left from Group 18
  - Group-16
  - Period-4
- Center:** A table showing the d-series elements (Transition Metals):
 

|    |     |  |  |           |    |     |
|----|-----|--|--|-----------|----|-----|
| 21 |     |  |  | 3d Series | 29 | 30  |
| 39 |     |  |  | 4d Series |    | 48  |
| 57 | 72  |  |  | 5d Series |    | 80  |
| 89 | 104 |  |  | 6d Series |    | 112 |
- Right:** A table showing the p-series elements (Groups 13-18):
 

|     |  |  |  |    |    |     |
|-----|--|--|--|----|----|-----|
| 5   |  |  |  |    | 2  | 10  |
| 13  |  |  |  |    |    | 18  |
| 31  |  |  |  | 34 | 36 |     |
| 49  |  |  |  |    |    | 54  |
| 81  |  |  |  |    |    | 86  |
| 113 |  |  |  |    |    | 118 |
- Bottom:** A table showing the f-series elements (Lanthanoids and Actinoids):
 

|    |  |  |  |  |           |  |  |    |  |     |
|----|--|--|--|--|-----------|--|--|----|--|-----|
| 58 |  |  |  |  | 4f Series |  |  | 69 |  | 71  |
| 90 |  |  |  |  | 5f Series |  |  |    |  | 103 |
- Bottom Right:** A callout for  $Z = 69$  (Erbium) with properties:
  - 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<sub>57</sub>

Ce<sub>58</sub> → Lu<sub>71</sub>

Ac<sub>89</sub>

Th<sub>90</sub> → Lr<sub>103</sub>

Hf<sub>72</sub>

Rf<sub>104</sub>

Lanthanoid Series

Actinoid Series

Period No.

6

Group No.

3

Period No.

7

Group No.

3

MODERN PERIODIC TABLE

|                       |    | s-Block (ns)                   |     | d-Block (n - 1)d |     |    |     |       |      |    |    |    |     | p-Block (np) |     |    |     |      |       |
|-----------------------|----|--------------------------------|-----|------------------|-----|----|-----|-------|------|----|----|----|-----|--------------|-----|----|-----|------|-------|
| Group                 |    | 1                              | 2   | 3                | 4   | 5  | 6   | 7     | 8    | 9  | 10 | 11 | 12  | 13           | 14  | 15 | 16  | 17   | 18    |
| Period                |    | IA                             | IIA | IIIB             | IVB | VB | VIB | VII B | VIII |    |    | IB | IIB | IIIA         | IVA | VA | VIA | VIIA | VIIIA |
| 1<br>(1s)             | H  | Transition Metals<br>(d-Block) |     |                  |     |    |     |       |      |    |    |    |     |              |     |    |     |      | He    |
| 2<br>(2s, 2p)         | Li | Be                             |     |                  |     |    |     |       |      |    |    |    | B   | C            | N   | O  | F   | Ne   |       |
| 3<br>(3s, 3p)         | Na | Mg                             |     |                  |     |    |     |       |      |    |    |    | Al  | Si           | P   | S  | Cl  | Ar   |       |
| 4<br>(4s, 3d, 4p)     | K  | Ca                             | Sc  | Ti               | V   | Cr | Mn  | Fe    | Co   | Ni | Cu | Zn | Ga  | Ge           | As  | Se | Br  | Kr   |       |
| 5<br>(5s, 4d, 5p)     | Rb | Sr                             | Y   | Zr               | Nb  | Mo | Tc  | Ru    | Rh   | Pd | Ag | Cd | In  | Sn           | Sb  | Te | I   | Xe   |       |
| 6<br>(6s, 4f, 5d, 6p) | Cs | Ba                             | La  | Hf               | Ta  | W  | Re  | Os    | Ir   | Pt | Au | Hg | Tl  | Pb           | Bi  | Po | At  | Rn   |       |
| 7<br>(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)<br>Period : 6 | Ce                        | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|         | Actinide series (5f)<br>Period : 7   | Th                        | Pa | U  | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |





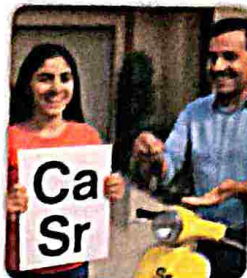
# देशी जुगाड़

## 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

## 1<sup>st</sup> Transition Series: 3d Series



Science Ticher Very Cruel  
Mange Fees Copy Niha  
Cukker Zindabad

## 2<sup>nd</sup> Transition Series: 4d Series



Yari Zra Nibhana  
Mout Tc Rukawat Rah  
Pde Age Cudo

## 3<sup>rd</sup> Transition Series: 5d Series



La Hafta Warna Re  
Osama Idher  
Pitayi Aur Hogi

## 4<sup>th</sup> 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



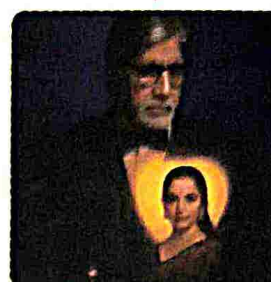
Vo Nabab Tha Dabang

Group-6



Crying Moti Wife

Group-7



Maan Tac\* Rekha

Group-8 and 9

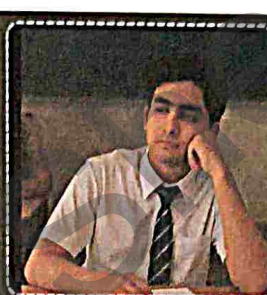


Fer\* Rouya Osama  
Con\* Rahega Iran me

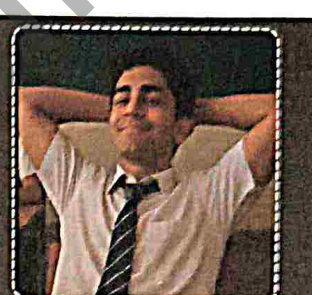
Group-10, 11, 12



Nahi Padoge to Pitoge



Cyu Aage Aau



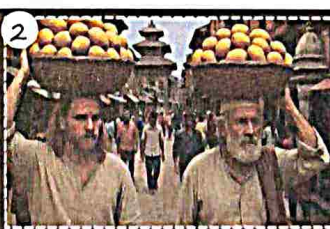
Zindagi Cadbury Hogyi

Lanthanide → 1st Inner Transition Series (Part of Group 3)



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

Actinoids → 11<sup>th</sup> 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

- Mendeleev [101] ko mila Jobel [102] in Lawrence [103]
- Rutherford [104] Dube [105] Sea [106] me Bohr [107] Hass [108] Meit [109]
- Dar [110] se Roe [111] Coper [112]
- 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)**

Period-4, Group-17

|  |     |
|--|-----|
|  | 2   |
|  | 10  |
|  | 18  |
|  | 35  |
|  | 36  |
|  | 54  |
|  | 86  |
|  | 118 |



#### 4. Match List-I with List-II

[30 Jan, 2023 (Shift-1)]

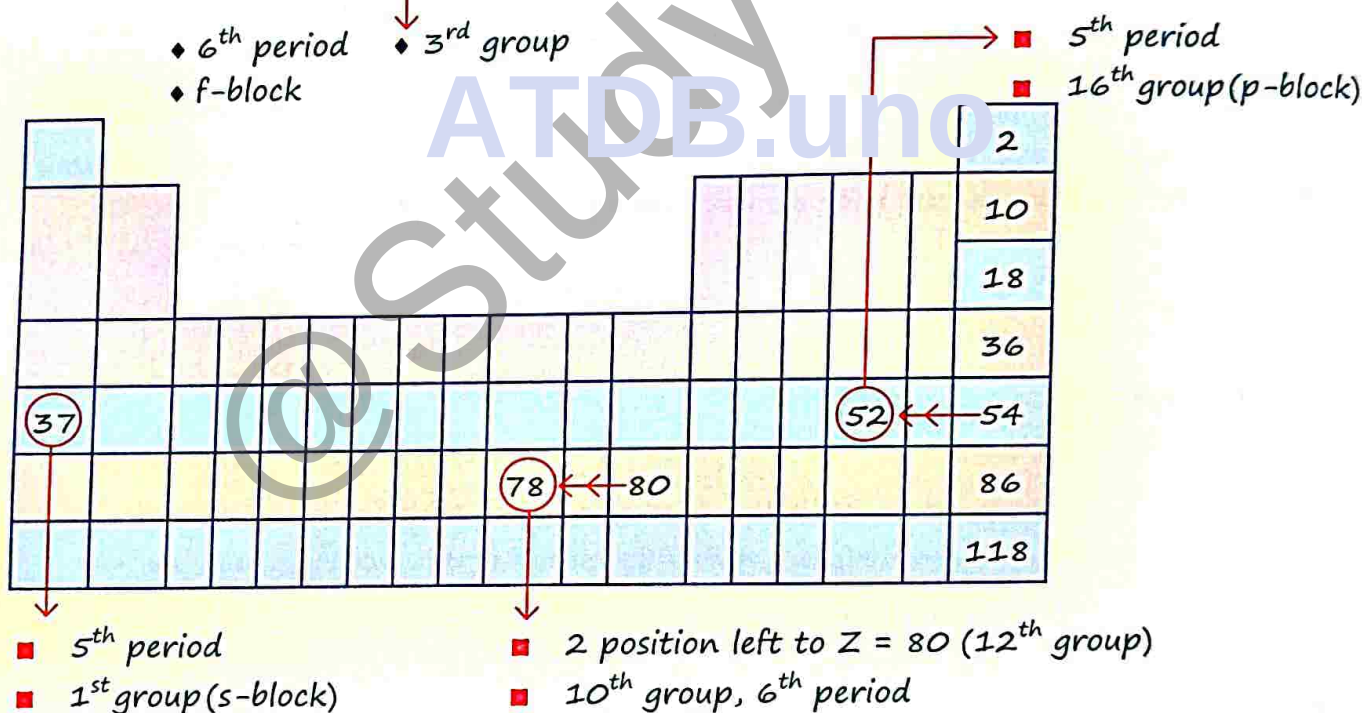
| List-I (Atomic Number) |    | List-II (Block of Periodic Table) |         |
|------------------------|----|-----------------------------------|---------|
| (A)                    | 37 | (i)                               | p-block |
| (B)                    | 78 | (ii)                              | 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 ( $58 < 65 < 71$ )



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

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CHEMISTRY



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

Diagram illustrating the periodic table structure, highlighting the 8th period and the 1st, 2nd, 17th, and 18th groups.

The diagram shows the following elements and their positions:

- 1st group (Alkali metals):** Element 119 is highlighted in red and circled.
- 2nd group (Alkaline Earth metal):** Element 120 is highlighted in red and circled.
- 17th group (Halogen family):** Element 117 is highlighted in red and circled.
- 18th group (Noble gases):** Element 118 is highlighted in red and circled.

The diagram also shows the cumulative number of elements in each period up to the 8th period:

- Period 1: 2 elements
- Period 2: 10 elements
- Period 3: 18 elements
- Period 4: 36 elements
- Period 5: 54 elements
- Period 6: 86 elements
- Period 7: 118 elements

The diagram is labeled with the following regions:

- d-block:** The central region of the periodic table.
- p-block:** The region on the right side of the periodic table.

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]  $\rightarrow$  Roentgenium

## METAL, NON-METAL AND METALLOID

## Metal



- ❑ 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.

## Classification of Elements and Periodicity in Properties



## Non-metal



- 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

आज सब से तेजी  
Aas Sab Se Te Ge

## s-BLOCK

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



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

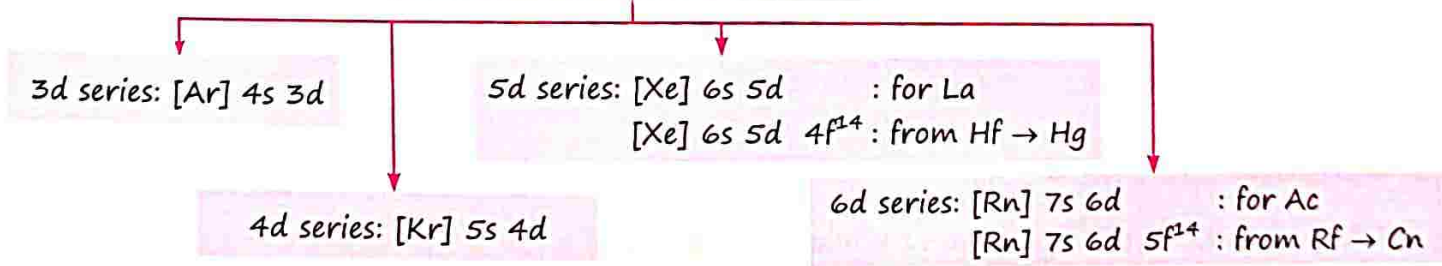
When shells upto (n – 1) are completely filled and differentiating electron enters the p-orbital of the n<sup>th</sup> orbit, elements of this class are called p-block elements.

- ❑ Group 13 to 18
- ❑ General electronic configuration: [inert gas] ns<sup>2</sup> np<sup>1-6</sup>
- ❑ 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 <sub>21</sub>           | Ti <sub>22</sub>  | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn <sub>30</sub>  |
| 4d-series               | Y <sub>39</sub>            | Zr <sub>40</sub>  | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd <sub>48</sub>  |
| 5d-series               | La <sub>57</sub> 4f Series | Hf <sub>72</sub>  | Ta | W  | Re | Os | Ir | Pt | Au | Hg <sub>80</sub>  |
| 6d-series               | Ac <sub>89</sub> 5f Series | Rf <sub>104</sub> | Db | Sg | Bh | Hs | Mt | Ds | Rg | Cn <sub>112</sub> |

Electronic Configuration







## 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 <sup>1</sup> |    |    |    |    |

|                 |
|-----------------|
| Pd              |
| ns <sup>0</sup> |

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

❑ Group : 3 to 12

❑ General electronic configuration : [inert gas] ns<sup>x-2</sup> (n-1)d<sup>1-10</sup>

(except, Pd : 4d<sup>10</sup> 5s<sup>0</sup>)

When outermost (n<sup>th</sup>) and penultimate shells (n-1)<sup>th</sup> 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 <sup>st</sup> Transition Series                  | 2 <sup>nd</sup> Transition Series                  |
|----------------------------------------------------|----------------------------------------------------|
| ❑ 3d series                                        | ❑ 4d series                                        |
| ❑ 10 elements                                      | ❑ 10 elements                                      |
| ❑ Starts from <sub>21</sub> Sc - <sub>30</sub> Zn. | ❑ Starts from <sub>39</sub> Y - <sub>48</sub> Cd   |
| ❑ Filling of electrons takes place in 3d subshell. | ❑ Filling of electrons takes place in 4d subshell. |

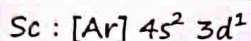
| 3 <sup>rd</sup> Transition Series                                    | 4 <sup>th</sup> Transition Series                                        |
|----------------------------------------------------------------------|--------------------------------------------------------------------------|
| ❑ 5d series                                                          | ❑ 6d series                                                              |
| ❑ 10 elements                                                        | ❑ 10 elements                                                            |
| ❑ Starts from <sub>57</sub> La, <sub>72</sub> Hf - <sub>80</sub> Hg. | ❑ Starts from <sub>89</sub> Ac , <sub>104</sub> Rf - <sub>112</sub> Uub. |
| ❑ Filling of electrons takes place in 5d subshell.                   | ❑ Filling of electrons takes place in 6d subshell.                       |



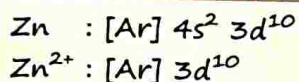
## Transition Metals

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

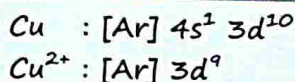
1. Sc is a transition metal because Sc has partially filled d-orbitals.



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



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



### Note

- ❑ Zn, Cd, Hg are not considered as transition elements because they have filled 'd<sup>10</sup> configuration' in atomic (M) and ionic (M<sup>2+</sup>) 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<sub>2</sub> (Non-metal)
  - ♦ Metals in Liquid State (at T < 40°C) - Rubi Mar Gayi Fir se  
Fr Hg Ga Fr Cs

## 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 <sub>58</sub> | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu <sub>71</sub>  |
| Actinoids   | Th <sub>90</sub> | Pa | U  | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr <sub>103</sub> |

- ❑ They are metals
- ❑ All f-block elements belong to 3<sup>rd</sup> group.

| 1 <sup>st</sup> Inner Transition Series - 4f series  | 2 <sup>nd</sup> Inner Transition Series- 5f series    |
|------------------------------------------------------|-------------------------------------------------------|
| ❑ 14 elements - <sub>58</sub> Ce to <sub>71</sub> Lu | ❑ 14 elements - <sub>90</sub> Th to <sub>103</sub> 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.

Classification of Elements and Periodicity in Properties

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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,  $[Rn]5f^{14}6d^{10}7s^27p^2$  (b) Oxygen family,  $[Rn]5f^{14}6d^{10}7s^27p^4$   
 (c) Nitrogen family,  $[Rn]5f^{14}6d^{10}7s^28p^6$  (d) Halogen family,  $[Rn]5f^{14}6d^{10}7s^27p^5$

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.  $Z = 32$

- $\rightarrow$  p-Block
- $\rightarrow$  Group Number - 14
- $\rightarrow$  Period - 4 (Carbon family)
- $\rightarrow$  EC  $\equiv [Ar] 4s^2 3d^{10} 4p^2$

$Z = 57$

- $\rightarrow$  d-Block
- $\rightarrow$  Group Number - 3
- $\rightarrow$  Period Number - 6
- $\rightarrow$  EC  $\equiv [Xe] 6s^2 5d^1$

$Z = 71$

- $\rightarrow$  f-Block (Lanthanoids)
- $\rightarrow$  Group Number - 3
- $\rightarrow$  Period Number - 6
- $\rightarrow$  EC  $\equiv [Xe] 6s^2 5d^1 4f^{14}$

$Z = 87$

- $\rightarrow$  Alkali metal
- $\rightarrow$  s-Block
- $\rightarrow$  Group 1 [ $7^{th}$  Period]
- $\rightarrow$  EC  $\equiv [Rn] 7s^1$

### 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  $\rightarrow$  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  $[Rn]5f^{14}6d^17s^2$  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  $\rightarrow$  33 [As] Non-metal Y  $\rightarrow$  53 [I] Metal Z  $\rightarrow$  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

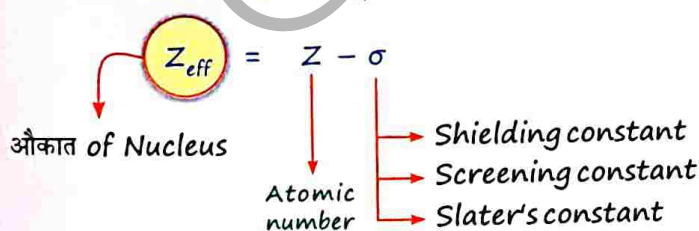
16. The number of d-electrons in  $Fe^{2+}$  ( $Z = 26$ ) is not equal to the number of electrons in which one of the following?  
 [NEET 2015]

- (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 ( $Z = 12$ )

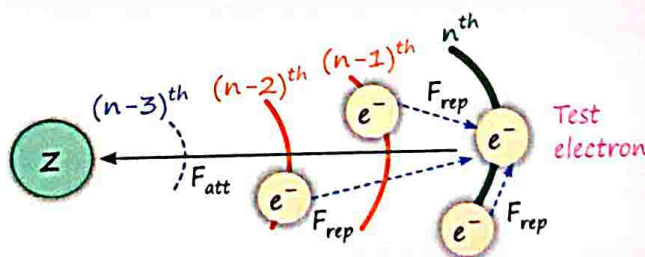
Sol. (a) Number of d-electrons in Fe  $\rightarrow 6$  [ $3d^6$ ]  
 Number of d-electrons in Fe  $\rightarrow 6$  [ $3d^6$ ]  
 Number of s-electrons in Mg  $\rightarrow 2$  [ $1s^2, 2s^2, 3s^2$ ]  
 Number of p-electrons in Cl  $\rightarrow 5$  [ $2p^6, 3p^5$ ]  
 Number of p-electrons in Ne  $\rightarrow 6$  [ $2p^6$ ]

## EFFECTIVE NUCLEAR CHARGE

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



Number of inner shell electrons  $\uparrow \Rightarrow \sigma \uparrow \Rightarrow Z_{\text{eff}} \downarrow$



- 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 ( $Z_{\text{eff}}$ ):** 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.

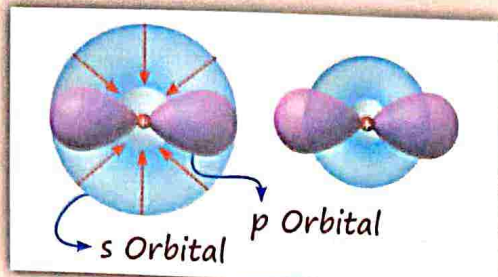
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## PENETRATION EFFECT

- 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.



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

Penetration effect :  $s > p > d > f$

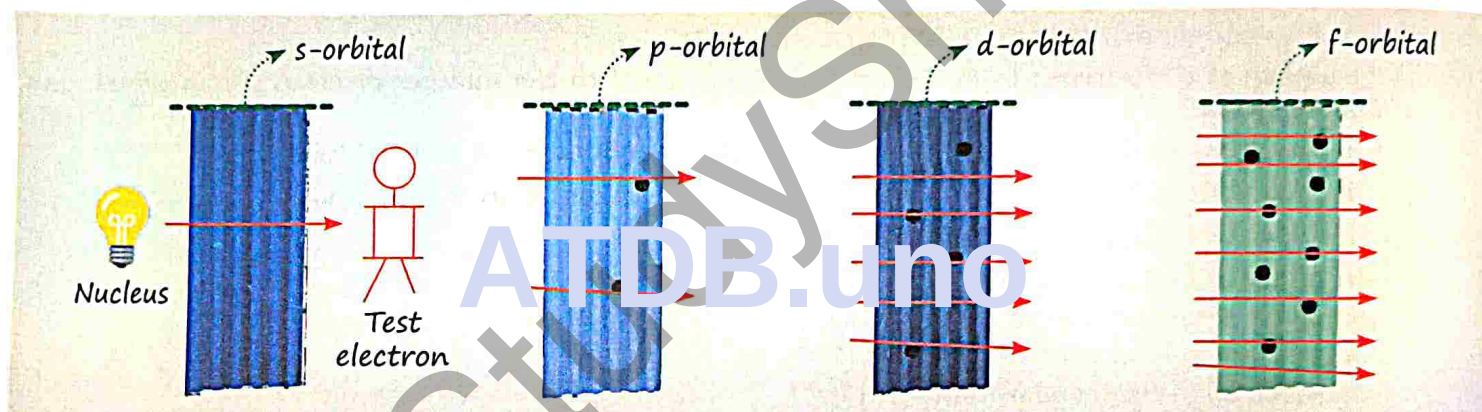
Screening effect/Shielding effect :  $s > p > d > f$

Poor shielding

Contribution of subshell in shielding constant ( $\sigma$ ) :

$ns > np > nd > nf$

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



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)  $\text{He}^+$

(b)  $\text{Li}^{2+}$

(c)  $\text{Be}^{3+}$

(d) In all cases

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

## Variation of $Z_{\text{eff}}$ in Periodic Table

$$Z_{\text{eff}} = Z - \sigma$$

$$1. Z_{\text{eff}} \propto Z$$

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

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

$n_e \rightarrow$  Total number of electrons in atom



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

$Z_{eff}$ : Li < Be

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

Li<sub>3</sub>

Be<sub>4</sub>

❑ Variation in a Group: When we move from top to bottom  
1.  $Z_{eff} \Rightarrow$  Constant [Generally valid in s and p blocks but not always]

Na<sub>11</sub>

11 P

$Z_{eff}$  is constant as no. of proton ↑ but distance between nucleus and test electron ↑.

K<sub>19</sub>

19 P

For Example

Al<sub>13</sub> → [Ne] 3s<sup>2</sup> 3p<sup>1</sup>

Ga<sub>31</sub> → [Ar] 4s<sup>2</sup> 3d<sup>10</sup> 4p<sup>1</sup>

Due to poor shielding of 3d<sup>10</sup> electrons, shielding constant σ decreases and  $Z_{eff} \uparrow$

$Z_{eff} : Al < Ga$

13 P

31 P

# ATOMIC RADIUS

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

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

| Covalent Radius                                                                                 | Metallic Radius                                                                             | vander Waal Radius                                                                                                                                  |
|-------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"><li>Covalent Bond</li><li>Non metal – non metal (H)</li></ul> | <ul style="list-style-type: none"><li>Metallic bond</li><li>Metal – metal (Na-Na)</li></ul> | <ul style="list-style-type: none"><li>VW – Force of attraction</li><li>Inert gas / molecules (He, Ne, Ar) (H<sub>2</sub>, Cl<sub>2</sub>)</li></ul> |
|                                                                                                 |                                                                                             |                                                                                                                                                     |



$$r_c = \frac{d_1}{2}$$

$$r_M = \frac{d_2}{2}$$

$$r_{vw} = \frac{d_3}{2}$$

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

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

# ATOMIC SIZE

**Variation in a Period:** Left  $\rightarrow$  Right  $\Rightarrow Z_{eff} \uparrow \Rightarrow$  Atomic Radius  $\downarrow$

${}_{10}\text{Ne} > {}_3\text{Li} > \text{Be} > \text{B} > \text{C} > \text{N} > \text{O} > \text{F}$  : Atomic Radius

vander Waal radii

**Variation in a Group:**

Top  $\rightarrow Z_{eff} \approx \text{constant}$

Bottom  $\rightarrow$  Due to addition of new shell  $\Rightarrow$  Atomic Radius  $\uparrow$

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

| Same Period Elements                                                               | Different Period Elements                                                        |
|------------------------------------------------------------------------------------|----------------------------------------------------------------------------------|
| <p>Left <math>\rightarrow</math> Right : Atomic Radius <math>\downarrow</math></p> | <p>Period Number <math>\uparrow</math> : Atomic Radius <math>\uparrow</math></p> |

$\text{Br} > \text{C} > \text{N} > \text{F}$   
 $n = 4$        $n = 2$

$\text{C} < \text{S} < \text{Al} < \text{Ca}$   
 $n = 2$        $n = 3$        $n = 4$

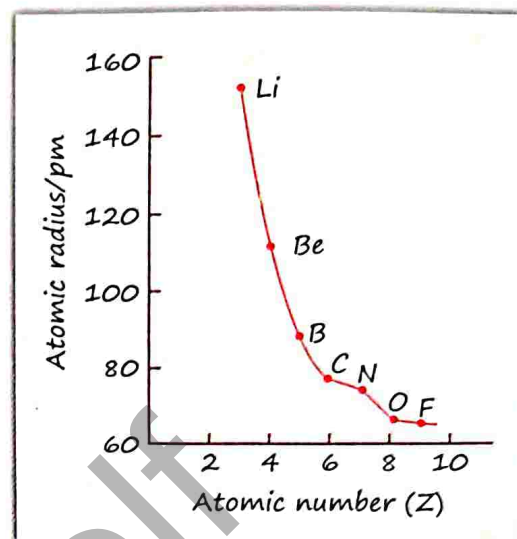
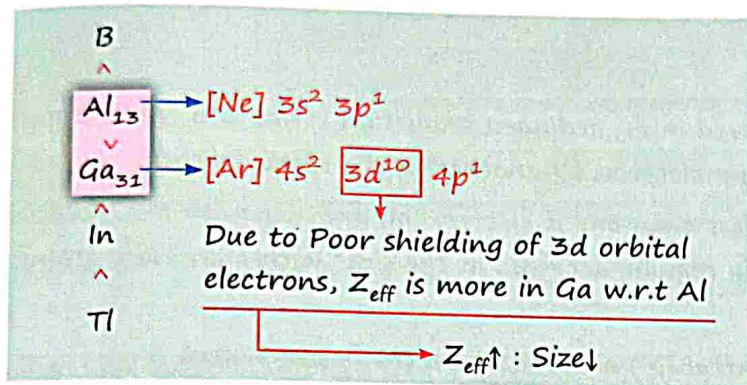
$\text{B} < \text{P} > \text{S} > \text{Cl} < \text{Br}$   
 $n = 2$      $n = 3$      $n = 3$      $n = 3$      $n = 4$

$\text{B} < \text{Cl} < \text{S} < \text{P} < \text{Br} \rightarrow$  Atomic Size



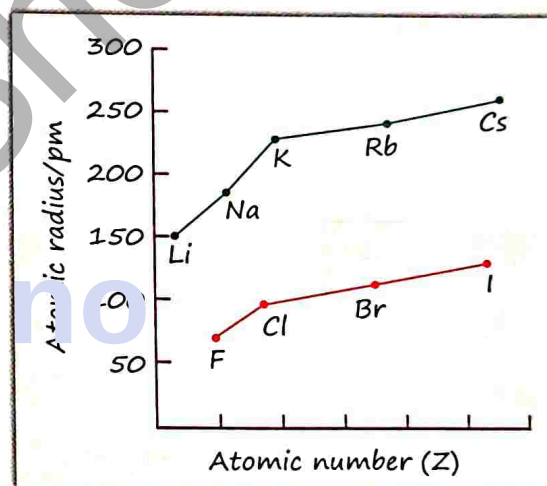
## Boron Family

नौटंकी Family



## Atomic Size Order in s and p Block

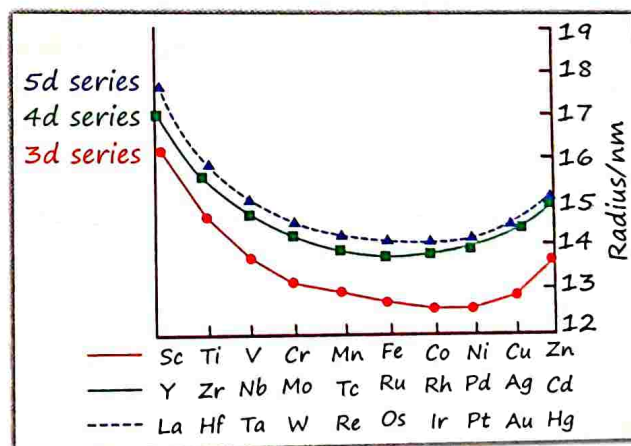
|    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|
| H  |    |    |    |    |    |    | He |
| Li | Be |    |    |    |    |    | Ne |
| Na | Mg | B  | C  | N  | O  | F  | Ar |
| K  | Ca | Al | Si | P  | S  | Cl | Kr |
| Rb | Sr | Ga | Ge | As | Se | Br | Xe |
| Cs |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



## Atomic Size of 3d Series

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

1. Nuclear charge [Nuclear charge  $\uparrow$  : size  $\downarrow$ ]
2. Interelectronic repulsion (IER) [IER  $\uparrow$  : size  $\uparrow$ ]



| Elements | Sc $\rightarrow$ Ti $\rightarrow$ V $\rightarrow$ Cr | Mn $\rightarrow$ Fe $\rightarrow$ Co $\rightarrow$ Ni | Cu $\rightarrow$ Zn               |
|----------|------------------------------------------------------|-------------------------------------------------------|-----------------------------------|
| Size     | Decreases                                            | Nearly constant                                       | Slightly increases                |
| Reason   | Nuclear charge dominates over IER                    | Nuclear charge $\approx$ IER                          | IER dominates over nuclear charge |

Classification of Elements and Periodicity in Properties

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## 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  $\rightarrow$  Atomic Radius : Eu > Ce

## Effect of Lanthanide Contraction on Size of d-Block Elements

|    |      |               |      |      |      |      |      |      |      |      |      |
|----|------|---------------|------|------|------|------|------|------|------|------|------|
| 3d | 21Sc | 22Ti          | 23V  | 24Cr | 25Mn | 26Fe | 27Co | 28Ni | 29Cu | 30Zn |      |
|    | ^    | ^             | ^    | ^    | ^    | ^    | ^    | ^    | ^    | ^    |      |
| 4d | 39Y  | 40Zr          | 41Nb | 42Mo | 43Tc | 44Ru | 45Rh | 46Pd | 47Ag | 48Cd |      |
|    | ^    | ^             | ^    | ^    | ^    | ^    | ^    | ^    | ^    | ^    |      |
| 5d | 57La | (58Ce → 71Lu) | 72Hf | 73Ta | 74W  | 75Re | 76Os | 77Ir | 78Pt | 79Au | 80Hg |
|    | ^    | ^             | ^    | ^    | ^    | ^    | ^    | ^    | ^    | ^    |      |

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 :

- Zr and Y have about the same radius
- Zr and Nb have similar oxidation state
- Zr and Hf have about the same radius.
- Zr and Zn have same oxidation state.

Sol. (c)

20. Which of the following has similar atomic radius with respect to Ag :

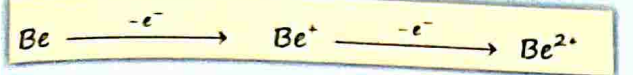
- La
- Zn
- Au
- Rf

Sol. (c)



## IONIC RADIUS

**Cation**  $\rightarrow$   $\oplus$  vely charged ion



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

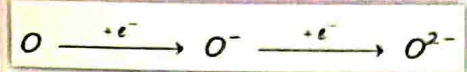
$$Z_{\text{eff}} : \text{Be} < \text{Be}^+ < \text{Be}^{2+}$$

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

: Mother atom > Cation

$$\blacklozenge \text{Mg} > \text{Mg}^+ > \text{Mg}^{2+} : \text{Size}$$

**Anion**  $\rightarrow$   $\ominus$  vely charged ion



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

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

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

: Mother atom < Anion

$$\blacklozenge \text{I} < \text{I}^- : \text{Size}$$

## ISOELECTRONIC SPECIES

- Species having same number of electrons are known as isoelectronic species.
- All ions  $\text{C}^{4-}$ ,  $\text{N}^{3-}$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  are isoelectronic because they all have 10 electrons.

|                                        | $\text{C}^{4-}$                                              | $\text{N}^{3-}$  | $\text{O}^{2-}$  | $\text{F}^-$     | $\text{Na}^+$                                   | $\text{Mg}^{2+}$  | $\text{Al}^{3+}$  |
|----------------------------------------|--------------------------------------------------------------|------------------|------------------|------------------|-------------------------------------------------|-------------------|-------------------|
| 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                |
| $Z_{\text{eff}} \propto \frac{Z}{e}$ : | $\frac{6}{10}$                                               | $< \frac{7}{10}$ | $< \frac{8}{10}$ | $< \frac{9}{10}$ | $< \frac{11}{10}$                               | $< \frac{12}{10}$ | $< \frac{13}{10}$ |
| Size :                                 | $\text{C}^{4-} > \text{N}^{3-} > \text{O}^{2-} > \text{F}^-$ |                  |                  |                  | $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$ |                   |                   |
|                                        | <div> <div></div> <div>Anions</div> </div>                   |                  |                  |                  | <div> <div></div> <div>Cations</div> </div>     |                   |                   |

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

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

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## Note

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

$$\begin{array}{cccc} \downarrow & \downarrow & \downarrow & \downarrow \\ 28 + 4(6 + 8) & 27 + 4(6 + 8) + 1 & 26 + 4(6 + 8) + 2 & 26 + 2(6 + 8) + 2(7 + 8) \\ \downarrow & \downarrow & \downarrow & \downarrow \\ 84 & 84 & 84 & 84 \end{array}$$

## Find the order of ionic radius?

- ❑  $S^{2-} > Cl^- > K^+ > Ca^{2+}$  : Size  
 $[16+2] \quad [17+1] \quad [19-1] \quad [20-2]$  : Number of electrons
- ❑  $Te^{2-} > I^-$  : Size  
 $[52+2] \quad [53+1]$  : Number of electrons
- ❑  $Ar > S^{2-} > Cl^- > K^+ > Ca^{2+}$  : Size  
 vander Waal radii
- ❑  $O^{2-} < N^{3-}$  : Size  
 Period Number  $\rightarrow 2$
- ❑  $K^+ > Na^+ > Li^+$  : Size  
 $[K > Na > Li]$  : Size
- ❑  $F^- < Cl^- < Br^- < I^-$  : Size  
 $[I > Br > Cl > F]$  : Size
- ❑  $O^{2-} < S^{2-} < Se^{2-} < Te^{2-}$  : Size

## 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  
 (a)  $\text{Ti}^{4+} < \text{Mn}^{7+}$  (b)  $^{35}\text{Cl}^- < ^{37}\text{Cl}^-$  (c)  $\text{K}^+ > \text{Cl}^-$  (d)  $\text{P}^{3+} > \text{P}^{5+}$  (IIT JEE 1999)

Sol. (d)

24. Among  $\text{V}(\text{CO})_6$ ,  $\text{Cr}(\text{CO})_5$ ,  $\text{Cu}(\text{CO})_3$ ,  $\text{Mn}(\text{CO})_5$ ,  $\text{Fe}(\text{CO})_5$ ,  $[\text{Co}(\text{CO})_3]^{3-}$ ,  $[\text{Cr}(\text{CO})_4]^{4-}$ , and  $\text{Ir}(\text{CO})_3$ , the total number of species isoelectronic with  $\text{Ni}(\text{CO})_4$  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  $\text{Ni}(\text{CO})_4 = 84$

| Species                  | Total electron |
|--------------------------|----------------|
| $\text{V}(\text{CO})_6$  | 107            |
| $\text{Cr}(\text{CO})_5$ | 94             |
| $\text{Cu}(\text{CO})_3$ | 71             |
| $\text{Mn}(\text{CO})_5$ | 95             |

| Species                         | Total electron |
|---------------------------------|----------------|
| $\text{Fe}(\text{CO})_5$        | 96             |
| $[\text{Co}(\text{CO})_3]^{3-}$ | 72             |
| $[\text{Cr}(\text{CO})_4]^{4-}$ | 84             |
| $\text{Ir}(\text{CO})_3$        | 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)  $\text{N}^{3-} > \text{O}^{2-} > \text{F}^- > \text{Na}^+$  : ionic size [All ions have noble gas configuration (Ne)]

26. Which one of the following represents all isoelectronic species? [NEET 2023-Manipur]  
 (a)  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{O}^-$ ,  $\text{NO}^+$  (b)  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_4$ ,  $\text{NO}^+$ ,  $\text{NO}$   
 (c)  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{O}^-$ ,  $\text{F}^-$  (d)  $\text{Cl}^{2-}$ ,  $\text{Ar}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$

Sol. (d)

27. From the following pairs of ions, which one is not an isoelectronic pair? [NEET 2021]  
 (a)  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  (b)  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  (c)  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  (d)  $\text{O}^{2-}$ ,  $\text{F}^-$

Sol. (c)

28. The species Ar,  $\text{K}^+$  and  $\text{Ca}^{2+}$  contain the same number of electrons. In which order do their radii increase? [NEET 2015]  
 (a)  $\text{Ca}^{2+} < \text{Ar} < \text{K}^+$  (b)  $\text{Ca}^{2+} < \text{K}^+ < \text{Ar}$  (c)  $\text{K}^+ < \text{Ar} < \text{Ca}^{2+}$  (d)  $\text{Ar} < \text{K}^+ < \text{Ca}^{2+}$

Sol. (b)

29.  $\text{Be}^{2+}$  is isoelectronic with which of the following ions? [NEET 2014]  
 (a)  $\text{Li}^+$  (b)  $\text{Na}^+$  (c)  $\text{Mg}^{2+}$  (d)  $\text{H}^+$

Sol. (a)

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

- Atomic radius of the elements decreases as one moves across from left to right in the 2<sup>nd</sup> period of the periodic table
- Amongst isoelectronic species, smaller the positive charge on the cation, smaller is the ionic radius
- Amongst isoelectronic species, greater the negative charge on the anion, larger is the ionic radius
- Atomic radius of the elements increases as one moves down the first group of the periodic table.

Sol. (b)



31. Ionic radii are:

- (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:

- (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<br>23 electrons 15 electrons<br>Entities having odd number of electrons are always paramagnetic. | He, Ne, $Zn^{2+}$ , Mg                 |

## IONISATION ENERGY

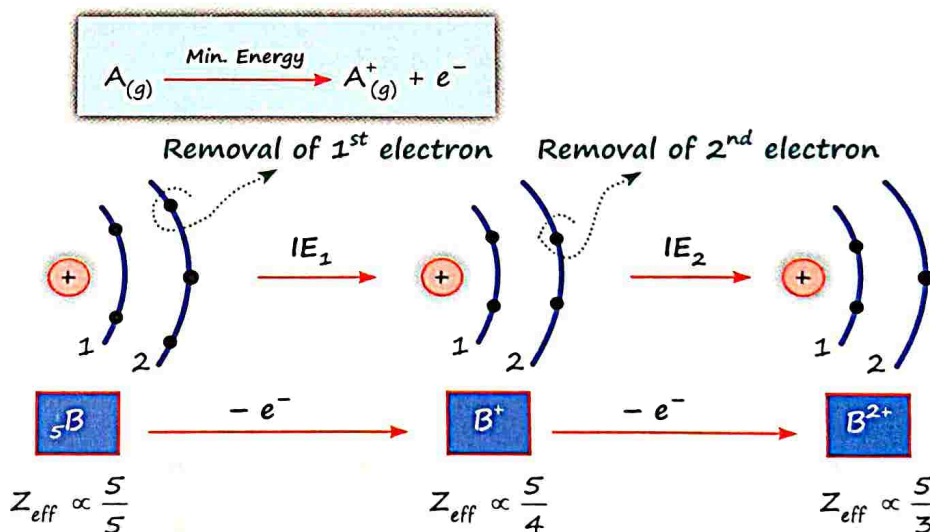
Minimum energy required to remove an electron from an isolated gaseous atom is known as ionisation energy (IE).

### Successive IE :

$$Z_{eff} : B < B^+ \\ IE : B < B^+$$

$$IE_1 \text{ of } B < IE_2 \text{ of } B$$

$$\square IE_2 \text{ of } B = IE_1 \text{ of } B^+ \\ IE_3 \text{ of } B = IE_1 \text{ of } B^{2+} \\ = IE_2 \text{ of } B^+$$





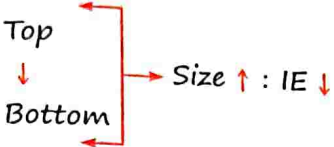
## Factors Affecting I.E.

### 1 $Z_{\text{eff}}$

Left  $\rightarrow$  Right  $\Rightarrow Z_{\text{eff}} \uparrow : \text{IE} \uparrow$



### 2 Size



Li  
 $\downarrow$   
Na  
 $\downarrow$   
K  
 $\downarrow$   
Rb  
 $\downarrow$   
Cs

As we move from top to bottom Size  $\uparrow : \text{IE} \downarrow$

### Metallic Character



- ♦ Tendency of an element to lose electrons and form positive ions or cations.
- ♦  $\text{IE} \downarrow : \text{Metallic character} \uparrow$
- ♦ Metallic character :  $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$

### 3 Electronic Configuration

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

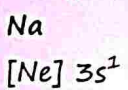
|                                                        |             |   |             |
|--------------------------------------------------------|-------------|---|-------------|
| IE :                                                   | N           | > | C           |
|                                                        | $2s^2 2p^3$ |   | $2s^2 2p^2$ |
| Removal of electron from half filled subshell is tough |             |   |             |
| IE :                                                   | P           | > | S           |
|                                                        | $3p^3$      |   | $3p^4$      |
| IE :                                                   | As          | > | Se          |
|                                                        | $4p^3$      |   | $4p^4$      |

$\text{C}(2p^2) \rightarrow \boxed{\uparrow\downarrow} \boxed{\uparrow} \boxed{\uparrow}$   $\text{N}(2p^3) \rightarrow \boxed{\uparrow\downarrow} \boxed{\uparrow} \boxed{\uparrow}$

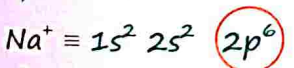
In the oxygen atom, two of the four 2p electrons must occupy the same 2p-orbital, resulting in an increased  $e^- - e^-$  repulsion. So, it is easier to remove the fourth 2p electron from oxygen than it is to remove one of the three 2p-electrons from nitrogen.

## Comparison of 2<sup>nd</sup> Ionisation Energy

### Group-1



$\downarrow \text{IE}_1$

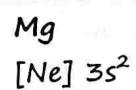


$\downarrow \text{IE}_2$



Removal of electron from 2<sup>nd</sup> shell is tough.

### Group-2



$\downarrow \text{IE}_1$



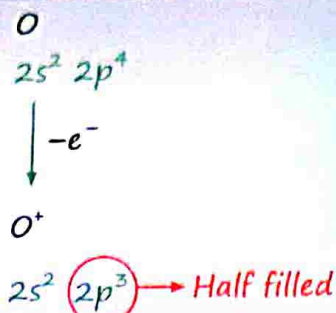
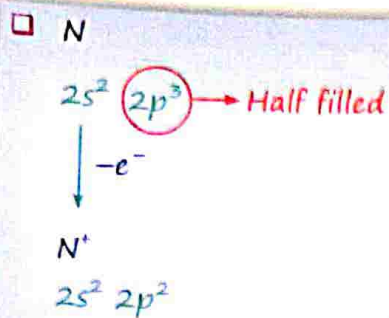
$\downarrow \text{IE}_2$



Removal of electron from 3<sup>rd</sup> shell is easy.

$\text{IE}_1 : \text{group 1} < \text{group 2}$   
 $\text{IE}_2 : \text{group 1} > \text{group 2}$

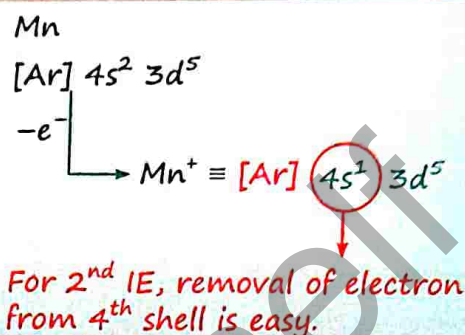
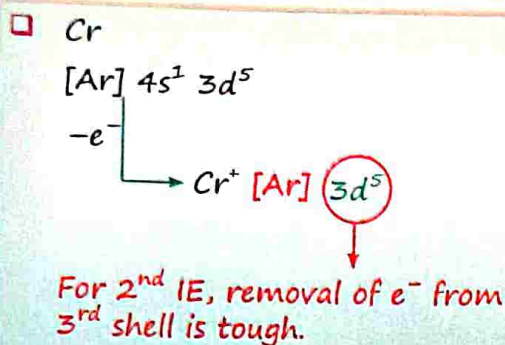




$$IE_1 : N > O$$

$$IE_2 : N < O$$

$$IE : N^+ < O^+$$

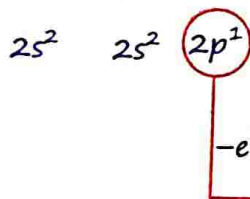


$$IE_2 : Cr > Mn$$

#### 4 Penetration Effect

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

♦ Be > B : IE



Removal of e<sup>-</sup> from 2p subshell is easy with respect to 2s (Be).

The penetration of a 2s -electron is more than that of a 2p electron; hence the 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)  $\text{Mn} [4s^2 3d^5] \xrightarrow[\text{IE}_1]{-e^-} \text{Mn}^+ [4s^1 3d^5] \xrightarrow[\text{IE}_2]{-e^-} \text{Mn}^{2+} [3d^5]$  Removal of 3<sup>rd</sup> electron from half filled subshell is tough, so, IE<sub>3</sub> will be highest among all.

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

- (a)  $\text{K} > \text{Na} > \text{Li}$       (b)  $\text{Be} > \text{Mg} > \text{Ca}$       (c)  $\text{B} > \text{C} > \text{N}$       (d)  $\text{Ge} > \text{Si} > \text{C}$

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:  $ns^1 < ns^2 > np^1 < np^2 < np^3 > np^4 < np^5 < np^6$

↓ due to penetration effect
↓ due to stable electronic configuration [np<sup>3</sup>]

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

|                                           |                 |                 |                 |                 |                 |                 |                 |
|-------------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 2s <sup>1</sup>                           | 2s <sup>2</sup> | 2p <sup>1</sup> | 2p <sup>2</sup> | 2p <sup>3</sup> | 2p <sup>4</sup> | 2p <sup>5</sup> | 2p <sup>6</sup> |
| Li                                        | Be              | B               | C               | N               | O               | F               | Ne              |
| Li < B < Be < C < O < N < F < Ne : IE     |                 |                 |                 |                 |                 |                 |                 |
| Na                                        | Mg              | Al              | Si              | P               | S               | Cl              | Ar              |
| Na < Al < Mg < Si < S < P < Cl < Ar : IE  |                 |                 |                 |                 |                 |                 |                 |
| K                                         | Ca              | Ga              | Ge              | As              | Se              | Br              | Kr              |
| K < Ga < Ca < Ge < Se < As < Br < Kr : IE |                 |                 |                 |                 |                 |                 |                 |

### Boron Family

B<sub>5</sub> : [He] 2s<sup>2</sup> 2p<sup>1</sup>

✓

Al<sub>13</sub> : [Ne] 3s<sup>2</sup> 3p<sup>1</sup>

^

Ga<sub>31</sub> : [Ar] 4s<sup>2</sup> 3d<sup>10</sup> 4p<sup>1</sup>

✓

poor shielding of 3d electrons

In<sub>49</sub> : [Kr] 5s<sup>2</sup> 4d<sup>10</sup> 5p<sup>1</sup>

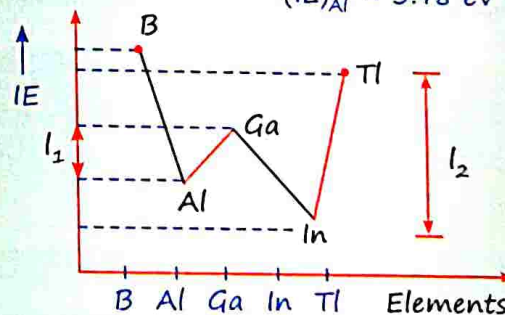
^

Tl<sub>81</sub> : [Xe] 6s<sup>2</sup> 4f<sup>14</sup> 5d<sup>10</sup> 6p<sup>1</sup>

poor shielding of 4f electrons

□  $\text{B} > \text{Tl} > \text{Ga} \geq \text{Al} > \text{In} : \text{IE}$

(IE)<sub>Ga</sub> = 5.99 eV and  
(IE)<sub>Al</sub> = 5.98 eV



- ♦  $(\text{IE}_{\text{Ga}} - \text{IE}_{\text{Al}} = I_1) < (\text{IE}_{\text{Tl}} - \text{IE}_{\text{In}} = I_2)$   
♦  $\Delta \text{IE}_{(\text{Ga}, \text{Al})} < \Delta \text{IE}_{(\text{Tl}, \text{In})}$

Classification of Elements and Periodicity in Properties



### 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 |

4d

5d

Size →

4d series ≈ 5d series

|      |               |      |    |    |    |    |    |    |    |    |
|------|---------------|------|----|----|----|----|----|----|----|----|
| 39Y  | (58Ce → 71Lu) | 40Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| 57La |               | 72Hf | Ta | W  | Re | Os | Ir | Pt | Au | Hg |

Free from the effect of Lanthanoid contraction

4d

5d

Ionisation Energy →

4d series < 5d series

|      |               |      |    |    |    |    |    |    |    |    |
|------|---------------|------|----|----|----|----|----|----|----|----|
| 39Y  | (58Ce → 71Lu) | 40Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| 57La |               | 72Hf | 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  $Z_{\text{eff}}$  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  $n^{\text{th}}$  ionisation energy just before **SUDDEN JUMP**

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

5.1
47.2
71.6
98.9

$IE_1$        $IE_2$        $IE_3$        $IE_4$

Sudden Jump

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

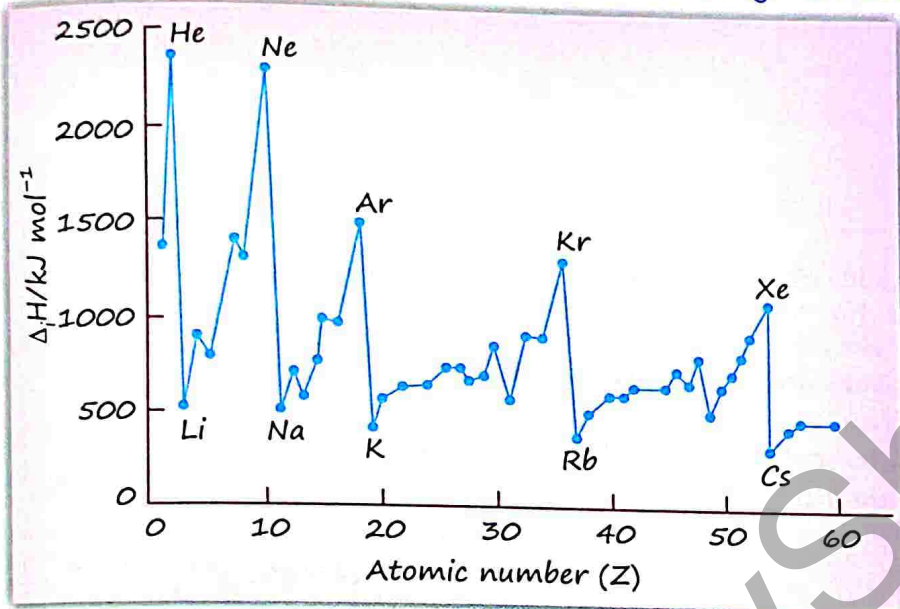
Removal of inner shell  $e^-$  is Tough

Removal of outer shell  $e^-$  is Easy

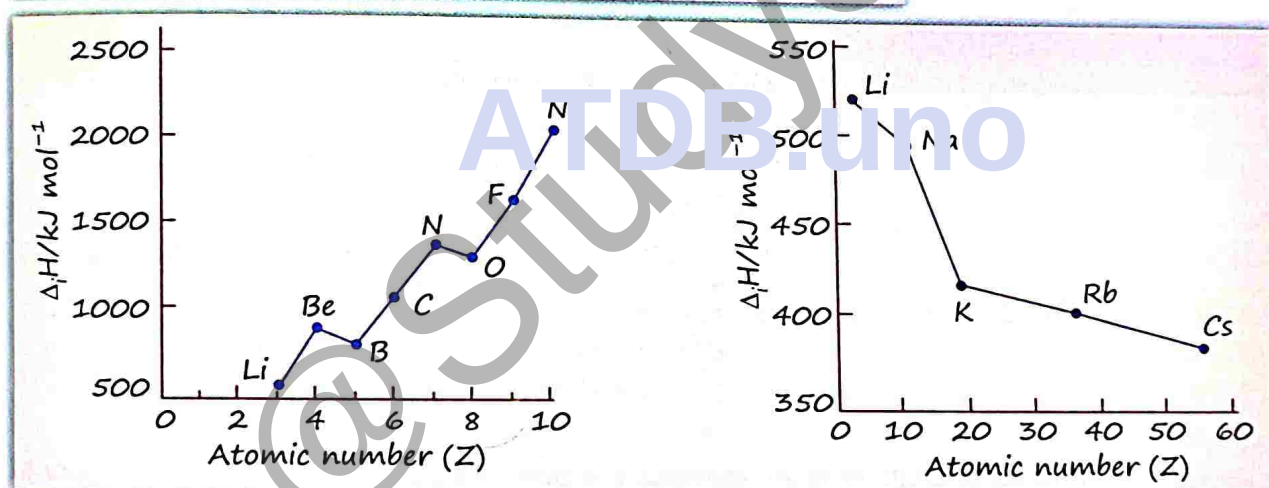
| Element | $IE_1$ | $IE_2$ | $IE_3$ | $IE_4$ | $IE_5$ | Number of valence electrons |
|---------|--------|--------|--------|--------|--------|-----------------------------|
| X       | 5.98   | 18.22  | 28.44  | 119.4  | —      | 3                           |
| Y       | 11.26  | 26.38  | 47.44  | 77.41  | 392.07 | 4                           |



- If the difference in ionisation energy  $\Delta(IE_2 - IE_1)$  is greater than  $16 \text{ eV atom}^{-1}$ , then the (+1) oxidation state is stable.  
 For Na,  $\Delta(IE_2 - IE_1) \approx 41 \text{ eV atom}^{-1} \Rightarrow \text{Na}^+$  is more stable.
- If value of  $\Delta(IE_2 - IE_1)$  is less than  $11 \text{ eV atom}^{-1}$  then the (+2) oxidation state is stable.  
 For Mg, value of  $\Delta(IE_2 - IE_1) \approx 7 \text{ eV atom}^{-1} \Rightarrow \text{Mg}^{2+}$  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) |                 |                 |
|---------|------------------------------|-----------------|-----------------|
|         | 1 <sup>st</sup>              | 2 <sup>nd</sup> | 3 <sup>rd</sup> |
| 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)  $\text{Si} < \text{Be} < \text{Mg} < \text{K}$  (b)  $\text{Be} < \text{Si} < \text{Mg} < \text{K}$  (c)  $\text{K} < \text{Mg} < \text{Be} < \text{Si}$  (d)  $\text{Be} < \text{Si} < \text{K} < \text{Mg}$

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)  $\text{IE} \rightarrow \text{Al} < \text{Mg} < \text{S} < \text{P}$

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

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                              |                  | List-II                            |      |
|-------------------------------------|------------------|------------------------------------|------|
| Electronic configuration of element |                  | $\Delta H$ in $\text{kJ mol}^{-1}$ |      |
| A.                                  | $1s^2 2s^2$      | I.                                 | 361  |
| 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)  $\text{N} > \text{O} > \text{Be} > \text{B}$

43. The five successive ionization enthalpies of an element are 800, 2427, 3658, 25024 and 32824  $\text{kJ mol}^{-1}$ . 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 3<sup>rd</sup> and 4<sup>th</sup> ionisation energies, the number of valence electrons is 3.

44. If first ionization enthalpies of elements X and Y are 419  $\text{kJ mol}^{-1}$  and 590  $\text{kJ mol}^{-1}$ , respectively and second ionization enthalpies of X and Y are 3069  $\text{kJ mol}^{-1}$  and 1145  $\text{kJ mol}^{-1}$ , 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)  $\text{X} \xrightarrow{419} \text{X}^+ \xrightarrow{3069} \text{X}^{2+}$   $\text{Y} \xrightarrow{590} \text{Y}^+ \xrightarrow{1145} \text{Y}^{2+}$   $[\text{IE}_1 : \text{X} < \text{Y}, \text{IE}_2 : \text{X} > \text{Y}]$



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

- (a) [Ne] 3s<sup>2</sup>3p<sup>2</sup> (b) [Ar] 3d<sup>10</sup>4s<sup>2</sup>4p<sup>3</sup> (c) [Ne] 3s<sup>2</sup>3p<sup>1</sup> (d) [Ne] 3s<sup>2</sup>3p<sup>3</sup>

Sol. (d)

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

- (a) 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>3</sup> (b) 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>5</sup> 3s<sup>1</sup> (c) 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> (d) 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>5</sup>

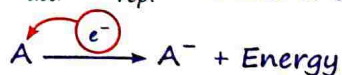
Sol. (b)

## ELECTRON GAIN ENTHALPY

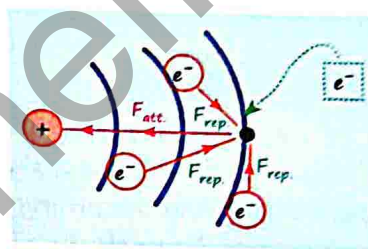
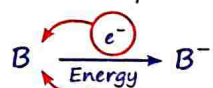
Enthalpy change in addition of an electron in an isolated gaseous atom is known as electron gain enthalpy.

□ 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



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



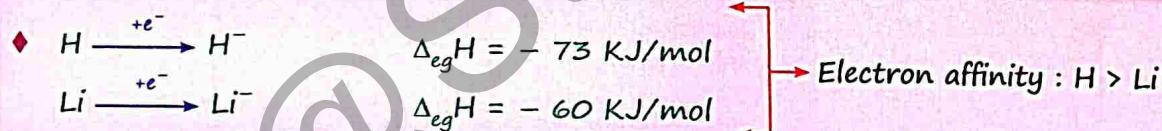
## Electron Affinity

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

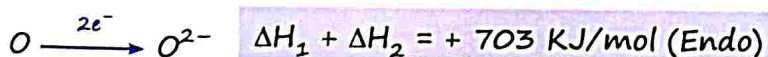
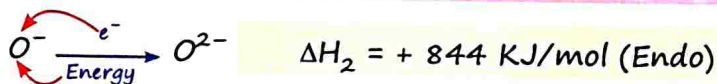
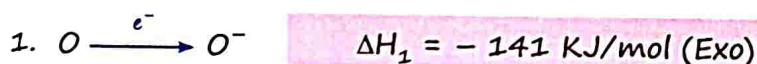
□ Electron affinity is measured in terms of EGE ( $\Delta H_{eg}$ ).

□ More -ve  $\Delta_{eg}H \Rightarrow$  more electron affinity

□ Less -ve  $\Delta_{eg}H \Rightarrow$  less electron affinity



□ Formation of multiple  $\ominus$ ve anion: Overall energy change during formation of multiple  $\ominus$ ve anion is always  $\oplus$ ve.



Classification of Elements and Periodicity in Properties

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## Factor Affecting Electron Affinity

1  $Z_{\text{eff}}$

Left  $\rightarrow$  Right :  $Z_{\text{eff}} \uparrow$  : EA  $\uparrow$

$O_8 < F_9$  : EA

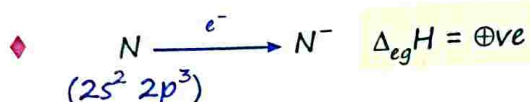
2 Size

Top  $\rightarrow$  Size  $\uparrow$   
 $\downarrow$   
 Bottom  $\rightarrow$  EA  $\downarrow$

EA : Cl > Br > I > At

3 Electronic Configuration

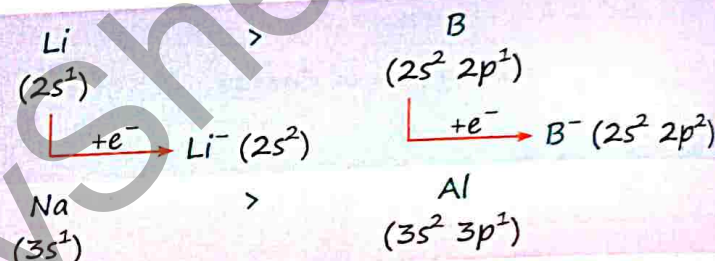
Generally for stable electronic configuration (half filled and fully filled)  $\Rightarrow \Delta H = \oplus ve$ .



4 Penetration Effect

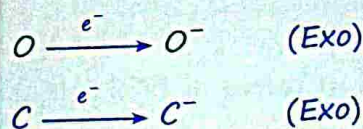
Addition of electron in s-orbital is more favorable than p-orbital because s-orbital is near to the nucleus and upcoming electron get more attraction by nucleus.

EA : K > Ga  
 : Rb > In  
 : Cs > Tl

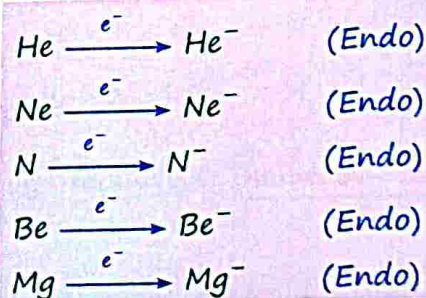


## Important Points

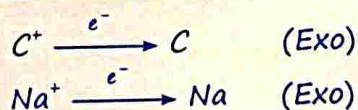
Generally For neutral atom :  $\Delta_{eg}H \equiv (-)ve$



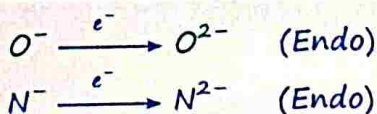
But For (Be, Mg, N) (Inert Gas) :  $\Delta_{eg}H \equiv (+)ve$



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



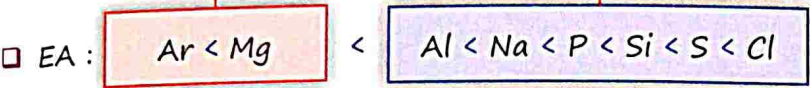
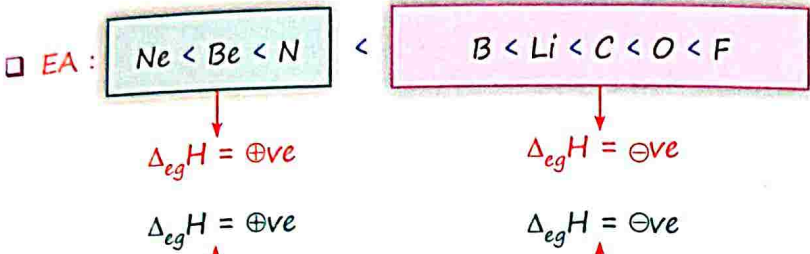
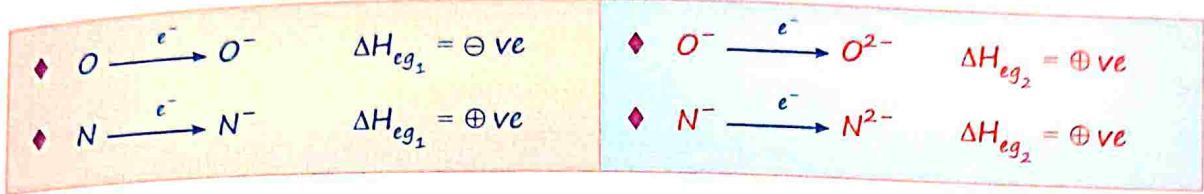
For all anions :  $\Delta_{eg}H \equiv (+)ve$



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



1<sup>st</sup> EGE [ $\Delta H_{eg_1}$ ] may be +ve/-ve. 2<sup>nd</sup> EGE [ $\Delta H_{eg_2}$ ] is always  $\oplus$ ve.



- EA: alkali metals > alkaline earth metals
- $ns^1 \xrightarrow{+e} ns^2$

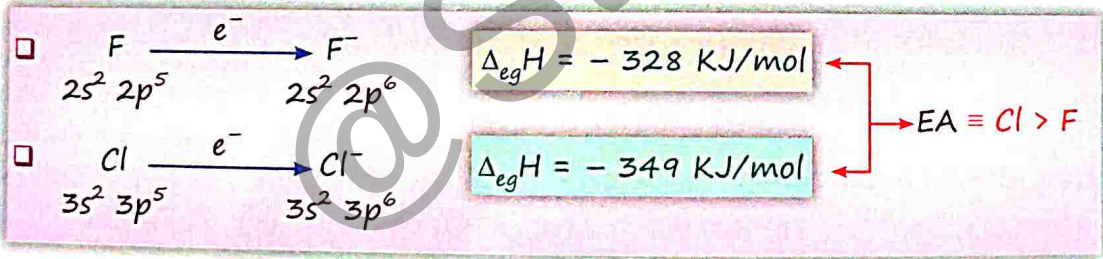
Fully-filled electronic configuration is achieved

$\Delta_{eg}H$  is (-)ve
- $ns^2 \xrightarrow{+e} ns^2 np^1$

Fully-filled electronic configuration is disturbed

$\Delta_{eg}H$  is (+)ve

Comparison b/w Electron Affinity of F & Cl



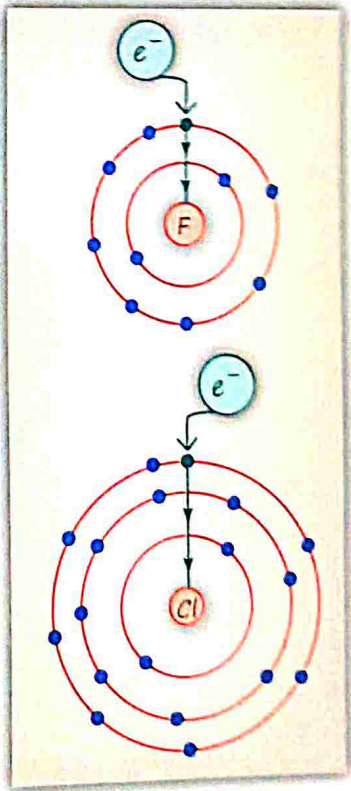
Adding an electron to the 2p-orbital (F) leads to greater repulsion than adding an electron to the larger 3p-orbital (Cl). Hence electron gain enthalpy of the Cl is more negative than F.

Note

- $\uparrow$

B C N O F (Period 2)
- $\uparrow$

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 enthalpy:  $H > Li > Na > \underline{K > Rb > Cs}$   
 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  $\Delta H_{eg}$  and Ne has most (+)ve  $\Delta H_{eg}$  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)  $Cl > Br > S > O : \Delta H_{eg}$  (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)  $\text{Xe} < \text{Kr} < \text{Ne} < \text{He}$  (b)  $\text{He} < \text{Ne} < \text{Kr} < \text{Xe}$   
 (c)  $\text{He} < \text{Xe} < \text{Kr} < \text{Ne}$  (d)  $\text{He} < \text{Kr} < \text{Xe} < \text{Ne}$

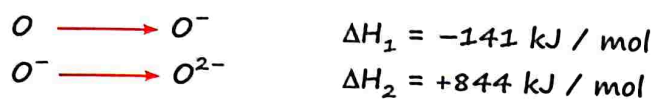
Sol. (c)

50. The first electron gain enthalpy ( $\Delta H_{eg}$ ) of oxygen is  $-141 \text{ kJ/mol}$ , 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 ion  $\text{O}^{2-}$  requires first an exothermic and then an endothermic step as shown below :



This is because:

- (a) Oxygen is more electronegative  
 (b) Oxygen has high electron affinity.  
 (c)  $\text{O}^-$  ion will tend to resist the addition of another electron.  
 (d)  $\text{O}^-$  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)  $\Delta_{eg}H(\text{Cl}) < \Delta_{eg}H(\text{F})$  (b)  $\Delta_{eg}H(\text{Se}) < \Delta_{eg}H(\text{S})$   
 (c)  $\Delta_{eg}H(\text{I}) < \Delta_{eg}H(\text{At})$  (d)  $\Delta_{eg}H(\text{Te}) < \Delta_{eg}H(\text{Po})$

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

53. The process that is NOT endothermic in nature is:

[4 Sept, 2020 (Shift-II)]

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

Sol. (a)

[IIT JEE 2002]

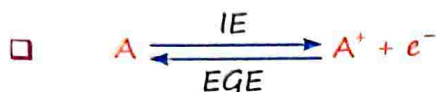
54. Identify the least stable ion amongst the following:

- (a)  $\text{Li}^-$  (b)  $\text{Be}^-$  (c)  $\text{B}^-$  (d)  $\text{C}^-$

Sol. (b)  $\text{Be}^-$  ion is formed by absorption of energy, so they have high energy  $\rightarrow$  means least stable.

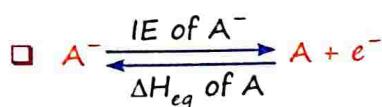


## Relation Between I.E. & E.G.E.

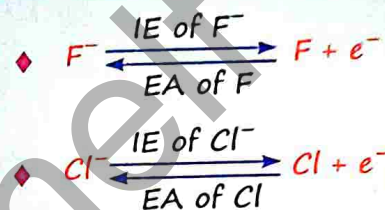
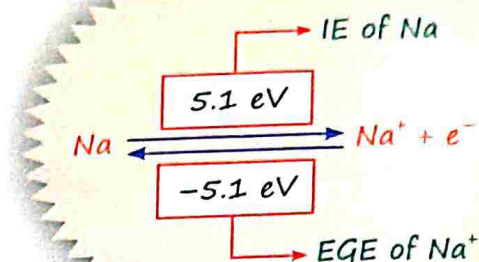


$$\text{IE of } A \equiv |\text{EGE of } A^+|$$

Order of IE :  $F > Cl$   
Order of EA :  $F^- > Cl^-$



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



$EA \equiv Cl^- > F^-$   
 $IE \equiv Cl^- > F^-$

## Note

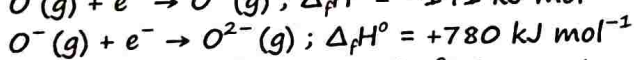
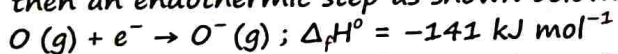
If energy is released when an electron is added to an atom, the electron affinity is taken as positive, contrary to thermodynamic convention. If energy has to be supplied to add an electron to an atom, then the electron affinity of the atom is assigned a negative sign. However, electron affinity is defined 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  $\Delta_r H^\circ = -A - 5/2 RT$ .

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]

- $Li < Na < K < Rb$  (increasing metallic radius)
- $Al^{3+} < Mg^{2+} < Na^+ < F^-$  (increasing ionic size)
- $B < C < N < O$  (increasing first ionization enthalpy)
- $I < Br < F < Cl$  (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:



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]

- $O^-$  ion has comparatively smaller size than oxygen atom
- Oxygen is more electronegative
- Addition of electron in oxygen results in larger size of the ion
- 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]

- $Cl < F < S < O$
- $O < S < F < Cl$
- $S < O < Cl < F$
- $F < Cl < O < S$

Sol. (b)



58. What is the value of electron gain enthalpy of  $\text{Na}^+$  if  $\text{IE}_1$  of  $\text{Na} = 5.1 \text{ eV}$ ? [NEET 2011 Mains]  
(a)  $+2.55 \text{ eV}$  (b)  $+10.2 \text{ eV}$  (c)  $-5.1 \text{ eV}$  (d)  $-10.2 \text{ eV}$   
Sol. (c)

## ELECTRONEGATIVITY

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

$-\delta$  : partial  $\ominus$ ve charge

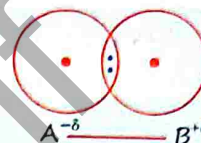


$$Z_{\text{eff}} : \text{A} > \text{B} \Rightarrow \text{EN} : \text{A} > \text{B}$$

1.  $Z_{\text{eff}} \uparrow : \text{EN} \uparrow$   $(Z_{\text{eff}})_{\text{A}} > (Z_{\text{eff}})_{\text{B}}$   
 $(\text{EN})_{\text{A}} > (\text{EN})_{\text{B}}$

Left  $\rightarrow$  Right  $\Rightarrow \text{EN} \uparrow$

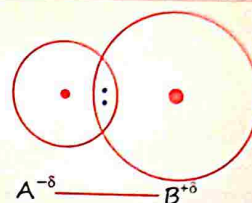
$\text{B} < \text{C} < \text{N} < \text{O} < \text{F} : \text{EN}$



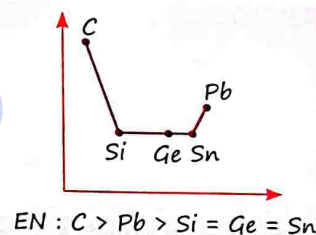
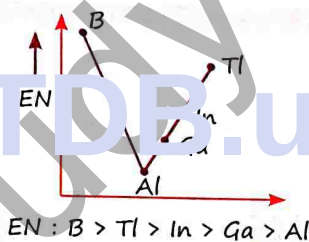
2.  $\text{Size} \uparrow : \text{EN} \downarrow$   $(\text{Size})_{\text{A}} < (\text{Size})_{\text{B}}$

Top  $\downarrow$  Bottom  $\Rightarrow \text{Size} \uparrow$   
 $\Rightarrow \text{EN} \downarrow$

F  
✓  
Cl  
✓  
Br  
✓  
I



Graph of Electronegativity Trends for Group 13 and Group 14 Elements



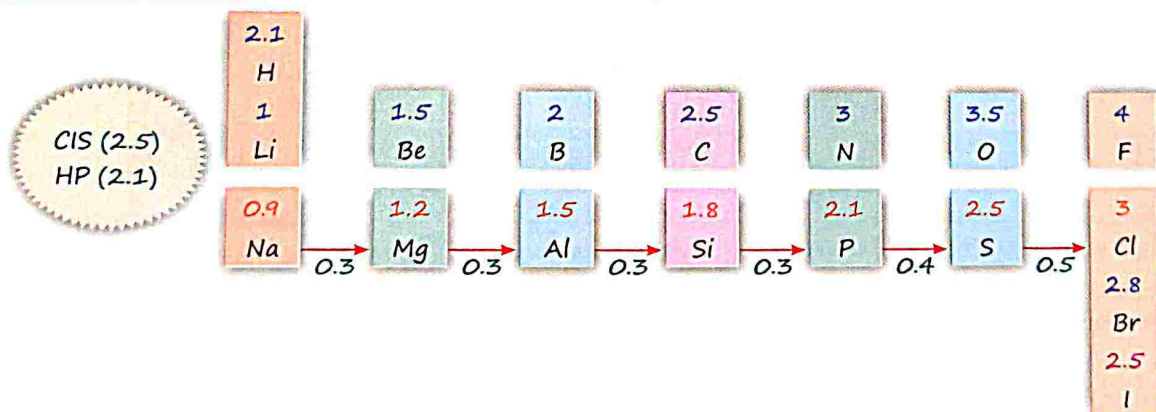
### Scale for Electronegativity

Pauling Scale

Mulliken Scale

Allred Rochow Scale

### Pauling Scale



Classification of Elements and Periodicity in Properties

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- Most electronegative element :  $F$
- Second most electronegative element :  $O$
- It is based on an empirical relation between energy of a bond and electronegativity.

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

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

$\Delta$  = Extra bond Energy

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

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

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

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

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

$$\chi_M = 2.8 \chi_P$$

I.E.  $\rightarrow$  Ionisation energy of an element in eV/atom.

E.A.  $\rightarrow$  Electron affinity of an element in eV/atom.

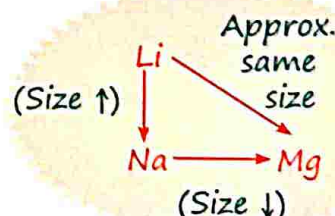
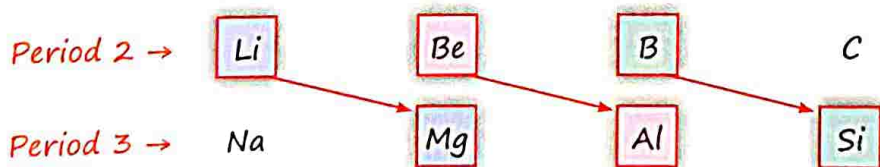
$\chi_M$   $\rightarrow$  Electronegativity of an element on Mulliken scale

$\chi_P$   $\rightarrow$  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 :  $Li \approx Mg$  , 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)

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61. Match List-I with List-II

| List-I<br>(Elements) |        | List-II<br>(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)<br>Group 1 : +1 | (Be → Ra)<br>Group 2 : +2 | Zn : +2<br>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.

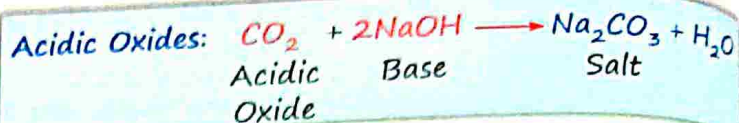
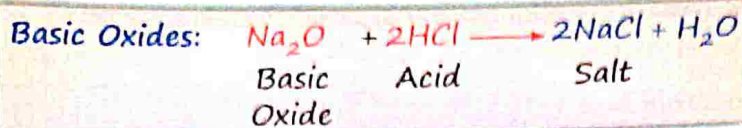
☐ Elements in rules 2, 3, 4, and 5 generally show the listed oxidation state but can also exhibit variable oxidation states in different compounds.

☐ Priority of rule: 1 > 2 > 3 > 4 > 5

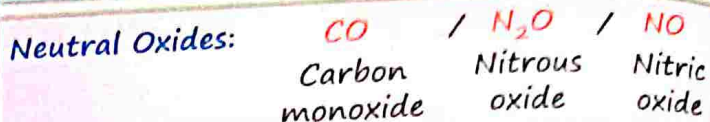
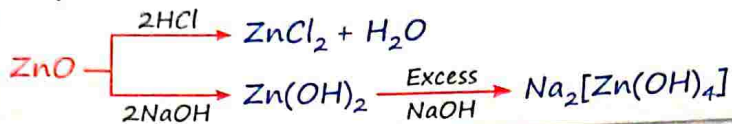
|                                          |                                                       |                                               |                                                |
|------------------------------------------|-------------------------------------------------------|-----------------------------------------------|------------------------------------------------|
| $Na^+$<br>$x = +1$                       | $N^{3-}$<br>$x = -3$                                  | $NO_3^-$<br>$x + 3(-2) = -1$<br>then $x = +5$ | $NH_4^+$<br>$x + 4(+1) = +1$<br>then $x = -3$  |
| $LiH$<br>$(+1) + x = 0$<br>then $x = -1$ | $H_2SO_4$<br>$2(+1) + x + 4(-2) = 0$<br>then $x = +6$ | $Na_2O$<br>$2(+1) + x = 0$<br>then $x = -2$   | $Na_2O_2$<br>$2(+1) + 2x = 0$<br>then $x = -1$ |



## OXIDES & HYDROXIDES



### Amphoteric Oxides:



## Amphoteric Oxides

□ As(+3)

Aas

Sb(+3)

Sab

Cr(+3)

Car

V(+5)

Vento

Te(+4)

Tera

□ Zn

Zaan

Sn

Suno

Be

Be

Al

Aaaliya

Pb

Pub

Ga

Gayi

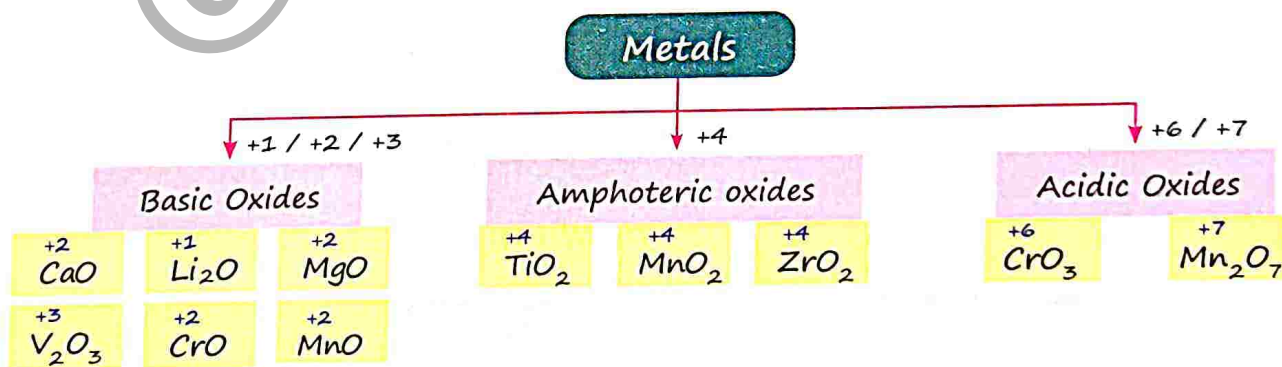
Example →

ZnO      BeO       $\text{Al}_2\text{O}_3$        $\text{Ga}_2\text{O}_3$       SnO       $\text{SnO}_2$        $\text{PbO}$        $\text{PbO}_2$        $\text{Pb}_3\text{O}_4$        $\text{Pb}_3\text{O}_2$

Amphoteric but predominantly acidic

## Basic Oxides

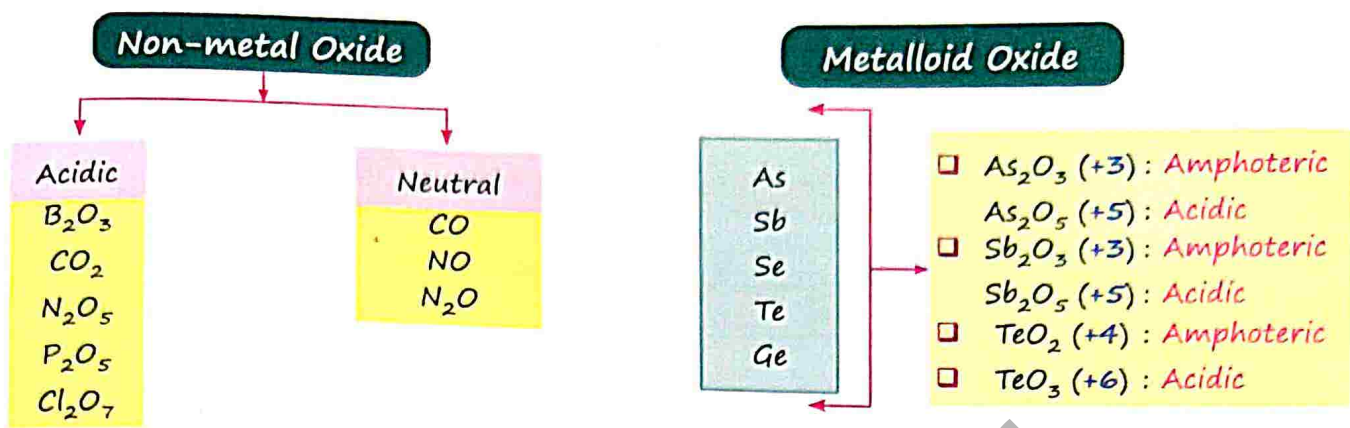
- Most common oxidation states for metals are +1, +2 and +3.
- Generally oxide of metals are basic in nature but some oxides are amphoteric and acidic also.



## Acidic Oxides

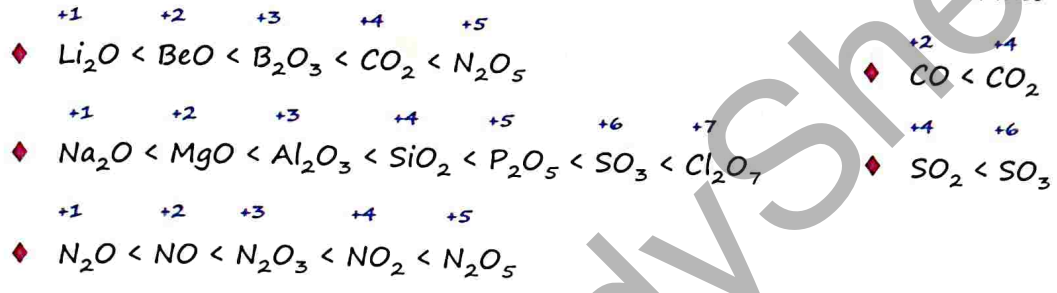
- Generally non-metal oxides are acidic except some neutral oxide [ $\text{CO}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ].
- Metalloid oxides are acidic except those which are considered already in amphoteric.





### Acidic Nature of Oxides

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



### 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 ⇌ M<sup>+</sup> + OH<sup>-</sup>

|χ<sub>O</sub> - χ<sub>M</sub>| > |χ<sub>O</sub> - χ<sub>H</sub>|

□ Cs—O—H is a base because

χ<sub>O</sub> - χ<sub>Cs</sub> = 3.5 - 0.7 = 2.8

χ<sub>O</sub> - χ<sub>H</sub> = 3.5 - 2.1 = 1.4

b. Acts as an acid when

M—O—H ⇌ MO<sup>-</sup> + H<sup>+</sup>

|χ<sub>O</sub> - χ<sub>H</sub>| > |χ<sub>O</sub> - χ<sub>M</sub>|

□ Cl—O—H is an acid because

χ<sub>O</sub> - χ<sub>Cl</sub> = 3.5 - 3.1 = 0.4

χ<sub>O</sub> - χ<sub>H</sub> = 3.5 - 2.1 = 1.4

| Basic Oxide       | Basic hydroxide     | Acidic oxide                  | Acidic hydroxide               | Amphoteric oxide               | Amphoteric hydroxide |
|-------------------|---------------------|-------------------------------|--------------------------------|--------------------------------|----------------------|
| Na <sub>2</sub> O | NaOH                | SiO <sub>2</sub>              | Si(OH) <sub>4</sub>            | Al <sub>2</sub> O <sub>3</sub> | Al(OH) <sub>3</sub>  |
| MgO               | Mg(OH) <sub>2</sub> | B <sub>2</sub> O <sub>3</sub> | B(OH) <sub>3</sub>             | ZnO                            | Zn(OH) <sub>2</sub>  |
| MnO               | Mn(OH) <sub>2</sub> | N <sub>2</sub> O <sub>5</sub> | HNO <sub>3</sub>               | BeO                            | Be(OH) <sub>2</sub>  |
| CuO               | Cu(OH) <sub>2</sub> | CO <sub>2</sub>               | H <sub>2</sub> CO <sub>3</sub> | PbO                            | Pb(OH) <sub>2</sub>  |



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-10)]

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

Sol. (c) Atomic number  $\rightarrow X$  (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<sub>2</sub>, CaO (b) ZnO, NO, CaO, CO<sub>2</sub>

(c) NO, CO<sub>2</sub>, ZnO, CaO (d) NO, CO<sub>2</sub>, 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  $\rightarrow A, B, C$

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

$M_A$  = 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  $\rightarrow$  24

Ca 40

S 32

Se  $\rightarrow$  79

Te 127

P 31

As  $\rightarrow$  75

Sb 120

H 1

F  $\rightarrow$  19

Cl 35.5

Sc : x

Y  $\rightarrow y = \frac{x+z}{2}$

La : z

## Newland's Law of Octaves

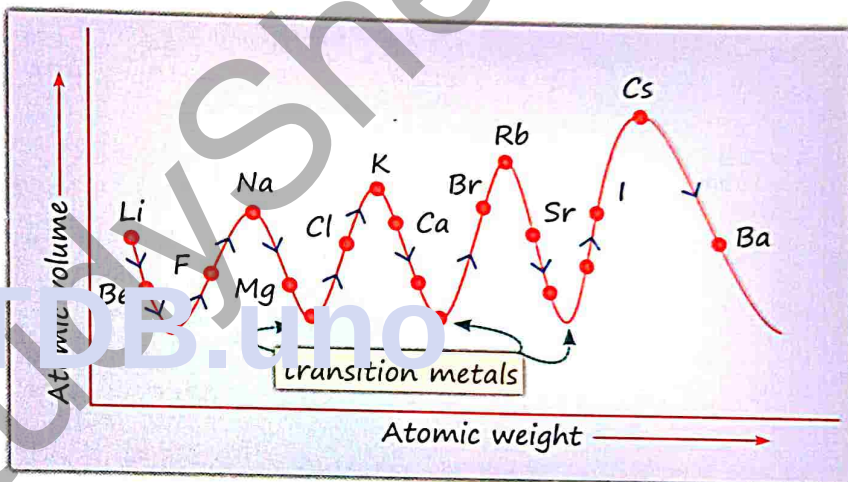
When elements are arranged in order of increasing atomic masses, every 8<sup>th</sup> element has properties similar to the first. Newlands called it law of octaves because similar relationship exists in the musical notes also.



| 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:

- It is based on atomic weight.
- 63 elements were known, noble gases were not discovered.
- He was the first scientist to classify the elements in a systematic manner (in horizontal rows and in vertical columns).
- Horizontal rows are called periods and there were 7 periods in Mendeleev's Periodic table.
- Vertical columns are called groups and there were 8 groups in Mendeleev's Periodic table.
- 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.
- The VIIIth group was consist of 9 elements in three rows (Transition metals group).
- The elements belonging to same group exhibit similar properties.

|    |    |    |
|----|----|----|
| Fe | Co | Ni |
| Ru | Rh | Pd |
| Os | Ir | Pt |

### Classification of Elements and Periodicity in Properties

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| Series | Groups of Elements |                  |             |                               |                                    |                                                                                                                                                                                |             |             |                 |             |             |
|--------|--------------------|------------------|-------------|-------------------------------|------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|-------------|-----------------|-------------|-------------|
|        | 0                  | I                | II          | III                           | IV                                 | V                                                                                                                                                                              | VI          | VII         | VIII            |             |             |
| 1      |                    | H<br>1.008       |             |                               |                                    |                                                                                                                                                                                |             |             |                 |             |             |
| 2      | He<br>4.0          | Li<br>7.03       | Be<br>9.1   | B<br>11.0                     | C<br>12.0                          | N<br>14.04                                                                                                                                                                     | O<br>16.00  | F<br>19.0   |                 |             |             |
| 3      | Ne<br>19.9         | Na<br>23.5       | Mg<br>24.3  | Al<br>27.0                    | Si<br>28.4                         | P<br>31.0                                                                                                                                                                      | S<br>32.06  | Cl<br>35.45 |                 |             |             |
| 4      | Ar<br>38           | K<br>39.1        | Ca<br>40.1  | Sc<br>44.1                    | Ti<br>48.1                         | V<br>51.4                                                                                                                                                                      | Cr<br>52.1  | Mn<br>55.0  | Fe<br>55.9      | Co<br>59    | Ni<br>59    |
| 5      |                    | Cu<br>63.6       | Zn<br>65.4  | Ga<br>70.0                    | Ge<br>72.3                         | As<br>75                                                                                                                                                                       | Se<br>79    | Br<br>79.95 |                 |             |             |
| 6      | Kr<br>81.8         | Rb<br>85.4       | Sr<br>87.6  | Y<br>89.0                     | Zr<br>90.6                         | Nb<br>94.0                                                                                                                                                                     | Mo<br>96.0  |             | Ru<br>101.7     | Rh<br>103.0 | Pd<br>106.5 |
| 7      |                    | Ag<br>107.9      | Cd<br>112.4 | In<br>114.0                   | Sn<br>119.0                        | Sb<br>120.0                                                                                                                                                                    | Te<br>127.6 | I<br>126.9  |                 |             |             |
| 8      | Xe<br>128          | Cs<br>132.9      | Ba<br>137.4 | La<br>139                     | Ce<br>140                          |                                                                                                                                                                                |             |             |                 |             |             |
| 9      |                    |                  |             |                               |                                    |                                                                                                                                                                                |             |             |                 |             |             |
| 10     |                    |                  |             | Yb<br>173                     | Ta<br>181                          | V<br>183                                                                                                                                                                       |             |             | Os<br>191       | Ir<br>193   | Pt<br>194.9 |
| 11     |                    | Au<br>197.2      | Hg<br>200.0 | Tl<br>204.1                   | Pb<br>206.9                        | Bi<br>208                                                                                                                                                                      |             |             |                 |             |             |
| 12     |                    |                  | Ra<br>224   |                               | Th<br>232                          |                                                                                                                                                                                | U<br>239    |             |                 |             |             |
|        | R                  | R <sub>2</sub> O | RO          | R <sub>2</sub> O <sub>3</sub> | RO <sub>2</sub><br>RH <sub>4</sub> | Higher Saline Oxides<br>R <sub>2</sub> O <sub>5</sub> RO <sub>3</sub> R <sub>2</sub> O <sub>7</sub><br>Higher Gaseous Hydrogen Compounds<br>RH <sub>3</sub> RH <sub>2</sub> RH |             |             | RO <sub>4</sub> |             |             |

## 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.

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CHEMISTRY



## Demerits in Mendeleev's Periodic Table:

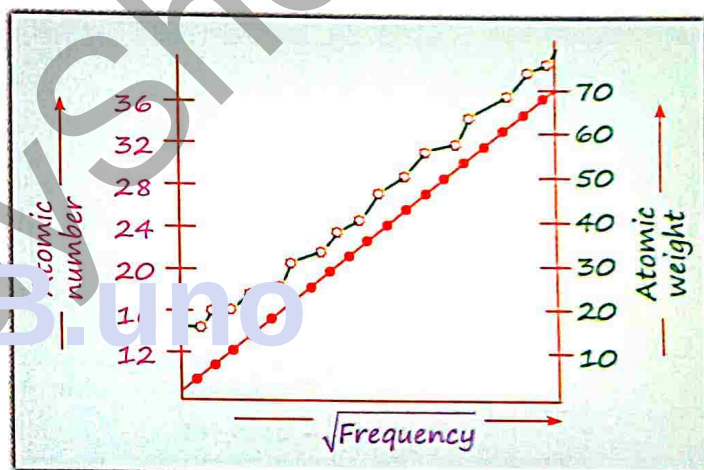
- ❑ Position of hydrogen is uncertain. It has been placed in IA and VIIA groups because of its resemblance with both the groups.
- ❑ No separate positions were given to isotopes.
- ❑ Anomalous positions of lanthanides and actinides in periodic table.
- ❑ Order of increasing atomic weights is not strictly 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  $\sqrt{\nu}$  (where  $\nu$  is frequency of X-rays emitted) against atomic number (Z) gave a straight line and not the plot of  $\sqrt{\nu}$  vs atomic mass.

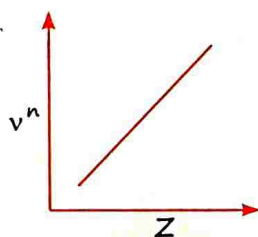
♦  $\sqrt{\nu} \propto Z$

$$\sqrt{\nu} = a(Z - b) \quad (a, b : \text{constant})$$



65. It is observed that characteristic X-ray spectra of elements show regularity. When frequency to the power 'n' i.e.  $\nu^n$  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

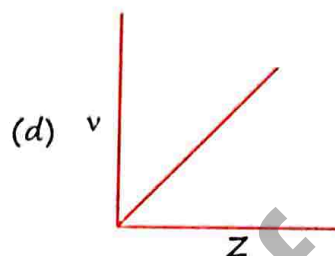
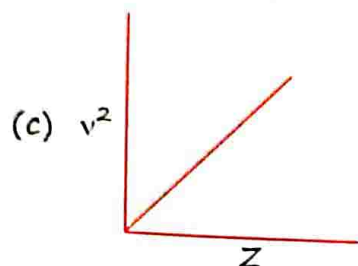
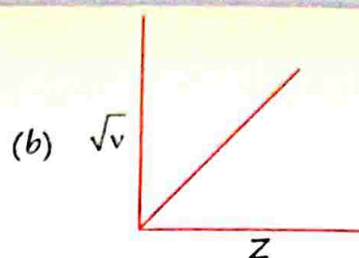
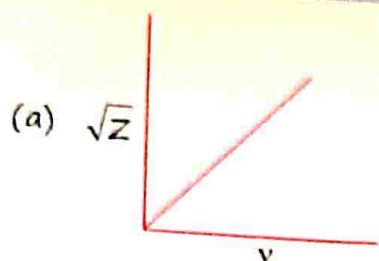
Sol. (c)

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

(Given:  $\nu$  = frequency of X-ray emitted; Z = atomic number)

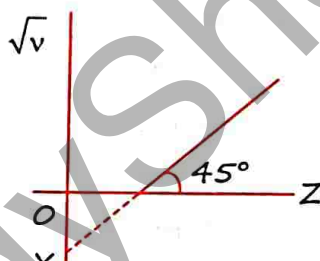
[8 April, 2023 (Shift-II)]





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

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) 60 Hz      (c) 50 Hz      (d) None

**Sol. (c)**

|                                                             |                                                                                                       |                                                                                            |                                |
|-------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|--------------------------------|
| $\sqrt{v} = a(z-b)$<br>$\sqrt{v} = az - ab$<br>$y = mx + c$ | $\text{Slope (m)} = a = \tan 45^\circ = 1$<br>$-ab = -1$<br>$-1 \cdot b = -1$<br>$\text{then } b = 1$ | $a = 1 \text{ \& } b = 1$<br>$\sqrt{v} = a(z-b)$<br>$\sqrt{v} = 1(z-1)$<br>$= 51 - 1 = 50$ | $v = (50)^2 = 2500 \text{ Hz}$ |
|-------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|--------------------------------|

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)  $\text{NO}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{SnO}_2$  (b)  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}$ ,  $\text{SnO}$ ,  $\text{PbO}$   
(c)  $\text{Cr}_2\text{O}_3$ ,  $\text{BeO}$ ,  $\text{SnO}$ ,  $\text{SnO}_2$  (d)  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{PbO}_2$

Sol. (c) and (d)

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als  
**CHEMISTRY** 



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)  | (i)  |
| (b) (iii) | (iv)  | (i)   | (ii) |
| (c) (iv)  | (iii) | (ii)  | (i)  |
| (d) (i)   | (ii)  | (iii) | (iv) |

Sol. (a)

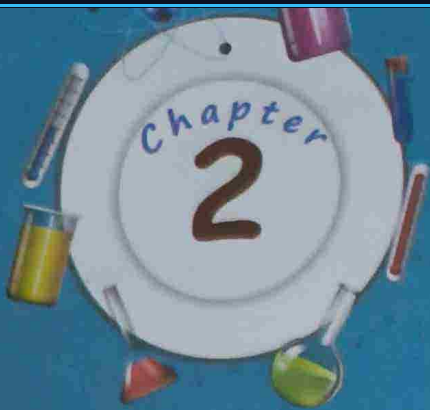
72. Which of the following oxide is amphoteric in nature?

[NEET 2020-Covid]

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

Sol. (d)





# Chemical Bonding and Molecular Structure

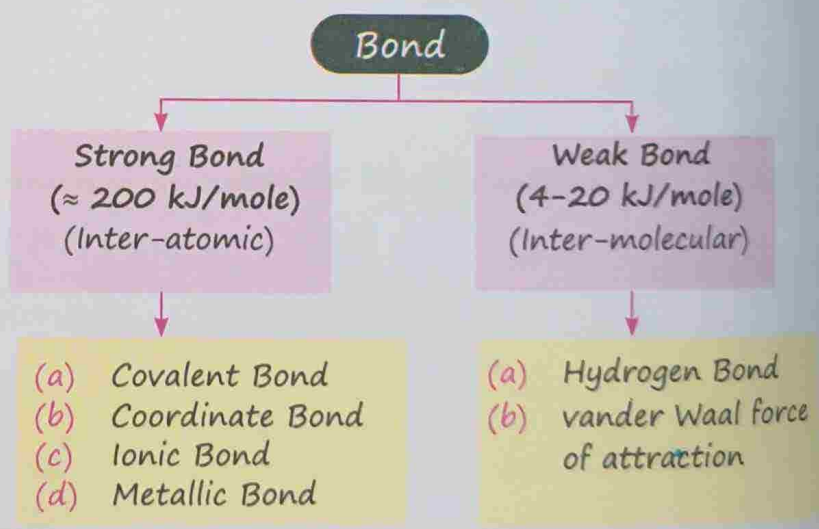
JEE Main & NEET

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**  $\equiv$  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**  $\rightarrow$  Exothermic Process



## Reason for Bond Formation

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

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# 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     | ·Li | ·Be· | ·B· | ·C· | ·N· | ·O· | ·F· | ·Ne· |

Lewis Symbol of Cl → ·Cl·  
 Lewis Symbol of S → ·S·

Lewis Symbol of P → ·P·  
 Lewis Symbol of Xe → ·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.

$$\text{Na} \cdot + \cdot \ddot{\text{Cl}}: \Rightarrow \text{Na}^{\oplus} : \ddot{\text{Cl}}:^{\ominus}$$

**Ionic bond**

$$\text{Na} : 1s^2 2s^2 2p^6 3s^1$$

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

$$\text{Cl} : 1s^2 2s^2 2p^6 3s^2 3p^5$$

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

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

**Covalent bond**

$$\text{F} : 1s^2 2s^2 2p^5$$

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.

$$\text{H}_2 \quad \text{H} \cdot \text{---} \cdot \text{H}$$

- NBE = Zero
- LP = Zero
- BP = 1

$$\text{O}_2 \quad :\ddot{\text{O}}::\ddot{\text{O}}:$$

- NBE = 8
- LP = 4
- BP = 2

$$\text{N}_2 \quad \text{:}\ddot{\text{N}}::\equiv::\ddot{\text{N}}\text{:}$$

- LP = 2
- BP = 3
- NBE = 4

- Non-bonding Electrons [NBE]
- Lone Pair [LP]
- Bond Pair [BP]



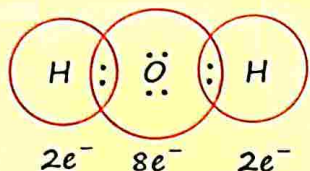
## Selection of Central Atom in a Molecule

### Central Atom

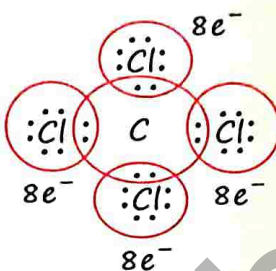
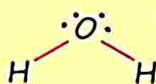
Less in number

Least electronegative

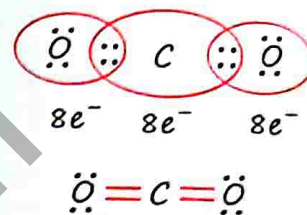
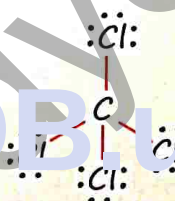
Tendency to form maximum number of bonds



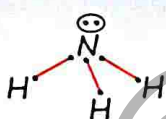
H atoms attain a duplet of electrons and O attain the octet



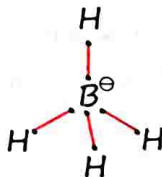
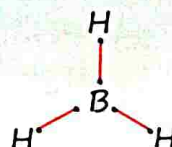
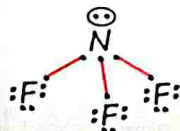
Each of the four Cl atoms along with the C atom attains octet of electrons



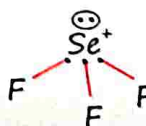
If two atoms share two pairs of electrons, the covalent bond between them is called a double bond.



We remove 1e<sup>-</sup> from nitrogen atom to get N<sup>+</sup>, So N<sup>+</sup> has 4e<sup>-</sup> in valence shell.



We add 1e<sup>-</sup> to boron atom to get B<sup>-</sup>.

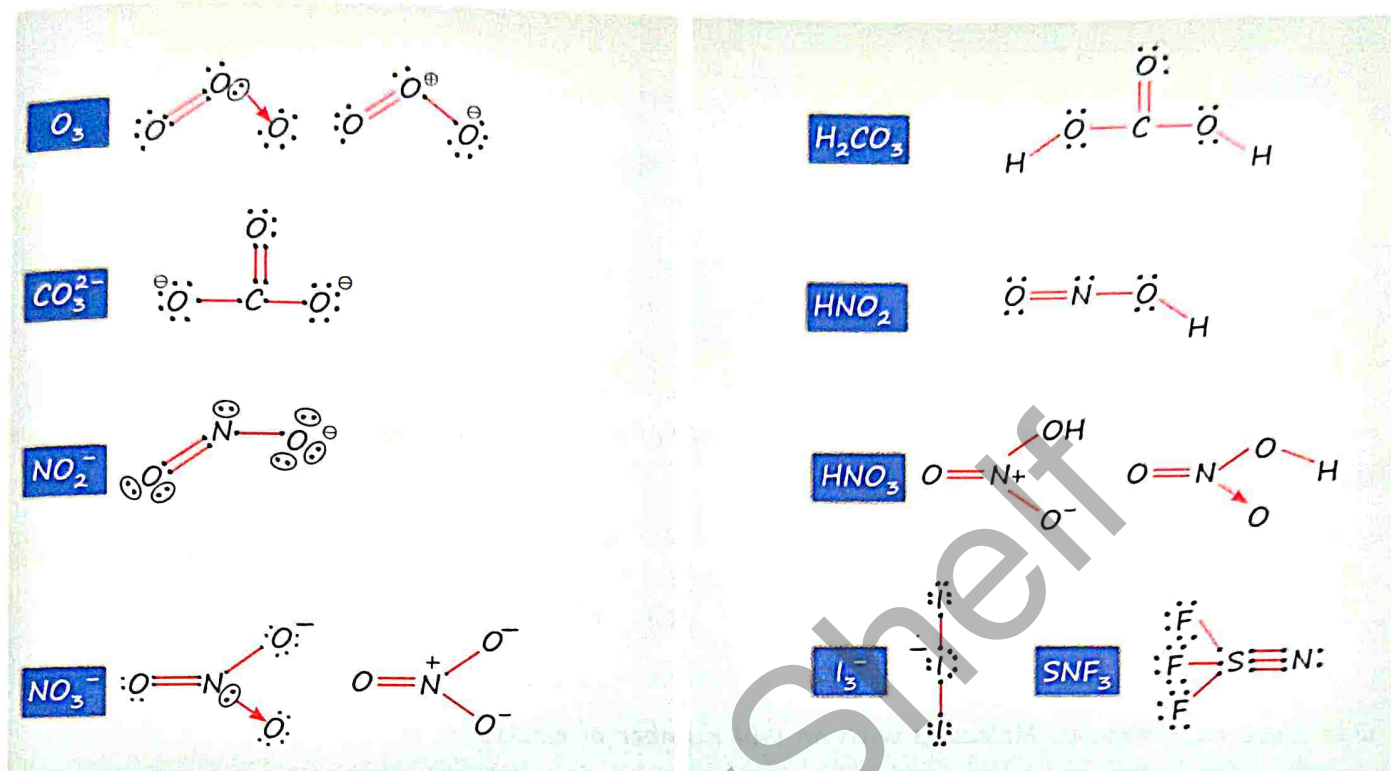


### Note

F & H can never act as central atom.

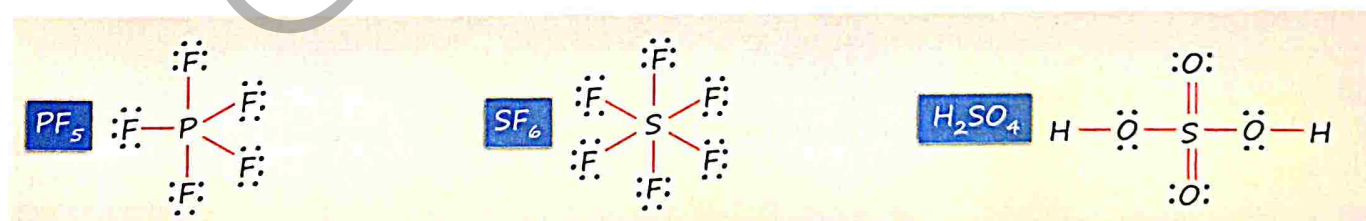
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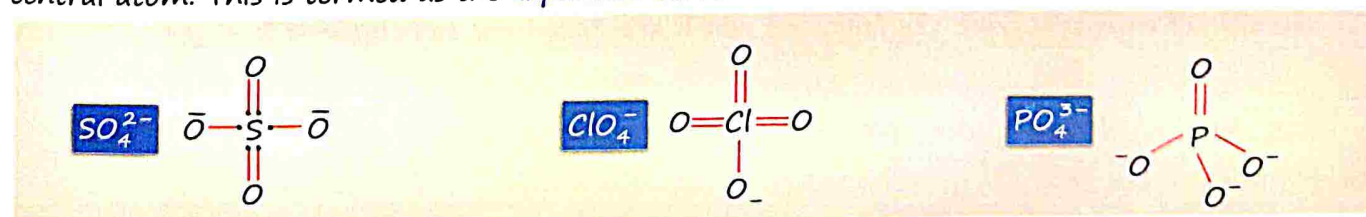


## Limitations of Octet Rule

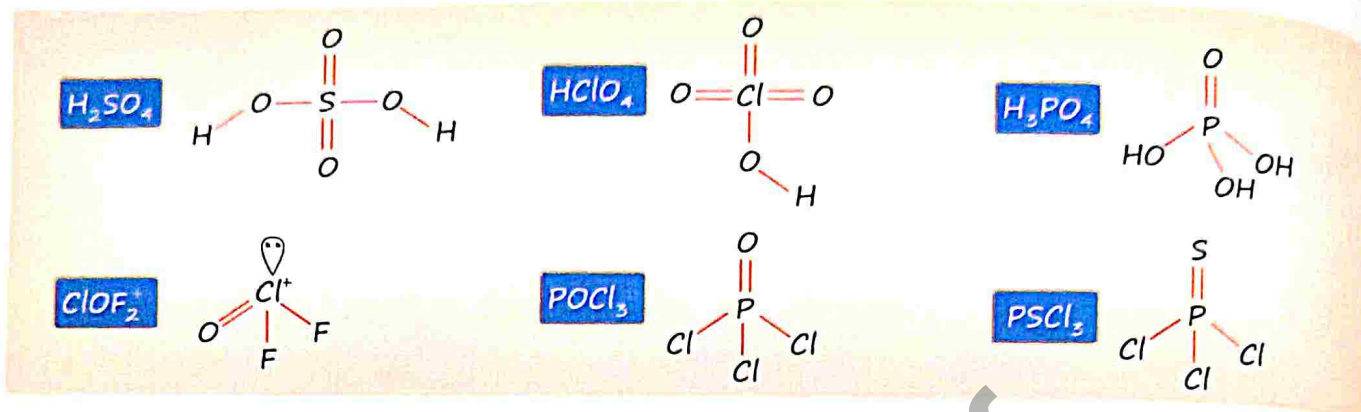
- It applies mainly to 2<sup>nd</sup> period elements.
  - 2<sup>nd</sup> Period elements [B, C, N, O, F]  $\rightarrow$  s + p subshell in valence shell  
 $\rightarrow$  maximum no. of electrons = 2 + 6 = 8
- Expanded or Super or Hypervalent Octet: Elements in and beyond the 3<sup>rd</sup> period of periodic table have d orbitals for bonding.
  - 3<sup>rd</sup> Period elements [Al, Si, P, S, Cl]  $\rightarrow$  s + p + d subshell in valence shell  
 $\rightarrow$  maximum no. of electrons = 2 + 6 + 10 = 18



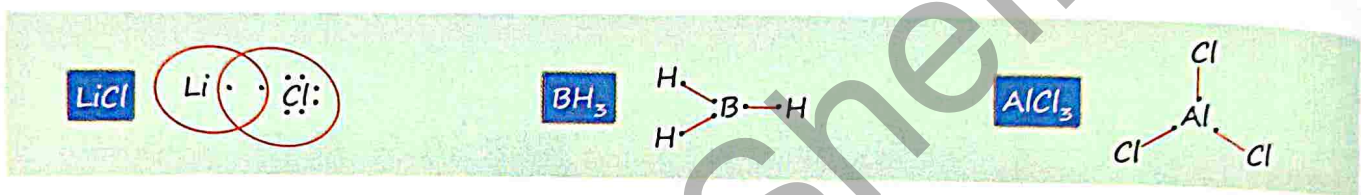
- In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the **expanded octet**.



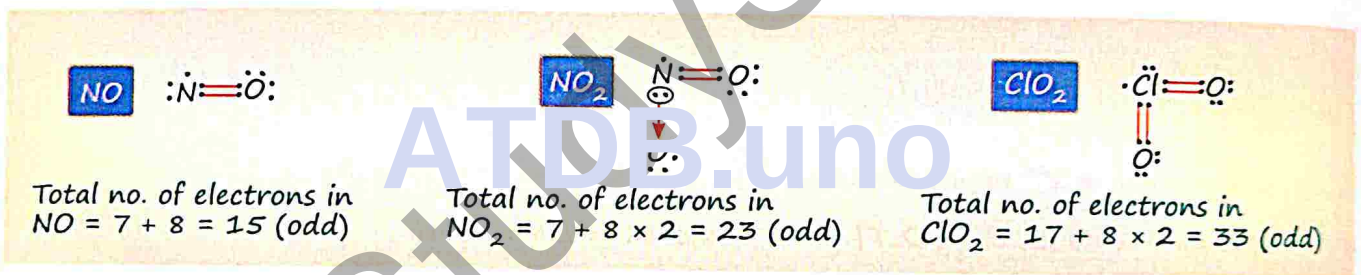




3. **Incomplete Octet:** In some compounds, the number of electrons surrounding the central atom is less than eight.

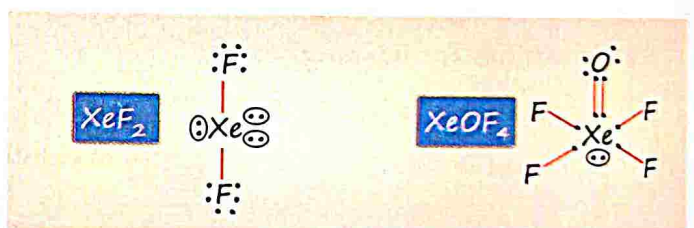


4. **Odd Electron Molecules:** Molecules with an odd number of electrons



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  $\text{XeF}_2$ ,  $\text{KrF}_2$ ,  $\text{XeOF}_4$  etc.



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)  $\text{NO}_2$  (b)  $\text{ICl}_4^-$  (c)  $\text{BrF}_3$  (d)  $\text{ClO}_2$  (e)  $\text{NO}_2^+$  (f)  $\text{NO}$

Sol. [3]  $\text{ICl}_4^-$ ,  $\text{BrF}_3$  and  $\text{NO}_2^+$  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)]

$\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{BF}_3$ ,  $\text{CH}_4$ ,  $\text{SiF}_4$ ,  $\text{ClO}_2$ ,  $\text{PCl}_5$ ,  $\text{BeF}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CHCl}_3$ ,  $\text{CBr}_4$

Sol. [6]  $\text{NO}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{BF}_3$ ,  $\text{ClO}_2$ ,  $\text{PCl}_5$ ,  $\text{BeF}_2$



3. Which of the following pair of molecules contain odd electron molecule and an expanded octet molecule?

- (a)  $\text{BCl}_3$  and  $\text{SF}_6$  (b)  $\text{NO}$  and  $\text{H}_2\text{SO}_4$  (c)  $\text{SF}_6$  and  $\text{H}_2\text{SO}_4$  (d)  $\text{BCl}_3$  and  $\text{NO}$

[29 July, 2022 (Shift-I)]

Sol. (b)

$\text{BCl}_3$  - electron deficient molecule

$\text{SF}_6$  - expanded octet molecule

$\text{NO}$  - odd electron containing molecule

$\text{H}_2\text{SO}_4$  - 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:  $\text{NH}_3$ ,  $\text{AlCl}_3$ ,  $\text{BeCl}_2$ ,  $\text{CCl}_4$ ,  $\text{PCl}_5$

[NEET 2023]

- (a) 1 (b) 3 (c) 2 (d) 4

Sol. (b)  $\text{AlCl}_3$ ,  $\text{BeCl}_2$ ,  $\text{PCl}_5$

5. Which of the following species contains equal number of  $\sigma$  and  $\pi$ -bonds?

[NEET 2015 Re]

- (a)  $(\text{CN})_2$  (b)  $(\text{CH})_2(\text{CN})_2$  (c)  $\text{HCO}_3^-$  (d)  $\text{XeO}_4$

Sol. (d)

6. Which one of the following molecules contains no  $\pi$  bond?

[NEET 2013]

- (a)  $\text{SO}_2$  (b)  $\text{NO}_2$  (c)  $\text{CO}_2$  (d)  $\text{H}_2\text{O}$

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 molecule.

$V$  = Total number of valence electrons in the free atom

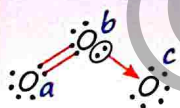
$$FC = V - N - \frac{B}{2}$$

$N$  = Number of non-bonding electrons

$B$  = Number of bonding electrons

|   | FC   |
|---|------|
| a | zero |
| b | +1   |
| c | -1   |

$\text{O}_3$



FC on "a"

$$\begin{aligned} V &= 6 \\ N &= 4 \\ B &= 4 \end{aligned} \rightarrow FC = 6 - 4 - \frac{4}{2} = 0$$

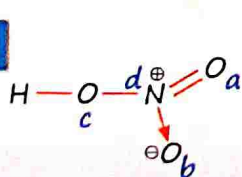
FC on "b"

$$\begin{aligned} V &= 6 \\ N &= 2 \\ B &= 6 \end{aligned} \rightarrow FC = 6 - 2 - \frac{6}{2} = +1$$

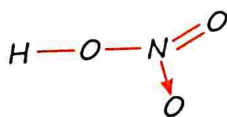
FC on "c"

$$\begin{aligned} V &= 6 \\ N &= 6 \\ B &= 2 \end{aligned} \rightarrow FC = 6 - 6 - \frac{2}{2} = -1$$

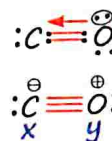
$\text{HNO}_3$



$$a = 0, b = -1, c = 0, d = +1$$



$\text{CO}$



$$\begin{aligned} x &= -1 \\ y &= +1 \end{aligned}$$



## OP\* Points

|                         |                                                                             |                                     |                                     |
|-------------------------|-----------------------------------------------------------------------------|-------------------------------------|-------------------------------------|
| Formal charge on Oxygen | FC = 0                                                                      | FC = -1                             | FC = +1                             |
|                         | $\text{:}\ddot{\text{O}}\text{:} \quad \text{---}\ddot{\text{O}}\text{---}$ | $\text{:}\ddot{\text{O}}\text{:}^-$ | $\text{:}\ddot{\text{O}}\text{:}^+$ |

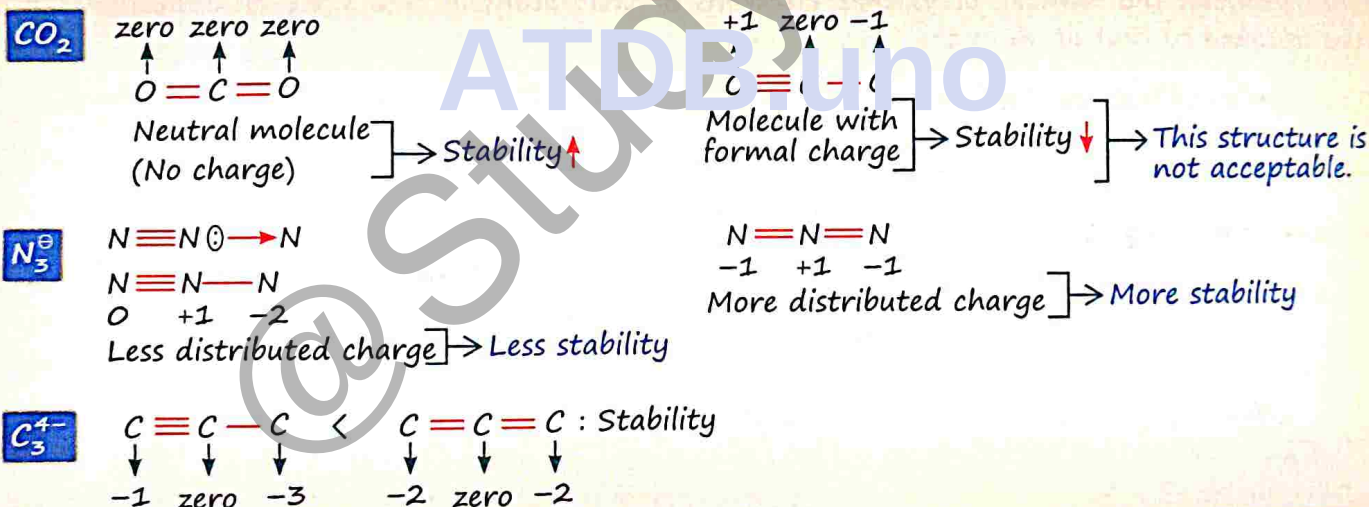
  

|                           |                                                                                                                |                                                                               |                                          |                                                                     |
|---------------------------|----------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|------------------------------------------|---------------------------------------------------------------------|
| Formal charge on Nitrogen | FC = 0                                                                                                         | FC = -1                                                                       | FC = -2                                  | FC = +1                                                             |
|                           | $\text{:}\text{N}\text{:} \quad \text{---}\ddot{\text{N}}\text{---} \quad \text{---}\ddot{\text{N}}\text{---}$ | $\text{:}\ddot{\text{N}}\text{:}^- \quad \text{---}\ddot{\text{N}}\text{:}^-$ | $\text{---}\ddot{\text{N}}\text{:}^{2-}$ | $\text{---}\text{N}^+\text{:} \quad \text{---}\text{N}^+\text{---}$ |

|                        |                                |                                  |                             |
|------------------------|--------------------------------|----------------------------------|-----------------------------|
| Formal charge on Boron | FC = 0                         | FC = -1                          | FC = +1                     |
|                        | $\text{---}\text{B}\text{---}$ | $\text{---}\text{B}^-\text{---}$ | $\text{H---B}^+\text{---H}$ |

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



## NATURE, SHAPE & PHASE OF ATOMIC ORBITAL



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

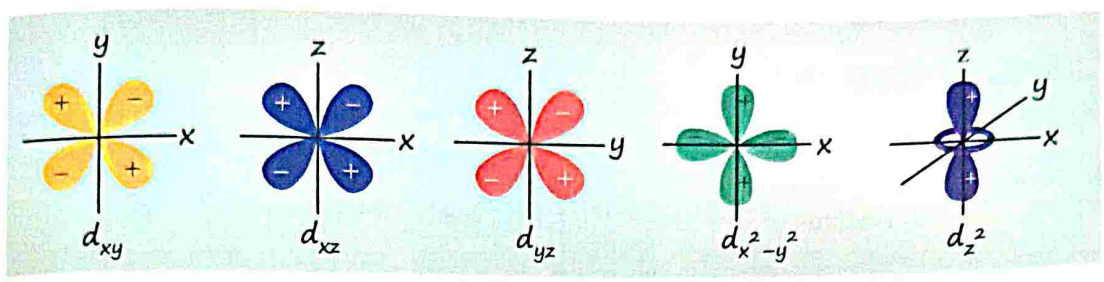
x axis



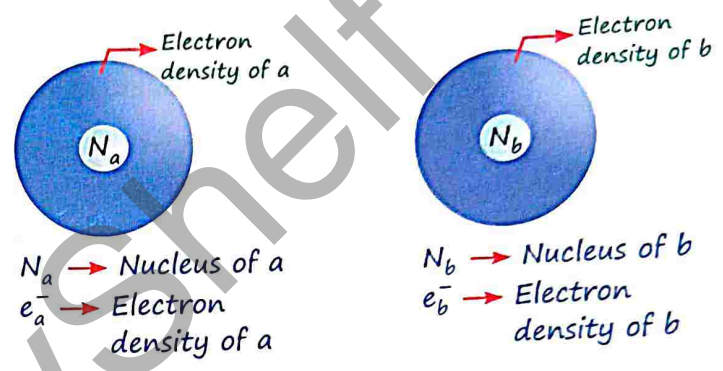
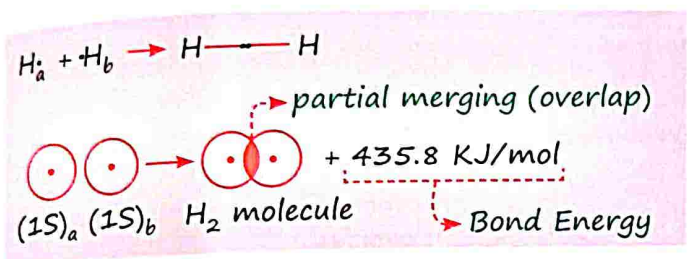
- ❑ p orbital (2 lobes)
- ❑ Directional nature
- ❑ p<sub>x</sub>, p<sub>y</sub>, p<sub>z</sub>



# d-Orbital

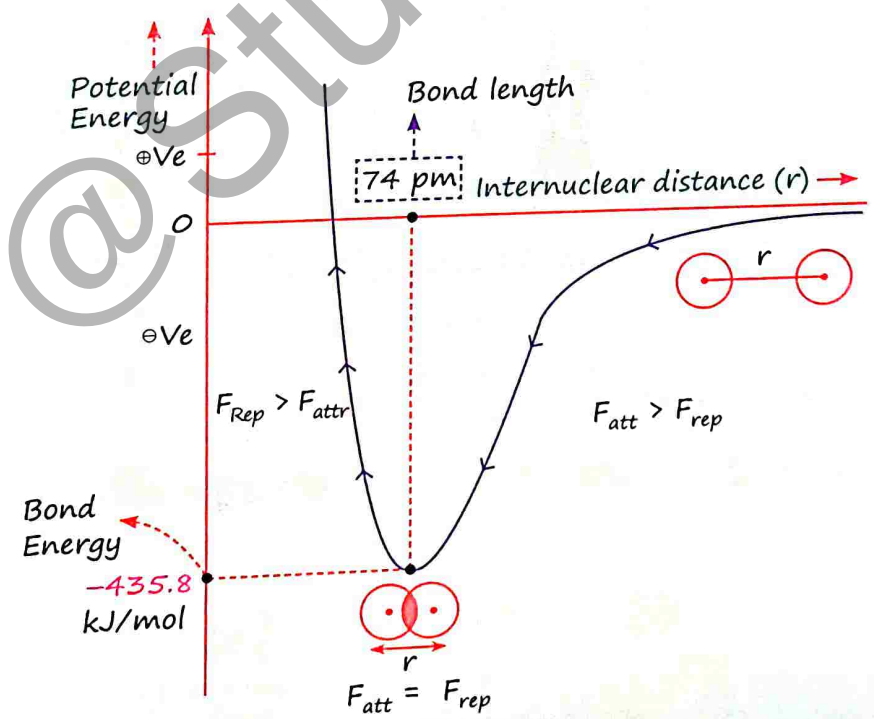


# VALENCE BOND THEORY



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

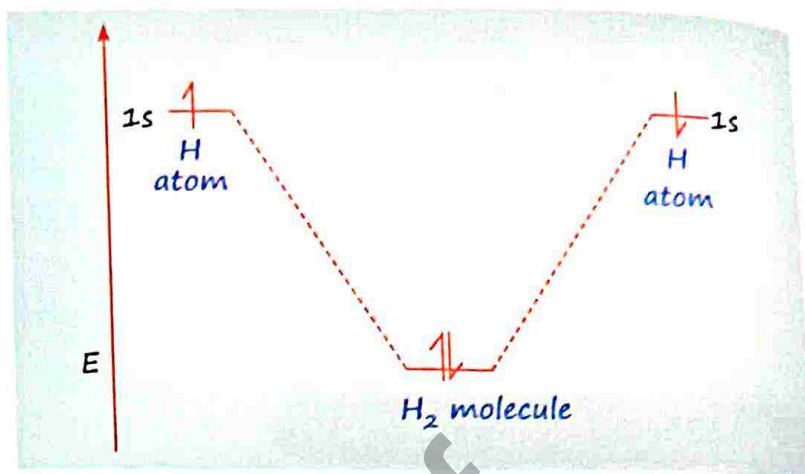
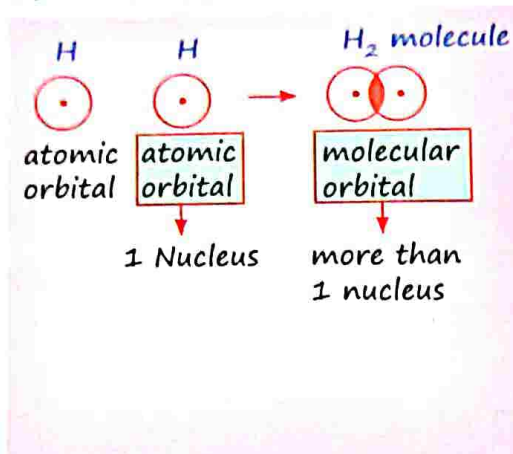
Force of repulsion: (i)  $(e^-)_a - (e^-)_b$   
(ii)  $(N)_a - (N)_b$



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.

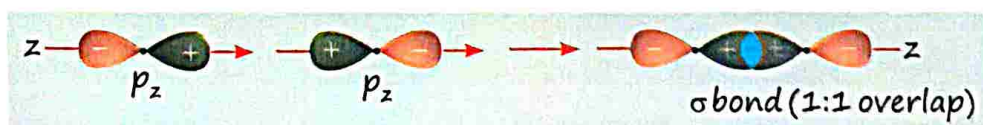


❑ Orbitals which are undergoing overlapping must have one electron with opposite spin for formation of covalent bond.

| Positive Overlap                                                                                                         | Negative Overlap                                                                                                         | Zero Overlap                                                                                                                                                             |
|--------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Same phase (sign) Overlap<br>+ +    - -                                                                                  | Opposite sign Overlap + -                                                                                                | i. No Overlap between 2 orbitals<br>ii. Both positive & negative overlap                                                                                                 |
| <p>Diagrams showing positive overlap: p<sub>z</sub>-p<sub>z</sub>, p<sub>z</sub>-s, and p<sub>x</sub>-p<sub>x</sub>.</p> | <p>Diagrams showing negative overlap: p<sub>z</sub>-p<sub>z</sub>, p<sub>z</sub>-s, and p<sub>x</sub>-p<sub>x</sub>.</p> | <p>Diagrams showing zero overlap: p<sub>y</sub>-s (positive overlap), p<sub>y</sub>-p<sub>x</sub> (negative overlap), and p<sub>y</sub>-p<sub>y</sub> (No, overlap).</p> |

## Sigma Bond

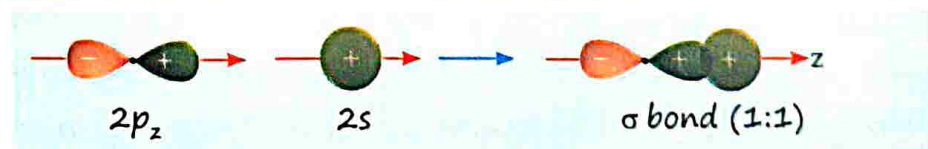
Overlapping along the molecular axis/Head on overlapping



i. s-s overlapping



ii. s-p overlapping





### iii. p-p overlapping



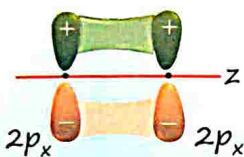
□ Extent of overlapping  $\uparrow \rightarrow$  Strength of bond  $\uparrow$   
 Extent of overlapping :  $2s - 2s < 2s - 2p < 2p - 2p$   
 Strength:  $2s-2s < 2s-2p < 2p-2p$

## Pi Bond

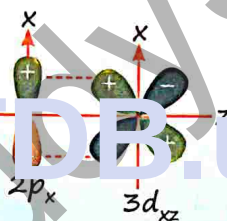
Overlapping  $\perp$  to molecular axis (Side ways overlapping)

Strength :  $\sigma \text{ bond} > \pi \text{ bond}$

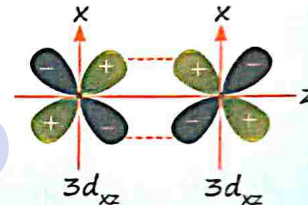
(i)  $p\pi-p\pi$  bond



(ii)  $p\pi-d\pi$  bond



(iii)  $d\pi-d\pi$  bond



□ Extent of overlapping  $\uparrow : (n_1 + n_2) \downarrow$   
 Extent of overlapping :  $2p-2p > 2p-3d > 3d-3d$   
 $n_1 + n_2 : (2 + 2) < (2 + 3) < (3 + 3)$   
 Strength of  $\pi$  bond :  $2p-2p > 2p-3d > 3d-3d$

## Strength of Bond

(i) When  $n_1 + n_2$  is same:  $2s-2s < 2s-2p < 2p-2p$  :  $\sigma$  bond strength

$(n_1 + n_2) \rightarrow (2 + 2) \quad (2 + 2) \quad (2 + 2)$

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

$1s - 1s > 2s - 2s > 3s - 3s$  :  $\sigma$  bond strength

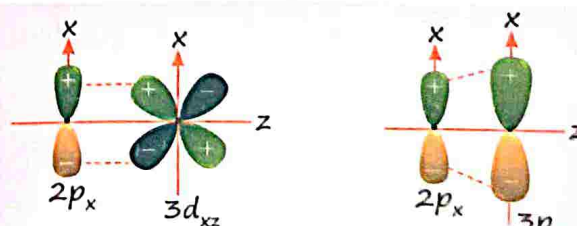
$(n_1 + n_2) \rightarrow (1 + 1) \quad (2 + 2) \quad (3 + 3)$

$2p - 2p > 2p - 3d$  :  $\pi$  bond strength

$(n_1 + n_2) \rightarrow (2 + 2) \quad (2 + 3)$

$2p - 3p < 2p - 3d$  :  $\pi$  bond strength

$(n_1 + n_2) \rightarrow (2 + 3) \quad (2 + 3)$

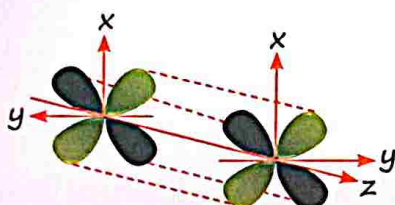


Better overlapping in  $2p-3d$  w.r.t  $2p-3p$

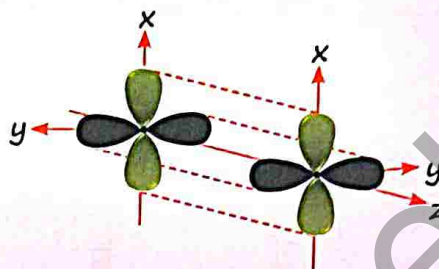
## Bonding in d-Orbitals

Delta Bond  $\rightarrow$  4 : 4 overlap

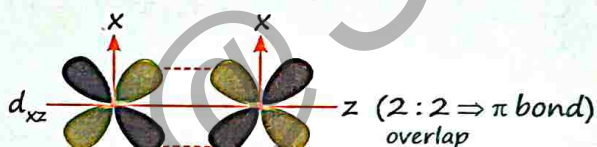
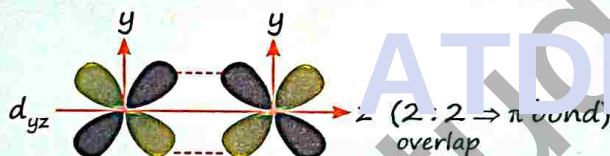
1.  $d_{xy}$  and  $d_{xy}$



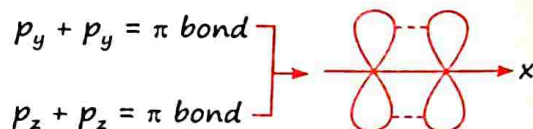
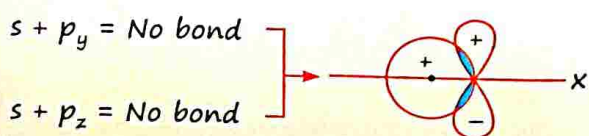
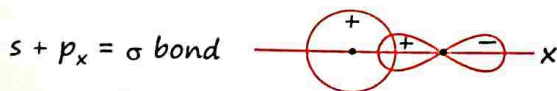
2.  $d_{x^2-y^2}$  and  $d_{x^2-y^2}$



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



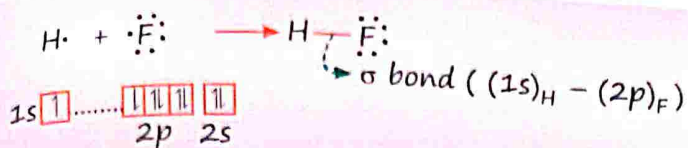
| Bond<br>Orbital | $\sigma$ | $\pi$ | $\delta$ |
|-----------------|----------|-------|----------|
| s               | ✓        | ✗     | ✗        |
| p               | ✓        | ✓     | ✗        |
| d               | ✓        | ✓     | ✓        |



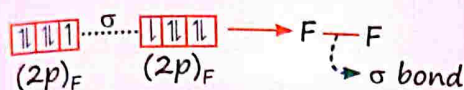
❑ Overlapping of orbitals when x axis is internuclear axis.



## HF Molecule



## F<sub>2</sub> Molecule



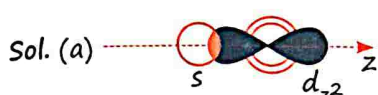
7. Draw the type of overlaps between given orbitals, Z is internuclear axis.

(a) s and d<sub>z<sup>2</sup></sub>

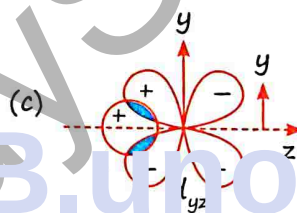
(b) s and d<sub>x<sup>2</sup>-y<sup>2</sup></sub>

(c) s and d<sub>yz</sub>

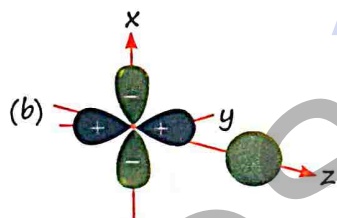
(d) p<sub>z</sub> and d<sub>z<sup>2</sup></sub>



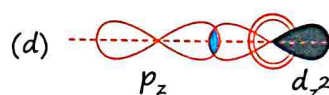
$\sigma \text{ bond}$



No bond



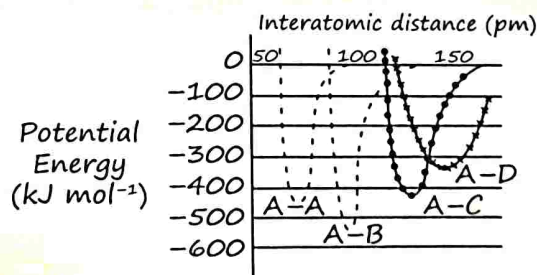
No bond



$\sigma \text{ bond}$

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

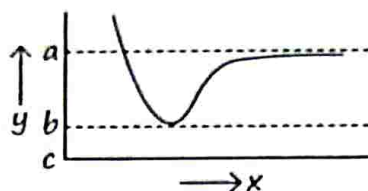
(b) A - D has the shortest bond length

(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-Contd.]



The bond energy of  $H_2$  is

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

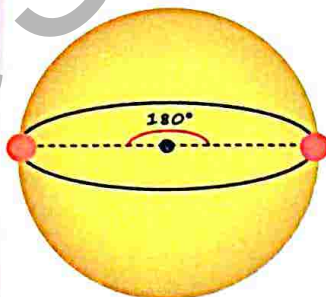
Sol. (d)

## VSEPR THEORY VALENCE SHELL ELECTRON PAIR REPULSION THEORY

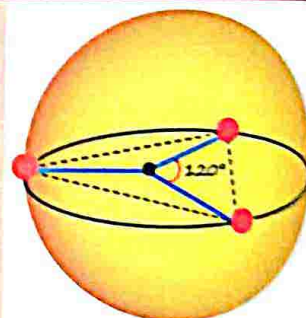
### Main Postulates

- ❑ 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.

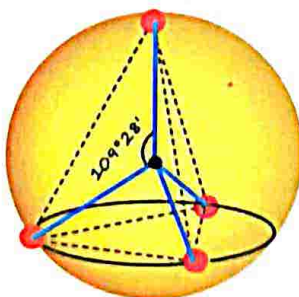
2 electron pairs are localised on spherical surface at maximum distance, when angle between them is  $180^\circ$ .



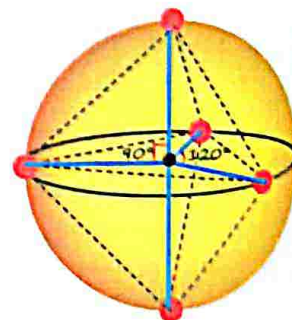
3 electron pairs are localised on spherical surface at maximum distance, when they are placed at corners of triangle.



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

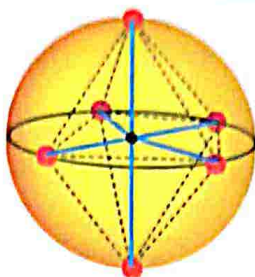


5 electron pairs are localised on spherical surface of central atom at maximum distance when 3 are placed at equatorial position [at angle  $120^\circ$ ] and 2 are placed at axial position [at angle  $90^\circ$ ]

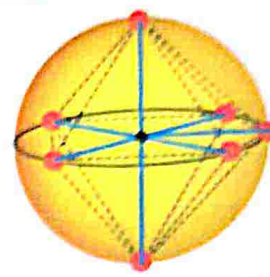




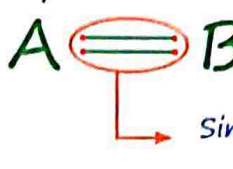
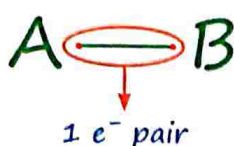
6 electron pairs are localised on spherical surface at maximum distance, when they are placed at corners of octahedron.



7 electron pairs at maximum distance is shown in figure



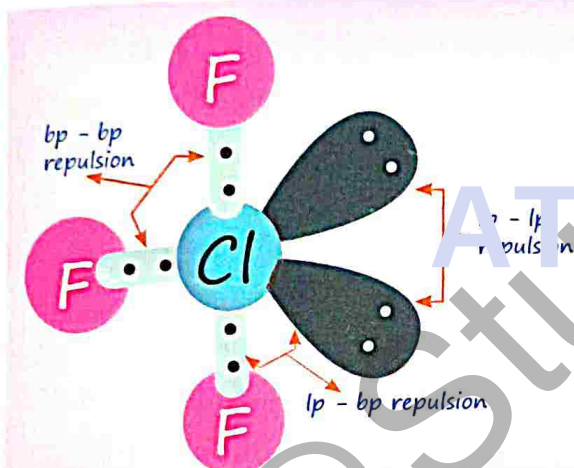
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.



- 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, but bond 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.

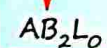
- We can represent any molecule in  $AB_xL_y$  form where, A  $\rightarrow$  Central atom, B  $\rightarrow$  Side atom, L  $\rightarrow$  Lone pair
- Number of valence shell electron pair decides the geometry of a molecule.

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

## AB<sub>2</sub> Type Molecule

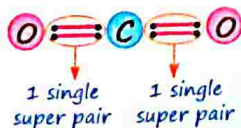


- Valence shell electron pair = 2
- Geometry  $\rightarrow$  Linear
- Bond angle  $\rightarrow 180^\circ$



$$x = 2$$

$$y = 0$$

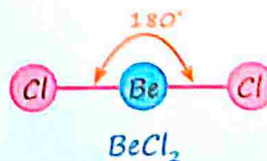


- Valence shell electron pair = 2
- Geometry  $\rightarrow$  Linear
- Bond angle  $\rightarrow 180^\circ$

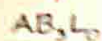


$$x = 2$$

$$y = 0$$

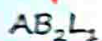
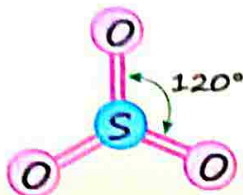


## AB<sub>3</sub> Type Molecule



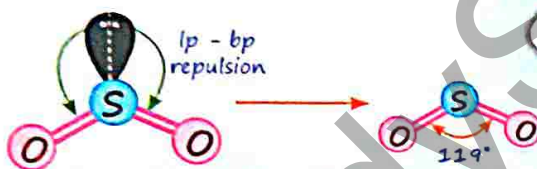
$x = 3$   
 $y = 0$

- Valence shell electron pair =  $3 + 0 = 3$
- Geometry → Trigonal planar
- Bond angle →  $120^\circ$



$x = 2$   
 $y = 1$

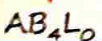
- Valence shell electron pair =  $2 + 1 = 3$
- Due to lp - bp repulsion, bond angle reduces from  $120^\circ$  to  $119^\circ$



Geometry → Trigonal planar      Shape → Bent

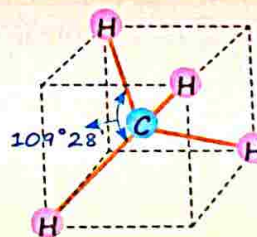
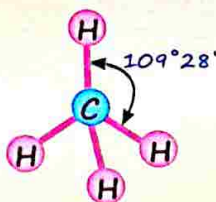
Structure with lone pair → Geometry  
Structure without lone pair → Shape

## AB<sub>4</sub> Type Molecule

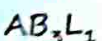


$x = 4$   
 $y = 0$

- Valence shell electron pair =  $4 + 0 = 4$
- Geometry → Tetrahedral
- Bond angle →  $109^\circ 28'$

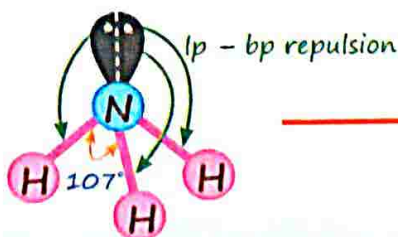


C → At body centre of cube  
H → At alternate corners of cube

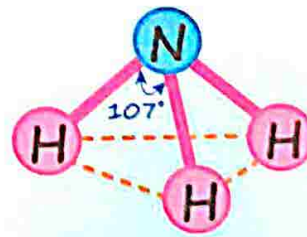


$x = 3$   
 $y = 1$

- Valence shell electron pair =  $3 + 1 = 4$
- Due to lp - bp repulsion, bond angle reduces from ideal tetrahedral angle  $109^\circ 28'$  to  $107^\circ$



Geometry — Tetrahedral

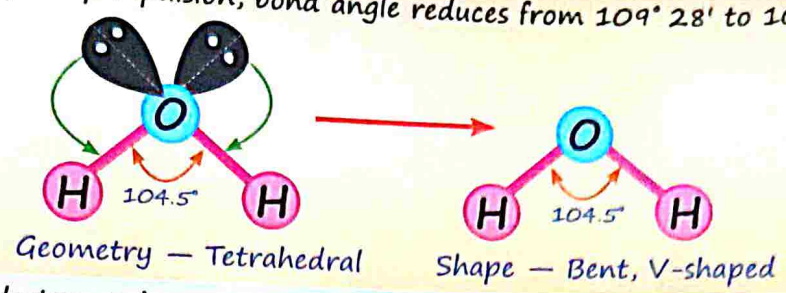


Shape — Pyramidal

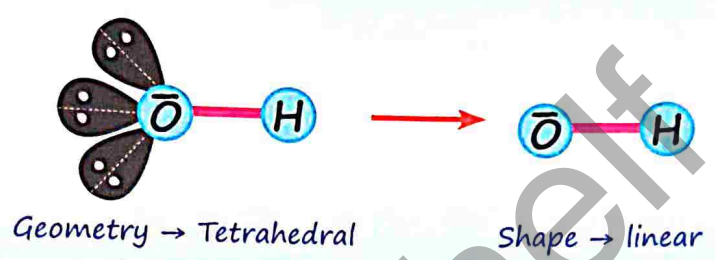




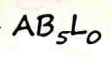
- Valence shell electron pair = 2 + 2 = 4
- Due to more lp - bp repulsion, bond angle reduces from 109° 28' to 104.5°



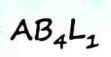
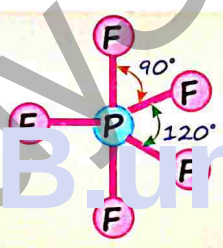
- Valence shell electron pair = 1 + 3 = 4



### AB<sub>5</sub> Type Molecule



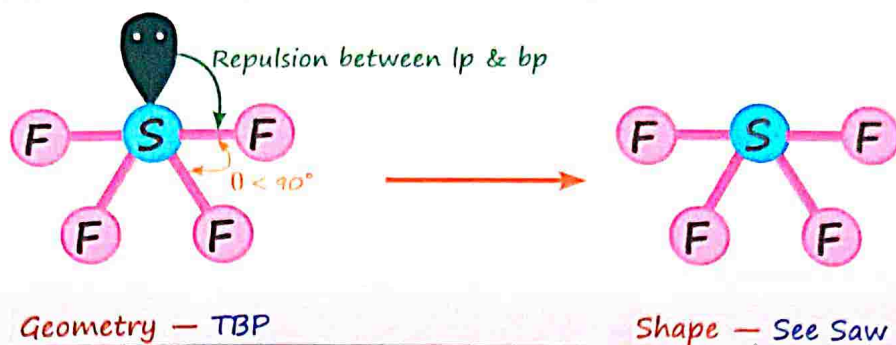
- Valence shell electron pair = 5 + 0 = 5
- Geometry → Trigonal bipyramidal
- θ → 90° and 120°



- Valence shell electron pair = 4 + 1 = 5

| Case-1<br>If lp is present at equatorial position                                                                                                                                                                                                                    | Case-2<br>If lp is present at axial position                                                                                                                                                                                                      |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>The diagram shows the equatorial lone pair in SF<sub>4</sub>. The sulfur atom is at the center, with four fluorine atoms and one lone pair. The lone pair is in an equatorial position, represented by two dots. The bond angles are labeled as 90° and 120°.</p> | <p>The diagram shows the axial lone pair in SF<sub>4</sub>. The sulfur atom is at the center, with four fluorine atoms and one lone pair. The lone pair is in an axial position, represented by two dots. The bond angles are labeled as 90°.</p> |
| □ 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.

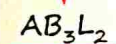


### Note

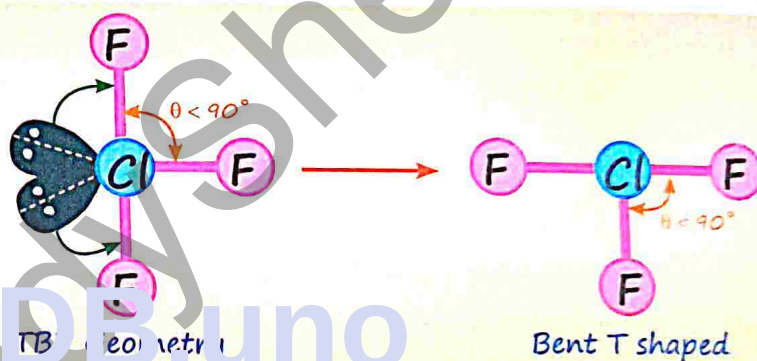
In TBP geometry due to less repulsion, more favorable position for lone pair is equatorial position.



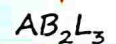
- Valence shell electron pair =  $3 + 2 = 5$



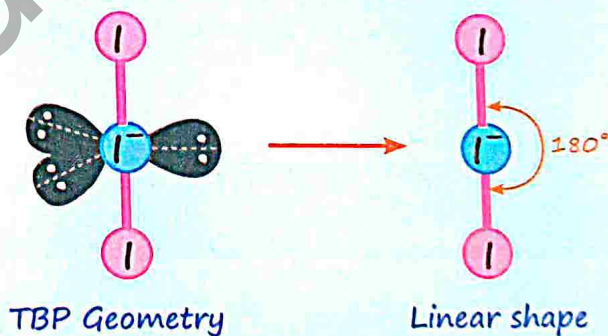
$x = 3$   
 $y = 2$



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



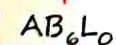
$x = 2$   
 $y = 3$



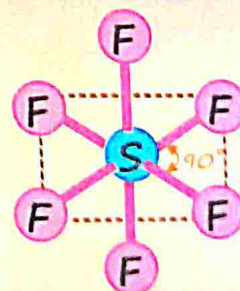
### $\text{AB}_6$ Type Molecule



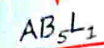
- Valence shell electron pair =  $6 + 0 = 6$
- Geometry  $\rightarrow$  Octahedral
- Bond angle  $\rightarrow 90^\circ$



$x = 6$   
 $y = 0$



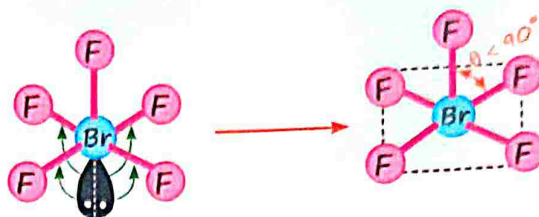




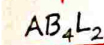
$x = 5$   
 $y = 1$

- Valence shell electron pair =  $5 + 1 = 6$
- All bond angles are less than  $90^\circ$

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

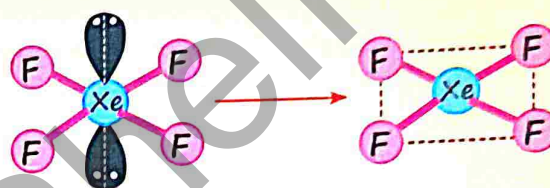


Geometry - Octahedral Shape  $\rightarrow$  Square Pyramidal



$x = 4$   
 $y = 2$

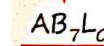
- Valence shell electron pair =  $4 + 2 = 6$
- Bond angle  $\rightarrow 90^\circ$



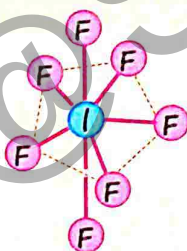
Geometry - octahedral

Shape - Square planar

### AB<sub>7</sub> Type Molecule



$x = 7$   
 $y = 0$



IF<sub>7</sub> [ $\theta = 72^\circ, 90^\circ$ ]  
 Pentagonal bipyramidal Geometry

10. In the structure of SF<sub>6</sub>, the lone pair of electrons on S is [27 June, 2022 (Shift-II)]
- Equatorial position and there are two lone pair - bond pair repulsions at  $90^\circ$ .
  - Equatorial position and there are three lone pair - bond pair repulsions at  $90^\circ$ .
  - Axial position and there are three lone pair - bond pair repulsion at  $90^\circ$ .
  - Axial position and there are two lone pair - bond pair repulsion at  $90^\circ$ .

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.                  | $\text{XeF}_4$ |
| B.             | Trigonal planar | II.                 | $\text{SF}_4$  |
| C.             | Square planar   | III.                | $\text{ClF}_3$ |
| D.             | See-saw         | IV.                 | $\text{BF}_3$  |

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

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

Sol. (b)

12. Match List-I with List-II.

| List-I (Compound) |                | List-II (Shape/geometry) |                    |
|-------------------|----------------|--------------------------|--------------------|
| A.                | $\text{NH}_3$  | I.                       | Trigonal Pyramidal |
| B.                | $\text{BrF}_5$ | II.                      | Square Planar      |
| C.                | $\text{XeF}_4$ | III.                     | Octahedral         |
| D.                | $\text{SF}_6$  | 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:

| List-I (molecules) |                | List-II (shape) |                      |
|--------------------|----------------|-----------------|----------------------|
| A.                 | $\text{NH}_3$  | I.              | square pyramidal     |
| B.                 | $\text{ClF}_3$ | II.             | trigonal bipyramidal |
| C.                 | $\text{PCl}_5$ | III.            | trigonal pyramidal   |
| D.                 | $\text{BrF}_5$ | 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)  $\text{XeF}_2$

(b)  $\text{ClF}_3$

(c)  $\text{IF}_5$

(d)  $\text{SF}_4$

Sol. (a)

15. Identify the incorrect statement related to  $\text{PCl}_5$  from the following: [NEET 2019]

(a) Three equatorial P-Cl bonds make an angle of  $120^\circ$  with each other

(b) Two axial P-Cl bonds make an angle of  $180^\circ$  with each other

(c) Axial P-Cl bonds are longer than equatorial P-Cl bonds

(d)  $\text{PCl}_5$  molecule is non-reactive

Sol. (d)



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16. Predict the correct order among the following:

[NEET 2016-I]

- Lone pair – bond pair > bond pair – bond pair > lone pair – lone pair
- Lone pair – lone pair > lone pair – bond pair > bond pair – bond pair
- Lone pair – lone pair > bond pair – bond pair > lone pair – bond pair
- 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]

- $\text{NO}_2^-$
- $\text{SO}_2$
- $\text{NO}_2^+$
- $\text{O}_3$

Sol. (c)

18. In  $\text{BrF}_3$  molecule, the lone pairs occupy equatorial positions to minimize:

[NEET 2004]

- Bond pair-bond pair repulsion only
- Lone pair-lone pair repulsion and lone pair-bond pair repulsion
- Lone pair-lone pair repulsion only
- Lone pair-bond pair repulsion only

Sol. (b)

19.  $\text{BCl}_3$  is a planar molecule whereas  $\text{NCl}_3$  is pyramidal because:

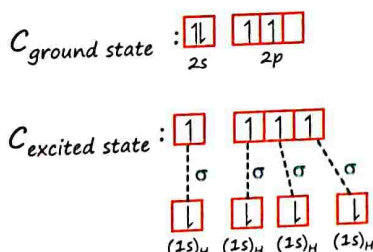
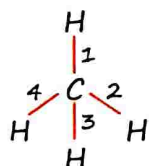
[NEET 1995]

- Nitrogen atom is smaller than boron atom
- $\text{BCl}_3$  has no lone pair but  $\text{NCl}_3$  has a lone pair of electrons
- B-Cl bond is more polar than N-Cl bond
- N-Cl bond is more covalent than B-Cl bond

Sol. (b)

## NEED OF NEW CONCEPT → (HYBRIDISATION)

### Bonding in $\text{CH}_4$ according to VBT



□ 2 different types of overlapping

→  $(2s)_C - (1s)_H$

→  $(2p)_C - (1s)_H$

□ 2 Different bond lengths.

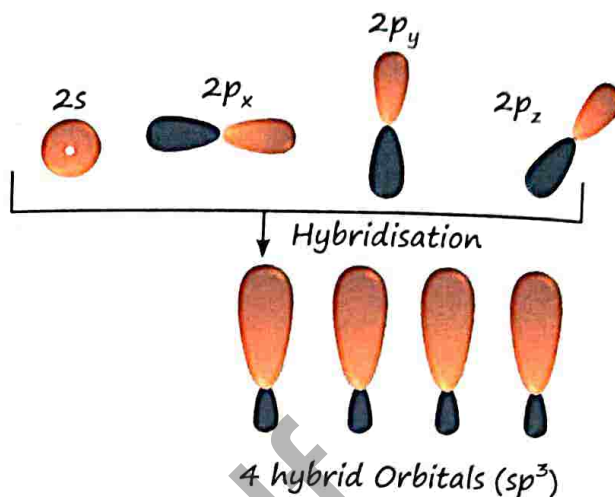
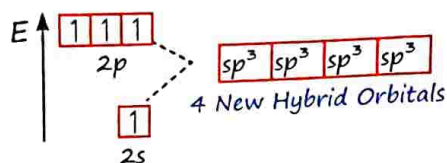
VBT predicts that the 3 bonds formed through s-p overlap would be the same and differ from the 4th bond formed through s-s overlap. This difference in bond types would result in unequal bond lengths which is not what is observed in methane.

**Experimental Fact** All C – H bonds are same in  $\text{CH}_4$ .

→ This fact can be explained by new theory ⇒ Hybridisation

## Hybridisation in $\text{CH}_4$

$\text{C}_{\text{excited state}}$  :  $\boxed{1} \boxed{1111}$   
 $2s \quad 2p$



4  $sp^3$  hybrid orbitals of carbon at  $109^\circ 28'$

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

- It is a hypothetical concept.
- Only those orbitals can take part in hybridisation which have comparable (almost equal) energies.
- The number of hybrid orbitals generated will be equal to the number of pure atomic orbitals taking part in hybridisation.
- All 3 type of orbitals (having a pair of electrons  $\boxed{1}$  or having a unpaired electron  $\boxed{1}$  or completely empty  $\boxed{}$ ) can take part in hybridisation.
- The hybrid orbital generated will be represented by

Bigger lobe will be used for bonding.

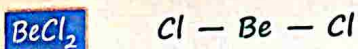


## Steric Number Rule

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

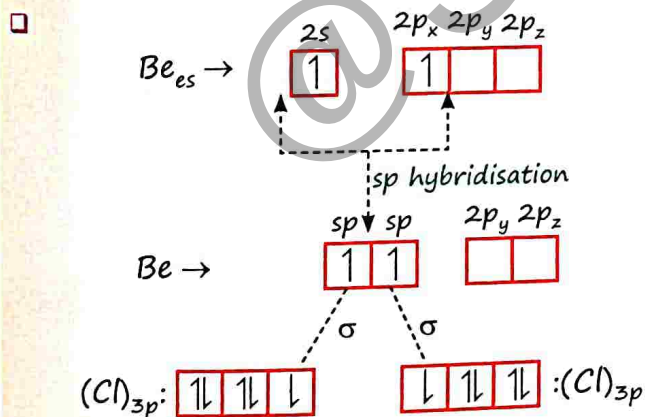
| SN | Geometry                | Hybridisation | Bond Angle                     |
|----|-------------------------|---------------|--------------------------------|
| 2  | Linear                  | $sp$          | $\theta = 180^\circ$           |
| 3  | Trigonal planar         | $sp^2$        | $\theta = 120^\circ$           |
| 4  | Tetrahedral             | $sp^3$        | $\theta = 109^\circ 28'$       |
| 5  | Trigonal bi-pyramidal   | $sp^3d$       | $\theta = 90^\circ, 120^\circ$ |
| 6  | Octahedral              | $sp^3d^2$     | $\theta = 90^\circ$            |
| 7  | Pentagonal bi-pyramidal | $sp^3d^3$     | $\theta = 90^\circ, 72^\circ$  |

## $sp$ Hybridisation



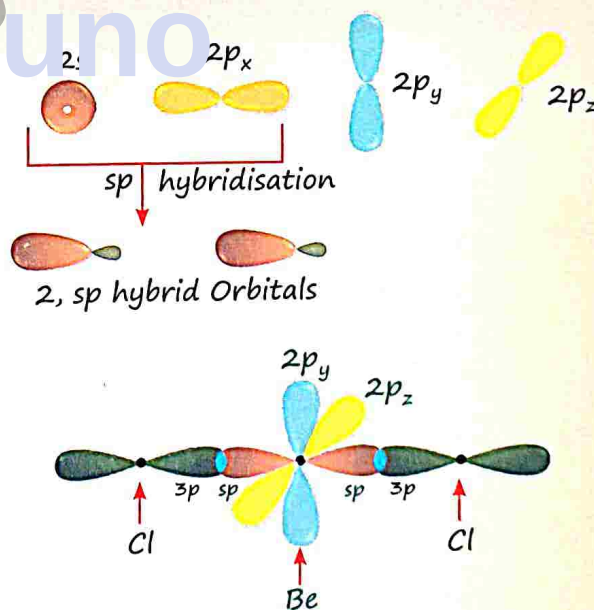
□  $SN = LP + SA = 0 + 2$

= 2 →  $sp$  hybridisation



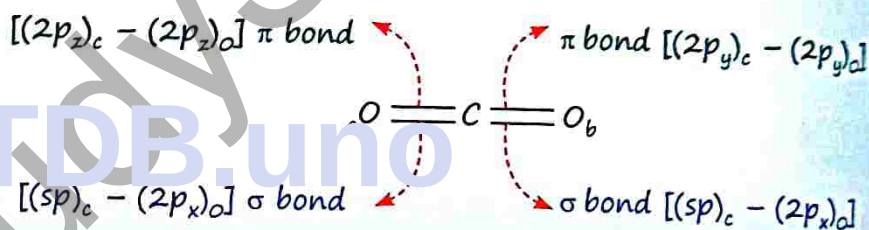
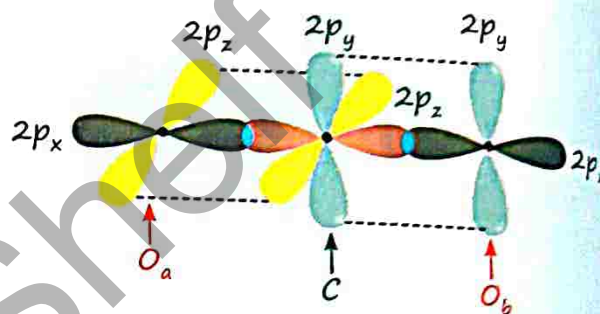
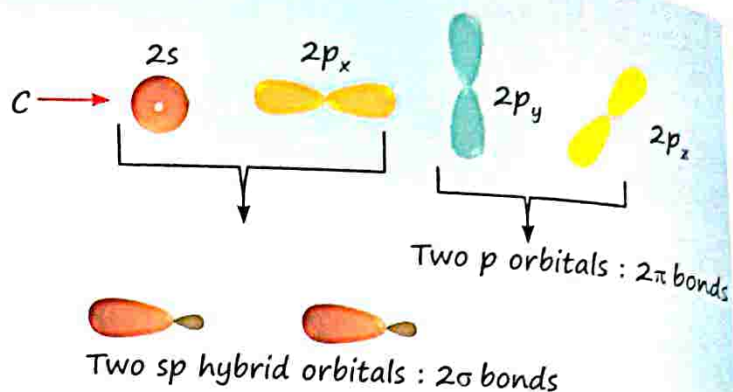
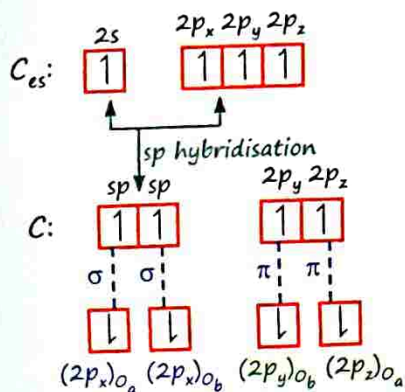
□ 2 Be — Cl  $\sigma$  bonds :  $(sp)_{Be} - (3p)_{Cl}$

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



# **CO<sub>2</sub>**      $O = C = O$

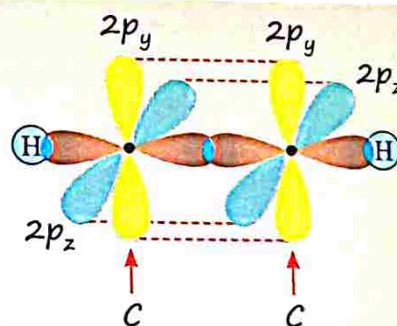
$\square$   $SN = LP + SA$   
 $= 0 + 2$   
 $= 2 \rightarrow sp \text{ hybridisation}$



## **C<sub>2</sub>H<sub>2</sub>**      $H - C \equiv C - H$

- $\square$  2 C-H  $\sigma$  bonds :  $(sp)_C - (1s)_H$
- $\square$  1 C-C  $\sigma$  bond :  $(sp)_C - (sp)_C$
- $\square$  2 C-C  $\pi$  bonds :  $(2p_y)_C - (2p_y)_C$  and  $(2p_z)_C - (2p_z)_C$

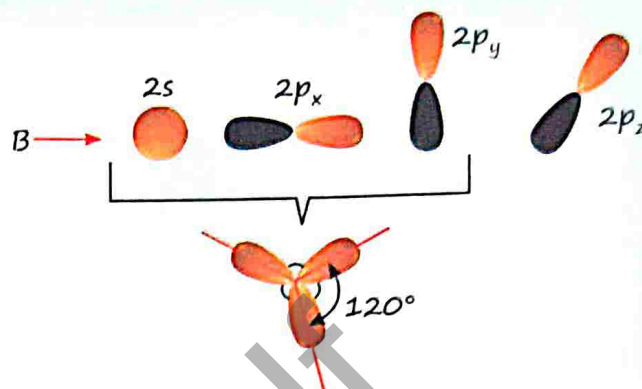
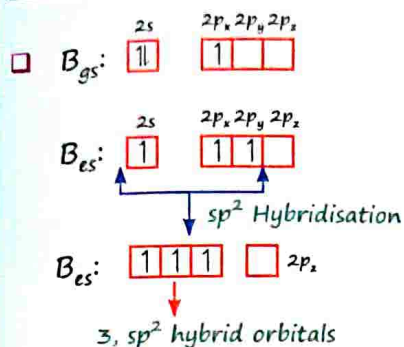
Molecular plane  $\rightarrow$   $H - C \equiv C - H$





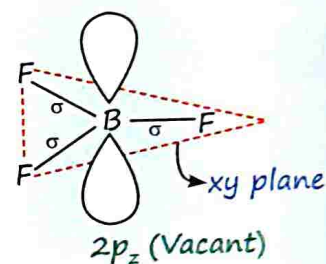
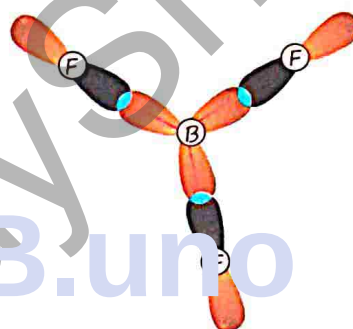
## $sp^2$ Hybridisation

### $BF_3$



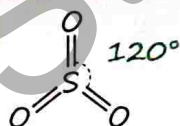
- 3  $sp^2$  hybrid orbitals are arranged at  $120^\circ$  before bonding.

- $F: \begin{array}{c} 2s \\ \boxed{\uparrow\downarrow} \end{array} \quad \begin{array}{c} 2p_x, 2p_y, 2p_z \\ \boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow} \end{array}$
- 3  $\sigma$  B - F bonds:  $(sp^2)_B - (2p_x)_F$
- $sp^2 \equiv s + p_x + p_y$



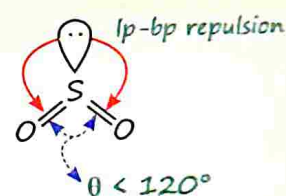
### $SO_3$

- $SN = 0 + 3 = 3$
- $hyb^n = sp^2$
- Shape = Trigonal planar



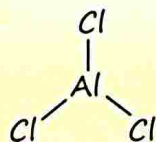
### $SO_2$

- $SN = 1 + 2 = 3$
- $sp^2$
- v shaped



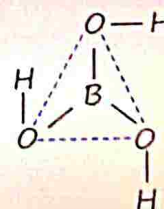
### $AlCl_3$

- $SN = 0 + 3 = 3$
- $sp^2$
- Trigonal planar

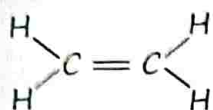


### $H_3BO_3$

- $SN = 0 + 3$
- $sp^2$
- Trigonal planar

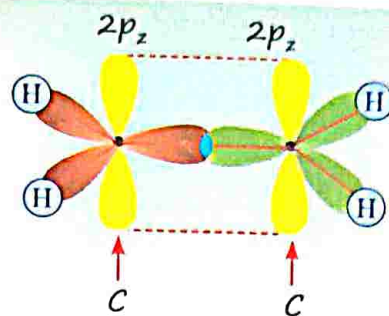
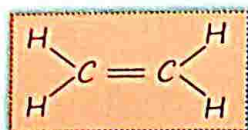


### $C_2H_4$



- $sp^2 \equiv s + p_x + p_y$
- 4 C-H  $\sigma$  bonds :  $(sp^2)_C - (1s)_H$
- 1 C-C  $\sigma$  bond :  $(sp^2)_C - (sp^2)_C$
- 1 C-C  $\pi$  bond :  $(2p)_C - (2p)_C$

Molecular plane  $\rightarrow$

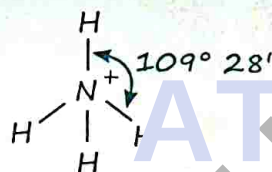


Max. no of atoms in a plane = 6

## $sp^3$ Hybridisation $\rightarrow$ Geometry : Tetrahedral

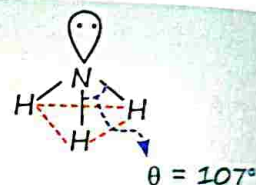
### $NH_4^+$

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



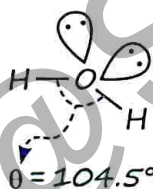
### $NH_3$

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



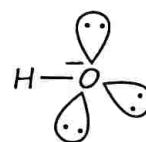
### $H_2O$

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



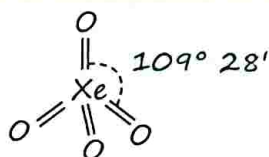
### $HO^-$

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



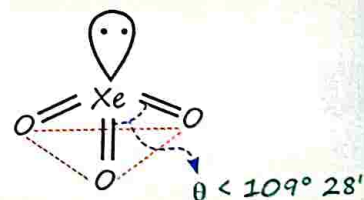
### $XeO_4$

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



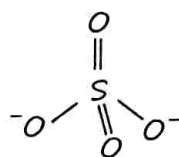
### $XeO_3$

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



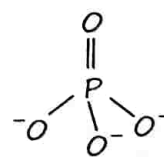
### $SO_4^{2-}$

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



### $PO_4^{3-}$

- 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 <sup>2</sup> hybrid orbital | 33.3%         | 66.6%         |
| sp <sup>3</sup> hybrid orbital | 25%           | 75%           |

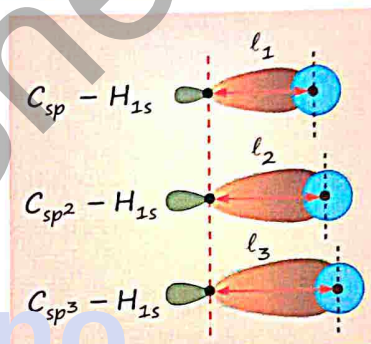
### Bond Length & % s Character

□ % s character:  $C_{sp} > C_{sp^2} > C_{sp^3}$

□ Bond length:  $l_1 < l_2 < l_3$

□ 
$$\text{Bond length} \propto \frac{1}{\% \text{ s character}}$$
  

$$\propto \% \text{ p character}$$



### Electronegativity & % s Character

□  $EN \propto \% \text{ s character}$

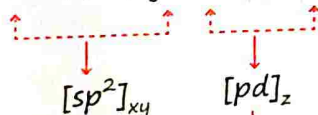
□ % s character:  $C_{sp} > C_{sp^2} > C_{sp^3}$

□ Electronegativity:  $C_{sp} > C_{sp^2} > C_{sp^3}$

**sp<sup>3</sup>d Hybridisation → Geometry: Trigonal bipyramidal (TBP)**

**PCl<sub>5</sub>**

$$sp^3d \equiv s + p_x + p_y + p_z + d_{z^2}$$



approx 100 % s character

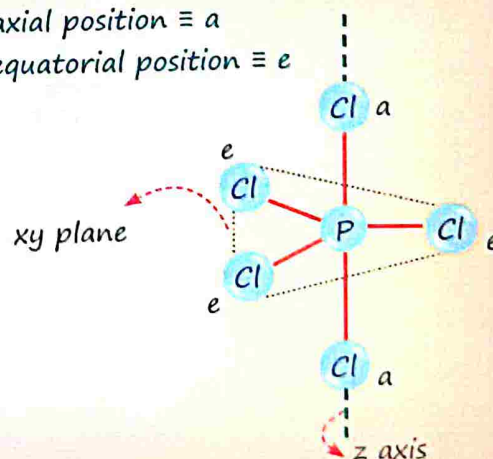
approx 0 % s character

Bond length : P - Cl<sub>e</sub>

<

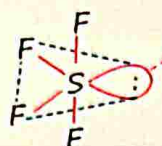
P - Cl<sub>a</sub>

axial position  $\equiv a$   
 equatorial position  $\equiv e$



## Bent's Rule

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

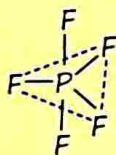
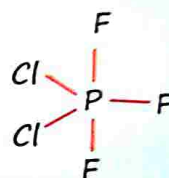
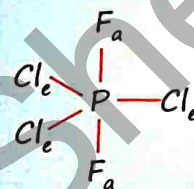
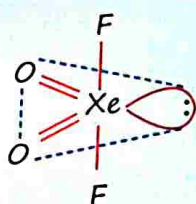


lone pair at equatorial position because it has more % s character than axial position.

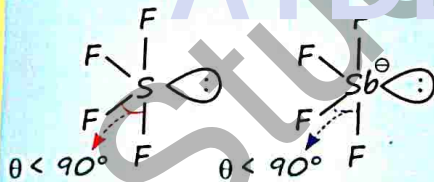
(2) A more electronegative atom prefers to occupy that hybrid orbital which has smaller % of s character (axial position).



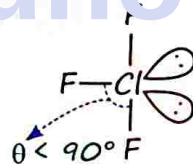
- $SN = LP + SA = 1 + 4 = 5$
- Geometry - TBP
- Shape - see saw



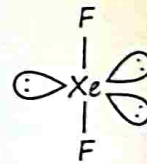
- $SN = 0 + 5$
- $sp^3d$
- TBP Shape
- $BL: P-F_a > P-F_e$



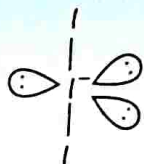
- $SN = 1 + 4 = 5$
- $sp^3d$
- See Saw Shape
- $BL: S-F_a > S-F_e$



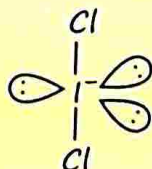
- $SN = 2 + 3 = 5$
- $sp^3d$
- Bent T shaped
- $BL: Cl-F_a > Cl-F_e$



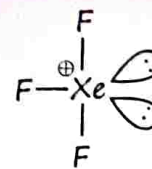
- $SN = 3 + 2 = 5$
- $sp^3d$
- Linear Shape



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



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



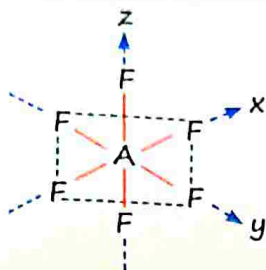
- $SN = LP + SA$   
 $= 2 + 3 = 5$
- Bent T shaped



## $sp^3d^2$ Hybridisation: Geometry $\rightarrow$ Octahedral

**AF<sub>6</sub>**

SF<sub>6</sub>  
PF<sub>6</sub><sup>-</sup>  
SiF<sub>6</sub><sup>2-</sup>  
AlF<sub>6</sub><sup>3-</sup>

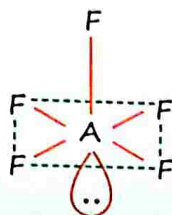


$$sp^3d^2 \equiv \underbrace{s + p_x + p_y + d_{x^2-y^2}}_{xy \text{ plane}} + \underbrace{p_z + d_{z^2}}_{z \text{ axis}}$$

| A                       | S | Si <sup>2+</sup> | P <sup>-</sup> | Al <sup>3-</sup> |
|-------------------------|---|------------------|----------------|------------------|
| Valence shell electrons | 6 | 4+2              | 5+1            | 3+3              |

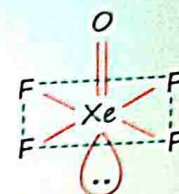
**BrF<sub>5</sub>, XeF<sub>5</sub><sup>+</sup>, ClF<sub>5</sub>, IF<sub>5</sub>, SF<sub>5</sub><sup>-</sup>**

- $AB_5 \rightarrow A = \text{Br, Xe}^+, \text{I, Cl, S}^-$
- $SN = 1 + 5 = 6$
- $sp^3d^2$
- Square pyramidal  $\rightarrow$  shape
- No of bond angles at  $90^\circ \rightarrow$  zero



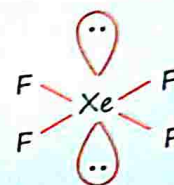
**XeOF<sub>4</sub>**

- $SN = 1 + 5 = 6$
- Square pyramidal  $\rightarrow$  shape



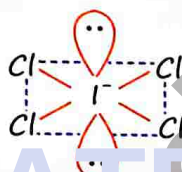
**XeF<sub>4</sub>**

- Square planar  $\rightarrow$  shape



**ICl<sub>4</sub>**

- $SN = 2 + 4 = 6$  ( $sp^3d^2$ )
- Square planar  $\rightarrow$  shape

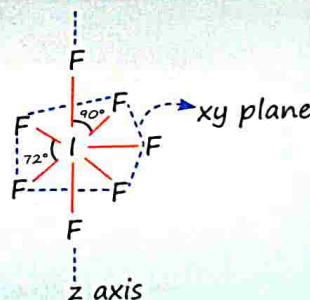


## $sp^3d^3$ Hybridisation

**IF<sub>7</sub>**

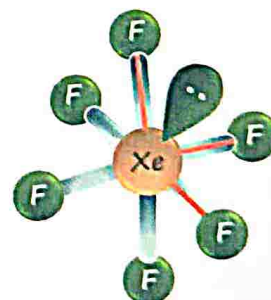
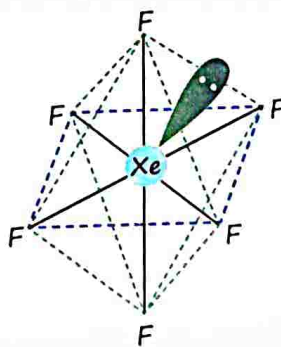
$$\underbrace{s + p_x + p_y + d_{x^2-y^2} + d_{xy}}_{xy \text{ plane}} + \underbrace{p_z + d_{z^2}}_{z \text{ axis}}$$

- $SN = LP + SA = 0 + 7 = 7$
- Pentagonal bipyramidal  $\rightarrow$  shape
- $\theta \rightarrow 90^\circ/72^\circ$

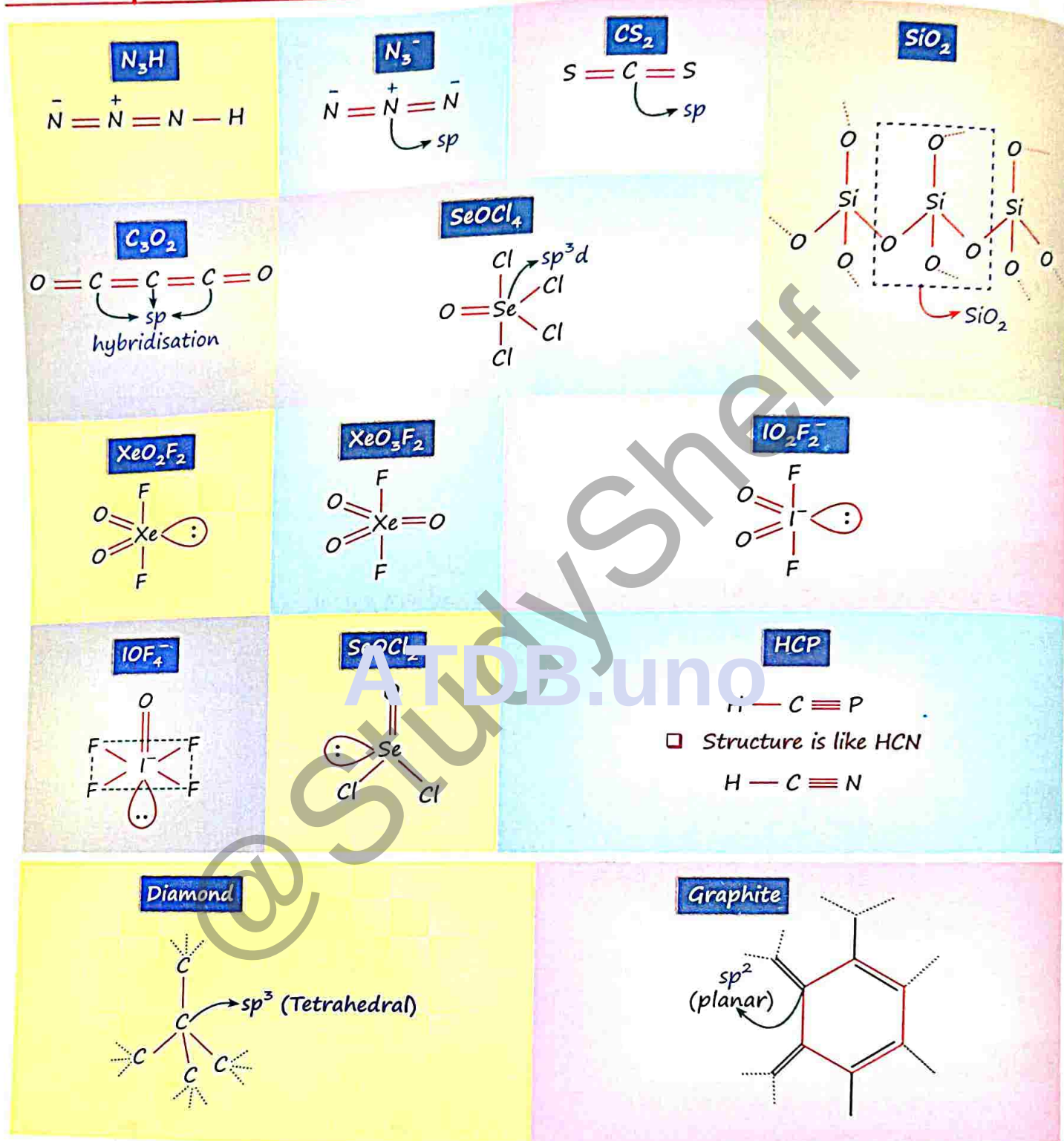


**XeF<sub>6</sub>(g), IF<sub>6</sub><sup>-</sup>, SeF<sub>6</sub><sup>2-</sup>**

- $SN = LP + SA = 1 + 6 = 7$
- Shape  $\rightarrow$  Distorted octahedral  
Capped octahedral



## Some Important Molecules-



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

(a) 0

(b) 1

(c) 2

(d) 3

(IIT JEE 2004)

Sol. (b)



21. Molecular shape of  $\text{SF}_4$ ,  $\text{CF}_4$  and  $\text{XeF}_4$  are (IIT JEE 2000)
- the same, with 2, 0 and 1 lone pair of electrons respectively
  - the same, with 1, 1 and 1 lone pair of electrons respectively
  - the different, with 0, 1 and 2 lone pair of electrons respectively
  - the different, with 1, 0 and 2 lone pair of electrons respectively

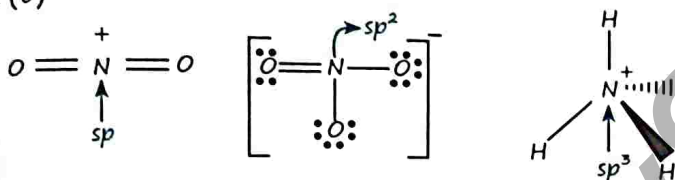
Sol. (d)

22. Based on VSEPR theory, the number of  $90^\circ$  F-Br-F angles in  $\text{BrF}_5$  is \_\_\_\_\_. (IIT JEE 2010)

Sol. [0]

23. The hybridisation of atomic orbitals of nitrogen in  $\text{NO}_2^+$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are (IIT JEE 2000)
- $sp$ ,  $sp^3$  and  $sp^2$  respectively
  - $sp$ ,  $sp^2$  and  $sp^3$  respectively
  - $sp^2$ ,  $sp$  and  $sp^3$  respectively
  - $sp^3$ ,  $sp^3$  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. $\text{XeF}_2$           | I. 0                                                           |
| B. $\text{XeO}_2\text{F}_2$ | II. 1                                                          |
| C. $\text{XeO}_3\text{F}_2$ | III. 2                                                         |
| D. $\text{XeF}_4$           | IV. 3                                                          |

Choose the most appropriate answer from the options given below:

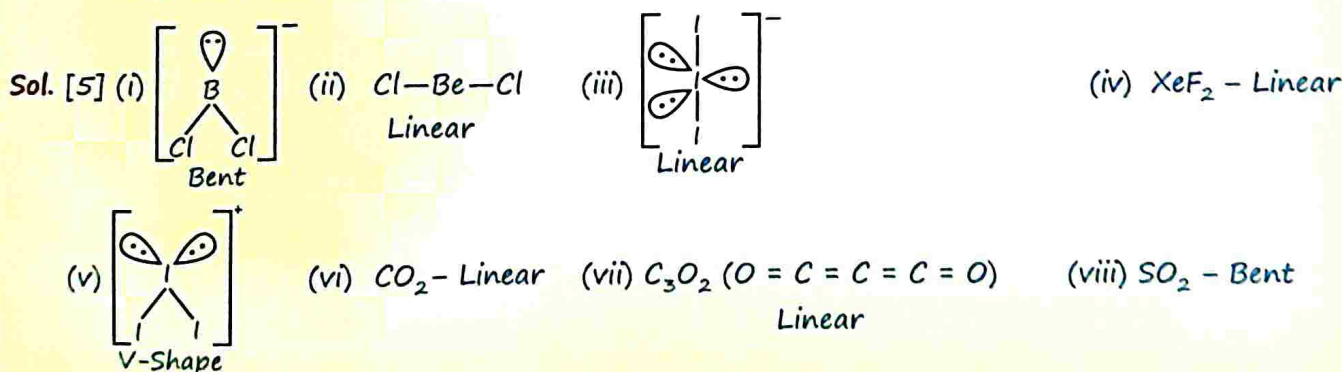
- (A)-(IV), (B)-(I), (C)-(II), (D)-(III)
- (A)-(III), (B)-(II), (C)-(IV), (D)-(I)
- (A)-(III), (B)-(IV), (C)-(II), (D)-(I)
- (A)-(IV), (B)-(II), (C)-(I), (D)-(III)

Sol. (d)  $\text{XeF}_2$        $\text{XeO}_2\text{F}_2$        $\text{XeO}_3\text{F}_2$        $\text{XeF}_4$   
 Lone Pair = 3      Lone Pair = 1      Lone Pair = 0      Lone Pair = 2

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

$\text{XeF}_2$ ,  $\text{I}_3^+$ ,  $\text{C}_3\text{O}_2$ ,  $\text{I}_3^-$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{BeCl}_2$  and  $\text{BCl}_2^-$

[30 Jan, 2023 (Shift-II)]





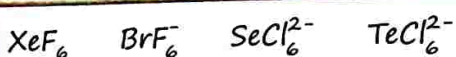
26. Which of the following statements is not correct for sigma- and pi-bonds formed between two carbon atoms? [NEET 2003]
- Sigma-bond is stronger than a pi-bond
  - Bond energies of sigma- and pi-bonds are of the order of 264 kJ/mol and 347 kJ/mol, respectively
  - Free rotation of atoms about a sigma bond is allowed but not in case of a pi-bond
  - 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
- $\text{CH}_4 \rightarrow \text{SN} = 0 + 4$  (Tetrahedral)
- $\text{CCl}_4 \rightarrow \text{SN} = 0 + 4$  (Tetrahedral)



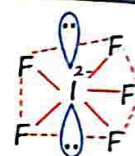
- Shape  $\rightarrow$  Distorted octahedral
- $\text{Xe} \equiv \text{Br}^- \equiv \text{Se}^{2-} \equiv \text{Te}^{2-}$
- No. of  $e^-$  in valence shell  $\rightarrow 8$

### Iso-electronic Species

- Species having same no. of electrons
- $\text{CH}_4 \rightarrow \text{no. of } e^- \equiv 6 + 4 \times 1 = 10 e^-$
- $\text{NH}_4^+ \rightarrow \text{no. of } e^- \equiv 7 + 4 \times 1 - 1 = 10 e^-$



- $\text{Xe} \equiv \text{I}^{2-} \rightarrow 8e^-$  in valence shell
- Shape  $\rightarrow$  Pentagonal planar
- no. of  $e^-$  in  $\text{XeF}_5^- \equiv 54 + 5 \times 9 + 1 = 100$
- no. of  $e^-$  in  $\text{IF}_5^{2-} \equiv 53 + 5 \times 9 + 2 = 100$



## Hybridisation in Solid State

- (1)  $2\text{PCl}_{5(s)} \rightarrow \text{PCl}_4^+ \text{PCl}_6^-$
- hyb<sup>n</sup> of cationic part of  $\text{PCl}_5 \equiv \text{PCl}_4^+ \equiv sp^3$  [Tetrahedral]
  - hyb<sup>n</sup> of anionic part of  $\text{PCl}_5 \equiv \text{PCl}_6^- \equiv sp^3d^2$  [Octahedral]

- (2)  $\text{PBr}_{5(s)} \rightarrow \text{PBr}_4^+ \text{Br}^-$
- $\rightarrow sp^3 \text{ hyb}^n$  [Tetrahedral]

- (3)  $\text{XeF}_{6(s)} \rightarrow \text{XeF}_5^+ \text{F}^-$
- $\rightarrow sp^3d^2$  [Sq. Pyramidal]

- (4)  $\text{N}_2\text{O}_{5(s)} \rightarrow \text{NO}_2^+ \text{NO}_3^-$

| Cation                                                                                          | Anion                                                                                                      |
|-------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------|
| $\text{O}=\text{N}^+=\text{O}$                                                                  | $\text{O}=\text{N}(\text{O})-\text{O}^-$                                                                   |
| <ul style="list-style-type: none"> <li><math>sp \text{ hyb}^n</math></li> <li>Linear</li> </ul> | <ul style="list-style-type: none"> <li><math>sp^2 \text{ hyb}^n</math></li> <li>Trigonal planar</li> </ul> |

- (5)  $\text{N}_2\text{O}_{3(s)} \rightarrow \text{NO}^+ \text{NO}_2^-$

- (6)  $\text{Cl}_2\text{O}_{6(s)} \rightarrow \text{ClO}_2^+ \text{ClO}_4^-$

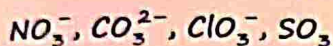


27. Which of the following contains a maximum number of lone pairs on the central atom?  
(IIT JEE 2005)

- (a)  $\text{ClO}_3^-$                       (b)  $\text{XeF}_4$                       (c)  $\text{SF}_4$                       (d)  $\text{I}_3^-$

Sol. (d)

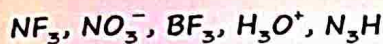
28. Which of the following are isoelectronic and isostructural?  
(IIT JEE 2003)



- (a)  $\text{NO}_3^-, \text{CO}_3^{2-}$                       (b)  $\text{SO}_3, \text{NO}_3^-$                       (c)  $\text{ClO}_3^-, \text{CO}_3^{2-}$                       (d)  $\text{CO}_3^{2-}, \text{SO}_3$

Sol. (a)

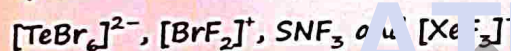
29. Among the following species, identify the isostructural pairs.  
(IIT JEE 1996)



- (a)  $[\text{NF}_3, \text{NO}_3^-]$  and  $[\text{BF}_3, \text{H}_3\text{O}^+]$                       (b)  $[\text{NF}_3, \text{HN}_3]$  and  $[\text{NO}_3^-, \text{BF}_3]$   
(c)  $[\text{NF}_3, \text{H}_3\text{O}^+]$  and  $[\text{NO}_3^-, \text{BF}_3]$                       (d)  $[\text{NF}_3, \text{H}_3\text{O}^+]$  and  $[\text{HN}_3, \text{BF}_3]$

Sol. (c)

30. The sum of the number of lone pairs of electrons on each central atom in the following species is



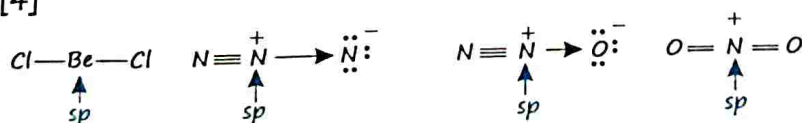
(Atomic numbers : N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54)                      (JEE Adv. 2017)

Sol. [6]

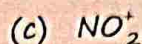
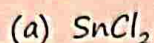
| S.N.  | Species                   | No. of $\sigma$ - bonds with central atom | No. of LP at central atom |
|-------|---------------------------|-------------------------------------------|---------------------------|
| (i)   | In $[\text{TeBr}_6]^{2-}$ | 6                                         | 1                         |
| (ii)  | In $[\text{BrF}_2]^+$     | 2                                         | 2                         |
| (iii) | In $\text{SNF}_3$         | 4                                         | 0                         |
| (iv)  | In $[\text{XeF}_3]^-$     | 3                                         | 3                         |

31. Among the triatomic molecules/ions  $\text{BeCl}_2, \text{N}_3^-, \text{N}_2\text{O}, \text{NO}_2^+, \text{O}_3, \text{SCl}_2, \text{ICl}_2^-, \text{I}_3^-$  and  $\text{XeF}_2$ , the total number of linear molecules/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)

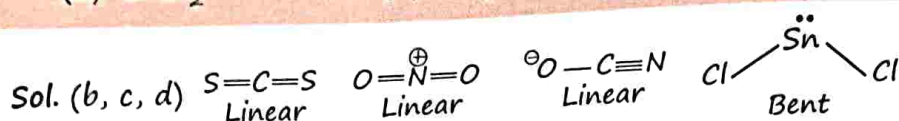
Sol. [4]



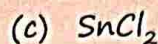
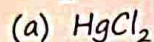
32. The linear structure assumed by



(IIT JEE 1991)



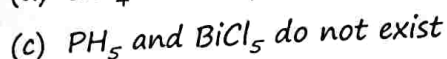
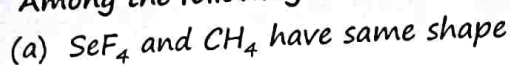
33.  $\text{CO}_2$  is isostructural with



(IIT JEE 1986)

Sol. (a, b)  $\text{CO}_2$ ,  $\text{HgCl}_2$ ,  $\text{C}_2\text{H}_2$  are all linear.

34. Among the following which one is a wrong statement?

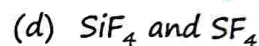
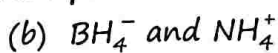
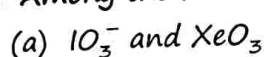


[NEET 2016-II]

Sol. (a)

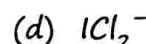
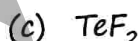
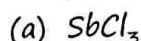
35. Among the following, the pair in which the two species are not isostructural is:

[NEET 2004]



Sol. (d)

36.  $\text{XeF}_2$  is isostructural with

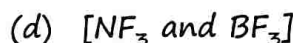
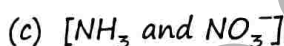
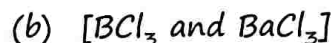
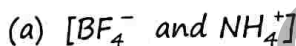


[NEET 2013]

Sol. (d)

37. Which one of the following pairs is iso-structural (i.e., having the same shape and hybridization)?

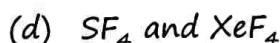
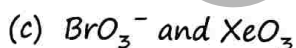
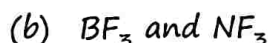
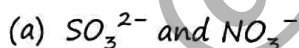
[NEET 2012 Pre]



Sol. (a)

38. In which of the following pairs, the two species are isostructural?

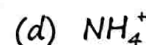
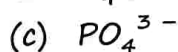
[NEET 2007]



Sol. (c)

39. Which of the following is not iso-structural with  $\text{SiCl}_4$ ?

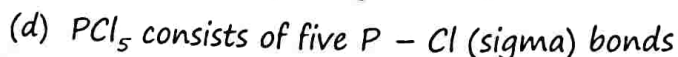
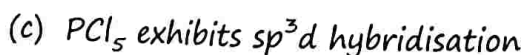
[NEET 2006]



Sol. (a)

40. Identify the incorrect statement about  $\text{PCl}_5$

[NEET 2024 Re]



Sol. (b)

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CHEMISTRY



41. The hybridisation of atomic orbitals of nitrogen in  $\text{NO}_2^+$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  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?

$\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{SCN}^-$

[NEET 2011 Pre]

- (a)  $\text{NO}_2^-$  and  $\text{NH}_2^-$     (b)  $\text{NO}_2^-$  and  $\text{NO}_3^-$   
 (c)  $\text{NH}_4^+$  and  $\text{NO}_3^-$     (d)  $\text{SCN}^-$  and  $\text{NH}_2^-$

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  $\text{N}_2$ , but phosphorus form  $\text{P}_2$ , but after some time convert in  $\text{P}_4$ , reason is:

[NEET 2001]

- (a) Triple bond present between phosphorous atom  
 (b)  $p\pi - p\pi$  bonding is weak  
 (c)  $p\pi - p\pi$  bonding is strong  
 (d) Multiple bond form easily

Sol. (b)

45.  $d\pi - p\pi$  bond is present i.:

[NEET 2000]

- (a)  $\text{CO}_3^{2-}$     (b)  $\text{PO}_4^{3-}$     (c)  $\text{NO}_3^-$     (d)  $\text{NO}_2^-$

Sol. (b)

### NO. OF $p\pi - p\pi$ BONDS/NO. OF $p\pi - d\pi$ BONDS

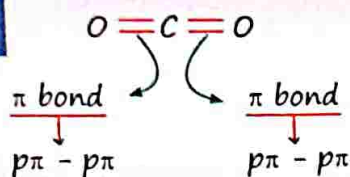
| Orbital | $\pi$ Bond              |
|---------|-------------------------|
| s       | Can not form $\pi$ bond |
| p       | Can form $\pi$ bond     |
| d       | Can form $\pi$ bond     |

| Period no = 2 | $\pi$ Bond                                           |
|---------------|------------------------------------------------------|
| s             | X                                                    |
| p             | ✓                                                    |
| d             | not available<br>in 2 <sup>nd</sup> period elements. |

| Period no > 2 | $\pi$ Bond |
|---------------|------------|
| s             | X          |
| p             | ✓          |
| d             | ✓          |

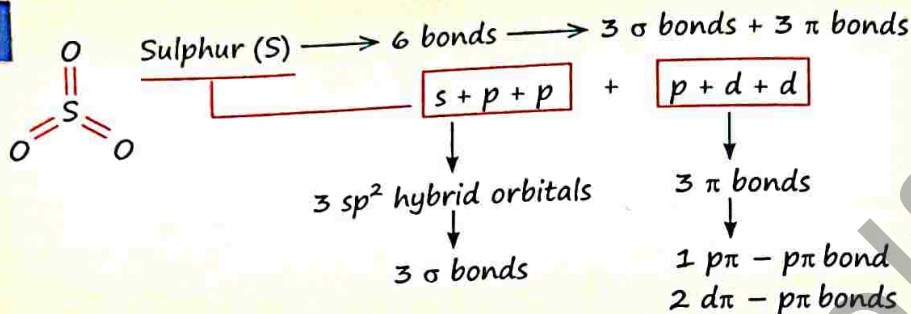
- ❑ If central atom or side atom is from period no 2 (B,C,N,O) then only p orbital can make  $\pi$  bond.
- ❑ If central atom or side atom is from period no > 2 (Al, Si, P, S, Cl, Xe) then p and d both can make  $\pi$  bond.

CO<sub>2</sub>



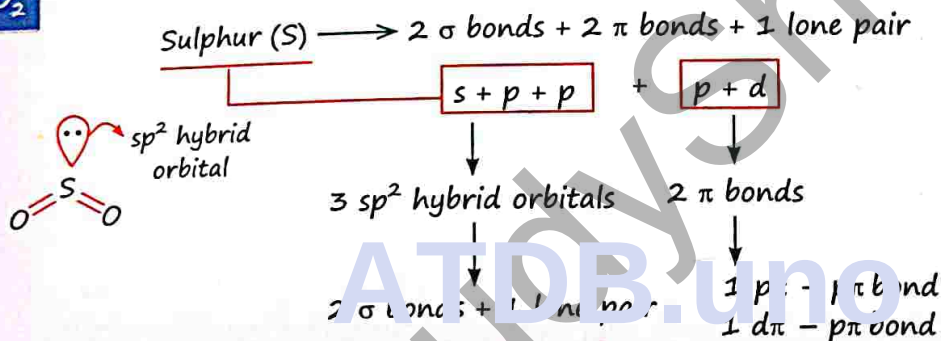
- overlapping between p orbital of carbon and p orbital of oxygen makes π bond.
- No. of pπ - pπ bonds = 2

SO<sub>3</sub>



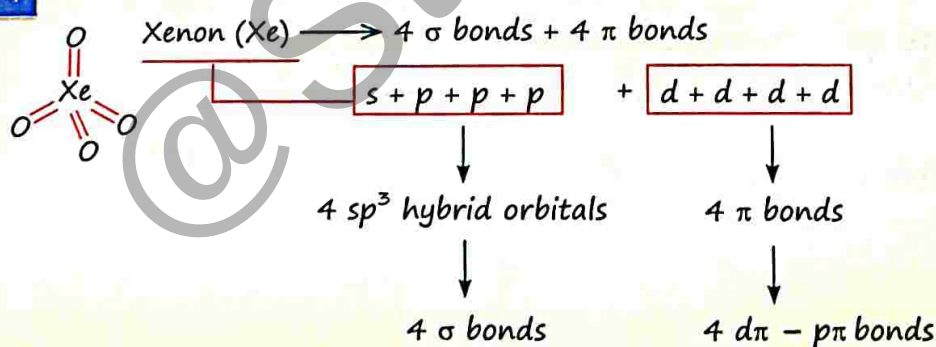
| 3 π bonds |        |
|-----------|--------|
| Sulphur   | Oxygen |
| 1. p      | p      |
| 2. d      | p      |
| 3. d      | p      |

SO<sub>2</sub>



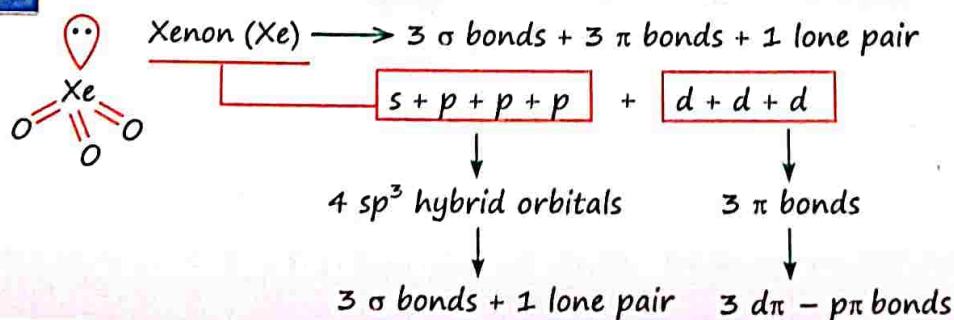
| 2 π bonds |        |
|-----------|--------|
| Sulphur   | Oxygen |
| 1. p      | p      |
| 2. d      | p      |

XeO<sub>4</sub>



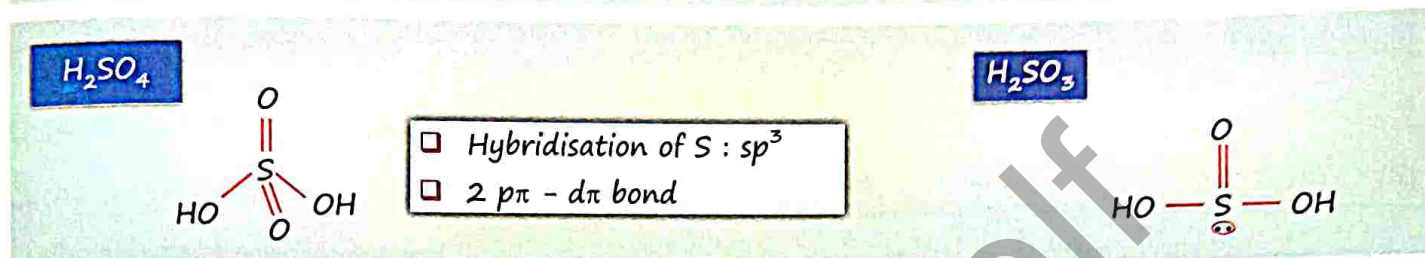
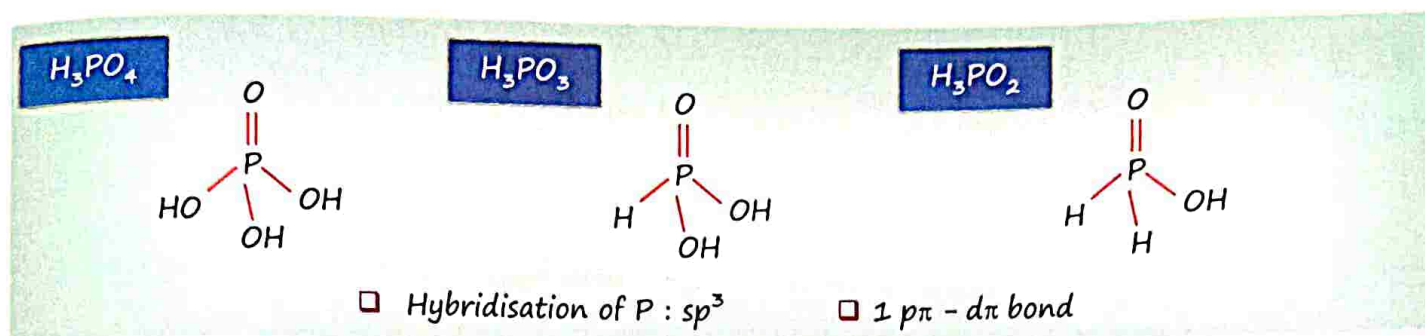
| 4 π bonds |        |
|-----------|--------|
| Xenon     | Oxygen |
| 1. d      | p      |
| 2. d      | p      |
| 3. d      | p      |
| 4. d      | p      |

XeO<sub>3</sub>



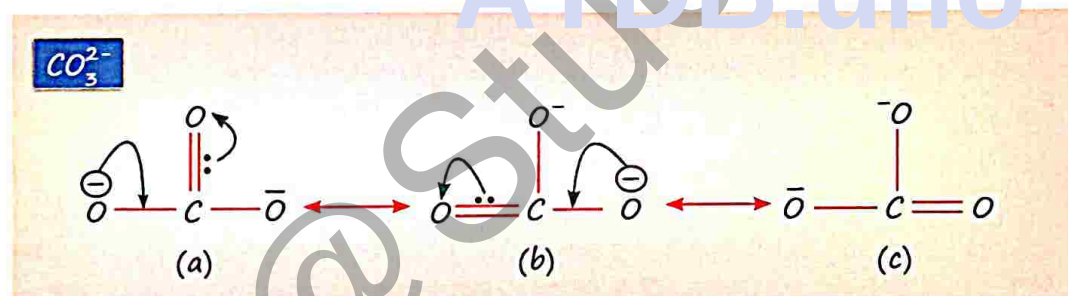
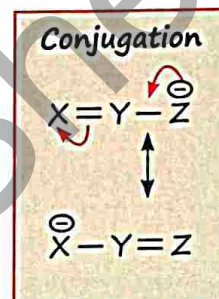
| 4 π bonds |        |
|-----------|--------|
| Xenon     | Oxygen |
| 1. d      | p      |
| 2. d      | p      |
| 3. d      | p      |



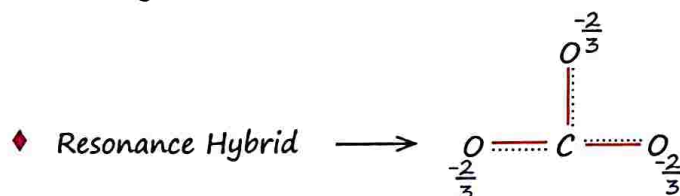


## RESONANCE

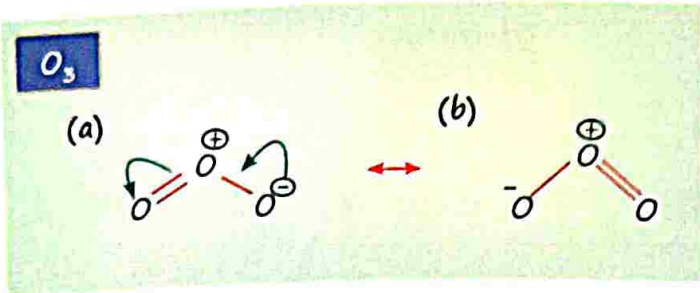
- Delocalisation of pi electrons
- Conjugation** - Necessary condition for resonance



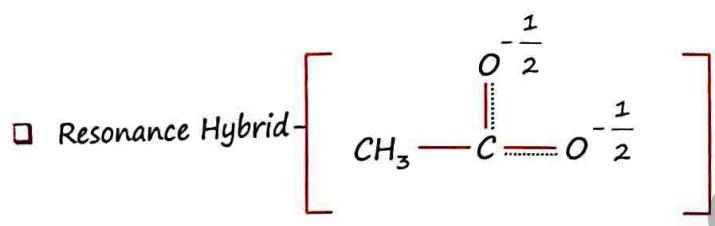
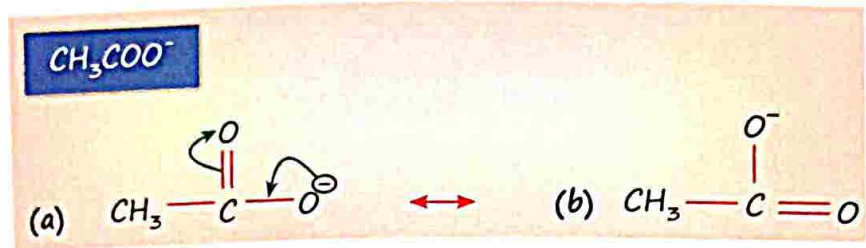
- Resonating structures  $\equiv$  a, b, c



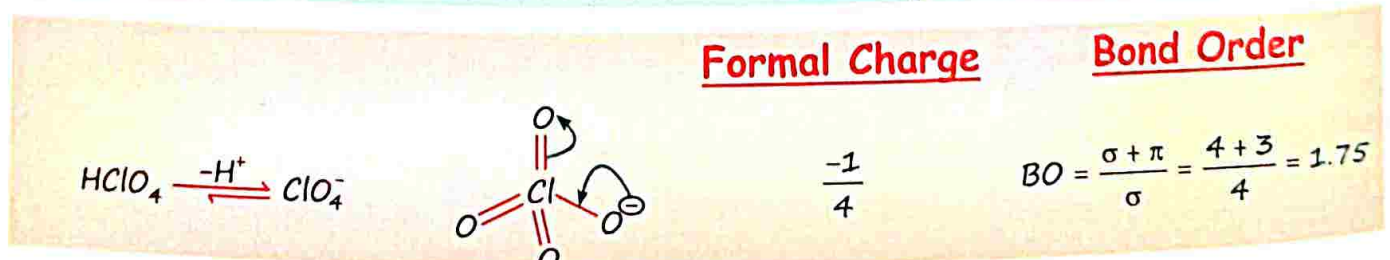
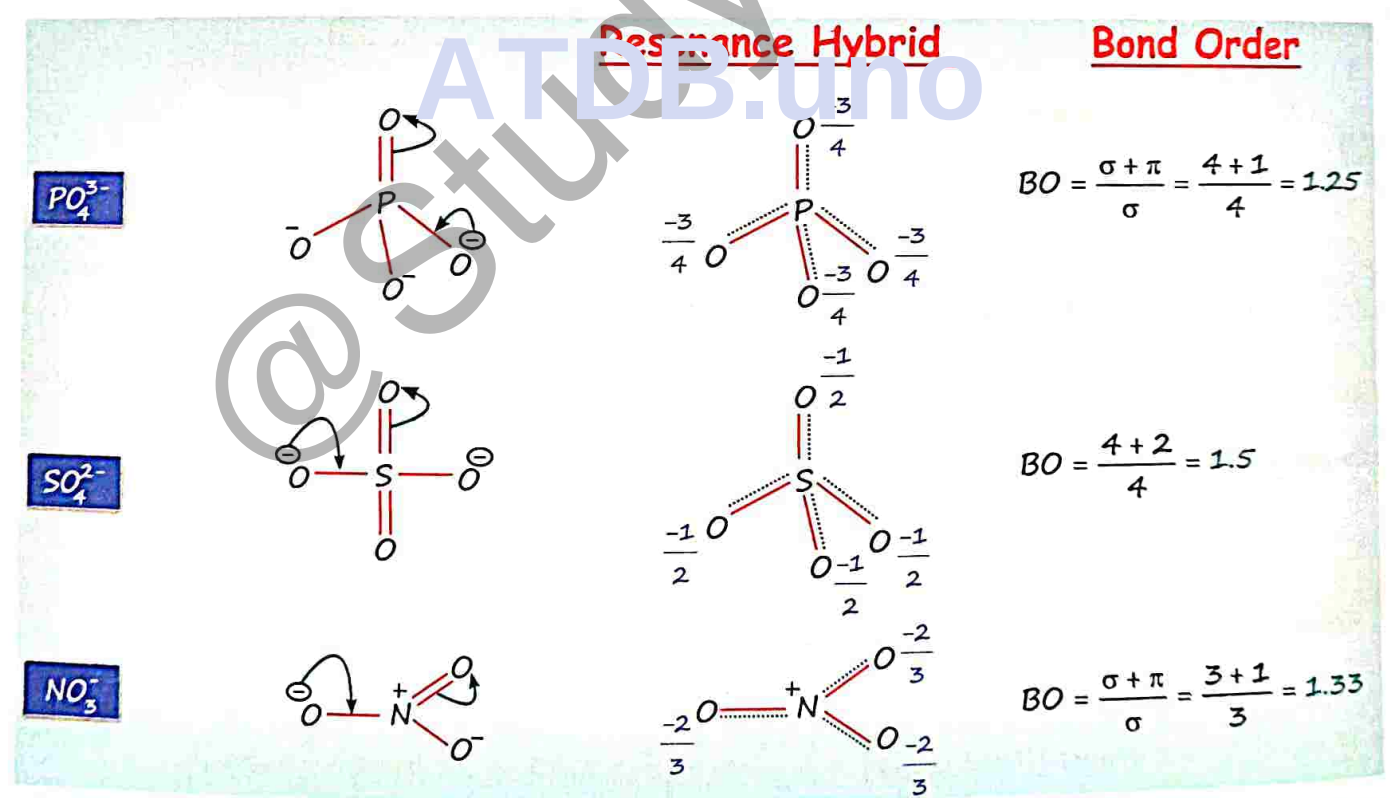
- No. of bonds b/w 2 atoms [Bond order]  $= \frac{\sigma + \pi}{\sigma} = \frac{3+1}{3} = 1.33 \rightarrow 1\sigma$  bond  $+ \frac{1}{3}\pi$  bonds.
- Formal charge on oxygen  $\equiv \frac{-2}{3}$
- Bond length  $\equiv$  All C - O bonds are same due to resonance



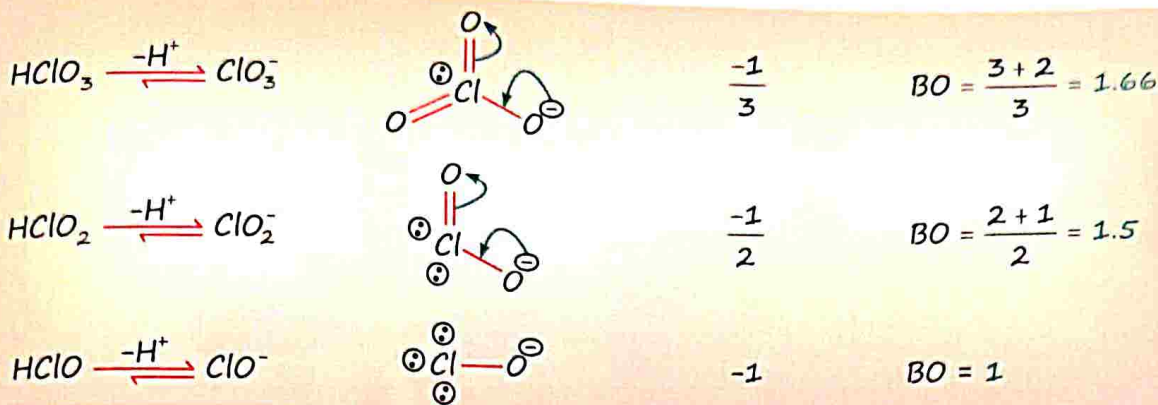
- Resonating structures = a & b
- Resonance Hybrid =
- Bond order =  $\frac{\sigma + \pi}{\sigma} = \frac{2 + 1}{2} = 1.5$
- Bond length = All O - O bonds are same.



- CO bond order =  $\frac{\sigma + \pi}{\sigma} = \frac{2 + 1}{2} = 1.5$
- Bond length = All C - O bonds are same







- Acidity  $\propto$  Stability of conjugate base  $\propto \frac{1}{\text{formal charge}}$
- Acidic Strength :  $a > b > c > d$

### (JEE. Adv 2015)

46. The correct statement(s) regarding,

- (i)  $\text{HClO}$ , (ii)  $\text{HClO}_2$ , (iii)  $\text{HClO}_3$  and (iv)  $\text{HClO}_4$  is (are)
- (a) The number of  $\text{Cl} = \text{O}$  bonds in (ii) and (iii) together is two
  - (b) the number of lone pair of electrons on  $\text{Cl}$  in (ii) and (iii) together is three
  - (c) the hybridisation of  $\text{Cl}$  in (iv) is  $\text{sp}^3$
  - (d) amongst (i) to (iv), the strongest acid is (i)

Sol. (b, c)

47. In  $\text{PO}_4^{3-}$  ion, the formal charge on each oxygen atom and  $\text{P}-\text{O}$  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  $90^\circ$ .

$\text{NH}_3 \rightarrow 107^\circ$

$\text{H}_2\text{O} \rightarrow 104.5^\circ$

bond angle  $\theta$  is near to ideal angle  $109^\circ 28'$  of  $\text{sp}^3$  hybridisation.

$\text{PH}_3 \rightarrow 93.6^\circ$

$\text{H}_2\text{S} \rightarrow 92^\circ$

bond angle  $\theta \approx 90^\circ$

No, Hybridisation

$\text{AsH}_3 \rightarrow 91.8^\circ$

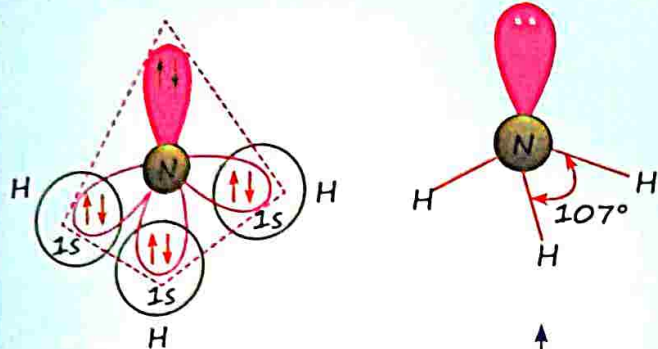
$\text{H}_2\text{Se} \rightarrow 91^\circ$

Pure  $p$  orbital of central atom overlaps to  $1s$  atomic orbital of side atom  $\text{H}$ .

$\text{SbH}_3 \rightarrow 91.3^\circ$

$\text{H}_2\text{Te} \rightarrow 90^\circ$

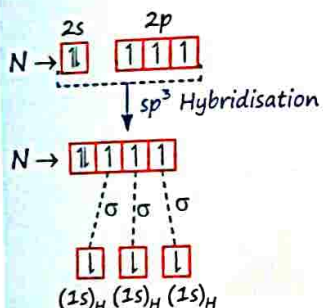
## Bonding in NH<sub>3</sub>



### Orbital overlap in NH<sub>3</sub>

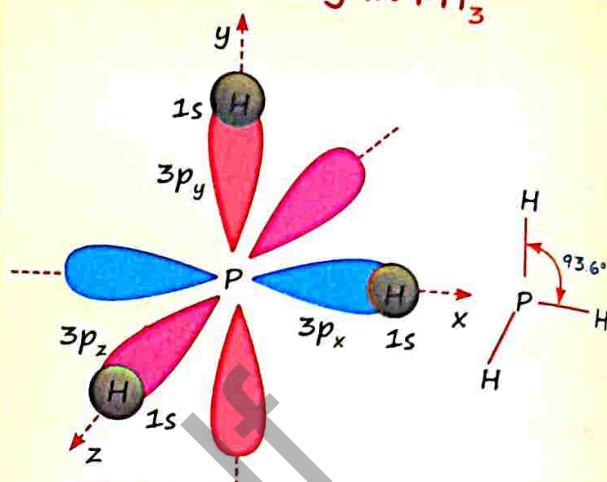
### Pyramidal shape

In order to make N – H bonds  $sp^3$  hybrid orbitals of nitrogen overlap with  $1s$  atomic orbital of hydrogens.



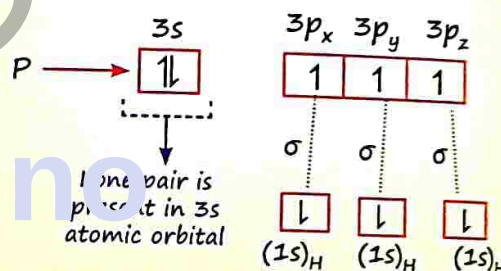
- 3 N – H  $\sigma$  bonds :  $(sp^3)_N - (1s)_H$
- 1 lone pair in  $sp^3$  hybrid orbital of nitrogen.

## Bonding in PH<sub>3</sub>



### Orbital overlap in PH<sub>3</sub>

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

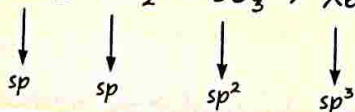
Hybridisation  $\rightarrow \theta : sp > sp^2 > sp^3$

$\theta : CO_2 > CO_3^{2-} > CH_4$



$\theta : CF_4 = CH_4 = NH_4^+ = XeO_4 = 109^\circ 28'$  [  $sp^3$  hybridisation ]

$\theta : NO_2^+ = CO_2 > SO_3 > XeO_4$



$\theta : BF_3 = BCl_3 = BBr_3 = 120^\circ$

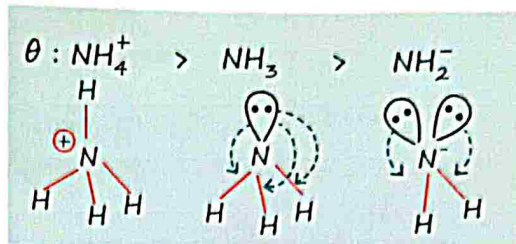
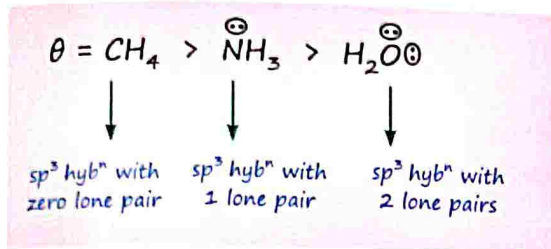
[  $sp^2$  hybridisation ]

|               |        |                          |
|---------------|--------|--------------------------|
| % s character | $sp$   | $\theta = 180^\circ$     |
|               | $sp^2$ | $\theta = 120^\circ$     |
| bond angle    | $sp^3$ | $\theta = 109^\circ 28'$ |

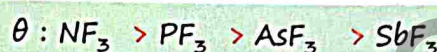
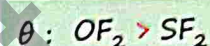
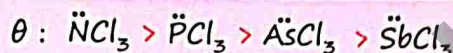
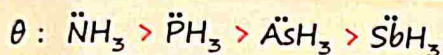


## Molecules with Lone Pair

1. If same Hybridisation  $\longrightarrow$  No of lone pair  $\uparrow$  :  $\theta \downarrow$

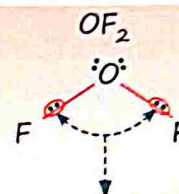
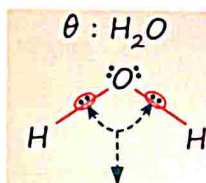
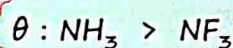


2. No. of lone pair : same  $\Rightarrow$  Size of CA  $\uparrow$  : Bond angle  $\downarrow$



3. No of lone pair : same

E.N. of S.A.  $\uparrow$  : Bond angle  $\downarrow$



□ Bond pair - bond pair repulsion  $\uparrow$

□ Bond pair - bond pair repulsion  $\downarrow$

□ Bond angle  $\uparrow$

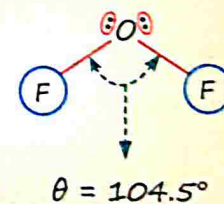
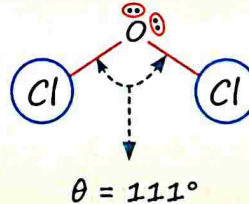
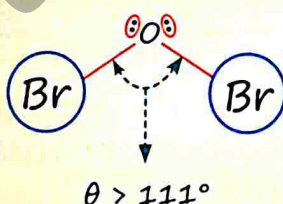
□  $\theta = 104.5^\circ$

□ Bond angle  $\downarrow$

□  $\theta < 104.5^\circ$

4. No of lone pair : same

Size of S.A.  $\uparrow$  : Bond angle  $\uparrow$

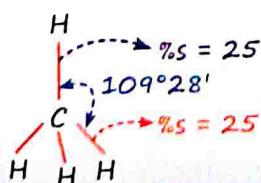


## Note

### Bent's Rule

% s character  $\uparrow$  : Bond Angle  $\uparrow$

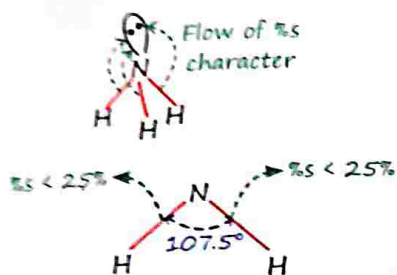
1. Lone pair orbitals must adopt a higher s character to stabilise the unshared, tightly bound nonbonding electrons.



□ Each C-H bond has 25% s character and bond angle is  $109^\circ 28'$ .

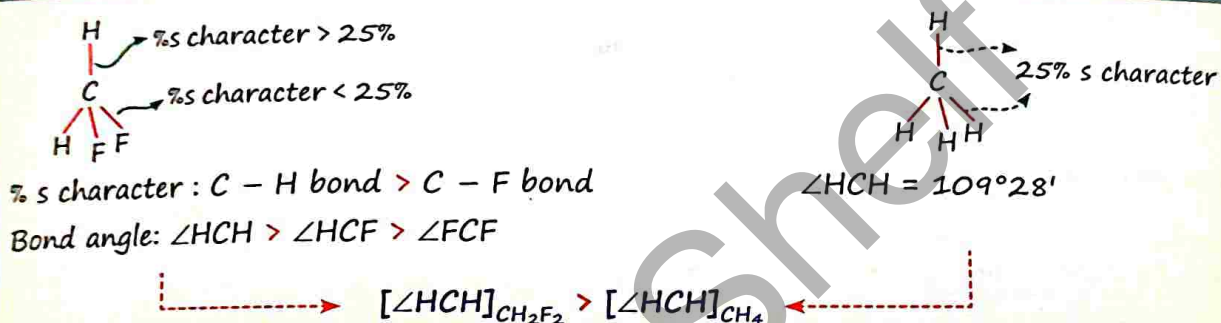


### NH<sub>3</sub>



- 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.



### (IIT JEE 1999)

48. In compounds of type  $\text{ECl}_3$ , where E = B, P, As or Bi, the angles  $\text{Cl}-\text{E}-\text{Cl}$  is in order  
 (a)  $\text{B} > \text{P} = \text{As} = \text{Bi}$  (b)  $\text{B} > \text{P} > \text{As} > \text{Bi}$  (c)  $\text{E} < \text{P} < \text{As} = \text{Bi}$  (d)  $\text{B} < \text{P} < \text{As} < \text{Bi}$

Sol. (b)

49. For  $\text{OF}_2$  molecule, consider the following:

[30 Jan, 2023 (Shift-0)]

- (A) Number of lone pairs on oxygen is 2. (B) FOF angle is less than  $104.5^\circ$ .  
 (C) Oxidation state of O is -2. (D) Molecule is bent 'V' shaped.  
 (E) Molecular geometry is linear.

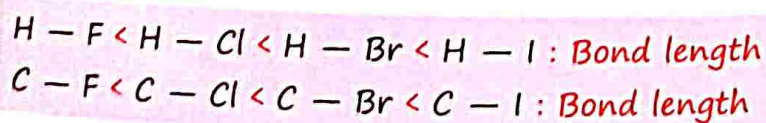
Correct options are:

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

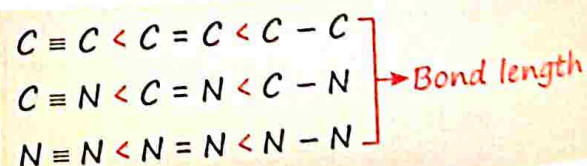
Sol. (d)

### Bond Length

Size  $\uparrow$ : Bond length  $\uparrow$



Bond order  $\downarrow$ : Bond length  $\uparrow$

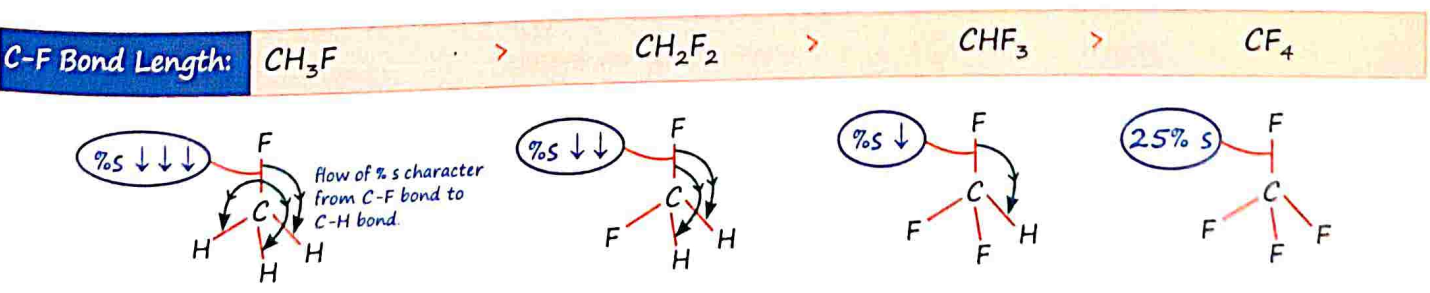
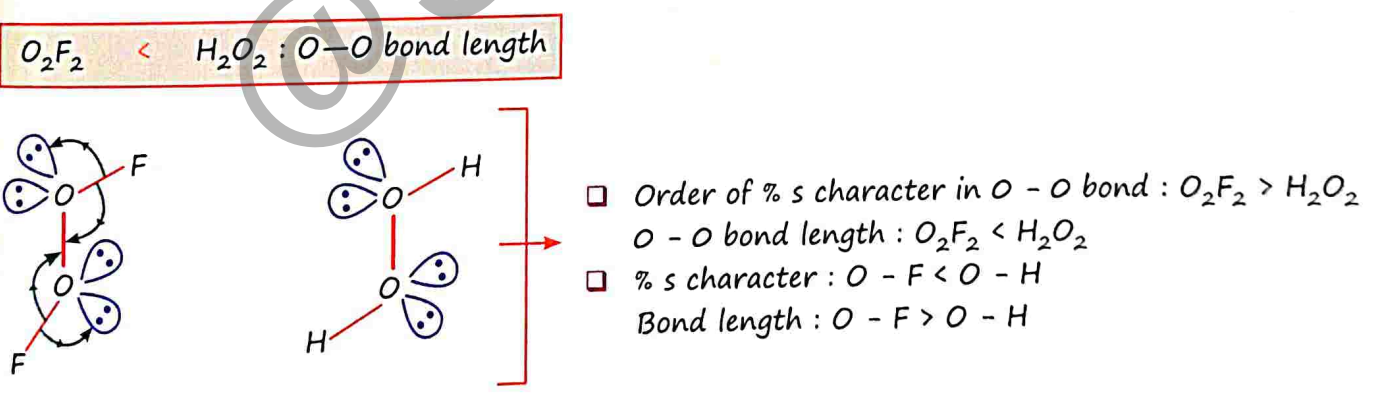
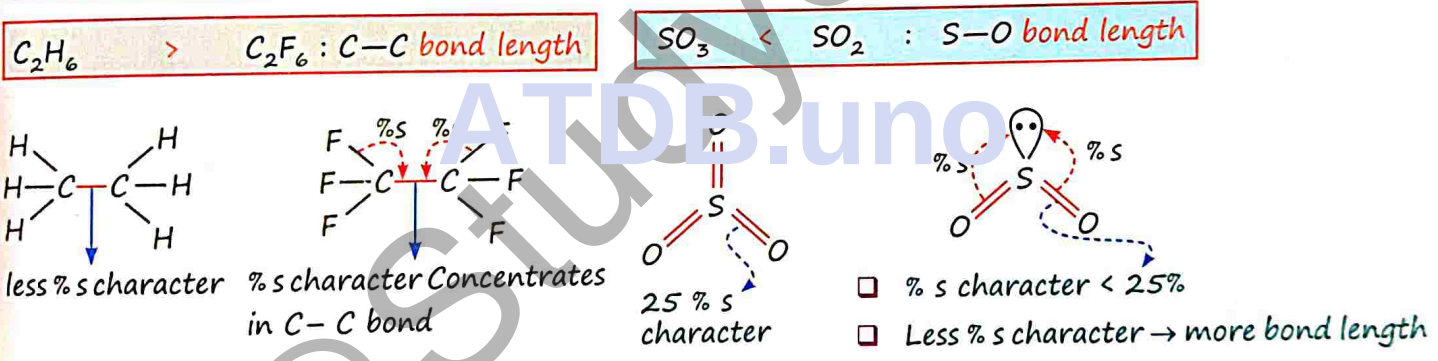
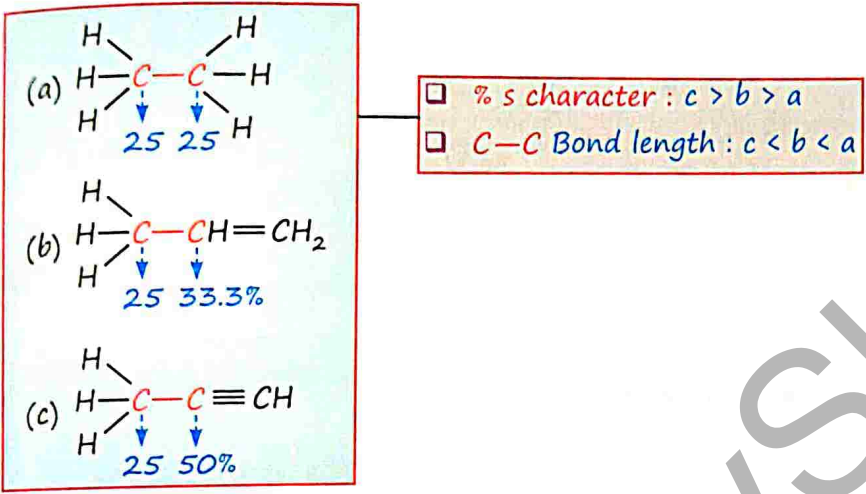
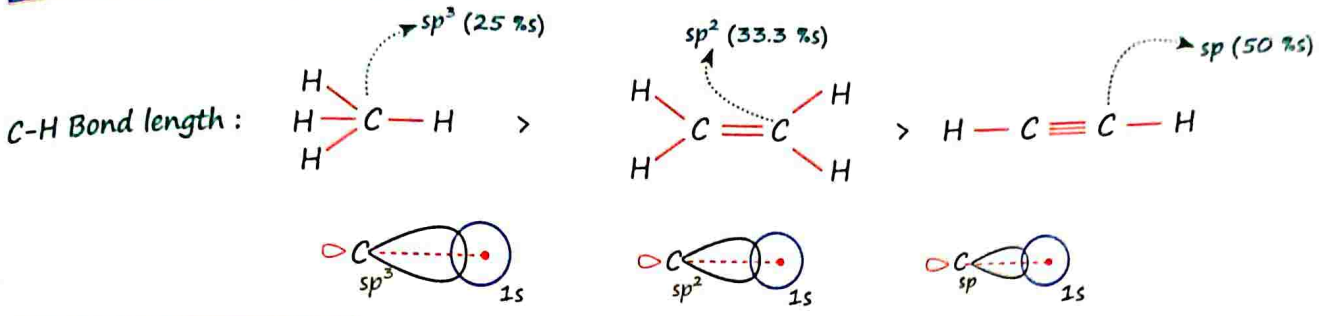


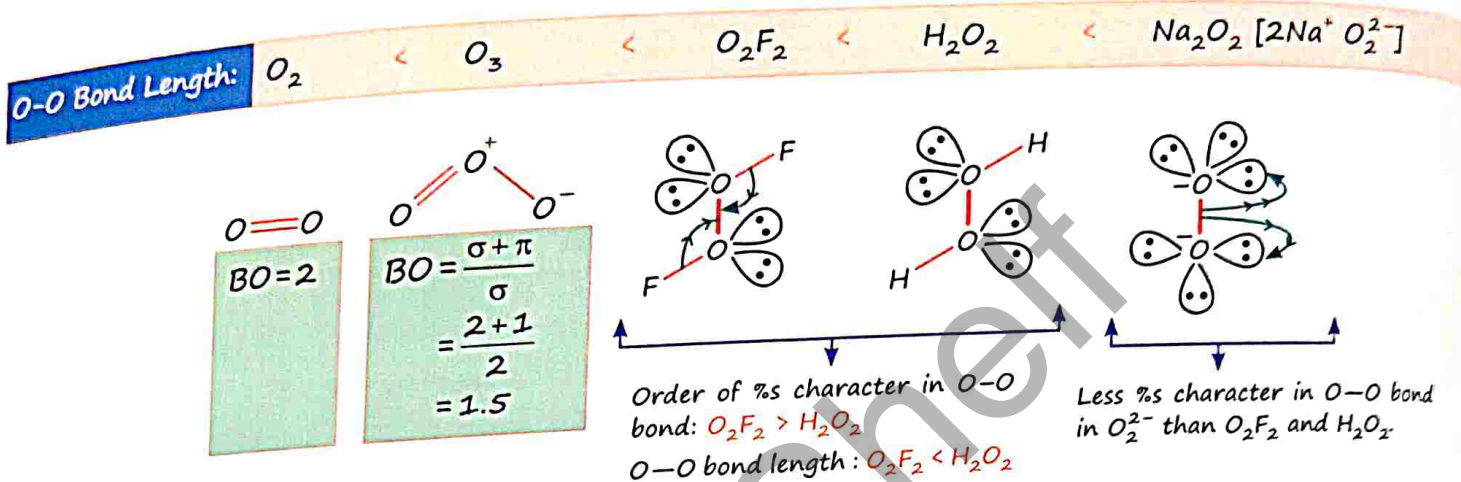
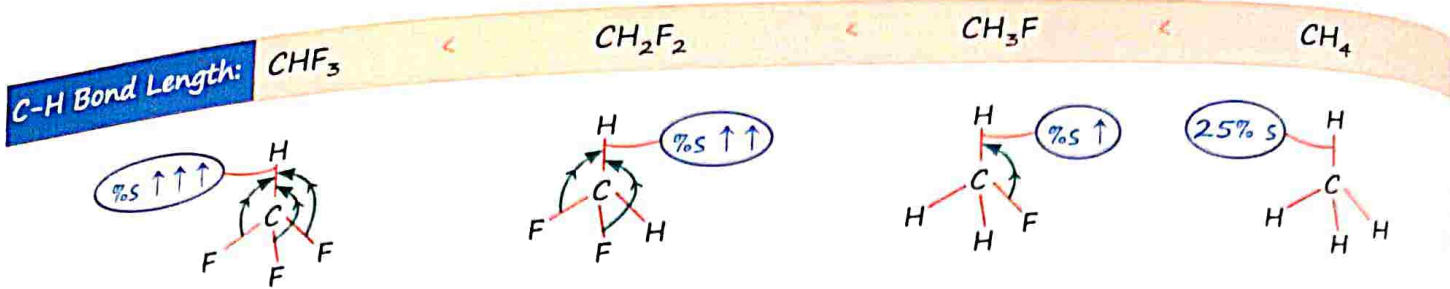
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CHEMISTRY



%s character↑ : Bond length↓





50. O-O bond length in  $\text{H}_2\text{O}_2$  is X than the O-O bond length in  $\text{F}_2\text{O}_2$ . The O-H bond length in  $\text{H}_2\text{O}_2$  is Y than that of the O-F bond in  $\text{F}_2\text{O}_2$ .

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

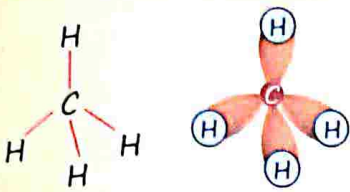
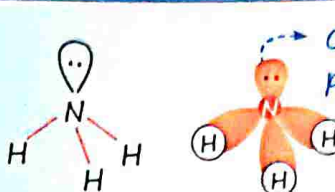
Sol. (d)

[1 Feb, 2023 (Shift-I)]

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CHEMISTRY

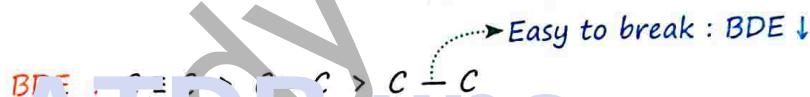


| Equivalent Hybrid Orbitals                                                                                                                                                                                                                                                                                                                                    | Non-equivalent Hybrid Orbitals                                                                                                                                                                                                                                                                                                                                                             |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  <p>□ All 4 hybrid orbitals are equivalent in energy and size.</p> <p>□ Central atom without lone pair and attached with same side atoms has equivalent hybrid orbitals.</p> <p>Example: <math>\text{XeO}_4</math>, <math>\text{BeCl}_2</math>, <math>\text{BF}_3</math></p> |  <p>Orbital having lone pair is small in size due to more %s character.</p> <p>□ Central atom with lone pair or attached with different side atoms has non-equivalent hybrid orbitals.</p> <p>Example: <math>\text{H}_2\text{O}</math>, <math>\text{NH}_3</math>, <math>\text{CH}_2\text{F}_2</math></p> |

## Bond Dissociation Energy

Minimum energy required to break a bond is known as bond dissociation energy.

### (1) $\text{BDE} \propto \text{Bond Order}$

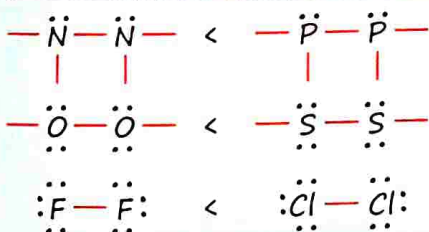


### (2) $\text{BDE} \downarrow : \text{Bond Length} \uparrow$



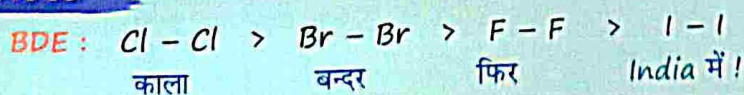
Order of bond length:  $\text{C} - \text{C} < \text{Si} - \text{Si}$   
 Bond dissociation energy:  $\text{C} - \text{C} > \text{Si} - \text{Si}$

### (3) $\text{BDE} \downarrow : \text{LP-LP Repulsion} \uparrow$



- 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



51. The table shown below gives the bond dissociation energies ( $E_{diss}$ ) for single covalent bonds of carbon atoms with element A, B, C and D. Which element has the smallest atoms? [NEET 1994]

| Bond | $E_{diss}$ (kJ mol <sup>-1</sup> ) |
|------|------------------------------------|
| 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:

| List-I<br>Molecule | List-II<br>Bond enthalpy (kJmol <sup>-1</sup> ) |
|--------------------|-------------------------------------------------|
| A. HCl             | I. 435.8                                        |
| B. N <sub>2</sub>  | II. 498                                         |
| C. H <sub>2</sub>  | III. 946.0                                      |
| D. O <sub>2</sub>  | 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-V, B-III, C-I, D-II

Sol. (d)

53. The correct order of bond angles in the following compounds/ species is: [NEET 2022 R]

- (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 angle in  $H_2O$  are all greater than  $90^\circ$ .  
 (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)

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CHEMISTRY



# PH<sub>3</sub> HAS NO HYBRIDISATION BUT PF<sub>3</sub> & PH<sub>4</sub><sup>+</sup> HAS ? WHY

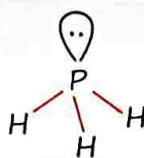
Complete or partial +ve charge on central atom supports **ORBITAL CONTRACTION**, which leads hybridisation of atomic orbitals.

**PH<sub>3</sub>**

P:  $\boxed{1\downarrow}\boxed{1}\boxed{1}\boxed{1}$

3s 3p

⇒ P in PH<sub>3</sub> has no hybridisation



**PF<sub>3</sub>**

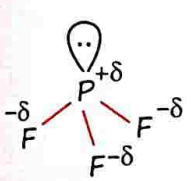
<sup>+δ</sup>P:  $\boxed{1\downarrow}\boxed{1}\boxed{1}\boxed{1}$

3s 3p

↓

$\boxed{1\downarrow}\boxed{1}\boxed{1}\boxed{1}$

4 sp<sup>3</sup> hybrid orbitals



⇒ P in PF<sub>3</sub> is sp<sup>3</sup> hybridised

**PH<sub>4</sub><sup>+</sup>**

P<sup>+</sup>:  $\boxed{1\downarrow}\boxed{1}\boxed{1}\boxed{1}$

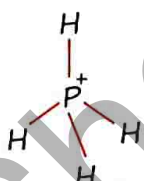
3s 3p

P<sub>es</sub><sup>+</sup>:  $\boxed{1}\boxed{1}\boxed{1}\boxed{1}$

↓

$\boxed{1}\boxed{1}\boxed{1}\boxed{1}$

4 sp<sup>3</sup> hybrid orbitals

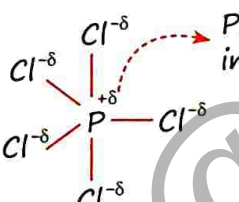


⇒ P in PH<sub>4</sub><sup>+</sup> is sp<sup>3</sup> hybridised

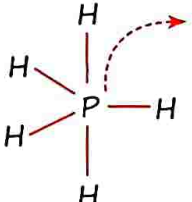
Bond Angle: PH<sub>3</sub> < PF<sub>3</sub> < PH<sub>4</sub><sup>+</sup>  
 [θ ≅ 90°] [θ > 90°] [θ = 109°28']

56. PCl<sub>5</sub> exists but not PH<sub>5</sub> ?

Sol. d-orbital contraction is possible in PCl<sub>5</sub> but not in PH<sub>5</sub>



Partial (+)ve charge on P helps in d orbital contraction



No charge on P.

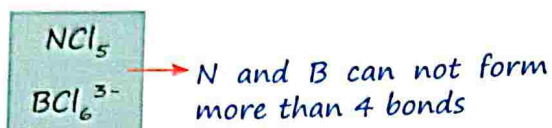
57. SF<sub>6</sub> exists but not SH<sub>6</sub> ?

Sol. d-orbital contraction is possible in SF<sub>6</sub> but not in SH<sub>6</sub>.

## EXISTENCE & NON-EXISTENCE

- 2<sup>nd</sup> Period elements → B/C/N/O/F → Can have maximum 8e<sup>-</sup> in valence shell
  - max. covalency ≡ 4
  - d orbitals are not available
  - Possible hybridisations are - sp, sp<sup>2</sup>, sp<sup>3</sup>

- 3<sup>rd</sup>/4<sup>th</sup>/5<sup>th</sup>/6<sup>th</sup>/7<sup>th</sup> 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.



### Note

#### Molecules That Do Not Exist

- (1)  $\text{SF}_4$ ,  $\text{SF}_6$  &  $\text{PF}_5$ , exist while  $\text{OF}_4$ ,  $\text{OF}_6$ ,  $\text{NF}_5$  do not exist
- (2) (a)  $\text{PI}_5(\text{vap})$  &  $\text{SCl}_6$  do not exist  
(b)  $\text{SCl}_6$  does not exist while  $\text{TeCl}_6$  exist due to steric effect.
- (3)  $\text{SF}_6$ ,  $\text{PF}_5$ ,  $\text{XeF}_6$ ,  $\text{XeF}_4$  &  $\text{XeF}_2$  exist while  $\text{SH}_6$ ,  $\text{PH}_5$ ,  $\text{XeH}_6$ ,  $\text{XeH}_4$ ,  $\text{XeH}_2$  do not exist.

## LEWIS BASE AND LEWIS ACID

### Lewis Acid → Electron pair acceptor

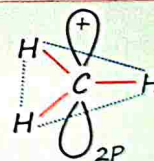
CA having vacant orbital:

(i) Vacant p orbital:  $\text{BF}_3$   
 $\text{B}(\text{OH})_3$   
 $\text{AlCl}_3$

(ii) Vacant d orbital:  $\text{SiF}_4$   
 $\text{PCl}_5$

CA with +ve charge having vacant orbital:

(i) Vacant s orbital:  $\text{H}^+$   
(ii) Vacant p orbital:  $\text{CH}_3^+$   
 $sp^2$



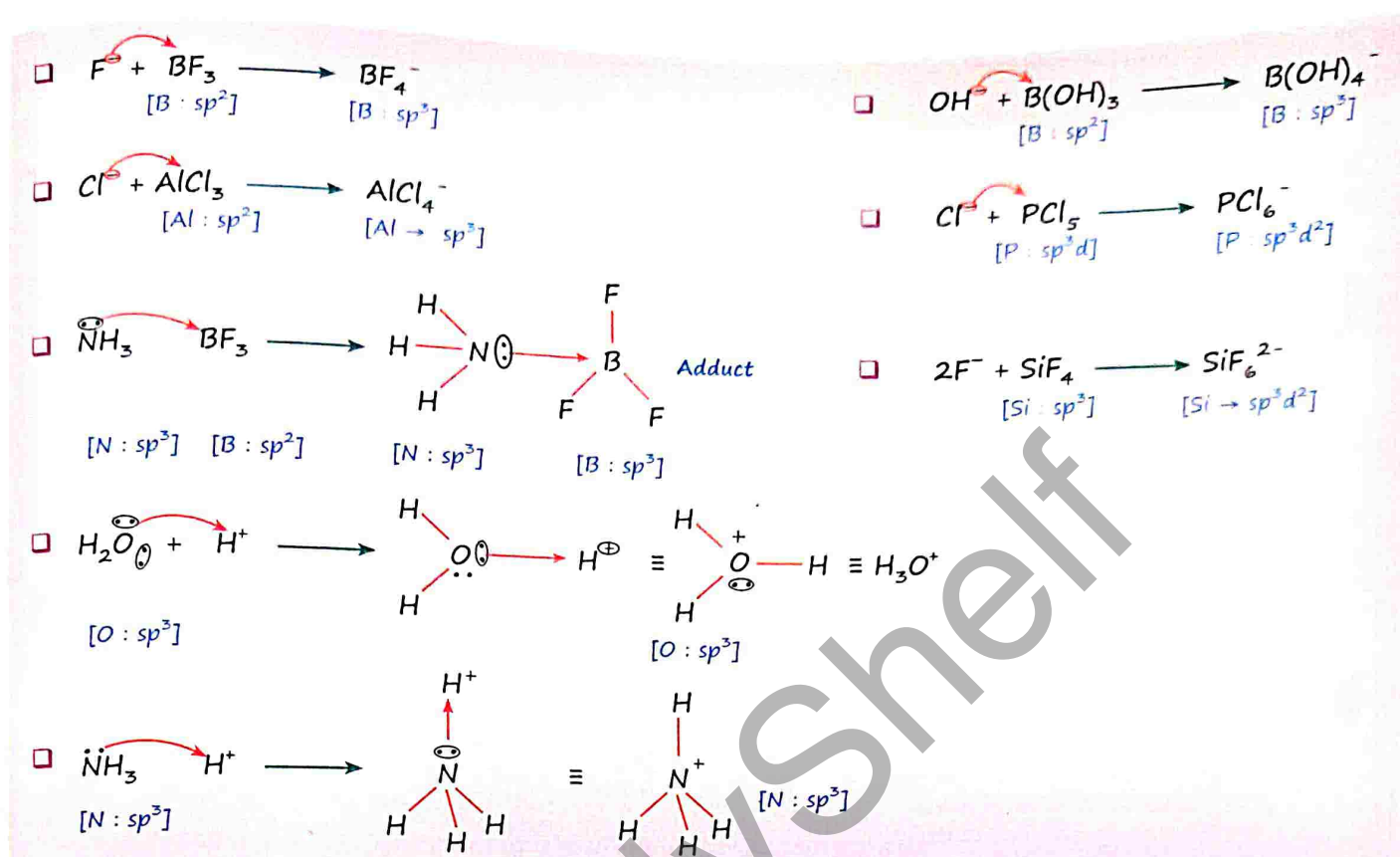
- $\text{NH}_4^+$  → not a Lewis Acid because there is no vacant orbital in N.

### Lewis Base → Electron pair donor

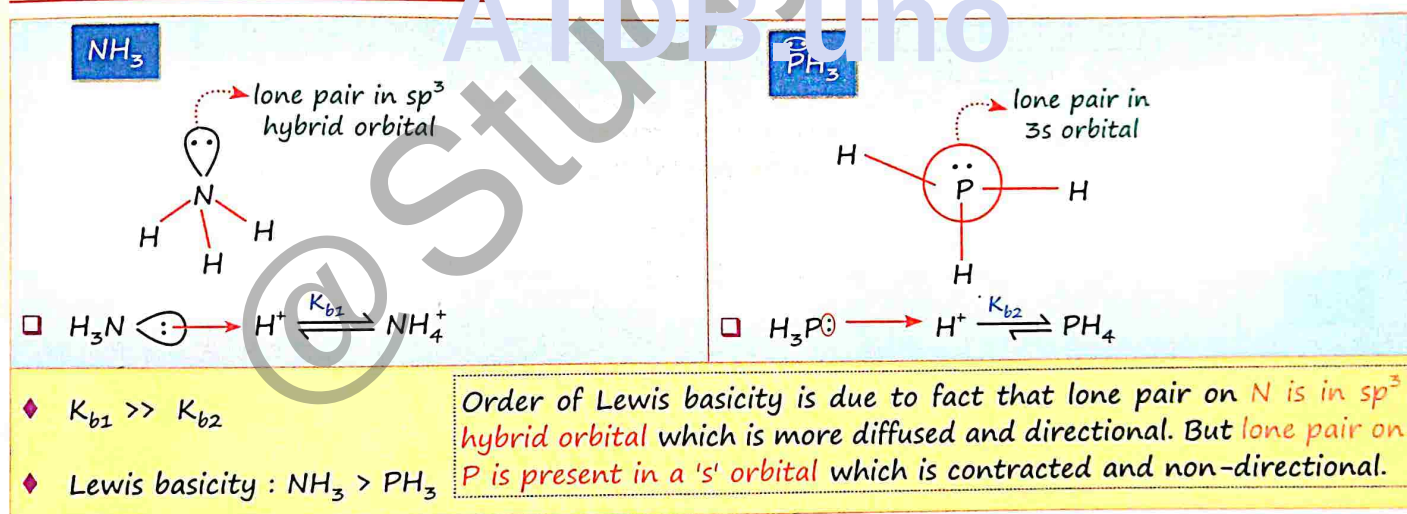
CA with lone pair :  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{O}$

CA with -ve charge :  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$





### Lewis Basicity $\text{NH}_3$ vs $\text{PH}_3$



(IIT JEE 2002)

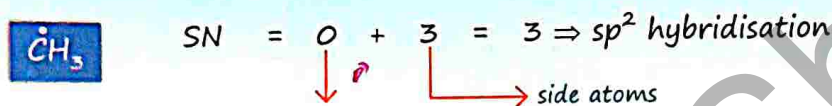
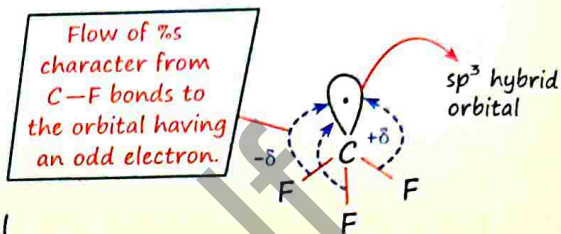
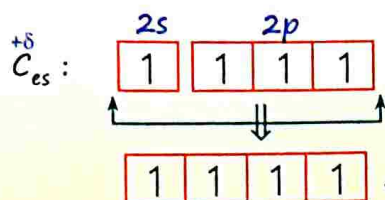
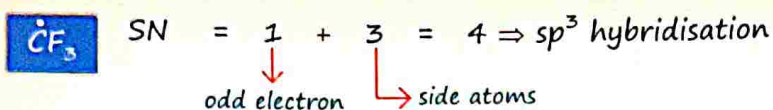
58. Specify the coordination geometry around and hybridising N and B atoms in a 1 : 1 complex of  $\text{BF}_3$  and  $\text{NH}_3$ .

- (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,  $sp^2$

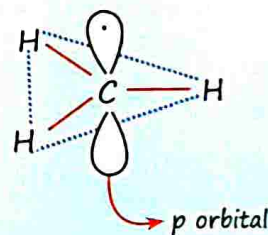
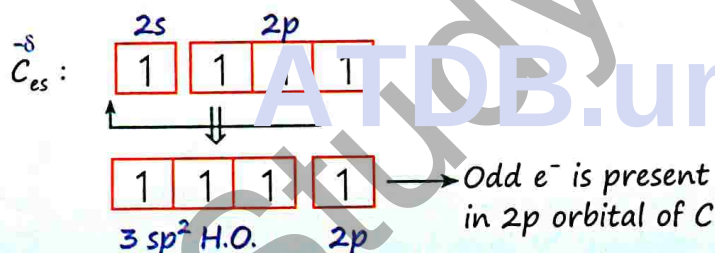
Sol. (a)

## HYBRIDISATION IN ODD ELECTRON SPECIES

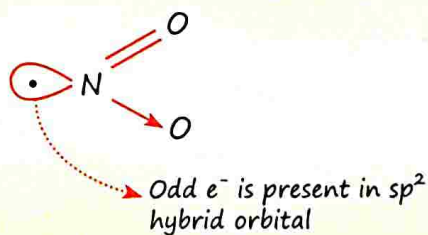
- When side atoms are more electronegative than central atom then odd electrons are considered in steric number to find hybridisation.



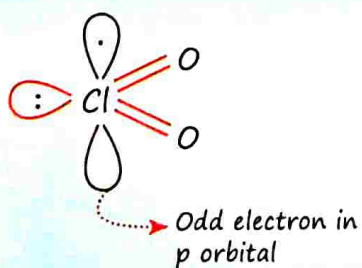
[odd electron is not considered because side atom H is less electronegative than central atom C]



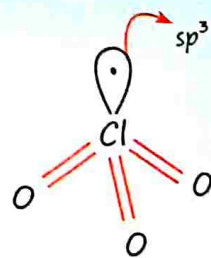
- SN = 1 + 2 = 3
- sp<sup>2</sup> hybridisation



- SN = 1 + 2 = 3
- sp<sup>2</sup> hybridisation



- SN = 1 + 3 = 4
- sp<sup>3</sup>

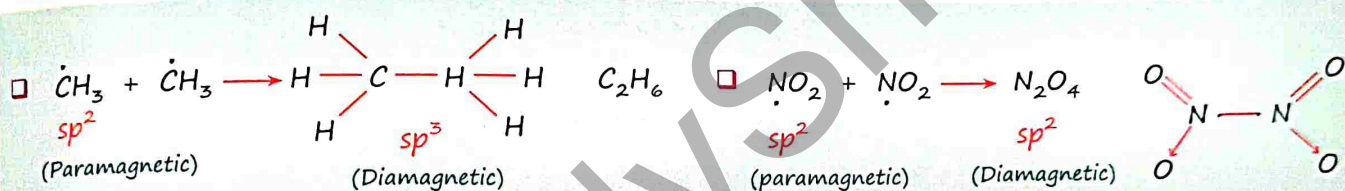




| Odd e <sup>-</sup> molecule        | Orbital having odd electron | hyb <sup>n</sup> of central atom |
|------------------------------------|-----------------------------|----------------------------------|
| $\dot{\text{C}}\text{H}_3$         | p                           | $sp^2$                           |
| $\dot{\text{C}}\text{F}_3$         | $sp^3$                      | $sp^3$                           |
| $\dot{\text{N}}\text{O}_2$         | $sp^2$                      | $sp^2$                           |
| $\dot{\text{C}}\text{I}\text{O}_3$ | $sp^3$                      | $sp^3$                           |
| $\dot{\text{C}}\text{I}\text{O}_2$ | p                           | $sp^2$                           |

### Dimer Formation - Hybridisation Change & Magnetic Behaviour

2 unit



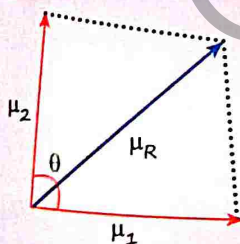
### DIPOLE MOMENT

Product of the magnitude of the charge and the distance between the centers of the positive and negative charges.

Dipole moment = charge  $\times$  distance of separation

$$\text{Dipole moment } \mu = q \cdot l$$

Dipole moment is a vector quantity when 2 vectors ( $\mu_1$  &  $\mu_2$ ) are separated by  $\theta$  then we can calculate resultant  $\mu_R$ .



$$\square \mu_R^2 = \mu_1^2 + \mu_2^2 + 2\mu_1 \cdot \mu_2 \cos \theta$$

$$\square \cos \theta \uparrow : \mu_R \uparrow$$

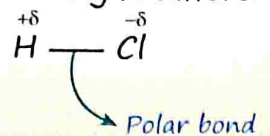
$$\square \theta \uparrow : \cos \theta \downarrow : \mu_R \downarrow$$

Unit  $\equiv \text{C} \cdot \text{m}$   
 $\equiv \text{esu} \cdot \text{cm}$   
 $\equiv \text{Debye [D]}$   
 C  $\rightarrow$  Coulomb  
 m  $\rightarrow$  metre  
 esu  $\rightarrow$  Electrostatic unit of charge

$$1 \text{ Debye} = 10^{-18} \text{ esu cm}$$

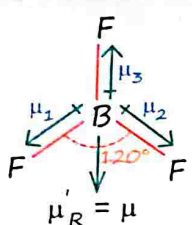
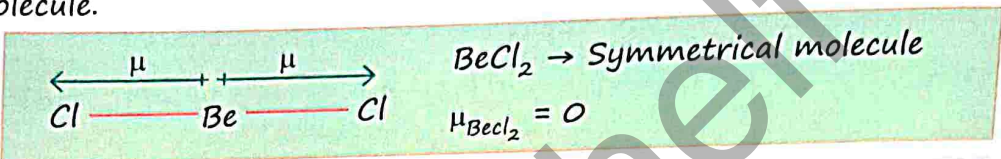
$$\text{Charge on } e^- \rightarrow q_e = 1.6 \times 10^{-19} \text{ C}$$

$$= 4.8 \times 10^{-10} \text{ esu}$$

| Polar Molecule ( $\mu_R \neq 0$ )                                                                                                                                                                                                                                                                               | Non-polar Molecule ( $\mu_R = 0$ )                                                                                                                                                                                                                                    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"><li>Hetero-nuclear diatomic</li><li>Molecule having 2 different atoms</li><li>HCl <math>\begin{array}{c} +\delta \quad -\delta \\ \text{H} \quad \text{Cl} \end{array}</math><br/></li></ul> | <ul style="list-style-type: none"><li>Homonuclear diatomic</li><li>Molecule having 2 same atoms</li><li><math>\text{H}_2, \text{F}_2, \text{O}_2, \text{N}_2</math><br/></li></ul> |

## Symmetry and Dipole Moment

A polyatomic molecule having polar covalent bonds and **symmetrical structure** indicates the zero dipole moment of the molecule.

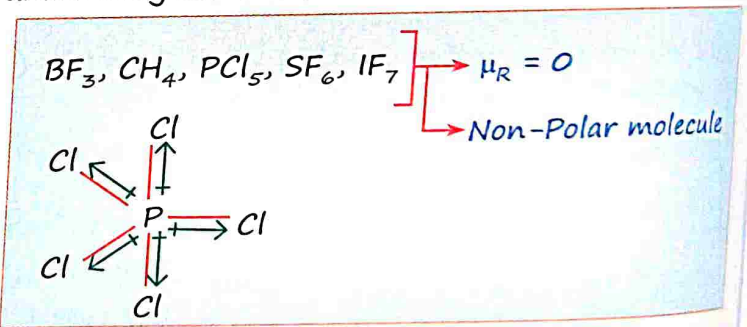
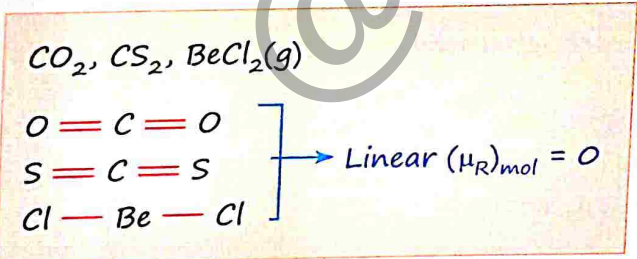


- $\text{BF}_3 \rightarrow$  Symmetrical molecule
- $\mu_{\text{BF}_3} = 0$
- $\text{BF}_3 \rightarrow$  Non polar molecule

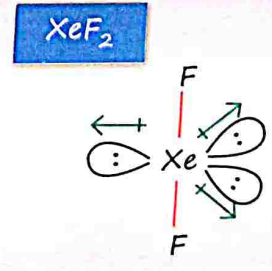
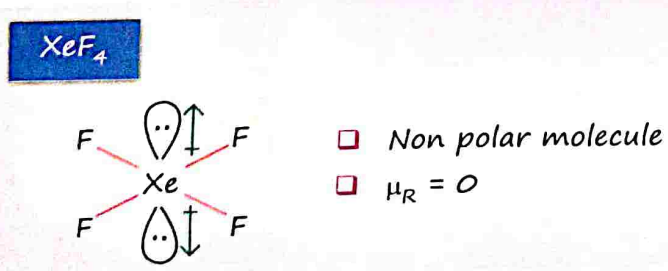
$\mu_R^2 = \mu_1^2 + \mu_2^2 + 2\mu_1 \cdot \mu_2 \cos 120^\circ$   
 $\mu_R = 0$  [  $\mu_1 = \mu_2 = \mu$  ]

## Symmetrical Molecule

- Symmetrical molecules are non-polar molecules.
- 1. Molecule having no lone pair on central atom and having same side atoms.



- 2. Molecule having lone pairs on central atom but in such a way that they can cancel each others dipole moment.

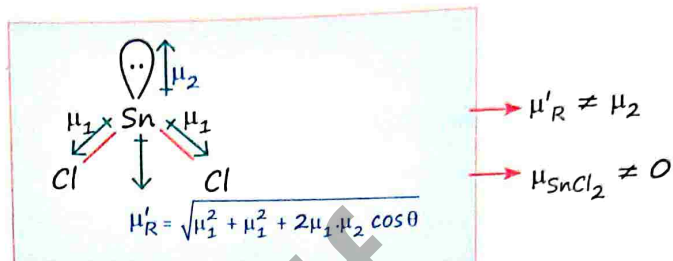




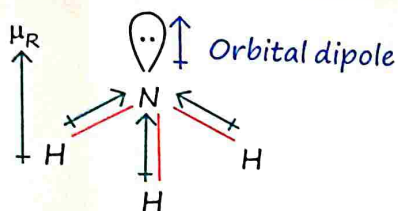
## Unsymmetrical Molecule

Molecule having lone pairs on central atom but in such a way that they can not cancel each others dipole moment.

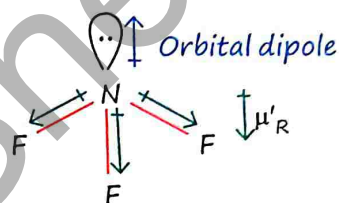
$\text{SnCl}_2, \text{PbCl}_2, \text{SO}_2$  : Angular mol. : Polar  
 $\text{NH}_3, \text{H}_2\text{O}, \text{NF}_3, \text{SF}_4, \text{H}_2\text{S}$  : Polar molecule



$\text{NH}_3$



$\text{NF}_3$  : Dipole moment

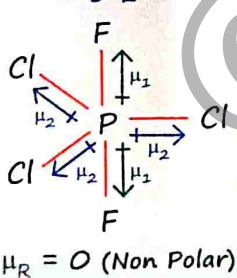


In case of  $\text{NH}_3$ , the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N - H bonds. In  $\text{NF}_3$ , the orbital dipole is in the direction opposite to the resultant dipole moment of the three N - F bonds.

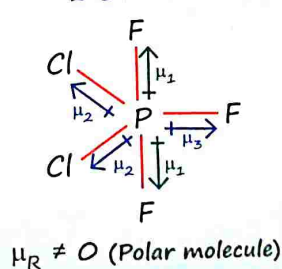
The orbital dipole because of lone pair decreases the effect of the resultant N - F bond moments, which results in the low dipole moment of  $\text{NF}_3$ .

□

$\text{PCl}_3\text{F}_2$

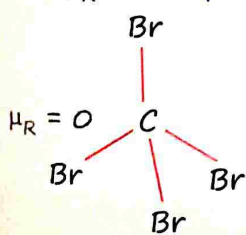


$\text{PCl}_2\text{F}_3$

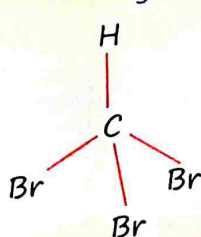


□

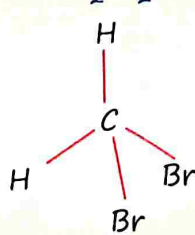
$\mu_R \rightarrow \text{CBr}_4$



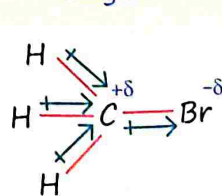
$\text{CHBr}_3$



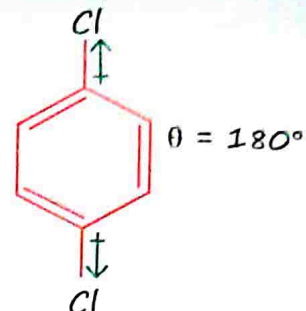
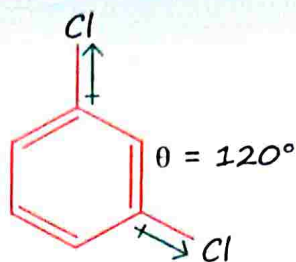
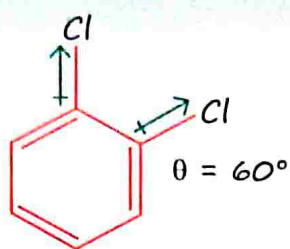
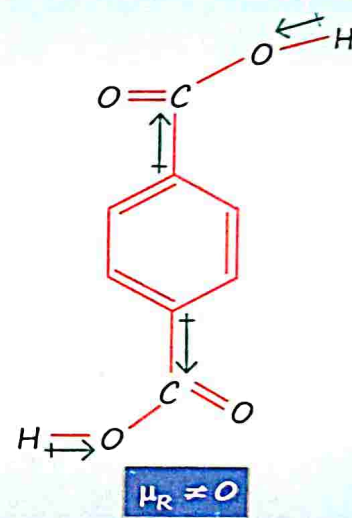
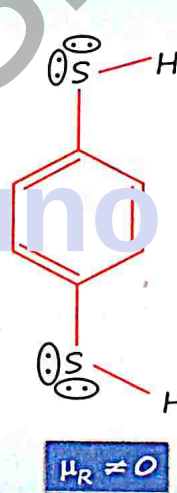
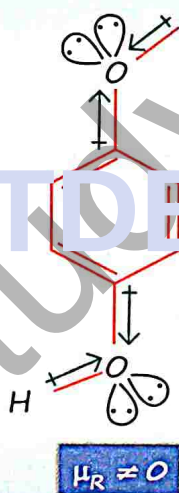
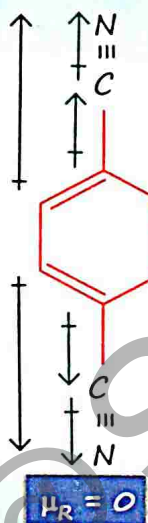
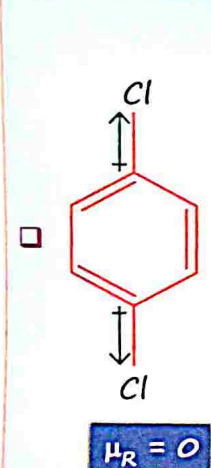
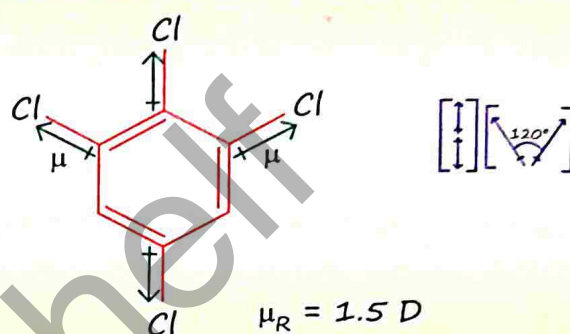
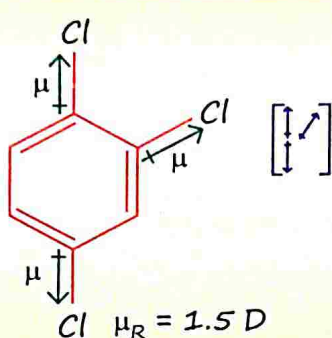
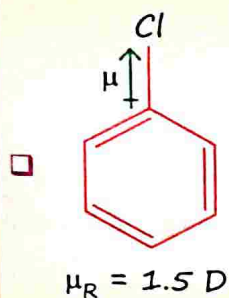
$\text{CH}_2\text{Br}_2$



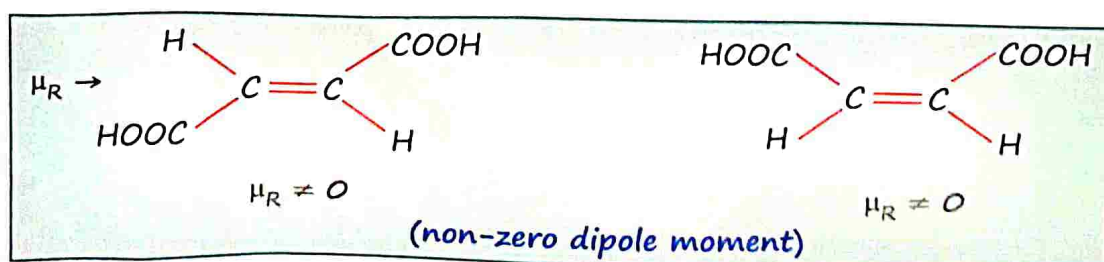
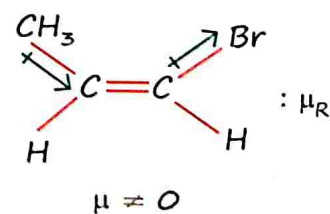
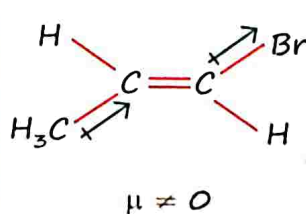
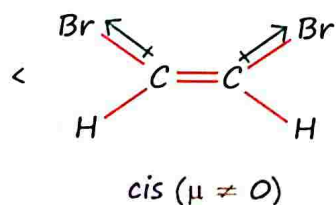
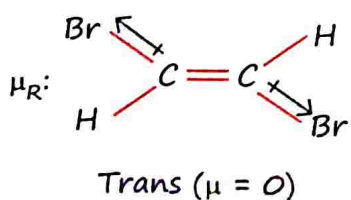
$\text{CH}_3\text{Br}$



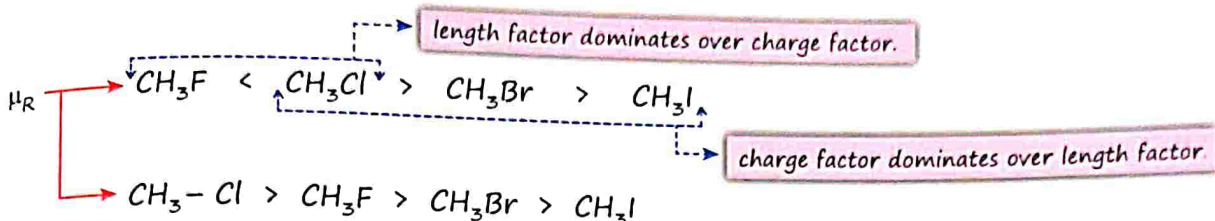
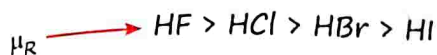
$$\mu_R \uparrow : \theta \downarrow : \cos\theta \uparrow$$


$$\mu_R: \text{ortho-dichlorobenzene} > \text{meta-dichlorobenzene} > \text{para-dichlorobenzene}$$


## Cis & Trans

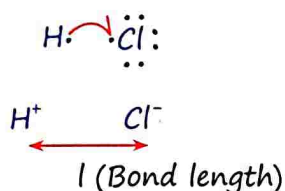






## % Ionic Character in Covalent Bond

$$\% \text{ ionic character} = \frac{\mu_{(exp/obs)}}{\mu_{(cal/theo)}} \times 100$$



For 100% ionic character—  
It is assumed that 1 electron is completely transferred from one atom to another.

59. For HCl gas molecule  $\mu = 1.03 \text{ D}$  and bond distance =  $1.275 \text{ \AA}$ . Calculate the % ionic character.

Sol.  $\mu_{\text{exp}} = 1.03 \text{ D}$

$$l = 1.275 \times 10^{-8} \text{ cm}$$

$\mu_{\text{cal}} = ?$

$$\mu_{\text{cal}} = q_e \cdot l$$

$$= (4.8 \times 10^{-10} \text{ esu}) \cdot (1.275 \times 10^{-8} \text{ cm})$$

$$= (4.8 \times 1.275) \cdot (10^{-18} \text{ esu} \cdot \text{cm}) = (4.8 \times 1.275) \text{ D}$$

$$\% \text{ ionic character} = \frac{1.03}{(4.8 \times 1.275)} \times 100\%$$

$$= 0.1683 \times 100 = 16.83\%$$

60. Among the following, the molecule with the highest dipole moment is (IIT JEE 2003)

- (a)  $\text{CH}_3\text{Cl}$  (b)  $\text{CH}_2\text{Cl}_2$  (c)  $\text{CHCl}_3$  (d)  $\text{CCl}_4$

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)  $\text{SO}_2$ ,  $\text{C}_6\text{H}_5\text{Cl}$ ,  $\text{H}_2\text{Se}$ ,  $\text{BrF}_5$  (b)  $\text{BeCl}_2$ ,  $\text{CO}_2$ ,  $\text{BCl}_3$ ,  $\text{CHCl}_3$   
 (c)  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{POCl}_3$ ,  $\text{CH}_3\text{Cl}$  (d)  $\text{BF}_3$ ,  $\text{O}_3$ ,  $\text{SF}_6$ ,  $\text{XeF}_6$

Sol. (a, c)

62. Which one of the following molecules has maximum dipole moment? [04 April, 2024 (Shift-I)]  
 (a)  $\text{NF}_3$  (b)  $\text{CH}_4$  (c)  $\text{NH}_3$  (d)  $\text{PF}_5$

Sol. (c)

63. Given below are two statements: one is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A):  $\text{NH}_3$  and  $\text{NF}_3$  molecule have pyramidal shape with a lone pair of electrons on nitrogen atom. The resultant dipole moment of  $\text{NH}_3$  is greater than that of  $\text{NF}_3$ .

Reason (R): In  $\text{NH}_3$ , 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-I)]

- (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)  $\text{CCl}_4$  (b)  $\text{HI}$  (c)  $\text{CO}_2$  (d)  $\text{BF}_3$

Sol. (b)

65. Identify the correct answer. [NEET 2024]

- (a) Dipole moment of  $\text{NF}_3$  is greater than that of  $\text{NH}_3$ .  
 (b) Three canonical forms can be drawn for  $\text{NO}_2^-$ .  
 (c) Three resonance structures can be drawn for ozone.  
 (d)  $\text{BF}_3$  has non-zero dipole moment.

Sol. (b)

66. The correct order of dipole moments for molecules  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{CH}_4$  and  $\text{HF}$ , is: [NEET 2023-Manipur]  
 (a)  $\text{CH}_4 > \text{H}_2\text{S} > \text{NH}_3 > \text{HF}$  (b)  $\text{H}_2\text{S} > \text{NH}_3 > \text{HF} > \text{CH}_4$   
 (c)  $\text{NH}_3 > \text{HF} > \text{CH}_4 > \text{H}_2\text{S}$  (d)  $\text{HF} > \text{NH}_3 > \text{H}_2\text{S} > \text{CH}_4$

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-dichlorobenzene  
 (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  $\text{NH}_3$  (1.5 D) is larger than that of  $\text{NF}_3$  (0.2 D). This is because: [NEET 2006]

- (a) In  $\text{NH}_3$  as well as in  $\text{NF}_3$ , the atomic dipole and bond dipole are in the same direction  
 (b) In  $\text{NH}_3$ , the atomic dipole and bond dipole are in the same direction whereas in  $\text{NF}_3$  these are in opposite directions  
 (c) In  $\text{NH}_3$ , as well as  $\text{NF}_3$  the atomic dipole and bond dipole are in opposite directions  
 (d) In  $\text{NH}_3$ , the atomic dipole and bond dipole are in the opposite directions whereas, in  $\text{NF}_3$  these are in the same directions

Sol. (b)



69. Identify the correct orders against the property mentioned
- $\text{H}_2\text{O} > \text{NH}_3 > \text{CHCl}_3$  – dipole moment
  - $\text{XeF}_4 > \text{XeO}_3 > \text{XeF}_2$  – number of lone pairs on central atom
  - $\text{O} - \text{H} > \text{C} - \text{H} > \text{N} - \text{O}$  – bond length
  - $\text{N}_2 > \text{O}_2 > \text{H}_2$  – bond enthalpy

Choose the correct answer from the options given below:

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

[NEET 2025]

Sol. (a)

70.  $\text{H}_2\text{O}$  is dipolar, whereas  $\text{BeF}_2$  is not. It is because

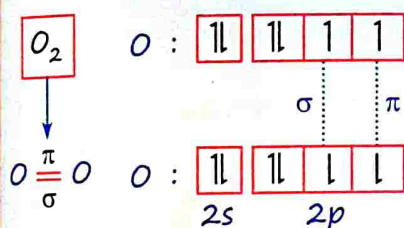
- $\text{H}_2\text{O}$  involves hydrogen bonding whereas  $\text{BeF}_2$  is a discrete molecule
- $\text{H}_2\text{O}$  is linear and  $\text{BeF}_2$  is angular
- $\text{H}_2\text{O}$  is angular and  $\text{BeF}_2$  is linear
- The electronegativity of F is greater than that of O

[2004]

Sol. (c)

## MOLECULAR ORBITAL THEORY

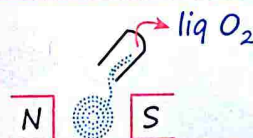
According to VBT



- All electrons are paired.
- $\text{O}_2$  is a diamagnetic molecule

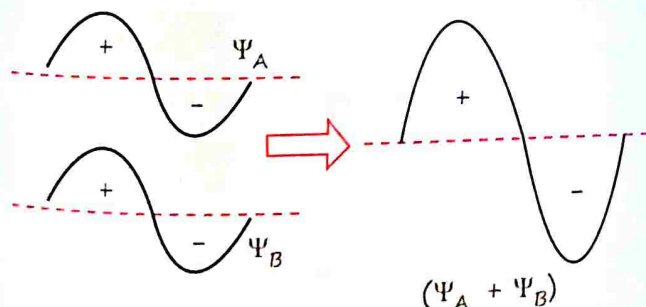
Need of new theory

- Experimental fact → (i)  $\text{O}_2$  is a paramagnetic molecule
- (i)  $\text{O}_2$  has 2 unpaired electrons

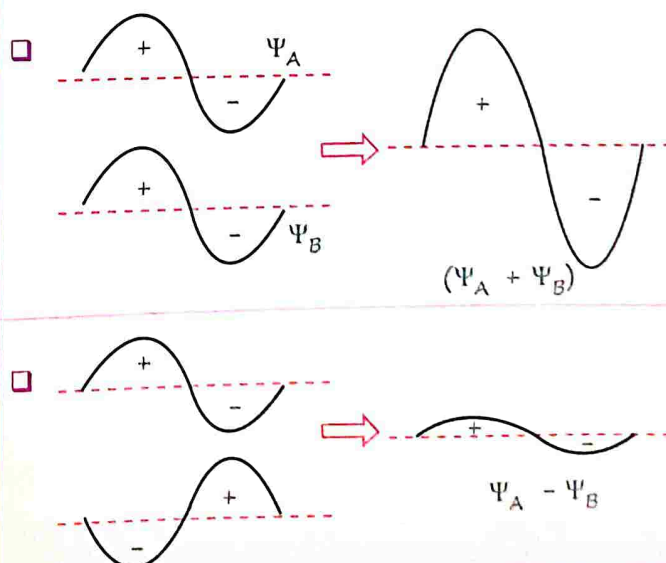


- Interaction between liq.  $\text{O}_2$  and magnetic field.

Valence Bond Theory



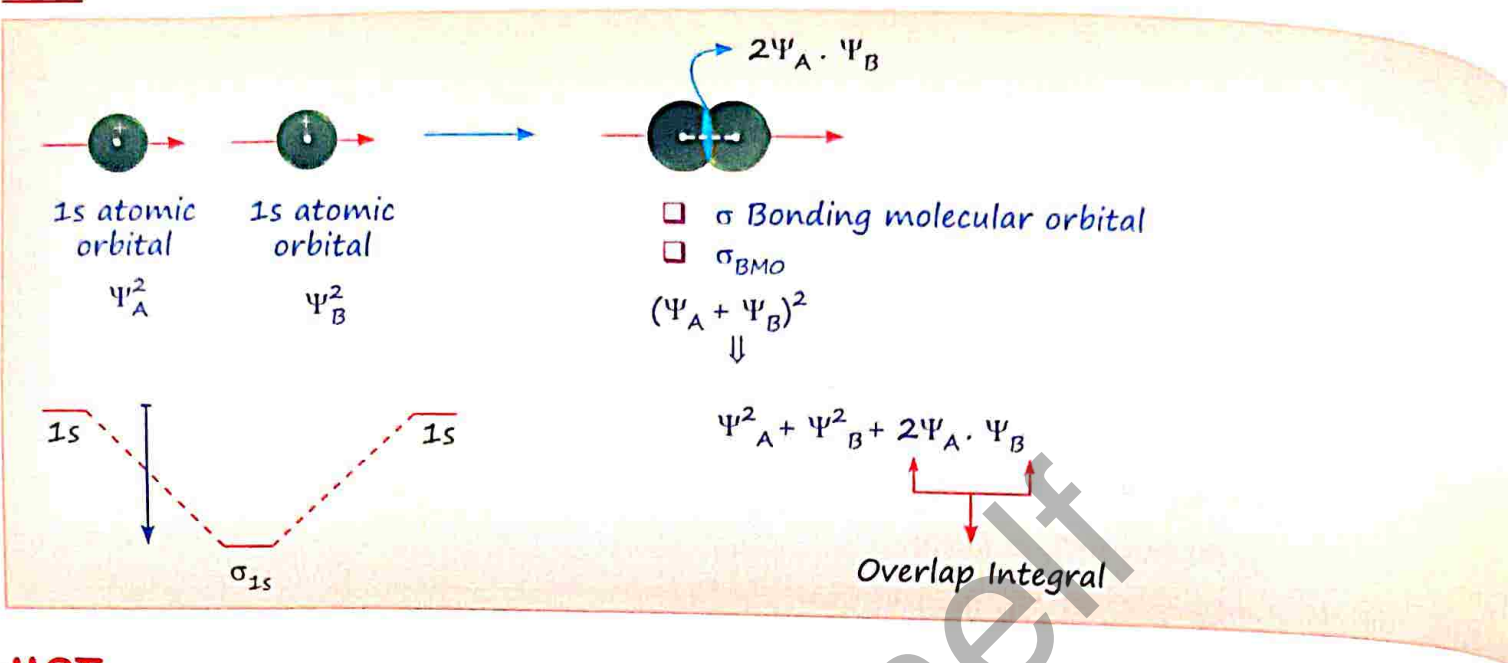
Molecular Orbital Theory



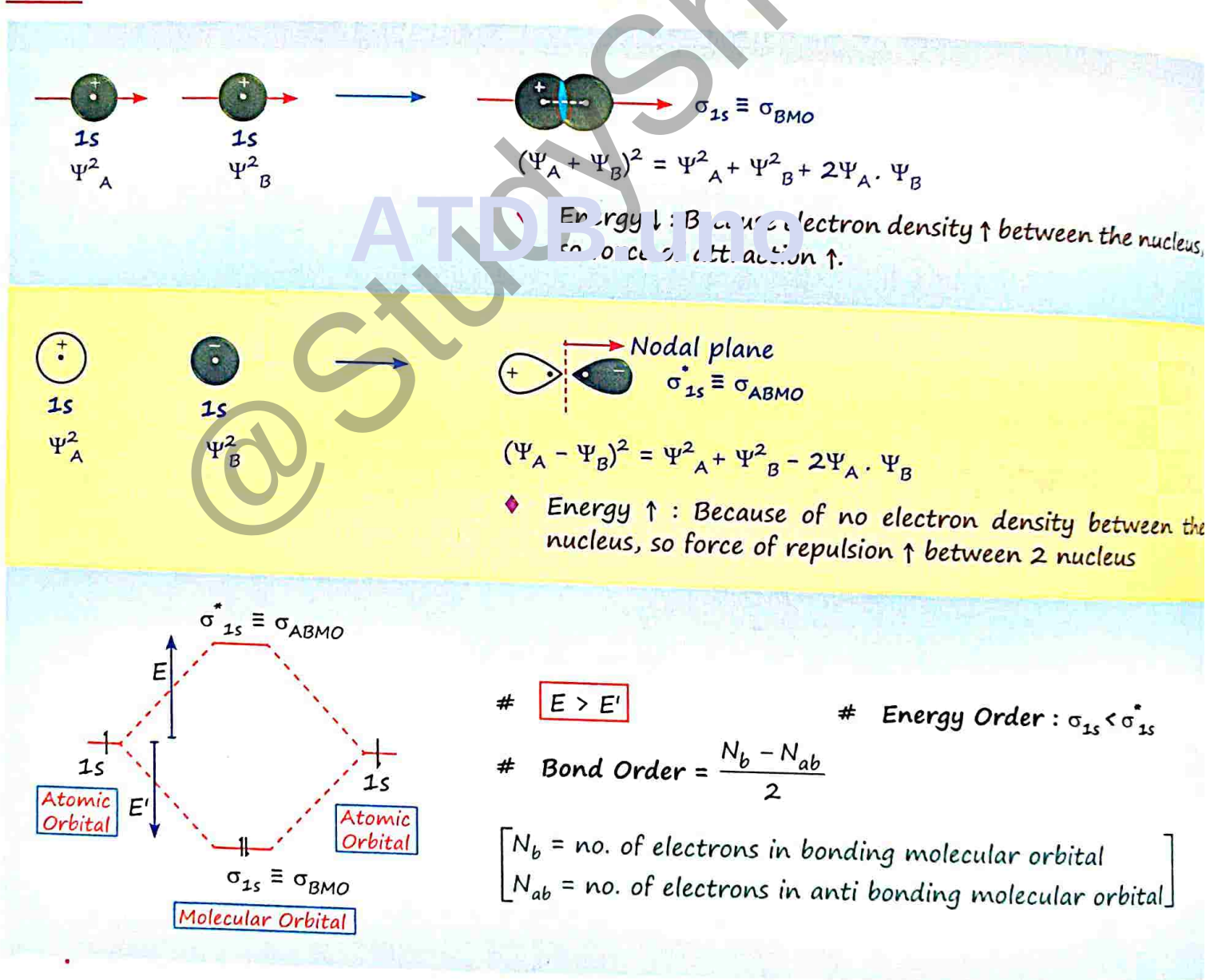
- VBT & MOT both are quantum mechanical theories of chemical bonding.

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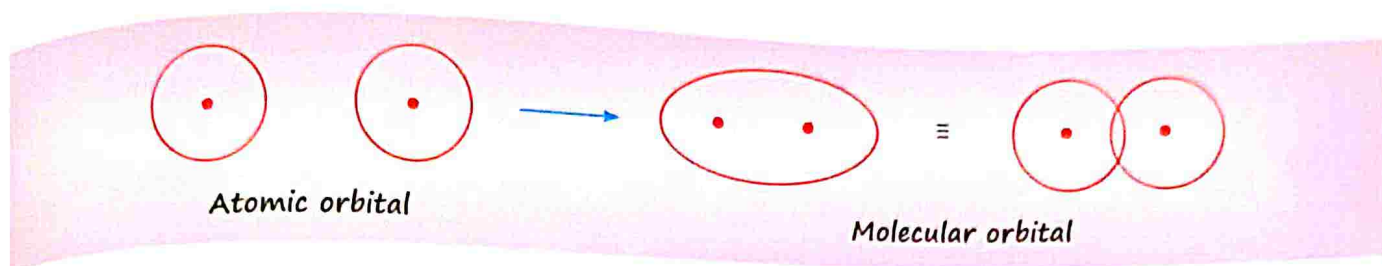
VBT



MOT

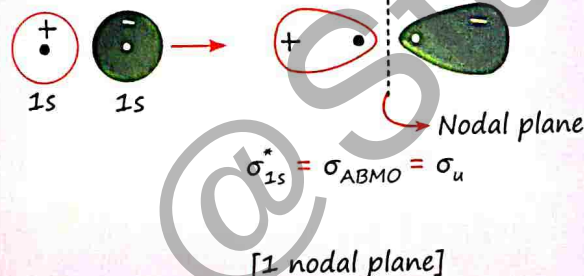
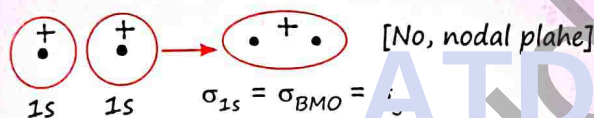






- ❑ An atomic orbital is **monocentric** while a molecular orbital is **polycentric**.
- ❑ Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.
- ❑ 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

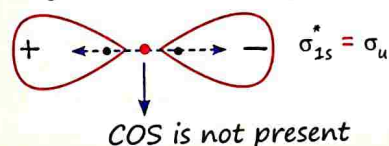


### Symmetry Term

- ❑ Gerade: Centre of symmetry is present

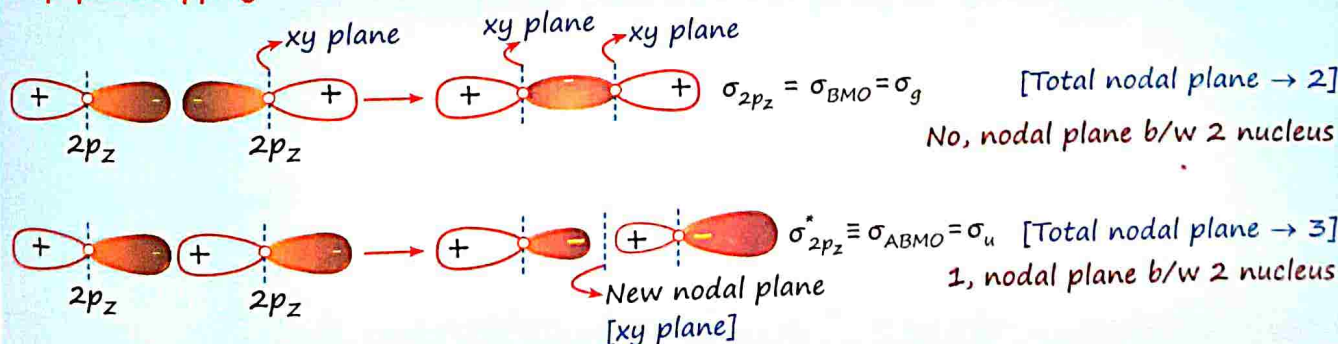


- ❑ Ungerade: COS is not present

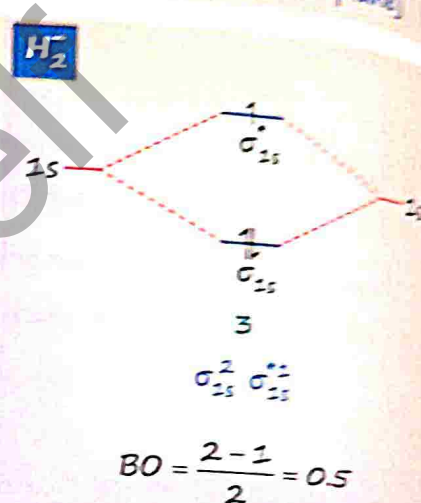
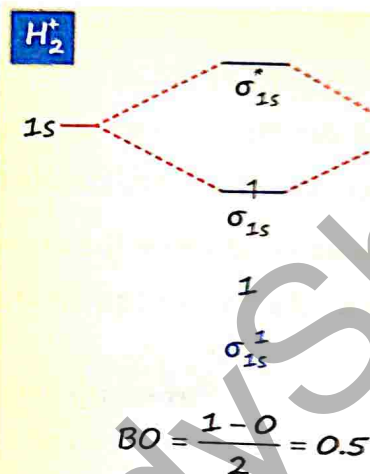
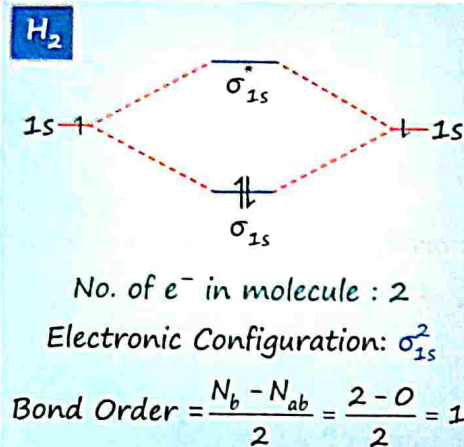
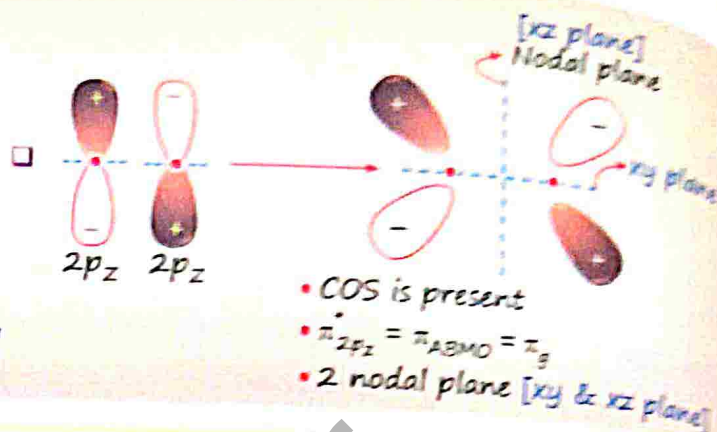
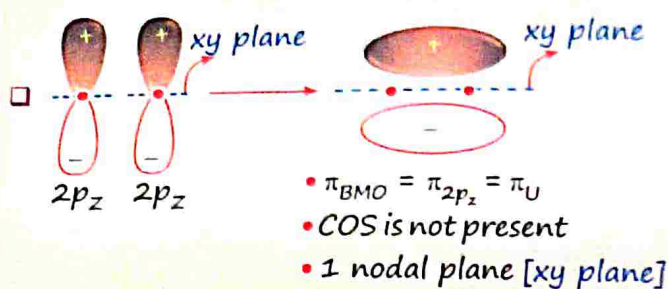


**COS** : A molecular orbital has a centre of symmetry when, for any molecular orbital in the molecule, an identical lobes (phase-wise, + or -) exists diametrically opposite to this centre at an equal distance.

### p-p overlapping



### p-p overlapping



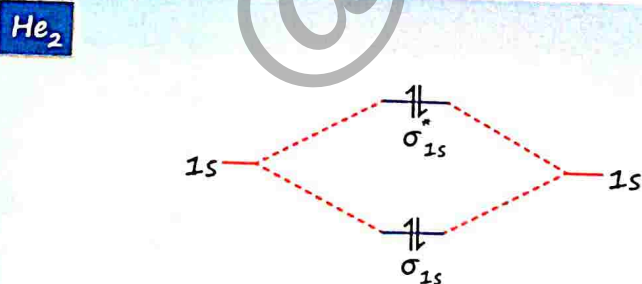
Bond Length:  $\text{H}_2 < \text{H}_2^+ < \text{H}_2^-$   
 Magnetic Behaviour: Diamagnetic

Paramagnetic

Paramagnetic

### Note

- If bond order is same  $\rightarrow N_{ab} \uparrow$  : Bond Length  $\uparrow$

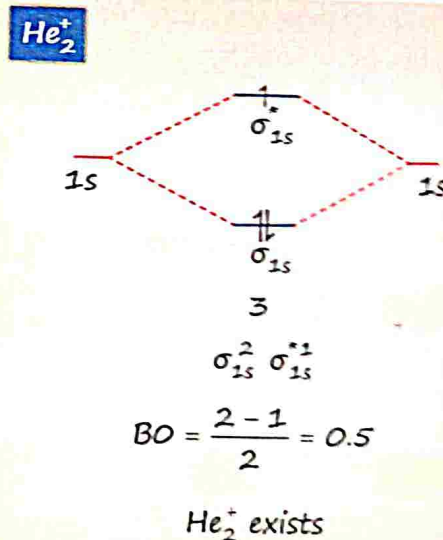


No. of e<sup>-</sup> in a molecule  $\rightarrow 4$

Electronic configuration  $\rightarrow \sigma_{1s}^2 \sigma_{1s}^{*2}$

Bond Order  $\rightarrow \frac{N_b - N_{ab}}{2} = \frac{2 - 2}{2} = 0$

Existence  $\rightarrow \text{He}_2$  molecule does not exist because He atoms are not bonded to each other.

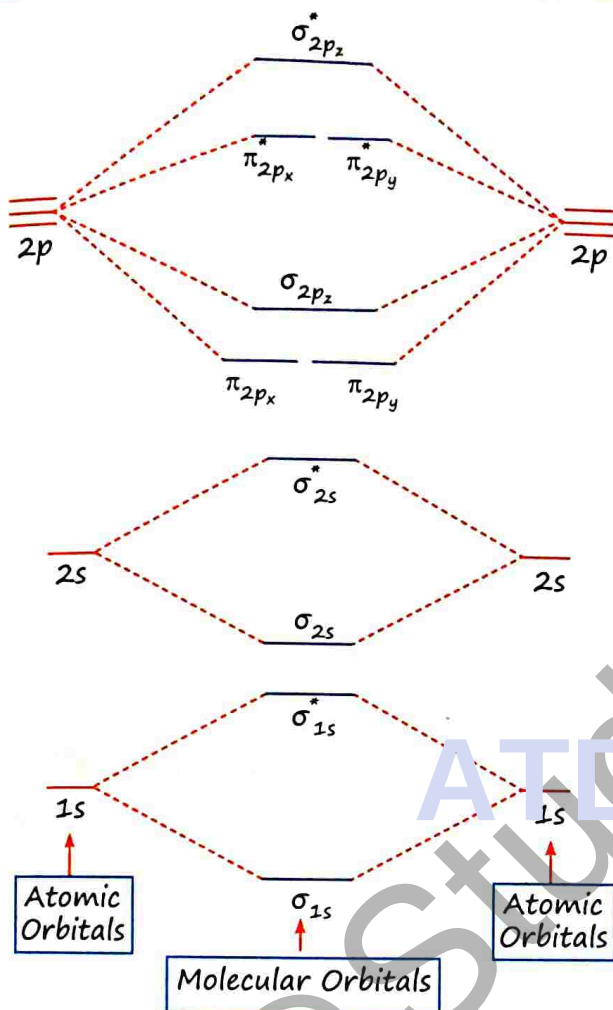




# Electronic Configuration

$n \leq 14$

[ $n \rightarrow$  no. of electrons in molecules, ions]



Energy Increases  $\rightarrow$

- 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:  $\pi_{2p} < \sigma_{2p}$

**B<sub>2</sub>**  $\rightarrow \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \left[ \begin{matrix} \pi_{2p}^1 \\ \pi_{2p}^1 \end{matrix} \right]$

(i)  $n \equiv 10$   
 (ii)  $BO \equiv \frac{N_b - N_a}{2} = \frac{6 - 4}{2} = 1$   
 (iii) 2 unpaired  $e^- \equiv$  paramagnetic behaviour

**C<sub>2</sub>**  $\rightarrow \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \left[ \begin{matrix} \pi_{2p}^2 \\ \pi_{2p}^2 \end{matrix} \right]$

(i)  $n \equiv 12$   
 (ii)  $BO \equiv 2$   
 (iii) Diamagnetic

4 electrons are present in  $\pi_{BMO}$  which indicates the presence of two  $\pi$  bonds between carbon atoms with no  $\sigma$  bond.

**N<sub>2</sub>**  $\rightarrow \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \left[ \begin{matrix} \pi_{2p}^2 \\ \pi_{2p}^2 \end{matrix} \right] \sigma_{2p}^2$

(i)  $n \equiv 14$   
 (ii)  $BO \equiv 3$   
 (iii) Diamagnetic  
 (iv) HOMO  $\rightarrow$  Highest occupied MO  $\rightarrow \sigma_{2p}$   
 (v) LUMO  $\rightarrow$  Lowest unoccupied MO  $\rightarrow \pi_{2p}^*$

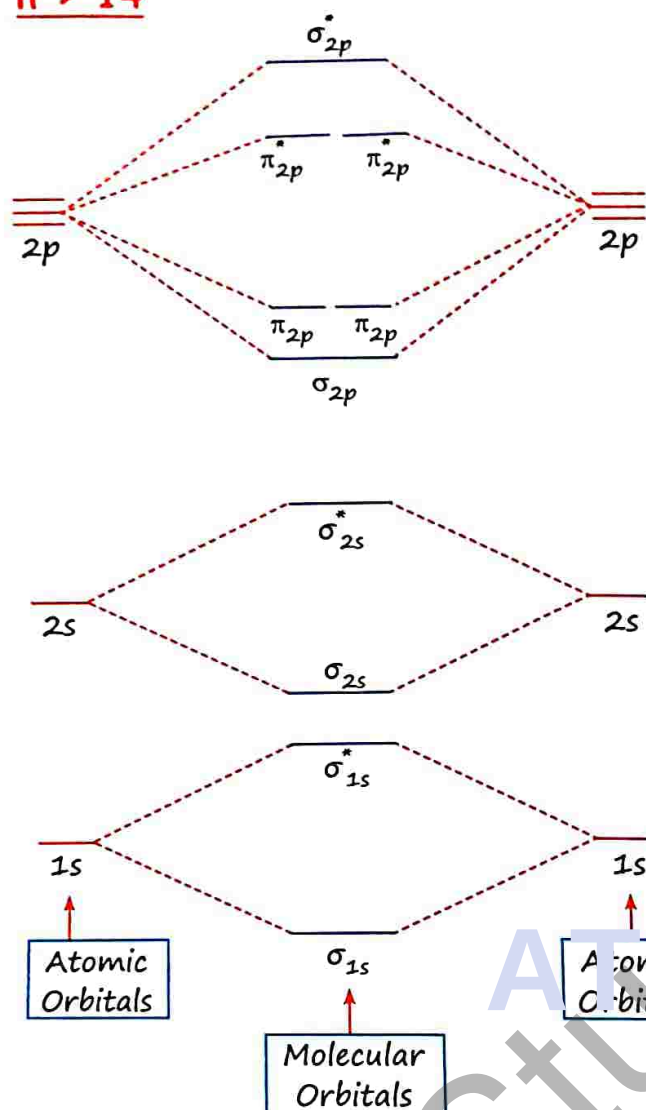
|                              | $N_2$                 | $N_2^+$       | $N_2^-$      |
|------------------------------|-----------------------|---------------|--------------|
| $N_b$                        | 10                    | 9             | 10           |
| $N_{ab}$                     | 4                     | 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 | —                     | $\sigma_{2p}$ | $\pi_{2p}^*$ |

**N<sub>2</sub>** Remove 1  $e^-$  from  $\sigma_{2p}$   $\rightarrow$  **N<sub>2</sub><sup>+</sup>** Energy Order  $\rightarrow \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \left[ \begin{matrix} \pi_{2p}^2 \\ \pi_{2p}^2 \end{matrix} \right] \sigma_{2p}^1$

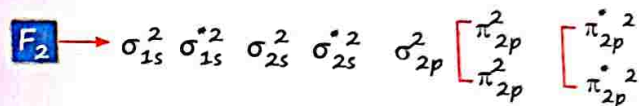
Add 1  $e^-$  in  $\pi_{2p}^*$   $\rightarrow$  **N<sub>2</sub><sup>-</sup>** Energy Order:  $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \left[ \begin{matrix} \pi_{2p}^2 \\ \pi_{2p}^2 \end{matrix} \right] \sigma_{2p}^2 \left[ \begin{matrix} \pi_{2p}^{*1} \\ \pi_{2p}^{*1} \end{matrix} \right]$

□ We can remove an electron from  $\sigma_{2p}$  molecular orbital of  $N_2$  by applying ionisation energy of  $N_2$  molecule.

$n > 14$



- Energy Increases  $\rightarrow$
- Energy Order:  $\sigma_{1s} \sigma_{1s}^* \sigma_{2s} \sigma_{2s}^* \sigma_{2p} \left[ \begin{matrix} \pi_{2p_x} \\ \pi_{2p_y} \end{matrix} \right] \left[ \begin{matrix} \pi_{2p_x}^* \\ \pi_{2p_y}^* \end{matrix} \right] \sigma_{2p}^*$
  - No, s-p mixing  $\rightarrow$  Energy:  $\sigma_{2p} < \pi_{2p}$



(i)  $n \equiv 18$

(ii)  $BO \equiv \frac{10 - 8}{2} = 1$

(iii) HOMO  $\rightarrow$  Highest occupied MO  $\rightarrow \pi_{2p}^*$

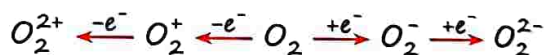
(iv) LUMO  $\rightarrow$  Lowest unoccupied MO  $\rightarrow \sigma_{2p}^*$

(v) Colour  $\rightarrow$  Pale yellow [HOMO to LUMO electronic transition is the reason behind colour]

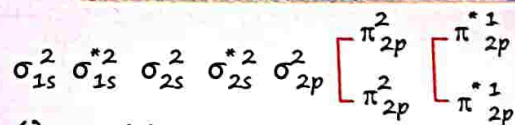
(vi) Magnetic Behaviour : Diamagnetic

$F_2$ ,  $Cl_2$ ,  $Br_2$  and  $I_2$ , all 4 are diamagnetic in nature and are colored (due to transition of electron from HOMO to LUMO  $\equiv \pi^*$  to  $\sigma^*$ ).

|                       | $O_2^{2+}$                                  | $O_2^+$ | $O_2$ | $O_2^-$ | $O_2^{2-}$ |
|-----------------------|---------------------------------------------|---------|-------|---------|------------|
| $N_b$                 | 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          |



### Electronic Configuration of $O_2$



(i)  $n = 16$

(ii) Bond order = 2

(iii) 2 unpaired electrons  $\rightarrow O_2$  is paramagnetic in nature

□ We can remove an electron from  $\pi_{2p}^*$  molecular orbital of  $O_2$  by applying 1<sup>st</sup> ionisation energy of  $O_2$  molecule.

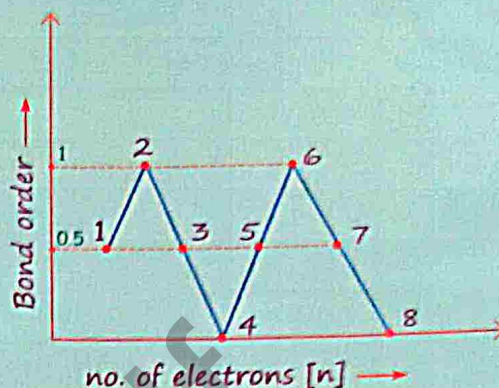


□  $S_2$  molecule is also paramagnetic with 2 unpaired electrons as  $O_2$  molecule.



## Note

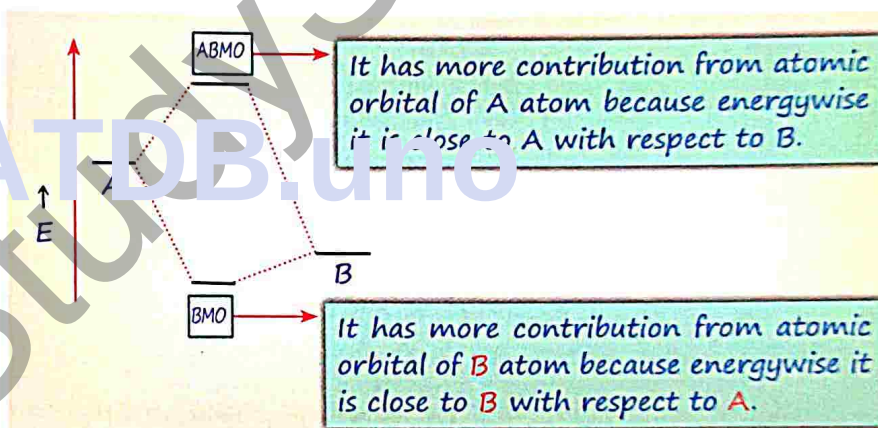
| n  | Bond Order | n  |
|----|------------|----|
| 14 | 3          |    |
| 13 | 2.5        | 15 |
| 12 | 2          | 16 |
| 11 | 1.5        | 17 |
| 10 | 1          | 18 |
| 9  | 0.5        | 19 |
| 8  | 0          | 20 |



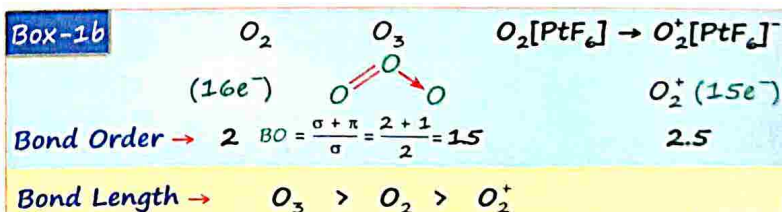
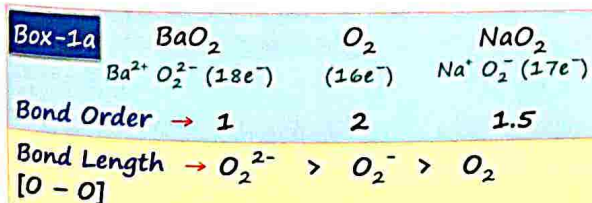
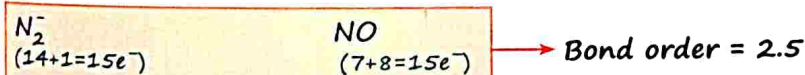
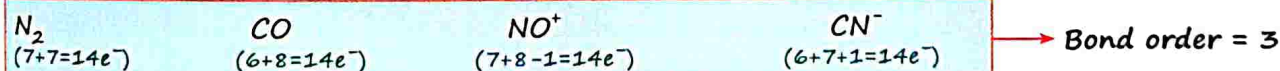
## MOT for Heteronuclear Diatomic

AB Type Molecule [ $\text{CO}$ ,  $\text{NO}$ ,  $\text{CN}^-$ ,  $\text{NO}^+$ ]

- Electronegativity:  $A < B$
- Energy of same orbital:  $A > B$



## Isoelectronic Species



Chemical Bonding and Molecular Structure

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|                                                                      |                   |                |                                       |
|----------------------------------------------------------------------|-------------------|----------------|---------------------------------------|
| <b>Box-2</b>                                                         | $KO_2 [K^+O_2^-]$ | $O_2$          | $O_2[BF_4] \rightarrow O_2^+[BF_4]^-$ |
| No. of $e^-$ in oxygen containing species $\rightarrow O_2^- (16+1)$ | 16                | $O_2^+ (16-1)$ |                                       |
| Bond Order $\rightarrow 1.5$                                         | 2                 | 2.5            |                                       |
| Bond Length $\rightarrow O_2^+ < O_2 < O_2^-$<br>[O - O]             |                   |                |                                       |

|                                                     |                 |        |             |                                                                                                                           |
|-----------------------------------------------------|-----------------|--------|-------------|---------------------------------------------------------------------------------------------------------------------------|
| <b>Box-3</b>                                        | $CO (6+8 = 14)$ | $CO_2$ | $CO_3^{2-}$ | $\begin{array}{c} O \\    \\ \bar{O}-C-\bar{O}^- \end{array}$ $BO = \frac{\sigma + \pi}{\sigma} = \frac{3 + 1}{3} = 1.33$ |
| Bond Order $\rightarrow 3$                          | 2               | 1.33   |             |                                                                                                                           |
| C-O Bond Length $\rightarrow CO < CO_2 < CO_3^{2-}$ |                 |        |             |                                                                                                                           |

|              |                                                                                                                                                             |                                  |  |
|--------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------|--|
| <b>Box-4</b> | <p><b>Bond Length:</b></p> $\begin{array}{ccc} NO & > & NO^+ \\ \downarrow & & \downarrow \\ \text{Bond order} = 2.5 & & \text{Bond order} = 3 \end{array}$ | $CO > CO^+ : \text{Bond length}$ |  |
|--------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------|--|

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)

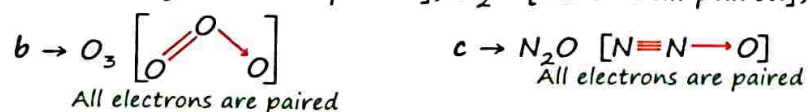
(a)  $NO^-$  (b)  $NO^+$  (c)  $CN^-$  (d)  $N_2$

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  $\rightarrow 2Na^+ [10 e^- : \text{all paired}], O_2^{2-} [18 e^- : \text{all paired}],$



d  $\rightarrow K^+ [18 e^- : \text{all paired}], O_2^- [17 e^- : 1 \text{ unpaired}]$



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 $\pi$ antibonding    |
| B.       |  | 2.        | d-d $\sigma$ bonding     |
| C.       |  | 3.        | p-d $\pi$ bonding        |
| D.       |  | 4.        | d-d $\sigma$ 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)
- $\sigma$  orbital has a total of two nodal planes.
  - $\sigma^*$  orbital has one node in the xz-plane containing the molecular axis.
  - $\pi$  orbital has one node in the plane which is perpendicular to the molecular axis and goes through the center of the molecule.
  - $\pi^*$  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)
- $C_2^{2-}$  is expected to be diamagnetic
  - $O_2^{2+}$  is expected to have a longer bond length than  $O_2$
  - $N_2^+$  and  $N_2^-$  have the same bond order
  - $He_2^+$  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)  $\sigma^*2p_z$  (b)  $\pi 2p_y$  (c)  $\pi^*2p_x$  (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-I)]

- (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)

|                                                                                   |                                                                                     |                                                                                      |                                                                                      |
|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| <input type="checkbox"/> $NO \longrightarrow NO^+$<br>B.O-2.5    3<br>Para    Dia | <input type="checkbox"/> $N_2 \longrightarrow N_2^+$<br>B.O-3    2.5<br>Dia    Para | <input type="checkbox"/> $O_2 \longrightarrow O_2^+$<br>B.O-2    2.5<br>Para    Para | <input type="checkbox"/> $O_2 \longrightarrow O_2^{2-}$<br>B.O-2    1<br>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  $\Rightarrow$  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 =  $NO_2$ ,  $NO$ ,  $ClO_2$ ,  $NO$

82. Match List-I with List-II.

[27 July, 2022 (Shift-I)]

| 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)

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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<sub>2</sub> (C) O<sub>2</sub> (D) C<sub>2</sub> (E) B<sub>2</sub>

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  $\pi$  bonding MO has lower electron density above and below the inter-nuclear axis.  
Statement-II: The  $\pi^*$  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<sub>2</sub> 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  $\pi^*$  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  $\pi$ -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  $\pi$  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  $\pi$  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)  $C_2^{2+} < C_2^+ < C_2$
- (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)  $\pi^*$  orbital
- (b)  $\pi$  orbital
- (c)  $\sigma^*$  orbital
- (d)  $\sigma$  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 2004]

- (a)  $\pi$  molecular orbital
- (b)  $\sigma$  molecular orbital
- (c)  $\delta$  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)

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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:

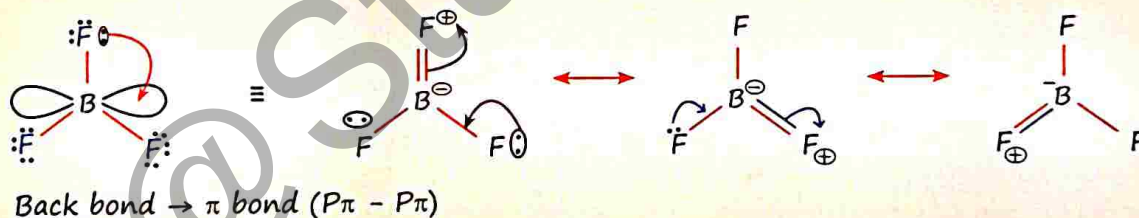
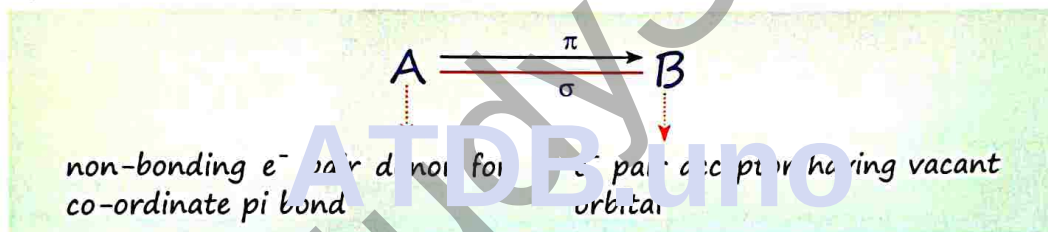
[NEET 2005]

- (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)

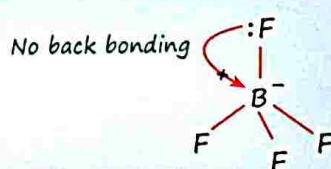
## BACK BONDING

□ Coordinate pi bond



□ Back bonding increases the bond strength and decreases the bond length.

B-F Bond length:  $BF_3 < BF_4^-$



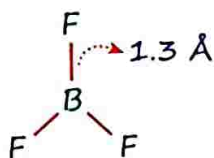
## Condition for Excellent Back Bonding

1. One atom from 2<sup>nd</sup> period
2. Second atom from 2<sup>nd</sup>/3<sup>rd</sup> period

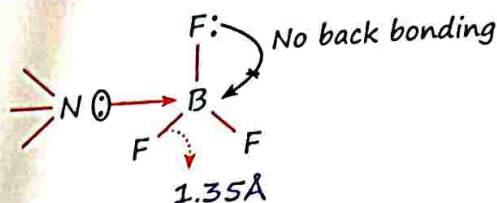
$\pi$  bond strength [back bond strength] :  $2p - 2p > 2p - 3d > 2p - 3p > 3p - 3p$

102. The B - F bond length in  $\text{Me}_3\text{N}.\text{BF}_3$  is  $1.35 \text{ \AA}$ , much longer than  $1.30 \text{ \AA}$  in  $\text{BF}_3$ . Explain?

Sol.



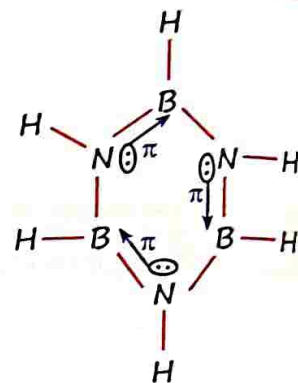
- back bonding from F to B  $\rightarrow$  small B - F bond



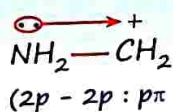
- No back bonding  $\rightarrow$  large B - F bond

### Inorganic Benzene ( $\text{B}_3\text{N}_3\text{H}_6$ )

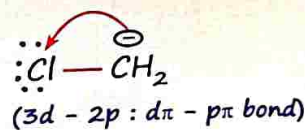
- Back bonding from N to B.
- $3\pi$  bonds [ $6\pi$  electrons]
- All nitrogen and boron are  $sp^2$  hybridised.
- Molecule is planar.
- It is an aromatic compound and isoelectronic as benzene [ $\text{C}_6\text{H}_6$ ].



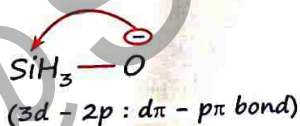
(1)



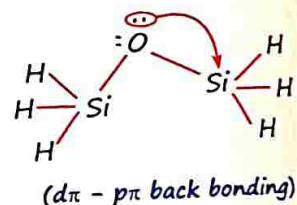
(2)



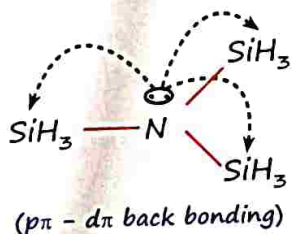
(3)



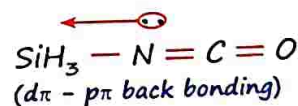
(4)  $\text{O}(\text{SiH}_3)_2$



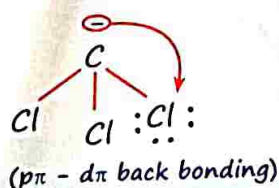
(5)



(6)



(7)



(8)

CO Molecule

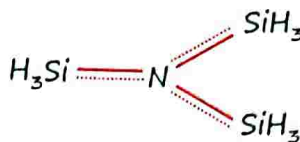
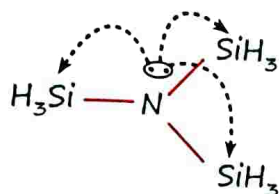




(JEE Adv. 2005)

103. Trisilylamine is a planar molecule and does not act as a Lewis base while trimethylamine is pyramidal and act as Lewis base!

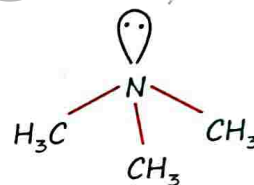
Sol.  $N(\text{SiH}_3) \rightarrow$  Trisilylamine



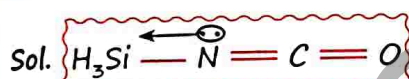
- ◆ Back bonding from N to Si
- ◆ Lone pair on nitrogen is delocalised as it is participating in back bonding with Si, so does not act as Lewis base.
- ◆ Steric no = LP + SA = 0 + 3 = 3
- ◆  $sp^2$  hybridisation (planar molecule)

$N(\text{CH}_3)_3 \rightarrow$  Trimethylamine

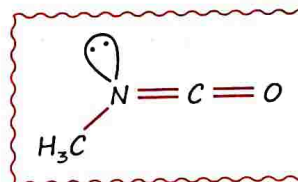
- ◆ No back bonding
- ◆ Lone pair is localised on nitrogen, so act as Lewis base
- ◆ Steric No = LP + SA = 1 + 3 = 4
- ◆  $sp^3$  hybridisation (pyramidal shape)



104. Silyl isocyanate ( $\text{SiH}_3\text{NCO}$ ) is linear but in the isocyanate ( $\text{C} \equiv \text{N}-\text{C}=\text{O}$ ) is bent explain!



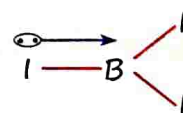
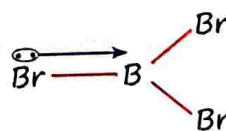
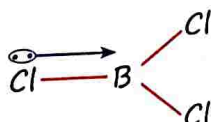
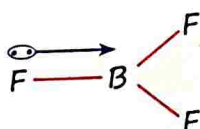
- ◆ Steric number of N : LP + SA = 0 + 2 = 2
- ◆  $sp$  hybridisation : Linear
- ◆ Back bonding from N to Si



- ◆ No back bonding
- ◆  $SN \equiv 1 + 2 \equiv 3$
- ◆  $sp^2$  hybridisation
- ◆ Bent shape

## Lewis Acidic Character

$\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$  : Lewis Acidity [Lone pair accepting tendency]



Extent of overlapping:  $2p - 2p > 3p - 2p > 4p - 2p > 5p - 2p$

(Back Bonding)

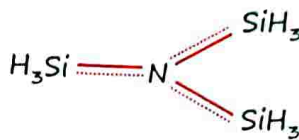
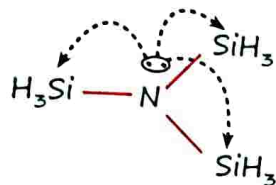
Lewis acidity:  $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$

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(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!

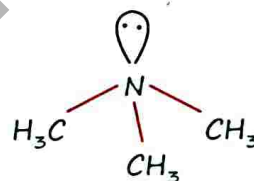
Sol.  $N(SiH_3)_3 \rightarrow$  Trisilylamine



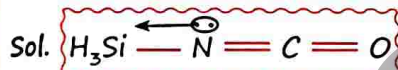
- ◆ Back bonding from N to Si
- ◆ Lone pair on nitrogen is delocalised as it is participating in back bonding with Si, so does not act as Lewis base.
- ◆ Steric no = LP + SA = 0 + 3 = 3
- ◆  $sp^2$  hybridisation (planar molecule)

$N(CH_3)_3 \rightarrow$  Trimethylamine

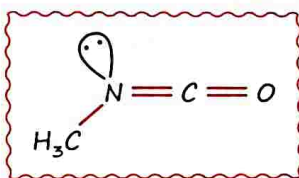
- ◆ No back bonding
- ◆ Lone pair is localised on nitrogen, so act as Lewis base
- ◆ Steric No = LP + SA = 1 + 3 = 4
- ◆  $sp^3$  hybridisation (pyramidal shape)



104. Silyl isocyanate ( $SiH_3NCO$ ) is linear but the  $C-N$  bond is bent explain!



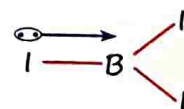
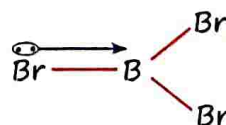
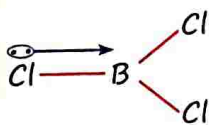
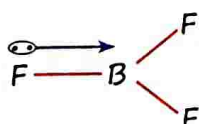
- ◆ Steric number of N : LP + SA = 0 + 2 = 2
- ◆  $sp$  hybridisation : Linear
- ◆ Back bonding from N to Si



- ◆ No back bonding
- ◆  $SN \equiv 1 + 2 \equiv 3$
- ◆  $sp^2$  hybridisation
- ◆ Bent shape

## Lewis Acidic Character

$BF_3 < BCl_3 < BBr_3 < BI_3$  : Lewis Acidity [Lone pair accepting tendency]

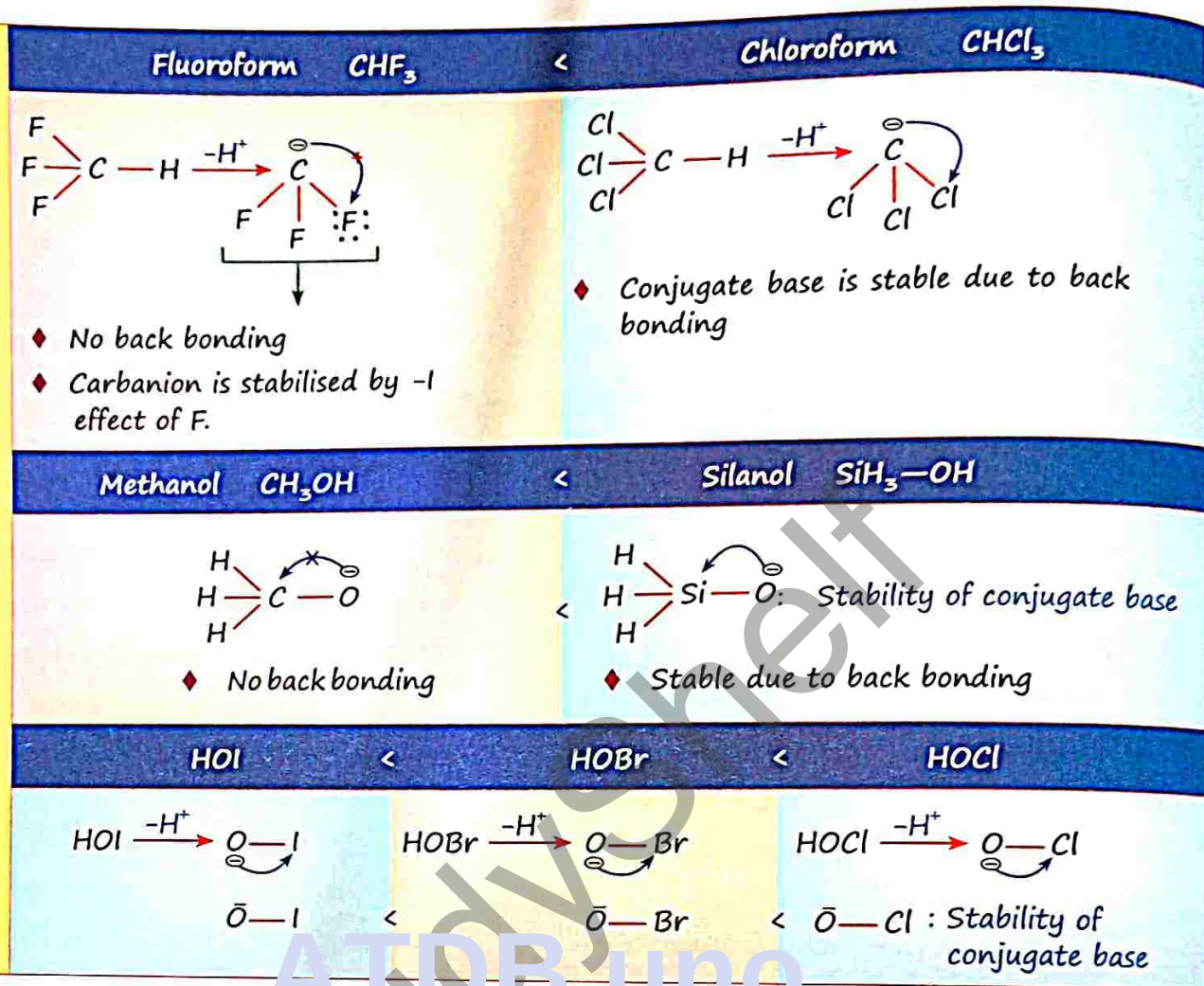


Extent of overlapping:  $2p - 2p > 3p - 2p > 4p - 2p > 5p - 2p$   
(Back Bonding)

Lewis acidity:  $BF_3 < BCl_3 < BBr_3 < BI_3$



## Acidic Nature



(IIT JEE. 1996)

105. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order.

$\text{ClOH}$  (I),  $\text{BrOH}$  (II),  $\text{IOH}$  (III)

(a)  $\text{I} > \text{II} > \text{III}$

(b)  $\text{II} > \text{I} > \text{III}$

(c)  $\text{III} > \text{II} > \text{I}$

(d)  $\text{I} > \text{III} > \text{II}$

Sol. (a)

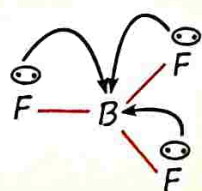
## DIMER FORMATION

**mer**  $\equiv$  Unit,

**mono-mer**  $\equiv$  Single Unit

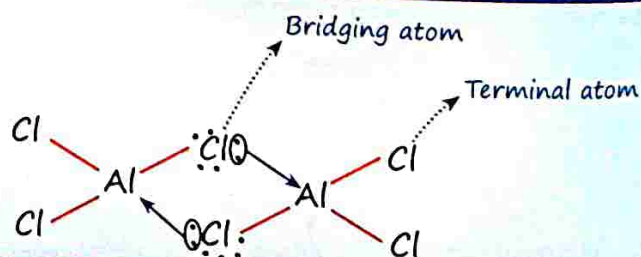
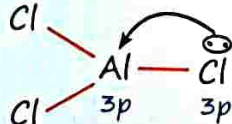
**Dimer**  $\equiv$  Combination of 2 unit

**Poly-mer**  $\equiv$  Combination of more than 2 unit



vs

$\text{AlCl}_3$



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CHEMISTRY

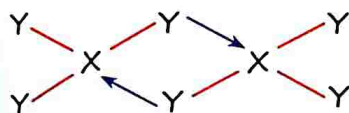
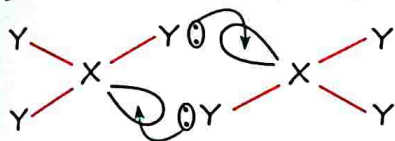


- monomer is stable due to excellent back bonding [2p - 2p]
- Monomer is not stable because back bonding from Cl to Al [3p - 3p] is not so good
- Dimer formation takes place through bridge bonding to attain stability
- $[AlCl_3]_2 \equiv Al_2Cl_6$

## BRIDGE BONDING

### Type-1

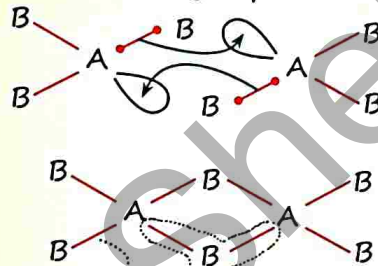
- Side atom has lone pair (Br, Cl)



- All bonds have  $2e^-$  in it  
[2 centre -  $2e^-$  bond]

### Type-2

- Side atom or group has no lone pair (-H, -CH<sub>3</sub>, -C<sub>6</sub>H<sub>5</sub>)



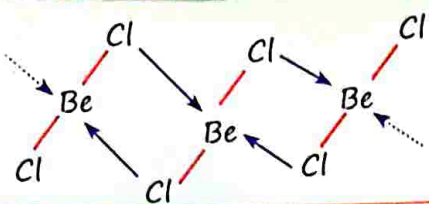
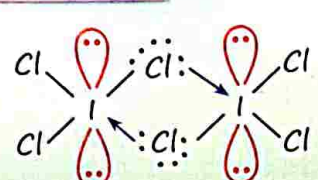
$2C - 2e^-$  bond

- Banana bond
- $3C - 2e^-$  bond
- Electron deficient bond

### Type-1

| Type-1                                                             | Hybridisation                                                                        | Max. No. of atom in same plane     |
|--------------------------------------------------------------------|--------------------------------------------------------------------------------------|------------------------------------|
| $Al_2Cl_6$<br>                                                     | Al - Cl $\rightarrow$ Al<br>$sp^3 - sp^3 - sp^3$                                     | 6<br>$[2Al, 4Cl]$<br>↓<br>Terminal |
| $BeCl_2$ at high temperature $\rightarrow$ Monomer<br>Cl - Be - Cl | Be $\rightarrow$ sp (Linear)                                                         | 3                                  |
| $BeCl_2$ in vapour phase $\rightarrow$ Dimer<br>                   | Be $\rightarrow$ $sp^2$ (planar)<br>Be - Cl $\rightarrow$ Be<br>$sp^2 - sp^3 - sp^2$ | 6                                  |

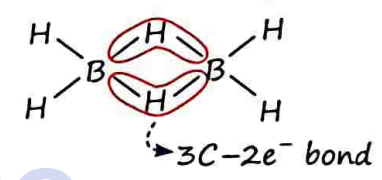


|                                                                                                                                                              |                                                                                                                                                      |                   |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|
| <p><b>BeCl<sub>2</sub> in solid phase</b> → Polymer</p>                     | <p>□ Be → sp<sup>3</sup> (Tetrahedral)<br/>                 □ Be - Cl → Be<br/>                 sp<sup>3</sup> - sp<sup>3</sup> - sp<sup>3</sup></p> | —                 |
| <p><b>I<sub>2</sub>Cl<sub>6</sub> in solid phase</b> → Planar molecule</p>  | <p>□ I - Cl - I<br/>                 sp<sup>3</sup>d<sup>2</sup> - sp<sup>3</sup> - sp<sup>3</sup>d<sup>2</sup></p>                                  | 8<br>[2I and 6Cl] |

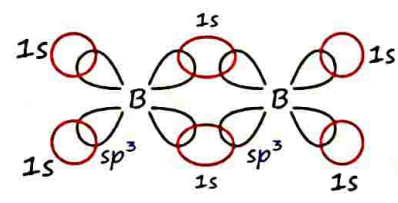
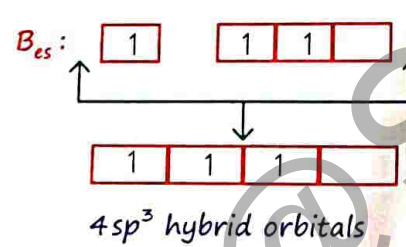
**Type-2**

**Diborane:** [BH<sub>3</sub>]<sub>2</sub> = B<sub>2</sub>H<sub>6</sub>

- B-H-B bond ≡ banana bond ≡ 3C - 2e<sup>-</sup> bond  
 ≡ Electron deficient bond



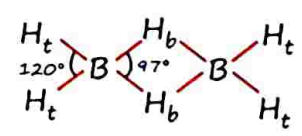
- Hybridisation of B → sp<sup>3</sup>



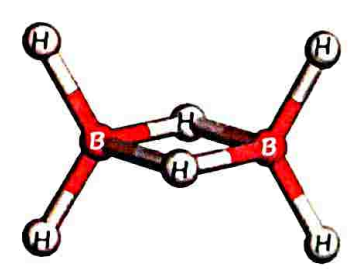
- B-H-B ⇒ sp<sup>3</sup> - 1s - sp<sup>3</sup>

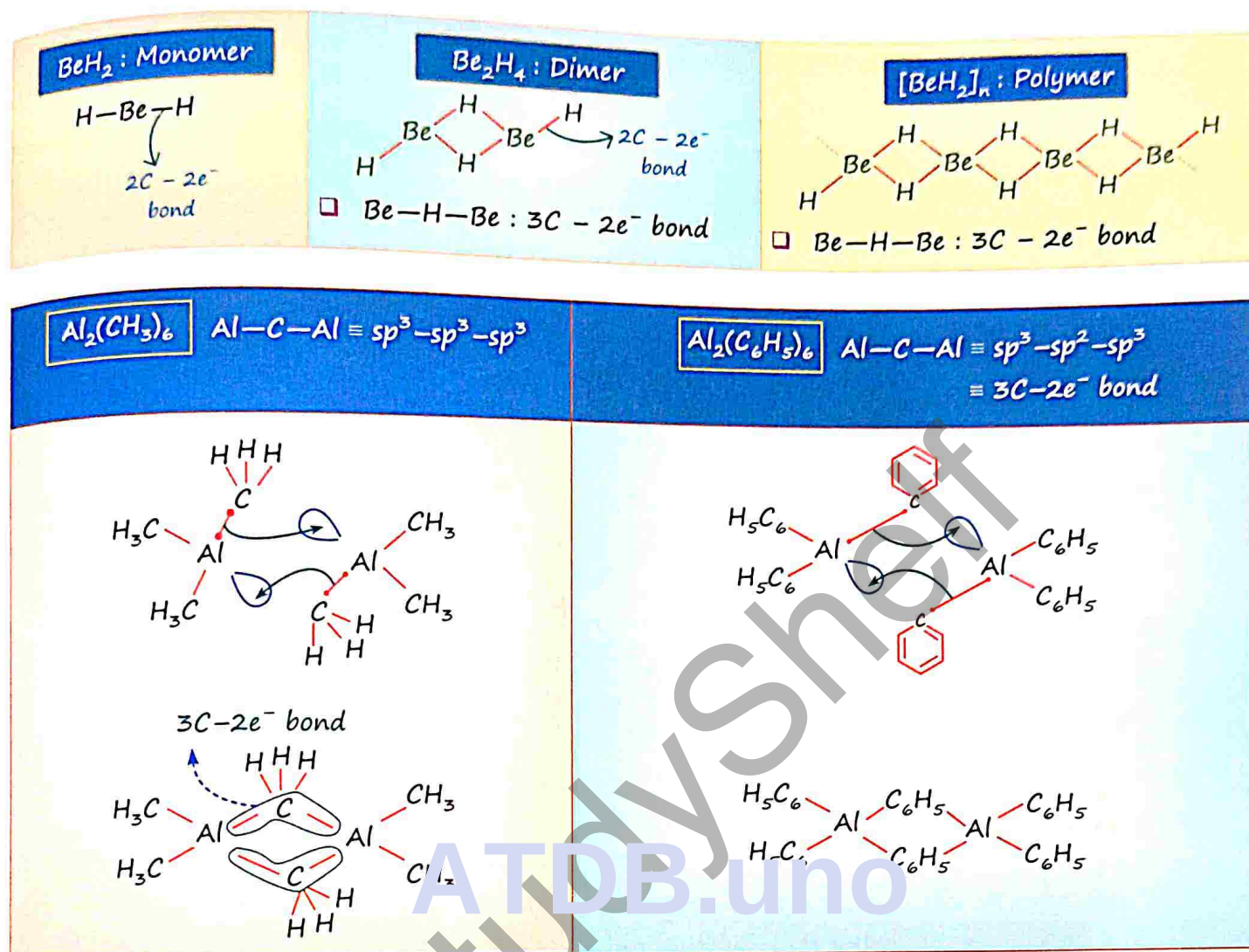
< H<sub>t</sub>BH<sub>t</sub> = 120° → θ↑ : %s↑ : %p↓ : Bond length↓

< H<sub>b</sub>BH<sub>b</sub> = 97° → θ↓ : %s↓ : %p↑ : Bond length↑



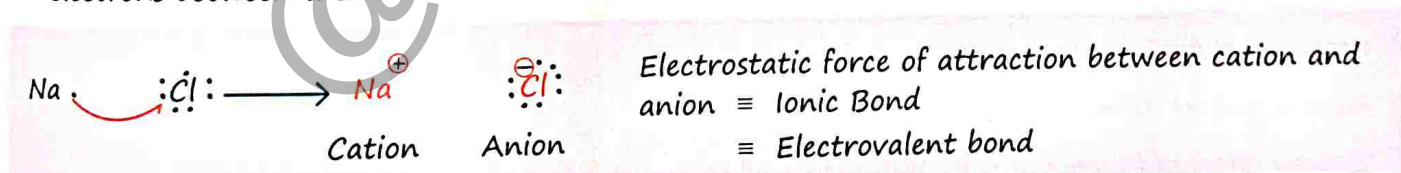
- Terminal B-H bonds have less p-character when compared to bridging bonds.
- Bond Length: B-H<sub>t</sub> < B-H<sub>b</sub>
- Bond Angle: H<sub>t</sub>BH<sub>t</sub> > H<sub>b</sub>BH<sub>b</sub>
- Max. No. of atoms in same plane: 6[2B, 4H<sub>t</sub>]



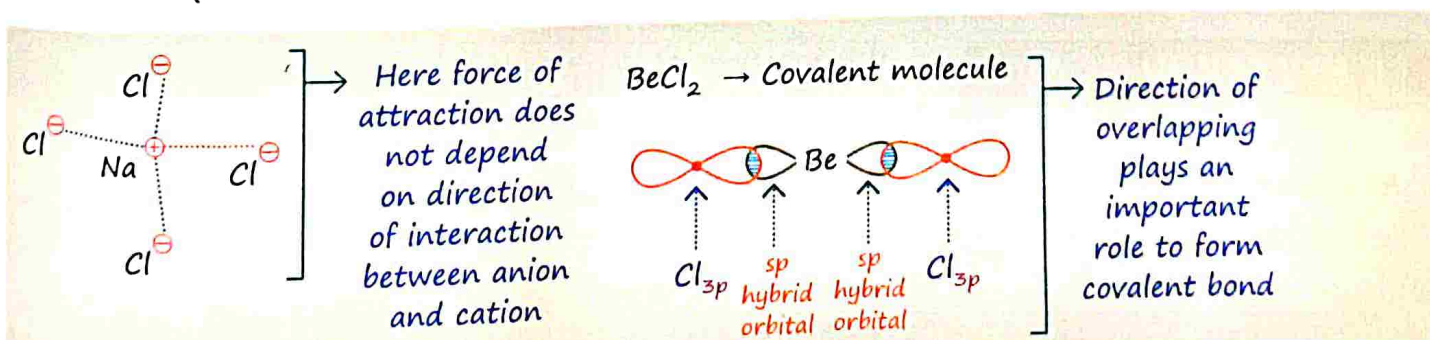


## IONIC BONDING

- The chemical bond formed between two or more atoms as a result of transfer of one or more electrons between them.



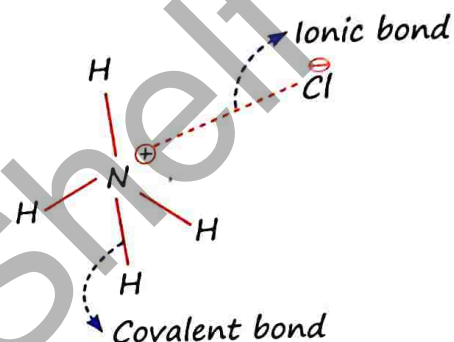
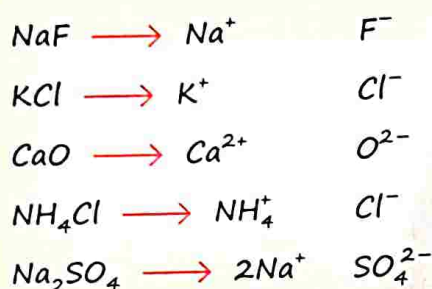
- Ionic bond (electrovalent bond) is **non-directional** in nature but covalent bond is directional in nature.



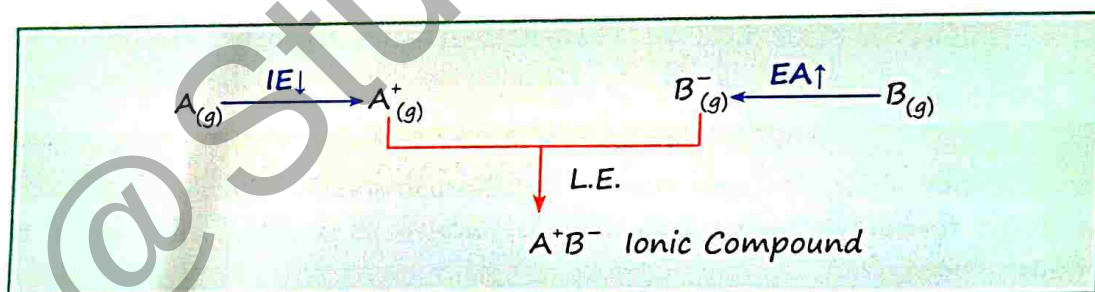


## Ionic Compounds

| A <sup>+</sup><br>Cation                                               | B <sup>-</sup><br>Anion                                                                                 |
|------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------|
| (a) Metal (Na, Mg)                                                     | (a) Non-Metal (B, C, N, S, O, F)                                                                        |
| (b) Group of atoms having (+)ve charge<br>NH <sub>4</sub> <sup>+</sup> | (b) Group of atoms having (-)ve charge<br>SO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup> |



## Favourable Condition for Ionic Bond

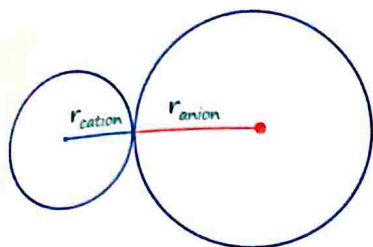


- Less Ionisation Energy for A
- More Electron Affinity for B
- Energy released because of the combination of cation (A<sup>+</sup>) and anion (B<sup>-</sup>) should be high. This energy is also defined in terms of lattice enthalpy.

## 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.





$$r = r_{\text{cation}} + r_{\text{anion}} \equiv \text{Internuclear Distance}$$

$$\text{Lattice Energy} \propto \frac{q_1 \cdot q_2}{r}$$

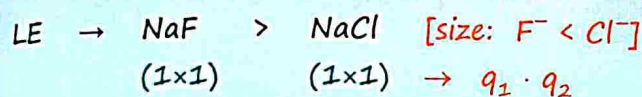
## Factors Affecting LE

(i) Charge  $\uparrow$  : LE  $\uparrow$

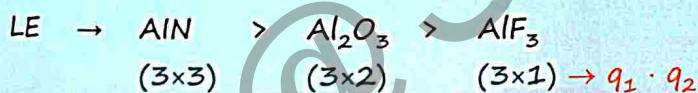
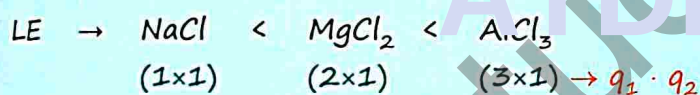
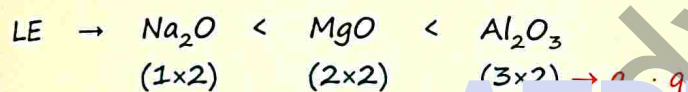
(ii) Size  $\uparrow$  : LE  $\downarrow$

$$1. \text{LE} \propto q_1 \cdot q_2$$

$$2. \text{LE} \propto \frac{1}{r_{\text{cation}} + r_{\text{anion}}}$$



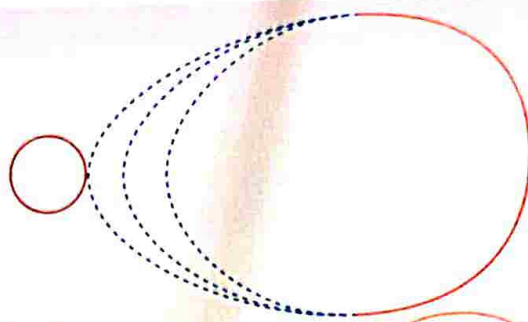
पहले charge  
फिर size



## 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<sup>-</sup> cloud is known as **polarisation**.
- Polarising power**  $\rightarrow$  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**  $\rightarrow$  tendency for an anion to become polarised.





- Cation**
- Polarising Power  $\uparrow$
- (i) Small size
  - (ii) More charge
  - (iii) Pseudo inert gas configuration of cation
- Anion**
- Polarisability  $\uparrow$
- (i) Large size
  - (ii) More charge



Polarising power of cation  $\rightarrow$   $\text{Li}^+ > \text{Na}^+ > \text{K}^+$   
 $\bullet \text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+}$

Polarisability of anion  $\rightarrow$   $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$   
 $\bullet \text{N}^{3-} > \text{O}^{2-} > \text{F}^-$

Covalent character  $\rightarrow$   $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}$

Size of cation  $\uparrow$  : Polarisation  $\downarrow$  : Covalent character  $\downarrow$

□  $\text{BeCl}_2$   $\text{MgCl}_2$   $\text{CaCl}_2$   $\text{SrCl}_2$   $\text{BaCl}_2$   
Size of cation  $\uparrow$  : Polarisation  $\downarrow$  : Covalent character  $\downarrow$

□  $\text{LiF}$   $\text{LiCl}$   $\text{LiBr}$   $\text{LiI}$   
- Size of anion  $\uparrow$   
- Polarisation  $\uparrow$   
- Covalent character  $\uparrow$

□  $\text{NaCl} < \text{MgCl}_2 < \text{AlCl}_3$  — Covalent character  
 $\text{Na}^+ \quad \text{Mg}^{+2} \quad \text{Al}^{+3}$   
- Charge of cation  $\uparrow$   
- Polarisation  $\uparrow$   
- Covalent character  $\uparrow$

□  $\text{AlF}_3 < \text{Al}_2\text{O}_3 < \text{AlN}$  — Covalent character  
 $\text{F}^- \quad \text{O}^{-2} \quad \text{N}^{-3}$   
- Charge on anion  $\uparrow$   
- Polarisation  $\uparrow$   
- Covalent Character  $\uparrow$

### Ionic Character

- $\text{AlN} < \text{Al}_2\text{O}_3 < \text{AlF}_3$  → less covalent character  
more ionic character
- $\text{AlF}_3 > \text{AlCl}_3$   
Ionic compound ( $\text{Al}^{3+} 3\text{F}^-$ )      Covalent compound
- $\text{BeCl}_2 < \text{MgCl}_2$   
Covalent molecule      Ionic compound ( $\text{Mg}^{2+} 2\text{Cl}^-$ )
- $\text{BeF}_2 > \text{BeCl}_2$   
( $\text{F}-\text{Be}-\text{F}$ )      ( $\text{Cl}-\text{Be}-\text{Cl}$ )  
[ $\text{BeF}_2$  has more ionic character than  $\text{BeCl}_2$ , but both are covalent molecules]

### Note

- Cation having pseudo-inert gas configuration, has more polarising power than other cations.



- Polarising power :  $\text{Cu}^+ > \text{Na}^+$

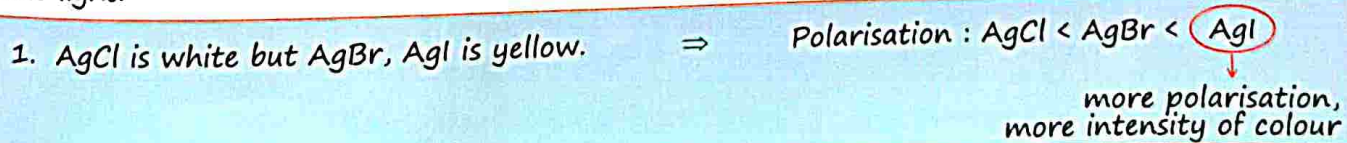
Melting point  $\uparrow$  : Ionic character  $\uparrow$

- ❑ Melting point of covalent compound < melting point of ionic compound.



### 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.





106. The number of following factors which affect the percent covalent character of the ionic bond is \_\_\_\_\_  
 [8 April, 2023 (Shift-I)]

- (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?

- (a)  $\text{BaCl}_2$  (b)  $\text{AgCl}$  (c)  $\text{KCl}$  (d)  $\text{CaCl}_2$

Sol. (b)  $\text{AgCl} < \text{CaCl}_2 < \text{BaCl}_2 < \text{KCl}$  (ionic character)

Reason:  $\text{Ag}^+$  has pseudo inert gas configuration

108. Arrange the bonds in order of increasing ionic character in the molecules  $\text{LiF}$ ,  $\text{K}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{SO}_2$  and  $\text{ClF}_3$ .  
 [01 Feb, 2024 (Shift-I)]

- (a)  $\text{ClF}_3 < \text{N}_2 < \text{SO}_2 < \text{K}_2\text{O} < \text{LiF}$
- (b)  $\text{LiF} < \text{K}_2\text{O} < \text{ClF}_3 < \text{SO}_2 < \text{N}_2$
- (c)  $\text{N}_2 < \text{SO}_2 < \text{ClF}_3 < \text{K}_2\text{O} < \text{LiF}$
- (d)  $\text{N}_2 < \text{ClF}_3 < \text{SO}_2 < \text{K}_2\text{O} < \text{LiF}$

Sol. (c) Increasing order of ionic character

$\text{N}_2 < \text{SO}_2 < \text{ClF}_3 < \text{K}_2\text{O} < \text{LiF}$

The degree of ionic character in a bond depends on the difference in electronegativity, which determines the bond polarity.

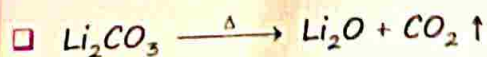
109. Order of Covalent bond;

- (A)  $\text{KF} > \text{KI}$ ;  $\text{LiF} > \text{KF}$  (B)  $\text{KF} < \text{KI}$ ;  $\text{LiF} > \text{KF}$
- (C)  $\text{SnCl}_4 > \text{SnCl}_2$ ;  $\text{CuCl} > \text{NaCl}$  (D)  $\text{LiF} > \text{KF}$ ;  $\text{CuCl} < \text{NaCl}$
- (E)  $\text{KF} < \text{KI}$ ;  $\text{CuCl} > \text{NaCl}$

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

Sol. (c)

## THERMAL STABILITY



☐ Thermally stable  $\rightarrow$  Strong lattice  $\rightarrow$

- (i) Lattice Energy  $\uparrow$
- (ii) Ionic Character  $\uparrow$

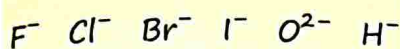
$\text{Li}_2\text{CO}_3$  is thermally unstable

$\text{Na}_2\text{CO}_3$  is thermally stable

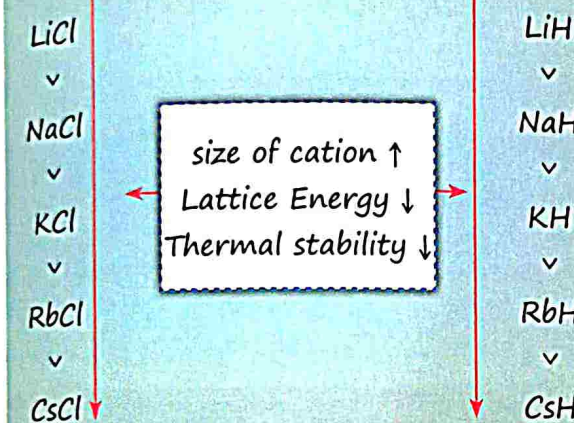


## Anions

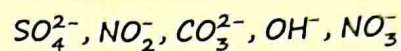
### Monoatomic anions



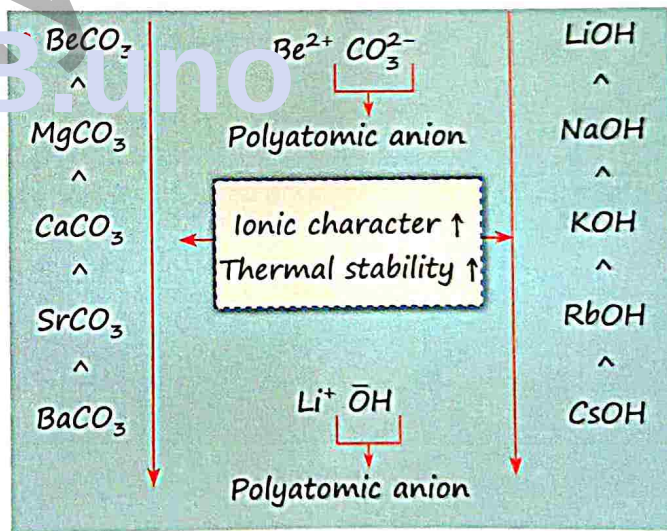
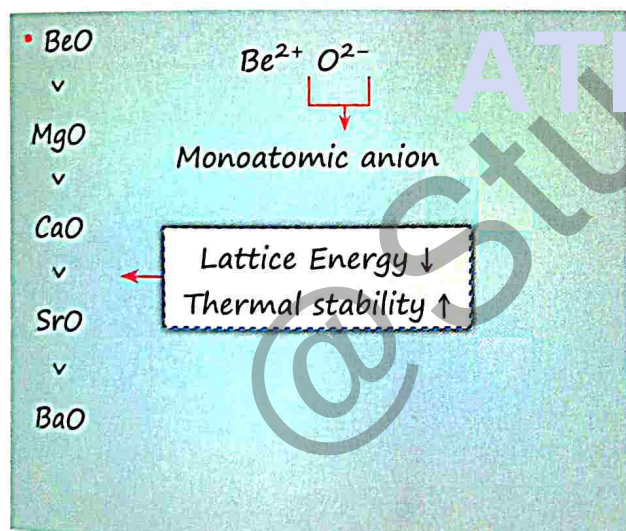
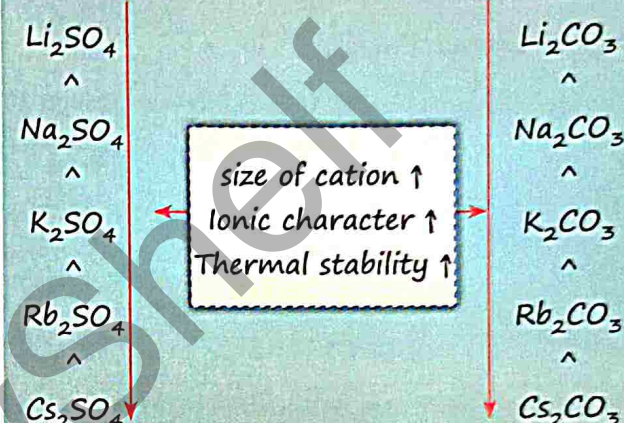
Apply **Lattice Energy** concept to get order for thermal stability



### Polyatomic anions



Apply **ionic character** concept to get order for thermal stability



## HEAT OF FORMATION

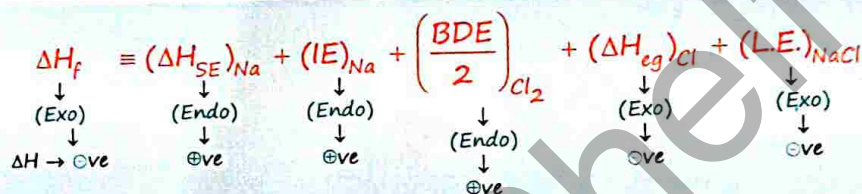
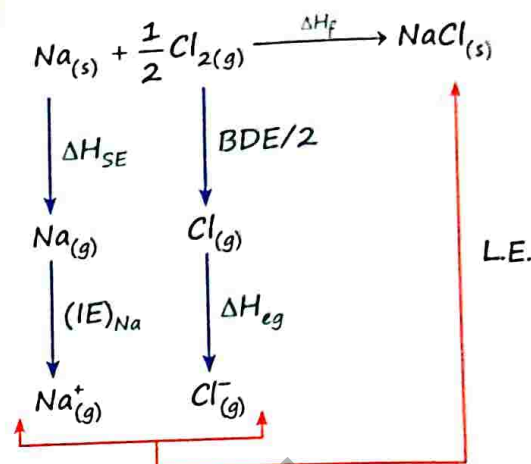
- Amount of heat released when 1 mole of substance is formed by its elements in pure and stable state.



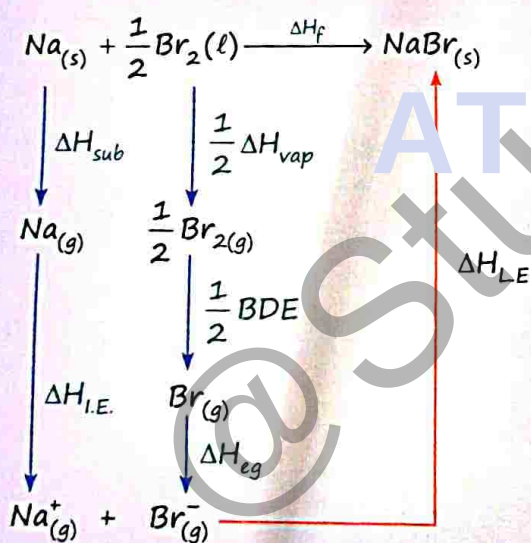


## BORN-HABER CYCLE

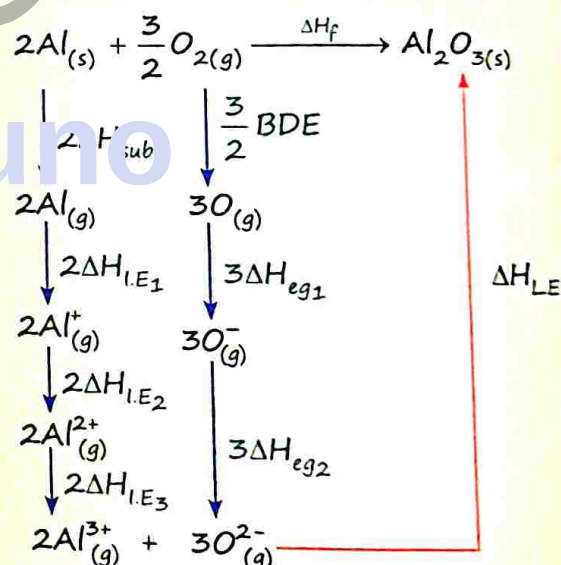
- $\Delta H_f \rightarrow$  Heat of formation of NaCl
- $[\Delta H_{SE}]_{Na} \rightarrow$  Sublimation energy of Na
- BDE  $\rightarrow$  Bond dissociation energy of 1 mole  $Cl_2$  molecule
- $\Delta H_{eg} \rightarrow$  Electron gain enthalpy of  $Cl_{(g)}$
- $\Delta H_{IE} \rightarrow$  Ionisation Energy
- $\Delta H_{LE} \rightarrow$  Lattice Energy



### Born Haber Cycle for NaBr



### Born Haber Cycle for $Al_2O_3(s)$



$$\Delta H_f = 2\Delta H_{sub} + 2\Delta H_{IE1} + 2\Delta H_{IE2} + 2\Delta H_{IE3} + \frac{3}{2}BDE + 3\Delta H_{eg1} + 3\Delta H_{eg2} + \Delta H_{LE}$$

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

$[Na^+ < Mg^{2+} < Al^{3+} < Si^{4+} < P^{5+} : \text{Charge}]$

111.  $\text{SnCl}_4$  has melting point  $-15^\circ\text{C}$  whereas  $\text{SnCl}_2$  has melting point  $535^\circ\text{C}$ . Why?

Sol. Covalent character :  $\text{SnCl}_4 > \text{SnCl}_2$

[Charge :  $\text{Sn}^{+4} > \text{Sn}^{+2}$ ]

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?

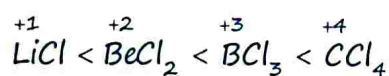
(a)  $\text{CCl}_4 < \text{BeCl}_2 < \text{BCl}_3 < \text{LiCl}$

(b)  $\text{LiCl} < \text{CCl}_4 < \text{BeCl}_2 < \text{BCl}_3$

(c)  $\text{LiCl} < \text{BeCl}_2 < \text{BCl}_3 < \text{CCl}_4$

(d)  $\text{LiCl} < \text{BeCl}_2 < \text{CCl}_4 < \text{BCl}_3$

Sol. (c) As charge on cations increases, their polarising power increases and thus covalent character increases.



113. Which of the following combination of ion will have highest polarisation?

(a)  $\text{Fe}^{2+}, \text{Br}^-$

(b)  $\text{Ni}^{4+}, \text{Br}^-$

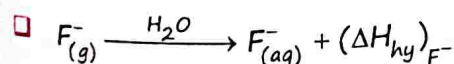
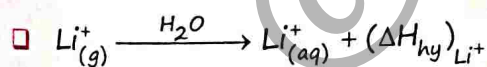
(c)  $\text{Ni}^{2+}, \text{Br}^-$

(d)  $\text{Fe}^{3+}, \text{Br}^-$

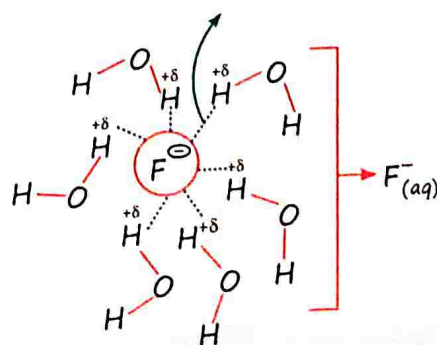
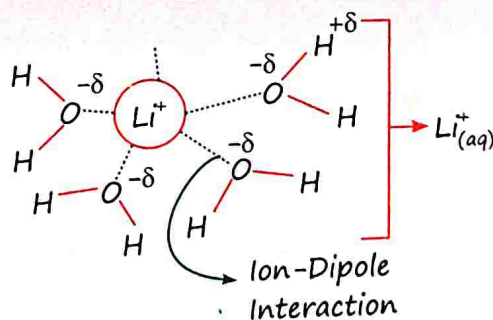
Sol. (b) Increase in oxidation state ( $\text{Ni}^{4+}$ ) increases the polarising power of cation and thus increases the polarisation of  $\text{Br}^-$  ions.

## HYDRATION ENERGY

Hydration energy is the amount of energy released when one mole of ions undergoes hydration.

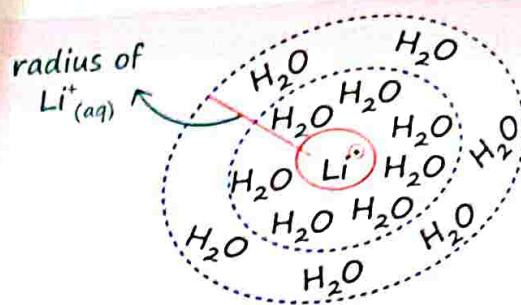


$$\text{Hydration Energy} \propto \frac{\text{charge } (q)}{\text{size } (r)}$$

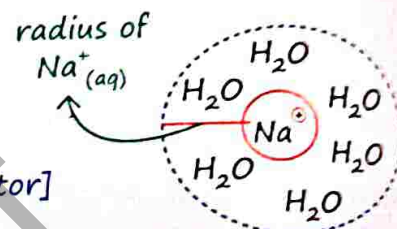




Radius<sub>(g)</sub> :  $\text{Li}^+ < \text{Na}^+$   
 Radius<sub>(aq)</sub> :  $\text{Li}^+_{(\text{aq})} > \text{Na}^+_{(\text{aq})}$   
 Mobility :  $\text{Li}^+_{(\text{aq})} < \text{Na}^+_{(\text{aq})}$



Ion Dipole Interaction :  $\text{Li}^+ > \text{Na}^+$   
 Hydration Energy :  $\text{Li}^+ > \text{Na}^+$   
 Hydration Energy :  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$  [Size factor]  
 :  $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$  [Size factor]  
 :  $\text{Na}^+ < \text{Mg}^{2+}$  [Charge factor]

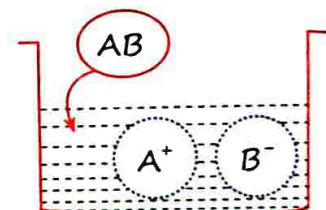
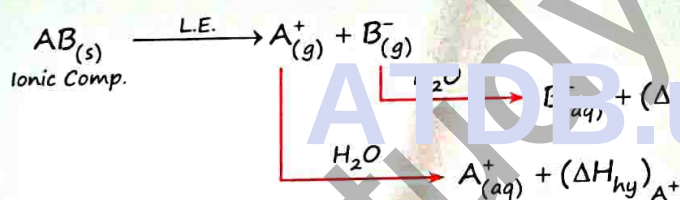


## Solubility in Water

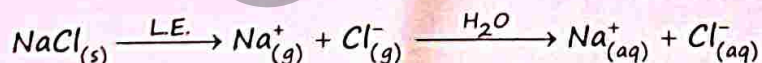
2 factors are responsible:

(i) Lattice energy of ionic compounds

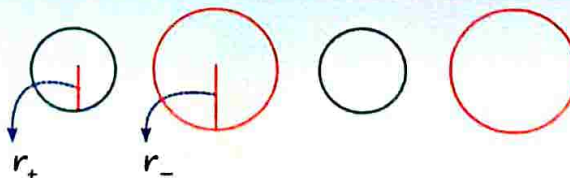
(ii) Hydration energy of component ions



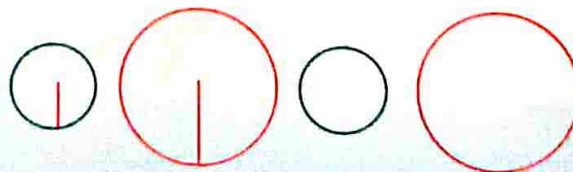
- Ionic Compound is soluble:  $\text{LE} < [(\Delta H_{\text{hy}})_{\text{A}^+} + (\Delta H_{\text{hy}})_{\text{B}^-}]$
- Ionic Compound is insoluble:  $\text{LE} > [(\Delta H_{\text{hy}})_{\text{A}^+} + (\Delta H_{\text{hy}})_{\text{B}^-}]$
- High solubility of  $\text{NaCl} \rightarrow (\text{LE})_{\text{NaCl}} < [(\Delta H_{\text{hy}})_{\text{Na}^+} + (\Delta H_{\text{hy}})_{\text{Cl}^-}]$



- Perfect lattice:  $r_+ \approx r_-$   
 Solubility  $\downarrow$

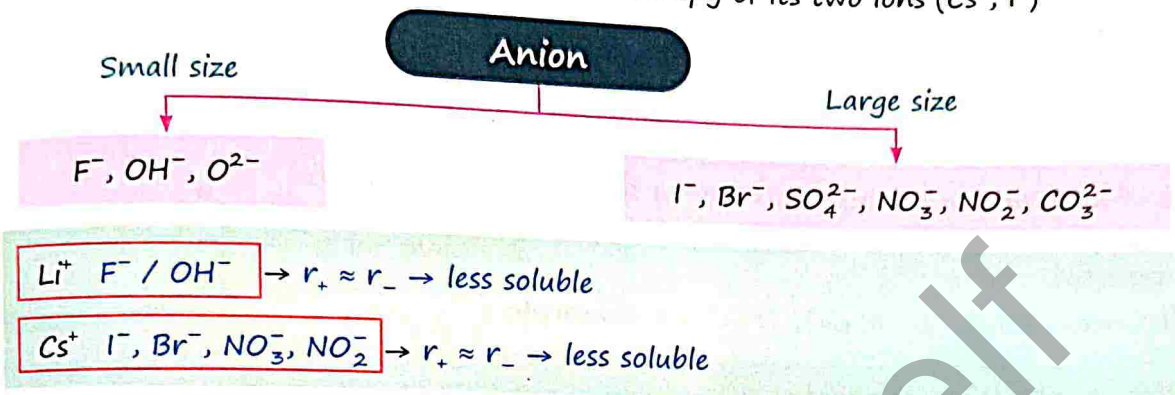


- Imperfect lattice:  $r_+ < r_-$   
 Solubility  $\uparrow$



- Extent of solubility  $\propto |r_- - r_+|$

- Solubility :  $\text{LiF} < \text{CsF}$   
Low solubility of  $\text{LiF}$  is due to its high lattice enthalpy
- Solubility :  $\text{LiI} > \text{CsI}$   
Low solubility of  $\text{CsI}$  is due to smaller hydration enthalpy of its two ions ( $\text{Cs}^+$ ,  $\text{I}^-$ )



- $\text{LiOH} < \text{NaOH} < \text{KOH} < \text{RbOH} < \text{CsOH}$
- $\text{Mg(OH)}_2 < \text{Ca(OH)}_2 < \text{Sr(OH)}_2 < \text{Ba(OH)}_2 < \text{Be(OH)}_2$  → Be compounds are generally more soluble than others due to high hydration of  $\text{Be}^{2+}$  ion.

$2\text{Li}^+ \text{CO}_3^{2-} / \text{SO}_4^{2-} \rightarrow 2r_+ \approx r_- \rightarrow \text{Solubility } \downarrow$

$2\text{Cs}^+ \text{CO}_3^{2-} / \text{SO}_4^{2-} \rightarrow 2r_+ > r_- \rightarrow \text{Solubility } \uparrow$

- $\text{Li}_2\text{SO}_4 < \text{Na}_2\text{SO}_4 < \text{K}_2\text{SO}_4 < \text{Rb}_2\text{SO}_4 < \text{Cs}_2\text{SO}_4$
- $\text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3 < \text{Cs}_2\text{CO}_3$
- $\text{LiHCO}_3 < \text{NaHCO}_3 < \text{KHCO}_3 < \text{RbHCO}_3 < \text{CsHCO}_3$  Same order for :  $\text{CO}_3^{2-} = \text{HCO}_3^-$

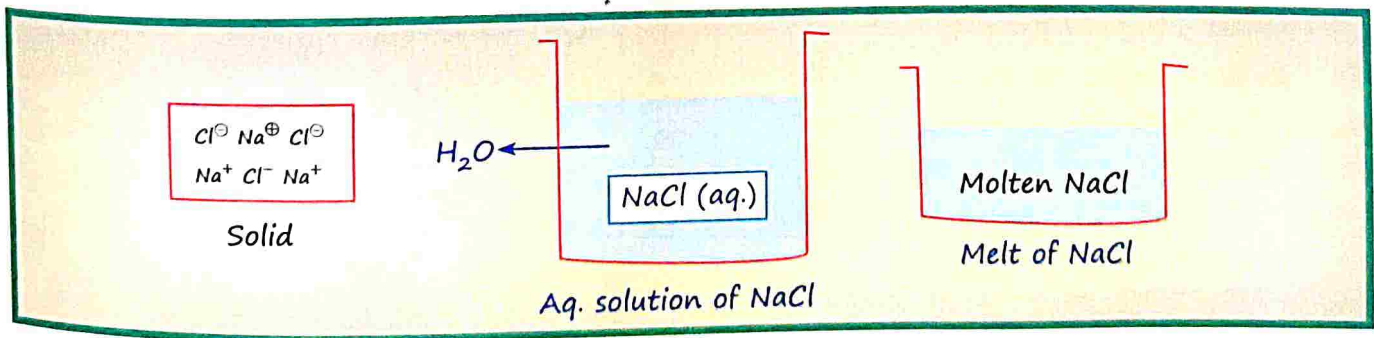
$\text{Be}^{2+} \text{CO}_3^{2-} / \text{SO}_4^{2-} \rightarrow r_+ < r_- \rightarrow \text{Solubility } \uparrow$

$\text{Ba}^{2+} \text{CO}_3^{2-} / \text{SO}_4^{2-} \rightarrow r_+ \approx r_- \rightarrow \text{Solubility } \downarrow$

- $\text{BeCO}_3 > \text{MgCO}_3 > \text{CaCO}_3 > \text{SrCO}_3 > \text{BaCO}_3$
- $\text{BeSO}_4 > \text{MgSO}_4 > \text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$

### 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  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ).

## 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.

Crystals having same shape of anion are isomorphs

Example:  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  &  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  are isomorphs.

- $\text{BaSO}_4$  &  $\text{KMnO}_4 \rightarrow$  isomorphs  
 $\rightarrow$  Both anions  $\text{SO}_4^{2-}$  and  $\text{MnO}_4^-$  are tetrahedral in shape.
- $\text{NaNO}_3$  &  $\text{NaClO}_3 \rightarrow$  not isomorphs  
 $\rightarrow$  Because anions have different shape.



114. Which of the following compounds has the lowest melting point?

- (a)  $\text{CaF}_2$  (b)  $\text{CaCl}_2$  (c)  $\text{CaBr}_2$  (d)  $\text{CaI}_2$

Sol. (d)

115. Among the following which one has the highest cation to anion size ratio?

- (a)  $\text{CsI}$  (b)  $\text{CsF}$  (c)  $\text{LiF}$  (d)  $\text{NaF}$

Sol. (b)

116. The sequence of ionic mobility in aqueous solution is:

- (a)  $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$  (b)  $\text{K}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Cs}^+$   
(c)  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+$  (d)  $\text{Rb}^+ > \text{K}^+ > \text{Cs}^+ > \text{Na}^+$

Sol. (c)

117. Among the following, which compound will show the highest lattice energy?

- (a)  $\text{KF}$  (b)  $\text{NaF}$  (c)  $\text{CsF}$  (d)  $\text{RbF}$

Sol. (b)

118. In the case of alkali metals, the covalent character decreases in the order:

- (a)  $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$  (b)  $\text{MF} > \text{MCl} > \text{MI} > \text{MBr}$   
(c)  $\text{MI} > \text{MBr} > \text{MCl} > \text{MF}$  (d)  $\text{MCl} > \text{MI} > \text{MBr} > \text{MF}$

Sol. (c)

119. Among  $\text{LiCl}$ ,  $\text{BeCl}_2$ ,  $\text{BCl}_3$  and  $\text{CCl}_4$ , the covalent bond character follows the order:

- (a)  $\text{BeCl}_2 > \text{BCl}_3 > \text{CCl}_4 > \text{LiCl}$  (b)  $\text{BeCl}_2 < \text{BCl}_3 < \text{CCl}_4 < \text{LiCl}$   
(c)  $\text{LiCl} < \text{BeCl}_2 < \text{BCl}_3 < \text{CCl}_4$  (d)  $\text{LiCl} > \text{BeCl}_2 > \text{BCl}_3 > \text{CCl}_4$

Sol. (c)

## INTER MOLECULAR FORCE OF ATTRACTION

Polar ( $\text{H}_2\text{O}$ ,  $\text{HCl}$ )

Molecules

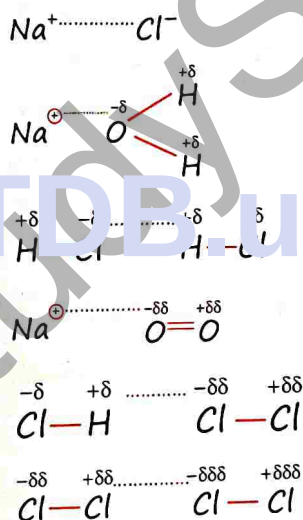
Non-polar ( $\text{Cl}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ )

- Interaction between Polar molecules
    - Dipole - dipole attraction
  - Interaction between Polar & non polar molecules
    - Dipole - induced dipole attraction
  - Interaction between non-polar molecules
    - Instantaneous induced dipole - induced dipole attraction [IID-ID]
    - Dispersion force
    - London force
- Vander Waal force of attraction includes 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> interactions.



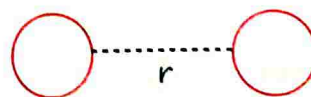
### Order of Inter-molecular Forces

- Ion - ion attraction
- Ion - dipole attraction
- Dipole - dipole attraction
- Ion-induced dipole attraction
- Dipole-induced dipole attraction
- Ins. Induced dipole - induced dipole



### Energy & Distance Relationship between 2 Interacting Particles

- Ion-ion attraction  $E \propto \frac{1}{r}$
- Ion-dipole attraction  $E \propto \frac{1}{r^2}$
- Dipole-dipole attraction  $E \propto \frac{1}{r^3}$
- Ion-induced dipole attraction  $E \propto \frac{1}{r^4}$
- Dipole - induced dipole attraction
- Ins. Induced dipole - induced dipole



$$\left. \begin{array}{l} \text{Dipole - induced dipole attraction} \\ \text{Ins. Induced dipole - induced dipole} \end{array} \right\} \rightarrow E \propto \frac{1}{r^6}$$

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).

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120. Identify type of Interaction present between following species

- (1) Xe and H<sub>2</sub>O (2) Na<sup>+</sup> and Br<sub>2</sub> (3) Br<sub>2</sub> and Br<sub>2</sub> (4) CO<sub>2</sub> and CO<sub>2</sub> (5) CCl<sub>4</sub> and CCl<sub>4</sub>  
 (6) K<sup>+</sup> and Cl<sup>-</sup> (7) Li<sup>+</sup> and H<sub>2</sub>O (8) H<sub>2</sub>S and H<sub>2</sub>S (9) Ne and Ne (10) I<sup>-</sup> and I<sub>2</sub>

Sol. 1. Xe, H<sub>2</sub>O → Dipole-induced dipole  
 [non polar - polar]

2. Na<sup>+</sup>, Br<sub>2</sub> → Ion-induced dipole  
 [ion - nonpolar]

3. Br<sub>2</sub>, Br<sub>2</sub> → London force/IID-ID  
 [nonpolar - nonpolar]

4. CO<sub>2</sub>, CO<sub>2</sub> → IID-ID  
 [nonpolar - nonpolar]

5. CCl<sub>4</sub>, CCl<sub>4</sub> → IID-ID  
 [nonpolar - nonpolar]

6. K<sup>+</sup>, Cl<sup>-</sup> → Ion-ion attraction  
 [ion - ion]

7. Li<sup>+</sup>, H<sub>2</sub>O → Ion-dipole attraction  
 [ion - polar molecule]

8. H<sub>2</sub>S, H<sub>2</sub>S → Dipole-dipole attraction  
 [polar - polar molecule]

9. Ne, Ne → London force  
 [nonpolar - nonpolar]

10. I<sup>-</sup>, I<sub>2</sub> → Ion-induced dipole attraction  
 [ion - nonpolar molecule]  
 $I^{\ominus} \cdots I^{\delta+} - I^{\delta-} \Rightarrow I_3^- \text{ ion}$

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

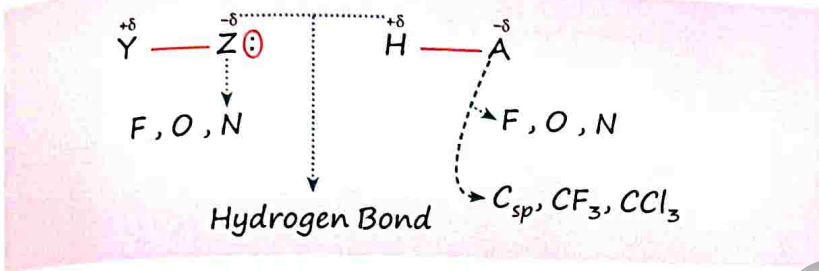
Molecular mass ↑ : Vander Waal force ↑  
 : Boiling Point ↑

| Order of Boiling Point |                   |     |
|------------------------|-------------------|-----|
| PH <sub>3</sub>        | H <sub>2</sub> S  | HCl |
| ^                      | ^                 | ^   |
| AsH <sub>3</sub>       | H <sub>2</sub> Se | HBr |
| ^                      | ^                 | ^   |
| SbH <sub>3</sub>       | H <sub>2</sub> Te | HI  |

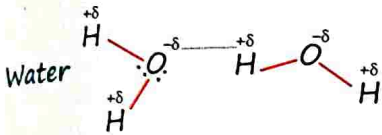
Size of the atom  $\uparrow$  : Vander Waal force  $\uparrow$  : BP  $\uparrow$   
 $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$  : BP/MP  
 Lowest B.P. (4.2 K) of any known substance

|    | 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             |

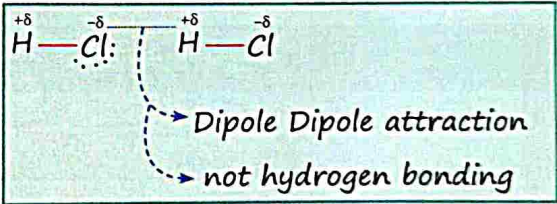
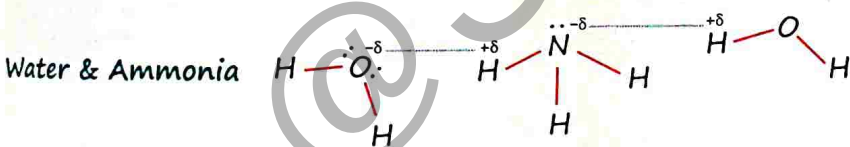
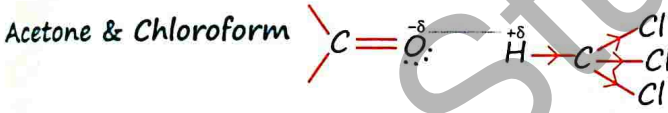
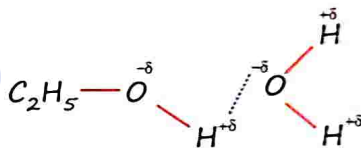
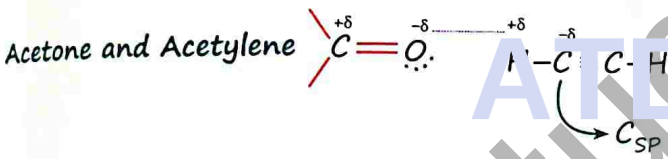
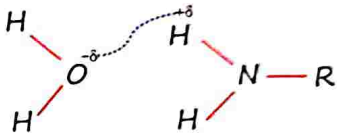
# HYDROGEN BONDING



Force of attraction : H-bonding  
 $\downarrow$   
 Van der Waals force of attraction

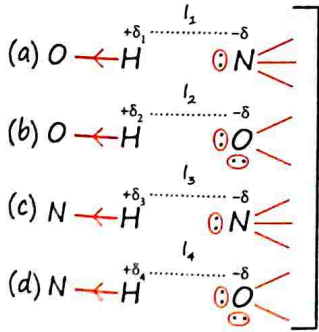


Water & Amine



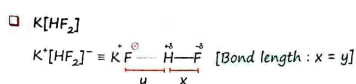
# Extent of H-bonding

Extent of H-bonding  $\uparrow$  : (i) Partial (+)ve charge on H  $\uparrow$   
 (ii) Electron density on Z  $\uparrow$

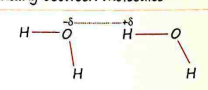
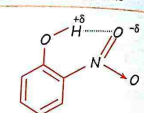
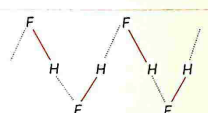
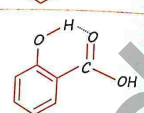


Extent of H-bonding :  $a > b > c > d$   
 Bond length :  $l_1 < l_2 < l_3 < l_4$   
 Order for partial charge :  $(\delta_1 = \delta_2) > (\delta_3 = \delta_4)$

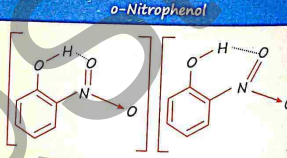




### Types of Hydrogen Bonding

| Inter-molecular H-bonding                                                                                                                                                       | Intra-molecular H-bonding                                                          |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
| H-bonding between molecules                                                                                                                                                     | H-bonding within a molecule                                                        |
|                                                                                                |   |
|                                                                                               |  |
| □ 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

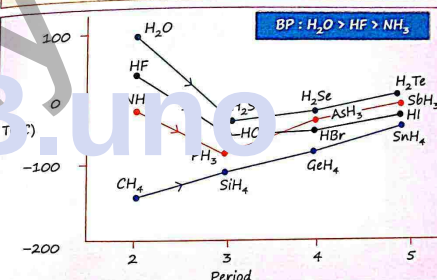
| p-Nitrophenol                                                                                                                                        | o-Nitrophenol                                                                                                                                                                                           |
|------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                                   |                                                                                                                      |
| □ Association of molecules due to inter-molecular H-bonding $\Rightarrow$ BP $\uparrow$                                                              | □ 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. |
| □ The intermolecular hydrogen bonding in p-nitrophenol requires more energy to break the intermolecular forces, resulting in a higher boiling point. |                                                                                                                                                                                                         |

### Order of Boiling Point

$NH_3, H_2O$  and  $HF \rightarrow$  Inter-molecular hydrogen bonding  $\Rightarrow$  BP  $\uparrow$

| Top $\rightarrow$ Bottom                   | CH <sub>4</sub>  | NH <sub>3</sub>  | PH <sub>3</sub>  | H <sub>2</sub> O  | H <sub>2</sub> S  | HF  | HCl |
|--------------------------------------------|------------------|------------------|------------------|-------------------|-------------------|-----|-----|
| Molecular Mass $\uparrow$                  | SiH <sub>4</sub> | PH <sub>3</sub>  | AsH <sub>3</sub> | H <sub>2</sub> S  | H <sub>2</sub> Se | HCl | HBr |
| Vander Waal Force of attraction $\uparrow$ | GeH <sub>4</sub> | AsH <sub>3</sub> | NH <sub>3</sub>  | H <sub>2</sub> Se | H <sub>2</sub> Te | HBr | HI  |
| BP $\uparrow$                              | SnH <sub>4</sub> | SbH <sub>3</sub> | SbH <sub>3</sub> | H <sub>2</sub> Te | H <sub>2</sub> O  | HI  | HF  |

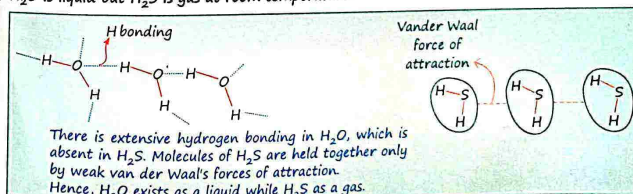
It has stronger intermolecular force of attraction (H-bonding) than others (having vander Waal force of attraction).



□ 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.

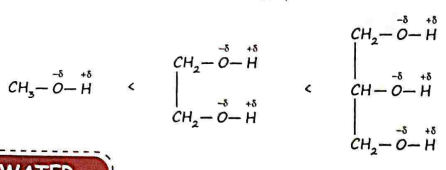


(ii)  $HF$  is liquid but  $HCl$  is gas. Think why?

Chemical Bonding and Molecular Structure

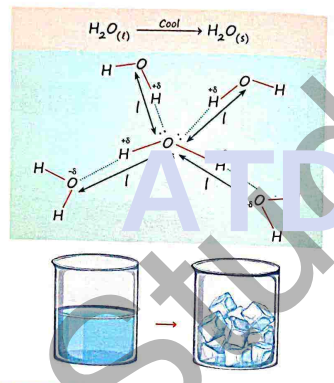
### B.P. & Viscosity

→ No. of Hydrogen bonds per molecule ↑ : viscosity ↑  
: BP ↑



### WATER

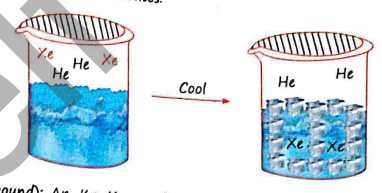
- No. of water molecules attached to 1 H<sub>2</sub>O molecule = 4
- Tetrahedrally bonded to a water molecule in solid state.  
Density : H<sub>2</sub>O<sub>(s)</sub> < H<sub>2</sub>O<sub>(l)</sub>  
Volume : H<sub>2</sub>O<sub>(s)</sub> > H<sub>2</sub>O<sub>(l)</sub>
- Volume of ice is more because of open cage like crystal structure, form by association of water molecules with the help of hydrogen bond.



| H <sub>2</sub> O <sub>(s)</sub> in H <sub>2</sub> O <sub>(l)</sub> | D <sub>2</sub> O <sub>(s)</sub> in H <sub>2</sub> O <sub>(l)</sub> | D <sub>2</sub> O <sub>(s)</sub> in D <sub>2</sub> O <sub>(l)</sub> |
|--------------------------------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------------|
| <p>density ↓</p> <p>Ice [H<sub>2</sub>O (s)] floats on water</p>   | <p>D<sub>2</sub>O (s) sinks into water</p>                         | <p>D<sub>2</sub>O (s) floats on heavy water</p>                    |

Due to open structure, ice is capable of forming Clathrates.

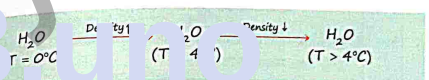
Clathrates compounds  
Cage like compounds



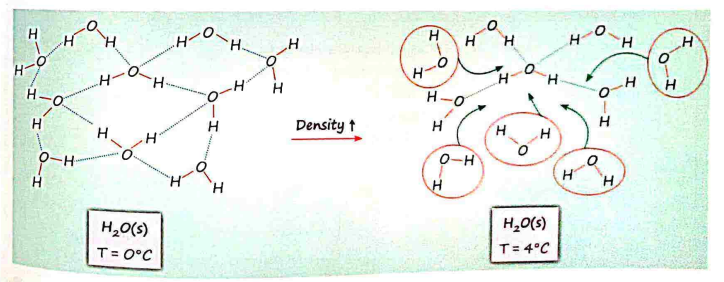
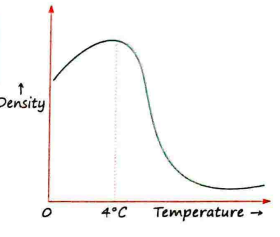
Noble gas hydrate (clathrate compound): Ar, Kr, Xe can form clathrate compounds but He, Ne cannot due to their smaller size.

Xe · 6H<sub>2</sub>O → formed only where  
Ar · 6H<sub>2</sub>O water freezes at high  
Kr · 6H<sub>2</sub>O pressure together with noble gas

### Variation of Density with Temperature



In this temperature region (0°C to 4°C), some of the ice melts and hence some H<sub>2</sub>O 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.



Chemical Bonding and Molecular Structure

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(IIT JEE 2000)

123. Amongst  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$ , the one with the highest boiling point is

- $\text{H}_2\text{O}$  because of hydrogen bonding
- $\text{H}_2\text{Te}$  because of higher molecular weight
- $\text{H}_2\text{S}$  because of hydrogen bonding
- $\text{H}_2\text{Te}$  because of lower molecular weight

Sol. (a)  $\text{H}_2\text{O}$  displays higher boiling point (in spite of lower molecular weight) on account of strong hydrogen bonding, while  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$  do not display H-bonding.

124. The correct statement/s about Hydrogen bonding is/are :

[04 April, 2024 (Shift-I)]

- Hydrogen bonding exists when H is covalently bonded to the highly electronegative atom.
- Intermolecular H bonding is present in o-nitrophenol
- Intramolecular Hs bonding is present in HF.
- The magnitude of H bonding depends on the physical state of the compound.
- H-bonding has powerful effect on the structure and properties of compounds.

Choose the correct answer from the options given below:

- A only
- A, D, E only
- A, B, D only
- A, B, C only

Sol. (b)

125. If the boiling point of  $\text{H}_2\text{O}$  is 373 K, the boiling point of  $\text{H}_2\text{S}$  will be :

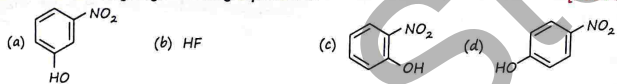
[3 Sep 2020 Shift-I]

- more than 373 K
- less than 300 K
- greater than 300 K but less than 373 K
- equal to 373 K

Sol. (b) Boiling point of  $\text{H}_2\text{S}$  is 213K.

126. Intramolecular hydrogen bonding is present in

[NEET 2024]



Sol. (c)

127. In  $\text{X}-\text{H}-\text{Y}$ , X and Y both are electronegative elements:

[NEET 2001]

- Electron density on X will increase and on H will decrease
- In both electron density will increase
- In both electron density will decrease
- On X electron density will decrease and on H increases

Sol. (a)

128. Strongest hydrogen bond is shown by:

[NEET 1992]

- Water
- Ammonia
- Hydrogen fluoride
- Hydrogen sulphide

Sol. (c)

129. Which one shows maximum hydrogen bonding?

- $\text{H}_2\text{O}$
- $\text{H}_2\text{Se}$
- $\text{H}_2\text{S}$
- HF

[NEET 1990]

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) $\text{XeF}_2$  | (i) Square planar      |
| (B) $\text{XeF}_4$  | (ii) Linear            |
| (C) $\text{XeO}_3$  | (iii) Square pyramidal |
| (D) $\text{XeOF}_4$ | (iv) Pyramidal         |

- A-ii B-i C-iv D-iii
- A-ii B-i C-iii D-iv
- A-ii B-iv C-iii D-i
- 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) $\text{XeF}_4$  | (i) Linear                 |
| (B) $\text{XeF}_6$  | (ii) Square planar         |
| (C) $\text{XeOF}_4$ | (iii) Distorted octahedral |
| (D) $\text{XeO}_3$  | (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]

- $\text{IF}_3$ ,  $\text{XeF}_2$
- $\text{BeCl}_2$ ,  $\text{XeF}_2$
- $\text{TeI}_2$ ,  $\text{XeF}_2$
- $\text{IBr}_2^-$ ,  $\text{XeF}_2$

Sol. (d)

133. The correct geometry and hybridization for  $\text{XeF}_4$  are:

[NEET 2016-II]

- Planar triangle,  $\text{sp}^3\text{d}^3$
- Square planar,  $\text{sp}^3\text{d}^2$
- Octahedral,  $\text{sp}^3\text{d}^2$
- Trigonal bipyramidal,  $\text{sp}^3\text{d}$

Sol. (b)

Chemical Bonding and Molecular Structure

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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)      | $\text{XeF}_6$  | (i)       | Distorted octahedral |
| (B)      | $\text{XeO}_3$  | (ii)      | Square planar        |
| (C)      | $\text{XeOF}_4$ | (iii)     | Pyramidal            |
| (D)      | $\text{XeF}_4$  | (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) $\text{XeF}_4$ , $\text{XeO}_4$ | (b) $\text{SiCl}_4$ , $\text{PCl}_4^+$ |
| (c) Diamond, silicon carbide        | (d) $\text{NH}_3$ , $\text{PH}_3$      |

Sol. (a)

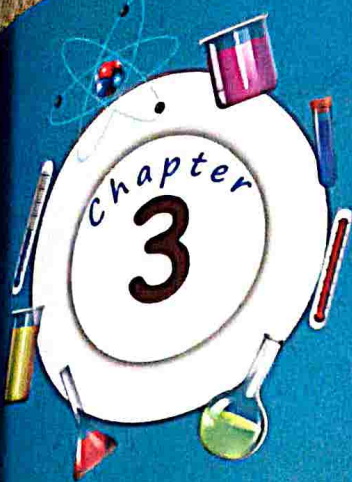
136.  $\text{XeF}_2$  is isostructural with:

- |                    |                   |                  |                     |
|--------------------|-------------------|------------------|---------------------|
| (a) $\text{TeF}_2$ | (b) $\text{Cl}_2$ | (c) $\text{I}_2$ | (d) $\text{BaCl}_2$ |
|--------------------|-------------------|------------------|---------------------|

[NEET 2013]

Sol. (b)





# Coordination Compounds

JEE Main & NEET

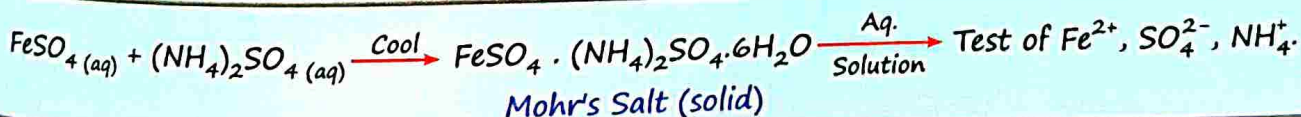
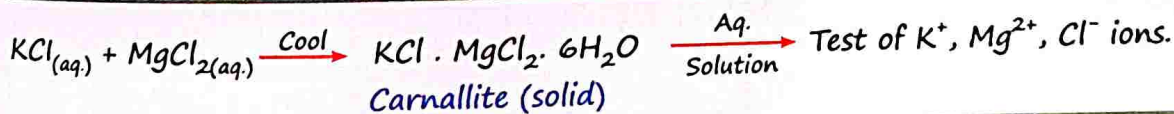
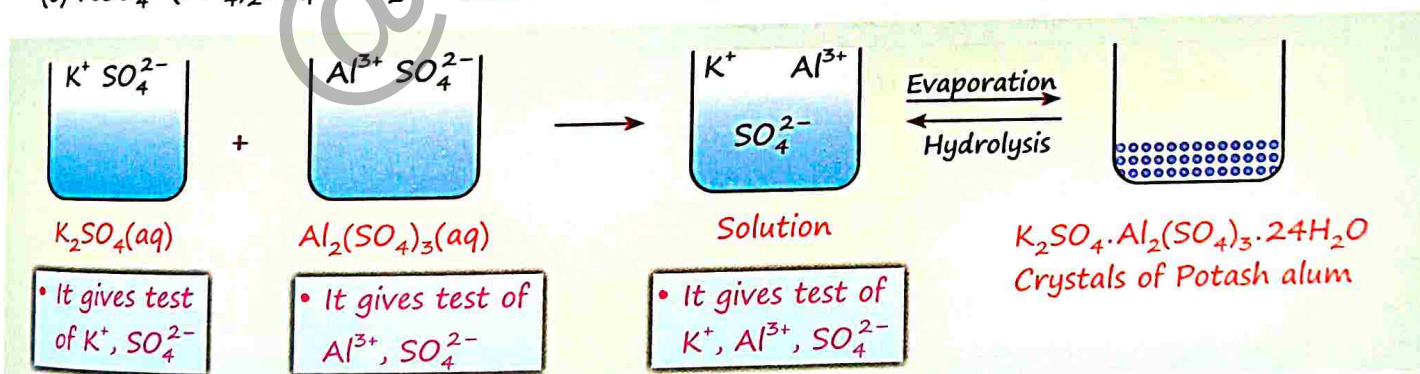
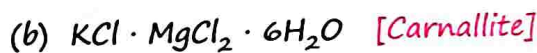
Syllabus

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

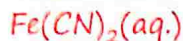
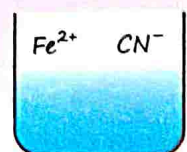
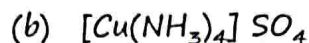
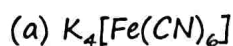
1. **Double Salts:** Ions in addition compound, don't lose their identity in aq. solution.



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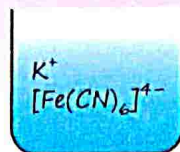
## 2. Coordination Compounds: Some ions in addition compound, lose their identity in aq. solution.



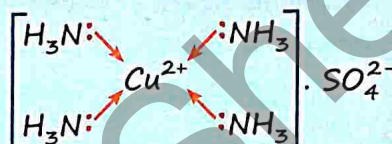
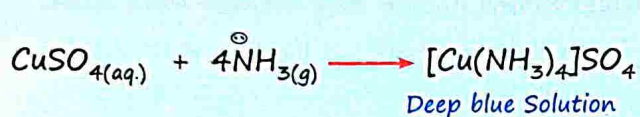
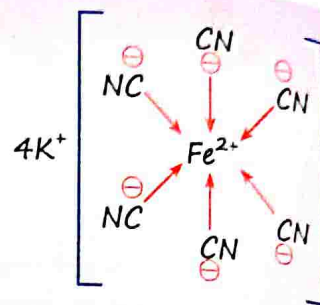
• It gives test of  $Fe^{2+}$ ,  $CN^-$



• It gives test of  $K^+$ ,  $CN^-$



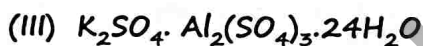
• It does not give test of  $Fe^{2+}$ ,  $CN^-$  because  $Fe^{2+}$  forms a complex ion with  $CN^-$ .



• It does not give test of  $Cu^{2+}$  and  $NH_3$

1. Which of the following are the examples of double salt?

(2023/01 Feb Shift-1)



Choose the correct answer.

(a) I and III only

(b) I and II only

(c) I, II and IV only

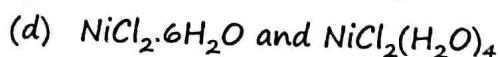
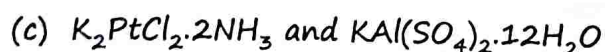
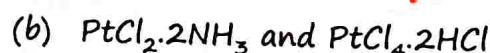
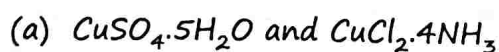
(d) II and IV only

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 |
| $KCl \cdot MgCl_2 \cdot 6H_2O$          | 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]



Sol. (c)

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## 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:  $[\text{Co}(\text{NH}_3)_6]^{2+}$

Here,  $\text{NH}_3$  is a ligand because it donates lone pair of electron to  $\text{Co}^{+2}$  ion.

3. **Denticity:** No. of coordinate bonds that a ligand can form with Metal

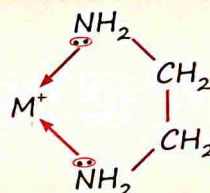
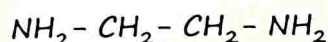
**Monodentate**  $\rightarrow$  Ligand having only 1 donor site.

Example:  $\text{F}^- / \text{Cl}^- / \text{Br}^- / \text{I}^- / \text{H}_2\text{O} / \text{NH}_3$  etc.

It is also called unidentate ligand.

**Bidentate**  $\rightarrow$  When a ligand can bind through 2 donor sites.

Example: Ethane-1, 2-diamine: ( $\text{en}$ )

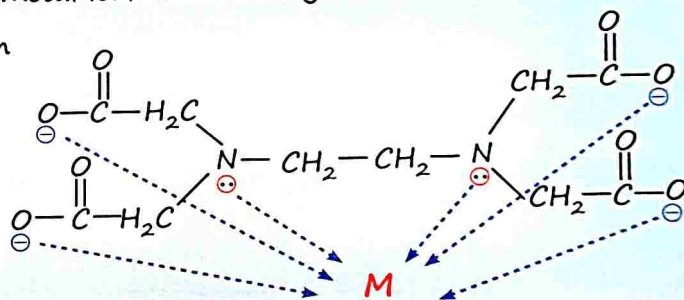


**Polydentate ligand**  $\rightarrow$  When a ligand can bind metal ion/atom through more than 2 donor sites.

Example:  $\text{EDTA}^{4-}$ : Ethylene diamine tetraacetate ion

4  $\ominus$ ve charges

Hexadentate ligand

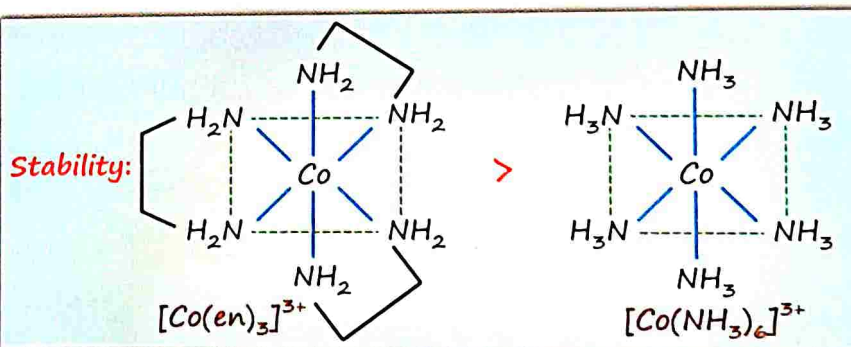


## 4. Chelation: Ring Formation

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.



## Coordination Compounds

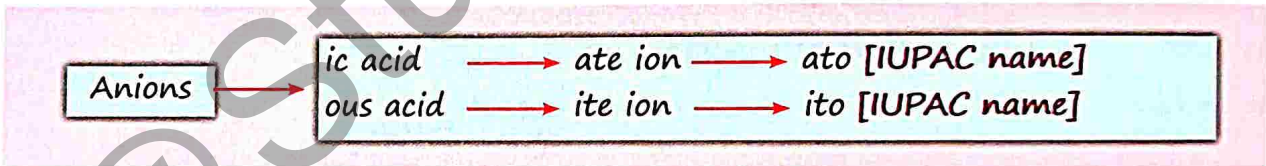
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# Naming of Ligands

## 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<br>$\text{HNO}_3$<br>Nitric acid                        |  | +5<br>$\text{H}_3\text{PO}_4$<br>Phosphoric acid      |  | +7<br>$\text{HClO}_4$<br>Perchloric acid |  |
| +3<br>$\text{HNO}_2$<br>Nitrous acid                       |  | +3<br>$\text{H}_3\text{PO}_3$<br>Phosphorous acid     |  | +5<br>$\text{HClO}_3$<br>Chloric acid    |  |
| +1<br>$\text{H}_2\text{N}_2\text{O}_2$<br>Hyponitrous acid |  | +1<br>$\text{H}_3\text{PO}_2$<br>Hypophosphorous acid |  | +3<br>$\text{HClO}_2$<br>Chlorous acid   |  |
|                                                            |  |                                                       |  | +1<br>$\text{HClO}$<br>Hypochlorous acid |  |



|                                                                                      | Ligand<br>[General Name]                                                      | IUPAC Name |                                                                                       | Ligand<br>[General Name]                                                       | IUPAC Name  |
|--------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|------------|---------------------------------------------------------------------------------------|--------------------------------------------------------------------------------|-------------|
| <div> <div><math>\text{HNO}_3</math></div> <div>Nitric acid</div> </div>             | <div> <div><math>\text{NO}_3^-</math></div> <div>Nitrate ion</div> </div>     | Nitrato    | <div> <div><math>\text{H}_3\text{PO}_4</math></div> <div>Phosphoric acid</div> </div> | <div> <div><math>\text{PO}_4^{3-}</math></div> <div>Phosphate ion</div> </div> | Phosphato   |
| <div> <div><math>\text{HNO}_2</math></div> <div>Nitrous acid</div> </div>            | <div> <div><math>\text{NO}_2^-</math></div> <div>Nitrite ion</div> </div>     | Nitrito    | <div> <div><math>\text{HClO}_4</math></div> <div>Perchloric acid</div> </div>         | <div> <div><math>\text{ClO}_4^-</math></div> <div>Perchlorate ion</div> </div> | Perchlorato |
| <div> <div><math>\text{H}_2\text{SO}_4</math></div> <div>Sulphuric acid</div> </div> | <div> <div><math>\text{SO}_4^{2-}</math></div> <div>Sulphate ion</div> </div> | Sulphato   | <div> <div><math>\text{HClO}_3</math></div> <div>Chloric acid</div> </div>            | <div> <div><math>\text{ClO}_3^-</math></div> <div>Chlorate ion</div> </div>    | Chlorato    |



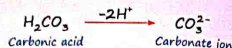
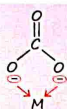
|                                                         |                                                 |              |                                     |                                    |              |
|---------------------------------------------------------|-------------------------------------------------|--------------|-------------------------------------|------------------------------------|--------------|
| $\text{H}_2\text{S}_2\text{O}_3$<br>Thio sulphuric acid | $\text{S}_2\text{O}_3^{2-}$<br>Thiosulphate ion | Thiosulphato | $\text{HClO}_2$<br>Chlorous acid    | $\text{ClO}_2^-$<br>chlorite ion   | Chlorito     |
| $\text{H}_2\text{SO}_3$<br>Sulphurous acid              | $\text{SO}_3^{2-}$<br>Sulphite ion              | Sulphito     | $\text{HClO}$<br>Hypo chlorous acid | $\text{ClO}^-$<br>Hypochlorite ion | Hypochlorito |

| Ligand               | IUPAC Name         | Ligand                                                                                                                                                                                                             | IUPAC Name      |
|----------------------|--------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|
| $\text{F}^-$         | Fluorido           | $\text{O}^{2-}$                                                                                                                                                                                                    | Oxo/oxido       |
| $\text{Cl}^-$        | Chlorido           | $\text{O}_2^{2-}$                                                                                                                                                                                                  | Peroxido/peroxo |
| $\text{I}^-$         | Iodido             | $\text{O}_2^-$                                                                                                                                                                                                     | Superoxo        |
| $\text{Br}^-$        | Bromido            | $\text{N}^{3-}$                                                                                                                                                                                                    | Nitrido         |
| $\text{NH}_2^-$      | Amido              | $\text{N}_3^-$                                                                                                                                                                                                     | Azido           |
| $\text{NH}^{2-}$     | Imido              | $\text{S}^{2-}$                                                                                                                                                                                                    | Sulphido        |
| $\text{OH}^-$        | Hydroxido          | $\text{H}^-$                                                                                                                                                                                                       | Hydrido         |
| $\text{CN}^-$        | Cyano / cyanido    | <div> <math display="block">\text{O}_2 \xrightarrow{+e^-} \text{O}_2^- \xrightarrow{+e^-} \text{O}_2^{2-} \longrightarrow \text{O}^{2-}</math> <div>Dioxygen      Superoxide      Peroxide      Oxide</div> </div> |                 |
| $\text{H}_2\text{O}$ | Aqua               | $\text{C}_5\text{H}_5\text{N}$                                                                                                                                                                                     | Pyridine        |
| $\text{CO}$          | Carbonyl           | $\text{CH}_3-\text{NH}_2$                                                                                                                                                                                          | Methylamine     |
| $\text{NO}$          | Nitrosyl           | $\text{NO}^+$                                                                                                                                                                                                      | Nitrosonium     |
| $\text{NH}_3$        | Ammine             | $\text{N}_2\text{H}_5^+$                                                                                                                                                                                           | Hydrazinium     |
| $\text{PPh}_3$       | Triphenylphosphine | <div> <math display="block">\text{NH}_2-\text{NH}_2 \xrightarrow{\text{H}^+} \text{NH}_2-\text{NH}_3^+</math> <div>Hydrazine      Hydrazinium ion</div> </div>                                                     |                 |

## Bidentate Ligand

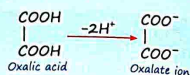
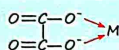
### $\text{CO}_3^{2-} \rightarrow$ Carbonate ion

- ☐ IUPAC: Carbonato
- ☐ 2 Ove charge
- ☐ 4 membered ring



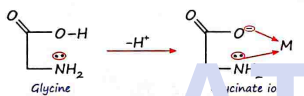
### $\text{Ox}^{2-} \rightarrow$ Oxalate ion ( $\text{C}_2\text{O}_4^{2-}$ )

- ☐ Oxalato
- ☐ 2 Ove charge
- ☐ Symmetrical ligand
- ☐ 5 membered ring



### $\text{Gly}^- \rightarrow$ Glycinate ion

- ☐ Glycinato
- ☐ 1 Ove charge
- ☐ 5 membered ring
- ☐ Unsymmetrical ligand

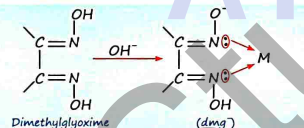


Glycine

Glycinate ion

### $\text{dmg}^- \rightarrow$ Dimethylglyoximate ion

- ☐ Charge  $\equiv -1$
- ☐ 5 membered ring

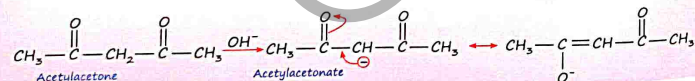
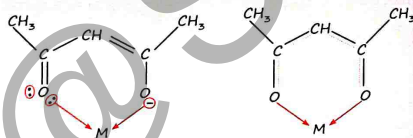


Dimethylglyoxime

(dmg)

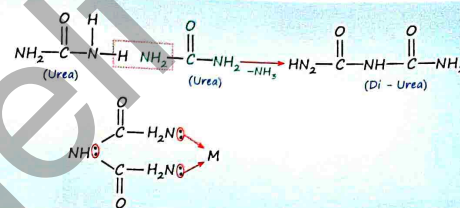
### $\text{acac}^- \rightarrow$ Acetylacetonate ion

- ☐ Charge  $\equiv -1$
- ☐ 6 membered ring
- ☐ Symmetrical ligand



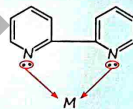
### Di-urea $\rightarrow$ Biurate

- ☐ Symmetrical ligand
- ☐ 6 membered ring
- ☐ Neutral ligand



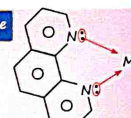
### dipy $\rightarrow$ Dipyridyl

- ☐ Neutral ligand
- ☐ 5 membered ring



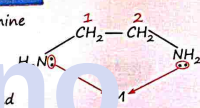
### o-phen $\rightarrow$ Ortho-phenanthroline

- ☐ Neutral ligand
- ☐ 5 membered ring



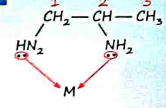
### en $\rightarrow$ Ethylene diamine

- ☐ Ethane-1,2-diamine
- ☐ Neutral ligand
- ☐ 5 membered ring
- ☐ Symmetrical ligand



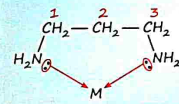
### pn $\rightarrow$ Propylene diamine

- ☐ Propane-1,2-diamine
- ☐ Neutral ligand
- ☐ 5 membered ring
- ☐ unsymmetrical ligand



### tn $\rightarrow$ Trimethylene diamine

- ☐ Propane-1,3-diamine
- ☐ Neutral ligand
- ☐ 6 membered ring
- ☐ Symmetrical ligand

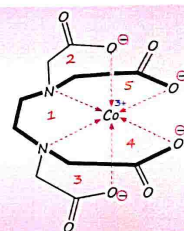


## Polydentate Ligands

### $\text{EDTA}^{4-} \rightarrow$ Ethylenediamine tetraacetate ion Denticity $\equiv 6$

#### $[\text{Co}(\text{EDTA})]^-$

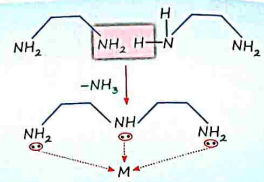
- ☐ Oxidation state of Co  $\equiv +3$
- ☐ No of 5 membered rings  $\equiv 5$
- ☐ No of O-M-O bond angles  $\equiv 6$
- ☐ No of N-M-N bond angles  $\equiv 1$





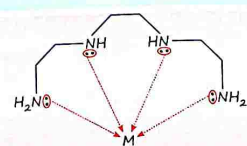
**dien → Diethylene triamine**

- Denticity  $\equiv 3$
- No of 5 membered rings  $\equiv 2$



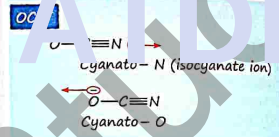
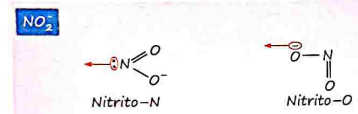
**trien → Tri-ethylene tetraamine**

- Denticity  $\equiv 4$
- No of 5 membered rings  $\equiv 3$



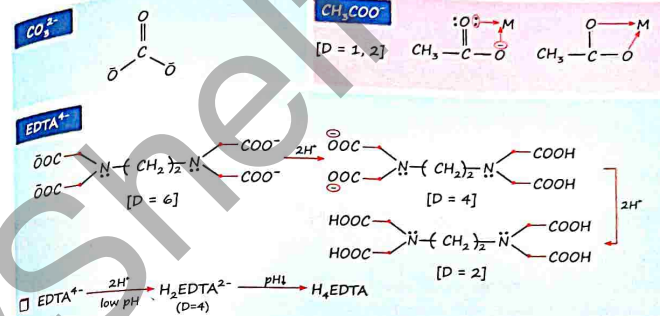
**Ambidentate Ligand**

Ligands that have more than one kind of donor sites.



**Flexidentate Ligand**

A polydentate ligand with different denticity in different coordination compounds.

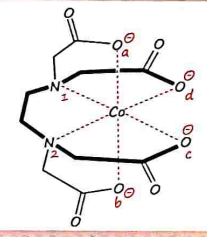


**(JEE Adv. 2013)**

3. EDTA is ethylenediaminetetraacetate ion. The total number of N - Co - O bond angles in [Co(EDTA)]<sup>3-</sup>

Sol. (8)

- |                                         |                                         |
|-----------------------------------------|-----------------------------------------|
| 1. N <sub>1</sub> - Co - O <sub>c</sub> | 2. N <sub>1</sub> - Co - O <sub>d</sub> |
| 3. N <sub>1</sub> - Co - O <sub>b</sub> | 4. N <sub>1</sub> - Co - O <sub>e</sub> |
| 5. N <sub>2</sub> - Co - O <sub>a</sub> | 6. N <sub>2</sub> - Co - O <sub>d</sub> |
| 7. N <sub>2</sub> - Co - O <sub>b</sub> | 8. N <sub>2</sub> - Co - O <sub>e</sub> |



4. Ethylene diaminetetraacetate ion is a/an:

- |                        |                        |
|------------------------|------------------------|
| (a) hexadentate ligand | (b) ambidentate ligand |
| (c) monodentate ligand | (d) bidentate ligand   |

[NEET 2024 R<sub>2</sub>]

5. Which of the following is not an ambidentate ligand?

- |                                                 |                      |                                  |                     |
|-------------------------------------------------|----------------------|----------------------------------|---------------------|
| (a) C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> | (b) SCN <sup>-</sup> | (c) NO <sub>2</sub> <sup>-</sup> | (d) CN <sup>-</sup> |
|-------------------------------------------------|----------------------|----------------------------------|---------------------|

[NEET 2024 R<sub>2</sub>]

6. Which complex compound is most stable?

- |                                                                         |                                                                                             |
|-------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|
| (a) [Co(NH <sub>3</sub> ) <sub>6</sub> ](SO <sub>4</sub> ) <sub>3</sub> | (b) [Co(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)Br](NO <sub>3</sub> ) <sub>2</sub> |
| (c) [Co(NH <sub>3</sub> ) <sub>3</sub> ](NO <sub>3</sub> ) <sub>3</sub> | (d) [CoCl <sub>2</sub> (en) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>                   |

[NEET 2023]

7. Ethylene diaminetetraacetate (EDTA) ion is: [NEET 2015]
- Unidentate ligand
  - Bidentate ligand with two "N" donor atoms
  - Tridentate ligand with three "N" donor atoms
  - Hexadentate ligand with four "O" and two "N" donor atoms
- Sol. (d)

### Homoleptic and Heteroleptic Complexes

| Homo-leptic complex                                                                                                                                  | Hetero-leptic complex                                                                                                                                      |
|------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Same Ligand                                                                                                                                          | Different Ligand                                                                                                                                           |
| Complex in which a metal is bound to only one kind of donor ligands.<br>[Co(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> : only one type of ligand | Complex in which a metal is bound to more than one kind of donor ligands.<br>[Co(H <sub>2</sub> O) <sub>4</sub> Br <sub>2</sub> ] : Two different ligands. |

8. Which of the following complex is homoleptic? [01 Feb, 2024 (Shift-II)]
- [Ni(CN)<sub>4</sub>]<sup>2-</sup>
  - [Ni(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]
  - [Fe(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>
  - [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>
- Sol. (a)

9. Given below are two statements: [NE 2012]
- Statement I: [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> is a homoleptic complex whereas [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> is a heteroleptic complex.
- Statement II: Complex [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> has only one kind of ligands but [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> has more than one kind of ligands.
- In the light of the above statements, choose the correct answer from the options given below:
- Statement I is true but Statement II is false.
  - Statement I is false but Statement II is true.
  - Both Statement I and Statement II are true.
  - Both Statement I and Statement II are false.
- Sol. (c)

### Coordination Number

No. of ligand donor atoms to which the metal is directly bonded.

$$\text{Coordination number} = \text{No. of ligands} \times \text{Denticity}$$

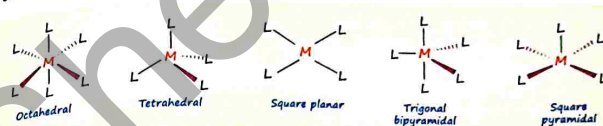
$$[\text{Co}(\text{NH}_3)_6]^{3+} \Rightarrow \text{Coordination number} = \text{No. of ligands} \times \text{Denticity} = 6 \times 1 = 6$$

$$[\text{Co}(\text{en})_2]^{2+} \Rightarrow \text{Coordination number} = 3 \times 2 = 6$$

$$[\text{Ni}(\text{NH}_3)_4]^{2+} \Rightarrow \text{Coordination number} = 4 \times 1 = 4$$

### 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. [Cr(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>                   | $\begin{aligned} x + 6(\text{charge on NH}_3) &= +3 \\ x + 6 \times 0 &= +3, \text{ then } x = +3 \end{aligned}$                                                              |
| 2. K <sub>2</sub> [Ni(CN) <sub>4</sub> ]                                | $\begin{aligned} 2(\text{charge on K}^+) + x + 4(\text{charge on CN}^-) &= 0 \\ 2(1) + x + 4(-1) &= 0 \text{ then } x = +2 \end{aligned}$                                     |
| 3. [Cr(H <sub>2</sub> O) <sub>3</sub> Cl] <sub>2</sub> H <sub>2</sub> O | $\begin{aligned} \text{oxidation state of Cr} + 6(\text{charge on H}_2\text{O}) + 3(\text{charge on Cl}^-) &= 0 \\ x + 6(0) + 3(-1) &= 0, \text{ then } x = +3 \end{aligned}$ |
| 4. Ni(CO) <sub>4</sub>                                                  | $\begin{aligned} \text{oxidation state of Ni} + 4(\text{charge on CO}) &= 0 \\ x + 4(0) &= 0 \text{ then } x = 0 \end{aligned}$                                               |

10. The coordination environment of Ca<sup>2+</sup> ion in its complex with EDTA<sup>4-</sup> is: [09 April, 2024 (Shift-II)]
- tetrahedral
  - octahedral
  - square planar
  - trigonal prismatic
- Sol. (b)

11. The sum of coordination number and oxidation number of the metal M in the complex [M(en)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)]Cl (where en is ethylenediamine) is: [NEET 2015 Re]
- 6
  - 7
  - 8
  - 9
- Sol. (d)

### Coordination Compounds

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# IUPAC NOMENCLATURE

## Rules for Writing Formula of Coordination Compounds

- Formula of cation [simple or complex] is written first.
- Co-ordination entity is enclosed in square bracket.
- In coordination sphere, metal atom is written first, followed by ligands in alphabetical order of their names.
- First letter of abbreviation is considered in abbreviated ligands [like en, Ox, EDTA]
- When ligands are polyatomic, their formulas are enclosed in parenthesis.  
For example: (H<sub>2</sub>O), (NH<sub>3</sub>).
- There should be no space between the ligands and the metal.
- 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<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, [CrCl<sub>4</sub>]<sup>1-</sup>.
- 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<br>K <sub>4</sub> [Fe(CN) <sub>6</sub> ] | Complex cation + Complex anion<br>[Cr(NH <sub>3</sub> ) <sub>6</sub> ][Co(CN) <sub>6</sub> ] | Complex cation + Simple anion<br>[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub> |

- Complex cation is named first followed by anion (if present).
- The ligands are named in alphabetical order before the name of metal atom/ion.

| Cationic part                                                     | Anionic part                    |                                    |
|-------------------------------------------------------------------|---------------------------------|------------------------------------|
| [Co(NH <sub>3</sub> ) <sub>4</sub> Br <sub>2</sub> ] <sup>+</sup> | [Cl <sub>2</sub> ] <sup>-</sup> | Alphabetical order: ammine > Bromo |

- | Ligands                                       | Suffix                            |
|-----------------------------------------------|-----------------------------------|
| Anionic (Cl <sup>-</sup> / CN <sup>-</sup> )  | - o (chlorido / cyanido)          |
| Neutral (H <sub>2</sub> O / NH <sub>3</sub> ) | No special suffix (aqua / ammine) |
| Cationic (NO <sup>+</sup> )                   | - ium (nitrosonium)               |
- To indicate the number of ligands, we use prefix as mono, di, tri, tetra for number of ligands.  
(H<sub>2</sub>O)<sub>3</sub> : triaqua, (NH<sub>3</sub>)<sub>4</sub> : tetraammine
- 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)<sub>2</sub> : bis(ethane - 1, 2-diammine)
- Oxidation state of metal is indicated by roman numerical in parenthesis (I) (II) (III) etc.

| Complex | Name of metal   | Complex                                            | Name of metal |
|---------|-----------------|----------------------------------------------------|---------------|
| Cation  | Same as element | [Ni(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> | Nickel        |
| Anion   | Ends with ate   | [NiCl <sub>4</sub> ] <sup>1-</sup>                 | Nickelate     |
| Neutral | Same as element | [Ni(CO) <sub>4</sub> ]                             | 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           |

- K<sub>3</sub>[Fe(CN)<sub>6</sub>] → Potassium hexacyanido**ferrate** (III)
- Ni(CO)<sub>4</sub> → Tetracarbonyl**nickel** (0)
- [Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]Br<sub>2</sub> → Tetraammine**diaqua**cobalt (II) bromide
- [Ag(NH<sub>3</sub>)<sub>2</sub>][Ag(CN)<sub>2</sub>] → Diamminesilver (I) dicyanido**argentate** (I)

Note

Silver always has +1 oxidation state in its compound.  
Cationic part: [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>: diamminesilver (I)  
Anionic part: [Ag(CN)<sub>2</sub>]<sup>-</sup>: dicyanidoargentate (I)

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8. If there is any water of crystallization, it is to included in the name. For example,  
 $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O \rightarrow$  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(dimethylglyoximate)nickel(II)                    |
| 3.    | $Na_2[Fe(CN)_5(NO)]$                 | Sodium pentacyanonitrosoumiron(II) ferrate(II)       |
| 4.    | $[Fe(H_2O)_5(NO)]SO_4$               | Pentaaquanitrosoumiron(II) sulphate                  |
| 5.    | $[Cu(CN)_4]^{3-}$                    | Tetracyanidocuprate(II) ion                          |
| 6.    | $[Co(NH_3)_5(CO_3)]Cl$               | Pentaamminecarbonatocobalt(III) chloride             |
| 7.    | $[Cr(CO)_5(PPh_3)]$                  | Pentacarbonyltriphenylphosphinechromium(0)           |
| 8.    | $(NH_4)[Cr(NH_3)_2(NCS)_4]$          | Ammonium diamminetetra(thiocyanato-N) chromate (III) |
| 9.    | $[Pt(NH_3)_2Cl_2]$                   | Diamminetetrachloridoplatinum (IV)                   |
| 10.   | $[NiCl_2(PPh_3)_2]$                  | Dichloridobis(triphenylphosphine)nickel (II)         |
| 11.   | $[Cr(NH_3)_3(H_2O)_2]Cl_3$           | Triamminetriaquachromium (III) chloride              |
| 12.   | $[Pt(NH_3)_2Cl]Br_3$                 | Pentaamminechloridoplatinum (IV) bromide             |
| 13.   | $(NH_4)_2[Ni(C_2O_4)_2(H_2O)_2]$     | Ammonium diaquadioxalatonicke(II)                    |
| 14.   | $[Pt(H_2NCH_2CH_2NH_2)_2Cl_2]Cl_2$   | Dichloridobis(ethylenediamine)platinum (IV) chloride |
| 15.   | $Fe(CO)_5$                           | Pentacarbonyliron (0)                                |
| 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.   | $NaCr(OH)_4 \cdot Na^+ [Cr(OH)_4]^-$ | 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.    | Dicyanidoaurate(I) ion                                | $[Au(CN)_2]^-$                     |
| 2.    | Sodium hexafluoroaluminate(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 (0)                           | $[(CO)_5Mn-Mn(CO)_5]$              |
| 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  $[Co(H_2O)_4(NH_3)_2]Cl_2$  is (IIT JEE 2012)
- (a) tetraaquadiamminecobalt (III) chloride (b) tetraaquadiamminecobalt (III) chloride  
 (c) diamminetetraaquacobalt (III) chloride (d) diamminetetraaquacobalt (III) chloride

Sol. (d)

13. The IUPAC name of  $[NiCl_4]^{2-}$  is (IIT JEE 2008)
- (a) tetrachloronickel (II)  
 (b) Tetraamminenickel (II) tetrachloronickel (II)  
 (c) Tetraamminenickel (II) tetrachloronickelate (II)  
 (d) Tetrachloronickel (II) tetraamminenickelate (0)

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)

## Coordination Compounds

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TESTS TO CONFIRM STRUCTURE OF COORDINATION COMPOUNDS

Aq. AgNO<sub>3</sub> Test

$[Cr(NH_3)_5Cl]Cl_2(aq) \xrightarrow[\text{excess}]{AgNO_3} 2AgCl \downarrow$ 

(White ppt.)

$[Cr(NH_3)_5Cl]Br_2(aq) \xrightarrow[\text{excess}]{AgNO_3} 2AgBr \downarrow$ 

(Yellow ppt.)

$[Cr(NH_3)_5Cl]Cl_2 \equiv [Cr(NH_3)_5Cl]^{2+} 2Cl^-$ 

[2 moles of white ppt (AgCl) indicates that 2 Cl<sup>-</sup> ions are outside the coordination sphere]

$[Cr(NH_3)_5Cl]Br_2 \equiv [Cr(NH_3)_5Cl]^{2+} 2Br^-$ 

[2 moles of yellow ppt (AgBr) indicates that 2 Br<sup>-</sup> ions are outside the coordination sphere]

BaSO<sub>4</sub> Test

$[Cr(NH_3)_5Cl]SO_4(aq) \xrightarrow[\text{excess}]{BaCl_2(aq)} BaSO_4 \downarrow$ 

(White)

$[Cr(NH_3)_5(SO_4)]Cl \xrightarrow[\text{excess}]{Ba(NO_3)_2} \text{No ppt}$ 

This indicates that SO<sub>4</sub><sup>2-</sup> is not present outside the coordination sphere.

$[Cr(NH_3)_5Cl]SO_4 \equiv [Cr(NH_3)_5Cl]^{2+} SO_4^{2-}$ 

[White ppt with BaCl<sub>2</sub> indicates presence of SO<sub>4</sub><sup>2-</sup> ion outside the coordination sphere]

16. Mixture X = 0.02 mole of [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>]Br and 0.02 mole of [Co(NH<sub>3</sub>)<sub>5</sub>Br]SO<sub>4</sub> was prepared in 2L of solution.

1L of mixture X + excess AgNO<sub>3</sub> → Y

1L of mixture X + excess BaCl<sub>2</sub> → Z

Number of moles of Y and Z are

(a) 0.01, 0.01

(b) 0.02, 0.01

(c) 0.01, 0.02

(d) 0.02, 0.02

(IIT JEE 2003)

Sol. (a) In 1L of solution, 0.01 mole of each [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>]Br and [Co(NH<sub>3</sub>)<sub>5</sub>Br]SO<sub>4</sub> will be present.

Adding of excess of AgNO<sub>3</sub> will give 0.01 mole of AgBr. On adding of excess BaCl<sub>2</sub>, 0.01 mole of BaSO<sub>4</sub> will be formed.

17. The correct order of the stoichiometries of AgCl formed when AgNO<sub>3</sub> in excess is treated with the complexes CoCl<sub>3</sub>·6NH<sub>3</sub>, CoCl<sub>3</sub>·5NH<sub>3</sub>, CoCl<sub>3</sub>·4NH<sub>3</sub> 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<sub>3</sub>·4NH<sub>3</sub>

(b) CoCl<sub>3</sub>·5NH<sub>3</sub>

(c) CoCl<sub>3</sub>·6NH<sub>3</sub>

(d) CoCl<sub>3</sub>·3NH<sub>3</sub>

Sol. (d)

Molar Conductivity Measurement

Molar conductivity ∝ No. of Charges

|                   | No. of Charges                        | Molar Conductivity (ohm <sup>-2</sup> cm <sup>2</sup> mol <sup>-1</sup> ) |
|-------------------|---------------------------------------|---------------------------------------------------------------------------|
| LiCl              | Li <sup>+</sup> Cl <sup>-</sup> ≡ 2   | 112                                                                       |
| MgCl <sub>2</sub> | Mg <sup>2+</sup> 2Cl <sup>-</sup> ≡ 4 | 260.8                                                                     |
| LaCl <sub>3</sub> | La <sup>3+</sup> 3Cl <sup>-</sup> ≡ 6 | 393.5                                                                     |

a. [Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl ≡ [Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl<sup>+</sup> → No. of charges = 2

b. [Cr(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> ≡ [Cr(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> 2Cl<sup>-</sup> → No. of charges = 4

Order of molar conductivity: a < b

19. Consider the following complexes:

(i) K<sub>2</sub>PtCl<sub>6</sub>      (ii) PtCl<sub>4</sub>·2NH<sub>3</sub>      (iii) PtCl<sub>4</sub>·3NH<sub>3</sub>      (iv) PtCl<sub>4</sub>·5NH<sub>3</sub>

their electrical conductance in aqueous solutions are:

(a) 2, 3, 4, 9, 404

(b) 404, 0, 97, 256

(c) 2, 3, 4, 0, 0

(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<sub>2</sub>[PtCl<sub>6</sub>] → 2K<sup>+</sup> + [PtCl<sub>6</sub>]<sup>2-</sup>

(ii) [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>] → [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>]

(iii) [Pt(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>]Cl → [Pt(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>]<sup>+</sup> + Cl<sup>-</sup>

(iv) [Pt(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>3</sub> → [Pt(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>3+</sup> + 3Cl<sup>-</sup>

Cryoscopic Measurement

The reduction in the freezing point of solvents due to the addition of solutes (salt).

Depression in freezing point ∝ no of particles

LiCl → Li<sup>+</sup> + Cl<sup>-</sup> ⇒ No of particles ≡ 2

MgCl<sub>2</sub> → Mg<sup>2+</sup> + 2Cl<sup>-</sup> ⇒ No of particles ≡ 3

Depression in freezing point: LiCl < MgCl<sub>2</sub>

a. [Cr(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> = No of particles ≡ 3

b. [Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl = No of particles ≡ 2

Depression in freezing point: a > b

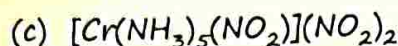
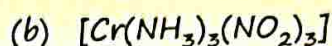
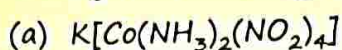
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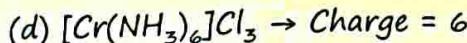
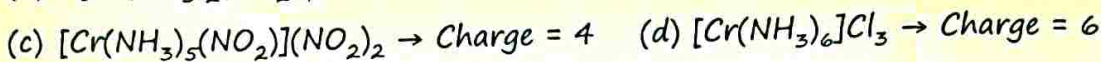
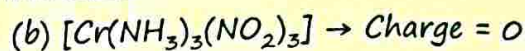
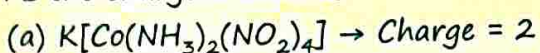
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20. Arrange the following compounds in order of increasing molar conductivity.



Sol. As the charge increases, molar conductivity increases.



(b) < (a) < (c) < (d) : Molar conductivity

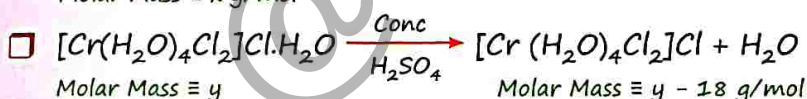
### Establishing the Structure of Complexes

| 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           | $[Co(NH_3)_3Cl_3]$             |
| $Co(NO_2)_3 \cdot KNO_2 \cdot 2NH_3$ | 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          | $3K^+ [Co(NO_2)_6]^{3-}$       |

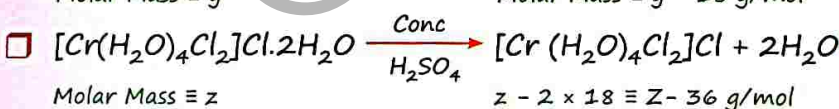
### Dehydrating Agents-Conc. $H_2SO_4$ , $P_2O_5$



[No loss of weight]



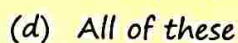
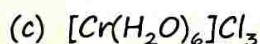
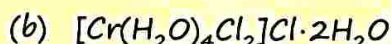
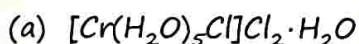
[Loss of 1 mole  $H_2O \equiv \text{loss of } 18 \text{ g/mol}$ ]



[Loss of 2 moles of  $H_2O \equiv \text{loss of } 36 \text{ g/mol}$ ]

Loss of weight by using dehydrating agent  $\rightarrow c > b > a$

21. Which of the following complexes will be dehydrated to relatively minimum extent by conc.  $H_2SO_4$  under identical condition.



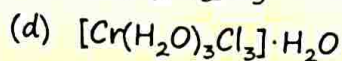
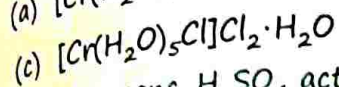
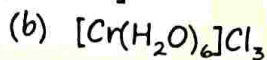
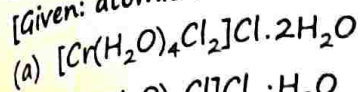
Sol. (c) Under identical conditions, the complex  $[Cr(H_2O)_6]Cl_3$  will be dehydrated the least by concentrated  $H_2SO_4$  because the water molecules are directly coordinated to the metal ion, making them less likely to be removed.



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-1I)]



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 i.e. they 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  $\equiv$  oxidation state of metal.
- ☐ It is represented by dotted line (.....)

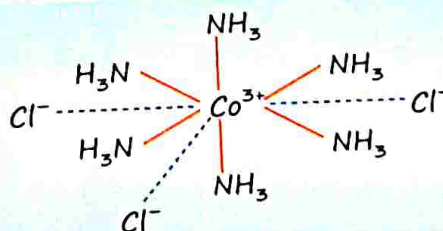
### Secondary Valency

- ☐ Non-ionisable Valency
- ☐ Directional in nature
- ☐ Secondary valencies are satisfied by neutral molecules or negatively charged ions or both
- ☐ Secondary valency  $\equiv$  coordination number of metal.
- ☐ It is represented by solid line (\_\_\_\_\_).

Example:  $CoCl_3 \cdot 6NH_3 = [Co(NH_3)_6]Cl_3$

Primary Valency  $\rightarrow 3$

Secondary valency  $\rightarrow 6$



Coordination Compounds [Click Here To Join @StudyShelf For More Study Materials](#)



## Modern Formulation

Primary valency  $\equiv$  oxidation state of metal.

Secondary valency  $\equiv$  coordination number of metal.

| Complex                                          | Primary Valency/Oxidation state                      | Secondary Valency/Coordination No.                                               |
|--------------------------------------------------|------------------------------------------------------|----------------------------------------------------------------------------------|
| $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$          | 3<br>(this valency is satisfied by $3\text{Cl}^-$ )  | 6<br>(this valency is satisfied by $6\text{NH}_3$ )                              |
| $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ | +3<br>(this valency is satisfied by $3\text{Cl}^-$ ) | $5 + 1 = 6$<br>(this valency is satisfied by $5\text{NH}_3$ and $1\text{Cl}^-$ ) |
| $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ | +3<br>(this valency is satisfied by $3\text{Cl}^-$ ) | $4 + 2 = 6$<br>(this valency is satisfied by $4\text{NH}_3$ and $2\text{Cl}^-$ ) |

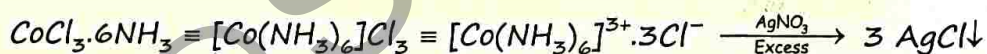
## Experiments

### 1. Precipitation Reaction with $\text{AgNO}_3$

In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of chloride ions could be precipitated as  $\text{AgCl}$  on adding excess  $\text{AgNO}_3$  solution but some remained in solution.

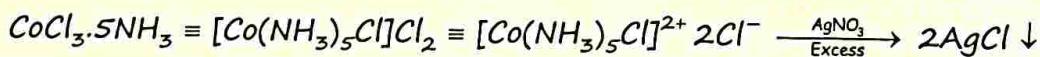
(a)

It means that 3 mol  $\text{Cl}^-$  were present in aq. solution of  $\text{CoCl}_3 \cdot 6\text{NH}_3$



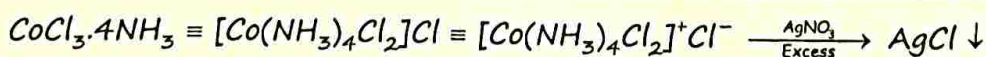
(b)

It means that 2 mol  $\text{Cl}^-$  were present in aq. Solution of  $\text{CoCl}_3 \cdot 5\text{NH}_3$



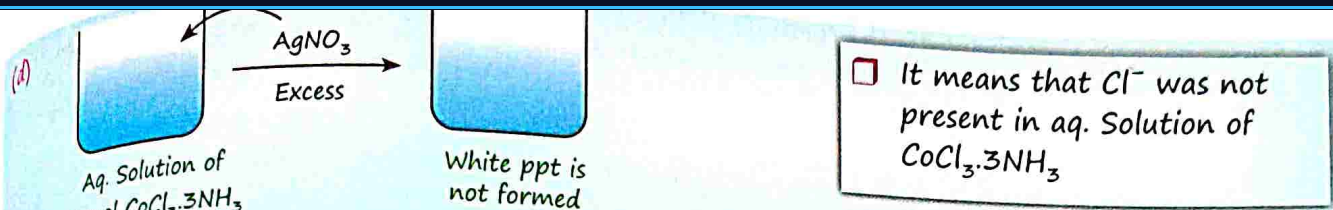
(c)

It means that 1 mol  $\text{Cl}^-$  was present in aq. Solution of  $\text{CoCl}_3 \cdot 4\text{NH}_3$



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23. An octahedral complex with the formula  $\text{CoCl}_3 \cdot n\text{NH}_3$  upon reaction with excess of  $\text{AgNO}_3$  solution given 2 moles of  $\text{AgCl}$ . 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)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 + \text{excess AgNO}_3 \rightarrow 2\text{AgCl}$  (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  $\text{CoCl}_3(\text{NH}_3)_4$  corresponds to 1 : 1 electrolyte, then the primary valency of central metal ion is \_\_\_\_\_. [27 July, 2022 (Shift-I)]

Sol. [3] Complex is  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

Primary valency = oxidation no. = +3.

25. Complex X of composition  $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_n$  has a spin only magnetic moment of 3.83 BM. It reacts with  $\text{AgNO}_3$  and shows geometrical isomerism. The IUPAC nomenclature of X is: [9 Jan, 2020 (Shift-I)]

- (a) Dichloridotetraaquachromium (IV) chloride dihydrate  
 (b) Hexaaquachromium (III) chloride  
 (c) Tetraaquadichloridochromium (III) chloride dihydrate  
 (d) Tetraaquadichloridochromium (IV) chloride dihydrate

Sol. (c)  $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_n \rightarrow \mu_{\text{spin}} = 3.83 \text{ B.M.}$

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  $\text{AgNO}_3$  therefore, formula of complex is  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ .

IUPAC Name: Tetraaquadichloridochromium(III) chloride dihydrate.

26. The primary and secondary valencies of cobalt respectively in  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$  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  $\text{AgCl}$  precipitated with excess of  $\text{AgNO}_3$  is given?

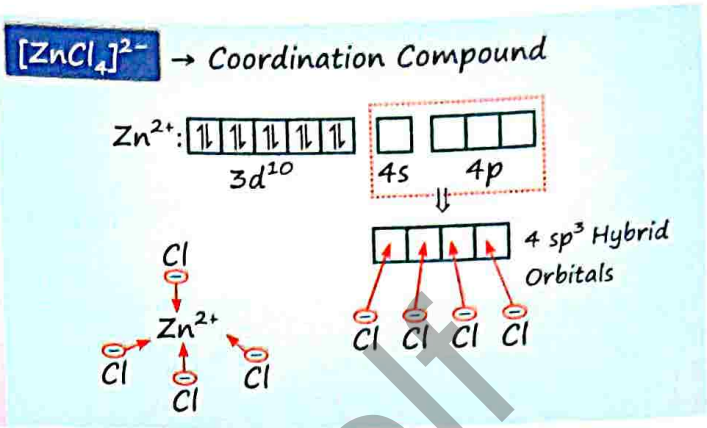
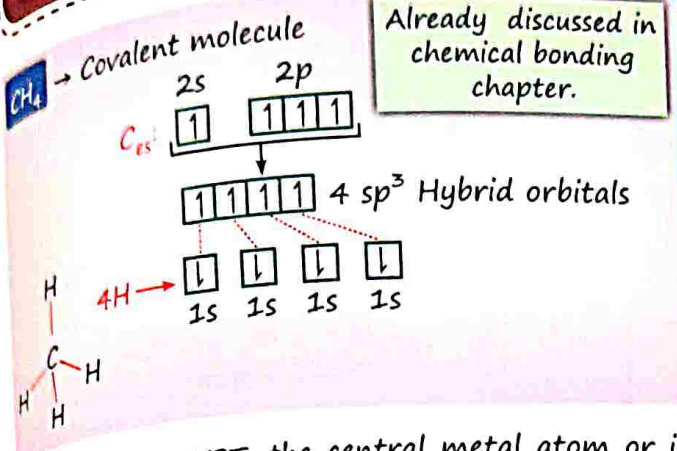
$\text{PtCl}_2 \cdot 2\text{NH}_3$ ,  $\text{CoCl}_3 \cdot 4\text{NH}_3$ ,  $\text{PtCl}_4 \cdot 2\text{HCl}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{PdCl}_2 \cdot 4\text{NH}_3$

Sol.

| Molecular Formula                         | Moles of $\text{AgCl}$ precipitated with excess of $\text{AgNO}_3$ | Compound                                         | Secondary valency (Coordination number) |
|-------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------|-----------------------------------------|
| $\text{PtCl}_2 \cdot 2\text{NH}_3$        | 0                                                                  | $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$          | 4                                       |
| $\text{CoCl}_3 \cdot 4\text{NH}_3$        | 1                                                                  | $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ | 6                                       |
| $\text{PtCl}_4 \cdot 2\text{HCl}$         | 0                                                                  | $\text{H}_2[\text{PtCl}_6]$                      | 6                                       |
| $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ | 2                                                                  | $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$   | 6                                       |
| $\text{PdCl}_2 \cdot 4\text{NH}_3$        | 2                                                                  | $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$          | 4                                       |



# VALENCE BOND THEORY



$[V(H_2O)_6]^{2+}$

$V^{2+}$

$[Ar]4s^0 3d^3$

$V^{2+}$

$3d$

$4s$

$V^{2+}$

$3d$

$d^2sp^3$  Hybridization

$[V(H_2O)_6]^{2+}$

$3d$

$H_2O$   $H_2O$   $H_2O$   $H_2O$   $H_2O$   $H_2O$

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, 6  $H_2O$  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].

$[Zn(H_2O)_6]^{2+}$

$Zn^{2+}$

$4s^0 3d^{10}$

$Zn^{2+}$

$3d$

$4s$

$4p$

$4d$

$Zn^{2+}$

$3d$

$6, sp^3d^2$  hybrid orbitals

$[Zn(H_2O)_6]^{2+}$

$3d$

$H_2O$   $H_2O$   $H_2O$   $H_2O$   $H_2O$   $H_2O$

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, 6  $H_2O$  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.

$d^0$   $d^1$   $d^2$   $d^3$

Always  $d^2sp^3$

Because two inner d-orbitals are always available for hybridisation

$d^4$   $d^5$   $d^6$   $d^7$

$d^2sp^3/sp^3d^2$

Both type of hybridisation are possible. It can be determined by value of magnetic moment or magnetic behaviour.

$d^7$   $d^8$   $d^9$   $d^{10}$

Always  $sp^3d^2$

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.

$Co^{3+}$  ion:  $(3d^6)$

$3d$

$4s$

$4p$

Hybridisation:  $3d$

$d^2sp^3$ : Inner orbital hybridisation

$[Co(NH_3)_6]^{3+}$ : [Inner orbital complex]

$NH_3$   $NH_3$   $NH_3$   $NH_3$   $NH_3$   $NH_3$

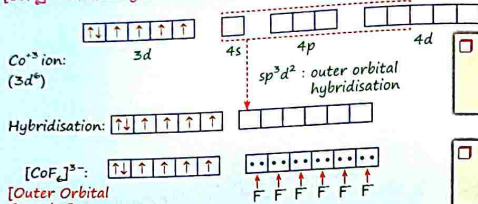
It is given that complex is diamagnetic, so all electrons should be paired

Here, 6  $NH_3$  ligands are donating lone pair in vacant hybrid orbitals.

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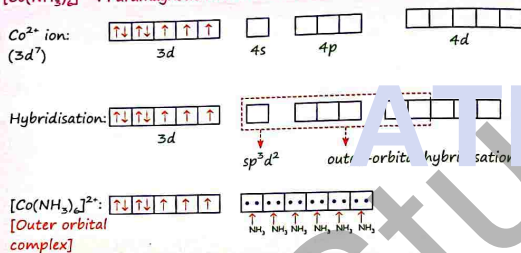


## 2. $[\text{CoF}_6]^{3-}$ : Paramagnetic octahedral complex

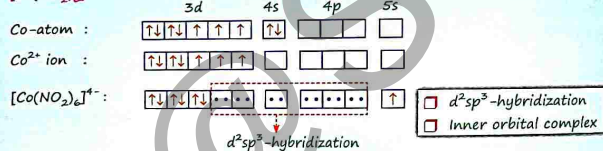


## For $d^7$ complex

### 1. $[\text{Co}(\text{NH}_3)_6]^{2+}$ : Paramagnetic in nature with 3.87 BM



### 2. $[\text{Co}(\text{NO}_2)_6]^{4-}$ :



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  $[\text{Co}(\text{NO}_2)_6]^{4-}$  is oxidized by air or  $\text{H}_2\text{O}_2$  easily to give  $[\text{Co}(\text{NO}_2)_6]^{3-}$ . This indicates that the complex  $[\text{Co}(\text{NO}_2)_6]^{4-}$  is unstable in air.

## Hybridization in Complex having Coordination No-4

### Hybridization in Complex having Coordination No-4

Tetrahedral ( $sp^3$ )

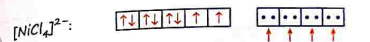
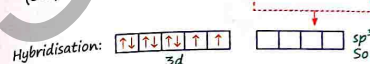
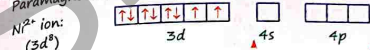
$[\text{NiCl}_4]^{2-}$ ,  $[\text{Ni}(\text{CO})_4]$

Square planar ( $dsp^2$ ) ( $d = d_{x^2-y^2}$ )

$[\text{Ni}(\text{CN})_4]^{2-}$

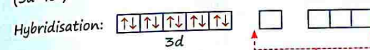
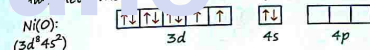
### 1. $[\text{NiCl}_4]^{2-}$ : Paramagnetic in nature.

Paramagnetic means unpaired electrons are present.

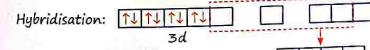
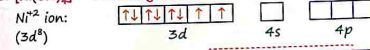


### 2. $[\text{Ni}(\text{CO})_4]$ : Diamagnetic in nature.

Diamagnetic means all electrons are paired.



### 3. $[\text{Ni}(\text{CN})_4]^{2-}$ : Diamagnetic.

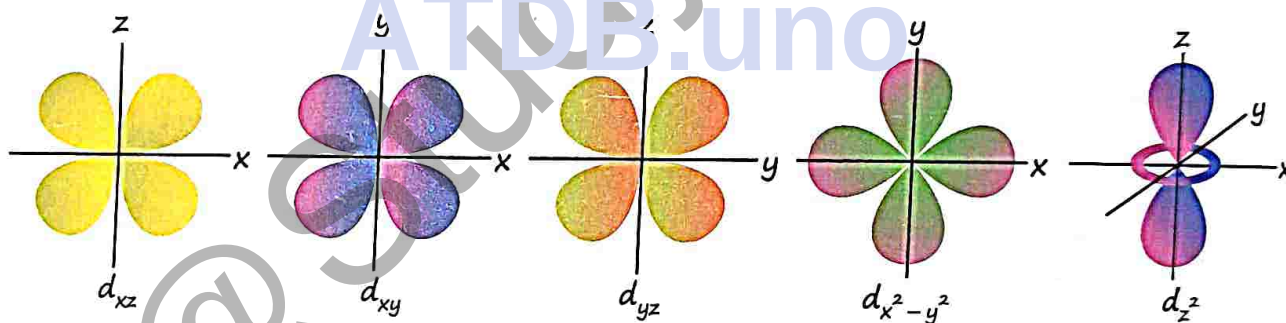


## Limitation of VBT

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 |
|------------------|---------------------|------------------|---------------------|
| $\text{Cu}^+$    | 2, 4                | $\text{Fe}^{2+}$ | 6                   |
| $\text{Ag}^+$    | 2                   | $\text{Fe}^{3+}$ | 6                   |
| $\text{Au}^+$    | 2, 4                | $\text{Co}^{2+}$ | 4, 6                |
| $\text{Cu}^{2+}$ | 4, 6                | $\text{Co}^{3+}$ | 6                   |
| $\text{Pt}^{2+}$ | 4                   | $\text{Al}^{3+}$ | 6                   |
| $\text{Pd}^{2+}$ | 4                   | $\text{Pt}^{4+}$ | 6                   |
| $\text{Mg}^{2+}$ | 6                   | $\text{Pd}^{4+}$ | 6                   |
| $\text{Ni}^{2+}$ | 4, 6                |                  |                     |

## SHAPES OF d-ORBITALS



## CRYSTAL FIELD THEORY

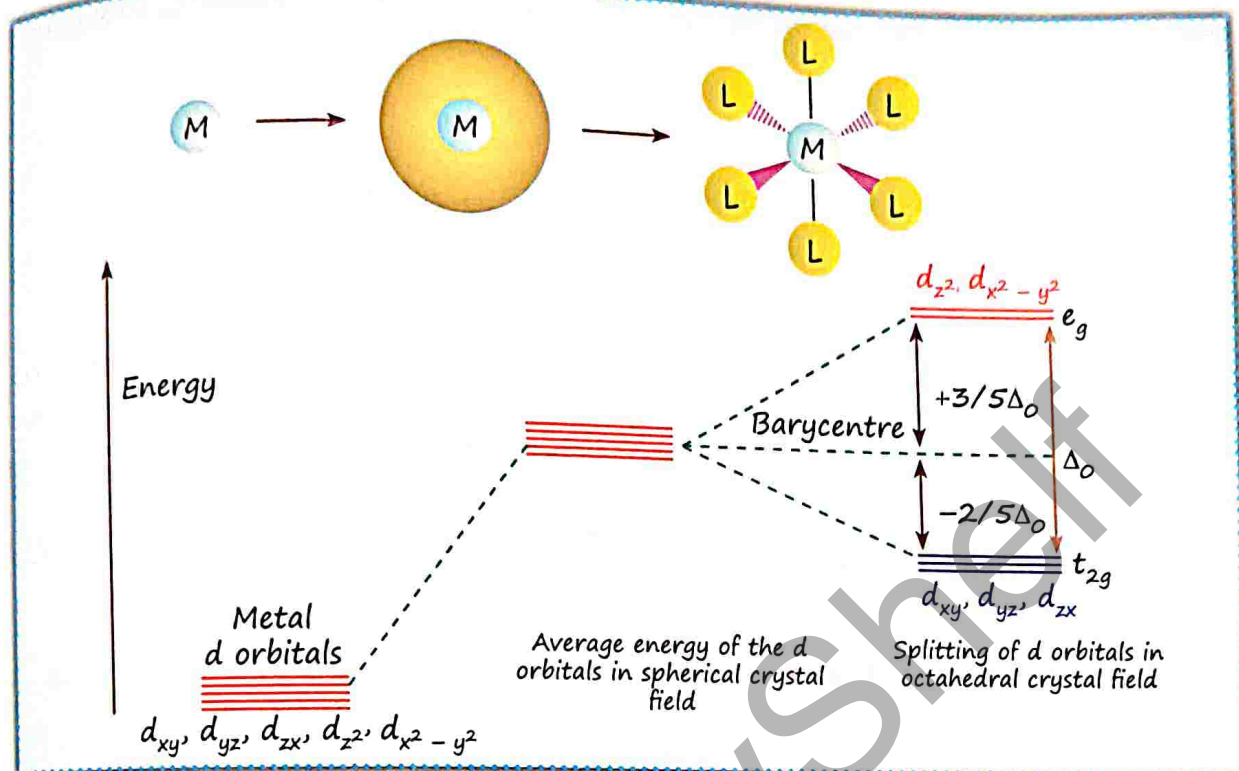
### Crystal Field Splitting in Octahedral Complexes

- 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).

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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  $\Delta_o$  [Crystal field splitting energy].



Crystal Field Stabilization Energy  $CFSE_{(octahedral)} = [-0.4n_{(t_{2g})} + 0.6n_{(e_g)}]\Delta_o$

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.

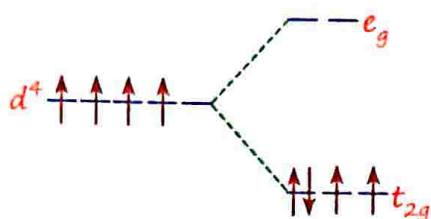
| $d^1$ Configuration                                                                                                                                                                                                                                                                                                                        | $d^2$ Configuration                                                                                                                                                                                                                                                                                                                        | $d^3$ Configuration                                                                                                                                                                                                                                                                                                                       |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                           |
| <p>Electronic configuration: <math>t_{2g}^1 e_g^0</math></p> <p>No. of unpaired electrons = 1</p> <p>Magnetic moment = <math>\sqrt{1(1+2)} \text{ BM}</math><br/> <math>= 1.73 \text{ BM}</math></p> <p>Example: <math>[\text{Ti}(\text{H}_2\text{O})_6]^{3+}</math></p> <p>CFSE = <math>1 \times -0.4 \Delta_o = -0.4 \Delta_o</math></p> | <p>Electronic configuration: <math>t_{2g}^2 e_g^0</math></p> <p>No. of unpaired electrons = 2</p> <p>Magnetic moment = <math>\sqrt{2(2+2)} \text{ BM}</math><br/> <math>= 2.82 \text{ BM}</math></p> <p>Example: <math>[\text{Ti}(\text{H}_2\text{O})_6]^{2+}</math></p> <p>CFSE = <math>2 \times -0.4 \Delta_o = -0.8 \Delta_o</math></p> | <p>Electronic configuration: <math>t_{2g}^3 e_g^0</math></p> <p>No. of unpaired electrons = 3</p> <p>Magnetic moment = <math>\sqrt{3(3+2)} \text{ BM}</math><br/> <math>= 3.87 \text{ BM}</math></p> <p>Example: <math>[\text{V}(\text{H}_2\text{O})_6]^{2+}</math></p> <p>CFSE = <math>3 \times -0.4 \Delta_o = -1.2 \Delta_o</math></p> |

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**Pairing Energy:** The energy required to force the two unpaired electrons in one orbital is called the pairing energy (P).

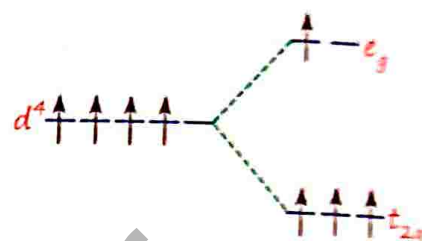
### $d^4$ Configuration

(i) If  $\Delta_o > P$  [ $P$  = pairing energy]



- If the crystal field splitting parameter ( $\Delta$ ) is large because of strong-bonding ligands, then the pairing energy will be smaller, and the complex will be low-spin.
- 4<sup>th</sup> electron enters into  $t_{2g}$  orbital and configuration =  $t_{2g}^4 e_g^0$
- Ligands for which  $\Delta_o > P$  are known as strong field ligand. [SFL]
- No. of unpaired electron = 2
- Magnetic moment =  $\sqrt{2(2+2)} = 2.828 \text{ BM}$
- CFSE =  $4 \times -0.4\Delta_o + P = -1.6\Delta_o + P$
- Example:  $[\text{Cr}(\text{CN})_6]^{4-}$

(ii) If  $\Delta_0 < P$



- If the crystal field splitting parameter ( $\Delta$ ) is small because of weak-bonding ligands, then the pairing energy will be larger and the complex will be high-spin.
- 4<sup>th</sup> electron enters into one of  $e_g$  orbitals giving the configuration  $t_{2g}^3 e_g^1$ .
- Ligands for which  $\Delta_o < P$  are known as weak field ligand. [WFL]
- No. of unpaired electrons = 4
- Magnetic moment =  $\sqrt{4(4+2)} = 4.89 \text{ BM}$
- CFSE =  $3 \times -0.4\Delta_o + 1 \times 0.6\Delta_o = -0.6\Delta_o$
- Example:  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$

## 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

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO \quad [NCERT]$$

| d series            | Charge on metal | Ligands         | Field strength |
|---------------------|-----------------|-----------------|----------------|
| 3d series           | +2              | $I^-$ to en     | Weak           |
| Sc $\rightarrow$ Zn | +3              | $I^-$ to $H_2O$ | Weak*          |
|                     | +4              | $I^-$ to CO     | Strong         |
| 4d series           | +2 / +3 / +4    | $I^-$ to CO     | Strong         |
| Y $\rightarrow$ Cd  |                 |                 |                |
| 5d series           | +2 / +3 / +4    | $I^-$ to CO     | Strong         |
| La $\rightarrow$ Hg |                 |                 |                |



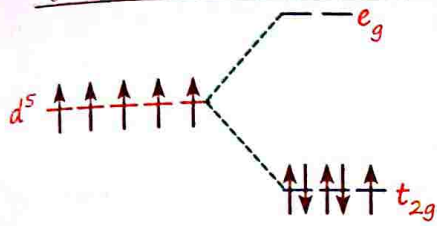
For  $\text{Co}^{3+}$  all oxygen / nitrogen / carbon donor ligands are strong field ligand.

- $[\text{Co}(\text{NH}_3)_6]^{2+}$  :  $\text{NH}_3$  as WFL with  $\text{Co}^{2+}$  :  $\Delta_o < P$
- $[\text{Co}(\text{NH}_3)_6]^{3+}$  :  $\text{NH}_3$  as SFL with  $\text{Co}^{3+}$  :  $\Delta_o > P$
- $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  :  $\text{H}_2\text{O}$  as SFL with  $\text{Co}^{3+}$  :  $\Delta_o > P$
- $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  :  $\text{H}_2\text{O}$  as WFL with  $\text{Ni}^{2+}$  :  $\Delta_o < P$
- $[\text{NiCl}_4]^{2-}$  :  $\text{Cl}^-$  as WFL with  $\text{Ni}^{2+}$  :  $\Delta_o < P$
- $[\text{NiF}_6]^{2-}$  :  $\text{F}^-$  as SFL with  $\text{Ni}^{2+}$  :  $\Delta_o > P$

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{NO}_2^- < \text{N}_3^- < \text{F}^- < \text{OH}^-$   
 $< \text{C}_2\text{O}_4^{2-} < \text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{CH}_3\text{C}\equiv\text{N} < \text{EDTA}^{4-}$   
 $< \text{py} < \text{NH}_3 < \text{en} < \text{bipy} < \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$   
 (The donor atoms are indicated by bold letters.)

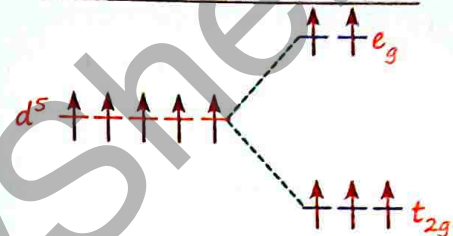
### d<sup>5</sup> System

#### $\Delta_o > P$ : Low Spin Complex



Electronic configuration =  $t_{2g}^5 e_g^0$   
 No. of unpaired electrons = 1  
 Magnetic moment =  $\sqrt{1(1+2)} \text{ BM} = 1.73 \text{ BM}$   
 CFSE =  $5 \times -0.4\Delta_o + 2P = -2.0\Delta_o + 2P$   
 Example =  $[\text{Fe}(\text{CN})_6]^{3-}$

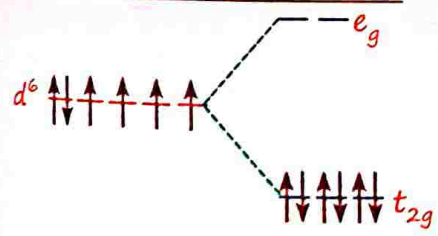
#### $\Delta_o < P$ : High Spin Complex



Electronic configuration =  $t_{2g}^3 e_g^2$   
 No. of unpaired electrons = 5  
 Magnetic moment =  $\sqrt{5(5+2)} \text{ BM} = 5.91 \text{ BM}$   
 CFSE =  $3 \times -0.4\Delta_o + 2 \times 0.6\Delta_o = 0$   
 Example =  $[\text{FeF}_6]^{3-}$

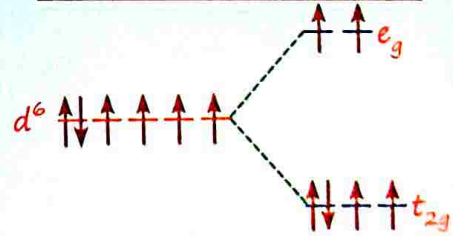
### d<sup>6</sup> System

#### $\Delta_o > P$ : Low Spin Complex



Electronic configuration =  $t_{2g}^6 e_g^0$   
 No. of unpaired electrons = 0 (Diamagnetic)  
 Magnetic moment = 0  
 CFSE =  $6 \times -0.4\Delta_o + 2P = -2.4\Delta_o + 2P$   
 Example =  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-} / [\text{Co}(\text{NH}_3)_6]^{3+}$

#### $\Delta_o < P$ : High Spin Complex



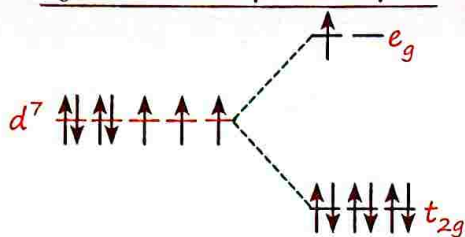
Electronic configuration =  $t_{2g}^4 e_g^2$   
 No. of unpaired electrons = (Paramagnetic : 4 unpaired electrons)  
 Magnetic moment =  $\sqrt{4(4+2)} \text{ BM} = 4.89 \text{ BM}$   
 CFSE =  $4 \times -0.4\Delta_o + 2 \times 0.6\Delta_o = -0.4\Delta_o$   
 Example =  $[\text{CoF}_6]^{3-}$



| Complex                                                            | Configuration  | $\Delta_o$ (cm <sup>-1</sup> ) | P (cm <sup>-1</sup> ) | Predicted | Found     |
|--------------------------------------------------------------------|----------------|--------------------------------|-----------------------|-----------|-----------|
| [Fe <sup>II</sup> (H <sub>2</sub> O)] <sup>2+</sup>                | d <sup>6</sup> | 10400                          | 17600                 | High spin | High spin |
| [Fe <sup>II</sup> (CN) <sub>6</sub> ] <sup>4-</sup>                | d <sup>6</sup> | 32850                          | 17600                 | Low spin  | Low spin  |
| [Co <sup>III</sup> F <sub>6</sub> ] <sup>3-</sup>                  | d <sup>6</sup> | 13000                          | 21000                 | High spin | High spin |
| [Co <sup>III</sup> (NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> | d <sup>6</sup> | 23000                          | 21000                 | Low spin  | Low spin  |

### d<sup>7</sup> System

$\Delta_o > P$  : Low Spin Complex



Electronic configuration =  $t_{2g}^6 e_g^1$

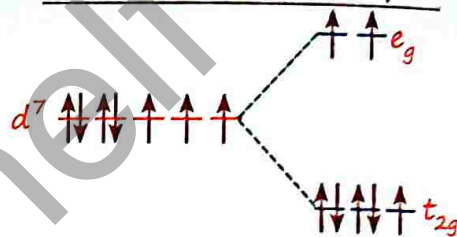
No. of unpaired electrons = Paramagnetic with 1 unpaired electron

Magnetic moment =  $\sqrt{1(1+2)}\text{BM} = 1.73\text{ BM}$

CFSE =  $6 \times -0.4\Delta_o + 1 \times 0.6\Delta_o = -1.0\Delta_o$

Example = [Co(CN)<sub>6</sub>]<sup>4-</sup>

$\Delta_o < P$  : High Spin Complex



Electronic configuration =  $t_{2g}^5 e_g^2$

No. of unpaired electrons = Paramagnetic with 3 unpaired electrons

Magnetic moment =  $\sqrt{4(4+2)}\text{BM} = 3.87\text{ BM}$

CFSE =  $4 \times -0.4\Delta_o + 2 \times 0.6\Delta_o = -0.8\Delta_o$

Example = [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>

## 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 $\Delta_o$ | Spin only magnetic moment $\mu_s(\text{BM})$ | $t_{2g}$                           | $e_g$ | CFSE $\Delta_o$ | Spin only magnetic moment $\mu_s(\text{BM})$ |
| d <sup>1</sup>        |                                  |       | -0.4            | 1.73                                         |                                    |       | -0.4            | 1.73                                         |
| d <sup>2</sup>        |                                  |       | -0.8            | 2.83                                         |                                    |       | -0.8            | 2.83                                         |
| d <sup>3</sup>        |                                  |       | -1.2            | 3.87                                         |                                    |       | -1.2            | 3.87                                         |
| d <sup>4</sup>        |                                  |       | -0.6            | 4.90                                         |                                    |       | -1.6            | 2.83                                         |
| d <sup>5</sup>        |                                  |       | 0               | 5.92                                         |                                    |       | -2.0            | 1.73                                         |
| d <sup>6</sup>        |                                  |       | -0.4            | 4.90                                         |                                    |       | -2.4            | 0.00                                         |
| d <sup>7</sup>        |                                  |       | -0.8            | 3.87                                         |                                    |       | -1.8            | 1.73                                         |
| d <sup>8</sup>        |                                  |       | -1.2            | 2.83                                         |                                    |       | -1.2            | 2.83                                         |
| d <sup>9</sup>        |                                  |       | -0.6            | 1.73                                         |                                    |       | -0.6            | 1.73                                         |
| d <sup>10</sup>       |                                  |       | 0               | 0                                            |                                    |       | 0               | 0                                            |

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$\Delta_o$  depends on

- (i) Charge on metal  $\Rightarrow$  Charge on metal  $\uparrow : \Delta_o \uparrow$   
 $\Rightarrow \Delta_o : 3d \text{ Series} < 4d \text{ Series} < 5d \text{ Series}$
- (ii) d Series
- (iii) Position of ligand in spectrochemical series.

| Crystal field splittings by various ligands    |                      |                          |
|------------------------------------------------|----------------------|--------------------------|
| Complex                                        | Absorption peak      |                          |
|                                                | ( $\text{cm}^{-1}$ ) | ( $\text{kJ mol}^{-1}$ ) |
| $[\text{Cr}^{III}\text{Cl}_6]^{3-}$            | 13640                | 163                      |
| $[\text{Cr}^{III}(\text{H}_2\text{O})_6]^{3+}$ | 17830                | 213                      |
| $[\text{Cr}^{III}(\text{NH}_3)_6]^{3+}$        | 21680                | 259                      |
| $[\text{Cr}^{III}(\text{CN})_6]^{3-}$          | 26280                | 314                      |

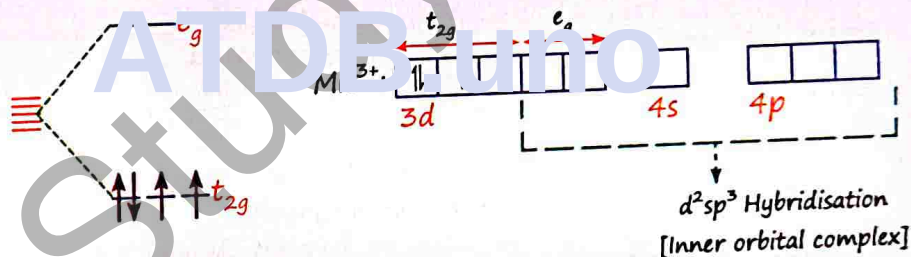
| $\Delta_o$ crystal field splittings in one group |                      |                          |
|--------------------------------------------------|----------------------|--------------------------|
|                                                  | ( $\text{cm}^{-1}$ ) | ( $\text{kJ mol}^{-1}$ ) |
| $[\text{Co}(\text{NH}_3)_6]^{3+}$                | 24800                | 296                      |
| $[\text{Rh}(\text{NH}_3)_6]^{3+}$                | 34000                | 406                      |
| $[\text{Ir}(\text{NH}_3)_6]^{3+}$                | 41000                | 490                      |

## Prediction of Hybridisation with Help of CFT



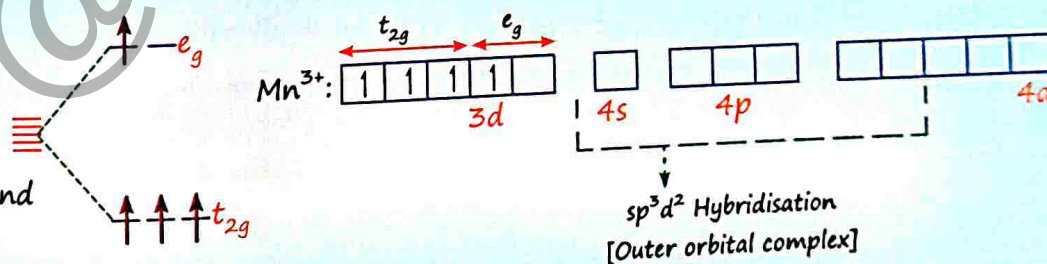
$\text{Mn}^{3+} : 3d^4$

$\text{CN}^-$  : Strong field ligand



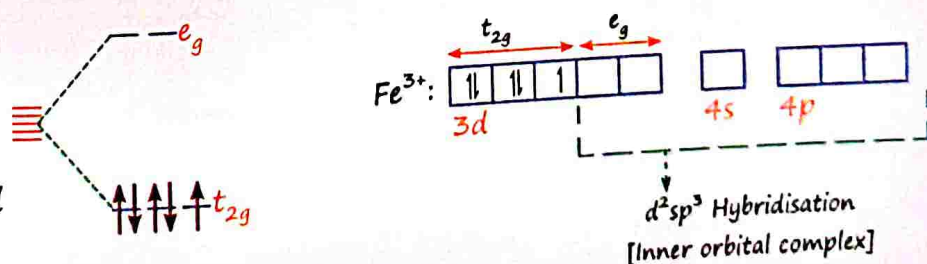
$\text{Mn}^{3+} : 3d^4$

$\text{Cl}^-$  : Weak field ligand



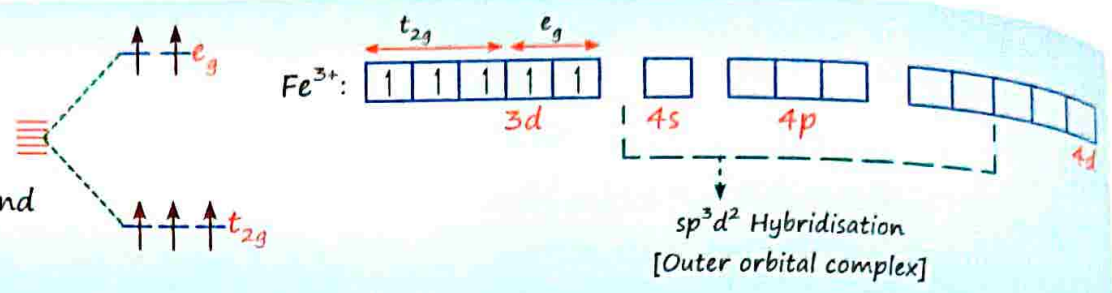
$\text{Fe}^{3+} : 3d^5$

$\text{CN}^-$  : Strong field Ligand



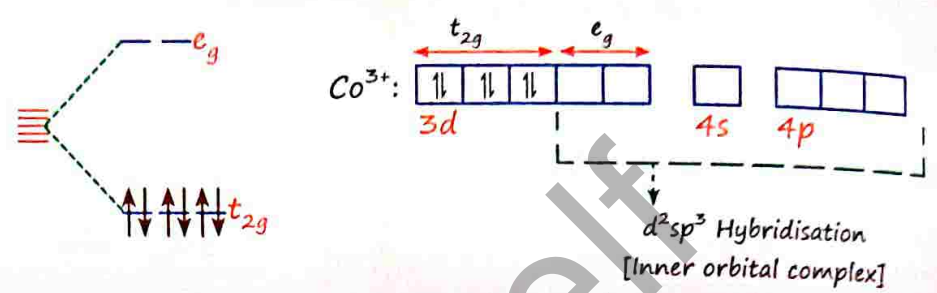
**[FeF<sub>6</sub>]<sup>3-</sup>**

- ☐ Fe<sup>3+</sup> : 3d<sup>5</sup>
- ☐ F<sup>-</sup> : Weak field ligand



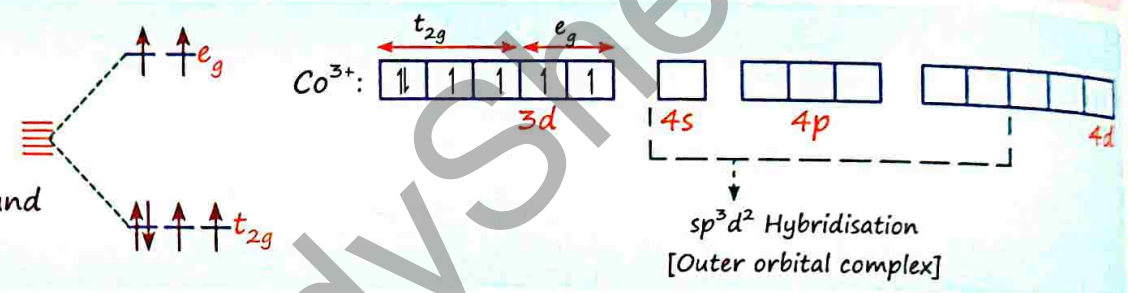
**[Co(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup>**

- ☐ Co<sup>3+</sup> : 3d<sup>6</sup>
- ☐ C<sub>2</sub>O<sub>4</sub><sup>2-</sup> : Strong field Ligand



**[CoF<sub>6</sub>]<sup>3-</sup>**

- ☐ Co<sup>3+</sup> : 3d<sup>6</sup>
- ☐ F<sup>-</sup> : Weak field ligand



28. [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> and [CoF<sub>6</sub>]<sup>3-</sup> are respectively known as [01 Feb, 2024 (Shift-II)]
- Spin free Complex, Spin paired Complex
  - Spin paired Complex, Spin free Complex
  - Outer orbital Complex, Inner orbital Complex
  - Inner orbital Complex, Spin paired Complex

Sol. (b)

29. Match List-I with List-II

| List-I<br>Complex |                                                    | List-II<br>Crystal Field splitting energy ( $\Delta_o$ ) |      |
|-------------------|----------------------------------------------------|----------------------------------------------------------|------|
| (A)               | [Ti(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> | (I)                                                      | -1.2 |
| (B)               | [V(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>  | (II)                                                     | -0.6 |
| (C)               | [Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> | (III)                                                    | 0    |
| (D)               | [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> | (IV)                                                     | -0.8 |

Choose the correct answer from the options given below: [10 April, 2023 (Shift-I)]

- (A) - (II), (B) - (IV), (C) - (I), (D) - (III)
- (A) - (IV), (B) - (I), (C) - (II), (D) - (III)
- (A) - (IV), (B) - (I), (C) - (III), (D) - (II)
- (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  
 (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  $d_{yz}$  [12 Jan, 2019 (Shift-I)]

Sol. (b)  
 31. For a  $d^4$  metal ion in an octahedral field, the correct electronic configuration is  
 (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  $\Delta_o < P$  [06 Sep, 2020 (Shift-II)]

Sol. (d)  
 32. The Crystal Field Stabilization Energy (CFSE) of  $[CoF_3(H_2O)_3]$  ( $\Delta_o < P$ ) is  
 (a)  $-0.8 \Delta_o$  (b)  $-0.8 \Delta_o + 2P$  (c)  $-0.4 \Delta_o$  (d)  $-0.4 \Delta_o + P$  [04 Sep, 2020 (Shift-II)]

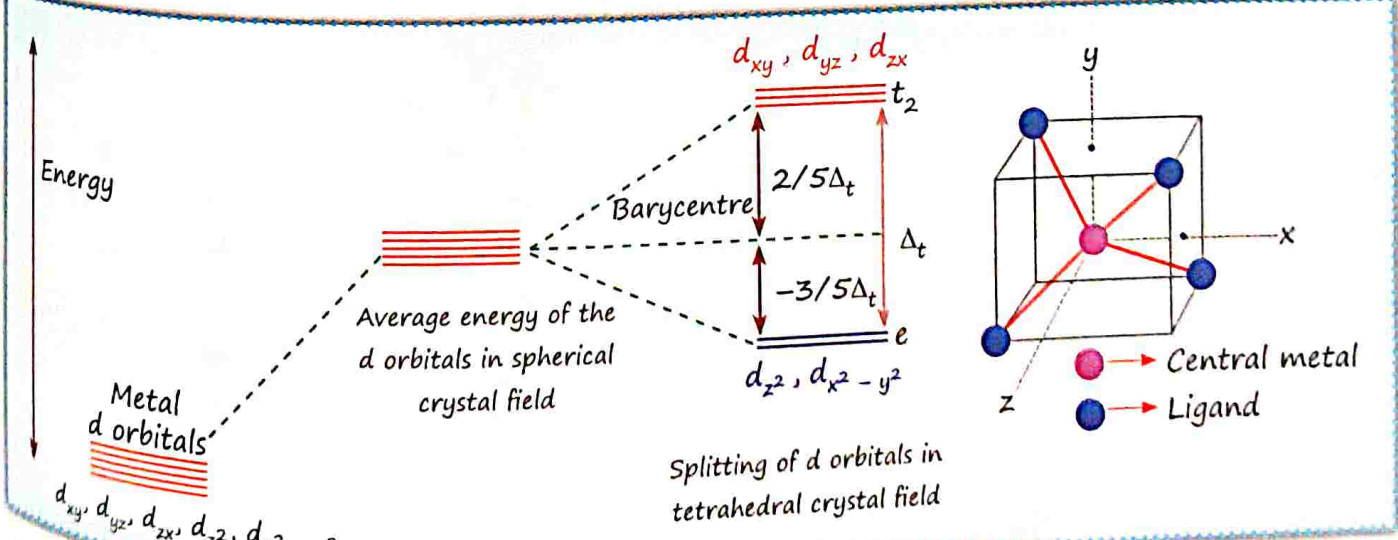
Sol. (c)  $[CoF_3(H_2O)_3] \Rightarrow Co^{3+} \Rightarrow d^6$  or  $t_{2g}^4 e_g^2$ , CFSE =  $[4 \times -0.4 + 2 \times 0.6] \Delta_o = -0.4 \Delta_o$   
 33. The crystal field stabilization energy (CFSE) value, for  $[Ti(H_2O)_6]^{3+}$  that has absorption maximum at 492 nm is  
 (a)  $20,325 \text{ cm}^{-1}$  (b)  $12,195 \text{ cm}^{-1}$  (c)  $10,162 \text{ cm}^{-1}$  (d)  $8,130 \text{ cm}^{-1}$

Sol. (d) Absorption maximum,  $\lambda = 492 \text{ nm} = 492 \times 10^{-7} \text{ cm}$   

$$\Delta_o = \frac{1}{\lambda} = \frac{1}{492 \times 10^{-7}} = 20325 \text{ cm}^{-1}$$
  
 CFSE =  $-0.4 \times 1 \times \Delta_o = -0.4 \Delta_o = -0.4 \times 20325 = -8130 \text{ cm}^{-1}$

## 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.



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- ☐ 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) <sub>Tetrahedral</sub> |
|-----------------------|-------------------------------------------|-----------------------------------------|---------------------------|-------------------------------|
|                       | e                                         | t <sub>2</sub>                          | $\mu(BM)$                 | $\Delta_t$                    |
| $d^1$                 | $\uparrow \square$                        | $\square \square \square$               | 1.73                      | -0.6                          |
| $d^2$                 | $\uparrow \uparrow$                       | $\square \square \square$               | 2.83                      | -1.2                          |
| $d^3$                 | $\uparrow \uparrow$                       | $\uparrow \square \square$              | 3.87                      | $-1.2 + 0.4 = -0.8$           |
| $d^4$                 | $\uparrow \uparrow$                       | $\uparrow \uparrow \square$             | 4.90                      | $-1.2 + 0.8 = -0.4$           |
| $d^5$                 | $\uparrow \uparrow$                       | $\uparrow \uparrow \uparrow$            | 5.92                      | $-1.2 + 1.2 = 0.0$            |
| $d^6$                 | $\uparrow \downarrow \uparrow$            | $\uparrow \uparrow \uparrow$            | 4.90                      | $-1.8 + 1.2 = -0.6$           |
| $d^7$                 | $\uparrow \downarrow \uparrow \downarrow$ | $\uparrow \uparrow \uparrow$            | 3.87                      | $-2.4 + 1.2 = -1.2$           |
| $d^8$                 | $\uparrow \downarrow \uparrow \downarrow$ | $\uparrow \downarrow \uparrow \uparrow$ | 2.83                      | $-2.4 + 1.6 = -0.8$           |
| $d^9$                 | $\uparrow \downarrow \uparrow \downarrow$ | $\uparrow \downarrow \uparrow \uparrow$ | 1.73                      | $-2.4 + 2.0 = -0.4$           |
| $d^{10}$              | $\uparrow \downarrow \uparrow \downarrow$ | $\uparrow \downarrow \uparrow \uparrow$ | 0.00                      | $-2.4 + 2.4 = 0.0$            |

$d^6$  configuration



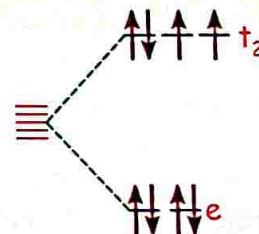
Oxidation state of Ni:  $x - 4 = -2 \Rightarrow x = -2 + 4 = +2$

Electronic configuration of Ni:  $[Ar]3d^8 4s^2$

Electronic configuration of  $Ni^{2+}$ :  $[Ar]3d^8$

No. of unpaired electrons = 2

Electronic configuration:  $e^4 t_2^4$



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  $\rightarrow [4 \times -0.4 \Delta_o + 2 \times 0.6 \Delta_o]$

Tetrahedral  $\rightarrow [3 \times -0.6 \Delta_o + 3 \times 0.4 \Delta_o]$

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)  $\approx$  (I) > (IV) > (III)

Sol. (c) No. of unpaired electrons  $\Rightarrow$  (I) 4

(II) Zero

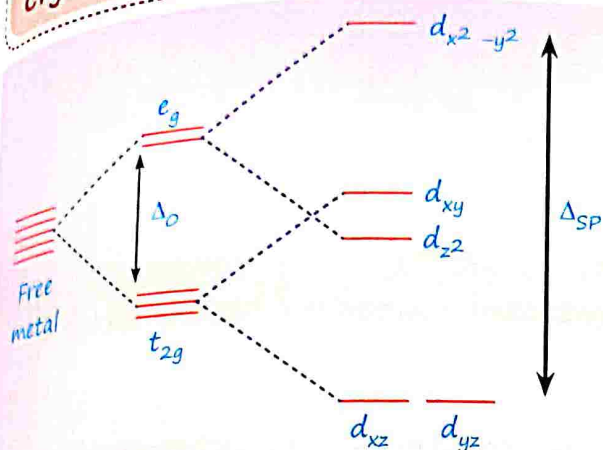
(III) 1

(IV) 3

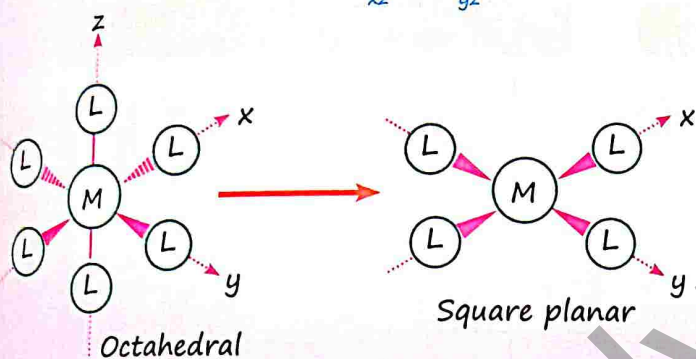
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## Crystal Field Splitting in Square Planar Complex



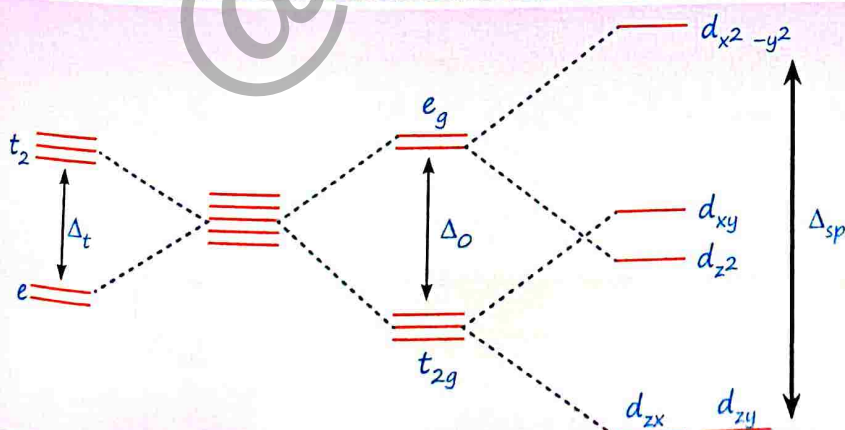
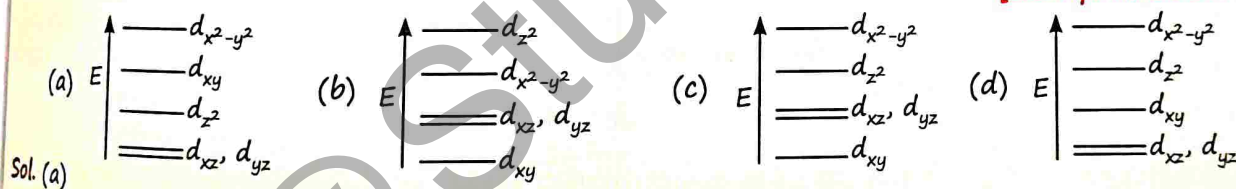
Energy order for sq. planar Complex:  
 $d_{x^2-y^2} > d_{xy} > d_{z^2} > (d_{xz} = d_{yz})$



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 pattern? (relative orbital energies not on scale)

[12 April, 2019 (Shift-I)]



$$\Delta_{sp} > \Delta_0 > \Delta_t$$

$$\Delta_{sp} = 1.3 \Delta_0$$

$$\Delta_t = \frac{4}{9} \Delta_0$$

Tetrahedral

$$(\Delta_t \ll P)$$

Octahedral

$$1. (\Delta_0 \gg P)$$

$$2. (\Delta_0 \ll P)$$

Square Planar

$$(\Delta_{sp} \gg P)$$

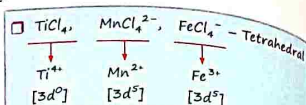
pairing energy

### Tetrahedral & Square Planar $ML_4$



Tetrahedral or Square planar

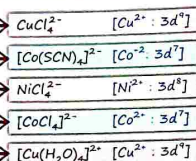
→ Tetrahedral



3d series metal in +2 oxidation state with  $d^7$ ,  $d^8$ ,  $d^9$  Configuration

$[I^- \text{ to } H_2O]$

### Tetrahedral Complex

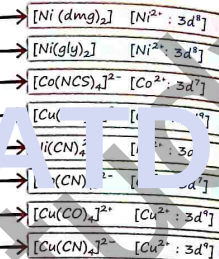


### Remember

$[\text{Co}(\text{NH}_3)_4]^{2+}$  has tetrahedral geometry with  $3d^7$  configuration.

[NH<sub>3</sub> to CO]

### Square Planar Complex



□ 4d and 5d series metal with  $d^8$ ,  $d^9$  configuration in +2, +3, +4 oxidation state with any ligand

→ Square planar geometry

$[\text{AuCl}_4]^-$  : Square planar  $[\text{Au}^{3+} : 5d^8]$

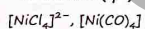
$[Pt(NH_3)_4]^{2+}$ ,  $[PtCl_4]^{2-}$ : Square planar  $[Pt^{2+}: 5d^8]$

$[PdCl_4]^{2-}$  : Square planar  $[Pd^{2+} : 4d^8]$

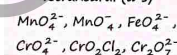
$[AgF_4]^-$ : Square planar  $[Ag^{3+} : 4d^8]$

### Hybridization in Complex having Coordination No-4

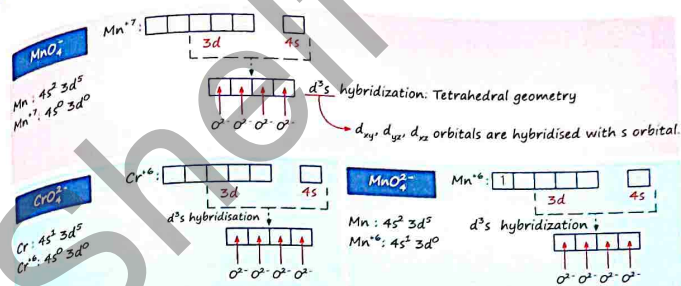
Tetrahedral ( $sp^3$ )



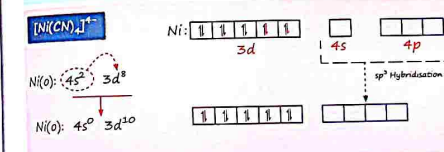
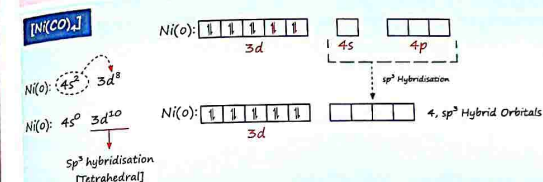
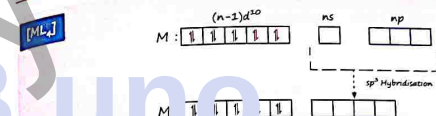
Tetrahedral ( $d^3s$ )



Square planar ( $dsp^2$ )



$d^{10}$  configuration of central metal  $\rightarrow$  Always Tetrahedral ( $sp^3$  hybridisation)



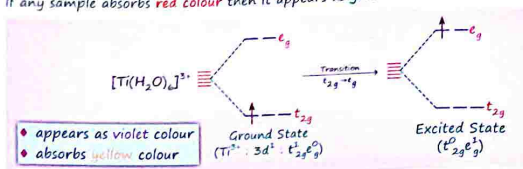
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## COLOUR IN COORDINATION COMPLEX

- 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)  $\uparrow \Rightarrow$  Large splitting  $\Rightarrow$  field strength  $\uparrow$
  - Absorbed wavelength of light for transition ( $\lambda$ )  $\downarrow \Rightarrow$  field strength  $\uparrow$
- (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)  $[Cu(H_2O)_6]^{2+}$ : It has tetrahedral geometry ( $\Delta_4 < \Delta_6$ ). 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 ( $Be_3Al_2Si_6O_{18}$ ).

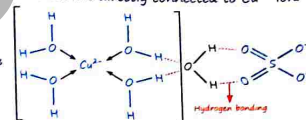
In absence of ligand crystal field splitting does not occur and hence the substance is colourless.

- $[Ti(H_2O)_6]Cl_3 \xrightarrow{-6H_2O} TiCl_3$  (colourless)
- $CuSO_4 \cdot 5H_2O \xrightarrow{-5H_2O} CuSO_4$  (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  $CuSO_4 \cdot 5H_2O$  respectively are  
(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 [18 March, 2021 (Shift-II)]

46. Given below are two statements:  
Statement-I: In  $CuSO_4 \cdot 5H_2O$ , Cu-O bonds are present.  
Statement-II: In  $CuSO_4 \cdot 5H_2O$ , 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. $[Cu(H_2O)_6]^{2+}$       | 600                               | Red                      | Blue                          |

Coordination Compounds

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# 48. Match List-I with List-II

| List-I<br>(Coordination entity)              | List-II<br>(Wavelength of light absorbed in nm) |
|----------------------------------------------|-------------------------------------------------|
| (A) $[\text{CoCl}(\text{NH}_3)_5]^{2+}$      | (I) 310                                         |
| (B) $[\text{Co}(\text{NH}_3)_6]^{3+}$        | (II) 475                                        |
| (C) $[\text{Co}(\text{CN})_6]^{3-}$          | (III) 535                                       |
| (D) $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ | (IV) 600                                        |

Choose the correct answer from the options given below:

[25 Jan, 2023 (Shift-I)]

- (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  $\text{M}^{3+}$  with three monodentate ligands  $\text{L}_1$ ,  $\text{L}_2$  and  $\text{L}_3$  absorb wavelengths in the region of green, blue and red respectively. The increasing order of the ligand strength is:

[09 Jan, 2019 (Shift-I)]

- (a)  $\text{L}_3 < \text{L}_1 < \text{L}_2$       (b)  $\text{L}_3 < \text{L}_2 < \text{L}_1$       (c)  $\text{L}_1 < \text{L}_2 < \text{L}_3$       (d)  $\text{L}_2 < \text{L}_1 < \text{L}_3$

Sol. (a)

- Order of wavelength  $\lambda \rightarrow \text{Red} > \text{Green} > \text{Blue}$   
 $(\text{L}_3) > (\text{L}_1) > (\text{L}_2)$
- Strength of ligand  $\propto \Delta \propto 1/\lambda$
- Strength of ligand  $\rightarrow \text{L}_2 > \text{L}_1 > \text{L}_3$

50. The electronic spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  shows a single broad peak with maximum at 20,300 cm. The crystal field stabilization energy (CFSE) of the complex ion, in kJ mol<sup>-1</sup>, is: (1 kJ mol<sup>-1</sup> = 83.7 cm<sup>-1</sup>)

[03 Sep, 2020 (Shift-I)]

- (a) 242.5      (b) 97      (c) 83.7      (d) 145.5

Sol. (b) CFSE =  $-0.4 \Delta_o = -0.4 \times 20300 = -8120 \text{ cm}^{-1}$

$$\text{CFSE (in kJ)} = \frac{8120}{83.7} = 97 \text{ kJ/mol}$$

51. If the CFSE of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is -96.0 kJ/mol, this complex will absorb maximum at wavelength \_\_\_\_\_ nm. (nearest integer)

Assume Planck's constant ( $h$ ) =  $6.4 \times 10^{-34}$  Js, Speed of light ( $c$ ) =  $3.0 \times 10^8$  m/s and Avogadro's constant ( $N_A$ ) =  $6 \times 10^{23}$ /mol.

[31 Jan, 2023 (Shift-I)]

Sol. [480]  $[\text{Ti}^{3+}(\text{H}_2\text{O})_6]^{3+} \rightarrow$  configuration of  $\text{Ti}^{3+}$  is  $3d^3$

$$\text{C.F.S.E.} = -0.4 \times \Delta_o = -\frac{96 \times 10^3}{N_A} \text{ J}$$

$$\Delta_o = \frac{96 \times 10^3}{0.4 \times 6 \times 10^{23}} \Rightarrow \frac{hc}{\lambda} = \frac{96 \times 10^3}{0.4 \times 6 \times 10^{23}}$$

$$\lambda = \frac{0.4 \times 6 \times 10^{23} \times 6.4 \times 10^{-34} \times 3 \times 10^8}{96 \times 10^3} = 0.48 \times 10^{-6} \text{ m} = 480 \times 10^{-9} \text{ m} = 480 \text{ nm}$$

# Colours of the First Row (aquated) Transition Metal ions $[\text{M}(\text{H}_2\text{O})_6]^{3+}$

| Configuration | Example                          | Colour     |
|---------------|----------------------------------|------------|
| $3d^0$        | $\text{Sc}^{3+}$                 | colourless |
| $3d^0$        | $\text{Ti}^{4+}$                 | colourless |
| $3d^1$        | $\text{Ti}^{3+}$                 | purple     |
| $3d^1$        | $\text{V}^{4+}$                  | blue       |
| $3d^2$        | $\text{V}^{3+}$                  | green      |
| $3d^3$        | $\text{V}^{2+}$                  | violet     |
| $3d^3$        | $\text{Cr}^{3+}$                 | violet     |
| $3d^4$        | $\text{Mn}^{2+}$                 | violet     |
| $3d^4$        | $\text{Cr}^{2+}$                 | blue       |
| $3d^5$        | $\text{Mn}^{2+}$                 | pink       |
| $3d^5$        | $\text{Fe}^{3+}$                 | yellow     |
| $3d^6$        | $\text{Fe}^{2+}$                 | green      |
| $3d^6, 3d^7$  | $\text{Co}^{3+}, \text{Co}^{2+}$ | blue, pink |
| $3d^8$        | $\text{Ni}^{2+}$                 | green      |
| $3d^9$        | $\text{Cu}^{2+}$                 | blue       |
| $3d^{10}$     | $\text{Zn}^{2+}$                 | colourless |

The colourless ion in the first row of the d series is  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ .



देशी जुगाड़

1. Fe Ko Ni Van me green lakdiyon

$\text{Fe}^{2+}, \text{Ni}^{2+}, \text{V}^{3+} \rightarrow \text{Green}$

2. Tumhe CuCr Co V blue kar diya

$\text{Cu}^{2+}, \text{Cr}^{2+}, \text{Co}^{3+}, \text{V}^{4+} \rightarrow \text{Blue}$

3. Vo Man Cre Karu Violence

$\text{V}^{2+}, \text{Mn}^{3+}, \text{Cr}^{3+} \rightarrow \text{Violet}$

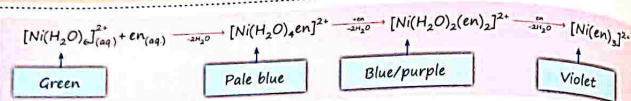
4. Yello Fer, Mn Co Kar diya pink

$\text{Fe}^{3+} \rightarrow \text{Yellow}$

$\text{Mn}^{2+}, \text{Co}^{2+} \rightarrow \text{pink}$



### Influence of the Ligand on Colour



### 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**  
 $\text{MnO}_4^-$   
 $\text{Mn}^{+7} : d^0 \rightarrow$  No d-d transition  
 $\text{MnO}_4^-$  : Colour is due to electron transfer from  $\text{O}^{2-} \rightarrow \text{Mn}^{+7}$ .

$\text{O}=\text{Mn}(\text{O})_3$

**Red Orange Colour**  
 $\text{Cr}_2\text{O}_7^{2-}$   
 $\text{Cr}^{+6} : d^0 \rightarrow$

$\text{O}=\text{Cr}(\text{O})_2-\text{O}-\text{Cr}(\text{O})_2=\text{O}$

**Green Colour**  
 $\text{MnO}_4^{2-}$   
 $\text{Mn}^{+6} : d^1 \rightarrow$

$\text{O}=\text{Mn}(\text{O})_3$

**Yellow Colour**  
 $\text{CrO}_4^{2-}$   
 $\text{Cr}^{+6} : d^0 \rightarrow$

$\text{O}=\text{Cr}(\text{O})_3$

#### 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.

$$1. \text{Fe}^{2+} + [\text{Fe}(\text{CN})_6]^{3-} \rightarrow [\text{Fe}_3(\text{Fe}(\text{CN})_6)_2]$$

Ferrous ferricyanide [Turn bulls blue]

$$2. \text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{4-} \rightarrow [\text{Fe}_3(\text{Fe}(\text{CN})_6)_3]$$

Ferric ferrocyanide [Prussian blue]

$$3. \text{Pb}_3\text{O}_4 \text{ (red colour)} \rightleftharpoons \text{PbO}_2 \cdot 2\text{PbO}$$

Red lead ( $\text{Pb}_3\text{O}_4$ ) 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.



The correct order of A, B, C and D in terms of wavenumber of light absorbed is:

- (a)  $C < D < A < B$     (b)  $D < A < C < B$     (c)  $A < C < B < D$     (d)  $B < C < A < D$   
 [06 April, 2024 (Shift-I)]  
 Sol. (b) As the ligand field strength increase, light of more energy is absorbed. Ligand strength can be determined by spectrochemical series.  
 Also, Energy  $\propto$  wave number ( $\nu$ )

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. $[\text{Cu}(\text{NH}_3)_4]^{2+}$        | I. -0.6   |
| B. $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ | II. -2.0  |
| C. $[\text{Fe}(\text{CN})_6]^{3-}$          | III. -1.2 |
| D. $[\text{NiF}_6]^{4-}$                    | IV. -0.4  |

Choose the correct option from the options given below: [12 April, 2023 (Shift-I)]

- (a) A-I, B-II, C-III, D-IV    (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):  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  absorbs at lower wavelength of light with respect to  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . 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

- 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.
- Further, it does not take into account the covalent character of bonding between the ligand and the central atom

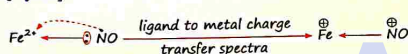
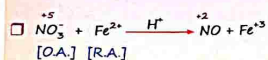
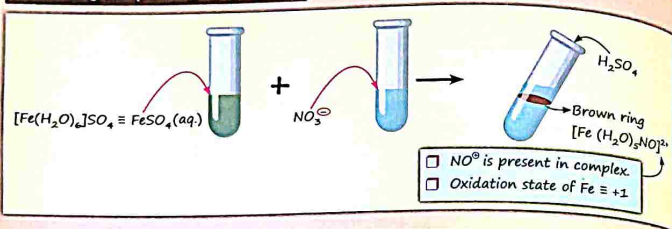
Coordination Compounds

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## Discussion About Some Important Complexes

### Brown Ring Complex $\Rightarrow [Fe(H_2O)_5NO]^{2+}$



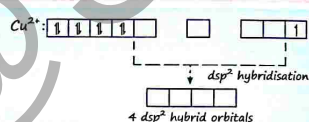
### $[Fe(H_2O)_5NO]^{2+}$

- ☐  $Fe^+ : 4s^5 : 3d^6$   
 $Fe^{2+} : 3d^6 : 4s^0$
- ☐ Hybridisation =  $sp^3d^2$
- ☐ No of unpaired electrons = 3
- ☐ Magnetic Moment =  $\sqrt{3(3+2)} \text{ BM}$   
 $= 3.87 \text{ BM}$



### $[Cu(NH_3)_4]^{2+}$

- ☐ Square planar  
 $[Cu^{2+} : 3d^9]$
- ☐ Hybridization =  $dsp^2$
- ☐ No of unpaired electrons = 1
- ☐ Colour = deep Blue



### $[Ni(dmg)_2]$

- ☐  $dmg$   $\rightarrow$  -1 charge
- ☐ Bidentate (nitrogen donor ligand)
- ☐  $Ni^{2+} : 3d^8$



- ☐ Complex acquires stability through chelation and intramolecular H-bonding.

- ☐ Hybridisation & Geometry = Square planar/ $dsp^2$
- ☐ Types of bonds = H-bond, Covalent, Co-ordinate bond
- ☐ No of unpaired electrons = Zero
- ☐ Types of rings = 5 and 6 membered
- ☐ Colour = Rosy Red / Scarlet Red
- ☐ No of rings = 4 [Two  $\odot$  and Two  $\ominus$  membered rings]

### $[RhCl(PPh_3)_3]$ Catalyst: Chloridotris(triphenylphosphine)rhodium(I)



### $[IrCl(CO)(PPh_3)_2]$ Vaska complex: Trans-carbonylchlorobis(triphenylphosphine)iridium(I)



### $Na_2[Fe(CN)_5NO]$ Sodium Nitroprusside

- Oxidation state of NO  $\equiv +1$
- If oxidation state of Fe is x.
- $(2 \times 1) + x + 5(-1) + (+1) = 0$ , then  $x = 2$

### $Na_2[Fe(CN)_5NOS]$ Sodium thionitroprusside

- Oxidation state of NOS  $\equiv -1$
- If oxidation state of Fe is x.
- $(4 \times 1) + x + 5(-1) + (-1) = 0$ , 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)

Coordination Compounds

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57. Which of the following are paramagnetic?  
A.  $[\text{NiCl}_4]^{2-}$  B.  $\text{Ni}(\text{CO})_4$  C.  $[\text{Ni}(\text{CN})_4]^{2-}$   
D.  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  E.  $\text{Ni}(\text{PPh}_3)_4$   
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,  
A.  $[\text{Co}(\text{NH}_3)_6]^{3+}$  B.  $[\text{Co}(\text{CN})_6]^{3-}$  C.  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  D.  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$   
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:  
Statement I: Both  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{CoF}_6]^{3-}$  complexes are octahedral but differ in their magnetic behaviour.

Statement II:  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is diamagnetic whereas  $[\text{CoF}_6]^{3-}$  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  
A.  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  B.  $[\text{Ni}(\text{H}_2\text{O})_6(\text{en})]^{2+}$  and C.  $[\text{Ni}(\text{en})_3]^{2+}$  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.

| List-I                                       | List-II       |
|----------------------------------------------|---------------|
| (A) $[\text{Fe}(\text{CN})_6]^{3-}$          | (i) 5.92 BM   |
| (B) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ | (ii) 0 BM     |
| (C) $[\text{Fe}(\text{CN})_6]^{4-}$          | (iii) 4.90 BM |
| (D) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | (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?  
(a)  $\text{SCN}^- < \text{F}^- < \text{CN}^- < \text{C}_2\text{O}_4^{2-}$  (b)  $\text{F}^- < \text{SCN}^- < \text{C}_2\text{O}_4^{2-} < \text{CN}^-$   
(c)  $\text{CN}^- < \text{C}_2\text{O}_4^{2-} < \text{SCN}^- < \text{F}^-$  (d)  $\text{SCN}^- < \text{F}^- < \text{C}_2\text{O}_4^{2-} < \text{CN}^-$

- Sol. (d)  
63. Match the coordination number and type of hybridisation with distribution of hybrid orbitals in space based on Valence bond theory.

| 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. (c)  
64. The electronic configuration of the central atom in  $\text{K}_4[\text{Fe}(\text{CN})_6]$  based on crystal field theory is:  
(a)  $t_{2g}^4 e_g^4$  (b)  $t_{2g}^5 e_g^3$  (c)  $e^2 t_{2g}^3$  (d)  $e^4 t_{2g}^3$

- Sol. (b)  
65. The geometry and magnetic behaviour of the complex  $[\text{Ni}(\text{CO})_4]$  are?  
(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  $\text{Co}^{3+}$  is:  
(a)  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{en})_3]^{3+}$ ,  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  (b)  $[\text{Co}(\text{en})_3]^{3+}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$   
(c)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Co}(\text{en})_3]^{3+}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (d)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{en})_3]^{3+}$

- Sol. (b)  
67. Pick out the correct statement with respect to  $[\text{Mn}(\text{CN})_6]^{3-}$   
(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  $[\text{Ni}(\text{CN})_4]^{2-}$  is (Atomic Number Ni = 28)  
(a)  $d^2sp^3$  (b)  $dsp^2$  (c)  $sp^3$  (d)  $d^2sp^2$

- Sol. (b)



69. Which of these statements about  $[\text{Co}(\text{CN})_6]^{3-}$  is true? [NEET 2015]
- $[\text{Co}(\text{CN})_6]^{3-}$  has four unpaired electrons and will be in a low-spin configuration
  - $[\text{Co}(\text{CN})_6]^{3-}$  has four unpaired electrons and will be in a high-spin configuration
  - $[\text{Co}(\text{CN})_6]^{3-}$  has no unpaired electrons and will be in a high-spin configuration
  - $[\text{Co}(\text{CN})_6]^{3-}$  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]
- $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
  - $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
  - $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
  - $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$
- Sol. (a)
71. A magnetic moment of 1.73 BM will be shown by one among the following: [NEET 2013]
- $[\text{Cu}(\text{NH}_3)_4]^{2+}$
  - $[\text{Ni}(\text{CN})_4]^{2-}$
  - $\text{TiCl}_4$
  - $[\text{CoCl}_4]^{4-}$
- Sol. (a)
72. Low spin complex of  $d^6$  - cation in an octahedral field will have the following energy: [NEET 2012 Mains]
- $-\frac{2}{5}\Delta_o + P$
  - $-\frac{12}{5}\Delta_o + P$
  - $-\frac{12}{5}\Delta_o + 3P$
  - $-\frac{2}{5}\Delta_o + 2P$
- Sol. (c)
73. Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour? [NEET 2012 Pre]
- $[\text{Co}(\text{NH}_3)_6]^{3+}$
  - $[\text{Ni}(\text{NH}_3)_6]^{2+}$
  - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
  - $[\text{Fe}(\text{NH}_3)_6]^{2+}$
- Sol. (b)
74. Red precipitate is obtained when ethanol solution of dimethylglyoxime is added to ammoniacal  $\text{Ni}(\text{II})$ . Which of the following statements is not true? [NEET 2012 Mains]
- Red complex has a square planar geometry
  - Complex has symmetrical H-bonding
  - Red complex has a tetrahedral geometry
  - Dimethylglyoxime functions as bidentate ligand
- $\text{dimethylglyoxime} = \begin{array}{c} \text{H}_3\text{C}-\text{C}=\text{N}-\text{OH} \\ | \\ \text{H}_3\text{C}-\text{C}=\text{N}-\text{OH} \end{array}$

$\left[ \begin{array}{c} \text{H}_3\text{C}-\text{C}=\text{N}-\text{OH} \\ | \\ \text{H}_3\text{C}-\text{C}=\text{N}-\text{OH} \end{array} \right]$
- Sol. (c)
75. Of the following complex ions, which is diamagnetic in nature? [NEET 2011 Pre]
- $[\text{CoF}_6]^{3-}$
  - $[\text{NiCl}_4]^{2-}$
  - $[\text{Ni}(\text{CN})_4]^{2-}$
  - $[\text{CuCl}_4]^{2-}$
- Sol. (c)
76. Which of the following complex compounds will exhibit highest paramagnetic behaviour? [NEET 2011 Mains]
- (Atomic Number  $\text{Ti} = 22$ ,  $\text{Cr} = 24$ ,  $\text{Co} = 27$ ,  $\text{Zn} = 30$ )
- $[\text{Co}(\text{NH}_3)_6]^{3+}$
  - $[\text{Zn}(\text{NH}_3)_6]^{2+}$
  - $[\text{Ti}(\text{NH}_3)_6]^{3+}$
  - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
- Sol. (d)

77. The d-electron configurations of  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  are  $d^3$ ,  $d^5$ ,  $d^6$  and  $d^7$  respectively. Which one of the following will exhibit minimum paramagnetic behaviour? [NEET 2011 Pre, 2007]
- (Atomic Number  $\text{Cr} = 24$ ,  $\text{Mn} = 25$ ,  $\text{Fe} = 26$ ,  $\text{Co} = 27$ )
- $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
  - $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
  - $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
  - $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
- Sol. (d)
78. Crystal field stabilization energy for high spin  $d^4$  octahedral complex is: [NEET 2010 Pre]
- $-0.6\Delta_o$
  - $-1.8\Delta_o$
  - $-1.6\Delta_o + P$
  - $-1.2\Delta_o$
- Sol. (a)
79. Which of the following complex ion is not expected to absorb visible light? [NEET 2010 Pre]
- $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
  - $[\text{Ni}(\text{CN})_6]^{2-}$
  - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
  - $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
- Sol. (b)
80. Which of the following complex ions is expected to absorb visible light? [NEET 2009]
- (Atomic number  $\text{Zn} = 30$ ,  $\text{Sc} = 21$ ,  $\text{Ti} = 22$ ,  $\text{Cr} = 24$ )
- $[\text{Ti}(\text{en})_2(\text{NH}_3)_2]^{4+}$
  - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
  - $[\text{Zn}(\text{NH}_3)_6]^{2+}$
  - $[\text{Sc}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{3+}$
- Sol. (b)
81. Out of  $\text{TiF}_6^{2-}$ ,  $\text{CoF}_6^{3-}$ ,  $\text{Cu}_2\text{Cl}_2$  and  $\text{NiCl}_4^{2-}$  ( $\text{Z}$  of  $\text{Ti} = 22$ ,  $\text{Co} = 27$ ,  $\text{Cu} = 29$ ,  $\text{Ni} = 28$ ), the colourless species are: [NEET 2009]
- $\text{Cu}_2\text{Cl}_2$  and  $\text{NiCl}_4^{2-}$
  - $\text{TiF}_6^{2-}$  and  $\text{Cu}_2\text{Cl}_2$
  - $\text{CoF}_6^{3-}$  and  $\text{NiCl}_4^{2-}$
  - $\text{TiF}_6^{2-}$  and  $\text{CoF}_6^{3-}$
- Sol. (d)
82. Which of the following coordination entities the magnitude of  $\Delta_o$  (CFSE in octahedral field) will be maximum: (atomic number  $\text{Co} = 27$ )? [NEET 2008]
- $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$
  - $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
  - $[\text{Co}(\text{NH}_3)_6]^{3+}$
  - $[\text{Co}(\text{CN})_6]^{3-}$
- Sol. (d)
83. Which of the following complexes exhibits the highest paramagnetic behaviour? Where gly = glycine, en = ethylenediamine and bpy = bipyridyl moieties. (Atomic number  $\text{Ti} = 22$ ,  $\text{V} = 23$ ,  $\text{Fe} = 26$ ,  $\text{Co} = 27$ ): [NEET 2008]
- $[\text{Ti}(\text{NH}_3)_6]^{3+}$
  - $[\text{V}(\text{gly})_2(\text{OH})_2(\text{NH}_3)_2]^+$
  - $[\text{Fe}(\text{en})(\text{bpy})(\text{NH}_3)_2]^{2+}$
  - $[\text{Co}(\text{Ox})_2(\text{OH})_2]^-$
- Sol. (c)
84.  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (atomic number of  $\text{Cr} = 24$ ) has a magnetic moment of 3.83 BM, the correct distribution of 3d electrons in the chromium of the complex is: [NEET 2006]
- $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1$
  - $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1$
  - $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1$
  - $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1$
- Sol. (c)
85. Which one of the following is an inner orbital complex as well as diamagnetic in behaviour? [NEET 2005]
- (Atomic number:  $\text{Zn} = 30$ ,  $\text{Cr} = 24$ ,  $\text{Co} = 27$ ,  $\text{Ni} = 28$ )
- $[\text{Zn}(\text{NH}_3)_6]^{2+}$
  - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
  - $[\text{Co}(\text{NH}_3)_6]^{3+}$
  - $[\text{Ni}(\text{NH}_3)_6]^{2+}$
- Sol. (c)

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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)  $d_{z^2}, d_{xy}$ 
 (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: [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 26. Which of the following is paramagnetic with the spin of electron? [NEET 2021]
 

(a)  $[Cr(CO)_6]$ 
 (b)  $[Fe(CO)_5]$ 
 (c)  $[Fe(NH_3)_6]^{2+}$ 
 (d)  $[Cr(NH_3)_6]^{3+}$

 Sol. (d)

TYPES OF LIGANDS
 

Simple Ligands:  $\sigma$  Donor Ligands
 

$H_2O$ 
 $NH_3$ 
 $H_2O-R$ 
 $H_2N-R$ 
 $H_3C^-$ 
 $H^-$

Non-Classical Ligands  $\sigma$  Donor &  $\pi$  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  $\pi^*$  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  $\sigma$  and  $\pi$  character. CO is a  $\pi$  donor and  $\pi$  acceptor ligand ( $\pi$  acid).
 (a) The  $M-C$   $\sigma$  bond is formed by the donation of lone pair of electrons from the carbonyl carbon to a vacant orbital of metal.
 (b) The  $M-C$   $\pi$  bond is formed by the donation of a pair of electron from a filled d-orbital of metal to vacant  $\pi^*$  orbital of CO.

Filled d orbital of metal (M)
 Vacant  $\pi^*$  orbital of CO
 Synergic bonding

$\sigma$  Bond Between M & C
  $\pi$  Bond Between M & C

Due to back-bonding  $\rightarrow$  M-C bond order  $\uparrow$  : M-C bond strength  $\uparrow$  : M-C Bond length  $\downarrow$   
 C-O bond order  $\downarrow$  : C-O bond strength  $\downarrow$  : C-O Bond length  $\uparrow$

The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.
 Electron density on metal  $\uparrow$  : Back bonding  $\uparrow$  : M - C Bond strength  $\uparrow$  : C-O Bond strength  $\downarrow$

(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:  $a < b < c < d$

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(JEE Adv. 2007)

92. Among the following metal carbonyls, the C - O bond order is lowest in:

- (a)  $[\text{Mn}(\text{CO})_6]^+$  (b)  $[\text{V}(\text{CO})_6]^-$  (c)  $[\text{Cr}(\text{CO})_6]$  (d)  $[\text{Fe}(\text{CO})_5]$

Sol. (d) The C-O bond order is lowest in  $[\text{Fe}(\text{CO})_5]$  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  $1.128 \text{ \AA}$ , what will be the order of bond length of CO in  $\text{CO}^+$  and  $\text{Fe}(\text{CO})_5$  with respect to free CO?

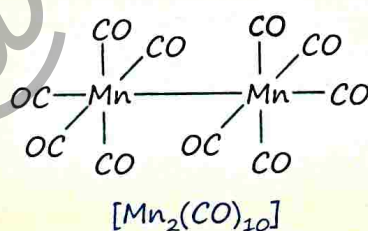
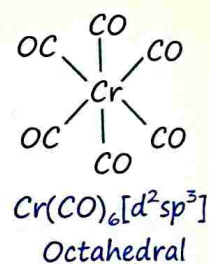
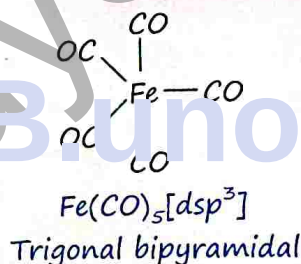
Sol.

$\text{CO}^+$   
bond Order  $> 3$   
(Bond order is approximately 3.5 for  $\text{CO}^+$  according to MOT)

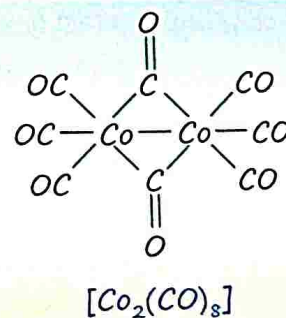
Free  $\text{C} \equiv \text{O}$   
bond Order = 3

$\text{Fe}(\text{CO})_5$   
  
Bond order  $< 3$   
(due to back bonding)

C-O Bond length :  $\text{Fe}(\text{CO})_5 > \text{CO} > \text{CO}^+$



Number of metal to metal bond  $[\text{Mn} - \text{Mn}]$ : 1  
 Number of bridging CO: 0  
 Number of terminal CO: 10



Number of metal to metal bond  $[\text{Co} - \text{Co}]$ : 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?

- (a)  $[\text{Co}_2(\text{CO})_8]$  (b)  $[\text{Mn}_2(\text{CO})_{10}]$  (c)  $[\text{Os}_3(\text{CO})_{12}]$  (d)  $[\text{Ru}_3(\text{CO})_{12}]$

Sol. (a)

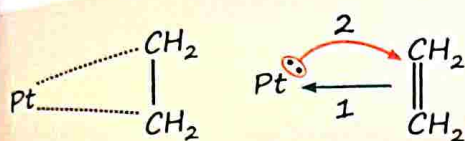
[29 Jan, 2024 (Shift-)]

45. The number of bridging CO ligand(s) and Co-Co bond (s) in  $\text{Co}_2(\text{CO})_8$  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)  
 46. Low oxidation state of metals in their complexes are common when ligands: [27 July, 2022 (Shift-II)]  
 (a) have good  $\pi$ -accepting character (b) have good  $\sigma$ -donor character  
 (c) are having good  $\pi$ -donating ability (d) are having poor  $\sigma$ -donating ability

Sol. (a)

## $\pi$ DONOR AND $\pi$ ACCEPTOR LIGANDS



1. Donation of  $\pi e^-$  from  $\text{C}_2\text{H}_4$  to Pt
2. Donation of  $e^-$  from Pt ( $d e^-$ ) to  $\pi^*$  of  $\text{C}_2\text{H}_4$ .

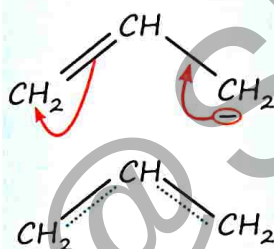
## Hepticity of Ligand

□ No of atoms involved in donation of  $\pi$  electron.

$\text{C}_2\text{H}_4$

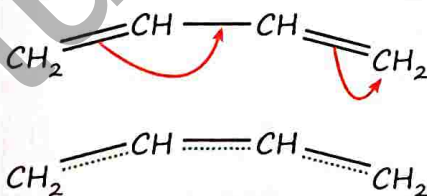
- $\eta^2-\text{C}_2\text{H}_4$
- $2e^-$  donor

$\text{C}_3\text{H}_5^-$



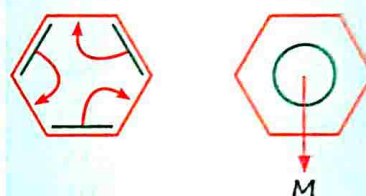
- $\eta^3-\text{C}_3\text{H}_5^-$
- $4e^-$  Donor

$\text{C}_4\text{H}_6$



- $\eta^4-\text{C}_4\text{H}_6$
- $4e^-$  Donor

$\text{C}_6\text{H}_6$

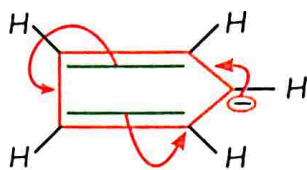


- $\eta^6-\text{C}_6\text{H}_6 \equiv \pi-\text{C}_6\text{H}_6$
- $6e^-$  Donor

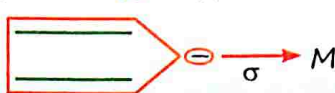
$\text{C}_5\text{H}_5^-$

Cyclopentadienyl [ $\text{cp}$ ]

1.  $\pi-\text{C}_5\text{H}_5^-$   
 $6e^-$  donor



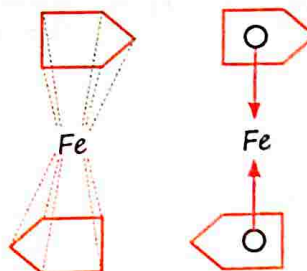
2.  $\sigma-\text{C}_5\text{H}_5^-$   
 $2e^-$  donor



Ferrocene

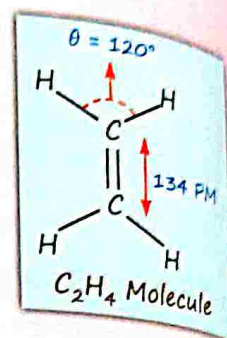
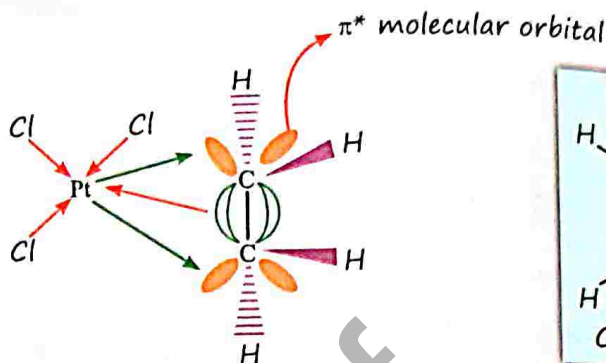
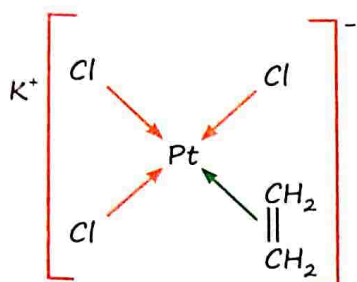
$\text{Fe}(\text{C}_5\text{H}_5)_2$   
 $\text{Fe}(\text{Cp})_2$

Oxidation state of Fe  
 $+2(\text{charge on cp}) = 0$





## Zeise's Salt $K^+ [PtCl_3 (\eta^2 - C_2H_4)]^-$



- 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  $\pi^*$  of  $C_2H_4$  makes C-C bond weak in Zeise salt

## EFFECTIVE ATOMIC NUMBER

### Sidgwick EAN Rule:-

The metal complex is stable when EAN is equal to the nearest noble gas configuration.

$$EAN = Z - n + [2 \times CN]$$

$Z$  → Atomic no. of metal  
 $n$  → Oxidation state of metal  
 $CN$  → Coordination number

$$[Cr(CO)_6] \quad EAN = 24 - 0 + (6 \times 2) = 36 \equiv [Kr]$$

$$[Pd(NH_3)_6]^{4+} \quad EAN = 46 - 4 + (6 \times 2) = 54 \equiv [Xe]$$

$$[PtCl_6]^{2-} \quad EAN = 78 - 4 + (6 \times 2) = 86 \equiv [Rn]$$

$$\square [Pt(NH_3)_4]^{2+} \quad EAN = 78 - 2 + (4 \times 2)$$

$$\square [Ti(\sigma - C_5H_5)_2(\pi - C_5H_5)_2] \quad EAN = 22 - 4 + 16 = 34$$

If  $x$  is the oxidation state of Ti.

$$x + 2(-1) + 2(-1) = 0 \text{ then } x = 4$$

$$\square [Fe(\pi - C_5H_5)_2] \quad EAN = 26 - 2 + 12 = 36$$

Oxidation state of Fe is  $x$ , then

$$x + 2(-1) = 0 \Rightarrow x = 2$$

$$\square [Fe(CO)_2(NO)_2] \quad EAN = 26 - 0 + (2 \times 2 + 2 \times 3) = 36$$

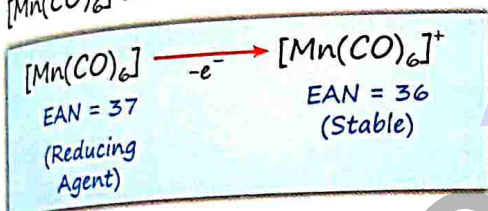
- ♦ All donations contribute two electrons, while NO is considered as a 3-electron donor.

$$\begin{aligned} \sigma - C_5H_5 &: 2e^- \text{ donor} \\ \pi - C_5H_5 &: 6e^- \text{ donor} \end{aligned}$$

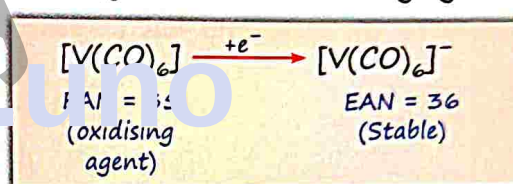
## Effective Atomic Numbers of Some Metals in Complexes

| Atom | Atomic number | Complex                           | Electrons lost in ion formation | Electrons gained by coordination | EAN |
|------|---------------|-----------------------------------|---------------------------------|----------------------------------|-----|
| Fe   | 26            | $[\text{Fe}(\text{CN})_6]^{4-}$   | 2                               | 12                               | 36  |
| Fe   | 26            | $[\text{Fe}(\text{CO})_5]$        | 0                               | 10                               | 36  |
| Co   | 27            | $[\text{Co}(\text{NH}_3)_6]^{3+}$ | 3                               | 12                               | 36  |
| Ni   | 28            | $[\text{Ni}(\text{CO})_4]$        | 0                               | 8                                | 36  |
| Cu   | 29            | $[\text{Cu}(\text{CN})_4]^{3-}$   | 1                               | 8                                | 36  |
| Fe   | 26            | $[\text{Fe}(\text{CN})_6]^{3-}$   | 3                               | 12                               | 35  |
| Ni   | 28            | $[\text{Ni}(\text{NH}_3)_6]^{2+}$ | 2                               | 12                               | 38  |
| Pd   | 46            | $[\text{PdCl}_4]^{2-}$            | 2                               | 8                                | 52  |
| Co   | 27            | $[\text{Co}(\text{CO})_4]^-$      | -1                              | 8                                | 36  |
| V    | 23            | $[\text{V}(\text{CO})]^-$         | -1                              | 12                               | 36  |

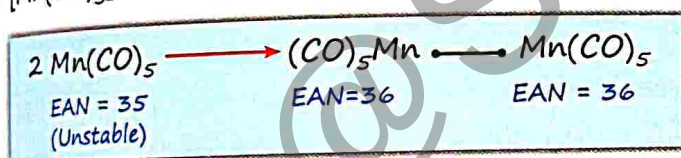
☐  $[\text{Mn}(\text{CO})_6]$  can act as a reducing agent.



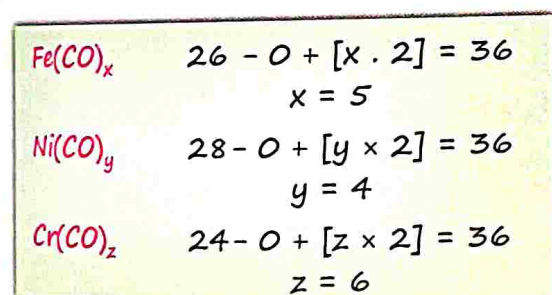
☐  $[\text{V}(\text{CO})_6]$  can act as oxidizing agent.



☐  $[\text{Mn}(\text{CO})_5]$  undergoes dimerization to attain the noble gas configuration.



☐ The number of CO molecule attached in mononuclear carbonyls can be predicted.



97.  $\text{Mn}_2(\text{CO})_{10}$  is an organometallic 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.  $[\text{Mn}_2(\text{CO})_{10}]$  and  $[\text{Co}_2(\text{CO})_8]$  structures have

- 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).  
Assertion (A): The metal carbon bond in metal carbonyls possesses both  $\sigma$  and  $\pi$  character.  
Reason (R): The ligand to metal bond is a  $\pi$  bond and metal to ligand bond is a  $\sigma$  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,  $\text{Fe}(\text{CO})_5$  is

- (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 Å)

- (a)  $[\text{Mn}(\text{CO})_6]$  (b)  $[\text{Ni}(\text{CO})_4]$  (c)  $[\text{Co}(\text{CO})_4]^-$  (d)  $[\text{Fe}(\text{CO})_4]^{2-}$

Sol. (d)

102. Which of the following carbonyl's will have the strongest C - O bond?

- (a)  $\text{V}(\text{CO})_6^-$  (b)  $\text{Fe}(\text{CO})_5$  (c)  $\text{Mn}(\text{CO})_6^+$  (d)  $\text{Cr}(\text{CO})_6$

Sol. (c)

103. Which of the following does not have a metal- carbon bond?

- (a)  $\text{C}_2\text{H}_5\text{MgBr}$  (b)  $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$  (c)  $\text{Ni}(\text{CO})_4$  (d)  $\text{Al}(\text{OC}_2\text{H}_5)_3$

Sol. (d)

104. Among the following, which is not the  $\pi$ -bonded organometallic compound?

- (a)  $\text{K}[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]$  (b)  $\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2$   
(c)  $\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2$  (d)  $(\text{CH}_3)_4\text{Sn}$

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

## Isomerism

### Structural - Isomerism

Different structure

Same molecular formula

- Structure means atom to atom arrangement.
- Structural Isomers have different structures (different bonds).

### Stereo - Isomerism

Different Stereo

Same molecular formula

- Stereo means spatial arrangement in 3D space.
- Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement.

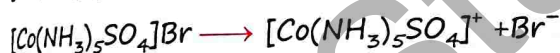
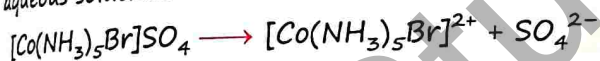
## STRUCTURAL ISOMERISM

### (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-

- $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  are ionisation isomers because they give different ions in aqueous solution.

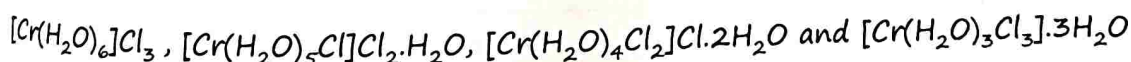


- $[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]\text{SO}_4$
  - $[\text{Co}(\text{en})_2(\text{NO}_2)(\text{SO}_4)]\text{Cl}$
  - $[\text{Co}(\text{en})_2\text{Cl}(\text{SO}_4)]\text{NO}_2$
- Ionisation isomers

### (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-



### (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.

Coordination Compounds



Example-

- ☐ (a)  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$   
 (b)  $[\text{Cr}(\text{NH}_3)_5(\text{NCS})]\text{Br}_2$  and  $[\text{Cr}(\text{NH}_3)_5(\text{SCN})]\text{Br}_2$   
☐ (a)  $[\text{Co}(\text{en})_2(\text{NCS})(\text{NO}_2)]\text{Cl} \rightarrow 4$  linkage isomers  
 (b)  $[\text{Co}(\text{en})_2(\text{NCS})(\text{ONO})]\text{Cl}$   
 (c)  $[\text{Co}(\text{en})_2(\text{SCN})(\text{NO}_2)]\text{Cl}$   
 (d)  $[\text{Co}(\text{en})_2(\text{SCN})(\text{ONO})]\text{Cl}$   
☐ 4 linkage isomers are possible for square planar  $[\text{Pd FCl}(\text{SCN})(\text{NO}_2)]^{2+}$  -  
 (a)  $[\text{Pd FCl}(\text{SCN})(\text{NO}_2)]^{2+}$  (b)  $[\text{Pd FCl}(\text{SCN})(\text{ONO})]^{2+}$   
 (c)  $[\text{Pd FCl}(\text{NCS})(\text{NO}_2)]^{2+}$  (d)  $[\text{Pd FCl}(\text{NCS})(\text{ONO})]^{2+}$

1.  $\text{NCS}^-$   $\text{NO}_2^-$
2.  $\text{NCS}^-$   $\text{ONO}^-$
3.  $\text{SCN}^-$   $\text{NO}_2^-$
4.  $\text{SCN}^-$   $\text{ONO}^-$

#### (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.  $[\text{Co}(\text{en})_2][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{en})_2][\text{Co}(\text{CN})_6]$  b.  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$  and  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$

Q. Find total structural isomers in  $[\text{Co}(\text{en})_2(\text{NCS})(\text{NO}_2)]\text{Cl}$  complex

|      |                                                              |                                                            |                                                            |
|------|--------------------------------------------------------------|------------------------------------------------------------|------------------------------------------------------------|
| Ans. | $[\text{Co}(\text{en})_2(\text{NCS})(\text{NO}_2)]\text{Cl}$ | $[\text{Co}(\text{en})_2\text{Cl}(\text{NO}_2)]\text{NCS}$ | $[\text{Co}(\text{en})_2(\text{NO}_2)]\text{NCS}$          |
|      | $[\text{Co}(\text{en})_2(\text{NCS})(\text{ONO})]\text{Cl}$  | $[\text{Co}(\text{en})_2\text{Cl}(\text{ONO})]\text{NCS}$  | $[\text{Co}(\text{en})_2(\text{SCN})\text{Cl}]\text{NO}_2$ |
|      | $[\text{Co}(\text{en})_2(\text{SCN})(\text{NO}_2)]\text{Cl}$ |                                                            |                                                            |
|      | $[\text{Co}(\text{en})_2(\text{SCN})(\text{ONO})]\text{Cl}$  |                                                            |                                                            |

Total No. of structural isomers = 8

105. Match List-I with List-II.

| List-I<br>(Complex)                                     | List-II<br>(Type of Isomerism) |
|---------------------------------------------------------|--------------------------------|
| A. $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ | I. Solvate isomerism           |
| B. $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$   | II. Linkage isomerism          |
| C. $[\text{Co}(\text{NH}_3)_5][\text{Cr}(\text{CN})_6]$ | III. Ionization isomerism      |
| D. $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$       | 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  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ ,  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ ,  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  and the value of coordination number (CN) of central metal ion in all these compounds, respectively is:

- (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:

| List-I<br>(Complexes)                                                                                                                  | List-II<br>(Types)         |
|----------------------------------------------------------------------------------------------------------------------------------------|----------------------------|
| A. $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$                        | I. ionization isomerism    |
| B. $[\text{Cr}(\text{NH}_3)_4][\text{Co}(\text{CN})_6]$ and $[\text{Cr}(\text{CN})_6][\text{Co}(\text{NH}_3)_4]$                       | II. coordination isomerism |
| C. $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$                             | III. linkage isomerism     |
| D. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ | 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-I, B-II, C-IV, D-I (d) A-III, B-II, C-I, D-IV

Sol. (c)

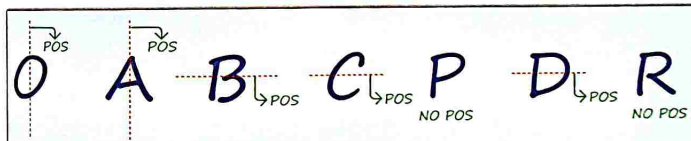
108. The complexes  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Cr}(\text{CN})_6]^{3-}$  and  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$  are the examples of which type of isomerism?

- (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.



Coordination Compounds

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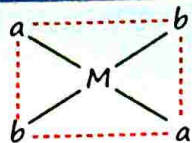
## POS and Anti-pairs in Square Planar Complex

$a, b, c, d \dots \rightarrow$  monodentate ligand [ $\text{Cl}^-$ ,  $\text{NH}_3$  etc.]

AA  $\rightarrow$  Symmetrical bidentate ligand [en]

AB  $\rightarrow$  Unsymmetrical bidentate ligand [gly $^-$ ]

Complex-1



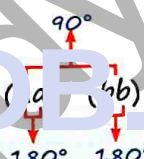
☐  $a$  is Anti to  $a \rightarrow (aa)$

$\angle aMa = 180^\circ$

☐  $b$  is Anti to  $b \rightarrow (bb)$

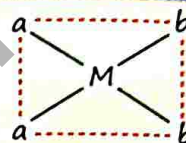
$\angle bMb = 180^\circ$

☐ Anti pair  $\rightarrow (aa) (bb)$   
for complex-1



☐ POS is present.

Complex-2



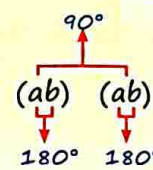
☐  $a$  is Anti to  $b \rightarrow (ab)$

$\angle aMb = 180^\circ$

☐  $a$  is Anti to  $b \rightarrow (ab)$

$\angle aMb = 180^\circ$

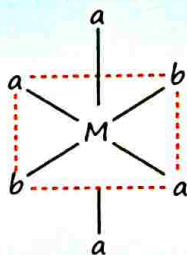
☐ Anti pair  $\rightarrow (ab) (ab)$   
for complex-2



☐ POS is present.

## POS and Anti-pairs in Octahedral Complex

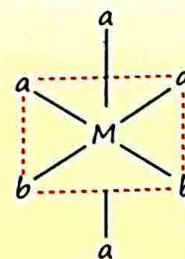
Complex-1



☐ Anti pair  $\rightarrow (aa) (aa) (bb)$

☐ POS is present.

Complex-2



☐ Anti pair  $\rightarrow (aa) (ab) (ab)$

☐ POS is present.



# STEREISOMERS

Isomers having-

- Different arrangement of the atoms in space (3D)
- or Different spatial arrangement of atoms / ligands.

## Stereoisomers



## GEOMETRICAL ISOMERISM

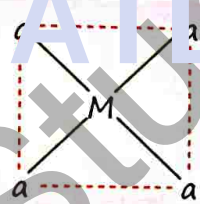
Same molecular formula but different geometry.

- Bond angles must be different between 2 ligands ( $\theta = 90^\circ / (180^\circ)$ )
- 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 ( $\theta$ ) should be  $90^\circ$  but in Trans form,  $\theta$  should be  $180^\circ$ .

No. of geometrical isomers  $\Rightarrow$  No. of set of anti-pairs

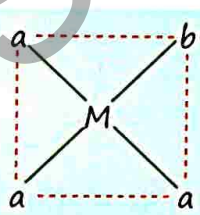
## Geometrical Isomerism in Square Planar Complex

$Ma_4$  (aa) (aa)



□ No geometrical isomer

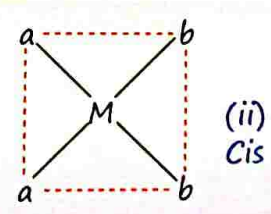
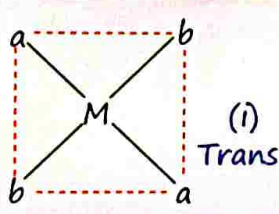
$Ma_3b$  (aa) (ab)



□ No geometrical isomer

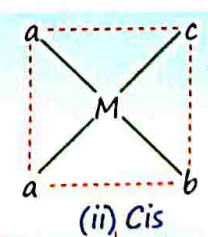
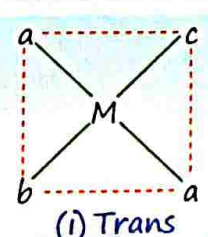
$Ma_2b_2$  (i) (aa) (bb)  
(ii) (ab) (ab)

Example -  $[Pt(NH_3)_2Cl_2]$



$Ma_2bc$  (i) (aa) (bc)  
(ii) (ab) (ac)

Example -  $[Pd(NH_3)_2ClBr]$



2 geometrical isomers

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Mabcd

(i) (ab)(cd)

(ii) (ac) (bd)

(iii) (ad) (cb)

**Example-**  $[Pt\ NH_3\ Br\ Cl\ Py] \rightarrow 3$  geometrical isomers

M(AA)a<sub>2</sub>

(Aa)(Aa)

**Example-**  $[Pt\ (en)Cl_2]$

No geometrical isomer is possible.

$\angle AMA = 90^\circ$  (always).

M(AB)ab

(i) (Aa)(Bb)

(ii) (Ab) (Ba)

**Example-**  $[Pd\ (gly)\ (NH_3)Cl]$

(iii) (AB) (ab)

- This is not possible because  $\angle AMB$  should always be equal to  $90^\circ$  (not  $180^\circ$ ).

M(AA)<sub>2</sub>

(AA)(AA)

**Example-**  $[Pt\ (en)_2]^{2+}$

M(AB)<sub>2</sub>

(i) (AA)(BB)

(ii) (AB) (BA)

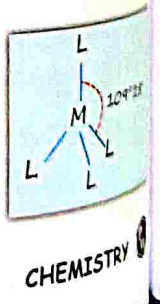
**Example-**  $[Pt\ (gly)_2]$

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

\* 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

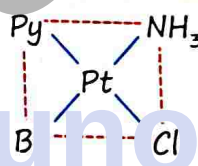
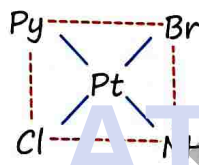
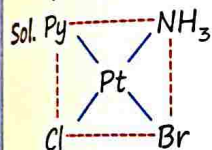
Generally, square planar complexes have plane of symmetry. So they can not show optical isomerism.

109. The complex,  $[\text{Pt}(\text{Py})(\text{NH}_3)\text{BrCl}]$  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  $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{py})]$  and how many of these will exhibit optical isomers?



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  $[\text{M}(\text{F})(\text{Cl})(\text{SCN})(\text{NO}_2)]$  is

[10 Jan, 2019 (Shift-I)]

- (a) 16 (b) 8 (c) 4 (d) 12

Sol. (d)

4 linkage isomers are possible for square planar  $[\text{M}(\text{F})(\text{Cl})(\text{SCN})(\text{NO}_2)]$  -

- $[\text{M}(\text{F})(\text{Cl})(\text{SCN})(\text{NO}_2)]$
- $[\text{M}(\text{F})(\text{Cl})(\text{SCN})(\text{ONO})]$
- $[\text{M}(\text{F})(\text{Cl})(\text{NCS})(\text{NO}_2)]$
- $[\text{M}(\text{F})(\text{Cl})(\text{NCS})(\text{ONO})]$

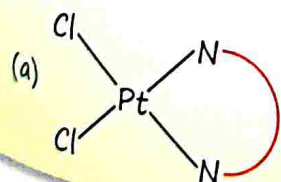
Through every linkage isomers we can make 3 geometrical isomers. So total =  $4 \times 3 = 12$ .

112. The species that can have a trans-isomer is:

(en = ethane-1, 2-diamine, ox = oxalate)

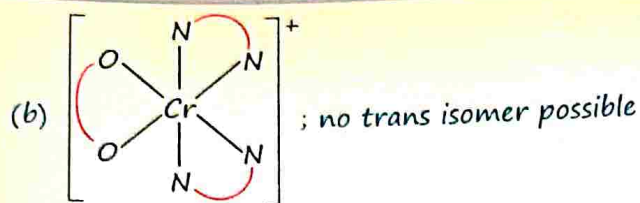
- (a)  $[\text{Pt}(\text{en})\text{Cl}_2]$  (b)  $[\text{Cr}(\text{en})_2(\text{ox})]^+$  (c)  $[\text{Zn}(\text{en})\text{Cl}_2]$  (d)  $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$

Sol. (d)

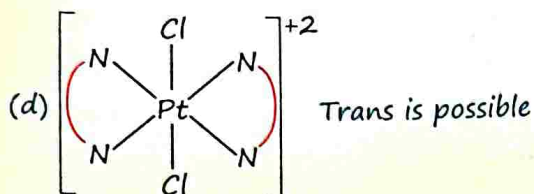


no trans isomer possible because bidentate ligand will be co-ordinating only at  $90^\circ$  angle in square planar complex

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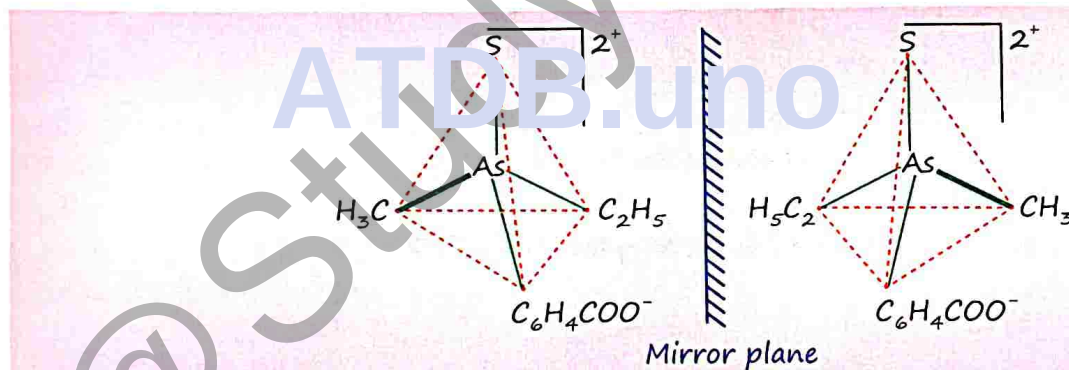
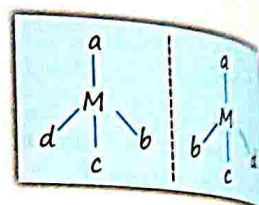


(c)  $[\text{Zn}(\text{en})\text{Cl}_2] \rightarrow \text{Tetrahedral} \rightarrow sp^3$  hybridized so no trans possible



### Optical Isomerism in Tetrahedral Complex

- ☐ Tetrahedral complexes are optically active only when all ligands are different.
- ☐ For example  $[\text{As}(\text{III})(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{S})(\text{C}_6\text{H}_4\text{COO})]^{2+}$ , shows optical isomerism.



113. The number of possible optical isomers for the complexes  $\text{MA}_2\text{B}_2$  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-I)]

- (a) 0 and 0      (b) 2 and 2      (c) 0 and 2      (d) 0 and 1

Sol. (a) POS is present in  $\text{MA}_2\text{B}_2$  in both tetrahedral ( $sp^3$ ) and square planar ( $dsp^2$ ).

114. The metal atom present in the complex  $\text{MABXL}$  (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-I)]

- (a) 4      (b) 0      (c) 2      (d) 3

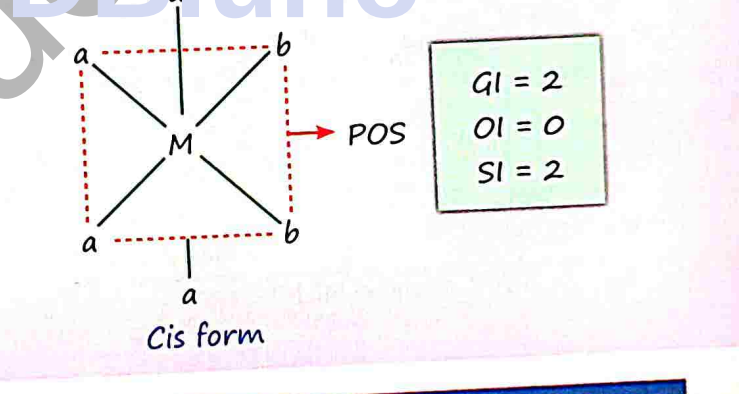
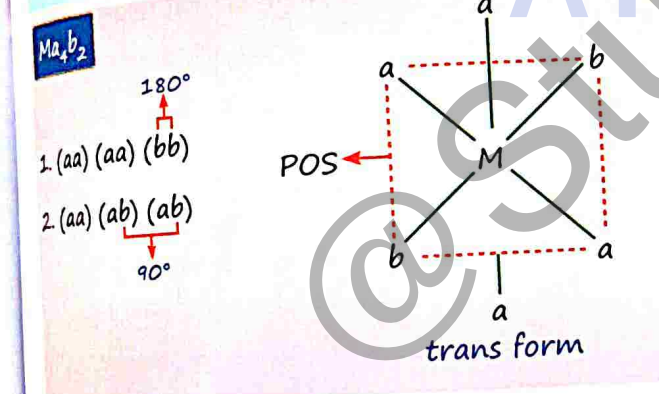
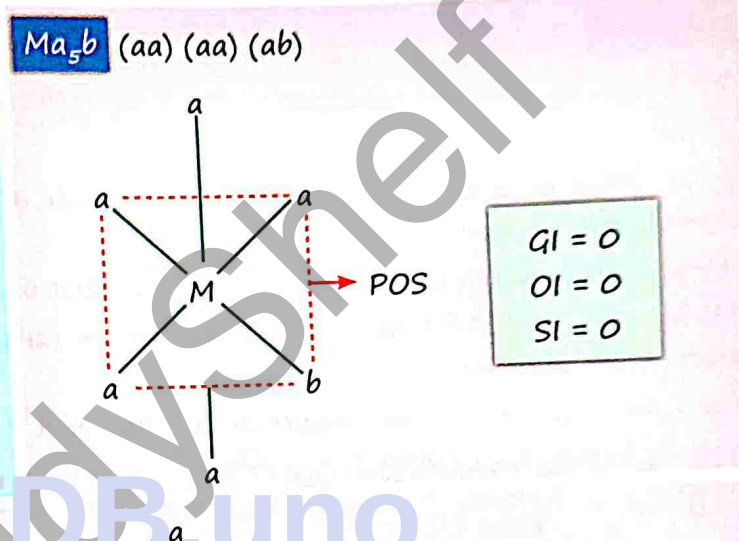
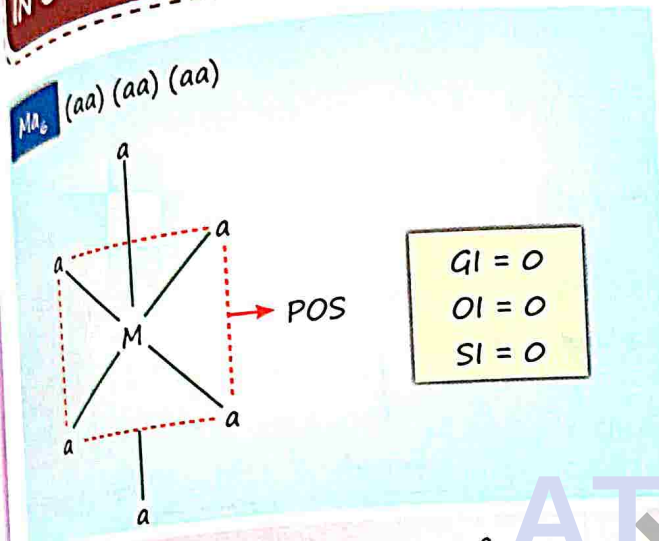
Sol. (b) Tetrahedral complex ( $sp^3$ ) does not show geometrical isomerism.



**(IIT JEE 2010)**  
 1.5 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  $\rightarrow$  Geometrical isomers
- OI  $\rightarrow$  Optical isomers
- SI  $\rightarrow$  Stereo-isomers

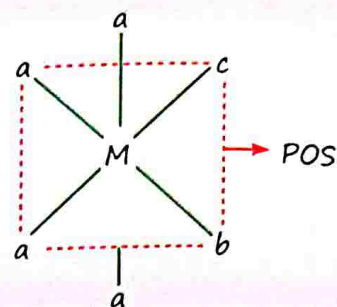
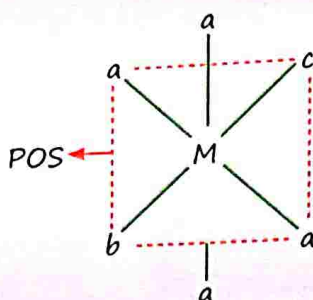


**Plane of symmetry and optical activity in geometrical isomers of  $[Co(NH_3)_4Cl_2]$ .**

| Trans form                                                               | Cis form                                                                                             |
|--------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|
| <p>This plane bisects the molecule in 2 equal halves. So it has POS.</p> | <p>Here, Plane of symmetry is present because this plane bisects the molecule in 2 equal halves.</p> |
| <input type="checkbox"/> Optically Inactive Compound.                    | <input type="checkbox"/> Optically Inactive Compound                                                 |

### Ma<sub>4</sub>bc

- (aa) (aa) (bc)
- (aa) (ab) (ac)



$$\begin{aligned} QI &= 2 \\ OI &= 0 \\ SI &= 2 \end{aligned}$$

### Ma<sub>3</sub>b<sub>3</sub>

- (a a) (a b) (b b)  $\rightarrow$  meridional
- (ab) (ab) (ab)  $\rightarrow$  facial

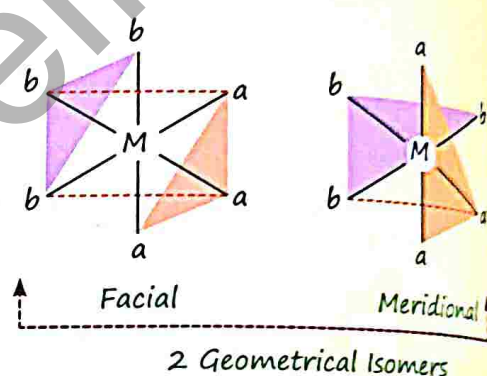
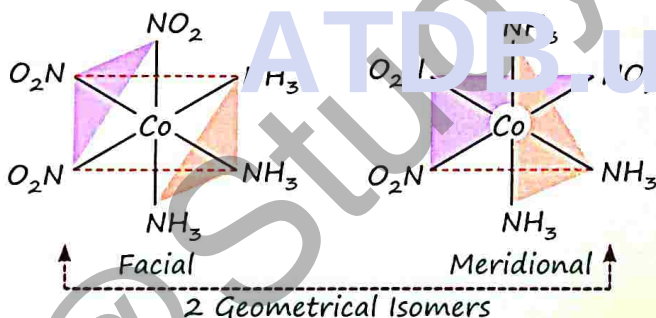
**Facial [fac]:** All 3 same ligands are at the corner of face of octahedron

Bond angle between same ligands  $\Rightarrow \theta = 90^\circ$  (but  $\theta \neq 180^\circ$ )

**Meridional [mer]:** All 3 same ligands are on the same plane that bisects octahedron

Bond angle between same ligands  $\Rightarrow (\theta = 90^\circ \text{ \& } \theta = 180^\circ)$

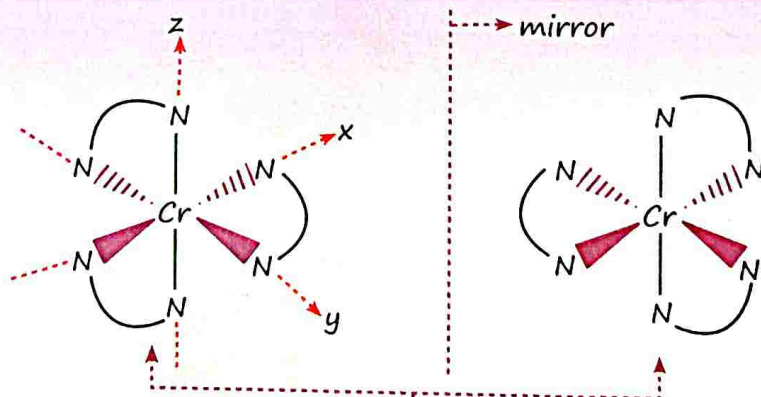
**Example:**  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$



### M(AA)<sub>3</sub>

(A A) (A A) (A A)

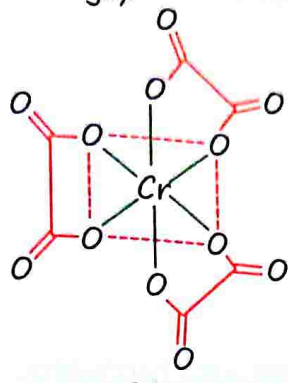
$\square [\text{Cr}(\text{en})_3]$



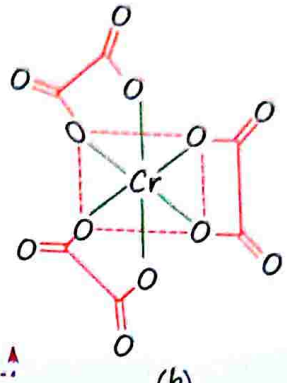
- $\square$  Enantiomeric Pair
- $\square$  POS is absent.



$[Cr(C_2O_4)_3]^{3-}$  is an optically active compound because it does not have POS (So it is non-superimposable on its mirror image).



(a)



(b)

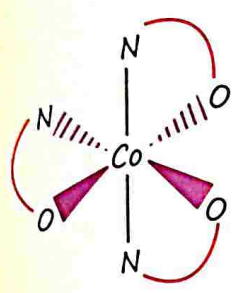
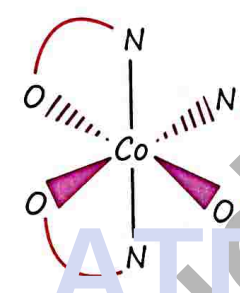
• (a) and (b) are optical isomers.

Mirror Image

$[M(AB)_3]^{3+} \rightarrow$

(i) (AB) (AB) (AB)

Enantiomeric Pair

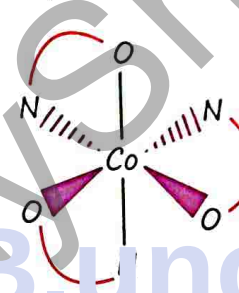
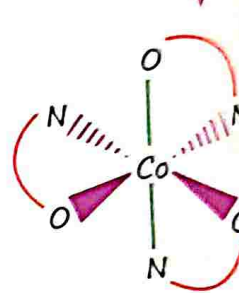



☐  $\theta = 180^\circ, 90^\circ$   
☐ meridional

☐ POS is absent  
☐ optically active

(ii) (AB) (A A) (B B)

Enantiomeric Pair

☐  $\theta = 90^\circ$   
☐ Facial

☐ POS is absent  
☐ Optically active

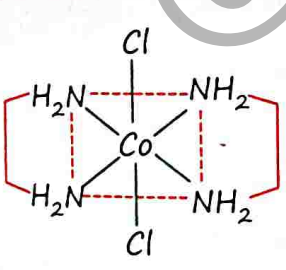
GI = 2, Enantiomeric pairs = 2

OI = 4

SI = 4

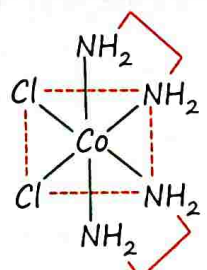
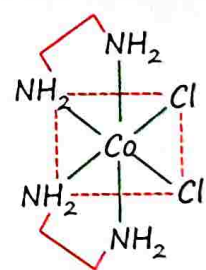
$[M(AA)_2a_2] \rightarrow$

(i) (A A) (A A) (a a)



Trans form is optically inactive because it has plane of symmetry.

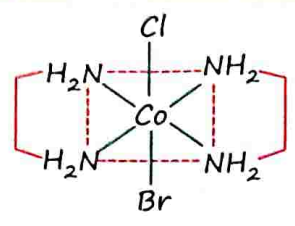
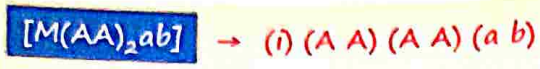
(ii) (A A) (A a) (A a)

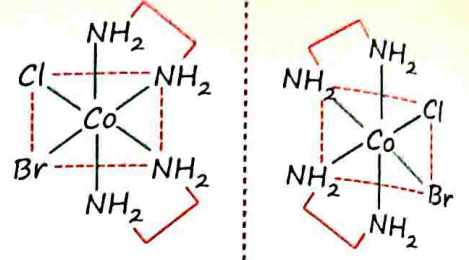
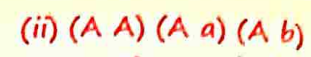
Cis form is optically active because it does not have plane of symmetry.

Enantiomeric Pair

Geometrical isomers  $\rightarrow 2$  } Stereoisomers : 3  
 Optical isomers  $\rightarrow 2$



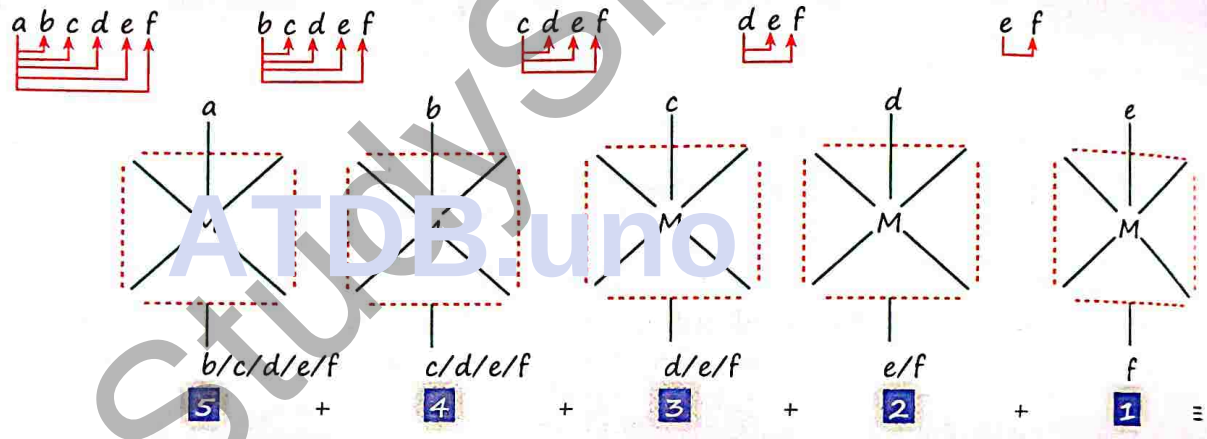
Trans form is optically inactive because it has plane of symmetry.



Enantiomeric Pair

Cis form is optically active because it does not have plane of symmetry.

Geometrical isomers → 2  
 Optical isomers → 2  
 Stereoisomers → 3



☐ All 15 geometrical isomers are optically active because 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<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>] complex is/are: [30 Jan, 2023 (Shift-I)]  
 (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-I)]  
 (a) [Co(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>]      (b) [CoCl<sub>2</sub>(en)<sub>2</sub>]      (c) [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>      (d) [Co(CN)<sub>5</sub>(NC)]<sup>3-</sup>  
 Sol. (d)
118. If Ni<sup>2+</sup> is replaced by Pt<sup>2+</sup> in the complex [NiCl<sub>2</sub>Br<sub>2</sub>]<sup>2-</sup>, which of the following properties are expected to get changed? [11 April, 2023 (Shift-I)]  
 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)  $[\text{NiBr}_2\text{Cl}_2]^{2-}$  — tetrahedral ( $3d^8$  : paramagnetic)  
 $[\text{PtBr}_2\text{Cl}_2]^{2-}$  — Square planar ( $5d^8$  : diamagnetic)

119. Match List-I with List-II:

| List-I |                                                      | List-II |                        |
|--------|------------------------------------------------------|---------|------------------------|
| (A)    | $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ | (I)     | Linkage isomerism      |
| (B)    | $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$          | (II)    | Solvate isomerism      |
| (C)    | $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$       | (III)   | Coordination isomerism |
| (D)    | cis - $[\text{CrCl}_2(\text{ox})_2]^{3-}$            | (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]  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3] \rightarrow X = 2$ ,  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-} \rightarrow Y = 0$

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)  $\text{CoCl}_3 + 2 \text{ en} \rightarrow [\text{CoCl}_2(\text{en})_2]\text{Cl}$  : Cis and trans isomerism

122. Which kind of isomerism is shown by  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl}$ ?

(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  $[\text{Pt}(\text{NH}_3)_2\text{Br}_2]$ , is (are) [JEE Adv. 2023]

- [en =  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ]  
 (a)  $[\text{Pt}(\text{en})(\text{SCN})_2]$  (b)  $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$  (c)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$  (d)  $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})(\text{SO}_4)]^+$

Sol. (c, d)

In  $[\text{Pt}(\text{NH}_3)_2\text{Br}_2]$ , the hybridisation of Pt is  $\text{dsp}^2$  and geometry is square planar. It exhibits cis and trans isomerism:

- (a)  $[\text{Pt}(\text{en})(\text{SCN})_2]$  : square planar and cis-trans not possible  
 (b)  $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$  : tetrahedral and cis-trans not possible  
 (c)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$  : octahedral and cis-trans possible  
 (d)  $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})\text{SO}_4]^+$  : Octahedral  $\rightarrow$  cis-trans

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124. The correct option(s) regarding the complex  $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$  ( $\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ) (JEE Adv. 2013)
- (a) It has two geometrical isomers  
(b) It will have three geometrical isomers, if bidentate 'en' is replaced by two cyanide ligands  
(c) It is paramagnetic  
(d) It absorbs light at longer wavelength as compared to  $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$

Sol. (a, b, d)

- (a)  $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$  complex is type of  $[\text{M}(\text{AA})\text{b}_3\text{c}]$  which will have two geometrical isomers.  
(b) If (en) is replaced by two cyanide ligands, complex will be type of  $[\text{Ma}_2\text{b}_3\text{c}]$  and have 3 geometrical isomers.  $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+} \xrightarrow[+ 2 \text{CN}^-]{- \text{en}} [\text{Co}(\text{CN})_2(\text{NH}_3)_3(\text{H}_2\text{O})]^+$   
(c)  $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$  have  $d^6$  configuration ( $t_{2g}^6$ ) on central metal with strong field ligands, therefore it is diamagnetic in nature.  
(d)  $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+} < [\text{Co}(\text{en})(\text{NH}_3)_4]^{3+} : \Delta_o$  value  
 $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+} > [\text{Co}(\text{en})(\text{NH}_3)_4]^{3+} : \lambda$  absorbed

125. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is/are (JEE Adv. 2013)

- (a)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  (b)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  and  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$   
(c)  $[\text{CoBr}_2\text{Cl}_2]^{2-}$  and  $[\text{PtBr}_2\text{Cl}_2]^{2-}$  (d)  $[\text{Pt}(\text{NH}_3)_3(\text{NO}_2)]\text{Cl}$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$

Sol. (b, d) ☐ Octahedral  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  and square planar  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$  which shows geometrical (cis-trans) isomerism.

- ☐ Square planar  $[\text{Pt}(\text{NH}_3)_3(\text{NO}_2)]\text{Cl}$  and square planar  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$  shows ionization isomerism.  
☐  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  neither shows structural nor stereoisomerism.  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  shows geometrical (cis trans) isomerism.  
☐ Tetrahedral  $[\text{CoBr}_2\text{Cl}_2]^{2-}$  and square planar  $[\text{PtBr}_2\text{Cl}_2]^{2-}$  do not show the same type of isomerism.

126. The compound(s) that exhibit(s) geometrical isomerism is/are (IIT JEE 2007)

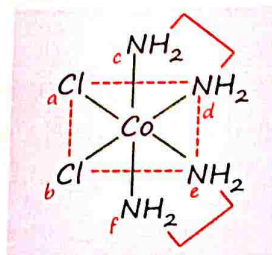
- (a)  $[\text{Pt}(\text{en})\text{Cl}_2]$  (b)  $[\text{Pt}(\text{en})_2]\text{Cl}_2$  (c)  $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$  (d)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

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  $[\text{Mn}(\text{en})_2\text{Cl}_2]$  complex is ..... (JEE Adv. 2014)  
( $\text{en} = \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ )

Sol. [6]  $\angle \text{ClCoN} = 90^\circ$

1.  $\angle_a \text{ClCoN}_c$  4.  $\angle_b \text{ClCoN}_c$   
2.  $\angle_a \text{ClCoN}_d$  5.  $\angle_b \text{ClCoN}_e$   
3.  $\angle_a \text{ClCoN}_f$  6.  $\angle_b \text{ClCoN}_f$





128. The type of isomerism exhibited by the complex  $[\text{CoCl}_2(\text{en})_2]$  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  $[\text{Co}(\text{en})_2\text{Cl}_2]$  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)  $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  (b)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$   
 (c)  $[\text{Ni}(\text{NH}_3)_2\text{Cl}_2]$  (d)  $[\text{Ni}(\text{en})_3]^{2+}$

Sol. (c)  
 131. The existence of two different coloured complexes with the composition of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  is due to: [NEET 2010 Pre]  
 (a) Ionization isomerism (b) Linkage isomerism  
 (c) Geometrical isomerism (d) Coordination isomerism

Sol. (c)  
 132. Which of the following does not show optical isomerism? [NEET 2009]  
 (a)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^{0}$  (b)  $[\text{Co}(\text{en})\text{Cl}_2(\text{NH}_3)_2]^+$   
 (c)  $[\text{Co}(\text{en})_3]^{3+}$  (d)  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$   
 (en = ethylenediamine)

Sol. (a)  
 133.  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$  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- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  (b) trans- $[\text{Co}(\text{en})_2\text{Cl}_2]$   
 (c) trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  (d) cis- $[\text{Co}(\text{en})_2\text{Cl}_2]$

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)  
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136. Which one of the following octahedral complexes will not show geometric isomerism? (A and B are monodentate ligands)

- (a)  $[MA_2B_4]$  (b)  $[MA_3B_3]$  (c)  $[MA_4B_2]$  (d)  $[MA_5B]$

Sol. (d)

137. The hypothetical complex chloro diaquatrimmine cobalt (III) chloride can be represented as

- (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



- ☐ Value of equilibrium constant  $\uparrow \Rightarrow$  Stability of  $[ML_4]$  complex  $\uparrow$
- ☐ Stepwise stability constant ( $k_1, k_2, \dots$ ): The equilibrium constant of each step of a complex reaction called stepwise stability constants.
- ☐ Overall stability constant ( $\beta_4$ ): The equilibrium constant for net reaction



Then  $\rightarrow \beta_4 = k_1 \cdot k_2 \cdot k_3 \cdot k_4$

138. Which of the following complexes formed by  $Cu^{2+}$  ions is most stable?

- (a)  $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$ ,  $\log K = 11.6$   
(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)  $Cu^{2+} + 4H_2O \rightleftharpoons [Cu(H_2O)_4]^{2+}$ ,  $\log K = 8.9$

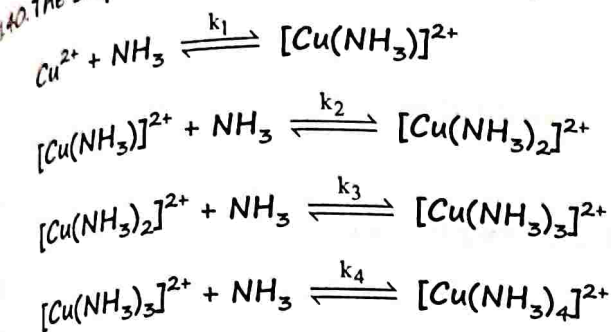
Sol. (b) The greater the value of  $\log K$ , the greater will be stability of complex compound formed.



39. Calculate the stability constant ( $\beta_4$ ) for this complex is  $2.1 \times 10^{13}$ .  
 (a)  $8.27 \times 10^{-13}$  (b)  $4.76 \times 10^{-14}$  (c)  $2.39 \times 10^{-7}$  (d)  $1.83 \times 10^{14}$

Sol. (b)  $[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$   
 Dissociation constant ( $k$ ) is the reciprocal of the stability constant  $\beta_4$  ( $k = 1/\beta_4$ ).  
 $k = \frac{1}{2.1 \times 10^{13}} \Rightarrow 4.76 \times 10^{-14}$

40. The stepwise formation of  $[Cu(NH_3)_4]^{2+}$  is given below:



The value of stability constants  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  are  $10^4$ ,  $1.58 \times 10^3$ ,  $5 \times 10^2$  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)

Sol. [1] Overall stability constant  $K$  will be calculated as:

$$K = K_1 \times K_2 \times K_3 \times K_4 = 7.9 \times 10^{11}$$

Now, calculate the overall equilibrium constant for dissociation of  $[Cu(NH_3)_4]^{2+}$  as:

$$K' = \frac{1}{K} = \frac{1}{7.9 \times 10^{11}} = 0.126 \times 10^{-11} = 1.26 \times 10^{-12} \approx 1 \times 10^{-12}$$

[24 Feb, 2021 (Shift-I)]

## 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),  $\alpha$ -nitroso- $\beta$ -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.

Coordination Compounds Here To Join @StudyShelf For More Study Materials

### Water Hardness Testing-

- ❑ The hardness of water can be measured by a simple titration with  $\text{Na}_2\text{EDTA}$ . Calcium ( $\text{Ca}^{2+}$ ) magnesium ( $\text{Mg}^{2+}$ ) ions form stable complexes with EDTA, allowing for their selective estimation to differences in the stability constants of their respective complexes.

### Metal Extraction-

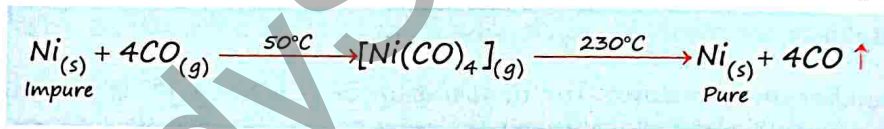
- ❑ Coordination compounds are also crucial in the extraction of metals, such as silver and gold. instance, gold forms a coordination entity,  $[\text{Au}(\text{CN})_2]^-$ , in the presence of cyanide, oxygen, and wa This allows gold to be separated from the solution in its metallic form by adding zinc.

### Metal Purification-

- ❑ The purification of metals can be achieved by forming coordination compounds, which can later decomposed to isolate the pure metal.



For example, impure nickel is converted to  $[\text{Ni}(\text{CO})_4]$ , which is decomposed to yield pure nickel.



### Electroplating-

- ❑ Articles can be electroplated with silver and gold more smoothly and evenly using solutions of the complexes  $[\text{Ag}(\text{CN})_2]^-$  and  $[\text{Au}(\text{CN})_2]^-$  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  $\rightarrow$  Chelating agent  $\rightarrow$  Binds with Cu  $\rightarrow$  Treatment of wilson's disease.

Desferrioxamine B  $\rightarrow$  Chelator  $\rightarrow$  Binds with Fe

Cis platin cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$   $\rightarrow$  To inhibit the growth of tumours.

### In biological system-

Chlorophyll (Green Pigment Responsible for photosynthesis)  $\rightarrow$  Co-ordination compound of Mg

Haemoglobin (Red pigment of blood : Acts as oxygen carrier)  $\rightarrow$  Co-ordination compound of Fe

Vitamin  $\text{B}_{12}$  (Cyanocobalamine)  $\rightarrow$  Co-ordination compound of Co.

Carboxy peptidase A (Removes the amino acid residue from the C-terminal of a peptide chain)  $\rightarrow$  Coordination compound of Zn.

Carbonic Anhydrase (Catalyze the interconversion between  $\text{CO}_2$  &  $\text{H}_2\text{O}$  and  $\text{H}_2\text{CO}_3$ )  $\rightarrow$  coordination compound of Zn.



### photography-

7 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-

7 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  $-2.4 \Delta_o$

(c) 1.73 BM and  $-2.0 \Delta_o$

(d) 2.84 BM and  $-1.6 \Delta_o$

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  $t_{2g}^5 e_g^0$

•  $M = \sqrt{n(n+2)} = 1.73 \text{ B.M.}$

•  $CFSE = -0.4 \Delta_o \times n_{t_{2g}} + 0.6 \Delta_o \times n_{e_g} = -0.4 \Delta_o \times 5 = -2.0 \Delta_o$

142. Match List-I with List-II.

| List-I<br>(Substances)      | List-II<br>(Element Present) |
|-----------------------------|------------------------------|
| (A) Ziegler catalyst        | (I) Rhodium                  |
| (B) Blood Pigment           | (II) Cobalt                  |
| (C) Wilkinson catalyst      | (III) Iron                   |
| (D) Vitamin B <sub>12</sub> | (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)

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144. Match List-I with List-II.

| List-I                      | List-II        |
|-----------------------------|----------------|
| (A) Chlorophyll             | (I) Ruthenium  |
| (B) Vitamin-B <sub>12</sub> | (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-2)]

(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-2)]

(a) EDTA (b) Cis-platin (c) D-penicillamine (d) desferrioxime B

Sol. (a)

146. Among the complex ions,  $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2 - \text{NH}_2)_2\text{Cl}_2]^+$ ,  $[\text{CrCl}_2(\text{C}_2\text{O}_4)_2]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]$ ,  $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]$ ,  $[\text{Co}(\text{NH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2)_2(\text{NH}_3)\text{Cl}]^{2+}$  and  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$  the number of complex ion(s) that show(s) cis-trans isomerism is (JEE Adv. 2021)

Sol. [6] Among given complexes, all six complexes will show cis-trans isomerism.

147. Among the following complexes,  $[\text{Fe}(\text{CN})_6]^{4-}$  (K),  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (L),  $\text{Na}_3[\text{Co}(\text{Ox})_3]$  (M),  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$  (N),  $\text{K}_2[\text{Pt}(\text{CN})_4]$  (O) and  $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$  (P) the diamagnetic complexes are (IIT JEE 2021)

(a) K, L, M, N (b) K, M, O, P (c) L, M, O, P (d) L, M, N, O

Sol. (c) L & M  $\rightarrow \text{Co}^{3+} (d^6)$  with  $\text{NH}_3/\text{Ox}^{2-}$  (Strong field ligand), O  $\rightarrow \text{Pt}^{+2} (d^8)$ : Square planar: All electrons are paired, P  $\rightarrow \text{Zn}^{+2} (d^{10})$

148. The complex showing a spin only magnetic moment of 2.82 BM is (IIT JEE 2010)

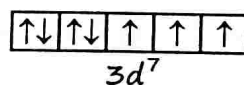
(a)  $\text{Ni}(\text{CO})_4$  (b)  $[\text{NiCl}_4]^{2-}$  (c)  $\text{Ni}(\text{PPh}_3)_4$  (d)  $[\text{Ni}(\text{CN})_4]^{2-}$

Sol. (b)  $\text{NiCl}_4^{2-}$ :  $\text{Ni}^{2+} (d^8)$ : Tetrahedral ( $sp^3$ ) with 2 unpaired electrons

149. Spin only magnetic moment of the compound  $\text{Hg}[\text{Co}(\text{SCN})_4]$  is (IIT JEE 2004)

(a)  $\sqrt{3}$  (b)  $\sqrt{15}$  (c)  $\sqrt{24}$  (d)  $\sqrt{8}$

Sol. (b) In complex,  $\text{Hg}[\text{Co}(\text{SCN})_4]$ ,  $\text{Co}^{2+}$  has  $3d^7$  electronic configuration.  $\text{SCN}^-$  weak ligand field, hence no pairing of electron occurs:



$$\mu = \sqrt{3(3+2)}\text{BM} = \sqrt{15}\text{BM}$$



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)  $[\text{FeCl}_4]^-$  and  $[\text{Fe}(\text{CO})_4]^{2-}$   
 (b)  $[\text{Co}(\text{CO})_4]^-$  and  $[\text{CoCl}_4]^{2-}$   
 (c)  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$   
 (d)  $[\text{Cu}(\text{py})_4]^+$  and  $[\text{Cu}(\text{CN})_4]^{3-}$

Sol. (a, b, d)

151. Which of the following complexes is used to be as an anticancer agent?

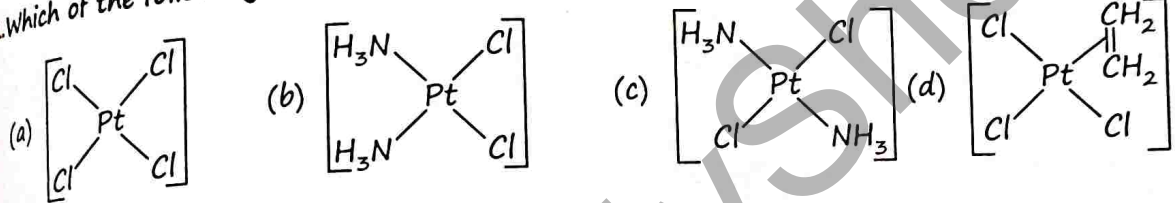
[NEET 2014]

- (a)  $\text{cis}-[\text{PtCl}_2(\text{NH}_3)_2]$   
 (b)  $\text{cis}-\text{K}_2[\text{PtCl}_2\text{Br}_2]$   
 (c)  $\text{Na}_2[\text{CoCl}_4]$   
 (d)  $\text{mer}-[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

Sol. (a)

152. Which of the following is considered to be an anticancer species?

[NEET 2004]



Sol. (b)

153. In the silver plating of copper,  $\text{K}[\text{Ag}(\text{CN})_2]$  is used instead of  $\text{AgNO}_3$ . The reason is: [NEET 2002]

- (a) A thin layer of Ag is formed on Cu  
 (b) More voltage is required  
 (c)  $\text{Ag}^+$  ions are completely removed from solution  
 (d) Less availability of  $\text{Ag}^+$  ions, as Cu cannot displace Ag from  $[\text{Ag}(\text{CN})_2]^-$  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.  $\text{Zn}^{2+}$ ,  $\text{Ti}^{2+}$       B.  $\text{Cr}^{2+}$ ,  $\text{Fe}^{2+}$       C.  $\text{Ti}^{3+}$ ,  $\text{Cu}^{2+}$       D.  $\text{V}^{2+}$ ,  $\text{Cu}^+$

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.  $\text{Ti}^{3+}$       B.  $\text{Cr}^{2+}$       C.  $\text{Mn}^{2+}$       D.  $\text{Fe}^{2+}$       E.  $\text{Sc}^{3+}$

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  $\text{Cr}^{2+}$  ion is [NEET 2020]

- (a) 4.90 BM      (b) 5.92 BM      (c) 2.84 BM      (d) 3.87 BM

Sol. (a)

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157. Magnetic moment 2.84 B.M. is given by: (Atomic numbers, Ni = 28, Ti = 22, Cr = 24, Co = 27)  
(a)  $Ti^{3+}$  (b)  $Cr^{2+}$  (c)  $Co^{2+}$  (d)  $Ni^{2+}$  [NEET 2015]

Sol. (d)

158. Magnetic moment 2.83 BM is given by which of the following ions?  
(Atomic Number Ti = 22, Cr = 24, Mn = 25, Ni = 28) [NEET 2014]

(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)

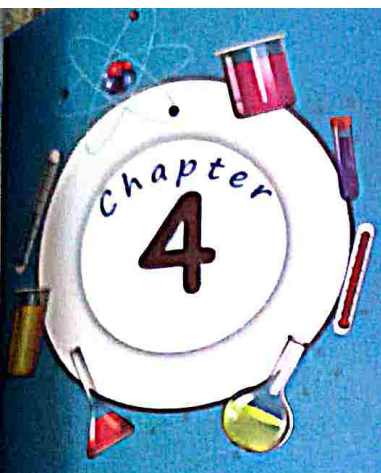
160. The aqueous solution containing which one of the following ions will be colourless? (Atomic number: Sc = 21, Fe = 26, Ti = 22, Mn = 25) [NEET 2005]

(a)  $Sc^{3+}$  (b)  $Fe^{2+}$  (c)  $Ti^{3+}$  (d)  $Mn^{2+}$

Sol. (a)

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# 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 <sup>2</sup> np <sup>1</sup>                                             | Group-14 : [IG]ns <sup>2</sup> np <sup>2</sup>                                             | Types of Element                                                                                                                                                                                                                                                                                                                                                                  |             |   |             |    |    |    |    |             |    |    |         |    |    |    |    |
|--------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|---|-------------|----|----|----|----|-------------|----|----|---------|----|----|----|----|
| B <sub>5</sub> : [He] 2s <sup>2</sup> 2p <sup>1</sup>                                      | C <sub>6</sub> : [He] 2s <sup>2</sup> 2p <sup>2</sup>                                      | <table><tr><td>B</td><td>C</td><td rowspan="2">→ Non-metal</td></tr><tr><td>Al</td><td>Si</td></tr><tr><td>Ga</td><td>Ge</td><td>→ Metalloid</td></tr><tr><td>In</td><td>Sn</td><td rowspan="3">→ Metal</td></tr><tr><td>Tl</td><td>Pb</td></tr><tr><td>Nh</td><td>Fl</td></tr></table> <p>❑ Nihonium (Nh) and Flerovium (Fl) are synthetically prepared radioactive element.</p> | B           | C | → Non-metal | Al | Si | Ga | Ge | → Metalloid | In | Sn | → Metal | Tl | Pb | Nh | Fl |
| B                                                                                          | C                                                                                          |                                                                                                                                                                                                                                                                                                                                                                                   | → Non-metal |   |             |    |    |    |    |             |    |    |         |    |    |    |    |
| Al                                                                                         | Si                                                                                         |                                                                                                                                                                                                                                                                                                                                                                                   |             |   |             |    |    |    |    |             |    |    |         |    |    |    |    |
| Ga                                                                                         | Ge                                                                                         |                                                                                                                                                                                                                                                                                                                                                                                   | → Metalloid |   |             |    |    |    |    |             |    |    |         |    |    |    |    |
| In                                                                                         | Sn                                                                                         |                                                                                                                                                                                                                                                                                                                                                                                   | → Metal     |   |             |    |    |    |    |             |    |    |         |    |    |    |    |
| Tl                                                                                         | Pb                                                                                         |                                                                                                                                                                                                                                                                                                                                                                                   |             |   |             |    |    |    |    |             |    |    |         |    |    |    |    |
| Nh                                                                                         | Fl                                                                                         |                                                                                                                                                                                                                                                                                                                                                                                   |             |   |             |    |    |    |    |             |    |    |         |    |    |    |    |
| Al <sub>13</sub> : [Ne] 3s <sup>2</sup> 3p <sup>1</sup>                                    | Si <sub>14</sub> : [Ne] 3s <sup>2</sup> 3p <sup>2</sup>                                    |                                                                                                                                                                                                                                                                                                                                                                                   |             |   |             |    |    |    |    |             |    |    |         |    |    |    |    |
| Ga <sub>31</sub> : [Ar] 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>1</sup>                   | Ge <sub>32</sub> : [Ar] 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>2</sup>                   |                                                                                                                                                                                                                                                                                                                                                                                   |             |   |             |    |    |    |    |             |    |    |         |    |    |    |    |
| In <sub>49</sub> : [Kr] 5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>1</sup>                   | Sn <sub>50</sub> : [Kr] 5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>2</sup>                   |                                                                                                                                                                                                                                                                                                                                                                                   |             |   |             |    |    |    |    |             |    |    |         |    |    |    |    |
| Tl <sub>81</sub> : [Xe] 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>1</sup>  | Pb <sub>82</sub> : [Xe] 6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>10</sup> 6p <sup>2</sup>  |                                                                                                                                                                                                                                                                                                                                                                                   |             |   |             |    |    |    |    |             |    |    |         |    |    |    |    |
| Nh <sub>113</sub> : [Rn] 7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>10</sup> 7p <sup>1</sup> | Fl <sub>114</sub> : [Rn] 7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>10</sup> 7p <sup>2</sup> |                                                                                                                                                                                                                                                                                                                                                                                   |             |   |             |    |    |    |    |             |    |    |         |    |    |    |    |

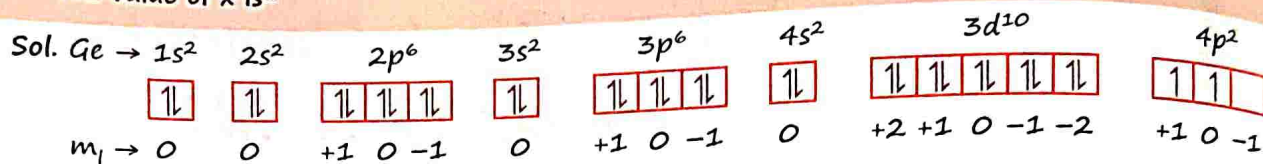
- ❑ Ga, Ge and Bi liquid expands when it forms the solid as water.
- ❑ Abundance in Earth Crust: O > Si > Al > Fe

GiGa Bite expand like water.  
O Simran Aloo Feka kro  
Jameen par.

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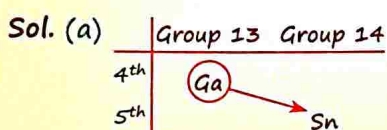
1. Ge ( $Z = 32$ ) in its ground state electronic configuration has  $x$  completely filled orbitals with  $m_l = 0$ . The value of  $x$  is-



Completely filled orbital with  $m_l = 0$  are 7

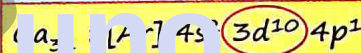
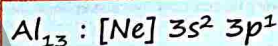
2. Outermost electronic configuration of group 13 element, E, is  $4s^2, 4p^1$ . The electronic configuration of an element of p-block period-five placed diagonally to element, E is:

(a)  $[\text{Kr}] 4d^{10} 5s^2 5p^2$  (b)  $[\text{Kr}] 3d^{10} 4s^2 4p^2$  (c)  $[\text{Xe}] 5d^{10} 6s^2 6p^2$  (d)  $[\text{Ar}] 3d^{10} 4s^2 4p^2$



E is Gallium, so diagonally placed element is Tin ( $[\text{Kr}] 5s^2 4d^{10} 5p^2$ ).

### Atomic Radius



poor shielding effect for outer electrons

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  |
| Covalent radius/pm <sup>a</sup> | 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)  $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$  (b)  $\text{Ga} < \text{Al} < \text{In} < \text{Tl}$  (c)  $\text{Al} < \text{In} < \text{Ga} < \text{Tl}$  (d)  $\text{Al} < \text{Ga} < \text{Tl} < \text{In}$

Sol. (b) Atomic radii tends to increase 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



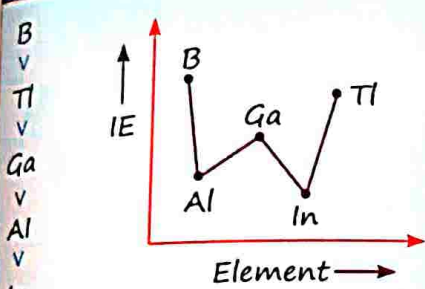
## Ionic Radius

□  $B^{3+} < Al^{3+} < Ga^{3+} < In^{3+} < Tl^{3+}$  : *Size*

□  $C^{4+} < Si^{4+} < Ge^{4+} < Sn^{4+} < Pb^{4+}$  : *Size*

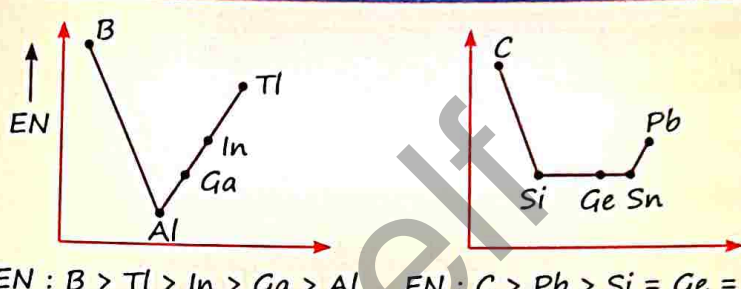
## Ionisation Energy and Electronegativity

### Ionisation Energy



C  
V  
Si  
V  
Ge  
V  
Pb  
^  
Sn

### Electronegativity



EN :  $B > Tl > In > Ga > Al$

EN :  $C > Pb > Si = Ge = Sn$

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.

Small decrease in  $\Delta H$  from Si to Ge to Sn and slight increase in  $\Delta H$  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, metalloid, as well as metallic elements.

In the light of the above statements, choose the most appropriate from the options given below:

- Statement-I is false but Statement-II is true
- Statement-I is true but Statement-II is false
- Both Statement-I and Statement-II are true
- Both Statement-I and Statement-II are false

[29 Jan, 2024 (Shift-I)]

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 :  $B < Al < Ga < In < Tl$

$C_{\text{graphite}} < Si < Ga < Sn < Pb$

$Si < C_{\text{diamond}} < Ga < Sn < Pb$



- Generally in group-13 and 14 Melting point (with some exception) and Boiling point (with exception) decreases as we move down the group.

Melting point :  $B > Al > Tl > In > Ga$

Due to very strong crystalline lattice, boron has unusually high melting point.

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.

:  $C > Si > Ge > Pb > Sn$  [Same order in IE]

## FIRST ATOM OF GROUP

1. 2<sup>nd</sup> period elements do not have d subshell, so possible hybridisations are  $sp, sp^2, sp^3$ .

First atom of group/2<sup>nd</sup> Period element →  $B \quad C \quad N \quad O \quad F$

♦ Maximum covalency of these elements is 4.

2. Small in size → Form multiple bond easily ( $P\pi-P\pi$  bond) [ $C=C, C\equiv C, C\equiv N, C=O$ ]

♦ This type of  $\pi$ -bonding is not particularly strong for the heavier p-block elements. The heavier elements do form  $\pi$  bond but this involves d orbitals ( $d\pi - p\pi$  or  $d\pi - d\pi$ ).

### Note

Using d-orbitals the 3<sup>rd</sup> period elements (Al, S, Si, P, Cl) or more than 3<sup>rd</sup> period elements can expand covalency above four

Existence:  $BF_4^-, AlF_6^-, SF_6, [Xe]Cl_6^{2-}, [Sn(OH)_6]^{2-}$

□  $BF_4^-, SiF_6^{2-}$  → 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  $p\pi-p\pi$  multiple bonds, is:

(a) Sn (b) C (c) Ge (d) Si

Sol. (b) The element that shows the greatest ability to form  $p\pi-p\pi$  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<sup>-</sup>: 6s e<sup>-</sup> pair does not take part in bonding.

### Stability of Oxidation State

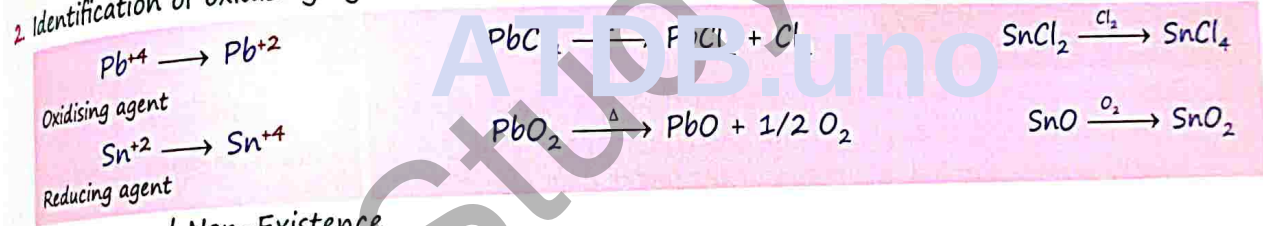
|                  |                  |                  |                  |                  |                  |
|------------------|------------------|------------------|------------------|------------------|------------------|
| B <sup>+3</sup>  | C <sup>+2</sup>  | N <sup>+3</sup>  | B <sup>+3</sup>  | C <sup>+4</sup>  | N <sup>+5</sup>  |
| ^                | ^                | ^                | ^                | ^                | ^                |
| Al <sup>+3</sup> | Si <sup>+2</sup> | P <sup>+3</sup>  | Al <sup>+3</sup> | Si <sup>+4</sup> | P <sup>+5</sup>  |
| ^                | ^                | ^                | ^                | ^                | ^                |
| Ga <sup>+3</sup> | Ge <sup>+2</sup> | As <sup>+3</sup> | Ga <sup>+3</sup> | Ge <sup>+4</sup> | As <sup>+5</sup> |
| ^                | ^                | ^                | ^                | ^                | ^                |
| In <sup>+3</sup> | Sn <sup>+2</sup> | Sb <sup>+3</sup> | In <sup>+3</sup> | Sn <sup>+4</sup> | Sb <sup>+5</sup> |
| ^                | ^                | ^                | ^                | ^                | ^                |
| Tl <sup>+3</sup> | Pb <sup>+2</sup> | Bi <sup>+3</sup> | Tl <sup>+3</sup> | Pb <sup>+4</sup> | Bi <sup>+5</sup> |

### Applications

#### 1. Stability of Compounds

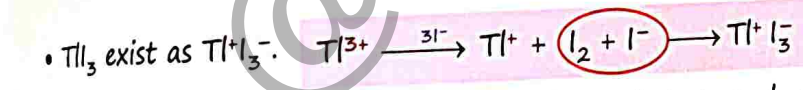
- (a)  $PbO > PbO_2$  (b)  $PbCl_2 > PbCl_4$  (c)  $SnCl_2 < SnCl_4$  (d)  $GeCl_2 < GeCl_4$

#### 2. Identification of oxidising agent and reducing agent

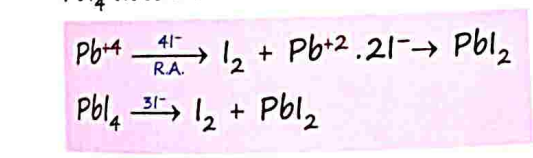


#### 3. Existence and Non-Existence

- $TlF_3$   $PbF_4$   $BiF_5$   $Tl_2O_3$   $PbO_2$  → Exist in nature [high oxidation state of element is stable with F and O].



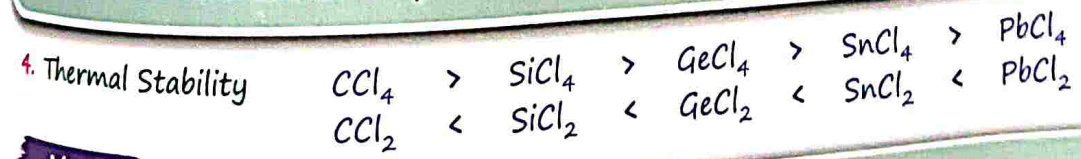
- $PbI_4$  does not exist because  $Pb^{+4}$  oxidises  $I^-$  into  $I_2$  and convert itself in  $PbI_2$ .



**'NCERT'** →  $PbI_4$  does not exist because Pb-I bond initially formed during the reaction does not release enough energy to unpair 6s<sup>2</sup> electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom.

### Note

The well characterised Bi compound is  $BiF_5$  due to strong oxidising power of  $F_2$ .



### Note

In  $GaCl_2$ , Ga exist in +3 and +1 oxidation state.  $2GaCl_2 \rightleftharpoons GaCl_3 \cdot GaCl$

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[08 April, 2024 (Shift-I)]

6. Given below are two statements: One is labelled as

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  $[\text{BF}_4]^-$ , are  
(a) 4 and 3 (b) 4 and 4 (c) 3 and 4 (d) 3 and 5

Sol. (a) In  $[\text{BF}_4]^-$ , 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  $\text{BF}_6^{3-}$

Reason (R): Size of B is very small.

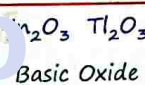
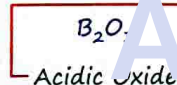
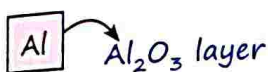
- (a) Both (A) and (R) are true and (R) is the correct explanation of (A)  
(b) Both (A) and (R) are true and (R) is NOT the correct explanation of (A)  
(c) (A) is true but (R) is false  
(d) (A) is false but (R) is true

Sol. (b) Boron do not form  $[\text{BF}_6]^{3-}$ . Since Boron does not have vacant d orbitals, it can not expand its octet.

## OXIDES

### Group 13

- B is unreactive in crystalline form. Air ( $\text{O}_2$ ,  $\text{N}_2$ ), 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.



### Group 14

CO Neutral

$\text{CO}_2$  Acidic

SiO exist only  
at High temp.

$\text{SiO}_2$  Acidic.

GeO Acidic

$\text{GeO}_2$  Acidic

Amphoteric Oxide

$\text{SnO}$ ,  $\text{PbO}$ ,  $\text{Pb}_2\text{O}_3$

$\text{SnO}_2$ ,  $\text{PbO}_2$ ,  $\text{Pb}_3\text{O}_4$

Red lead  $\text{Pb}_3\text{O}_4 \equiv 2\text{PbO} \cdot \text{PbO}_2$

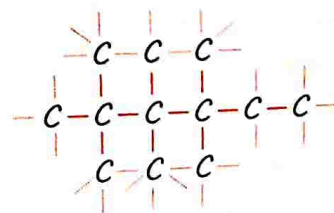
$\text{Pb}_2\text{O}_3 \equiv \text{PbO} \cdot \text{PbO}_2$

## BOND ENERGY

Bond dissociation energy:  $\text{C}-\text{C} > \text{Si}-\text{Si} > \text{Ge}-\text{Ge} > \text{Sn}-\text{Sn}$

## CATENATION PROPERTY

- Self linking property of an element is known as catenation property.
- More single bond formation tendency with itself  $\Rightarrow$  More Self-linking property.



- ❑ The order of catenation is  $C \gg Si > Ge \approx Sn$ .
- ❑ 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.

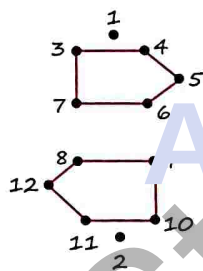
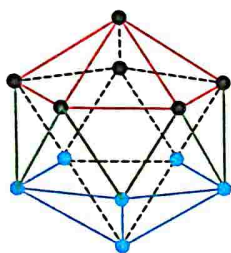
13. The correct order of bond enthalpy (kJ per mol) is:

- (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:  $^{10}B$  (9%)  $^{11}B$  (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.

- (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

[12 April, 2023 (Shift-I)]

Sol. (b)

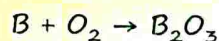
15. The number of neutrons present in the more abundant isotope of boron is 'x'. Amorphous boron upon heating with air forms a product, in which the oxidation state of boron is 'y'. The value of  $x + y$  is ...

[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.  
 $x = 6$



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)  $[GeCl_4]^-$  (c)  $[Sn(CH_3)_2]^-$  (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 ( ${}^2\text{He}$ ) - Noble gas     |
| 2.                     | Nitrogen ( ${}^7\text{N}$ ) - Non metal      | Oxygen ( ${}^8\text{O}$ ) - Non metal        | Fluorine ( ${}^9\text{F}$ ) - Non metal     | Neon ( ${}^{10}\text{Ne}$ ) - Noble gas    |
| 3.                     | Phosphorus ( ${}^{15}\text{P}$ ) - Non metal | Sulphur ( ${}^{16}\text{S}$ ) - Non metal    | Chlorine ( ${}^{17}\text{Cl}$ ) - Non metal | Argon ( ${}^{18}\text{Ar}$ ) - Noble gas   |
| 4.                     | Arsenic ( ${}^{33}\text{As}$ ) - Metalloid   | Selenium ( ${}^{34}\text{Se}$ ) - Metalloid  | Bromine ( ${}^{35}\text{Br}$ ) - Non metal  | Krypton ( ${}^{36}\text{Kr}$ ) - Noble gas |
| 5.                     | Antimony ( ${}^{51}\text{Sb}$ ) - Metalloid  | Tellurium ( ${}^{52}\text{Te}$ ) - Metalloid | Iodine ( ${}^{53}\text{I}$ ) - Non metal    | Xenon ( ${}^{54}\text{Xe}$ ) - Noble gas   |
| 6.                     | Bismuth ( ${}^{83}\text{Bi}$ ) - Metal       | Polonium ( ${}^{84}\text{Po}$ ) - Metal      | Astatine ( ${}^{85}\text{At}$ ) - Non metal | Radon ( ${}^{86}\text{Rn}$ ) - Noble gas   |

❑ Polonium, Astatine and 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: $[\text{He}] 2s^2 2p^3$                  | O: $[\text{He}] 2s^2 2p^4$                  | F: $[\text{He}] 2s^2 2p^5$                  | Ne: $[\text{He}] 2s^2 2p^6$                 |
| 3.                     | P: $[\text{Ne}] 3s^2 3p^3$                  | S: $[\text{Ne}] 3s^2 3p^4$                  | Cl: $[\text{Ne}] 3s^2 3p^5$                 | Ar: $[\text{Ne}] 3s^2 3p^6$                 |
| 4.                     | As: $[\text{Ar}] 4s^2 3d^{10} 4p^3$         | Se: $[\text{Ar}] 4s^2 3d^{10} 4p^4$         | Br: $[\text{Ar}] 4s^2 3d^{10} 4p^5$         | Kr: $[\text{Ar}] 4s^2 3d^{10} 4p^6$         |
| 5.                     | Sb: $[\text{Kr}] 5s^2 4d^{10} 5p^3$         | Te: $[\text{Kr}] 5s^2 4d^{10} 5p^4$         | I: $[\text{Kr}] 5s^2 4d^{10} 5p^5$          | Xe: $[\text{Kr}] 5s^2 4d^{10} 5p^6$         |
| 6.                     | Bi: $[\text{Xe}] 6s^2 4f^{14} 5d^{10} 6p^3$ | Po: $[\text{Xe}] 6s^2 4f^{14} 5d^{10} 6p^4$ | At: $[\text{Xe}] 6s^2 4f^{14} 5d^{10} 6p^5$ | Rn: $[\text{Xe}] 6s^2 4f^{14} 5d^{10} 6p^6$ |

❑ 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 |
|    |    |    | v  |
| N  | O  | F  | Ne |
| v  | v  | v  | v  |
| P  | S  | Cl | Ar |
| v  | v  | v  | v  |
| As | Se | Br | Kr |
| v  | v  | v  | v  |
| Sb | Te | I  | Xe |
| v  | v  |    |    |
| 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 electron as compared to group 16 elements.

## Electron Gain Enthalpy

| Group 16 | $\Delta_{eg}H$ | Group 17 | $\Delta_{eg}H$ | Group 18 | $\Delta_{eg}H$ |
|----------|----------------|----------|----------------|----------|----------------|
|          |                |          |                | 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 enthalpy:

$S > Se > Te > Po > O$   
 $Cl > F > Br > I > At$

[Chlorine has most (-)ve electron gain enthalpy in periodic table.]

- Order of (+)ve electron gain enthalpy:

$Ne > Ar = Kr > Xe > Rn > He$

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



## Electronegativity (Pauling Scale)

|     |      |     |
|-----|------|-----|
| N   | O    | F   |
| 3.0 | 3.5  | 4.0 |
| P   | S    | Cl  |
| 2.1 | 2.58 | 3.2 |
| As  | Se   | Br  |
| 2.0 | 2.55 | 3.0 |
| Sb  | Te   | I   |
| 1.9 | 2.01 | 2.7 |
| Bi  | Po   | At  |
| 1.9 | 1.76 | 2.2 |

| Group No. | Maximum oxidation state  |
|-----------|--------------------------|
| 13        | +3 (B $\rightarrow$ In)  |
| 14        | +4 (C $\rightarrow$ Sn)  |
| 15        | +5 (N $\rightarrow$ Sb)  |
| 16        | +6 (S $\rightarrow$ Te)* |
| 17        | +7 (Cl $\rightarrow$ I)* |
| 18        | +8 (Xe)                  |

\* O has +2 as maximum oxidation state (eg. OF<sub>2</sub>).

\* 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.

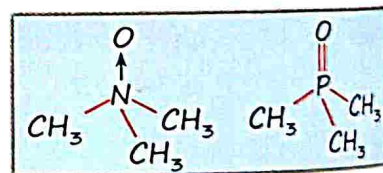
### Exception-

- Boiling Point: Sb > Bi
- Melting Point: N < P < As > Sb > Bi

- Melting Point and Boiling Point: Te > Po

## First Atom of Group

- First atom of the group has small size, so they can form  $\pi$  bond easily.
- First atom of the group (C, N, O) has 2<sup>nd</sup> 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<sup>2</sup>, sp<sup>3</sup>.
- 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<sub>6</sub><sup>-</sup>.
- Nitrogen cannot form d $\pi$  - p $\pi$  bond as the heavier elements can.
- Nitrogen has unique ability to form p $\pi$ -p $\pi$  multiple bonds with itself and with other elements having small size and high electronegativity (C, O).
- Heavier elements of this group do not form p $\pi$ -p $\pi$  bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.
- Phosphorus and arsenic can form d $\pi$ -d $\pi$  bond also with transition metals when their compounds like P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> 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 2<sup>nd</sup> period and cannot expand its octet.

26.  $\text{PCl}_5$  is well known, but  $\text{NCl}_5$  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)

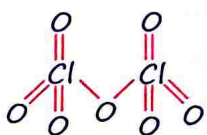
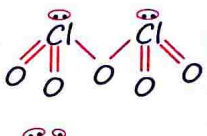
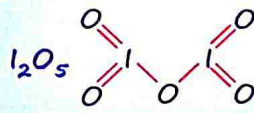
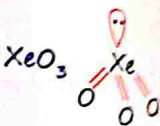
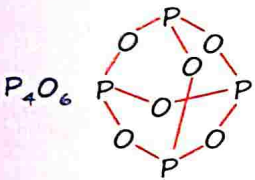
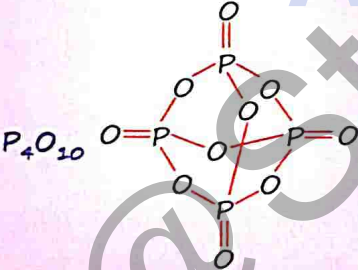
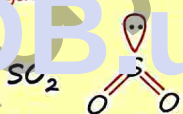
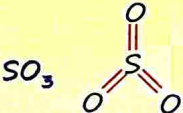
27. Statement-I: Although  $\text{PF}_5$ ,  $\text{PCl}_5$  and  $\text{PBr}_5$  are known, the pentahalides of nitrogen have not been observed.

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 <sub>2</sub> O : Neutral oxide                                                                                                                                   | SO <sub>2</sub> SeO <sub>2</sub> <span style="border: 1px solid black; padding: 2px;">TeO<sub>2</sub></span> → Amphoteric oxide                                                                                                                                                                                                                                                                                               | Cl <sub>2</sub> O <sub>7</sub> , I <sub>2</sub> O <sub>7</sub>                                                                                                                                                                                                                                                                                                                                                                       | XeO <sub>3</sub> , XeO <sub>4</sub>                                                 |
| N <sub>2</sub> O <sub>3</sub> , N <sub>2</sub> O <sub>5</sub> , NO <sub>2</sub><br>N <sub>2</sub> O <sub>4</sub> : Acidic oxide                                        | Acidic Oxide<br>SO <sub>3</sub> SeO <sub>3</sub> <span style="border: 1px solid black; padding: 2px;">TeO<sub>3</sub></span> <span style="border: 1px solid black; padding: 2px;">PoO</span> → Basic oxide                                                                                                                                                                                                                    | Cl <sub>2</sub> O <sub>5</sub> , I <sub>2</sub> O <sub>5</sub><br>ClO <sub>2</sub> , Cl <sub>2</sub> O <sub>4</sub> , BrO <sub>2</sub> , I <sub>2</sub> O <sub>4</sub><br>Cl <sub>2</sub> O <sub>3</sub> , Cl <sub>2</sub> O <sub>6</sub><br>Cl <sub>2</sub> O, Br <sub>2</sub> O                                                                                                                                                    |  |
| P <sub>4</sub> O <sub>6</sub> , P <sub>4</sub> O <sub>10</sub> : Acidic oxide                                                                                          | <div> <div>□ O<sub>3</sub> and SO<sub>2</sub> → gas</div> <div>SeO<sub>2</sub> → solid</div> </div> <div> <div>□ Reducing nature →</div> <div>SO<sub>2</sub> &gt; SeO<sub>2</sub> &gt; TeO<sub>2</sub></div> <div>Due to inert pair effect, stability of +6 oxidation state decreases as we go down the group.</div> </div> <div> <div>□ SO<sub>2</sub> is a reducing and TeO<sub>2</sub> is an oxidising agent.</div> </div> | <div> <div>□ Oxides of halogen are acidic in nature.</div> </div> <div>     </div> |  |
| As <sub>2</sub> O <sub>3</sub> , Sb <sub>2</sub> O <sub>3</sub> : Amphoteric oxide                                                                                     |                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                     |
| As <sub>2</sub> O <sub>5</sub> , Sb <sub>2</sub> O <sub>5</sub> : Acidic oxide                                                                                         |                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                     |
| Bi <sub>2</sub> O <sub>3</sub> : Basic Oxide                                                                                                                           |                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                     |
|   | <div> <div> <div>SO<sub>2</sub> <math>\xrightarrow{+4}</math> SO<sub>2</sub> <math>\xrightarrow{+6}</math> SO<sub>4</sub><sup>2-</sup> or SO<sub>3</sub> <math>\xrightarrow{+6}</math></div> <div>Reducing Agent</div> </div>   </div>                  |                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                     |

## OXO-ACIDS

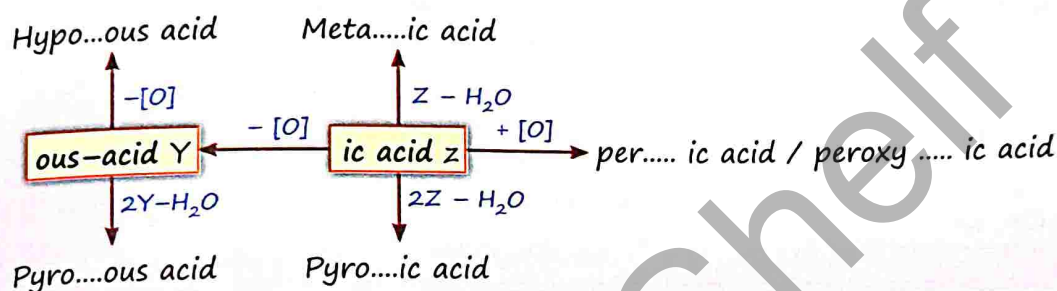
An oxyacid or oxoacid is a compound that contains hydrogen, oxygen, and at least one other element, with at least one hydrogen atom bonded to oxygen that can dissociate to produce the H<sup>+</sup> cation and the anion of the acid.

| 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) |                      |

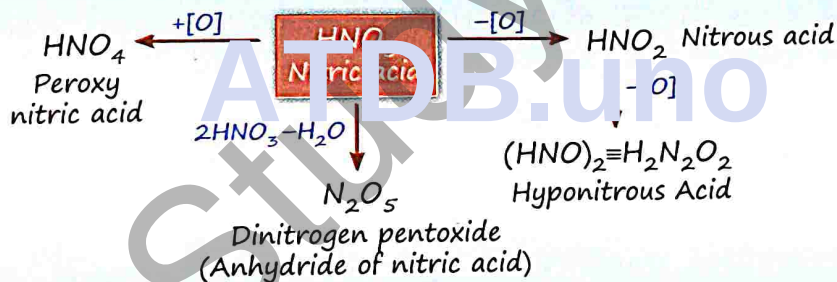


|                                                       |                                                  |                                            |                                     |                                           |
|-------------------------------------------------------|--------------------------------------------------|--------------------------------------------|-------------------------------------|-------------------------------------------|
| $\text{HNO}_3$<br>Nitric acid                         | $\text{H}_3\text{PO}_4$<br>Phosphoric acid       | $\text{H}_2\text{SO}_4$<br>Sulphuric acid  | $\text{HClO}_4$<br>Perchloric acid  | $\text{H}_4\text{XeO}_6$<br>Perxenic acid |
| $\text{HNO}_2$<br>Nitrous acid                        | $\text{H}_3\text{PO}_3$<br>Phosphorous acid      | $\text{H}_2\text{SO}_3$<br>Sulphurous acid | $\text{HClO}_3$<br>Chloric acid     | $\text{H}_4\text{XeO}_4$<br>Xenic acid    |
| $\text{H}_2\text{N}_2\text{O}_2$<br>Hypo nitrous acid | $\text{H}_3\text{PO}_2$<br>Hypo phosphorous acid |                                            | $\text{HClO}_2$<br>Chlorous acid    |                                           |
|                                                       |                                                  |                                            | $\text{HClO}$<br>Hypo chlorous acid |                                           |

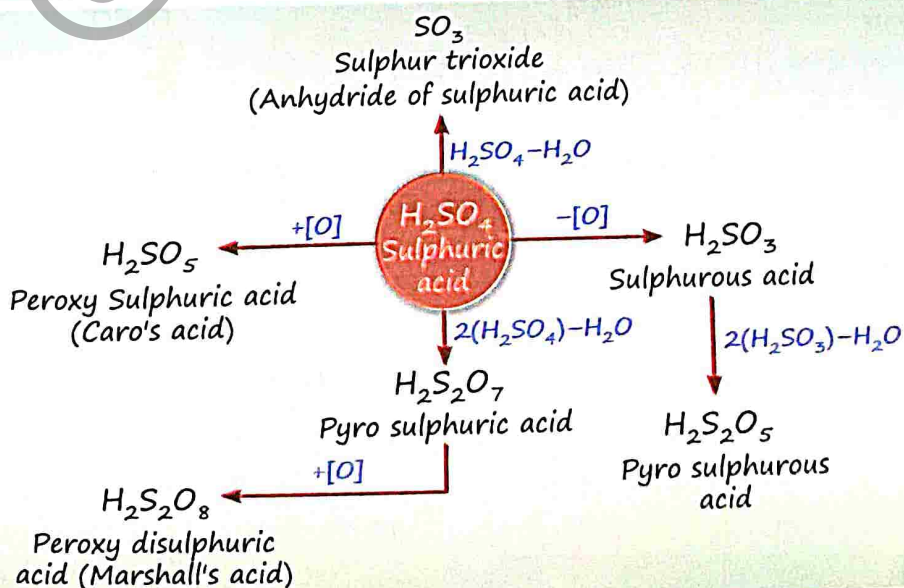
## Meta, Pyro, Peroxy Acids



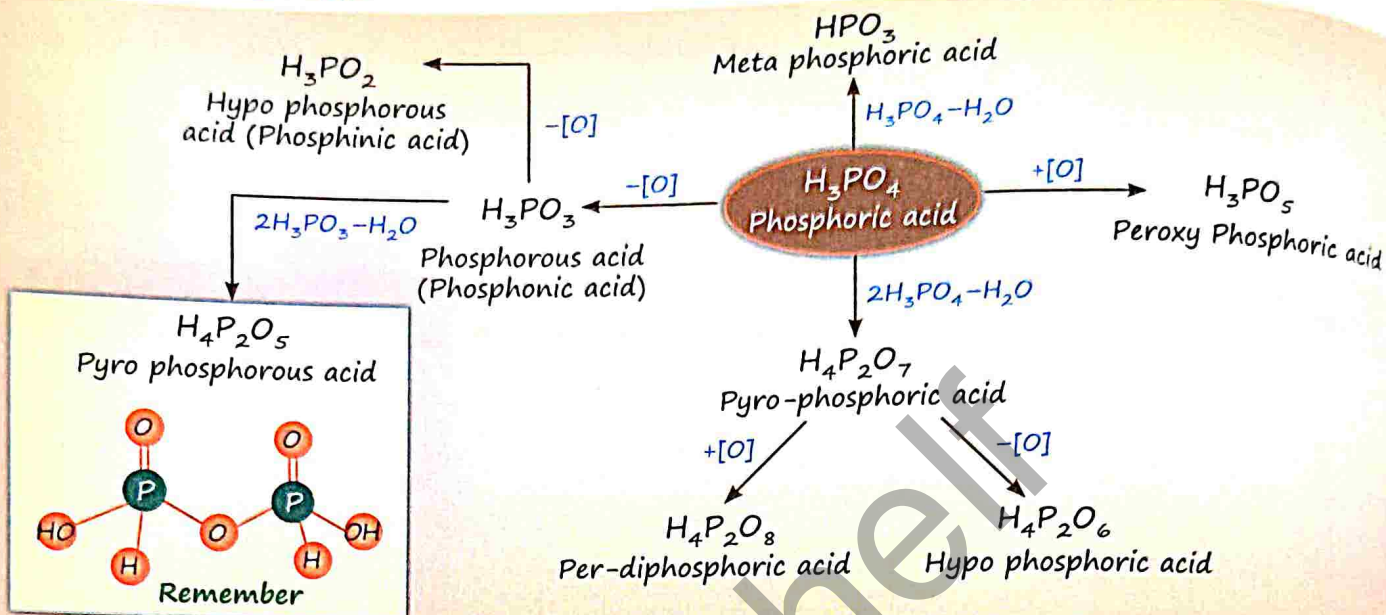
## Oxo-Acids of Nitrogen



## Oxo-Acids of Sulphur

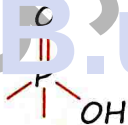


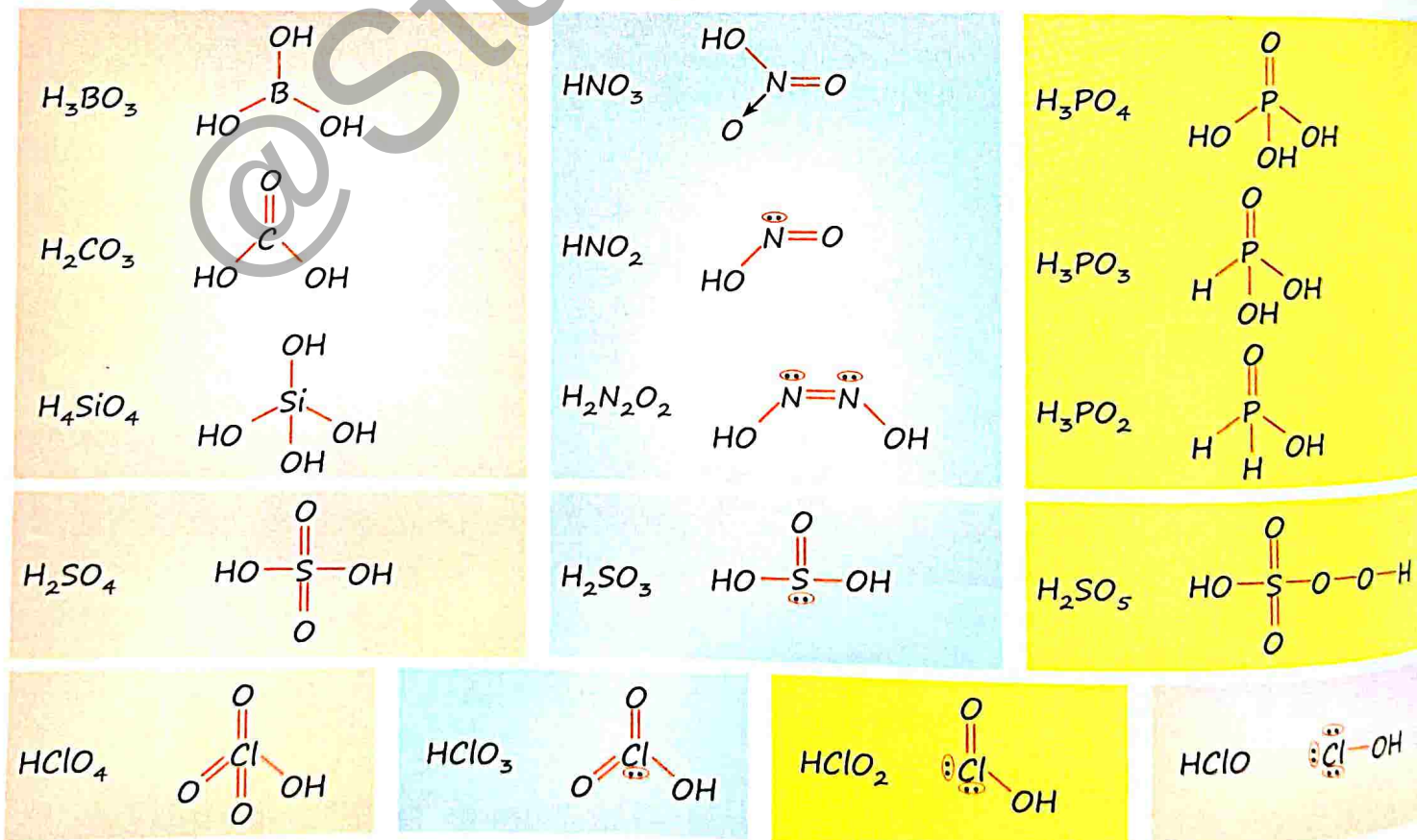
## Oxo-Acids of P



## Structure of Acids having Single Central Atom

- (i) Central atom from 2<sup>nd</sup> period (B, C, N) must be  $\text{sp}^2$  hybridised.  
 Central atom from 3<sup>rd</sup> period (Si, P, S) must be  $\text{sp}^3$  hybridised.

- (ii) Oxo-acids of phosphorus always has  structure.

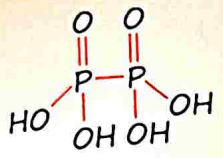




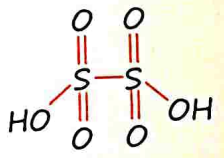
## Structure of Acids having Two Central Atom (Z)

- Calculate theoretical oxidation state (TOS) of central atom Z.
- Compare it with maximum oxidation state (MOS) of central atom.
- Then write type of bond between 2 central atoms.

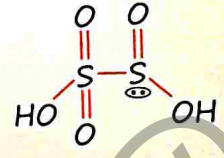
|                          |         |
|--------------------------|---------|
| Theoretical OS < Max. OS | Z—Z     |
| Theoretical OS = Max. OS | Z—O—Z   |
| Theoretical OS > Max. OS | Z—O—O—Z |



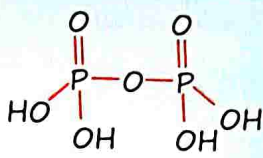
- $4 \times 1 + 2x + 6(-2) = 0$   
 $x = +4 = \text{T.O.S.}$
- T.O.S. < M.O.S. [M.O.S.]<sub>P</sub> = +5
- P—P bond



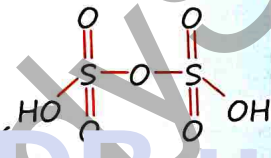
- [M.O.S.]<sub>S</sub> = +6  
[T.O.S.]<sub>S</sub> = +5



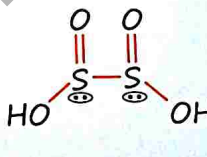
- [M.O.S.]<sub>S</sub> = +6  
[T.O.S.]<sub>S</sub> = +4



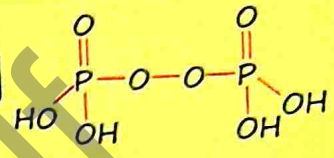
- $4 \times 1 + 2x + 7(-2) = 0$   
 $x = +5$
- T.O.S. = M.O.S.
- P—O—P bond



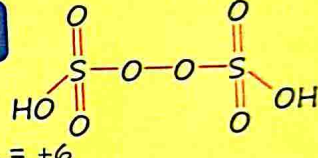
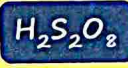
- [M.O.S.]<sub>S</sub> = +6  
[T.O.S.]<sub>S</sub> = +6



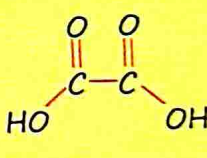
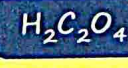
- [M.O.S.]<sub>S</sub> = +6  
[T.O.S.]<sub>S</sub> = +3



- $4 \times 1 + 2x + 8(-2) = 0$   
 $x = +6$
- T.O.S. > M.O.S.
- P—O—O—P bond



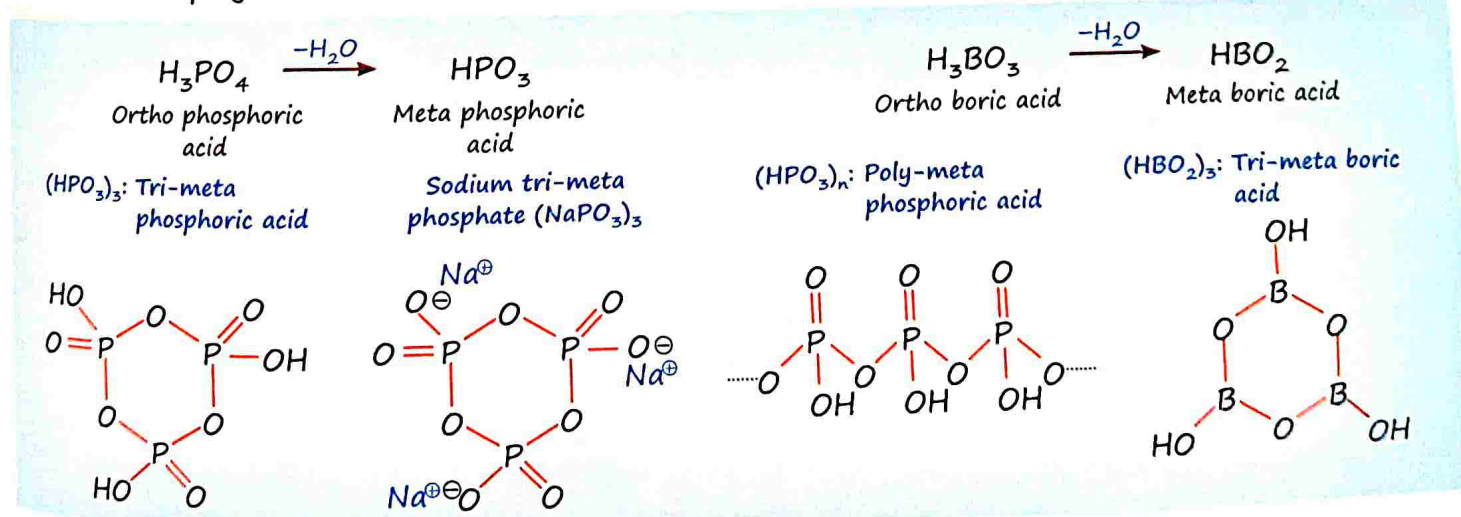
- [M.O.S.]<sub>S</sub> = +6  
[T.O.S.]<sub>S</sub> = +7



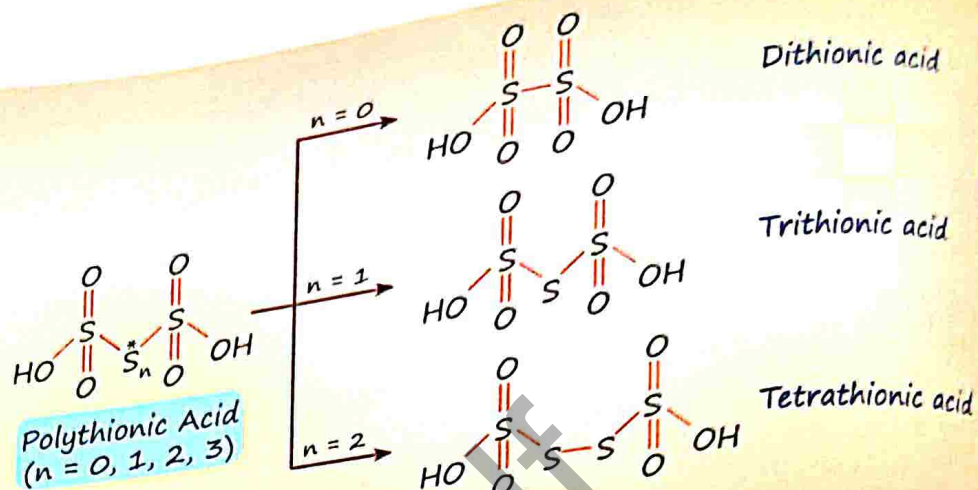
- [M.O.S.]<sub>C</sub> = +4  
[T.O.S.]<sub>C</sub> = +3

## Meta Acids

These acids are polymeric in nature or have cyclic structures.



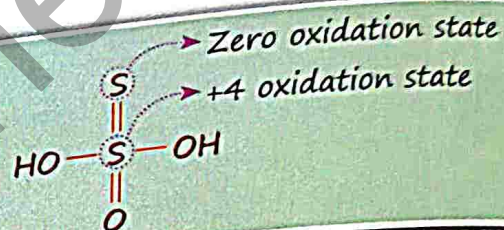
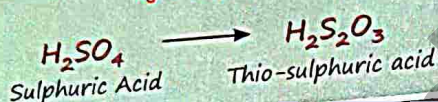
## Polythionic Acids



- Four  $d\pi - p\pi$  bonds are present.
- \* Marked sulphur has zero oxidation state and other 2 sulphur have +5 oxidation state.

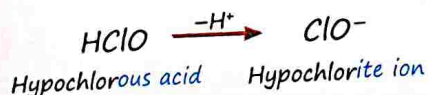
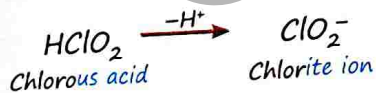
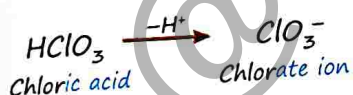
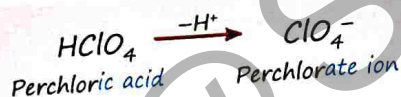
### Note

Oxy Acid  $\xrightarrow[\text{by 1 sulphur atom}]{\text{Exchange of 1 oxygen atom}}$  Thio Acid

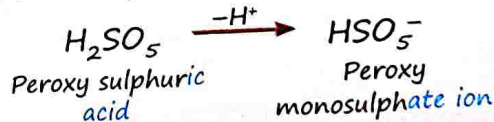
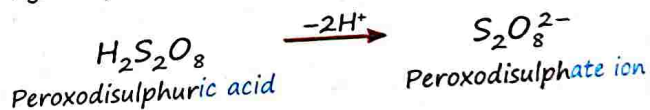
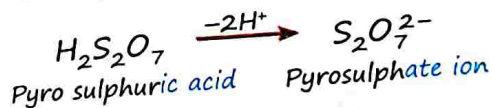
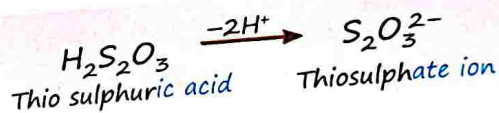


## Name of Anions

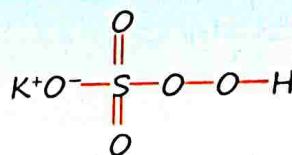
ic acid → ate ion



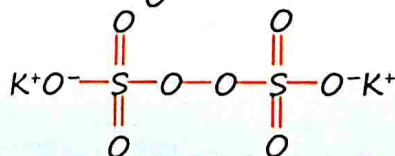
ous acid → ite ion



Potassium peroxymonosulphate [ $\text{KHSO}_5$ ]



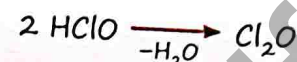
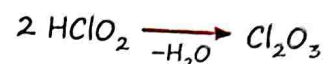
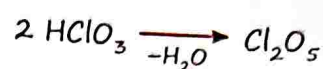
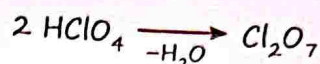
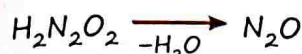
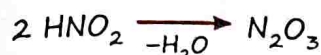
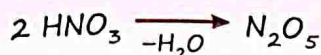
Potassium peroxodisulphate [ $\text{K}_2\text{S}_2\text{O}_8$ ]



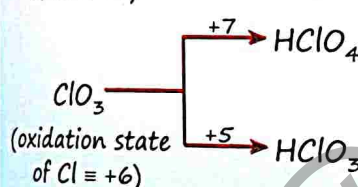
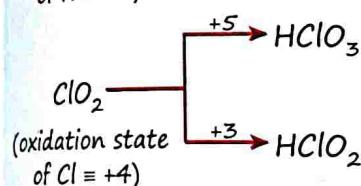
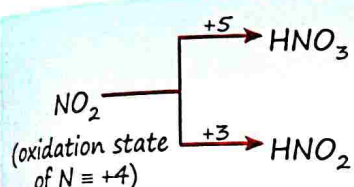


## Anhydride

To make anhydride (oxide) of any given acid remove all hydrogen from acid in the form of water ( $H_2O$ ) molecule.



## 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]

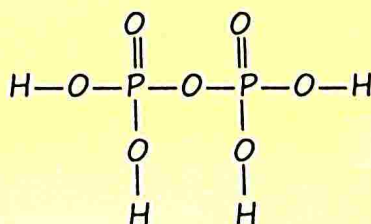
30. The ratio of sigma and  $\pi$  bonds present in pyrophosphoric acid is \_\_\_\_\_. [8 April, 2023 (Shift-II)]

Sol. [6] No. of  $\sigma$  bonds = 12

No. of  $\pi$  bonds = 2

$$\therefore \frac{\sigma}{\pi} = \frac{12}{2} = 6$$

Hence, ratio of  $\sigma$  and  $\pi$  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-1)]

- (a) + 3 and + 5 only  
 (b) + 6 only  
 (c) 0 and + 5 only  
 (d) + 5 only

Sol. (c)

(IIT JEE 2004)

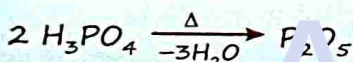
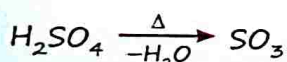
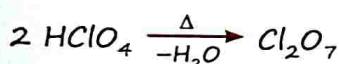
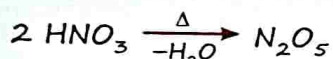
32. Which of the following has  $-O-O-$  linkage?

- (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



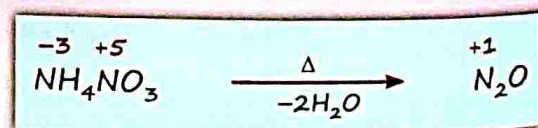
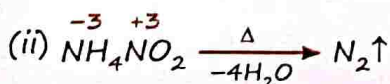
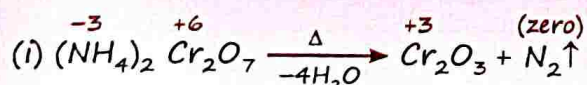
□ Oxyacid having intermediate oxidation state  $\xrightarrow{\Delta}$  ic acid + hydride/oxide (or lower oxidation state)



### HEATING OF AMMONIUM SALT

#### Type-1

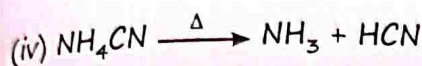
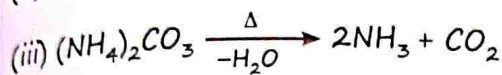
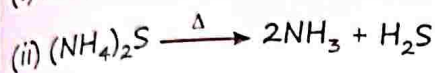
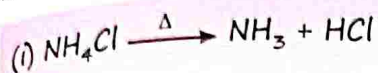
□ Heating of ammonium salt with oxidising anion  $\xrightarrow{\Delta}$   $N_2$  or  $N_2O$  + Side Product





## Type-2

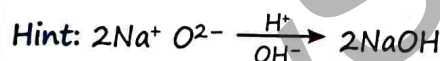
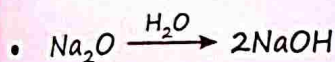
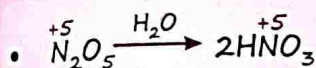
□ Heating of ammonium salt with non-oxidising anion  $\xrightarrow{\Delta}$   $\text{NH}_3$  + Side Product



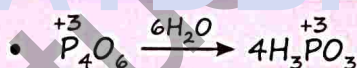
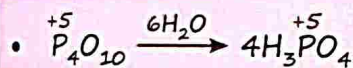
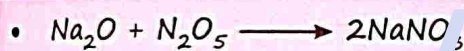
## HYDROLYSIS

### 1. Oxides

□ Hydrolysis of oxide does not change the oxidation state of central atom.



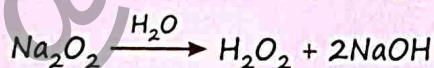
□ Hydrolysis helps to understand the mechanism behind the reactions.



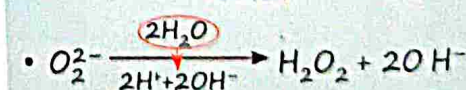
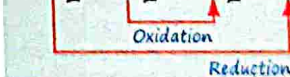
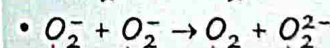
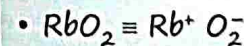
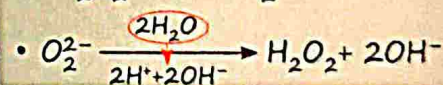
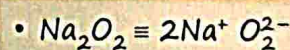
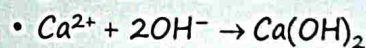
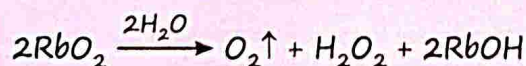
□ Oxides [ $\text{O}^{2-}$ ]



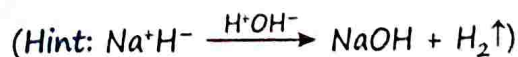
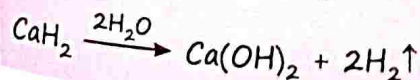
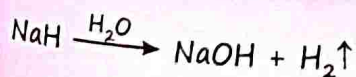
□ Peroxides [ $\text{O}_2^{2-}$ ]



□ Superoxides [ $\text{O}_2^-$ ]

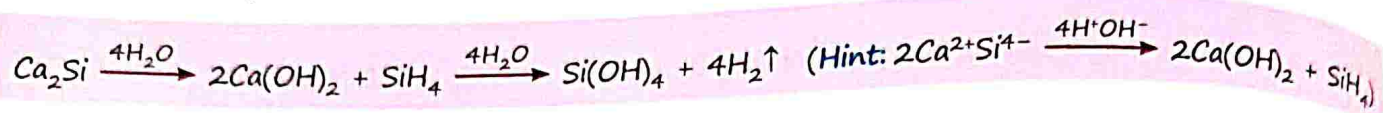


### 2. Hydride ( $\text{H}^-$ )

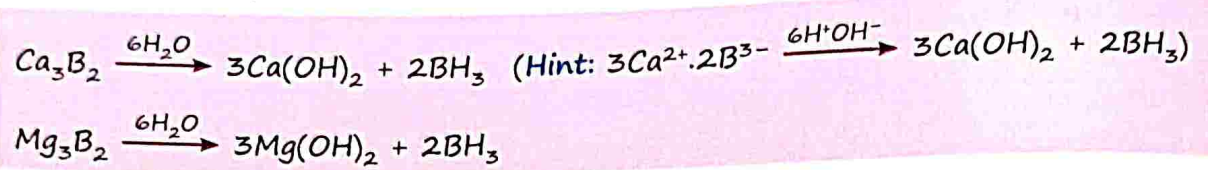


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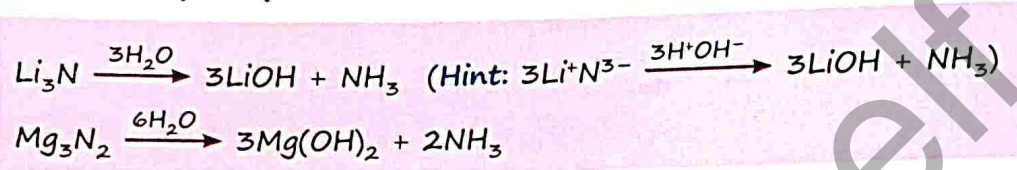
3. Silicide (Si<sup>4-</sup>)



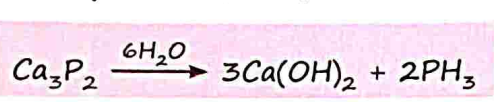
4. Borides (B<sup>3-</sup>)



5. Nitrides (N<sup>3-</sup>)



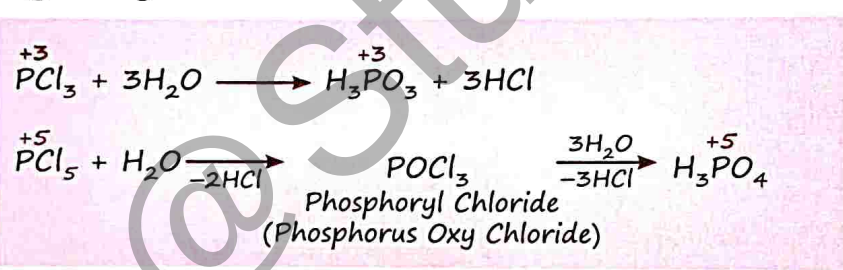
6. Phosphide (P<sup>3-</sup>)



7. Carbide

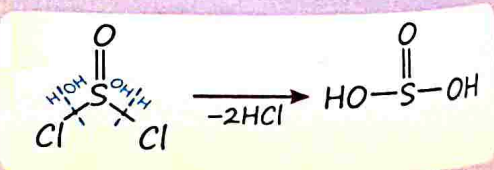
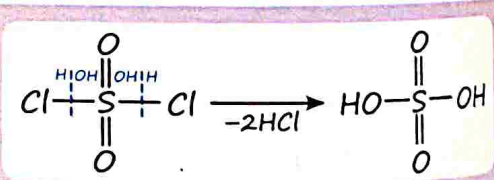
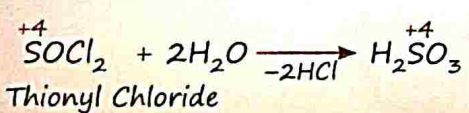
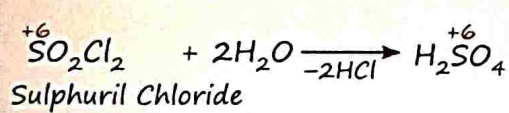


8. Hydrolysis of Halides



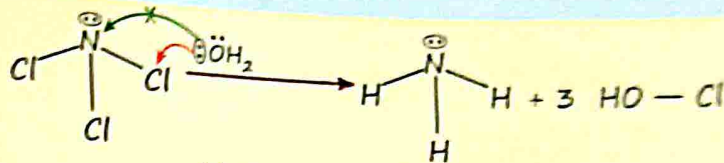
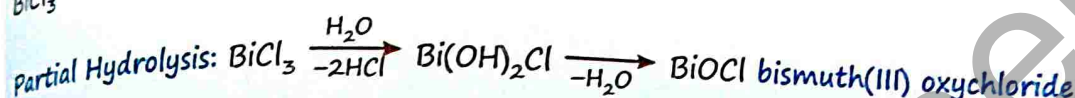
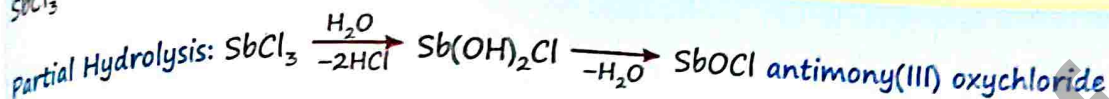
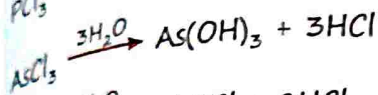
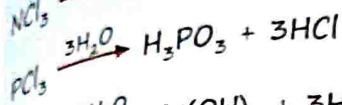
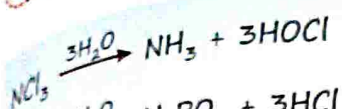
Note

PCl<sub>3</sub> hydrolyses in the presence of moisture giving fumes of HCl.



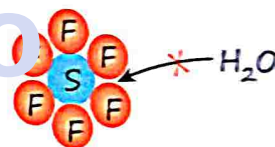
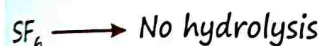
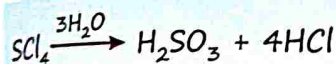


## Hydrolysis of Group-15 Halides



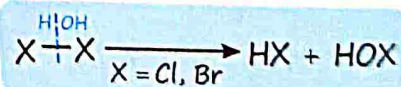
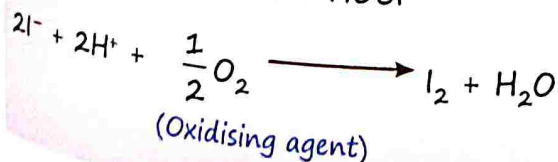
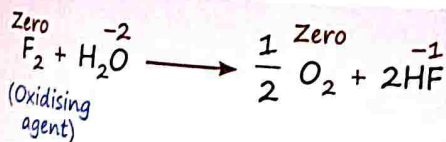
$\text{H}_2\text{O}$  attacks on Cl but not on N because Cl has vacant d orbital but N does not.

## Hydrolysis of Group-16 Halides



$\text{SF}_6$  is exceptionally stable for steric reasons. So, water can not reach to the sulphur for hydrolysis.

## 9. Hydrolysis of Halogens

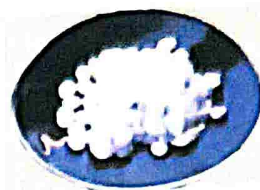
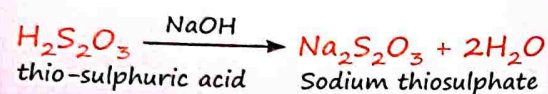
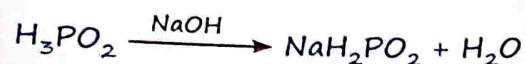
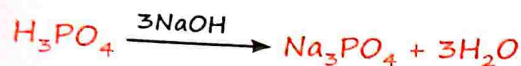
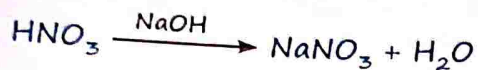
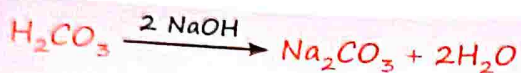


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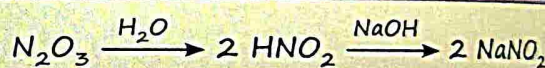
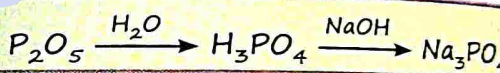
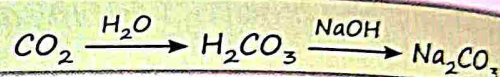
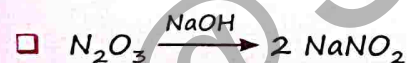
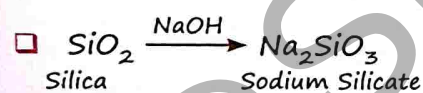
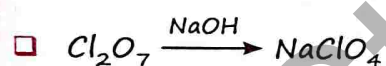
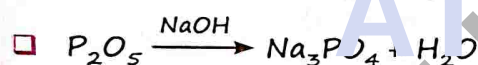
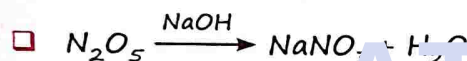
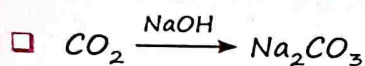
Chemical Name: Sodium Hydroxide.  
Common name: Caustic Soda.

- ☐  $\text{NaOH}$  is deliquescent in nature.

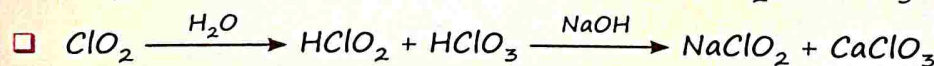
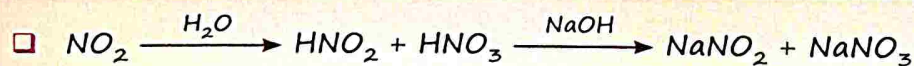


White translucent  
solid

| Deliquescent                                                    | Vs | Hygroscopic                       |
|-----------------------------------------------------------------|----|-----------------------------------|
| Ability to absorb so much water that it forms a liquid solution |    | Ability to absorb water.          |
| $\text{NaOH}$<br>$\text{CaCl}_2$<br>$\text{MgCl}_2$             |    | Sugar<br>$\text{Na}_2\text{CO}_3$ |

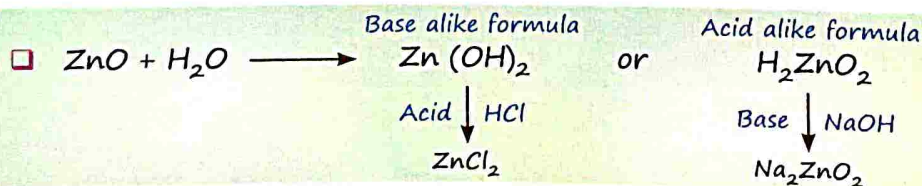


## Reaction with mixed Anhydride

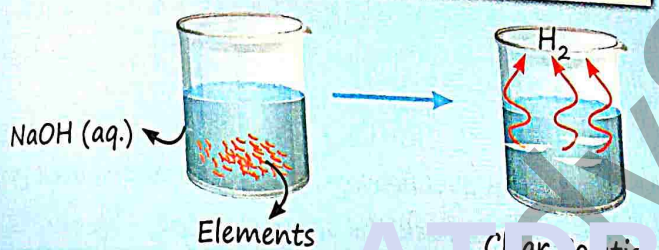
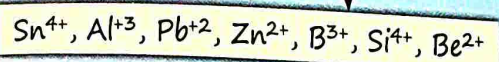
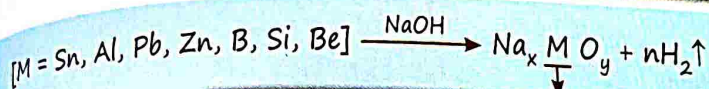
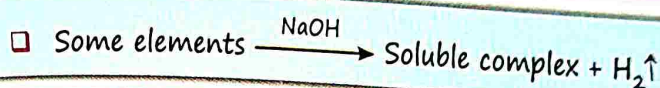
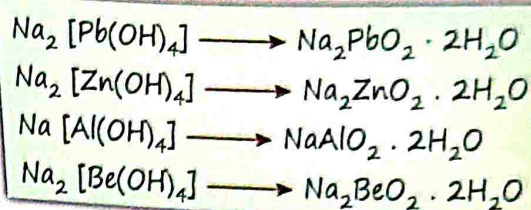
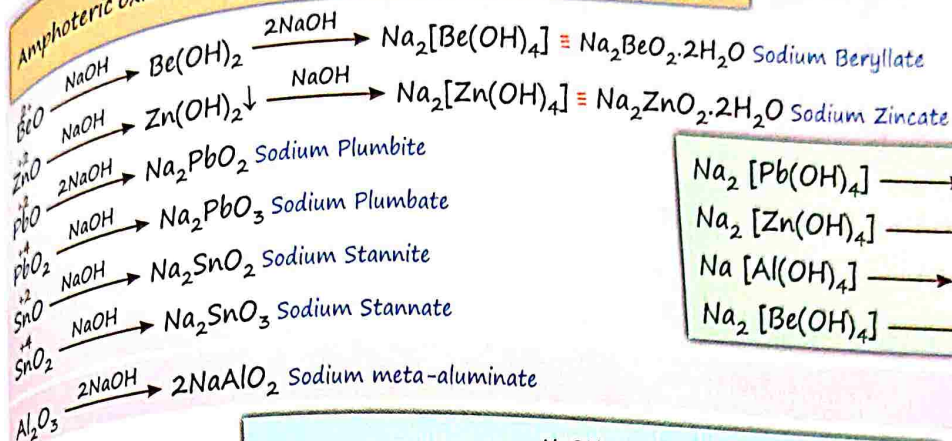
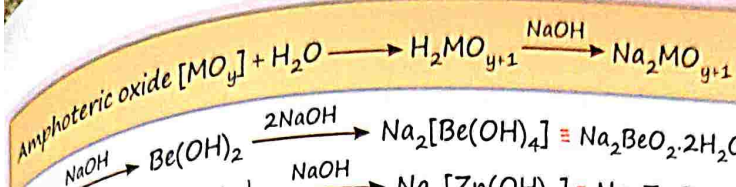


$N_2O$  is fairly soluble in water and  $NO$  is sparingly soluble in water. Both produces neutral solution in water. So they both do not react with  $NaOH$ .

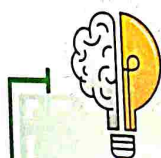
### Reaction with amphoteric Oxides



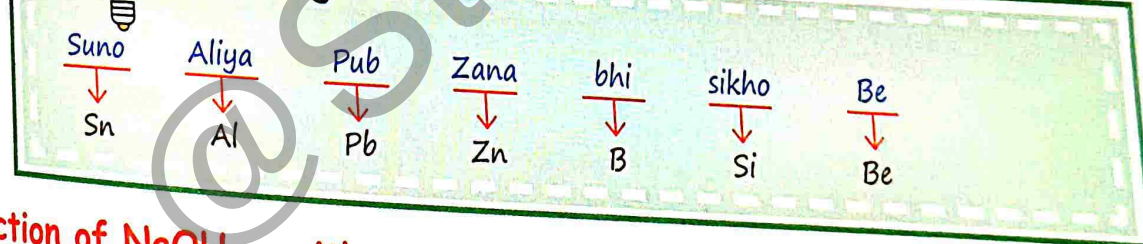




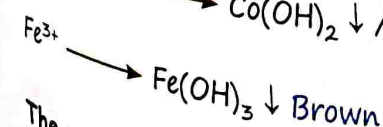
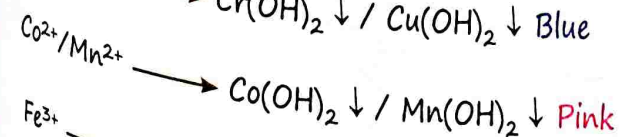
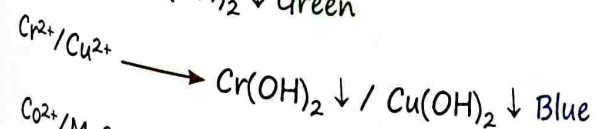
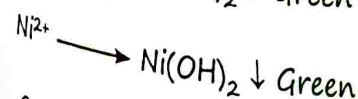
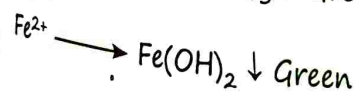
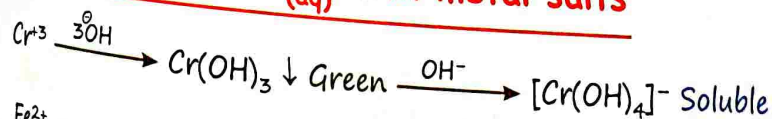
| Element (M) | $Na_x MO_y$ |
|-------------|-------------|
| Be          | $Na_2BeO_2$ |
| Pb          | $Na_2PbO_2$ |
| Sn          | $Na_2SnO_2$ |
| Si          | $Na_2SiO_3$ |
| Zn          | $Na_2ZnO_2$ |
| B           | $Na_3BO_3$  |
| Al          | $NaAlO_2$   |



देशी जुगाड़।



## Reaction of $NaOH_{(aq)}$ with metal salts

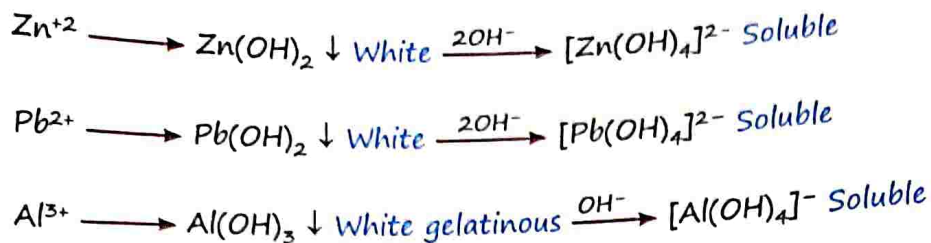


- Amphoteric hydroxides like  $Cr(OH)_3$ ,  $Pb(OH)_2$ ,  $Al(OH)_3$ ,  $Zn(OH)_2$  are soluble in base  $NaOH_{(aq)}$
- Basic hydroxides do not react with  $NaOH$ , so they are insoluble in  $NaOH_{(aq)}$
- Green **C**row **F**esa **N**ikalo  
Blue **CuCr** se  
**F**er Brown munde ne **Mn Co** Kr diya pink.
- Hydroxides of  $d^{10}$  system & p-block element

The p-Block elements (Group 13 to 18)

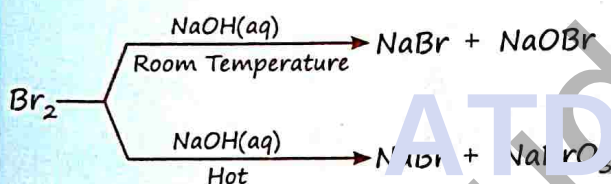
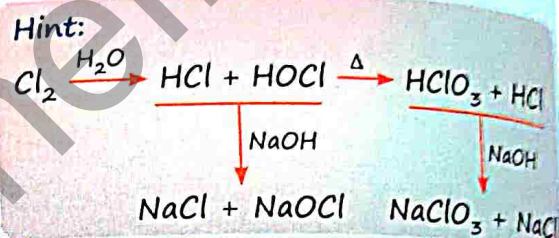
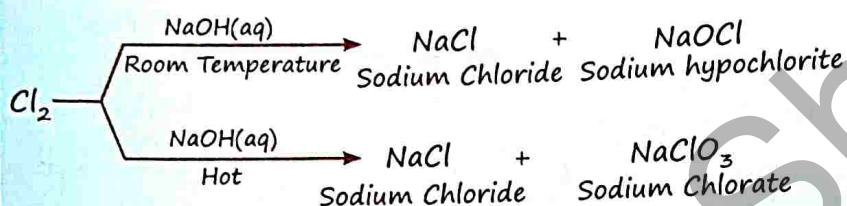
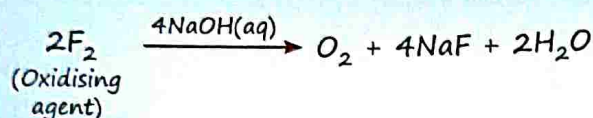
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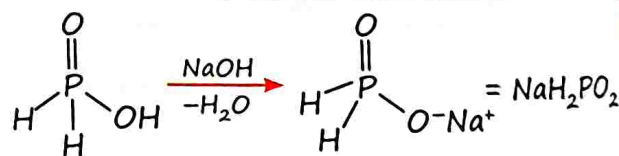
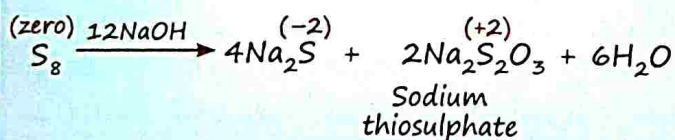
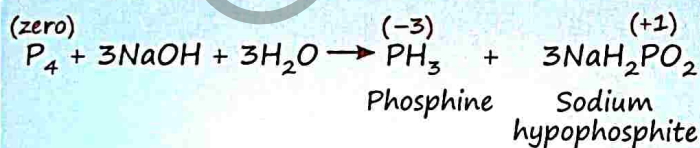
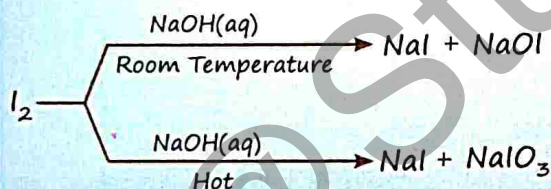
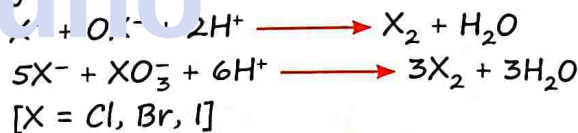


### Note

$\text{I}_2$ ,  $\text{P}_4$  and  $\text{S}_8$  do not react with water but they give disproportionation reaction with aq. NaOH.

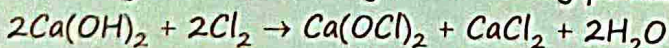


On acidification, the disproportionated product gives back the same element.



### Note

With dry slaked lime, it gives bleaching powder.

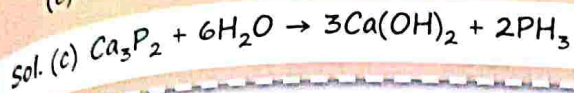




(IIT JEE 1999)

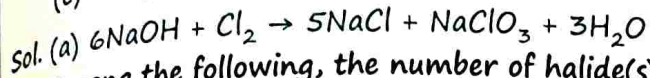
33. One mole of calcium phosphide on reaction with excess water gives

- (a) one mole of phosphine (b) two moles of phosphoric acid  
(c) two moles of phosphine (d) one mole of phosphorus pentoxide



34. Chlorine on reaction with hot and concentrated sodium hydroxide gives: [12 Jan, 2019 (Shift-II)]

- (a)  $\text{Cl}^-$  and  $\text{ClO}_3^-$  (b)  $\text{Cl}^-$  and  $\text{ClO}^-$   
(c)  $\text{ClO}_3^-$  and  $\text{ClO}_2^-$  (d)  $\text{Cl}^-$  and  $\text{ClO}_2^-$



35. Among the following, the number of halide(s) which is / are inert to hydrolysis is \_\_\_\_.

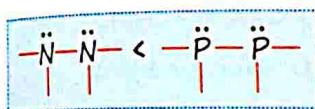
[25 Feb, 2021 (Shift-I)]

- (a)  $\text{BF}_3$  (b)  $\text{SiCl}_4$  (c)  $\text{PCl}_5$  (d)  $\text{SF}_6$

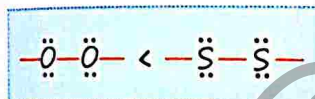
Sol. [1] Due to presence of steric crowding,  $\text{SF}_6$  does not undergo hydrolysis.

## CATENATION PROPERTY

- Self linking property of an element is known as catenation property.
- Single bond formation tendency  $\propto$  single bond strength.
- Single bond formation tendency : Catenation property  $\uparrow$



order of bond strength



order of 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:                       | a < b < c < d |
| (H <sup>+</sup> ion donation tendency) |               |
| Boiling point:                         | b < c < d < a |

The p-Block Elements (Group 13 to 18)

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(a)  $\text{NH}_3$  (Ammonia) (b)  $\text{PH}_3$  (Phosphine) (c)  $\text{AsH}_3$  (Arsine) (d)  $\text{SbH}_3$  (Stibine) (e)  $\text{BiH}_3$  (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 $\text{NH}_3$ is easy)           |
| Reducing power:           | $a < b < c < d < e$ ( $\text{H}^\ominus$ ion donation is easy with weak bond) |
| Boiling point:            | $b < c < a < d < e$                                                           |

(a)  $\text{H}_2\text{O}$  (b)  $\text{H}_2\text{S}$  (c)  $\text{H}_2\text{Se}$  (d)  $\text{H}_2\text{Te}$

|                           |                 |
|---------------------------|-----------------|
| 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-I)]

- A. The stability of the hydrides decreases in the order  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$   
B. The reducing ability of the hydrides increases in the order  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{BiH}_3$   
C. Among the hydrides,  $\text{NH}_3$  is strong reducing agent while  $\text{BiH}_3$  is mild reducing agent.  
D. The basicity of the hydrides increases in the order  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{BiH}_3$

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

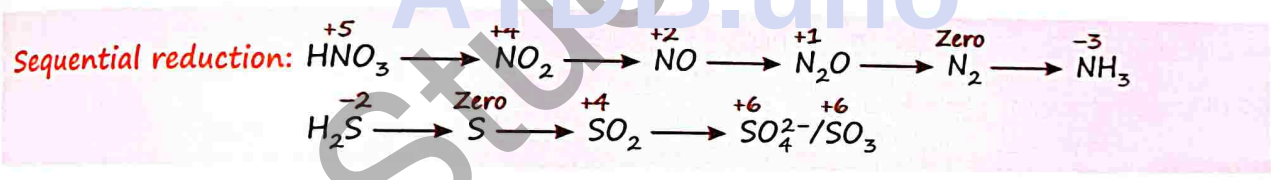
|    | Reactant         | Oxidised Product |    | Reactant                | Oxidised Product        |     | Reactant             | Oxidised Product |
|----|------------------|------------------|----|-------------------------|-------------------------|-----|----------------------|------------------|
| 1. | $\text{Fe}^{+2}$ | $\text{Fe}^{+3}$ | 7. | $\text{CO}$             | $\text{CO}_2$           | 13. | $\text{HNO}_2$       | $\text{HNO}_3$   |
| 2. | $\text{Cl}^-$    | $\text{Cl}_2$    | 8. | $\text{H}_3\text{PO}_3$ | $\text{H}_3\text{PO}_4$ | 14. | $\text{H}_2\text{O}$ | $\text{O}_2$     |
| 3. | $\text{Br}^-$    | $\text{Br}_2$    | 9. | $\text{H}_2\text{S}$    | $\text{S}$              | 15. | $\text{NO}$          | $\text{NO}_2$    |



|    |                               |                |     |                                              |                                                |     |                                       |                                       |
|----|-------------------------------|----------------|-----|----------------------------------------------|------------------------------------------------|-----|---------------------------------------|---------------------------------------|
| 4. | I <sup>-</sup>                | I <sub>2</sub> | 10. | Sn <sup>+2</sup>                             | Sn <sup>+4</sup>                               | 16. | H <sub>2</sub> SO <sub>3</sub>        | H <sub>2</sub> SO <sub>4</sub>        |
| 5. | NH <sub>3</sub>               | N <sub>2</sub> | 11. | H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> | CO <sub>2</sub>                                | 17. | S/S <sup>2-</sup>                     | SO <sub>2</sub>                       |
| 6. | H <sub>2</sub> O <sub>2</sub> | O <sub>2</sub> | 12. | SO <sub>2</sub>                              | SO <sub>3</sub> /SO <sub>4</sub> <sup>2-</sup> | 18. | K <sub>4</sub> [Fe(CN) <sub>6</sub> ] | K <sub>3</sub> [Fe(CN) <sub>6</sub> ] |

Reduction

| Reactant                         | Reduced Product                 | Reactant                          | Reduced Product               | Reactant                                                          | Reduced Product                                                                                                                             |
|----------------------------------|---------------------------------|-----------------------------------|-------------------------------|-------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------|
| 1. F <sub>2</sub>                | F <sup>-</sup>                  | 8. Pb <sup>+4</sup>               | Pb <sup>+2</sup>              | 15. K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> /H <sup>+</sup> | Cr <sup>+3</sup>                                                                                                                            |
| 2. Br <sub>2</sub>               | Br <sup>-</sup>                 | 9. Bi <sup>+5</sup>               | Bi <sup>+3</sup>              | 16. Fe <sup>+3</sup>                                              | Fe <sup>+2</sup>                                                                                                                            |
| 3. Cl <sub>2</sub>               | Cl <sup>-</sup>                 | 10. Cu <sup>+2</sup>              | Cu <sup>+1</sup>              | 17. HNO <sub>3</sub> (conc.)                                      | NO <sub>2</sub>                                                                                                                             |
| 4. I <sub>2</sub>                | I <sup>-</sup>                  | 11. CaOCl <sub>2</sub>            | CaCl <sub>2</sub>             | 18. HNO <sub>3</sub> (dil.)                                       | NO/N <sub>2</sub> O                                                                                                                         |
| 5. O <sub>3</sub>                | O <sub>2</sub> /O <sup>2-</sup> | 12. Ag <sup>+</sup>               | Ag                            | 19. HNO <sub>2</sub>                                              | NO                                                                                                                                          |
| 6. H <sub>2</sub> O <sub>2</sub> | H <sub>2</sub> O                | 13. Hg <sup>+2</sup>              | Hg <sub>2</sub> <sup>+2</sup> | 20. KMnO <sub>4</sub>                                             | <div> <div>H<sup>+</sup> → Mn<sup>+2</sup></div> <div>Neutral → MnO<sub>2</sub></div> <div>Base → MnO<sub>4</sub><sup>2-</sup></div> </div> |
| 7. MnO <sub>2</sub>              | Mn <sup>+2</sup>                | 14. Hg <sub>2</sub> <sup>+2</sup> | Hg                            |                                                                   |                                                                                                                                             |

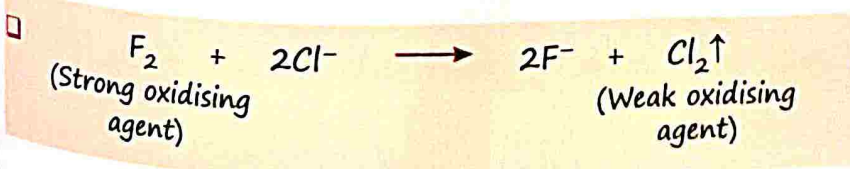


SRP Value and Oxidising Power

- Oxidising power: F<sub>2</sub> > Cl<sub>2</sub> > Br<sub>2</sub> > I<sub>2</sub>
- Three factors are responsible for E° order
  - (i) Bond dissociation energy
  - (ii) Electron gain enthalpy
  - (iii) Hydration energy

|              |                |                 |                 |                |
|--------------|----------------|-----------------|-----------------|----------------|
|              | F <sub>2</sub> | Cl <sub>2</sub> | Br <sub>2</sub> | I <sub>2</sub> |
| +ve E° value | 2.87           | 1.36            | 1.09            | 0.54           |

Oxidising & Reducing Agent





- ❑ Reactant having more oxidising power should be at reactant side and weak oxidising agent should be at product side.

Strong oxidising agent  $\xrightarrow{\text{Feasible}}$  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                                                                                                                                                                                         |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"> <li>❑ Elements with maximum oxidation state.</li> <li>❑ Conc. <math>H_2SO_4</math>, Conc. <math>HNO_3</math>, Conc. <math>HIO_3</math></li> <li>❑ <math>Pb^{4+}</math>, <math>Fe^{3+}</math>, <math>Bi^{5+}</math>, <math>Cu^{2+}</math></li> </ul> | <ul style="list-style-type: none"> <li>❑ Metals &amp; Elements with lower or minimum oxidation state.</li> <li>❑ Na, Li, Al, Mg etc.</li> <li>❑ HI, <math>SO_2</math>, <math>Fe^{2+}</math></li> </ul> |

### Oxidising Power

Strong oxidising agent  $\longrightarrow F_2, O_3, Cl_2, S_2O_8^{2-}, KMnO_4/H^+, H_2O_2/H^+, MnO_2, K_2Cr_2O_7/H^+$   
 Moderate oxidising agent  $\longrightarrow Cl_2, HNO_3, H_2O_2$   
 Weak oxidising agent  $\longrightarrow Br_2, HNO_2$   
 Weakest oxidising agent  $\longrightarrow I_2$

### Note

Some metal ions ( $Bi^{5+}$ ,  $Pb^{4+}$ ) are strong oxidising agent and some ions ( $Fe^{3+}$ ,  $Cu^{2+}$ ) are weak oxidising agent.

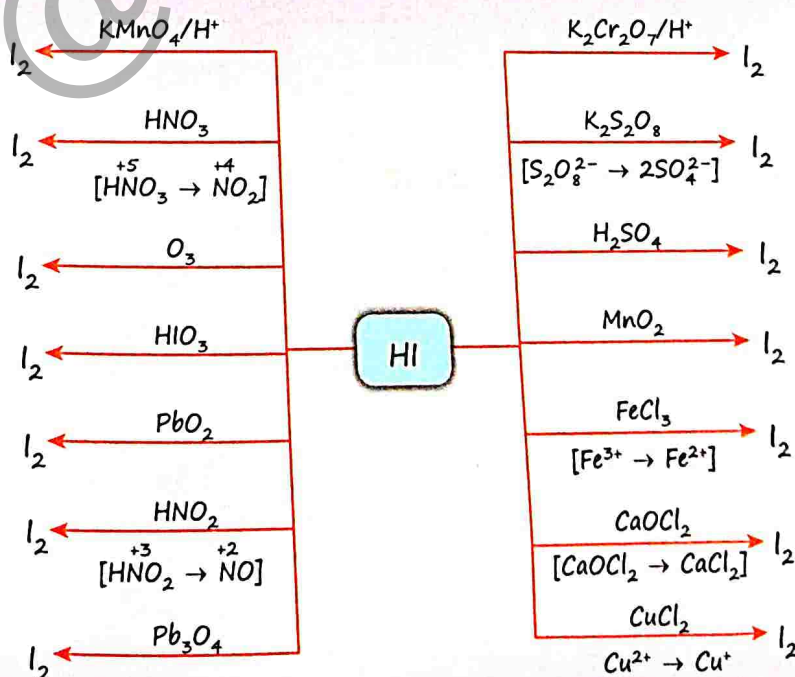
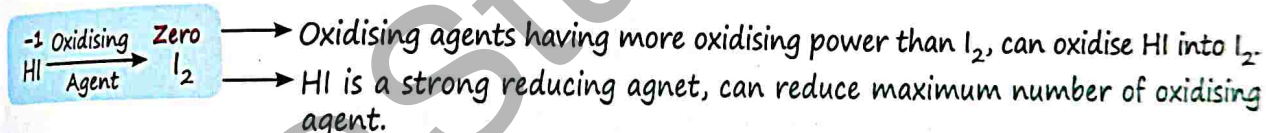
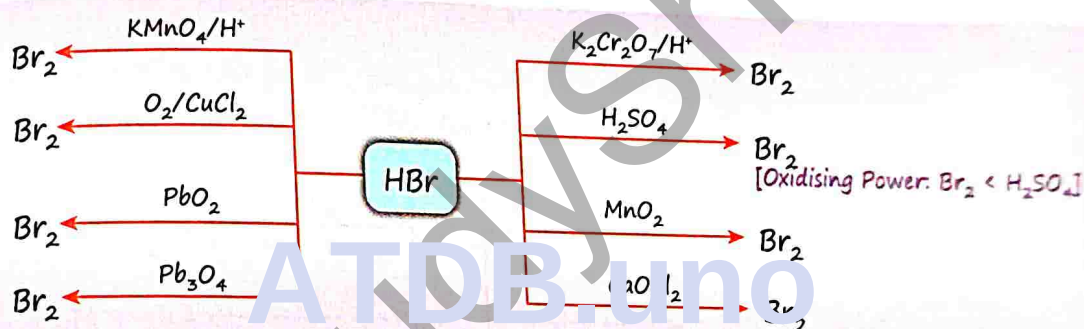
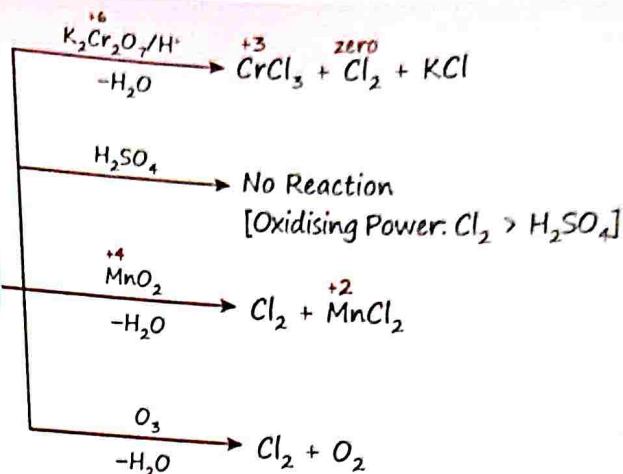
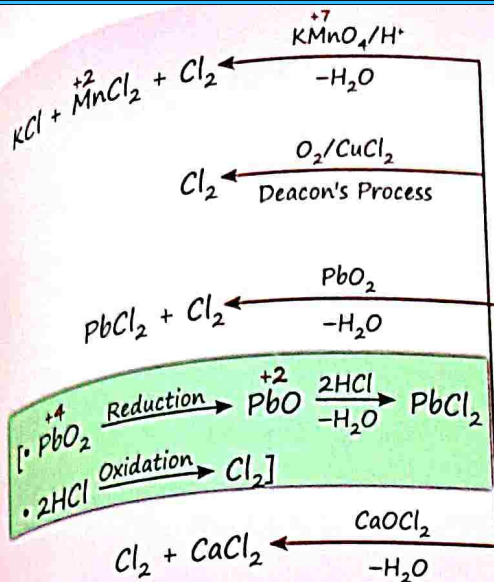
- ❑  $Mn^{2+} + PbO_2 \text{ (excess)} \longrightarrow KMnO_4$
- ❑  $Mn^{2+} + BiO_3^- \text{ (excess)} \longrightarrow KMnO_4$
- ❑  $Mn^{2+} + S_2O_8^{2-} \text{ (excess)} \longrightarrow KMnO_4$
- ❑  $Pb^{4+} + 2I^- \longrightarrow I_2 + Pb^{2+}$
- ❑  $Fe^{3+} + 2I^- \longrightarrow I_2 + Fe^{2+}$
- ❑  $2Cu^{+2} + 2I^- \longrightarrow I_2 + 2Cu^{+1}$

Due to oxidising nature of  $Pb^{4+}$ ,  $Fe^{3+}$ ,  $Cu^{2+}$  ions  $PbI_4$ ,  $FeI_3$  and  $CuI_2$  do not exist.

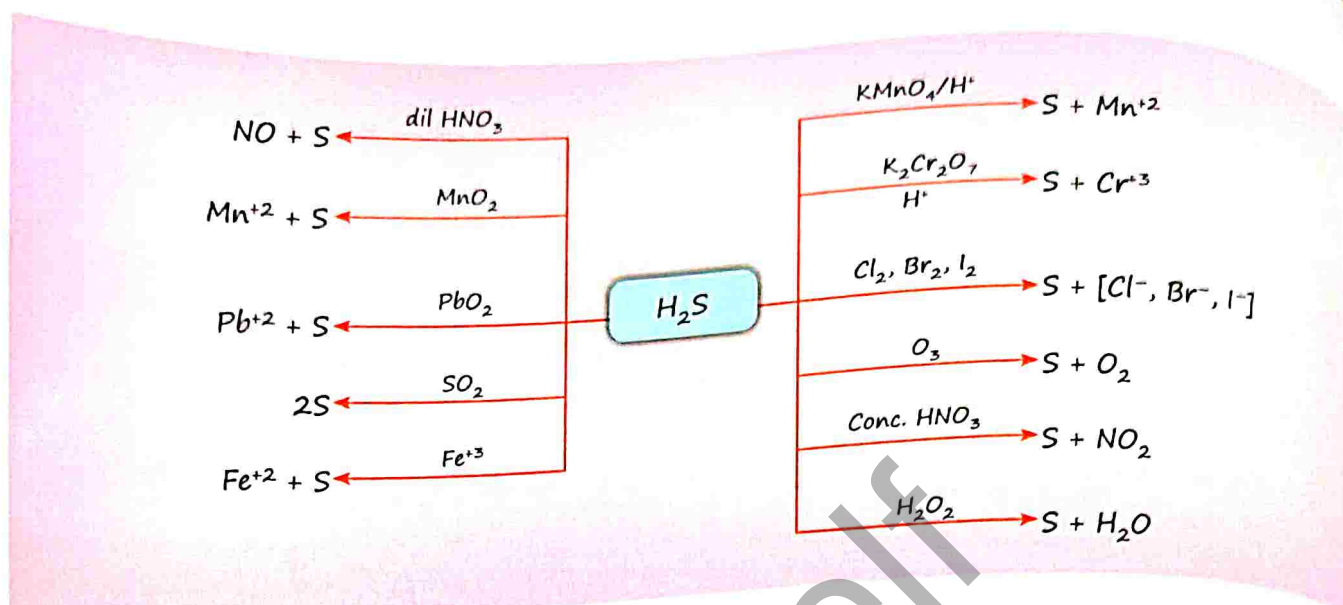
### Flow Chart Method for Reactions $\longrightarrow$ Great Method for Product Prediction

$\overset{-1}{HCl} \xrightarrow[\text{Agent}]{\text{Oxidising}} \overset{Zero}{Cl_2} \longrightarrow$  Oxidising agents having more oxidising power than  $Cl_2$ , can oxidise HCl into  $Cl_2$  gas.



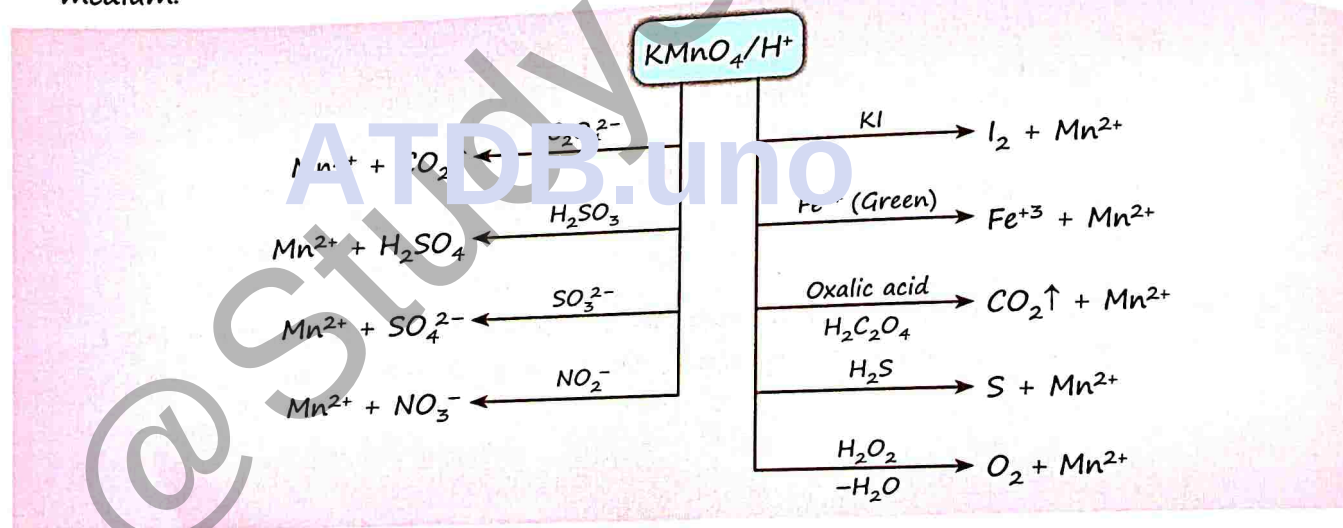


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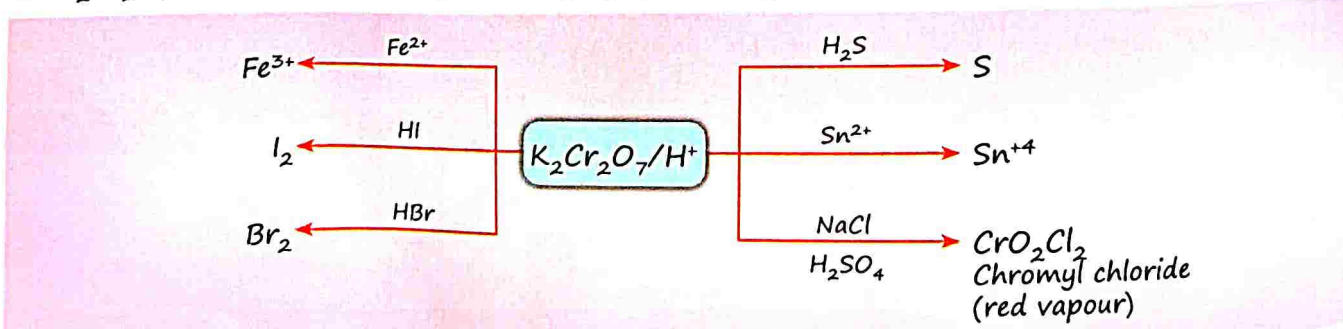
### $KMnO_4$ with Acid as Oxidising Agent

- $\square$   $KMnO_4$  is a strong oxidising agent, during reaction it reduces itself from  $Mn^{+7}$  to  $Mn^{+2}$  in acidic medium.



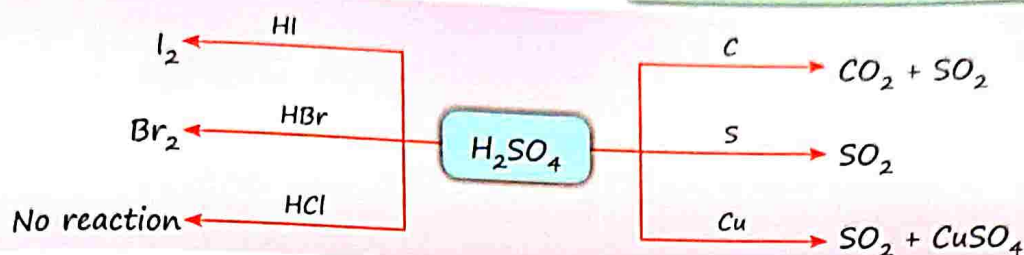
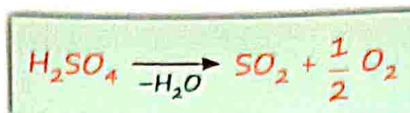
### $K_2Cr_2O_7$ with Acid as Oxidising Agent

- $\square$   $K_2Cr_2O_7$  with acid is a strong oxidising agent, during reaction it reduces itself from  $Cr^{+6}$  to  $Cr^{+3}$ .

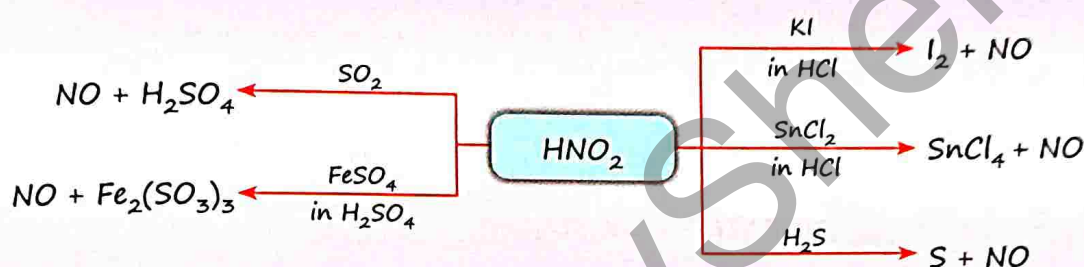




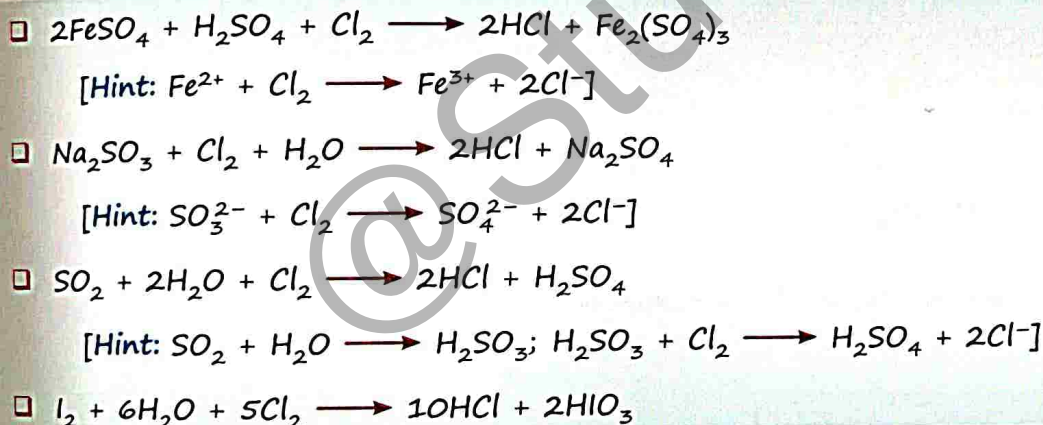
## $H_2SO_4$ as Oxidising Agent



## $HNO_2$



## Chlorine as Oxidising Agent



## GROUP-15 ELEMENTS

NITROGEN ( $_7N$ ), PHOSPHORUS ( $_{15}P$ ), ARSENIC ( $_{33}As$ ), ANTIMONY ( $_{51}Sb$ ), BISMUTH ( $_{83}Bi$ )

## Oxidation States and Trends in Chemical Reactivity

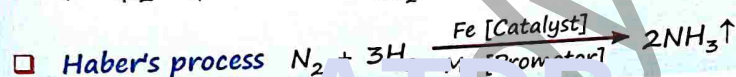
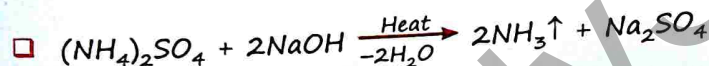
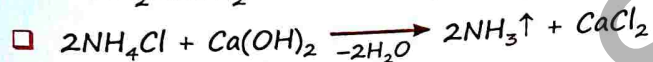
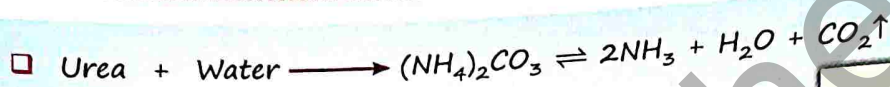
- Group 15 elements commonly have oxidation states of  $-3$ ,  $+3$ , and  $+5$ .
- The tendency to show a  $-3$  oxidation state decreases as you move down the group because the atoms get larger and more metallic. For example, bismuth, the last element in the group, rarely forms compounds with a  $-3$  oxidation state.

The p-Block Elements (Group 13 to 18) [Click Here To Join @StudyShelf For More Study Materials](#)

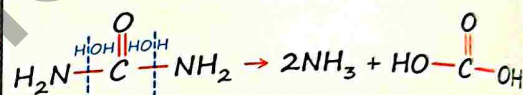
- ❑ The stability of the +5 oxidation state also decreases down the group. Bismuth's only well-known +5 compound is  $\text{BiF}_5$ .
- ❑ As you go down the group, the +5 oxidation state becomes less stable, while the +3 oxidation state becomes more stable due to the "inert pair effect."
- ❑ Nitrogen 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 $\text{NH}_3$

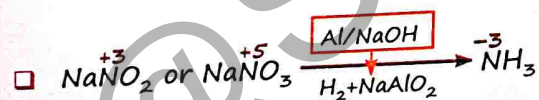
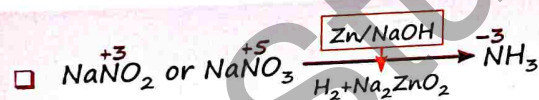
### Preparation Methods



Hint:



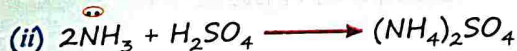
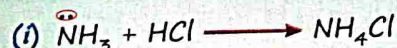
### From nitrate and nitrite-



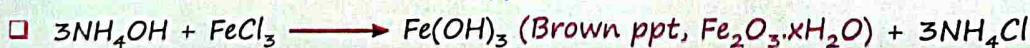
$\text{H}_2$  gas is responsible for reduction of  $\text{NO}_2^-$  or  $\text{NO}_3^-$  to  $\text{NH}_3$ .

### Reactions of $\text{NH}_3$

$\text{NH}_3$  acts as base.



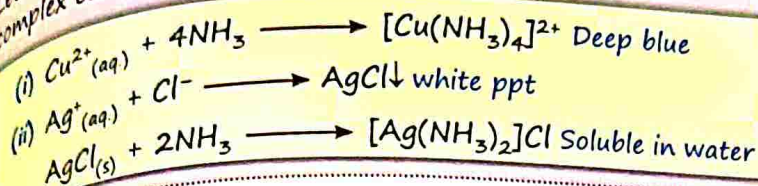
Aq.  $\text{NH}_3$  forms ammonium salts with acids. As a weak base, it precipitates the hydroxides or hydrated oxides.





## 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.



37. Urea reacts with water to form A which will decompose to form B. B when passed through  $\text{Cu}^{2+}(\text{aq})$ , deep blue colour solution C is formed. What is the formula of C from the following?

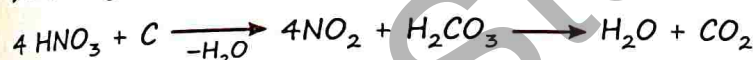
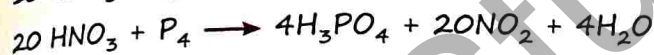
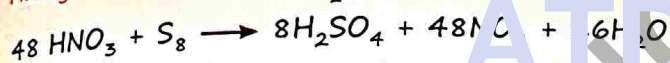
[NEET 2020]

- (a)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  (b)  $\text{Cu}(\text{OH})_2$   
(c)  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  (d)  $\text{CuSO}_4$

Sol. (a)

## Conc. $\text{HNO}_3$ as a Oxidising Agent

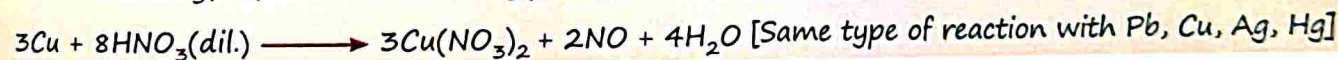
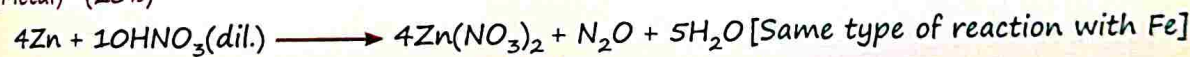
□  $\text{HNO}_3 + \text{Non metals} \xrightarrow{-\text{H}_2\text{O}} \text{-ic acid} + \text{NO}_2$  (Brown colour)



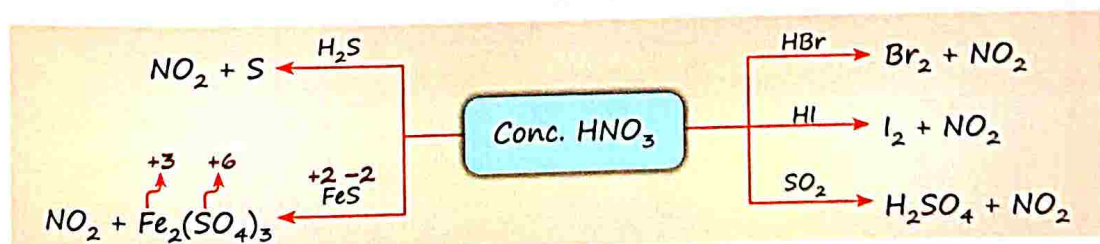
□  $\text{M} + \text{Conc. HNO}_3 \xrightarrow{-\text{H}_2\text{O}} \text{M}(\text{NO}_3)_y + \text{NO}_2$  (Brown)  
(Metal) (70%)



□  $\text{M} + \text{dil. HNO}_3 \xrightarrow{-\text{H}_2\text{O}} \text{M}(\text{NO}_3)_y + \text{N}_2\text{O}/\text{NO}$   
(Metal) (20%)



□ Noble Metals Au, Pt : Do not dissolve in  $\text{HNO}_3$



Some metals do not dissolve in concentrated  $\text{HNO}_3$  because of the formation of a passive film of oxide on the surface.

For example  $\rightarrow \text{Fe, Cr, Co, Ni, Al, Be}$

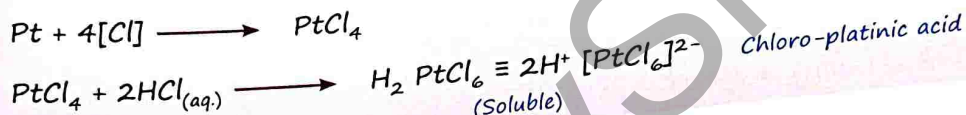
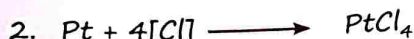
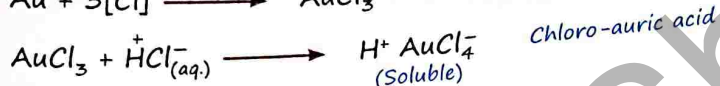
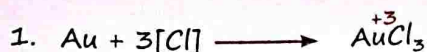
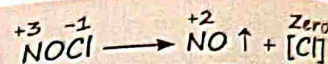


## Aqua Regia

Aqua Regia  $\rightarrow 3\text{HCl} + 1\text{HNO}_3$



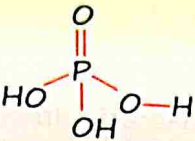
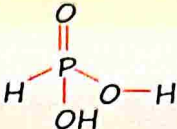
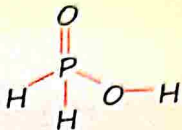
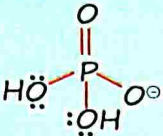
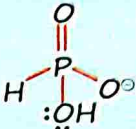
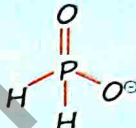
Au, Pt : Do not dissolve in  $\text{HNO}_3$



## OXIDES OF NITROGEN

| Formula                                         | Oxidation State | Structure                                                                                                                                       | Physical / Chemical Properties                                                                                                                                                  |
|-------------------------------------------------|-----------------|-------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{N}_2\text{O}$<br>Nitrous oxide           | +1              | $\text{N} \equiv \text{N} \rightarrow \text{O}$<br>$\text{N} \equiv \text{N}^+ - \text{O}^- \leftrightarrow \text{N}^- = \text{N}^+ = \text{O}$ | <ul style="list-style-type: none"><li>Gas</li><li>Neutral oxide</li></ul>                                                                                                       |
| $\text{NO}$<br>Nitric oxide                     | +2              | $:\text{N} = \ddot{\text{O}}: \leftrightarrow :\ddot{\text{N}} = \ddot{\text{O}}:$                                                              | <ul style="list-style-type: none"><li>Gas</li><li>Neutral oxide</li></ul>                                                                                                       |
| $\text{N}_2\text{O}_3$<br>Dinitrogen trioxide   | +3              |                                                                                                                                                 | Blue solid/liquid<br>$\text{N}_2\text{O}_3$ (Solid) : $\text{NO}^+ \text{NO}_2^-$                                                                                               |
| $\text{NO}_2$<br>Nitrogen dioxide               | +4              |                                                                                                                                                 | Brown gas/paramagnetic nature                                                                                                                                                   |
| $\text{N}_2\text{O}_4$<br>Dinitrogen Tetraoxide | +4              |                                                                                                                                                 | Colorless/diamagnetic nature                                                                                                                                                    |
| $\text{N}_2\text{O}_5$<br>Nitric Anhydride      | +5              |                                                                                                                                                 | <ul style="list-style-type: none"><li>Gas (covalent molecule)</li><li>Solid (ionic compound)</li></ul> $\text{N}_2\text{O}_5$ (Solid) $\rightarrow \text{NO}_2^+ \text{NO}_3^-$ |



| Reducing Properties of Oxoacids of Phosphorus                                                                                                                          |                                                                                   |                                                                                     |                                                                                       |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
|                                                                                                                                                                        |  |   |    |
| No. of replacable H <sup>+</sup>                                                                                                                                       | 3H <sup>+</sup> (Tribasic Acid)                                                   | 2H <sup>+</sup> (Dibasic Acid)                                                      | 1H <sup>+</sup> (Monobasic Acid)                                                      |
| Stability of Conjugate Base<br>(order is based on the effect of cross-conjugation)                                                                                     |  | <  | <  |
| Order of acidic nature                                                                                                                                                 | H <sub>3</sub> PO <sub>4</sub>                                                    | < H <sub>3</sub> PO <sub>3</sub>                                                    | < H <sub>3</sub> PO <sub>2</sub>                                                      |
| No. of P—H bond                                                                                                                                                        | Zero                                                                              | One                                                                                 | Two                                                                                   |
| Reducing property is directly proportional to number of P—H bonds. So, H <sub>3</sub> PO <sub>2</sub> is a better reducing agent than H <sub>3</sub> PO <sub>3</sub> . |                                                                                   |                                                                                     |                                                                                       |

38. The order of the oxidation state of the phosphorus atom in H<sub>3</sub>PO<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>PO<sub>3</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>6</sub> is (JEE Adv. 2017)

(a) H<sub>3</sub>PO<sub>4</sub> > H<sub>3</sub>PO<sub>2</sub> > H<sub>3</sub>PO<sub>3</sub> > H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>

(b) H<sub>3</sub>PO<sub>4</sub> > H<sub>4</sub>P<sub>2</sub>O<sub>6</sub> > H<sub>3</sub>PO<sub>3</sub> > H<sub>3</sub>PO<sub>2</sub>

(c) H<sub>3</sub>PO<sub>2</sub> > H<sub>3</sub>PO<sub>3</sub> > H<sub>4</sub>P<sub>2</sub>O<sub>6</sub> > H<sub>3</sub>PO<sub>4</sub>

(d) H<sub>3</sub>PO<sub>3</sub> > H<sub>3</sub>PO<sub>2</sub> > H<sub>3</sub>PO<sub>4</sub> > H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>

Sol. (b) H<sub>3</sub>PO<sub>2</sub> → +1, H<sub>3</sub>PO<sub>4</sub> → +5, H<sub>3</sub>PO<sub>3</sub> → +3, H<sub>4</sub>P<sub>2</sub>O<sub>6</sub> → +4

39. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen? (IIT JEE 2012)

(a) HNO<sub>3</sub>, NO, NH<sub>4</sub>Cl, N<sub>2</sub>

(b) HNO<sub>3</sub>, NO, N<sub>2</sub>, NH<sub>4</sub>Cl

(c) HNO<sub>3</sub>, NH<sub>4</sub>Cl, NO, N<sub>2</sub>

(d) NO, HNO<sub>3</sub>, NH<sub>4</sub>Cl, N<sub>2</sub>

Sol. (b) HNO<sub>3</sub> → +5, NO → +2, N<sub>2</sub> → 0, NH<sub>4</sub>Cl → -3

40. For H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>, the correct choice is (IIT JEE 2003)

(a) H<sub>3</sub>PO<sub>3</sub> is dibasic and reducing

(b) H<sub>3</sub>PO<sub>3</sub> is dibasic and non-reducing

(c) H<sub>3</sub>PO<sub>4</sub> is tribasic and reducing

(d) H<sub>3</sub>PO<sub>3</sub> is tribasic and non-reducing

Sol. (a)



## GROUP-16 ELEMENTS

OXYGEN ( ${}_8\text{O}$ ), SULPHUR ( ${}_{16}\text{S}$ ), SELENIUM ( ${}_{34}\text{Se}$ ), TELLURIUM ( ${}_{52}\text{Te}$ ), POLONIUM ( ${}_{84}\text{Po}$ )

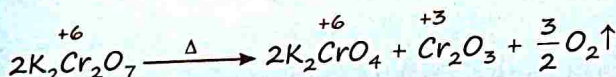
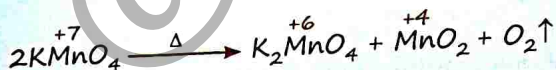
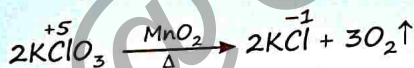
### Oxidation States and Trends in Chemical Reactivity

- For
- ❑ 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  $\text{OF}_2$ , 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 $\text{O}_2$

#### Preparation

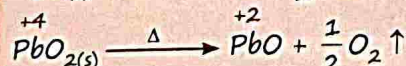
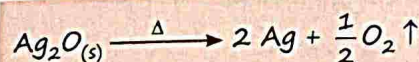
- ❑ By Heating:



- ❑ Decomposition of  $\text{H}_2\text{O}_2$



- ❑ By the thermal decomposition of the oxides of metals:





## GROUP-17 ELEMENTS

FLUORINE ( $_9\text{F}$ ), CHLORINE ( $_{17}\text{Cl}$ ), BROMINE ( $_{35}\text{Br}$ ), IODINE ( $_{53}\text{I}$ ), ASTATINE ( $_{85}\text{At}$ )

### 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:

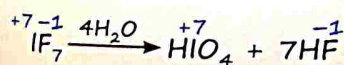
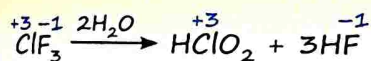
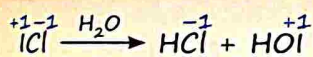
| Halogen atom in ground state | ns                   | np                                               | nd                                   |                                                                |
|------------------------------|----------------------|--------------------------------------------------|--------------------------------------|----------------------------------------------------------------|
|                              | $\uparrow\downarrow$ | $\uparrow\downarrow \uparrow\downarrow \uparrow$ | $\square \square \square \square$    | 1 unpaired electron accounts for $-1$ or $+1$ oxidation states |
| First excited state          | $\uparrow\downarrow$ | $\uparrow\downarrow \uparrow \uparrow$           | $\uparrow \square \square \square$   | 3 unpaired electron accounts for $+3$ oxidation states         |
| Second excited state         | $\uparrow\downarrow$ | $\uparrow \uparrow \uparrow$                     | $\uparrow \uparrow \square \square$  | 5 unpaired electron accounts for $+5$ oxidation states         |
| Third excited state          | $\uparrow$           | $\uparrow \uparrow \uparrow$                     | $\uparrow \uparrow \uparrow \square$ | 7 unpaired electron accounts for $+7$ oxidation states         |

- The fluorine atom has no d orbitals in its valence shell and hence it 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



These compounds undergo hydrolysis giving halide ion derived from the smaller halogen and an anion derived from larger halogen such as-

- hypohalite (when  $\text{AB}$ )
- halite (when  $\text{AB}_3$ )
- halate (when  $\text{AB}_5$ )
- perhalate (when  $\text{AB}_7$ )

## GROUP-18 ELEMENTS

HELIUM ( ${}^2\text{He}$ ), NEON ( ${}^{10}\text{Ne}$ ), ARGON ( ${}^{18}\text{Ar}$ ), KRYPTON ( ${}^{36}\text{Kr}$ ), XENON ( ${}^{54}\text{Xe}$ ), RADON ( ${}^{86}\text{Rn}$ )

- 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 passing through most commonly used laboratory materials such as rubber, glass or plastic.

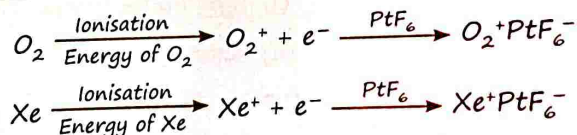
### Chemical Properties

Noble gases are least reactive because-

- The noble gases **except helium ( $1s^2$ )** have completely filled  $ns^2 np^6$  electronic configuration in their valence shell.
- They have high ionisation enthalpy and more positive electron gain enthalpy.

#### Interesting discovery of the reactivity of noble gases-

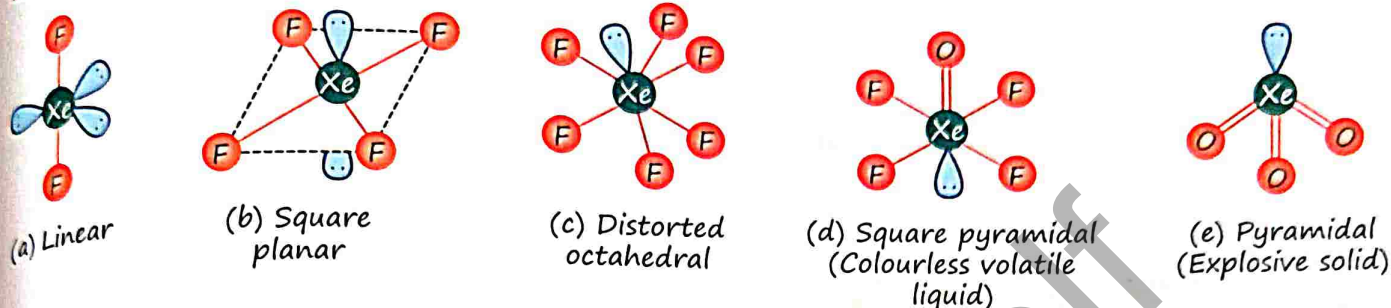
Neil Bartlett at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as  $\text{O}_2^+ \text{PtF}_6^-$ . He, then realised that the first ionisation enthalpy of molecular oxygen ( $1175 \text{ kJ mol}^{-1}$ ) was almost identical with that of xenon ( $1170 \text{ kJ mol}^{-1}$ ). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour compound  $\text{Xe}^+ \text{PtF}_6^-$  by mixing  $\text{PtF}_6$  and xenon.



First ionisation enthalpy of molecular oxygen :  $1175 \text{ kJ mol}^{-1}$   
First ionisation enthalpy of Xenon :  $1170 \text{ kJ mol}^{-1}$



- ❑ 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  $\text{KrF}_2$ ,  $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{XeF}_6$ ,  $\text{XeOF}_4$ ,  $\text{XeO}_2\text{F}_2$ ,  $\text{XeO}_4$ ,  $\text{XeO}_3$ ).
- ❑ Compounds of Rn have not been isolated but only identified (e.g.  $\text{RnF}_2$ ) by radiotracer technique.



### 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 medical breathing 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 ( $\text{NaNO}_3$ , known as Chile saltpetre) and potassium nitrate ( $\text{KNO}_3$ , known as Indian saltpetre).
- ❑ Present in proteins in plants and animals.

The p-Block Elements (Group 13 to 18)

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## Phosphorus

- Found in minerals of the apatite family, such as fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ), 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 -  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$   
Epsom salt -  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$   
Baryte -  $\text{BaSO}_4$

(ii) Sulphides : Galena -  $\text{PbS}$   
Zinc blende -  $\text{ZnS}$   
Copper pyrites -  $\text{CuFeS}_2$

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 ( $\text{CaF}_2$ ), cryolite ( $\text{Na}_3\text{AlF}_6$ ), and Fluoroapatite ( $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ ).
- 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 ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ).
- 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

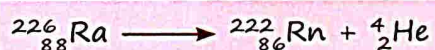
- All noble gases, except radon, are present in the atmosphere.
- They make up about 1% of the volume of dry air, with argon being the most abundant.

## Helium, Neon, Xenon and Radium

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 ( $^{226}\text{Ra}$ ).



41. Identify the incorrect pair from the following:

[29 Jan, 2024 (Shift-I)]

- |                                                                     |                                                                            |
|---------------------------------------------------------------------|----------------------------------------------------------------------------|
| (a) Fluorspar- $\text{BF}_3$                                        | (b) Cryolite- $\text{Na}_3\text{AlF}_6$                                    |
| (c) Fluoroapatite- $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ | (d) Carnallite- $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ |

Sol. (a)

42. The  $\text{F}^-$  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) $[3(\text{Ca}_3(\text{PO}_4)_2) \cdot \text{CaF}_2]$ | (b) $[3(\text{Ca}_2(\text{PO}_4)_2) \cdot \text{Ca}(\text{OH})_2]$ |
| (c) $[3(\text{Ca}_3(\text{PO}_4)_3) \cdot \text{CaF}_2]$ | (d) $[3(\text{Ca}_3(\text{PO}_4)_2) \cdot \text{Ca}(\text{OH})_2]$ |

Sol. (a)

The p- Block Elements (Group 13 to 18)

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43. Given below are two statements:

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.

- (a)  $\text{PET}_3$  and  $\text{AsPh}_3$  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

- (a)  $\text{HNO}_3$ , NO,  $\text{N}_2$ ,  $\text{NH}_4\text{Cl}$
- (b)  $\text{HNO}_3$ , NO,  $\text{NH}_4\text{Cl}$ ,  $\text{N}_2$
- (c)  $\text{NH}_4\text{Cl}$ ,  $\text{N}_2$ , NO,  $\text{HNO}_3$
- (d)  $\text{HNO}_3$ ,  $\text{NH}_4\text{Cl}$ , NO,  $\text{N}_2$

Sol. (a)

46. Strong reducing behavior of  $\text{H}_3\text{PO}_2$  is due to

- (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.  $\text{HNO}_3$  it produces:

- (a)  $\text{Cu}(\text{NO}_3)_2$  and  $\text{N}_2\text{O}$
- (b)  $\text{Cu}(\text{NO}_3)_2$  and  $\text{NO}_2$
- (c)  $\text{Cu}(\text{NO}_3)_2$  and NO
- (d)  $\text{Cu}(\text{NO}_3)_2$ , NO and  $\text{NO}_2$

Sol. (b)

48. Given below are two statements:

Statement-I: The boiling points of the following hydrides of group 16 elements increases in the order-  $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$ .

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)  $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$  : Increasing  $\text{pK}_a$  values
- (b)  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$  : Increasing acidic character
- (c)  $\text{CO}_2 < \text{SiO}_2 < \text{SnO}_2 < \text{PbO}_2$  : Increasing oxidizing power
- (d)  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$  : Increasing acidic strength

Sol. (a)  
50. Which of the following is the most basic oxide?

- (a)  $\text{Al}_2\text{O}_3$
- (b)  $\text{Sb}_2\text{O}_3$
- (c)  $\text{Bi}_2\text{O}_3$
- (d)  $\text{SeO}_2$

[NEET 2006]

Sol. (c)  
51. Given below are two statements:

Statement I: The boiling point of hydrides of Group 16 elements follow the order  $\text{H}_2\text{O} > \text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S}$ .

Statement II: On the basis of molecular mass,  $\text{H}_2\text{O}$  is expected to have lower boiling point than the other members of the group but due to the presence of extensive H-bonding in  $\text{H}_2\text{O}$ , 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.

[NEET 2024]

Sol. (c)  
52. Among Group 16 elements, which one does NOT show -2 oxidation state?

- (a) Te
- (b) Po
- (c) O
- (d) Se

[NEET 2024]

Sol. (b)  
53. Amongst the given options, which of the following molecules/ion acts as a Lewis acid?

- (a)  $\text{OH}^-$
- (b)  $\text{NH}_3$
- (c)  $\text{H}_2\text{O}$
- (d)  $\text{BF}_3$

[NEET 2023]

Sol. (d)  
54. Which is the correct thermal stability order for  $\text{H}_2\text{E}$  (E = O, S, Se, Te and Po)?

- (a)  $\text{H}_2\text{S} < \text{H}_2\text{O} < \text{H}_2\text{Se} < \text{H}_2\text{Te} < \text{H}_2\text{Po}$
- (b)  $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} < \text{H}_2\text{Po}$
- (c)  $\text{H}_2\text{Po} < \text{H}_2\text{Te} < \text{H}_2\text{Se} < \text{H}_2\text{S} < \text{H}_2\text{O}$
- (d)  $\text{H}_2\text{Se} < \text{H}_2\text{Te} < \text{H}_2\text{Po} < \text{H}_2\text{O} < \text{H}_2\text{S}$

[NEET 2019]

Sol. (c)  
55. Which of the statements given below is incorrect?

- (a)  $\text{O}_3$  molecule is bent
- (b) ONF is isoelectronic with  $\text{O}_2\text{N}^-$
- (c)  $\text{OF}_2$  is an oxide of fluorine
- (d)  $\text{Cl}_2\text{O}_7$  is an anhydride of perchloric acid

[NEET 2015 Re]

Sol. (c)

The p- Block Elements (Group 13 to 18)

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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 :

| 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]

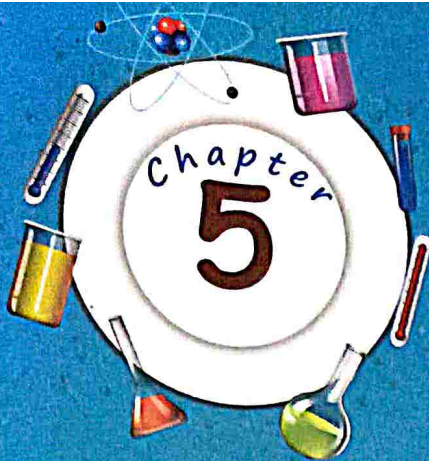
- (a) Noble gases have very high melting and boiling points
- (b) Noble gases have weak dispersion forces
- (c) Noble gases have large positive values of electron gain enthalpy
- (d) Noble gases are sparingly soluble in water

Sol. (a)

The p- Block Elements (Group 13 to 18)

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# 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, alloy formation, preparation, magnetic properties, complex formation, interstitial compounds, properties and uses of  $K_2Cr_2O_7$  and  $KMnO_4$ .

**Inner Transition Elements:**

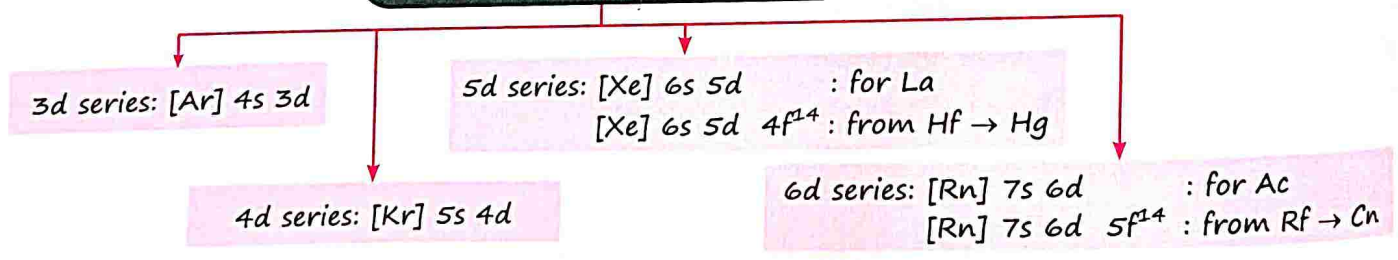
**Lanthanoids-** Electronic configuration, oxidation states and Lanthanoid contraction.

**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 <sub>21</sub> | Ti <sub>22</sub> | V                 | Cr | Mn | Fe | Co | Ni | Cu | Zn <sub>30</sub> |                   |
| 4d-series               | Y <sub>39</sub>  | Zr <sub>40</sub> | Nb                | Mo | Tc | Ru | Rh | Pd | Ag | Cd <sub>48</sub> |                   |
| 5d-series               | La <sub>57</sub> | 4f Series        | Hf <sub>72</sub>  | Ta | W  | Re | Os | Ir | Pt | Au               | Hg <sub>80</sub>  |
| 6d-series               | Ac <sub>89</sub> | 5f Series        | Rf <sub>104</sub> | Db | Sg | Bh | Hs | Mt | Ds | Rg               | Cn <sub>112</sub> |

### Electronic Configuration



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## 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 |
|----|----|----|----|----|----|----|----|----|----|

Pd  
↓  
ns<sup>0</sup>

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

1. Choose the correct option having all the elements with d<sup>10</sup> electronic configuration from the following: [27 Jan, 2024 (Shift-II)]

- (a) <sup>27</sup>Co, <sup>28</sup>Ni, <sup>26</sup>Fe, <sup>24</sup>Cr (b) <sup>29</sup>Cu, <sup>30</sup>Zn, <sup>48</sup>Cd, <sup>47</sup>Ag  
(c) <sup>46</sup>Pd, <sup>28</sup>Ni, <sup>26</sup>Fe, <sup>24</sup>Cr (d) <sup>20</sup>Ni, <sup>21</sup>Cr, <sup>25</sup>Mn, <sup>29</sup>Cu

Sol. (b)

[Cd] = [Kr] 5s<sup>2</sup> 4d<sup>10</sup>, [Cu] = [Ar] 4s<sup>1</sup> 3d<sup>10</sup>, [Ag] = [Kr] 5s<sup>1</sup> 4d<sup>10</sup>, [Zn] = [Ar] 4s<sup>2</sup> 3d<sup>10</sup>

2. Match List-I with List-II.

| List-I<br>(Species)  | List-II<br>(Electronic distribution) |
|----------------------|--------------------------------------|
| (A) Cr <sup>+2</sup> | (I) 3d <sup>8</sup>                  |
| (B) Mn <sup>+</sup>  | (II) 3d <sup>3</sup> 4s <sup>1</sup> |
| (C) Ni <sup>+2</sup> | (III) 3d <sup>4</sup>                |
| (D) V <sup>+</sup>   | (IV) 3d <sup>5</sup> 4s <sup>1</sup> |

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) <sup>24</sup>Cr → [Ar] 3d<sup>5</sup> 4s<sup>1</sup>; Cr<sup>2+</sup> → [Ar] 3d<sup>4</sup>

<sup>25</sup>Mn → [Ar] 3d<sup>5</sup> 4s<sup>2</sup>; Mn<sup>+</sup> → [Ar] 3d<sup>5</sup> 4s<sup>1</sup>

<sup>28</sup>Ni → [Ar] 3d<sup>8</sup> 4s<sup>2</sup>; Ni<sup>2+</sup> → [Ar] 3d<sup>8</sup>

<sup>23</sup>V → [Ar] 3d<sup>3</sup> 4s<sup>2</sup>; V<sup>+</sup> → [Ar] 3d<sup>3</sup> 4s<sup>1</sup>



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.



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



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



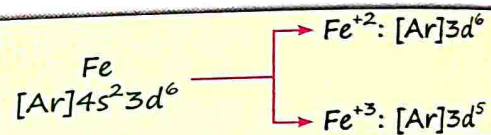
### Note

- 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 than  $Fe^{+2}$  due to half filled electronic configuration.



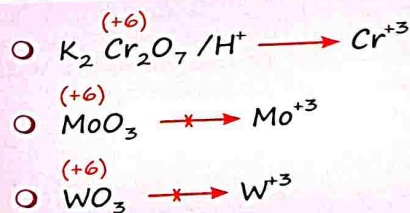
| Sc | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|----|----|----|----|----|----|----|----|----|----|
|    | +2 | +2 | +2 | +2 | +2 | +2 | +2 | +1 | +2 |
| +3 | +3 | +3 | +3 | +3 | +3 | +3 | +3 | +2 |    |
|    | +4 | +4 | +4 | +4 | +4 | +4 | +4 |    |    |
|    |    | +5 | +5 | +5 |    |    |    |    |    |
|    |    |    | +6 | +6 | +6 |    |    |    |    |
|    |    |    |    | +7 |    |    |    |    |    |



- Sc and Zn shows ONLY one oxidation state +3 and +2 respectively.
- Highest Oxidation State in 3d series : Mn (+7)  $[Mn_2O_7]$
- Highest Common Oxidation State in 3d series : +2
- Highest Oxidation state in d block  $\rightarrow$  Ru and Os : +8  $[RuO_4, OsO_4]$
- Sc<sup>3+</sup> is not known (Sc exist as only Sc<sup>3+</sup> ion because of stable inert gas configuration in Sc<sup>3+</sup> ion).
- Sc :  $[Ar]4s^2 3d^1$
- Sc<sup>3+</sup> :  $[Ar] 4s^0$  : Inert gas configuration
- Ti<sup>4+</sup> is more stable than Ti<sup>2+</sup> or Ti<sup>3+</sup> because Ti<sup>4+</sup> has inert gas configuration.
- Ti<sup>2+</sup> :  $[Ar] 4s^2 3d^2$       Ti<sup>3+</sup> :  $[Ar] 4s^0 3d^1$
- Ti :  $[Ar] 4s^2 3d^2$
- Ti<sup>4+</sup> :  $[Ar] 4s^0 3d^0$  : Inert gas configuration
- Zn shows only one oxidation state +2 because Zn<sup>2+</sup> has  $[Ar]3d^{10}$  configuration which is stable.
- Zn :  $[Ar] 4s^2 3d^{10}$
- Zn<sup>2+</sup> :  $[Ar] 3d^{10}$  : 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          |
|-------------------------------------------------------|-------------|-------------|-------------|-------------|-------------|
| Maximum oxidation state<br>[sum of s and d electrons] | $4s^2 3d^1$ | $4s^2 3d^2$ | $4s^2 3d^3$ | $4s^1 3d^5$ | $4s^2 3d^5$ |
|                                                       | 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 2 units ( $Pb^{2+}, Pb^{4+}$ ).
- In p block, due to inert pair effect lower oxidation state 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<sup>+</sup> is an oxidizing agent because Cr(+6) reduces itself to Cr(+3).
- Low or zero oxidation states of metal (Ni, Fe) are found when a complex compound has  $\sigma$  donor and  $\pi$  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.  $YBa_2Cu_3O_7$

$$\text{Let oxidation state of copper be } x \Rightarrow 3 + 2 \times 2 + 3 \times x - 2 \times 7 = 0$$

$$\Rightarrow x = +\frac{7}{3}$$

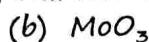
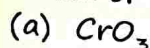


6. Match the properties given in Column-I with the metals given in Column-II.

| 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 |

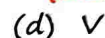
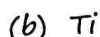
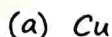
Sol. (i)  $\rightarrow$  (c), (ii)  $\rightarrow$  (a), (iii)  $\rightarrow$  (b)

7. Which of the following will not act as oxidising agents?



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:



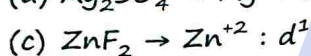
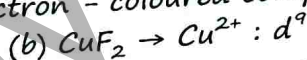
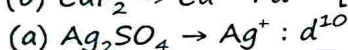
(2019/12th Jan/Shift-1)

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?



Sol. (b)  $\text{CuF}_2 \rightarrow \text{Cu}^{2+} : d^9$  [Unpaired electron - coloured compound]



(2023/29 Jan/Shift-2)

10. The set of correct statements is

(a) Manganese exhibits +7 oxidation state in its oxide.

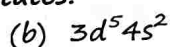
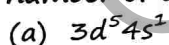
(b) Ruthenium and Osmium exhibit +8 oxidation in their oxides.

(c) Sc shows +4 oxidation state which is oxidising in nature.

(d) Cr shows oxidising nature in +6 oxidation state.

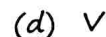
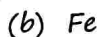
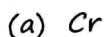
Sol. (a), (b) and (d)

11. Which one of the elements with the following outer orbital configurations may exhibit the largest number of oxidation states? [NEET 2009]



Sol. (b)

12. Which of the following shows maximum number of oxidation states? [NEET 2002]



Sol. (c)

## PHYSICAL PROPERTIES

d-block elements contains metals so they are

- Malleable** : Able to be pressed into shape without breaking or cracking.
- Sonorous** : Able to resonate sound.
- Ductile** : Able to be deformed without losing toughness.
- Lustrous** : Majority lose lustre on exposure to air (moist).



## ALLOY

- Mixture of element
- (i) Brass  $\rightarrow \text{Cu} + \text{Zn}$
- (ii) Gun metal/Bell metal  $\rightarrow \text{Cu} + \text{Zn} + \text{Sn}$
- (iii) German silver  $\rightarrow \text{Cu} + \text{Zn} + \text{Ni}$
- UK 'copper' coins are copper-coated steel.
- The 'silver' UK coins are a Cu/Ni alloy.

- (ii) Bronze  $\rightarrow \text{Cu} + \text{Sn}$
- (iv) Stainless steel  $\rightarrow \text{C} + \text{Fe} + \text{Cr} + \text{Ni}$

23. 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

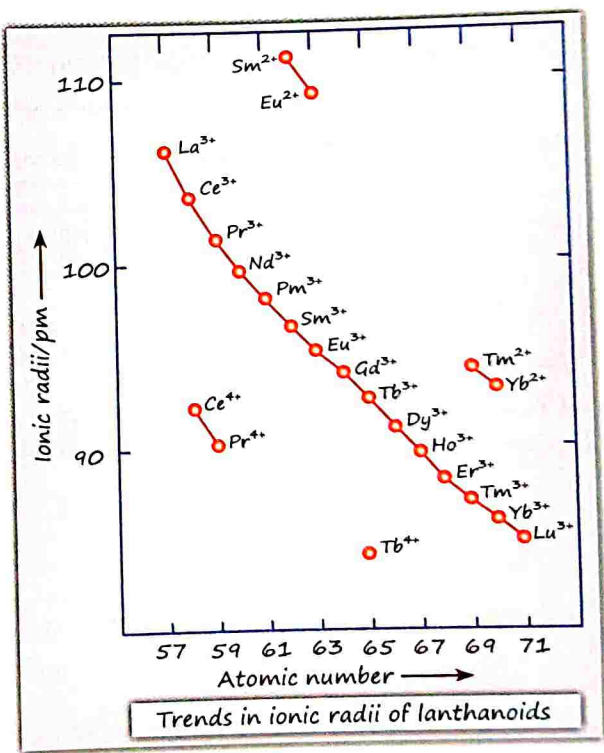
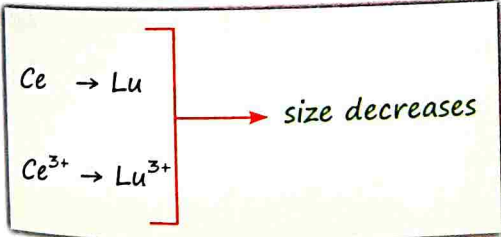
## ATOMIC SIZE

- 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 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 Ln and  $\text{Ln}^{3+}$  size orders.

**Remember, Atomic size :  $\text{Eu} > \text{Ce}$**



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-2)]

- (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

[illegible]

Free from effect of Lanthanide contraction

- 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.
- 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.

Assertion: Separation of Zr and Hf is difficult.  
Reason: Because Zr and Hf lie in the same group of the periodic table.

- 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: (b) Lanthanoid contraction

[NEET 2021]

- (a) Diagonal relationship (b) Lanthanoid contraction  
(c) Having similar chemical properties (d) Belonging to same group

**Sol. (b)**

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]

[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)  $Zr^{4+}$ ,  $Hf^{4+}$

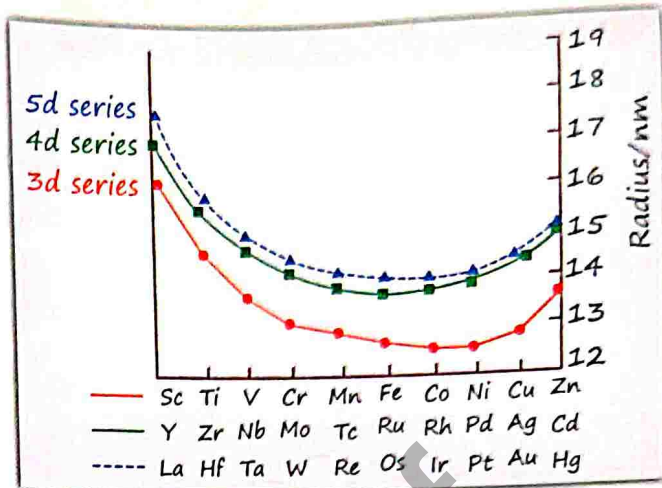
**Sol. (d)**



## Atomic Size of 3d Series

There are two factors in order to decide atomic radius of 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 <sup>3</sup> ) | 3.43 | 4.1 | 6.07 | 7.19 | 7.1 | 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).

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

□ Metallic radius of Zn is more than radius of Cu ⇒ [(Volume)<sub>Zn</sub> > (Volume)<sub>Cu</sub>].

So, density : Cu > Zn

□ Highest Density in d block-

Osmium (Os) = 22.51 g/cm<sup>3</sup>, Iridium (Ir) = 22.61 g/cm<sup>3</sup>

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)
20. The atomic radius of Ag is closest to: (2020/07 Jan/Shift-1)
- (a) Au (b) Ni (c) Cu (d) Hg
- Sol. (a) Atomic radius of Ag and Au is nearly same.
21. The pair that has similar atomic radii is: (2019/12<sup>th</sup> April/Shift-2)
- (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.

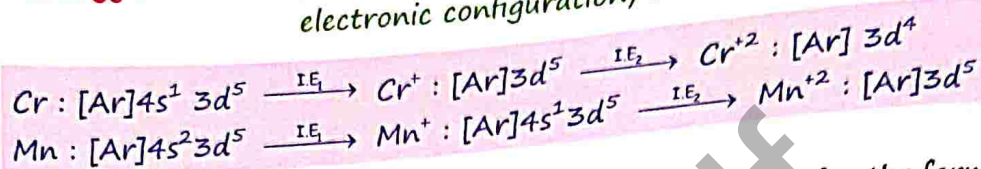
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The d- and f- Block Elements



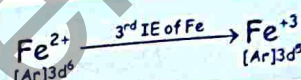
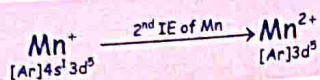
## IONISATION ENERGY

- 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  $IE_1$  due to their fully filled electronic configuration.
- 2<sup>nd</sup> Ionisation Energy** :  $Cr > Mn$  [Removal of electron from  $Cr^+$  is tough (due to half filled stable electronic configuration) with respect to  $Mn^+$ .]



- For an element :  $IE_1 < IE_2 < IE_3$
- The trend in steady increase in 2<sup>nd</sup> and 3<sup>rd</sup> ionisation enthalpy breaks for the formation of  $Mn^{2+}$  and  $Fe^{3+}$  respectively.

Explanation:



$Mn^{2+}$  and  $Fe^{3+}$  have  $d^5$  configuration which is relatively more stable due to higher exchange energy.

- 3<sup>rd</sup> Ionisation Energy** :  $Mn > Fe$

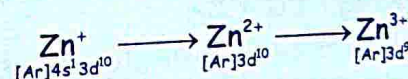
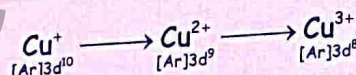


Removal of electron from  $Mn^{2+}$  to give  $d^4$  (not half filled  $d^5$  stable configuration) with respect to  $Fe^{2+}$ .

- Second ionisation enthalpy for Cr and Cu is high (due to removal of electron from ions  $Cr^+$  and  $Cu^+$  ions ( $d^5$  and  $d^{10}$  configuration respectively) is relatively tough.



- 2<sup>nd</sup> ionisation energy of Zn is low but 3<sup>rd</sup> ionisation energy is high with respect to Cu.



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 3<sup>rd</sup> 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:

(a) Co

(b) Fe

(c) Ni

(d) Mn

Sol. (b)  $Fe^{2+} \longrightarrow Fe^{3+}$

$3d^6 \longrightarrow 3d^5$  [half filled]

(2020/08<sup>th</sup> Jan/Shift-1)

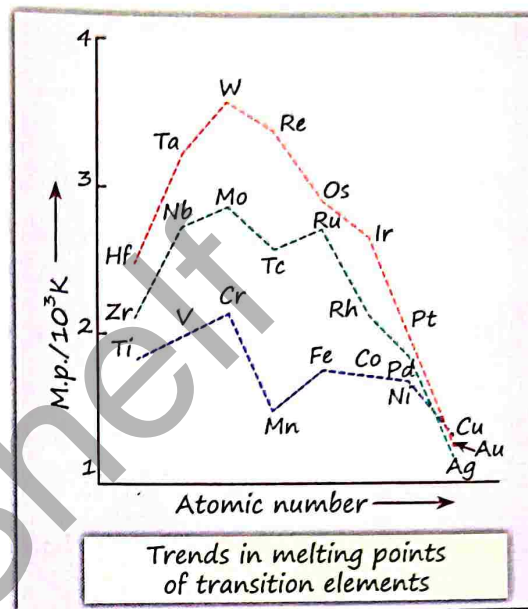


23. The correct order of decreasing second ionisation enthalpy of Ti (22), V (23), Cr (24) and Mn (25) is:
- (a)  $Ti > V > Cr > Mn$   
 (b)  $Cr > Mn > V > Ti$   
 (c)  $V > Mn > Cr > Ti$   
 (d)  $Mn > Cr > Ti > V$
- Sol. (b)

[NEET 2008]

## 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.



No. of unpaired electrons  $\uparrow$  : Metallic bonding  $\uparrow$  : MP / B.P.  $\uparrow$

| Metals                     | No. of unpaired electrons | Metals                        | No. of unpaired electrons |
|----------------------------|---------------------------|-------------------------------|---------------------------|
| $Sc \rightarrow 4s^2 3d^1$ | 1                         | $Fe \rightarrow 4s^2 3d^6$    | 4                         |
| $Ti \rightarrow 4s^2 3d^2$ | 2                         | $Co \rightarrow 4s^2 3d^7$    | 3                         |
| $V \rightarrow 4s^2 3d^3$  | 3                         | $Ni \rightarrow 4s^2 3d^8$    | 2                         |
| $Cr \rightarrow 4s^1 3d^5$ | 6                         | $Cu \rightarrow 4s^1 3d^{10}$ | 1                         |
| $Mn \rightarrow 4s^2 3d^5$ | 5                         | $Zn \rightarrow 4s^2 3d^{10}$ | 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.

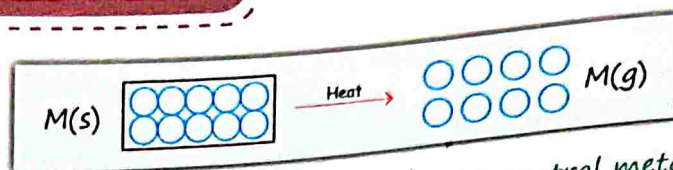
Metallic Bonding :  $Cr < Mo < W$

Melting Point :  $Cr < Mo < W$

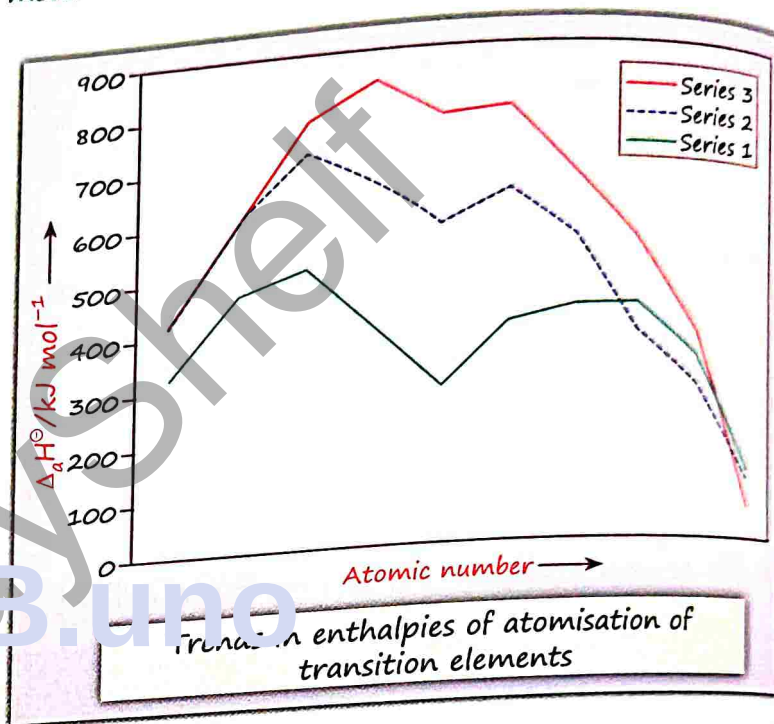
- As Mn and Zn has stable configuration, so they won't like to lose electron for delocalization leads to weak metallic bonding hence low M.P.
- Zn, Cd and Hg are more volatile than other d block elements because they do not have any unpaired electron.



## HEAT OF ATOMISATION



- The energy required to break 1 mole of metal lattice into neutral metal atom is known as heat of atomization.
- No. of unpaired electrons  $\uparrow$  : Metallic bonding  $\uparrow$  : Heat of atomization  $\uparrow$ .
- 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 ( $d^{10}$  : fully filled) has stable configuration. So they have weak metallic bonding hence low enthalpy of atomization.



24. The transition element that has lowest enthalpy of atomisation is: (2019/09<sup>th</sup> Jan/Shift-II)

(a) Fe (b) Cu (c) V (d) Zn

Sol. (b) Among Fe, Cu, V and Zn  $\rightarrow$  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?

- They exhibit high enthalpy of atomisation as the d-subshell is full.
- Zn and Cd do not show variable oxidation state while Hg shows +I and +II.
- Compounds of Zn, Cd and Hg are paramagnetic in nature.
- Zn, Cd and Hg are called soft metals.

Choose the most appropriate from the options given below:

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

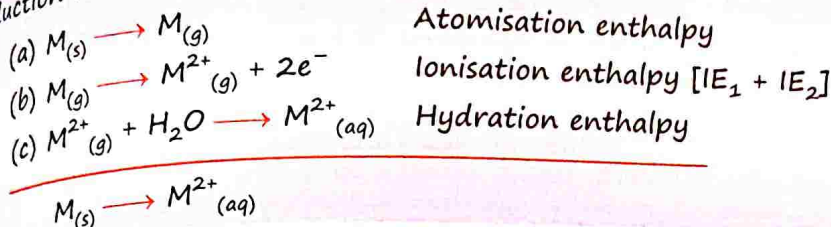
Sol. (a) (A) Zn, Cd, Hg exhibit lowest enthalpy of atomisation in respective transition series.  
(C) Compounds of Zn, Cd and Hg are diamagnetic in nature.



## REDUCTION POTENTIAL

### Reduction Potential $E^{\circ}_{M^{2+}/M}$

Reduction Potential depends on 3 following factors.



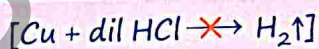
| Element                | V     | Cr    | Mn    | Fe    | Co    | Ni    | Cu    | Zn    |
|------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| $E^{\circ}_{M^{2+}/M}$ | -1.18 | -0.91 | -1.18 | -0.44 | -0.28 | -0.25 | +0.34 | -0.76 |

- $E^{\circ}$  = high (+) value means  $M^{2+}$  has great tendency to get reduced in Metal.
- $E^{\circ}$  = high (-) value means  $M^{2+}$  has low tendency to get reduced in Metal.

$M_{(s)} \rightarrow M^{2+}_{(aq)}$  becomes very spontaneous when

- Atomisation enthalpy of metal  $M_{(s)}$  is low.
- Sum of 1<sup>st</sup> and 2<sup>nd</sup> ionisation enthalpy of  $M_{(g)}$  is low.
- 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.



Heat of atomisation of metal      1<sup>st</sup> ionisation energy      2<sup>nd</sup> ionisation energy      Hydration Energy of  $M^{2+}$

| Element (M) | $\Delta H^{\circ} (M)$ | $\Delta_1 H^{\circ}_1$ | $\Delta_1 H^{\circ}_2$ | $\Delta_{\text{hyd}} H^{\circ} (M^{2+})$ | $E^{\circ} / V$ |
|-------------|------------------------|------------------------|------------------------|------------------------------------------|-----------------|
| 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           |



- $E^\circ$  values of Mn and Zn are more -ve than expected from the general trend

Less  $\Delta H_{\text{atom}}$  : More  $\ominus E^\circ_{\text{RP}}$

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)

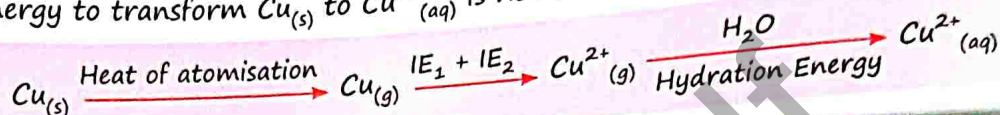
- $E^\circ$  value of Ni is more -ve than expected from the general trend.

More  $\Delta H_{\text{hyd}}$  : More  $\ominus E^\circ_{\text{RP}}$

$E^\circ$  for Ni is related to the highest negative hydration enthalpy  $\rightarrow$

- $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +\text{ve}$  because -

The high energy to transform  $\text{Cu}_{(\text{s})}$  to  $\text{Cu}^{2+}_{(\text{aq})}$  is not balanced by its hydration enthalpy.



26. Which of the following 3d-metal ion will give the lowest enthalpy of hydration ( $\Delta_{\text{hyd}}H$ ) when dissolved in water? [29 July, 2022 (Shift-1)]

- (a)  $\text{Cr}^{2+}$  (b)  $\text{Mn}^{2+}$  (c)  $\text{Fe}^{2+}$  (d)  $\text{Co}^{2+}$

Sol. (b)

27. Assertion : Cu cannot liberate hydrogen from acids.

Reason: Value of  $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$  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  $\text{Cu}^{2+}$  has greater tendency to get reduced in Cu metal. Cu cannot liberate  $\text{H}_2$  from acids.

28. The colour of light absorbed by an aqueous solution of  $\text{CuSO}_4$  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)  $\text{VOCl}_2$  ;  $\text{FeCl}_2$  (b)  $\text{CuCl}_2$  ;  $\text{VOCl}_2$   
 (c)  $\text{MnCl}_2$  ;  $\text{FeCl}_2$  (d)  $\text{FeCl}_2$  ;  $\text{CuCl}_2$

Sol. (b) Since both  $\text{Cu}^{2+}$  in  $\text{CuCl}_2$  and  $\text{V}^{4+}$  in  $\text{VOCl}_2$  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)  $\text{MnO}_2$  ,  $\text{FeCl}_3$  (b)  $[\text{MnO}_4]^-$  ,  $\text{CrO}_2\text{Cl}_2$   
 (c)  $[\text{Fe}(\text{CN})_6]^{3-}$  ,  $[\text{Co}(\text{CN})_3]$  (d)  $[\text{NiCl}_4]^{2-}$  ,  $[\text{CoCl}_4]^-$

Sol. (b)  $[\text{MnO}_4]^-$  contains Mn in the +7 oxidation state, and  $\text{CrO}_2\text{Cl}_2$  contains Cr in the +6 oxidation state, both representing the highest oxidation states of manganese and chromium.

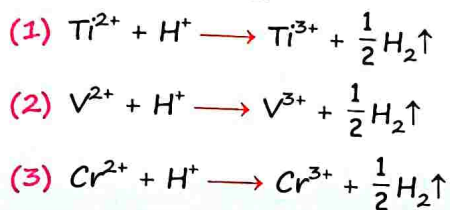


31. Amongst the following, identify the species with an atom in +6 oxidation state (JEE Adv. 2000)  
(a)  $\text{MnO}_4^-$  (b)  $\text{Cr}(\text{CN})_6^{3-}$  (c)  $\text{NiF}_6^{2-}$  (d)  $\text{CrO}_2\text{Cl}_2$

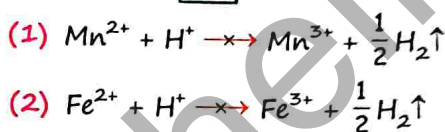
sol. (d) Chromium in  $\text{CrO}_2\text{Cl}_2$  is in the +6 oxidation state, which is the highest oxidation state for chromium in most compounds.

### Reduction Potential $M^{3+}/M^{2+}$

|                 |       |       |       |
|-----------------|-------|-------|-------|
|                 | Ti    | V     | Cr    |
| $M^{3+}/M^{2+}$ | -0.37 | -0.26 | -0.41 |
|                 | -ve   |       |       |



|  |      |      |      |
|--|------|------|------|
|  | Mn   | Fe   | Co   |
|  | 1.57 | 0.77 | 1.97 |
|  | +ve  |      |      |



### Note

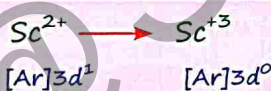
Aq. solution of  $\text{Ti}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{Cr}^{2+}$  ions are strong reducing agents, can evolve  $\text{H}_2$  from dil. acid.

### High Value for Mn and Zn:



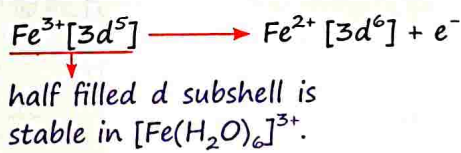
- The highest value for Zn is due to the removal of an electron from the stable  $d^{10}$  configuration of  $\text{Zn}^{2+}$  is tough.
- The comparatively high value for Mn shows that  $\text{Mn}^{2+}$  ( $d^5$ ) is particularly stable.

### Low Value for Sc:



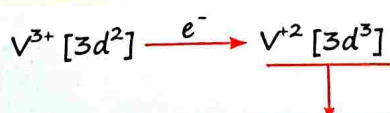
The low value for Sc reflects the stability of  $\text{Sc}^{3+}$  which has a noble gas configuration.

### Comparatively Low value (less +ve value) for Fe, with respect to Co and Mn

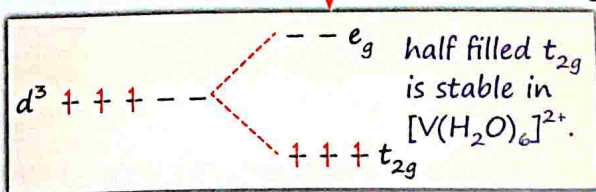


|      |      |      |
|------|------|------|
| Mn   | Fe   | Co   |
| 1.57 | 0.77 | 1.97 |
| +ve  |      |      |

### Comparatively Low value (less -ve value) for V, with respect to Ti and Cr



|       |       |       |
|-------|-------|-------|
| Ti    | V     | Cr    |
| -0.37 | -0.26 | -0.41 |
| -ve   |       |       |



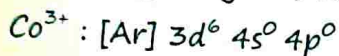
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32. Among  $\text{Co}^{3+}$ ,  $\text{Ti}^{2+}$ ,  $\text{V}^{2+}$  and  $\text{Cr}^{2+}$  ions, one if used as a reagent cannot liberate  $\text{H}_2$  from dilute mineral acid solution, its spin-only magnetic moment in gaseous state is \_\_\_\_ B.M. (Nearest integer) [25 July, 2022 (Shift-1)]

Sol. [5] Among the given,  $\text{Co}^{3+}$  can't liberate  $\text{H}_2$ .



Number of unpaired electrons = 4

$$\mu = \sqrt{4 \times 6} = 4.89 \text{ B.M.} \approx 5 \text{ B.M.}$$

33. The spin-only magnetic moment value of  $\text{M}^{3+}$  ion (in gaseous state) from the pairs  $\text{Cr}^{3+} / \text{Cr}^{2+}$ ,  $\text{Mn}^{3+} / \text{Mn}^{2+}$ ,  $\text{Fe}^{3+} / \text{Fe}^{2+}$  and  $\text{Co}^{3+} / \text{Co}^{2+}$  that has negative standard electrode potential, is \_\_\_\_ B.M [Nearest integer] [25 July, 2022 (Shift-2)]

Sol. [4] In given electrodes, only  $E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}}$  is negative

Electronic configuration of Cr in +3 o.s. is  $[\text{Ar}]3d^3 4s^0 4p^0$

Number of unpaired electrons = 3

$$\mu = \sqrt{n(n+2)}\text{BM} = \sqrt{3(3+2)}\text{BM} = 3.87\text{BM} \approx 4\text{BM}$$

34. Which of the following ions does not liberate hydrogen gas on reaction with dilute acids? (JEE Main 2017)

- (a)  $\text{Ti}^{2+}$  (b)  $\text{V}^{2+}$  (c)  $\text{Cr}^{2+}$  (d)  $\text{Mn}^{2+}$

Sol. (d)  $\text{Mn}^{2+}$  does not liberate hydrogen gas on reaction with dilute acids.

35. Which is a stronger reducing agent  $\text{Cr}^{2+}$  or  $\text{Fe}^{2+}$  and why?

Sol.  $\text{Cr}^{2+}$  is stronger reducing agent than  $\text{Fe}^{2+}$  in aqueous solution because  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  with  $d^4$  configuration converts easily into  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  with  $d^3$  configuration because in water  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ( $d^3$ ) is more stable as compared to  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  ( $d^4$ ) due to more CFSE in  $d^3$  configuration.

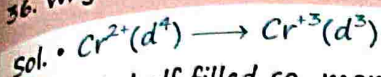
| $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} \longrightarrow [\text{Cr}(\text{H}_2\text{O})_6]^{3+}$    |                                                                                             | $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} \xrightarrow{\times} [\text{Fe}(\text{H}_2\text{O})_6]^{3+}$      |                                                                                                           |
|----------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|
| $d^4 \Rightarrow \begin{array}{l} \uparrow - e_g \\ \uparrow \uparrow \uparrow t_{2g} \end{array}$ | $d^3 \Rightarrow \begin{array}{l} - - e_g \\ \uparrow \uparrow \uparrow t_{2g} \end{array}$ | $d^6 \Rightarrow \begin{array}{l} \uparrow \uparrow e_g \\ \uparrow \uparrow \uparrow t_{2g} \end{array}$ | $d^5 \Rightarrow \begin{array}{l} \uparrow \uparrow e_g \\ \uparrow \uparrow \uparrow t_{2g} \end{array}$ |
| $\text{CFSE} = -3 \times 0.4 \Delta_o + 1 \times 0.6 \Delta_o$                                     | $\text{CFSE} = -3 \times 0.4 \Delta_o$                                                      | $\text{CFSE} = -4 \times 0.4 \Delta_o + 2 \times 0.6 \Delta_o$                                            | $\text{CFSE} = -3 \times 0.4 \Delta_o + 2 \times 0.6 \Delta_o$                                            |
| $= -0.6 \Delta_o$                                                                                  | $= -1.2 \Delta_o$                                                                           | $= -0.4 \Delta_o$                                                                                         | $= 0$                                                                                                     |

### Note

$\text{Fe}^{2+}$  ( $d^6$ ) does not convert into  $\text{Fe}^{3+}$  ( $d^5$ ) because  $d^5$  has zero CFSE.

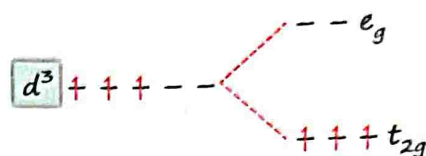
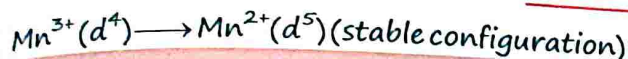


36. Why is  $\text{Cr}^{2+}$  reducing agent and  $\text{Mn}^{3+}$  oxidising agent when both have  $d^4$  configuration

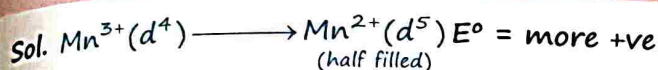


$t_{2g}$  is half filled so, more stable

•  $\text{Mn}^{2+}(d^5) \longrightarrow \text{Mn}^{3+}(d^4)$  is not possible because ionisation of  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  is not easy due to stability of  $d^5$  configuration. So  $\text{Mn}^{2+}$  is not a reducing agent but  $\text{Mn}^{3+}$  is an oxidizing agent.



37. Why is the  $E^\circ$  value for the  $\text{Mn}^{3+}/\text{Mn}^{2+}$  couple much more positive than that for  $\text{Cr}^{3+}/\text{Cr}^{2+}$  or  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ? Explain.



• 3<sup>rd</sup> Ionisation energy of  $\text{Mn}^{2+}$  is more than  $\text{Fe}^{+2}$  and  $\text{Cr}^{+2}$ .

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)  $\text{Mn}^{3+}$  and  $\text{Co}^{3+}$  are oxidising agents in aqueous solution
- (d)  $\text{Ti}^{2+}$  and  $\text{Cr}^{2+}$  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.



$$\text{CFSE} = -0.4 \Delta_o \times 5 + 2 \times 0.6 \Delta_o$$

$$= -0.8 \Delta_o$$

$$\text{CFSE} = -0.4 \Delta_o \times 6$$

$$= -2.4 \Delta_o$$

high CFSE favours the formation of  $\text{Co}^{3+}$ .

40. The  $E^\circ$  value for the  $\text{Mn}^{3+}/\text{Mn}^{2+}$  couple is more positive than that of  $\text{Cr}^{3+}/\text{Cr}^{2+}$  or  $\text{Fe}^{3+}/\text{Fe}^{2+}$  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]

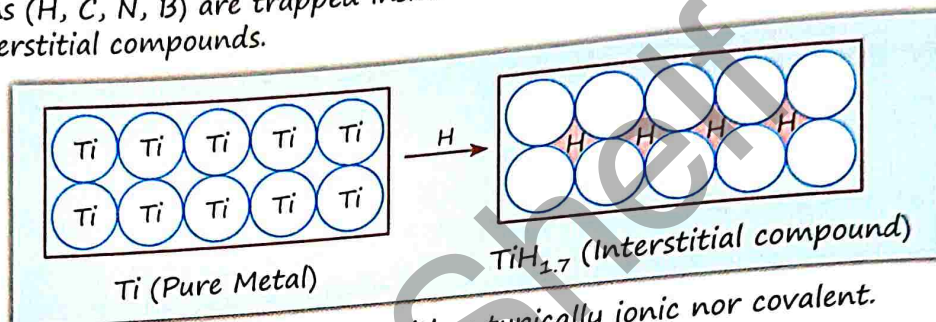
- (a)  $V^{3+}$  (b)  $Ti^{3+}$  (c)  $Mn^{3+}$  (d)  $Cr^{3+}$

(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.



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

- (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.

[MP :  $Ti < TiC$ ]

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: (2019/08<sup>th</sup> 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)

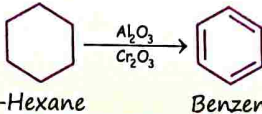
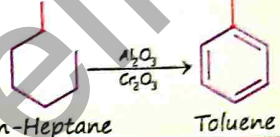
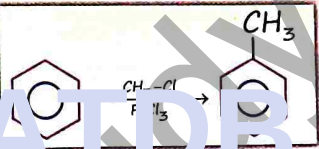


## CATALYTIC ACTIVITY

Factors responsible for catalytic activity of transition metals-

- Large surface area.
- Ability to form complexes.

- Variable oxidation state.
- Presence of empty d-orbital.

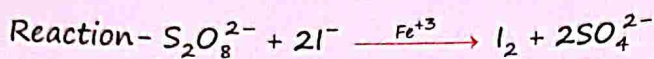
| Metal          | Catalyst                                        | Process/Reaction                                                                                                                                                                                                           |
|----------------|-------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Ti             | $\text{TiCl}_4 + \text{Et}_3\text{Al}$          | Ziegler Natta Catalyst : Preparation of polythene from ethene<br>$n\text{CH}_2 = \text{CH}_2 \xrightarrow{\text{TiCl}_4 + \text{Et}_3\text{Al}} \text{-(CH}_2 - \text{CH}_2\text{)}_n$                                     |
| V              | $\text{V}_2\text{O}_5$                          | $\text{V}_2\text{O}_5$ is used in contact process $\text{SO}_2 \xrightarrow[\text{O}_2]{\text{V}_2\text{O}_5} \text{SO}_3$                                                                                                 |
| Cr             | $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ | Used for aromatization<br><div>   </div>               |
| Mn             | $\text{MnO}_2$                                  | Used as catalyst in producing oxygen<br>$2\text{KClO}_3 \xrightarrow[\Delta]{\text{MnO}_2} 2\text{KCl} + 3\text{O}_2$                                                                                                      |
| Fe             | Anhydrous $\text{FeCl}_3$                       | Friedel Craft Reaction<br><div>  </div>                                                                                                  |
|                |                                                 | Used for preparation of benzene from acetylene<br>$3\text{HC} \equiv \text{CH} \longrightarrow \text{Benzene Ring}$                                                                                                        |
|                | Fe tube/ $\Delta$                               | Haber's Process<br>$\text{N}_2 + 3\text{H}_2 \xrightarrow[\text{Mo: As promoter}]{\text{Fe: As catalyst}} 2\text{NH}_3$                                                                                                    |
| Ni<br>Pd<br>Pt |                                                 | Hydrogenation of alkene and alkyne<br>$\text{CH}_2 = \text{CH}_2 \xrightarrow[\text{Pt}]{\text{H}_2} \text{CH}_3 - \text{CH}_3$ $\text{CH} \equiv \text{CH} \xrightarrow[\text{Pt}]{\text{H}_2} \text{CH}_3 - \text{CH}_3$ |
| Cu             |                                                 | Dehydrogenation of alcohol<br>$\text{CH}_3 - \text{CH}_2 - \text{OH} \xrightarrow[300^\circ\text{C}]{\text{Cu}} \text{CH}_3 - \overset{\text{O}}{\overset{\parallel}{\text{C}}} - \text{H}$                                |
| Ag             | AgBr                                            | The photographic industry relies on the special light-sensitive properties of AgBr                                                                                                                                         |
| Pd             |                                                 | Wacker process<br>$\text{CH}_2 = \text{CH}_2 \xrightarrow[\text{O}_2]{\text{PdCl}_2} \text{CH}_3 - \overset{\text{O}}{\overset{\parallel}{\text{C}}} - \text{H}$                                                           |



## Note

Transition metal ions can change their oxidation states, so they become more effective as catalyst.

- ❑  $\text{Fe}^{+3}$  catalyses the reaction between  $\text{I}^-$  and persulphate ion ( $\text{S}_2\text{O}_8^{2-}$ ).



### Mechanism:

- (i)  $2\text{Fe}^{+3} + 2\text{I}^- \longrightarrow 2\text{Fe}^{+2} + \text{I}_2$   
(ii)  $2\text{Fe}^{+2} + \text{S}_2\text{O}_8^{2-} \longrightarrow 2\text{Fe}^{+3} + 2\text{SO}_4^{2-}$

## Note

Some compounds are manufactured for special purposes such as  $\text{TiO}$  for the pigment industry and  $\text{MnO}_2$  for use in dry battery cells. The battery industry also requires  $\text{Zn}$  and  $\text{Ni/Cd}$ . The elements of Group 11 [ $\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Au}$ ] are still worthy of being called the coinage metals.

(2019/09<sup>th</sup> April/Shift-I)

45. Match the catalysts (Column-I) with products (Column-II).

| Column-I (Catalyst) |                                        | Column-II (Product) |                           |
|---------------------|----------------------------------------|---------------------|---------------------------|
| (A)                 | $\text{V}_2\text{O}_5$                 | (i)                 | Polyethylene              |
| (B)                 | $\text{TiCl}_4/\text{Al}(\text{Me})_3$ | (ii)                | $\text{e}^+\text{h}^-$ nr |
| (C)                 | $\text{PdCl}_2$                        | (iii)               | $\text{H}_2\text{SO}_4$   |
| (D)                 | Iron Oxide                             | (iv)                | $\text{NH}_3$             |

- (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)                 | Ziegler Natta catalyst           |
| (ii)                | $\text{Cu}_2\text{Cl}_2$                   | (b)                 | Contact process                  |
| (iii)               | $\text{V}_2\text{O}_5$                     | (c)                 | Vegetable oil to ghee            |
| (iv)                | Finely divided iron                        | (d)                 | Sandmeyer reaction               |
| (v)                 | $\text{TiCl}_4 + \text{Al}(\text{CH}_3)_3$ | (e)                 | Haber's Process                  |
|                     |                                            | (f)                 | Decomposition of $\text{KClO}_3$ |

Sol. (i)  $\rightarrow$  (c), (ii)  $\rightarrow$  (d), (iii)  $\rightarrow$  (b), (iv)  $\rightarrow$  (e), (v)  $\rightarrow$  (a)



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CHEMISTRY



47. In the context with the first transition series which of the following statement is incorrect?
- In the highest oxidation state of first five elements all the 4s and 3d are used for bonding.
  - Once the  $d^5$  configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.
  - Zero oxidation state is also shown by these elements in complexes.
  - 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?

- (a)  $Mn^{3+}$  (b)  $Fe^{3+}$  (c)  $Ti^{3+}$  (d)  $Cr^{3+}$

(2022/25 June/Shift-1)

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]

- $Cr^{2+}$  is a reducing agent
- $Mn^{3+}$  is an oxidising agent
- Both  $Cr^{2+}$  and  $Mn^{3+}$  exhibit  $d^4$  electronic configuration
- When  $Cr^{2+}$  is used as a reducing agent, the chromium ion attains  $d^5$  electronic configuration

Sol. (a), (b), (c)



[NEET 2025]

50. Match List-I with List-II.

| 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-I, B-II, C-IV, D-III
- A-II, B-III, C-I, D-IV
- A-I, B-II, C-III, D-IV
- A-I, B-IV, C-III, D-II

Sol. (c)

[NEET 2022 R4]

51. Given below are two statements:

Statement I:  $\text{Cr}^{2+}$  is oxidising and  $\text{Mn}^{3+}$  is reducing in nature.

Statement II:  $\text{Sc}^{3+}$  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  $E_{\text{M}^{2+}/\text{M}}$  has 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 containing 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)  $\text{Cr} > \text{Mn} > \text{Co} > \text{Fe}$
- (b)  $\text{Mn} > \text{Fe} > \text{Cr} > \text{Co}$
- (c)  $\text{Fe} > \text{Mn} > \text{Co} > \text{Cr}$
- (d)  $\text{Co} > \text{Mn} > \text{Fe} > \text{Cr}$

Sol. (b)  $\text{Mn}^{2+}$  being the most stable because after losing 2 electron it has now half filled stable configuration. Hence, stability of +2 oxidation state becomes:  
 $\text{Mn} > \text{Fe} > \text{Cr} > \text{Co}$

56. Which one of the following characteristics of the transition metals is associated with their catalytic activity? [NEET 2003]

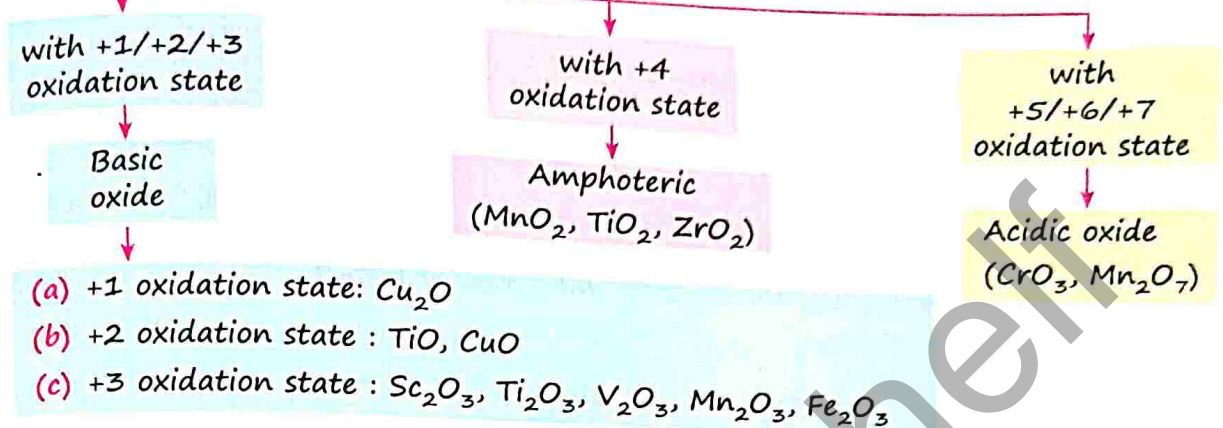
- (a) High enthalpy of atomization
- (b) Paramagnetic behaviour
- (c) Colour of hydrated ions
- (d) Variable oxidation states

Sol. (d)



# OXIDES OF TRANSITION ELEMENTS

## Oxides of Metal



**Note**  
 $\text{ZnO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  are amphoteric in nature. Remember  $\text{V}_2\text{O}_4$  is basic (less) in nature.

| Oxidation Number | Groups                         |                                |                               |                                |                                |                                |     |     |                   |     |
|------------------|--------------------------------|--------------------------------|-------------------------------|--------------------------------|--------------------------------|--------------------------------|-----|-----|-------------------|-----|
|                  | 3                              | 4                              | 5                             | 6                              | 7                              | 8                              | 9   | 10  | 11                | 12  |
| +7               |                                |                                |                               |                                | Mn <sub>2</sub> O <sub>7</sub> |                                |     |     |                   |     |
| +6               |                                |                                |                               | CrO <sub>3</sub>               |                                |                                |     |     |                   |     |
| +5               |                                |                                | V <sub>2</sub> O <sub>5</sub> |                                |                                |                                |     |     |                   |     |
| +4               |                                | TiO <sub>2</sub>               | V <sub>2</sub> O <sub>4</sub> |                                |                                |                                |     |     |                   |     |
| +3               | Sc <sub>2</sub> O <sub>3</sub> | Ti <sub>2</sub> O <sub>3</sub> | V <sub>2</sub> O <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | Mn <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> |     |     |                   |     |
| +2               |                                | TiO                            | VO                            | (CrO)                          | MnO                            | FeO                            | CoO | NiO | CuO               | ZnO |
| +1               |                                |                                |                               |                                |                                |                                |     |     | Cu <sub>2</sub> O |     |

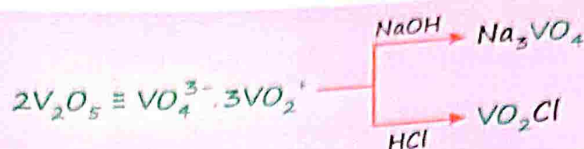
## Oxides, Oxo-anion and Oxo-cation

- As oxidation number of a metal increases, acidic character and covalent character increases.  
 For V :  $\text{V}_2\text{O}_3$  (basic)  $\rightarrow$   $\text{V}_2\text{O}_4$  (less basic)  $\rightarrow$   $\text{V}_2\text{O}_5$  (amphoteric)  
 For Cr :  $\text{CrO}$  (basic)  $\rightarrow$   $\text{Cr}_2\text{O}_3$  (amphoteric)  $\rightarrow$   $\text{CrO}_3$  (acidic)
- All metal except Sc form MO oxides which are ionic.  
 Example :  $\text{ZnO}$ ,  $\text{CuO}$ ,  $\text{TiO}$
- $\text{Mn}_2\text{O}_7$ ,  $\text{CrO}_3$ ,  $\text{V}_2\text{O}_5$  are covalent molecule.
- Generally covalent compounds ( $\text{CrO}_3$ ,  $\text{V}_2\text{O}_5$ ) have low melting point.
- $\text{V}_2\text{O}_5$  is amphoteric (predominantly acidic) because it reacts with alkalis ( $\text{NaOH}$ ) as well as acids ( $\text{HCl}$ ) to give  $\text{VO}_4^{3-}$  and  $\text{VO}_2^+$  respectively.

**According to Fajan's rule-**

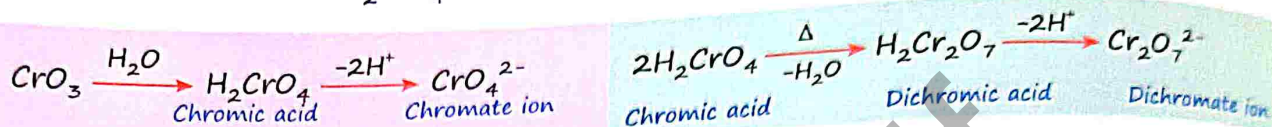
- Charge on cation  $\uparrow \equiv$  covalent character  $\uparrow$
- $\text{MnO}$  : Ionic compound
- $\text{Mn}_2\text{O}_7$  : Covalent compound



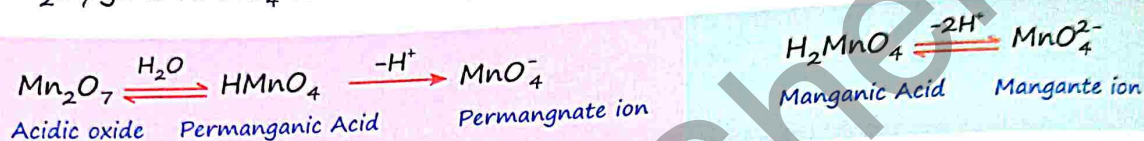


6. Remember  $V_2O_5$  is less basic in nature. It dissolves in acids to give  $VO^{2+}$  salts.

□  $CrO_3$  gives chromic acid  $H_2CrO_4$  and dichromic acid  $H_2Cr_2O_7$ .



□  $Mn_2O_7$  gives  $HMnO_4$  or we can say  $Mn_2O_7$  is an anhydride of  $HMnO_4$ .



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. [O]

'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)



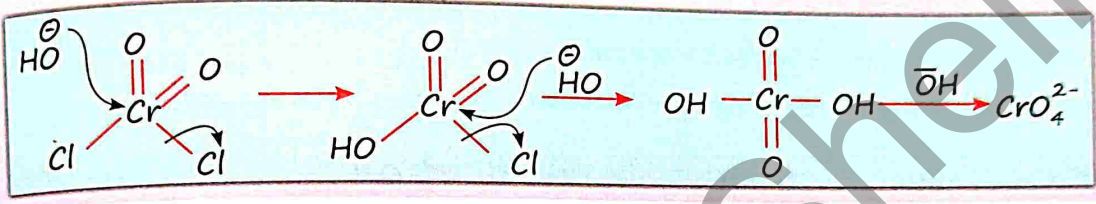
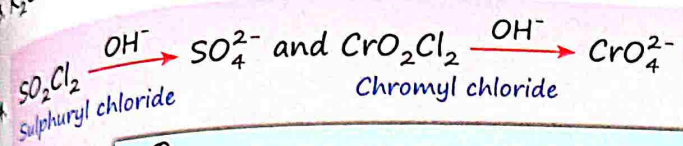
## SO<sub>3</sub> Vs CrO<sub>3</sub>

Hexavalent chromium shows similarities in properties with hexavalent sulphur compounds because both the elements have the same number of valence shell electrons.

SO<sub>3</sub> and CrO<sub>3</sub> are both acidic.

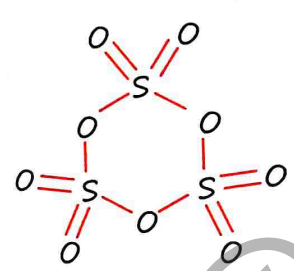
S forms SO<sub>4</sub><sup>2-</sup>, S<sub>2</sub>O<sub>7</sub><sup>2-</sup> and similarly Cr forms CrO<sub>4</sub><sup>2-</sup> (chromate), Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> (dichromate)

K<sub>2</sub>CrO<sub>4</sub> [2K<sup>+</sup> . CrO<sub>4</sub><sup>2-</sup>] and K<sub>2</sub>SO<sub>4</sub> [2K<sup>+</sup> . SO<sub>4</sub><sup>2-</sup>] are isomorphous (same crystal type)



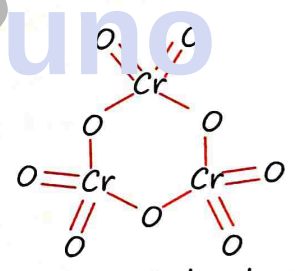
SO<sub>3</sub> and β(SO<sub>3</sub>) have the same structures.

β(SO<sub>3</sub>) ≡ (SO<sub>3</sub>)<sub>3</sub> ≡ S<sub>3</sub>O<sub>9</sub>  
 ≡ Trimer of SO<sub>3</sub> ≡ Cyclic Structure



- ♦ S - O - S bond : 3
- ♦ Type of p bond : 6 pπ - dπ
- ♦ Each sulphur is sp<sup>3</sup> hybridised.

(CrO<sub>3</sub>)<sub>3</sub> : Cr<sub>3</sub>O<sub>9</sub>



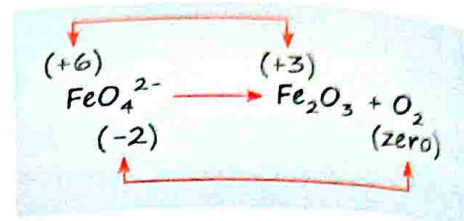
- ♦ Cr - O - Cr bond : 3
- ♦ Type of π bond : 6 pπ - dπ
- ♦ Each chromium is sp<sup>3</sup> hybridised.

## Oxo-anions

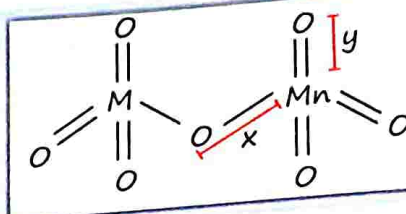
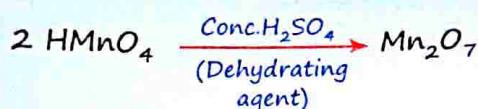
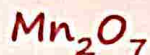
Tetrahedral [MO<sub>4</sub>]<sup>n-</sup> ions are known for V<sup>+5</sup>, Cr<sup>+6</sup>, Fe<sup>+6</sup>, Mn<sup>+6</sup>.

|                                                                                                 |                                                                                                                                                     |                                                 |                                               |
|-------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|-----------------------------------------------|
| VO <sub>4</sub> <sup>3-</sup><br>Vanadate                                                       | CrO <sub>4</sub> <sup>2-</sup><br>Chromate ion<br>MoO <sub>4</sub> <sup>2-</sup><br>Molybdate ion<br>WO <sub>4</sub> <sup>2-</sup><br>Tungstate ion | MnO <sub>4</sub> <sup>2-</sup><br>Manganate ion | FeO <sub>4</sub> <sup>2-</sup><br>Ferrate ion |
| <div> <input type="checkbox"/> These ions are stable in alkaline medium.                 </div> |                                                                                                                                                     |                                                 |                                               |

- $\text{FeO}_4^{2-}$  (ferrate ion has +6 oxidation state of Fe) are formed in alkaline media but it readily decompose to  $\text{Fe}_2\text{O}_3$  and  $\text{O}_2$ .



- V and Ti form oxo-cations  $\text{VO}_2^+$ ,  $\text{VO}^{2+}$ , and  $\text{TiO}^{2+}$ .



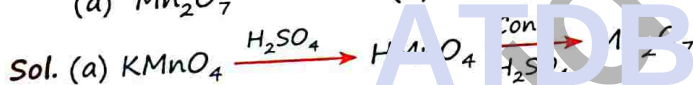
Bond length :  $y < x$   
 $\pi$  bond :  $p\pi - d\pi$

- Non-linear and symmetrical covalent molecule.
- Each Mn is tetrahedrally surrounded by O's including a Mn-O-Mn bridge.
- Highly explosive in nature.
- Green oily compound.



60. On addition of small amount of  $\text{KMnO}_4$  to concentrated  $\text{H}_2\text{SO}_4$ , a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following:

- (a)  $\text{Mn}_2\text{O}_7$  (b)  $\text{MnO}_2$  (c)  $\text{MnSO}_4$  (d)  $\text{Mn}_2\text{O}_3$



61. Highest oxidation state of Mn is exhibited in  $\text{Mn}_2\text{O}_7$ . The correct statements about  $\text{Mn}_2\text{O}_7$  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:

- (a)  $\text{CrO}_3$  (b)  $\text{Fe}_2\text{O}_3$  (c)  $\text{MnO}_2$  (d)  $\text{V}_2\text{O}_5$  (e)  $\text{Cu}_2\text{O}$  (2021/31 Aug)

Sol The oxidation state of the metal in each oxide:

- (a)  $\text{CrO}_3$  (b)  $\text{Fe}_2\text{O}_3$  (c)  $\text{MnO}_2$  (d)  $\text{V}_2\text{O}_5$  (e)  $\text{Cu}_2\text{O}$
- $\downarrow$                        $\downarrow$                        $\downarrow$                        $\downarrow$                        $\downarrow$   
 +6                      +3                      +4                      +5                      +1

Thus, the increasing order of oxidation numbers is:  $\text{Cu}_2\text{O} < \text{Fe}_2\text{O}_3 < \text{MnO}_2 < \text{V}_2\text{O}_5 < \text{CrO}_3$ .

(2023/31 Jan/Shift-I)

63. The correct order of basicity of oxides of vanadium is-

- (a)  $\text{V}_2\text{O}_3 > \text{V}_2\text{O}_4 > \text{V}_2\text{O}_5$  (b)  $\text{V}_2\text{O}_3 > \text{V}_2\text{O}_5 > \text{V}_2\text{O}_4$   
 (c)  $\text{V}_2\text{O}_4 > \text{V}_2\text{O}_3 > \text{V}_2\text{O}_5$  (d)  $\text{V}_2\text{O}_5 > \text{V}_2\text{O}_4 > \text{V}_2\text{O}_3$

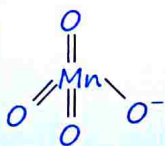
Sol. (a) The oxides in the lower oxidation states of the metals are basic and in their higher oxidation states they are acidic.



## PERMANGANATE AND MANGANATE ION

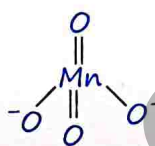
### Permanganate ion : $\text{MnO}_4^-$

- $\text{Mn}^{+7} : 3d^0$
- Colour : Purple
- Colour is due to charge transfer from  $\text{O}^{2-}$  to  $\text{Mn}^{+7}$ .
- Magnetic property  $\rightarrow$  Diamagnetic due to absence of unpaired electron.
- Structure :



### Manganate ion: $\text{MnO}_4^{2-}$

- $\text{Mn}^{+6} : 3d^1$
- Colour : Green
- Colour is due to charge transfer from  $\text{O}^{2-}$  to  $\text{Mn}^{+6}$ .
- Magnetic property  $\rightarrow$  Paramagnetic due to presence of 1 unpaired electron.
- $\text{MnO}_4^- \xrightleftharpoons[\text{H}^+]{\text{OH}^-} \text{MnO}_4^{2-}$
- Structure :



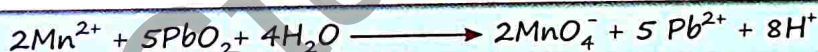
- All 4 Mn - O bonds are same in  $\text{MnO}_4^-$  and  $\text{MnO}_4^{2-}$ .
- In both ion,  $\pi$  bond is a  $p\pi - d\pi$  bond because  $\pi$  bonding takes place by overlap of p orbital of O and d orbital of Mn.

## Preparation of $\text{KMnO}_4$

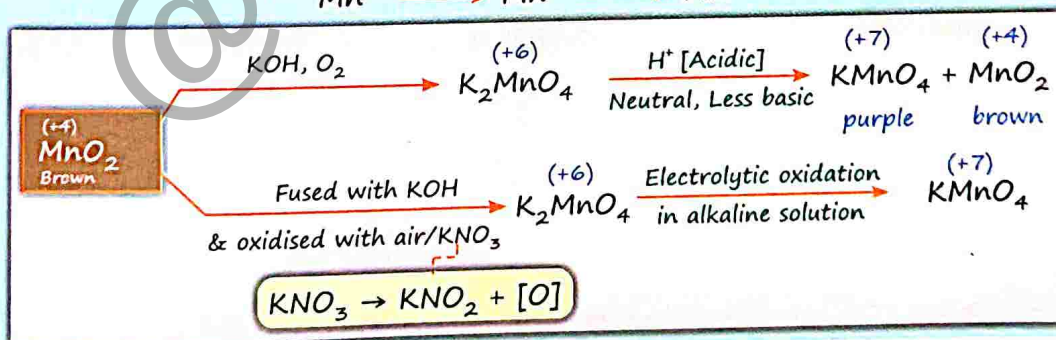
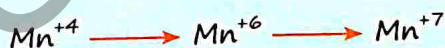
### From $\text{S}_2\text{O}_8^{2-}$ or $\text{PbO}_2$



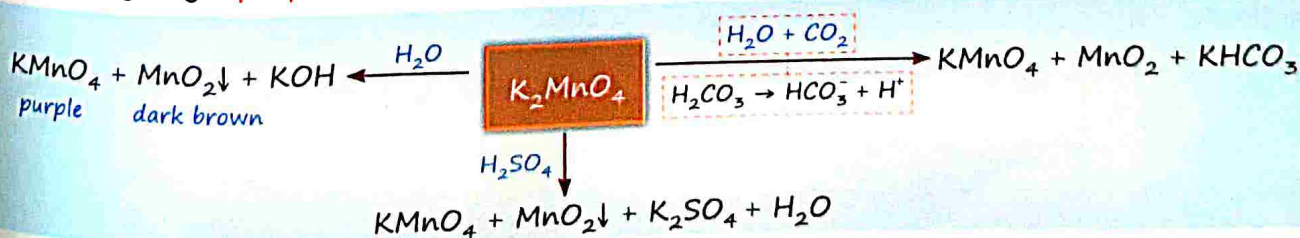
Manganese (II) ion salt is oxidised by peroxodisulphate ( $\text{S}_2\text{O}_8^{2-}$ ) to permanganate ( $\text{MnO}_4^-$ ).



### From $\text{MnO}_2$ (Pyrolusite)



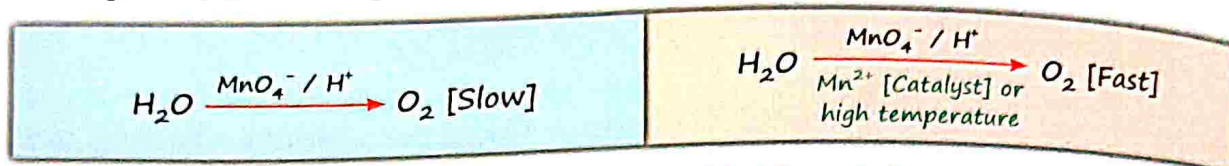
- Green solution ( $\text{K}_2\text{MnO}_4$ ) is quite stable in alkali, but in pure water and in presence of acids, depositing  $\text{MnO}_2$  and giving a **purple solution of permanganate**.



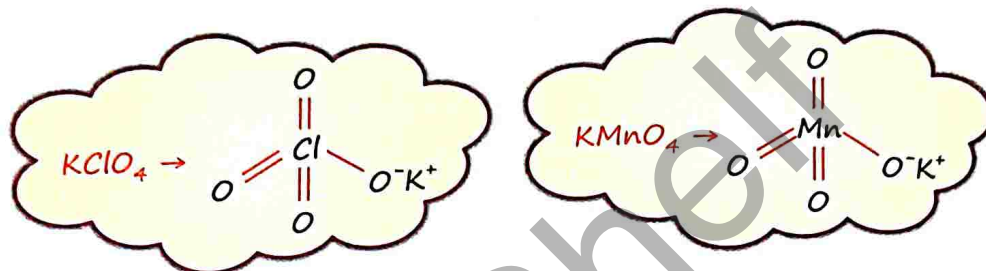
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## Properties of $\text{KMnO}_4$

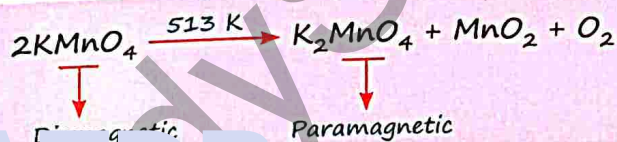
- ❑ Permanganate at  $[\text{H}^+] = 1$  should oxidise water but in practice the reaction is extremely slow unless either manganese(II) ions are present or the temperature is raised.



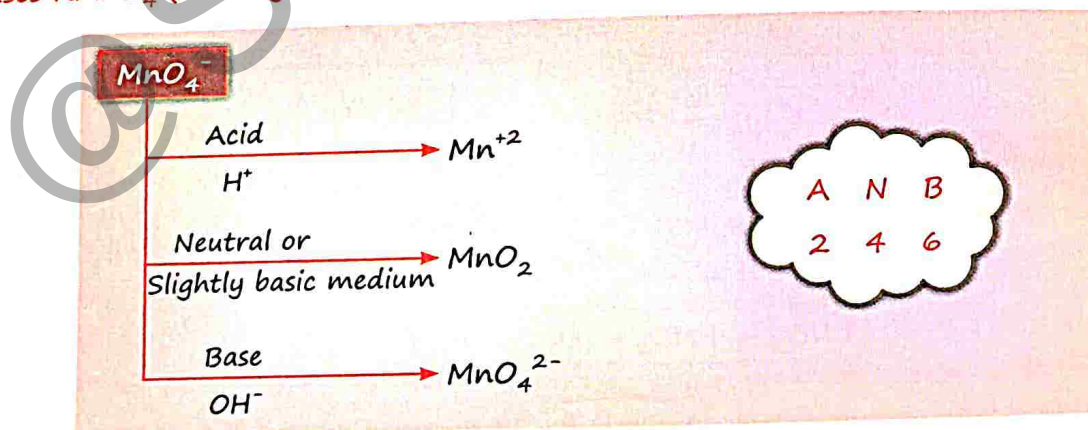
- ❑ Potassium permanganate forms **dark purple (almost black) crystals** which are isostructural with those of  $\text{KClO}_4$ .



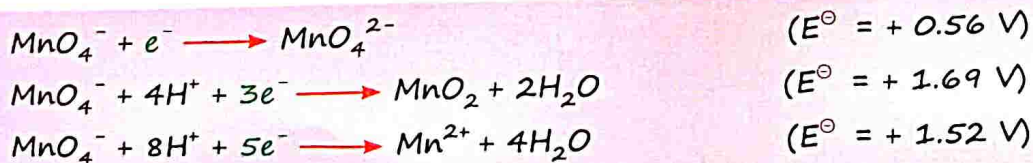
- ❑ The salt is not very soluble in water (6.4 g/100 g of water at 293 K), but when heated it decomposes at 513 K.



- ❑  $\text{KMnO}_4$  has 2 physical properties of **interest**
- Its **intense colour** and
  - Its diamagnetism along with temperature-dependent weak paramagnetism [As temperature increases  $\text{KMnO}_4$  (diamagnetic) converts into  $\text{K}_2\text{MnO}_4$  (weak paramagnetic)].



- ❑ The reduction of permanganate to manganate, manganese dioxide and manganese(II) salt by half-reactions,





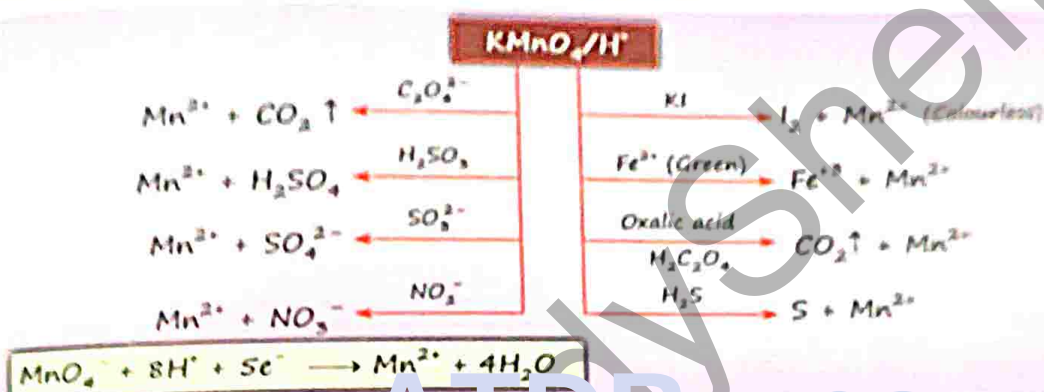
## Note

Appropriate situations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine



we can not use HCl to create acidic medium for  $\text{KMnO}_4$ , because HCl get oxidised to  $\text{Cl}_2$  by  $\text{KMnO}_4$ , so we use  $\text{H}_2\text{SO}_4$  to create acidic medium because  $\text{KMnO}_4$  cannot oxidise  $\text{H}_2\text{SO}_4$  as sulphur is in higher (+6) oxidation state.

## Reactions of $\text{KMnO}_4$ in Acidic Medium



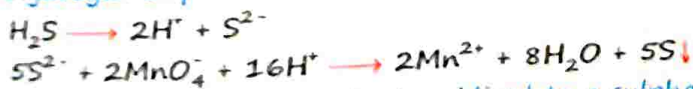
- (1) Iodine is liberated from potassium iodide ( $\text{KI}$ )  
 $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$   
 For balanced equation multiply equation (i) by 2 and (ii) by 5 -  
 $10\text{I}^- + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{I}_2$

- (2)  $\text{Fe}^{2+}$  ion (green) is converted to  $\text{Fe}^{3+}$  (yellow):  
 $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$   
 For balanced equation multiply equation (i) by 1 and (iii) by 5 -  
 $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$

- (3) Oxalate ion or oxalic acid is oxidised at 333 K:  
 $\text{COO}^- \rightarrow 2\text{CO}_2 + 2\text{e}^-$

- For balanced equation multiply equation (i) by 2 and (iv) by 5 -  
 $5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$

- (4) Hydrogen sulphide is oxidised, sulphur being precipitated.

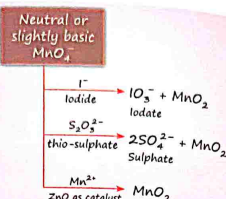


- (5) Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:  
 $5\text{SO}_3^{2-} + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{SO}_4^{2-}$

- (6) Nitrite is oxidised to nitrate:  
 $5\text{NO}_2^- + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{NO}_3^- + 3\text{H}_2\text{O}$

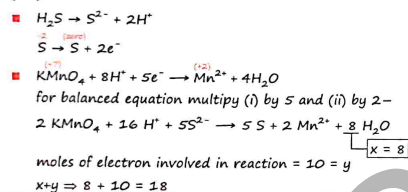
### Reactions of $\text{KMnO}_4$ in Neutral or Slightly Basic Medium

- (1) A notable reaction is the oxidation of iodide to iodate:  
 $2\text{MnO}_4^- + \text{H}_2\text{O} + \text{I}^- \longrightarrow 2\text{MnO}_2 + 2\text{OH}^- + \text{IO}_3^-$
- (2) Thiosulphate is oxidised almost quantitatively to sulphate:  
 $8\text{MnO}_4^- + 3\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \longrightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + 2\text{OH}^-$
- (3) Manganous salt is oxidised to  $\text{MnO}_2$ ; the presence of zinc sulphate or zinc oxide catalyses the oxidation:  
 $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \longrightarrow 5\text{MnO}_2 + 4\text{H}^+$



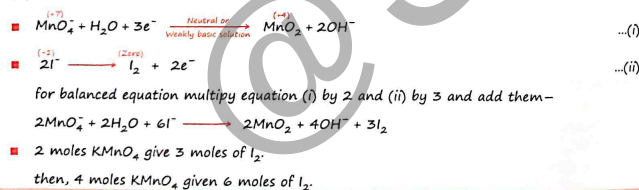
64.  $\text{H}_2\text{S}$  (5 moles) reacts completely with acidified aqueous potassium permanganate solution. In this reaction, the number of moles of water produced is  $x$ , and the number of moles of electrons involved is  $y$ . The value of  $(x + y)$  is \_\_\_\_ (JEE Adv. 2023)

Sol. (18)



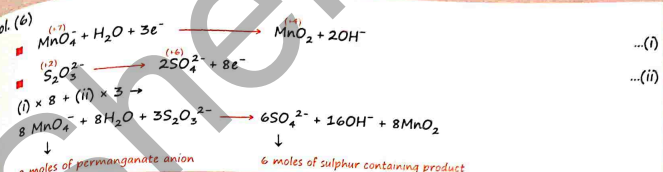
65. In the chemical reaction between stoichiometric quantities of  $\text{KMnO}_4$  and  $\text{KI}$  in weakly basic solution, what is the number of moles of  $\text{I}_2$  released for 4 moles of  $\text{KMnO}_4$  consumed? (JEE Adv. 2020)

Sol. (6)



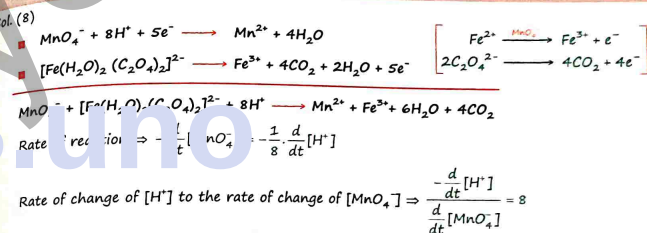
66. In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitatively oxidise thiosulphate anions to produce  $X$  moles of a sulphur containing product. The magnitude of  $X$  is \_\_\_\_ (JEE Adv. 2016)

Sol. (6)



67. In dilute aqueous  $\text{H}_2\text{SO}_4$  the complex diaquadioxalatoferate (II) is oxidised by  $\text{MnO}_4^-$ . For this reaction, the ratio of the rate of change of  $[\text{H}^+]$  to the rate of change of  $[\text{MnO}_4^-]$  is \_\_\_\_ (JEE Adv. 2015)

Sol. (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)  $\text{K}_2\text{MnO}_4$ ,  $\text{Mn}^{6+}$  contains one unpaired electron, thus paramagnetic, and green in colour.

69.  $\text{KMnO}_4$  oxidises  $\text{I}^-$  in acidic and neutral/faintly alkaline solution, respectively, to

- (a)  $\text{I}_2$  and  $\text{IO}_3^-$  (b)  $\text{I}_2$  and  $\text{I}_2$  (c)  $\text{IO}_3^-$  and  $\text{I}_2$  (d)  $\text{IO}_3^-$  and  $\text{IO}_3^-$

Sol. (a)

70. Incorrect statement about  $\text{K}_2\text{MnO}_4$ :

- (a) It's prepared by reaction of pyrolusite with  $\text{KOH}$  and air.  
 (b) It is tetrahedral, paramagnetic and green compound  
 (c)  $2p\pi - 3p\pi$  bonding is present  
 (d) In acidic medium, it is disproportionate to produce compound with  $\text{Mn(VII)}$  and  $\text{Mn(IV)}$ .

Sol. (c) The manganate ion is tetrahedral; the  $\pi$  bonding takes place by overlap of  $p$  orbitals of oxygen with  $d$  orbitals of manganese.

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71. When  $\text{MnO}_2$  is heated with fused  $\text{KOH}$  in presence of air, then the product formed is:

- (a)  $\text{KMnO}_4$ , Purple (b)  $\text{MnO}_3$ , Brown  
(c)  $\text{K}_2\text{MnO}_4$ , Green (d)  $\text{K}_2\text{MnO}_4$ , Black

Sol. (c)  $\text{MnO}_2 + \text{KOH} + \text{O}_2 \rightarrow \text{K}_2\text{MnO}_4$

72. Why is  $\text{HCl}$  not used to make the medium acidic in oxidation reactions of  $\text{KMnO}_4$  in acidic medium?

- (a) Both  $\text{HCl}$  and  $\text{KMnO}_4$  act as oxidizing agents  
(b)  $\text{KMnO}_4$  oxidises  $\text{HCl}$  into  $\text{Cl}_2$  which is also an oxidizing agent  
(c)  $\text{KMnO}_4$  is a weaker oxidizing agent than  $\text{HCl}$   
(d)  $\text{KMnO}_4$  acts as a reducing agent in the presence of  $\text{HCl}$

Sol. (b)  $\text{HCl} \xrightarrow{\text{MnO}_4^-} \text{Cl}_2$

73. Thermal decomposition of a Mn compound (X) at  $513\text{ K}$  results in compound Y,  $\text{MnO}_2$  and a gaseous product.  $\text{MnO}_2$  reacts with  $\text{NaCl}$  and concentrated  $\text{H}_2\text{SO}_4$  to give a pungent gas Z. X, Y and Z respectively, are :

- (a)  $\text{KMnO}_4$ ,  $\text{K}_2\text{MnO}_4$  and  $\text{Cl}_2$  (b)  $\text{K}_2\text{MnO}_4$ ,  $\text{KMnO}_4$  and  $\text{SO}_2$   
(c)  $\text{K}_2\text{MnO}_4$ ,  $\text{K}_2\text{MnO}_4$  and  $\text{Cl}_2$  (d)  $\text{K}_2\text{MnO}_4$ ,  $\text{KMnO}_4$  and  $\text{Cl}_2$

Sol. (a)  $\text{KMnO}_4 \xrightarrow{513\text{ K}} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{gas (O}_2\text{)}$   
(X) (Y)  
 $\text{NaCl} \xrightarrow{\text{H}_2\text{SO}_4} \text{Cl}_2 \uparrow \text{ (Z)}$

74.  $\text{A} \xrightarrow{4\text{KOH, O}_2} 2\text{B} + 2\text{H}_2\text{O}$   
(Green)

$\text{B} \xrightarrow{4\text{HCl}} 2\text{C} + \text{MnO}_2 + 2\text{H}_2\text{O}$   
(Purple)

$2\text{C} \xrightarrow{\text{H}_2\text{O, KI}} 2\text{A} + 2\text{KOH} + \text{D}$

In the above sequence of reactions, A and D, respectively, are:

- (a)  $\text{KI}$  and  $\text{KMnO}_4$  (b)  $\text{MnO}_2$  and  $\text{KIO}_3$   
(c)  $\text{KIO}_3$  and  $\text{MnO}_2$  (d)  $\text{KI}$  and  $\text{K}_2\text{MnO}_4$

Sol. (b)  $\text{MnO}_2 \text{ (A)} \xrightarrow[\text{O}_2]{4\text{KOH}} 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$   
[B]  $\rightarrow$  green

$\text{K}_2\text{MnO}_4 \xrightarrow{4\text{HCl}} 2\text{KMnO}_4 + \text{MnO}_2 + 2\text{H}_2\text{O}$   
[B] [C]  $\rightarrow$  purple

$2\text{KMnO}_4 \xrightarrow[\text{KI}]{\text{H}_2\text{O}} \text{MnO}_2 + \text{KIO}_3 + \text{KOH}$   
[C] [A] [D]

75.  $\text{MnO}_4^-$  can not be decolourised by:

- (a)  $\text{CO}_2$  (b)  $\text{SO}_2$   
(c) Ferrous Ammonium Sulphate (d)  $\text{HCl}$

Sol. (a)  $\text{MnO}_4^-$  can not oxidise  $\text{CO}_2$  because carbon is already in highest oxidation state.

$\text{MnO}_4^-$  can be decolourised by the oxidation reaction of  $\text{SO}_2$ ,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$  and  $\text{HCl}$ .

$\text{SO}_2 \rightarrow \text{SO}_3$   $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$   $\text{HCl} \rightarrow \text{Cl}_2$

76.  $3\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{MnO}_4^- + 4\text{OH}^- + \text{MnO}_2$

To increase % yield of  $\text{MnO}_4^-$ ,  $\text{OH}^-$  can be removed by help of:

- (a)  $\text{HCl}$  (b)  $\text{KOH}$  (c)  $\text{SO}_2$  (d)  $\text{CO}_2$

OR

$\text{KMnO}_4$  can be prepared from  $\text{K}_2\text{MnO}_4$  as per the reaction

$3\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{KMnO}_4 + \text{MnO}_2 + 4\text{OH}^-$

The reaction can go to completion by removing  $\text{OH}^-$  ions by additions:

- (a)  $\text{SO}_2$  (b)  $\text{HCl}$  (c)  $\text{KOH}$  (d)  $\text{CO}_2$

Sol. (d) By adding  $\text{CO}_2$ , the hydroxide ions are removed as  $\text{CO}_2$  reacts with  $\text{OH}^-$  to form carbonate, thereby driving the reaction to completion in favour of producing  $\text{KMnO}_4$ .

Amount of  $\text{MnO}_4^-$  decreases by adding  $\text{SO}_2$  and  $\text{HCl}$ , as we know  $\text{MnO}_4^-$  oxidises  $\text{SO}_2$  and  $\text{HCl}$ .

On adding  $\text{KOH}$ , equilibrium shifts in backward direction. So,  $[\text{MnO}_4^-]$  decreases.

77. For the reaction of  $\text{KMnO}_4$  with ferrous ammonium sulphate in  $\text{H}^+$  medium which of the following acid anion is not used?

- (a)  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$  (b)  $\text{HNO}_3$  (c) Dil.  $\text{H}_2\text{SO}_4$  (d) Conc.  $\text{H}_2\text{SO}_4$

Sol. (c) Volumetric titrations involving  $\text{KMnO}_4$  are carried out only in the presence of dilute  $\text{H}_2\text{SO}_4$  because it provides acidic medium but does not involve in any other reaction either with  $\text{KMnO}_4$  or  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$  [FAS].

$\text{Fe}^{2+} \xrightarrow{\text{HNO}_3} \text{Fe}^{3+}$  [ $\text{HNO}_3$  can not be used because it reduces amount of FAS]

[From FAS]

$\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI} \xrightarrow{\text{KMnO}_4} \text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$

$\text{KMnO}_4 \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{Mn}_2\text{O}_7$

78. When  $\text{KMnO}_4$  solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because:

- (a)  $\text{CO}_2$  is formed as the product (b) Reaction is exothermic  
(c)  $\text{MnO}_4^-$  catalyses the reaction (d)  $\text{Mn}^{2+}$  acts as autocatalyst

Sol. (d) When  $\text{KMnO}_4$  solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because  $\text{Mn}^{2+}$  acts as autocatalyst.

$2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$

End point of this reaction  $\rightarrow$  Colourless to light pink

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79.  $E^\circ_{\text{cell}}$  of reaction of  $\text{KMnO}_4$  with  $\text{H}_2\text{O}$  is +ve, even  $\text{KMnO}_4$  can be used as analytical reagent with  $\text{H}_2\text{O}$ . 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  $E^\circ_{\text{cell}}$ , meaning it takes a very long time to occur at room temperature, allowing for practical use in analysis. This slow reaction rate allows  $\text{KMnO}_4$  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

$$\text{CrO}_4^{2-} \xrightleftharpoons[\text{OH}^-]{\text{H}^+} \text{Cr}_2\text{O}_7^{2-}$$

- Chromate ion
- Yellow Colour
- $\text{Cr}^{6+} : d^0$
- Diamagnetic
- $d^3s$  (Tetrahedral)
- All Cr - O bonds are same due to resonance

- Dichromate ion
- Orange colour
- $\text{Cr}^{6+} : d^0$
- Diamagnetic
- $d^3s$  (tetrahedral)

Terminal Cr-O bond length (x) : Bridged Cr-O bond length (y)

small due to resonance

$\text{K}_2\text{Cr}_2\text{O}_7$  [ORANGE, SOLID]

Preparation of Potassium Dichromate

From Chromite Ore:  $\text{FeCr}_2\text{O}_4$  [ $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ]

$$\text{FeCr}_2\text{O}_4 + \text{Na}_2\text{CO}_3 + \text{O}_2 \rightarrow \text{Na}_2\text{CrO}_4 + \text{CO}_2 \uparrow + \text{Fe}_2\text{O}_3$$

$$\begin{matrix} \text{Na}_2\text{CO}_3 \equiv \text{Na}_2\text{O} \cdot \text{CO}_2 \\ \text{(Basic oxide)} \quad \text{(Acidic oxide)} \\ \text{FeCr}_2\text{O}_4 \equiv \text{FeO} \cdot \text{Cr}_2\text{O}_3 \xrightarrow{\text{O}_2} \text{Fe}_2\text{O}_3 + \text{CrO}_3 \\ \text{(Basic oxide)} \quad \text{(Acidic oxide)} \end{matrix} \rightarrow \text{Na}_2\text{O} + \text{CrO}_3 \rightarrow \text{Na}_2\text{CrO}_4$$

$$\text{Na}_2\text{CrO}_4 \xrightarrow[\text{H}^+]{\text{H}_2\text{SO}_4} \text{Na}_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{KCl}} \text{K}_2\text{Cr}_2\text{O}_7 \text{ (Orange crystals)} + \text{NaCl}$$

$\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{NaCl}$  both are water soluble and hence fractional crystallization is carried out.  $\text{NaCl}$  crystallizes out first and is filtered off. Then  $\text{K}_2\text{Cr}_2\text{O}_7$  is crystallized out further.

Reactions of  $\text{K}_2\text{Cr}_2\text{O}_7$

- $\text{K}_2\text{Cr}_2\text{O}_7$  is a very important chemical in leather industry and in the preparation of azo compounds.
- $\text{K}_2\text{Cr}_2\text{O}_7$  is used as a primary standard in volumetric analysis.
- In acidic medium,  $\text{Cr}_2\text{O}_7^{2-}$  acts as oxidising agent.

$$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad \text{---(i)}$$

$$\begin{aligned} 6\text{I}^- &\rightarrow 3\text{I}_2 + 6\text{e}^- \quad \text{---(ii)} \\ 3\text{H}_2\text{S} &\rightarrow 6\text{H}^+ + 3\text{S} + 6\text{e}^- \quad \text{---(iv)} \\ 3\text{Sn}^{2+} &\rightarrow 3\text{Sn}^{4+} + 6\text{e}^- \quad \text{---(iii)} \\ 6\text{Fe}^{2+} &\rightarrow 6\text{Fe}^{3+} + 6\text{e}^- \quad \text{---(v)} \end{aligned}$$

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)  $\rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- \rightarrow 3\text{I}_2 + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

By equation (i) & (iii)  $\rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 3\text{Sn}^{2+} \rightarrow 3\text{Sn}^{4+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

By equation (i) & (v)  $\rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$

Sodium and potassium dichromates are strong oxidising agents, the sodium salt has a greater solubility in water and is therefore used as an oxidising agent in organic chemistry.

Heating  $\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{Cr}_2\text{O}_3 + \text{K}_2\text{CrO}_4 + \text{O}_2$  (Zero)

Note

$$\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow[\text{Amyl Alcohol}]{\text{H}_2\text{O}_2} \text{CrO}_5$$

$\text{CrO}_5$  : Cr in +6 oxidation state, 2 peroxide bonds, Blue in Colour

Amyl alcohol  $\text{C}_5\text{H}_{11}\text{OH}$  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%  $\text{H}_2\text{O}_2$ , 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)

$$\text{K}_2\text{CrO}_4 \xrightarrow[\text{Amyl Alcohol}]{\text{H}_2\text{O}_2} \text{CrO}_5$$

$\text{CrO}_5$  : Blue colour in amyl alcohol

Chromium (VI) compound 'X'

No. of oxygen atoms bonded to Cr through only single bonds  $\equiv 4$



81.  $\text{Mn}^{2+}$  can be oxidised to  $\text{MnO}_4^-$  by ...  
( $\text{SnO}_2$ ,  $\text{PbO}_2$ ,  $\text{BaO}_2$ )

(IIT JEE 1981)

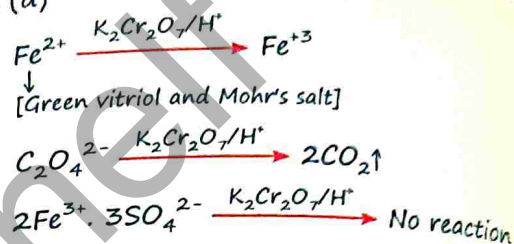
Sol. [Only  $\text{PbO}_2$ ]

- $2\text{Mn}^{2+} + 5\text{PbO}_2 + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + 5\text{Pb}^{2+} + 2\text{H}_2\text{O}$
- $\text{SnO}_2$  can not act as oxidising agent because  $\text{Sn}^{4+}$  is more stable [ $\text{SnO}_2$ ] than  $\text{Sn}^{+2}$  [ $\text{SnO}$ ].
- $\text{BaO}_2 \equiv \text{Ba}^{2+} \cdot \text{O}_2^{2-} \rightarrow$  Peroxide can act as an oxidising agent but not strong enough to oxidise  $\text{Mn}^{+2}$  to  $\text{MnO}_4^-$ .

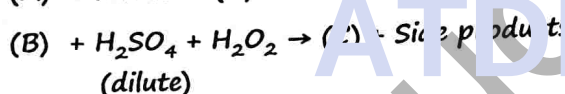
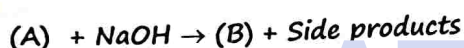
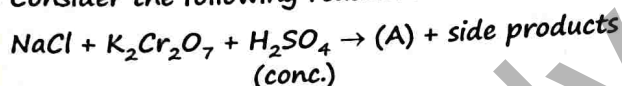
82. Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  can not oxidise:

- (a) Green vitriol  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$   
 (b) Mohr's salt  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$   
 (c) Ferric oxalate  $\text{Fe}_2(\text{C}_2\text{O}_4)_3$   
 (d) Ferric sulphate  $\text{Fe}_2(\text{SO}_4)_3$

Sol. (d)

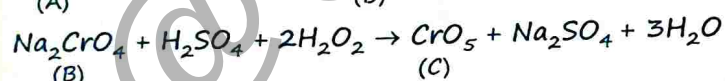
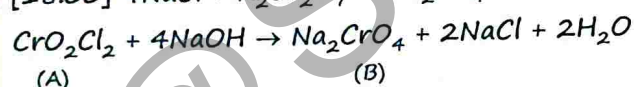
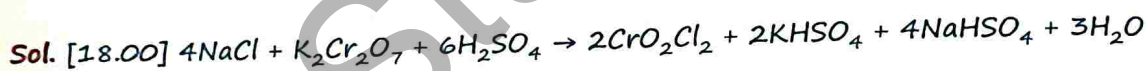


83. Consider the following reactions:



The sum of the total number of atoms in one molecule each of (A), (B) and (C) is \_\_\_\_.

[7 Jan, 2020 (Shift-II)]

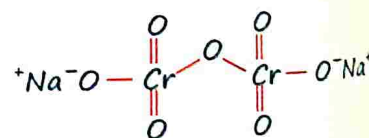
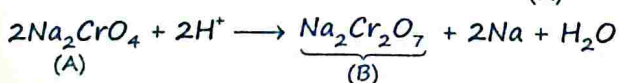
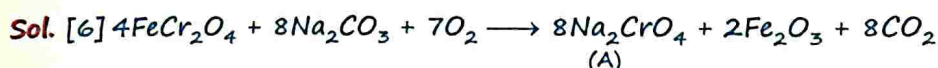
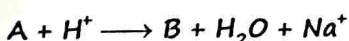
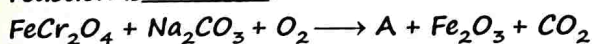


Total no. of atoms in A, B and C =  $5 + 7 + 6 = 18$

(A) =  $\text{CrO}_2\text{Cl}_2$ , (B) =  $\text{Na}_2\text{CrO}_4$ , (C) =  $\text{CrO}_5$

84. The number of terminal oxygen atoms present in the product B obtained from the following reaction is \_\_\_\_.

[29 June, 2022 (Shift-1)]



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

- (a) Green (b) Orange-Red (c) Yellow (d) Blue

Sol. (d) A solution of  $CrO_5$  in amyl alcohol has a blue colour.

87.  $Cr_2O_7^{2-} \xrightleftharpoons[X]{Y} 2CrO_4^{2-}$ , 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)  $Cr_2O_7^{2-} \xrightleftharpoons[H^+]{OH^-} CrO_4^{2-}$

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)  $Cr_2O_7^{2-}$

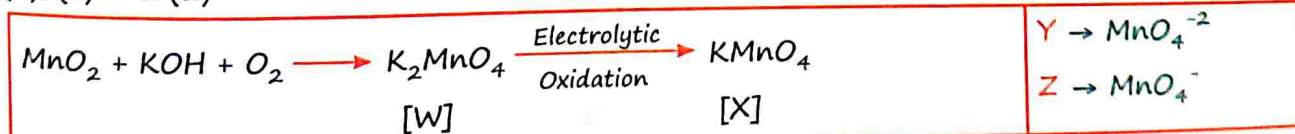
Sol. (d) In  $Cr_2O_7^{2-}$  ion, the two Cr-O bonds which share an oxygen atom at the common vertex of two tetrahedral units are longer than the other six equivalent Cr-O bonds.

### (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,  $\pi$ -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)





## HALIDES OF d-BLOCK ELEMENTS

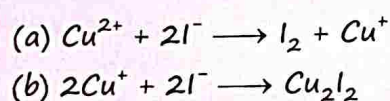
- The ability of F to stabilise the highest oxidation state is due to 2 factors-
  - High lattice energy [in ionic compound –  $\text{CoF}_3$ ]
  - High bond enthalpy [in covalent compound –  $\text{VF}_5$ ,  $\text{CrF}_6$ ]
- The +7 state for Mn is not represented in simple halides ( $\text{MnF}_7$  does not exist but oxohalide of Mn,  $\text{MnO}_3\text{F}$  has +7 oxidation state.)
- Highest Mn fluoride is  $\text{MnF}_4$  whereas the highest oxide is  $\text{Mn}_2\text{O}_7$ .  
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               |                                  |                | $\text{CrF}_6$ |                |                 |                |                |                  |                |  |
| +5               |                                  | $\text{VF}_5$  | $\text{CrF}_5$ |                |                 |                |                |                  |                |  |
| +4               | $\text{TiX}_4$                   | $\text{VX}_4'$ | $\text{CrX}_4$ | $\text{MnF}_4$ |                 |                |                |                  |                |  |
| +3               | $\text{TiX}_3$                   | $\text{VX}_3$  | $\text{CrX}_3$ | $\text{MnF}_3$ | $\text{FeX}_3'$ | $\text{CoF}_3$ |                |                  |                |  |
| +2               | $\text{TiX}_2''$                 | $\text{VX}_2$  | $\text{CrX}_2$ | $\text{MnX}_2$ | $\text{FeX}_2$  | $\text{CoX}_2$ | $\text{NiX}_2$ | $\text{CuX}_2''$ | $\text{ZnX}_2$ |  |
| +1               |                                  |                |                |                |                 |                |                | $\text{CuX}''$   |                |  |

Key:  $\text{X} = \text{F} \rightarrow \text{I}$ ;  $\text{X}' = \text{F} \rightarrow \text{Br}$ ;  $\text{X}'' = \text{F}, \text{Cl}$ ;  $\text{X}''' = \text{Cl} \rightarrow$

- $\text{V}^{+5}$  is represented only by  $\text{VF}_5$ . The other halides, however, undergo hydrolysis to give oxohalides  $\text{VOY}_3$ , ( $\text{Y} = \text{Cl}, \text{Br}, \text{I}$ ).  

$$\text{VCl}_5 (\text{unstable}) \xrightarrow{\text{moist}} \text{VOCl}_3 + 2\text{HCl}$$
- Another feature of fluorides is their instability in the low oxidation states  $\text{VY}_2$  ( $\text{Y} = \text{Cl}, \text{Br}, \text{or I}$ ).
- All Cu(II) halides are known except the iodide because  $\text{Cu}^{2+}$  oxidises  $\text{I}^-$  to  $\text{I}_2$ .  $\text{CuF}_2$ ,  $\text{CuCl}_2$  &  $\text{CuBr}_2$  exist but  $\text{CuI}_2$  does not exist because-



- Many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.



- Hydration Energy :  $\text{Cu}^{2+} > \text{Cu}^+$
- $[\text{Hydration Energy}]_{\text{Cu}^{2+}} \gg [\text{Second ionisation energy}]_{\text{Cu}}$

The stability of  $\text{Cu}^{2+}_{(\text{aq})}$  rather than  $\text{Cu}^+_{(\text{aq})}$  is due to the much more negative  $\Delta H_{\text{hyd}}$  of  $\text{Cu}^{2+}_{(\text{aq})}$  than  $\text{Cu}^+$ , which more than compensates for the second ionisation enthalpy of Cu.

90. When  $\text{Cu}^{2+}$  ion is treated with KI, a white precipitate is formed. Explain the reaction with the help of a chemical equation.

Sol. Reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  takes place due to reaction with  $\text{I}^-$  ion.



91. Out of  $\text{Cu}_2\text{Cl}_2$  and  $\text{CuCl}_2$ , which is more stable and why?

Sol.  $\text{CuCl}_2$  is more stable than  $\text{Cu}_2\text{Cl}_2$ . The stability of  $\text{CuCl}_2$  is because of higher enthalpy of hydration of  $\text{Cu}^{2+}(\text{aq})$  than that of  $\text{Cu}^+(\text{aq})$ .

92.  $\text{Cu}^{2+}$  salt reacts with potassium iodide to give

(2021/20 July)

- (a)  $\text{Cu}_2\text{I}_2$  (b)  $\text{Cu}_2\text{I}_3$  (c)  $\text{CuI}$  (d)  $\text{Cu}(\text{I}_3)_2$

Sol. (a)  $\text{Cu}^{2+} + 2\text{KI} \longrightarrow \underset{\text{Unstable}}{\text{CuI}_2\downarrow} + 2\text{K}^+$

$\text{I}^-$  is strong R.A. It reduces  $\text{Cu}^{2+}$  to  $\text{Cu}^+$   
 $2\text{CuI}_2 \longrightarrow \text{Cu}_2\text{I}_2\downarrow + \text{I}_2$

93. The stability of  $\text{Cu}^{2+}$  is more than  $\text{Cu}^+$  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 10 oxides which are ionic.  
 B. The highest oxidation number corresponding to the group number in transition metal oxides is attained in  $\text{Sc}_2\text{O}_3$  to  $\text{Mn}_2\text{O}_7$ .  
 C. Basic character increases from  $\text{V}_2\text{O}_3$  to  $\text{V}_2\text{O}_4$  to  $\text{V}_2\text{O}_5$ .  
 D.  $\text{V}_2\text{O}_4$  dissolves in acids to give  $\text{VO}_4^{3-}$  salts.  
 E.  $\text{CrO}$  is basic but  $\text{Cr}_2\text{O}_3$  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,  $\text{KMnO}_4$  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  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are not the same.  
 (d)  $\text{Cr}^{2+}(\text{d}^4)$  is a stronger reducing agent than  $\text{Fe}^{2+}(\text{d}^6)$  in water.

Sol. (c)

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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)  $\text{CrO}_4^{2-}$
- (b)  $\text{Cr}_2\text{O}_7^{2-}$
- (c)  $\text{MnO}_4^{2-}$
- (d)  $\text{MnO}_4^-$

Sol. (c)

99. Name the gas that can readily decolourise acidified  $\text{KMnO}_4$  solution:

[NEET 2017-Delhi]

- (a)  $\text{P}_2\text{O}_5$
- (b)  $\text{CO}_2$
- (c)  $\text{SO}_2$
- (d)  $\text{NO}_2$

Sol. (c)

100. Which one of the following statements is correct when  $\text{SO}_2$  is passed through acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution? [NEET 2016-I]

- (a)  $\text{SO}_2$  is reduced
- (b) Green  $\text{Cr}_2(\text{SO}_4)_3$  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  $\text{KMnO}_4$  for complete oxidation? [NEET 2015 Re]

- (a)  $\text{Fe}(\text{NO}_2)_2$
- (b)  $\text{FeSO}_4$
- (c)  $\text{FeSO}_3$
- (d)  $\text{FeC}_2\text{O}_4$

Sol. (b)

102. Which of the statements is not true?

[NEET 2012 Re]

- (a)  $\text{K}_2\text{Cr}_2\text{O}_7$  solution becomes yellow on increasing the pH beyond 7
- (b) On passing  $\text{H}_2\text{S}$  through acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, a milky colour is observed
- (c)  $\text{Na}_2\text{Cr}_2\text{O}_7$  is preferred over  $\text{K}_2\text{Cr}_2\text{O}_7$  in volumetric analysis
- (d)  $\text{K}_2\text{Cr}_2\text{O}_7$  solution in acidic medium is orange

Sol. (c)

103. Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution turns green when  $\text{Na}_2\text{SO}_3$  is added to it. This is due to the formation of:

[NEET 2011 Pre]

- (a)  $\text{CrSO}_4$
- (b)  $\text{Cr}_2(\text{SO}_4)_3$
- (c)  $\text{CrO}_4^{2-}$
- (d)  $\text{Cr}_2(\text{SO}_3)_3$

Sol. (b)

104. The number of moles of  $\text{KMnO}_4$  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  $\text{KMnO}_4$  reduced by one mole of  $\text{KI}$  in alkaline medium is: [NEET 2005]

- (a)  $2/5$
- (b) 5
- (c) 1
- (d) 2

Sol. (d)

## f-BLOCK ELEMENT

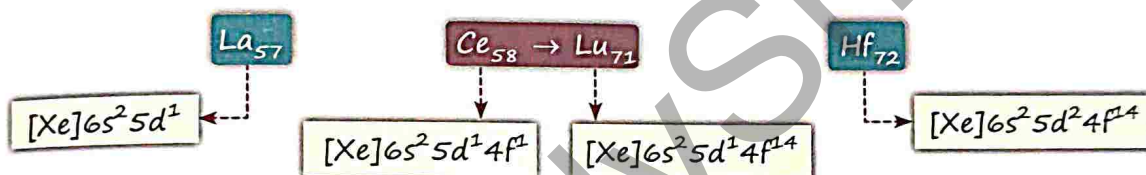
The f-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium).

|             |                  |    |    |    |    |    |    |    |    |    |    |    |    |                   |
|-------------|------------------|----|----|----|----|----|----|----|----|----|----|----|----|-------------------|
| Lanthanoids | Ce <sub>58</sub> | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu <sub>71</sub>  |
| Actinoids   | Th <sub>90</sub> | Pa | U  | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr <sub>103</sub> |

- 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



| Atomic Number | Name         | Symbol | 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

1<sup>st</sup> element  $\rightarrow$  Ce:  $[\text{Xe}] 4f^1 5d^1 6s^2$   
 7<sup>th</sup> element  $\rightarrow$  Gd:  $[\text{Xe}] 4f^7 5d^1 6s^2$   
 14<sup>th</sup> element  $\rightarrow$  Lu:  $[\text{Xe}] 4f^{14} 5d^1 6s^2$

- 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  $\text{Ho}^{3+}$  ion is \_\_\_\_\_. (Given atomic number of Ho = 67)  
Sol. [10]  ${}_{67}\text{Ho} = [\text{Xe}] 4f^{11} 6s^2$   $\text{Ho}^{3+} = [\text{Xe}] 4f^{10} 6s^0$
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)
- | Element | Atomic Number | Ground State Configuration   |
|---------|---------------|------------------------------|
| Sm      | 62            | $[\text{Xe}] 4f^6 6s^2$      |
| Eu      | 63            | $[\text{Xe}] 4f^7 6s^2$      |
| Tb      | 65            | $[\text{Xe}] 4f^9 6s^2$      |
| Gd      | 64            | $[\text{Xe}] 4f^7 5d^1 6s^2$ |
108. The electronic configurations of bivalent europium and trivalent cerium are: (atomic number: Xe = 54, Ce = 58, Eu = 63)  
(a)  $[\text{Xe}] 4f^2$  and  $[\text{Xe}] 4f^7$  (b)  $[\text{Xe}] 4f^7$  and  $[\text{Xe}] 4f^2$   
(c)  $[\text{Xe}] 4f^7 6s^2$  and  $[\text{Xe}] 4f^2 6s^2$  (d)  $[\text{Xe}] 4f^4$  and  $[\text{Xe}] 4f^9$   
Sol. (b) Eu  $\rightarrow [\text{Xe}] 6s^2 4f^7$   $\text{Eu}^{2+} \rightarrow [\text{Xe}] 4f^7$   
Ce  $\rightarrow [\text{Xe}] 6s^2 5d^1 4f^1$   $\text{Ce}^{3+} \rightarrow [\text{Xe}] 4f^1$

### Oxidation State

- Lanthanoids generally show +3 oxidation state.
  - $\text{Yb}^{2+}$  and  $\text{Eu}^{2+}$  are reducing agent but  $\text{Ce}^{4+}$  is an oxidising agent because they convert themselves into higher oxidation state (+3) of lanthanides.
- | Reducing Agent                                                     | Oxidising Agent                                                    |
|--------------------------------------------------------------------|--------------------------------------------------------------------|
| (a) $\text{Yb}^{2+} \xrightarrow{\text{oxidation}} \text{Yb}^{3+}$ | (a) $\text{Ce}^{4+} \xrightarrow{\text{reduction}} \text{Ce}^{3+}$ |
| (b) $\text{Eu}^{2+} \xrightarrow{\text{oxidation}} \text{Eu}^{3+}$ | (b) $\text{Tb}^{4+} \xrightarrow{\text{reduction}} \text{Tb}^{3+}$ |
- $E^\circ$  value for  $\text{Ce}^{4+}/\text{Ce}^{3+}$  is 1.74 V which suggests that  $\text{Ce}^{4+}$  can oxidise water ( $\text{H}_2\text{O} \rightarrow \text{O}_2$ ) but this reaction is very slow and hence  $\text{Ce(IV)}$  is a good analytical reagent (a kind of chemical reagent used for analysis and testing).
  - In organic chemistry, we use  $\text{Ce(IV)}$  reagent (ceric ammonium nitrate) to test presence of alcoholic group ( $-\text{OH}$ ).
  - Metal having +4 oxidation state in their oxides ( $\text{MO}_2$ ) 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  $\text{Ce}^{4+}$  is favoured by its noble gas configuration.  
Statement-II:  $\text{Ce}^{4+}$  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)

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- Strong reducing and oxidizing agents among the following, respectively, are  
(a)  $\text{Ce}^{4+}$  and  $\text{Eu}^{2+}$  (b)  $\text{Ce}^{4+}$  and  $\text{Tb}^{4+}$   
(c)  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  (d)  $\text{Eu}^{2+}$  and  $\text{Ce}^{4+}$  [6 April, 2023 (Shift-I)]

### Magnetic Properties

- $f^0$  Type  $[\text{La}^{3+}, \text{Ce}^{4+}]$ : Diamagnetic (because all electrons are paired)  
 $f^{14}$  Type  $[\text{Lu}^{3+}, \text{Yb}^{2+}]$ : Diamagnetic (because all electrons are paired)  
 $f^1$  to  $f^{13}$   $[\text{Ln}^{3+}]$ : 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.  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$  B.  $\text{Gd}(\text{NO}_3)_3$  and C.  $\text{Eu}(\text{NO}_3)_3$

Answer is:

- (a) (A) < (C) < (B) (b) (B) < (A) < (C) (c) (C) < (A) < (B) (d) (A) < (B) < (C)

- Sol. (a) In  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6] \rightarrow \text{Ce}^{4+} \Rightarrow 4f^0 \Rightarrow n = 0$   
 $\text{Eu}(\text{NO}_3)_3 \rightarrow \text{Eu}^{3+} \Rightarrow 4f^6 \Rightarrow n = 6$   
 $\text{Gd}(\text{NO}_3)_3 \rightarrow \text{Gd}^{3+} \Rightarrow 4f^7 \Rightarrow n = 7$

The complex with higher number of unpaired electrons has high magnetic moment.

### Colour

- Many trivalent lanthanoid ions  $\text{Ln}^{3+}$  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  $f^0$  and  $f^{14}$  type of ion do not show any colour because f-f transition is not possible in this case.

- $f^0$  Type  $[\text{La}^{3+}, \text{Ce}^{4+}]$ : colourless  
 $f^{14}$  Type  $[\text{Lu}^{3+}, \text{Yb}^{2+}]$ : 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)]  
 $\text{Eu}^{3+}, \text{Lu}^{3+}, \text{Nd}^{3+}, \text{La}^{3+}, \text{Sm}^{3+}$

Sol. [2] Colour arises due to the presence of unpaired electrons.

$\text{La}^{3+} - [\text{Xe}] 4f^0, \text{Sm}^{3+} - [\text{Xe}] 4f^5, \text{Lu}^{3+} - [\text{Xe}] 4f^{14}, \text{Nd}^{3+} - [\text{Xe}] 4f^3, \text{Eu}^{3+} - [\text{Xe}] 4f^6$   
Hence,  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$  do not show any colour because unpaired electron are absent in them.

113. Which one of the following lanthanoids does not form  $\text{MO}_2$ ? (2021/26 Feb)

[M is lanthanoid metal]

- (a) Nd (b) Dy (c) Yb (d) Pr

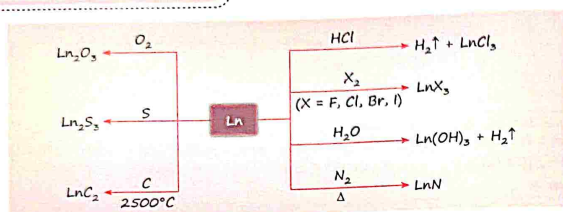
Sol. (c) Yb is the element that do not form  $\text{MO}_2$  type oxide

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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  $\text{Ln}_2\text{O}_3$  and hydroxide  $\text{Ln}(\text{OH})_3$  and both are basic like alkaline earth metal (such as Ca) oxides and hydroxides.

On moving from left to right, basicity of lanthanoid hydroxide decreases.

Basicity:  $\text{La}(\text{OH})_3 > \text{Ce}(\text{OH})_3 > \dots > \text{Lu}(\text{OH})_3$

Size:  $\text{La}^{3+} > \text{Ce}^{3+} > \dots > \text{Lu}^{3+}$

Bigger cation has less polarising power so it has more ionic character in  $\text{La}-\text{OH}$  bond. Hence more basic.

Smaller cation has more polarising power so it has more covalent character in  $\text{Lu}-\text{OH}$  bond. Hence least basic.

Basic nature gradually decreases from  $\text{Ce}(\text{OH})_3$  to  $\text{Lu}(\text{OH})_3$ , due to high polarisation caused by gradual decrease in size  $\text{M}^{3+}$  ion. The hydroxides of lanthanoids  $\text{Ln}(\text{OH})_3$  are less basic than  $\text{Ca}(\text{OH})_2$  and more basic than  $\text{Al}(\text{OH})_3$ .

The first ionisation enthalpies of the lanthanoids are around  $600 \text{ kJ mol}^{-2}$ , the second about  $1200 \text{ kJ mol}^{-2}$  comparable with those of calcium.

$3^{\text{rd}}$  ionisation enthalpy of La, Gd, Lu is low.

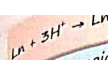
Because  $\text{La}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Lu}^{3+}$  have stable electronic configuration  $4f^0$ ,  $4f^7$  and  $4f^{14}$  respectively.



$1^{\text{st}}$  and  $11^{\text{th}}$  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.

$E_{\text{Ln}^{3+}/\text{Ln}^{2+}}^{\circ}$  values are in range of  $-2.2$  to  $-2.4 \text{ V}$  except for Eu ( $E_{\text{Eu}^{3+}/\text{Eu}^{2+}}^{\circ} = 2.0 \text{ V}$ )



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 ( $\sim 95\%$ ) and iron ( $\sim 5\%$ ) and traces of S, C, Ca and Al.

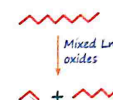
An unseparated mixture of La and the lanthanoids called Misch metal is added to steel to improve its strength and workability. It is pyrophoric and also used in gas lighters.

#### Mischmetal & Mg based alloy



Individual Ln Oxide  $\rightarrow$  As phosphors

#### Petroleum Cracking



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.  $\text{W(VI)}$  is more stable than  $\text{Cr(VI)}$ .

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)

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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)  $\rightarrow$  (b), (ii)  $\rightarrow$  (a), (iii)  $\rightarrow$  (d), (iv)  $\rightarrow$  (e), (v)  $\rightarrow$  (c)

117. Which one amongst the following are good oxidising agents?  
(A)  $\text{Sm}^{2+}$  (B)  $\text{Ce}^{2+}$  (C)  $\text{Ce}^{4+}$  (D)  $\text{Tb}^{4+}$

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)  $\text{Ce}^{4+}$  and  $\text{Tb}^{4+}$  ions are good oxidising agents.

118. Select reducing agent from  $\text{Eu}^{+2}$ ,  $\text{Yb}^{+2}$ ,  $\text{Ce}^{+4}$ ,  $\text{Mn}^{+2}$ ,  $\text{Cr}^{+2}$ ,  $\text{M}^{+3}$ .  
(a)  $\text{Mn}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Eu}^{2+}$  (b)  $\text{Eu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{2+}$   
(c)  $\text{Cr}^{3+}$ ,  $\text{Eu}^{2+}$ ,  $\text{Yb}^{2+}$  (d)  $\text{Cu}^{+}$ ,  $\text{Yb}^{2+}$ ,  $\text{M}^{3+}$

Sol. (b) Reducing agents are species that readily donate electrons. In the given list,  $\text{Eu}^{2+}$  and  $\text{Yb}^{2+}$  are well-known strong reducing agents because they easily oxidize to their +3 states. Similarly,  $\text{Cr}^{2+}$  is a strong reducing agent, as it tends to be oxidized to  $\text{Cr}^{3+}$ .

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

$\text{Ac}_{89}$   
 $[\text{Rn}]7s^2 6d^2$

$\text{Th}_{90} \rightarrow \text{Lr}_{103}$   
 $[\text{Rn}]7s^2 6d^2$

$\text{Rf}_{104}$   
 $[\text{Rn}]7s^2 6d^2 5f^{14}$

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| Atomic Number | Name         | Symbol | Electronic Configuration |
|---------------|--------------|--------|--------------------------|
| 90            | Thorium      | Th     | $6d^2 7s^2$              |
| 91            | Protactinium | Pa     | $5f^2 6d^1 7s^2$         |
| 92            | Uranium      | U      | $5f^3 6d^1 7s^2$         |
| 93            | Neptunium    | Np     | $5f^4 6d^1 7s^2$         |
| 94            | Plutonium    | Pu     | $5f^6 7s^2$              |
| 95            | Americium    | Am     | $5f^7 7s^2$              |
| 96            | Curium       | Cm     | $5f^7 6d^1 7s^2$         |
| 97            | Berkelium    | Bk     | $5f^9 7s^2$              |
| 98            | Californium  | Cf     | $5f^{10} 7s^2$           |
| 99            | Einsteinium  | 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     | $5f^{14} 6d^1 7s^2$      |

Uranium is the heaviest naturally occurring element.

After uranium, 12 new elements have been artificially synthesized (having atomic number more than 92) and are sometimes 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  $\text{M}^{3+}$  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.

Radial 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.

The d- and f- Block Elements

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## 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:

(10<sup>th</sup> 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:

(09<sup>th</sup> 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)  $\text{Lu}^{3+}$  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.

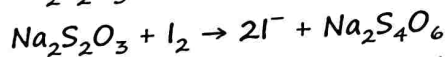
Sol. (d) Nd is a lanthanide (f-block) and Np is an actinide (f-block), but Nb (niobium) is a d-block element, making option (d) incorrect.

(JEE Adv. 2014)

125. Consider the following list of reagents, acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ , alkaline  $\text{KMnO}_4$ ,  $\text{CuSO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_3$ ,  $\text{FeCl}_3$ ,  $\text{HNO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$ . The total number of reagents that can oxidise aqueous iodide to iodine is

Sol. (7)

- Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CuSO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_3$ ,  $\text{FeCl}_3$  and  $\text{HNO}_3$  oxidise aq. iodide to iodine.
- Alkaline  $\text{KMnO}_4$  oxidise aq. iodide to  $\text{IO}_3^-$ .
- $\text{Na}_2\text{S}_2\text{O}_3$  is a strong reducing agent which on reaction with  $\text{I}_2$  produces  $\text{I}^-$

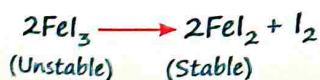


Therefore, no reaction takes place between  $\text{Na}_2\text{S}_2\text{O}_3$  and iodide ion.

126.  $\text{Fe}_x$  and  $\text{Fe}_y$  are known when x and y are

- (a)  $x = \text{F, Cl, Br, I}$  and  $y = \text{F, Cl, Br}$  (b)  $x = \text{Cl, Br, I}$  and  $y = \text{F, Cl, Br, I}$   
(c)  $x = \text{F, Cl, Br, I}$  and  $y = \text{F, Cl, Br, I}$  (d)  $x = \text{F, Cl, Br}$  and  $y = \text{F, Cl, Br, I}$

Sol. (a)



Due to strong reducing nature of  $\text{I}^-$



Remaining halides of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are stable.

[NEET 2020-Covid]

127. Match the following aspects with the respective metal.

| 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.       | $\text{Co}^{3+}$ | i.        | 8 B.M           |
| B.       | $\text{Cr}^{3+}$ | ii.       | $\sqrt{35}$ B.M |
| C.       | $\text{Fe}^{3+}$ | iii.      | $\sqrt{3}$ B.M  |
| D.       | $\text{Ni}^{2+}$ | 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  $\text{CuSO}_4$  solution by iron  
 (b) Formation of  $\text{Fe}(\text{CO})_5$  from Fe  
 (c) Liberation of  $\text{H}_2$  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 2<sup>nd</sup> 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<br>(Block/group in periodic table) |                 | List-II<br>(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  
(c) A-I, B-IV, C-II, D-III

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

- (a) high basic character (b) small size  
(c) high exchange enthalpy (d) high electronegativity

[NEET 2022]

Sol. (c)

141. The incorrect statement among the following is:

- (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

[NEET 2021]

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  $[Xe]4f^7 6s^2$
- (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-Rs]

- (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)

[NEET 2014]

148. Reason of lanthanoid contraction is:

- (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)

[NEET 2012 Mains]

150. Which of the following exhibits only +3 oxidation state?

- (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)



# Salt Analysis

Syllabus

JEE Main & NEET

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



### 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 $\uparrow$

$A + B \rightleftharpoons C + D$   
 (Soluble) (Soluble)

$K_{sp}$  of A >  $K_{sp}$  of C  $\rightarrow$  Then equilibrium shifts in forward direction.

$K_{sp}$  of C >  $K_{sp}$  of A  $\rightarrow$  Backward reaction is favourable.

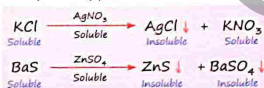
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|                                        |                                                                                                                                                                                       |
|----------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{CO}_3^{2-}/\text{SO}_3^{2-}$    | All are water insoluble $\rightarrow$ $\text{NH}_4^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$ carbonates are water soluble                                                 |
| $\text{HCO}_3^-/\text{HSO}_3^-$        | All are water soluble $\rightarrow$ $\text{NaHCO}_3$ is sparingly soluble                                                                                                             |
| $\text{SO}_4^{2-}$                     | All are water soluble $\rightarrow$ $\text{Ag}^+, \text{Hg}_2^{2+}, \text{Pb}^{2+}, \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}$ sulphates are water insoluble                     |
| $\text{NO}_3^-/\text{NO}_2^-$          | All are water soluble $\rightarrow$ $\text{AgNO}_2$ is water insoluble                                                                                                                |
| $\text{OH}^-$                          | All are water insoluble $\rightarrow$ $\text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+, \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}$ hydroxides are water soluble |
| $\text{NH}_4^+$                        | All are water soluble                                                                                                                                                                 |
| $\text{Cl}^-, \text{Br}^-, \text{I}^-$ | All are water soluble $\rightarrow$ $\text{Ag}^+, \text{Hg}_2^{2+}, \text{Pb}^{2+}$ halides are water insoluble $[\text{HgI}_2, \text{BiI}_3 : \text{Insoluble}]$                     |
| $\text{S}^{2-}$                        | All are water insoluble $\rightarrow$ $\text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}, \text{NH}_4^+$ sulphides are water soluble  |
| $\text{CH}_3\text{COO}^-$              | All are water soluble $\rightarrow$ $\text{Ag}^+, \text{Hg}_2^{2+}, \text{Cu}^+$ acetates are slightly soluble in water                                                               |

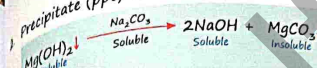
|                                            |                                     |                                          |
|--------------------------------------------|-------------------------------------|------------------------------------------|
| $\text{CuS} \times$ (Insoluble)            | $\text{Ca(OH)}_2 \checkmark$        | $\text{Pb(CH}_3\text{COO)}_2 \checkmark$ |
| $\text{NiS} \times$                        | $\text{Fe(OH)}_3 \times$            | $\text{BaCl}_2 \checkmark$               |
| $\text{PbS} \times$                        | $\text{PbSO}_4 \times$              | $\text{CuSO}_4 \checkmark$               |
| $\text{Na}_2\text{S} \checkmark$ (Soluble) | $\text{Al(OH)}_3 \times$            | $\text{ZnCl}_2 \checkmark$               |
| $(\text{NH}_4)_2\text{S} \checkmark$       | $\text{Mg(OH)}_2 \times$            | $\text{Na}_2\text{SO}_4 \checkmark$      |
| $\text{KNO}_2 \checkmark$                  | $\text{Pb(OH)}_2 \times$            | $\text{CaCl}_2 \checkmark$               |
| $\text{NaNO}_3 \checkmark$                 | $\text{Cr(OH)}_3 \times$            | $\text{Ag}_2\text{SO}_4 \times$          |
| $\text{Hg}_2\text{Cl}_2 \times$            | $\text{Na}_2\text{SO}_3 \checkmark$ | $\text{Hg}_2\text{Cl}_2 \times$          |
| $\text{CaCO}_3 \times$                     | $\text{Ba(OH)}_2 \checkmark$        | $\text{BaSO}_4 \times$                   |
| $\text{AgNO}_3 \checkmark$                 | $\text{NH}_4\text{OH} \checkmark$   | $\text{HgI}_2 \times$                    |
| $\text{Pb(NO}_3)_2 \checkmark$             | $\text{CaSO}_4 \times$              | $\text{MgCO}_3 \times$                   |

## TYPE OF REACTIONS

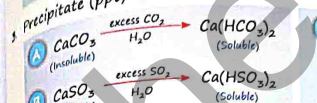
### 1. Precipitate (ppt) formation



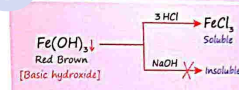
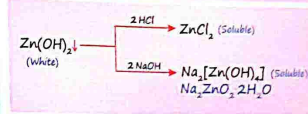
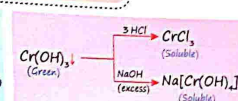
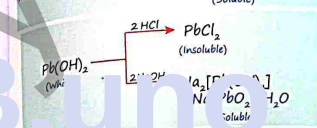
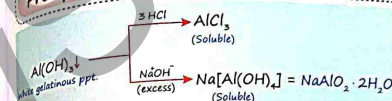
### Precipitate (ppt) Exchange



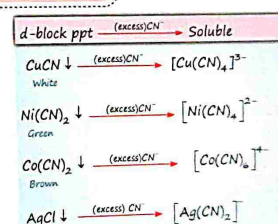
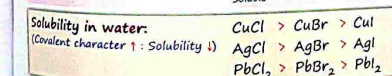
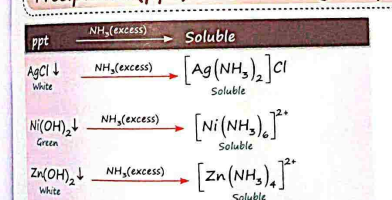
### Precipitate (ppt) dissolution



### Precipitate (ppt) Dissolution by Acid-Base Reaction



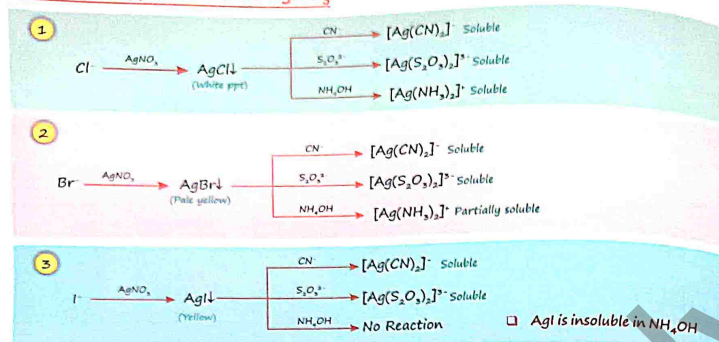
### Precipitate (ppt) Dissolution by Complex Formation



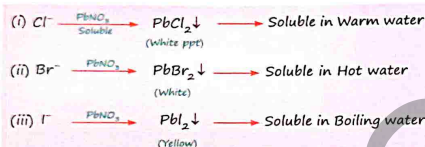
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### Precipitate (ppt) test with $\text{AgNO}_3$



### Precipitate (ppt) (with $\text{PbNO}_3$ )



Solubility in water:  $\text{PbI}_2 > \text{PbBr}_2 > \text{PbCl}_2$

more ionic character  $\rightarrow$  more soluble in water

more covalent character  $\rightarrow$  less soluble in water

1. Assertion: Sulphate is estimated as  $\text{BaSO}_4$  and not as  $\text{MgSO}_4$ .

Reason: Ionic radius of  $\text{Mg}^{2+}$  is smaller than that of  $\text{Ba}^{2+}$ .

(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  $\text{BaSO}_4$  because it is insoluble in water. But not as  $\text{MgSO}_4$  because  $\text{MgSO}_4$  is soluble in water.

2. The species present in solution when  $\text{CO}_2$  is dissolved in water are: (JEE 2016)

(a)  $\text{CO}_2, \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CO}_3^{2-}$

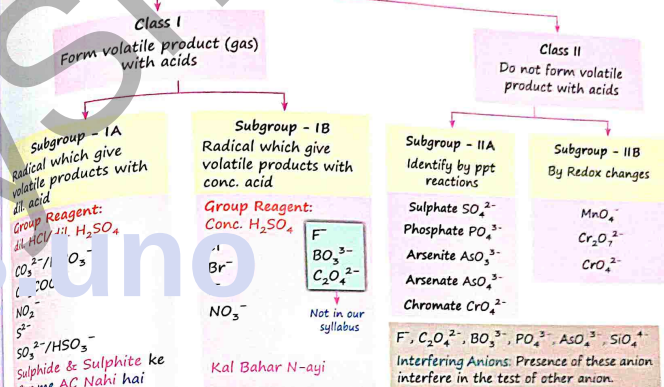
(b)  $\text{HCO}_3^-, \text{CO}_3^{2-}$

(c)  $\text{CO}_3^{2-}, \text{HCO}_3^-, \text{CO}_2$

(d)  $\text{CO}_2, \text{H}_2\text{CO}_3$



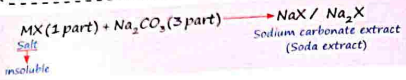
### Classification of Anions



| Observation                                                                                                                                                                                                                                                                  | Ions                                                                                                               |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|
| (i) Colourless and odourless gas with brisk effervescence $\text{CO}_2$                                                                                                                                                                                                      | $\text{CO}_3^{2-}$                                                                                                 |
| (ii) Colourless gas with odour $\text{H}_2\text{S}$ gas - Smells like rotten eggs<br>$\text{SO}_2$ gas - Suffocating smell of burning of sulphur<br>$\text{HCl}$ gas - Pungent smell<br>Acetic acid vapours - vinegar like smell<br>$\text{NH}_3$ gas - Characteristic smell | $\text{S}^{2-}$<br>$\text{SO}_3^{2-}$<br>$\text{Cl}^-$<br>$\text{CH}_3\text{COO}^-$<br>$\text{NH}_4^+/\text{NH}_3$ |
| (iii) Coloured gases - Pungent smell<br>$\text{NO}_2$ gas - Reddish brown<br>$\text{Cl}_2$ gas - Greenish yellow<br>$\text{Br}_2$ vapour - Reddish brown<br>$\text{I}_2$ vapours - Dark violet                                                                               | $\text{NO}_2^-$ or $\text{NO}_3^-$<br>$\text{Cl}^-$<br>$\text{Br}^-$<br>$\text{I}^-$                               |

Salt Analysis

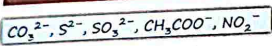
## SODIUM CARBONATE EXTRACT



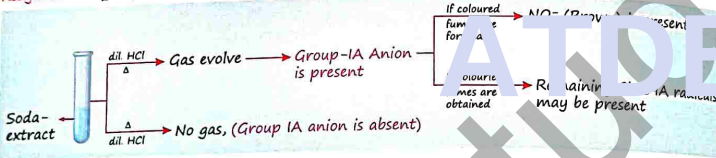
### Note

- If the given salt is insoluble in H<sub>2</sub>O, we add Na<sub>2</sub>CO<sub>3</sub> in the salt to get soda extract.
- Almost all sodium salts are water soluble. Na<sup>+</sup> displaces the cation of the salt to obtain soluble salt solution.
- Soda extract → Basic in nature (neutralise by small amount of acid like CH<sub>3</sub>COOH)
- We cannot use soda extract to identify CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> ion because CO<sub>3</sub><sup>2-</sup> ion is already present in soda extract.

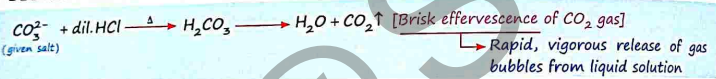
## TEST FOR GROUP-1A ANION



Reagent: dil. H<sub>2</sub>SO<sub>4</sub>/dil. HCl

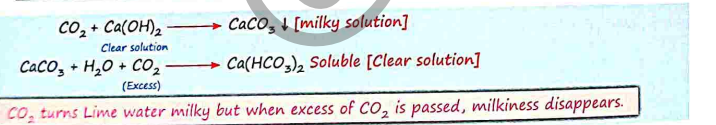


## TEST FOR CO<sub>3</sub><sup>2-</sup>

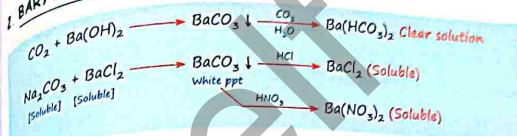


### Confirmatory Test

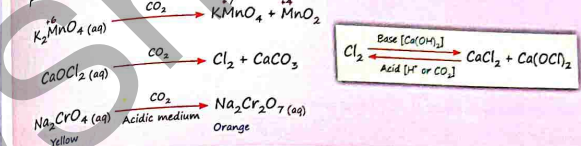
#### 1. LIME WATER [Ca(OH)<sub>2</sub>] TEST



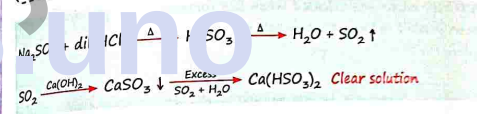
## BARYTA WATER [Ba(OH)<sub>2</sub>] TEST



CO<sub>2</sub> does not show redox reaction as it has maximum oxidation state (+4) of carbon but can provide acidic medium for many reactions:

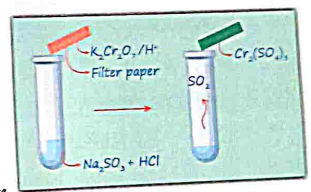
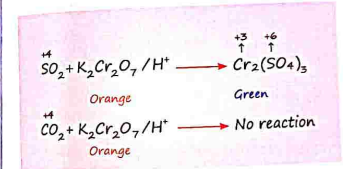


## TEST FOR SO<sub>3</sub><sup>2-</sup>

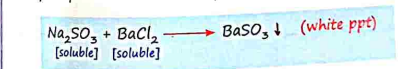


### Confirmatory Test:

1. The filter paper dipped in acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> turns green.



2. Sodium carbonate extract of the salt produces a white precipitate of barium sulphite on addition of barium chloride solution.





(i) This precipitate on treatment with dilute HCl, dissolves due to decomposition of sulphite by dilute HCl.

$$\text{BaSO}_3 \downarrow + 2\text{HCl} \rightarrow \text{BaCl}_2 + \text{H}_2\text{SO}_3 \rightarrow \text{H}_2\text{O} + \text{SO}_2 \uparrow$$

(ii) Precipitate of sulphite decolourises acidified  $\text{KMnO}_4$  solution (purple).

$$\text{BaSO}_3 \downarrow \xrightarrow[\text{Colourless}]{\text{KMnO}_4/\text{H}^+} \text{BaSO}_4 \downarrow$$

3. On treating a compound with warm dil.  $\text{H}_2\text{SO}_4$ , gas X is evolved which turns  $\text{K}_2\text{Cr}_2\text{O}_7$  paper acidified with dil.  $\text{H}_2\text{SO}_4$  to a green compound Y. X and Y respectively are: (JEE Mains 2021)

(a)  $\text{X} = \text{SO}_2$ ,  $\text{Y} = \text{Cr}_2\text{O}_3$  (b)  $\text{X} = \text{SO}_3$ ,  $\text{Y} = \text{Cr}_2\text{O}_3$   
 (c)  $\text{X} = \text{SO}_2$ ,  $\text{Y} = \text{Cr}_2(\text{SO}_4)_3$  (d)  $\text{X} = \text{SO}_3$ ,  $\text{Y} = \text{Cr}_2(\text{SO}_4)_3$

Sol. (c)

4.  $\text{K}_2\text{Cr}_2\text{O}_7$  paper acidified with dilute  $\text{H}_2\text{SO}_4$  turns green when exposed to (JEE Mains 2023)

(a) Hydrogen sulphide (b) Carbon dioxide  
 (c) Sulphur dioxide (d) Sulphur trioxide

5. A white precipitate was formed when  $\text{BaCl}_2$  was added to an extract of an inorganic salt. Further, a gas 'X' with characteristic odour was released when the white precipitate was dissolved in dilute HCl. The anion present in the inorganic salt is (JEE Mains 2021)

(a)  $\text{I}^-$  (b)  $\text{SO}_3^{2-}$  (c)  $\text{S}^{2-}$  (d)  $\text{NO}_2^-$

Sol. (b)

$$\text{BaCl}_2 + \text{SO}_3^{2-} \rightarrow \text{BaSO}_3 \downarrow \xrightarrow[\text{white}]{\text{dil. HCl}} \text{SO}_2 \uparrow \text{ (Burning sulphur like smell)}$$

6.  $[\text{X}] + \text{H}_2\text{SO}_4 \rightarrow [\text{Y}]$  a colourless gas with irritating smell  
 $[\text{Y}] + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{green solution}$ ; [X] and [Y] are (JEE Adv. 2003)

(a)  $\text{SO}_3^{2-}$ ,  $\text{SO}_2$  (b)  $\text{Cl}^-$ ,  $\text{HCl}$   
 (c)  $\text{S}^{2-}$ ,  $\text{H}_2\text{S}$  (d)  $\text{CO}_3^{2-}$ ,  $\text{CO}_2$

Sol. (a)

$$\text{SO}_3^{2-} + \text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \text{SO}_4^{2-}$$

$$3\text{SO}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$$

## TEST FOR SULPHIDE ( $\text{S}^{2-}$ ) ION

1.  $\text{Na}_2\text{S} + \text{dil. H}_2\text{SO}_4 \xrightarrow{\Delta} \text{H}_2\text{S} \uparrow$  Rotten egg like smell

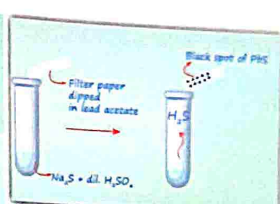
(a)  $(\text{CH}_3\text{COO})_2\text{Pb} + \text{H}_2\text{S} \rightarrow \text{PbS}$  Black  
 Filter Paper

(b)  $(\text{CH}_3\text{COO})_2\text{Cd} + \text{H}_2\text{S} \rightarrow \text{CdS}$  Yellow  
 Filter Paper

2.  $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \rightarrow \text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$   
 Sodium nitroprusside Sodium thio-nitroprusside  
 Brown red [ $\text{Fe}^{2+}$  with  $\text{NO}^+$ ] Violet [ $\text{Fe}^{2+}$  with  $\text{NOS}^-$ ]

$\text{NO}^+ + \text{S}^{2-} \rightarrow \text{NOS}^-$   
 (ionic sulphide)

$\text{NO}^+ + \text{H}_2\text{S} \rightarrow \text{No reaction}$  Sodium Nitroprusside Test



## Note

$\text{H}_2\text{S}$  does not provide sufficient concentration of  $\text{S}^{2-}$  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-II))

(a)  $[\text{Fe}(\text{CN})_6]^{4-}$  (b)  $[\text{Fe}(\text{SCN})_6]^{3-}$   
 (c)  $[\text{Fe}(\text{CN})_6]^{3-}$  (d)  $[\text{Fe}(\text{CN})_5]^{4-}$

Sol. (d)  $[\text{Fe}(\text{CN})_5\text{NOS}]^{4-} \rightarrow \text{Violet Colour}$

8. In which reaction no colour change will be observed?

(a)  $\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{CO}_2}$  (b)  $\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{SO}_2}$   
 (c)  $\text{Na}_2\text{CrO}_4 \xrightarrow{\text{CO}_2}$  (d)  $\text{Na}_2\text{S} \xrightarrow{\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]}$

Sol. (a)

9. In nitroprusside ion, the iron and NO exist. They exist as  $\text{Fe}^{\text{II}}$  and  $\text{NO}^+$  rather than  $\text{Fe}^{\text{III}}$  and NO. These forms can be differentiated by (JEE 1998)

(a) estimating the concentration of Iron. (b) measuring the concentration of  $\text{CN}^-$ .  
 (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  $\text{S}^{2-}$  anion.  
 (b)  $\text{H}_2\text{S}$  also gives positive test.  
 (c) Formation of  $\text{Na}_2[\text{Fe}(\text{H}_2\text{O})_2\text{NOS}]$  complex confirm the presence of  $\text{S}^{2-}$  anion.  
 (d) Iron has +2 oxidation state in sodiumthionitroprusside complex.

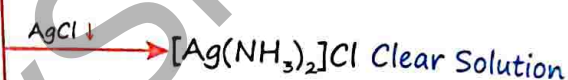
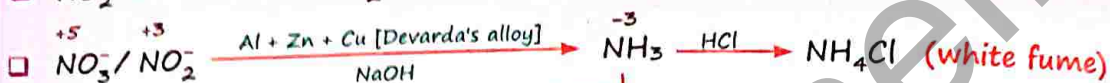
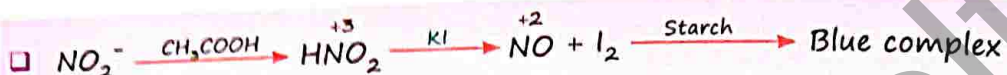
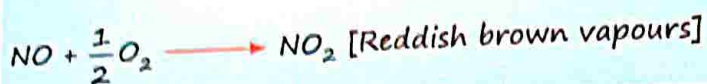
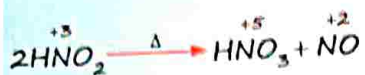
Sol. (a) and (d)

Salt Analysis

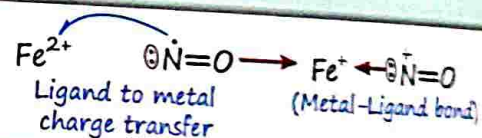
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## TEST FOR NO<sub>2</sub><sup>-</sup> ION

### Preliminary Test

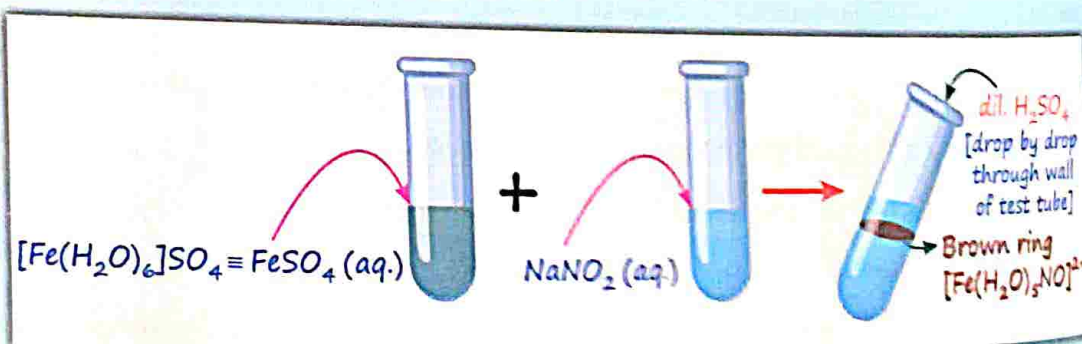


### Brown Ring Test $\Rightarrow$ Test for Nitrites



Reason for brown colour  $\rightarrow$  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.





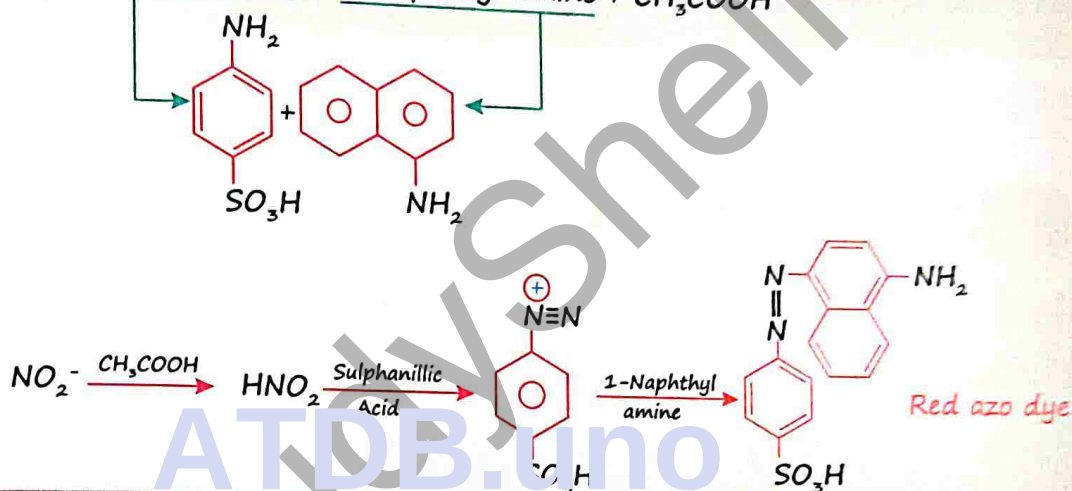
## Note

- FeSO<sub>4</sub> solution must be freshly prepared because Fe<sup>2+</sup> ion is very prone to aerial oxidation and gets converted to Fe<sup>3+</sup>, which does not give this test.
- Concentrated H<sub>2</sub>SO<sub>4</sub> cannot be used in this test instead of dil. H<sub>2</sub>SO<sub>4</sub> because it produces intense brown fumes with NO<sub>2</sub><sup>-</sup> and under these conditions no ring can be observed.
- Shaking and warming are not allowed for this test because [Fe(H<sub>2</sub>O)<sub>5</sub>NO]<sup>2+</sup> formed is unstable and liberates NO easily.

## Confirmatory Test for NO<sub>2</sub><sup>-</sup>

### Griss - Hosray Test

Sulphanillic Acid + 1-Naphthyl amine + CH<sub>3</sub>COOH



11. Reagent 1-naphthylamine and sulphanillic acid in acetic acid is used for the detection of:

(JEE Mains 2021)

- (a) N<sub>2</sub>O (b) NO<sub>2</sub><sup>-</sup> (c) NO<sub>3</sub><sup>-</sup> (d) NO

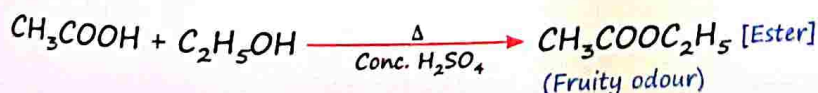
Sol. (b)

12. Which statement(s) is/are correct about Brown ring test?

- (a) The test is given by NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> anions.  
 (b) Brown ring test depend upon the reduction of NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> to Nitric oxide.  
 (c) Brown ring is formed due to formation of [Fe(H<sub>2</sub>O)<sub>5</sub>NO]<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>  
 (d) Charge on NO in brown ring complex is +1.

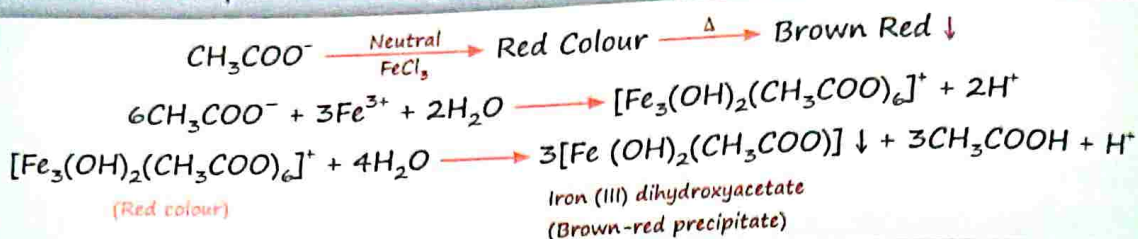
Sol. (a, b, d)

## TEST FOR ACETATE (CH<sub>3</sub>COO<sup>-</sup>) ION



### 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**.

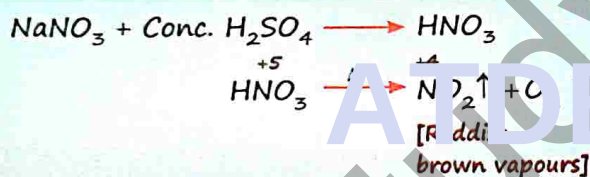


## TEST FOR GROUP 1B ( $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{NO}_3^-$ )

Reagent: Conc.  $\text{H}_2\text{SO}_4$

### TEST FOR $\text{NO}_3^-$ ION

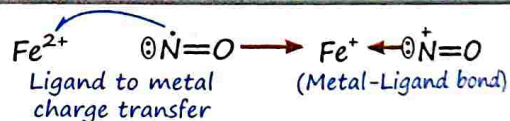
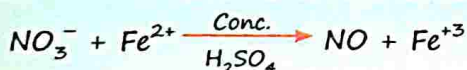
#### Preliminary Test



- If on heating the salt with conc.  $\text{H}_2\text{SO}_4$  light brown fumes are evolved then heat a small quantity of the given salt with few copper turnings or chips and conc.  $\text{H}_2\text{SO}_4$ , intensity of brown fume increases.

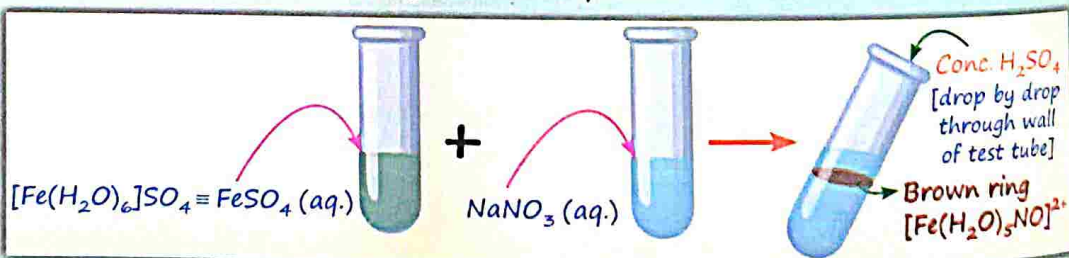


#### Brown Ring Test → Test for Nitrates



- Reason for brown colour → Ligand to metal charge transfer spectra

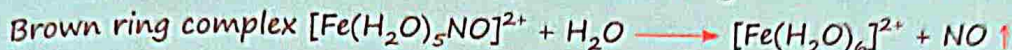
A brown ring at the interface between the solution and sulphuric acid layers indicates the presence of nitrate ion in solution.



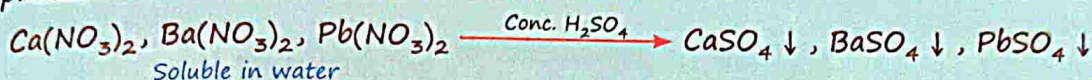


## Note

- On shaking or warming, the brown colour disappears and NO gas is evolved.

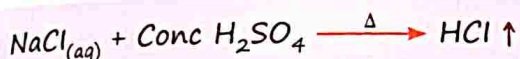


- Radicals such as  $\text{Br}^-$ ,  $\text{I}^-$  and  $\text{NO}_2^-$  must be absent because these produce coloured gases with conc.  $\text{H}_2\text{SO}_4$  like  $\text{Br}_2$ ,  $\text{I}_2$  and  $\text{NO}_2$  respectively and no ring is observed.
- $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$  do not respond to the test due to precipitation of their corresponding metal sulphates.



## TEST FOR $\text{Cl}^-$ ION

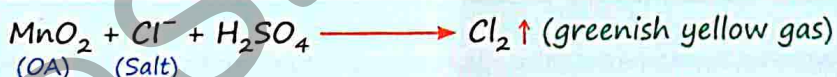
### 1. Preliminary Test:



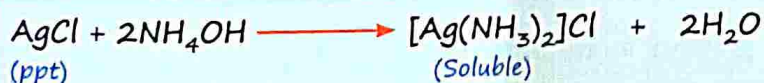
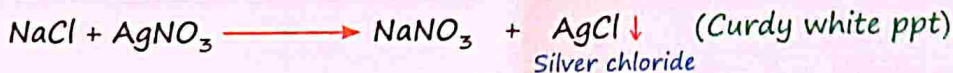
- A colourless gas with pungent smell, which gives dense white fumes when a rod dipped in ammonium hydroxide is brought near the mouth of the test tube.



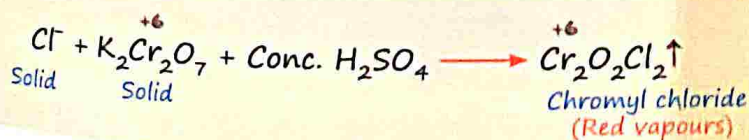
2. If a salt gives effervescence on heating with conc.  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$  and a light greenish yellow pungent gas is evolved, this indicates the presence of  $\text{Cl}^-$  ions.

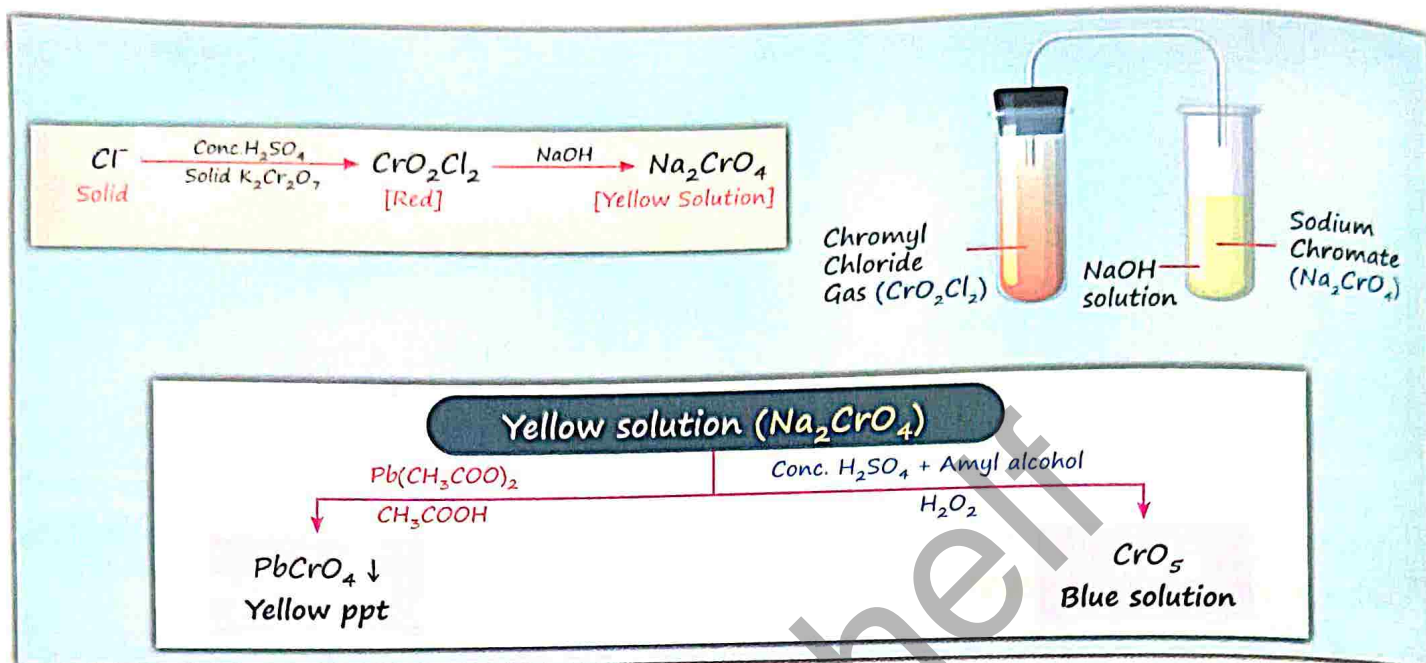


3. **Aq.  $\text{AgNO}_3$  Test:** Salt solution acidified with dilute  $\text{HNO}_3$  on addition of silver nitrate solution gives a curdy white precipitate soluble in ammonium hydroxide solution. This indicates the presence of  $\text{Cl}^-$  ions in the salt.



### 4. Chromyl Chloride Test:



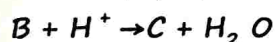
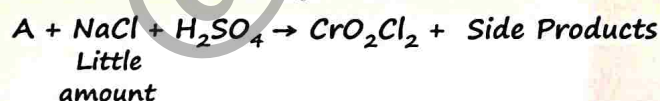


### Note

- ❑ Ionic chlorides can give this test ( $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{SnCl}_2$ ).
- ❑ Insoluble and covalent chlorides do not give this test ( $\text{AgCl}$ ,  $\text{HgCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{PbCl}_2$ ,  $\text{SnCl}_4$  &  $\text{CCl}_4$ ).
- ❑  $\text{Br}^-$  and  $\text{I}^-$  must be absent for this test as they are oxidized by  $\text{Cr}_2\text{O}_7^{2-}$  into  $\text{Br}_2$  (red vapours) and  $\text{I}_2$  (violet vapours) respectively.

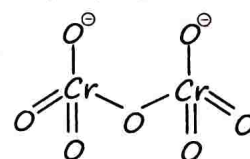
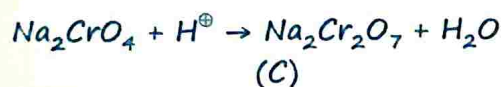
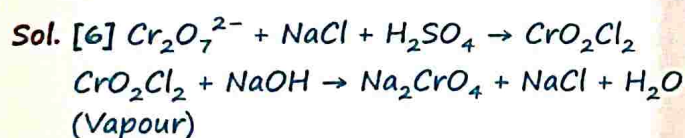


### 13. Consider the following reactions



The number of terminal 'O' present in the compound 'C' is \_\_\_\_.

[03 April, 2025 (Shift-I)]



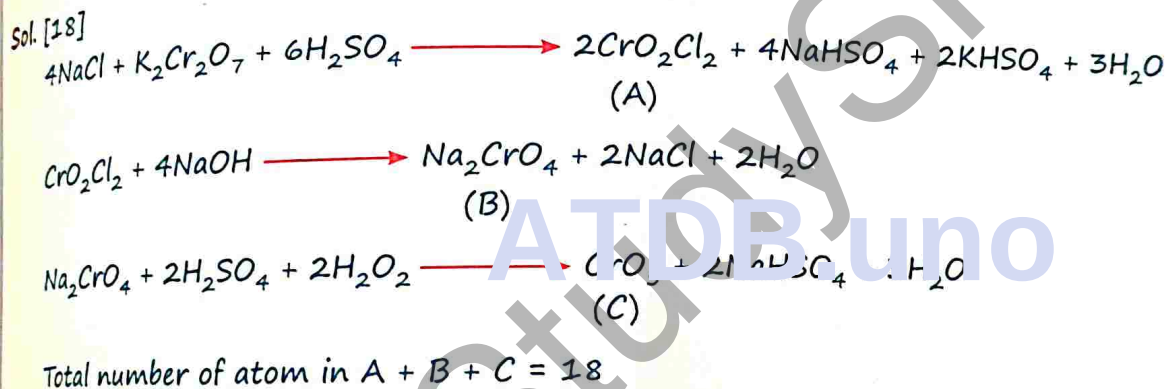
Number of terminal "O" = 6



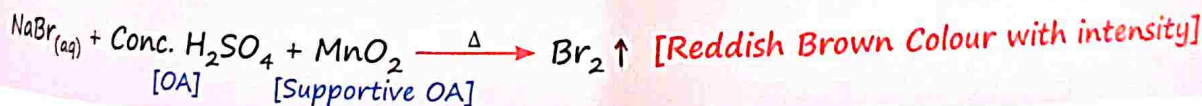
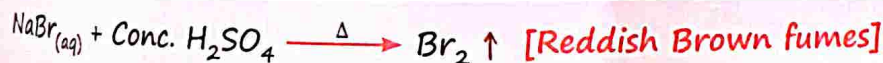
14. A solution of  $\text{CrO}_5$  in  $\text{H}_2\text{O}_2$  is (a) Blue (b) Yellow (c) Green (d) Orange-Red [JEE Mains 2023]

- Sol. (a)  
15. When a mixture of solid  $\text{NaCl}$ , solid  $\text{K}_2\text{Cr}_2\text{O}_7$  is heated with conc.  $\text{H}_2\text{SO}_4$ , orange red vapours are obtained. The compound formed is (a) Chromous chloride (b) Chromyl chloride (c) Chromic chloride (d) Chromic sulphate

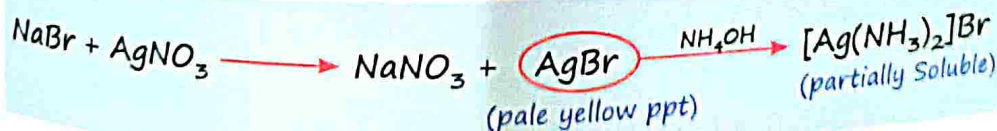
- Sol. (b)  
16. Choose the following reactions  
 $\text{NaCl} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow (\text{A}) + \text{side products}$   
 $(\text{A}) + \text{NaOH} \rightarrow (\text{B}) + \text{side products}$   
 $(\text{B}) + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow (\text{C}) + \text{Side products}$   
(dilute)  
The sum of the total number of atoms in one molecule each of (A), (B) and (C) is \_\_\_\_ [07 Jan, 2020 (shift-II)]



## TEST FOR $\text{Br}^-$ ION



- Q.  **$\text{AgNO}_3$  Test:** Acidify the sodium carbonate extract of the salt with dil.  $\text{HNO}_3$ . Add silver nitrate ( $\text{AgNO}_3$ ) solution and shake the test tube. A pale yellow precipitate is obtained which dissolves in ammonium hydroxide with difficulty.

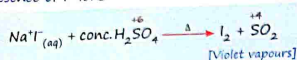


Salt Analysis

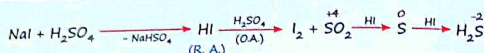
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### TEST FOR I<sup>-</sup> ION

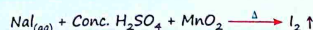
- ❑ If on heating the salt with conc. H<sub>2</sub>SO<sub>4</sub>, deep violet vapours with a pungent smell are evolved. These turns starch paper blue, a violet sublimate is formed on the sides of the test tube, it indicates the presence of I<sup>-</sup> ions.



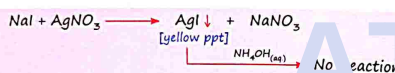
Some HI, sulphur dioxide, hydrogen sulphide, and sulphur are also formed due to the following reactions.



- ❑ On adding MnO<sub>2</sub> to the reaction mixture, the violet vapours become dense.



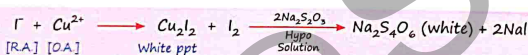
- ❑ **Aq. AgNO<sub>3</sub> Test:** Acidify sodium carbonate extract of the salt with dil. HNO<sub>3</sub> and add AgNO<sub>3</sub> solution. Appearance of a yellow precipitate insoluble in excess of NH<sub>4</sub>OH confirms the presence of iodide ions.



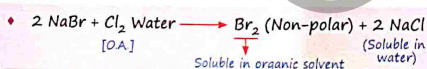
### From HgCl<sub>2</sub>



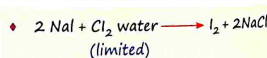
### From CuSO<sub>4</sub>



### Layer Test

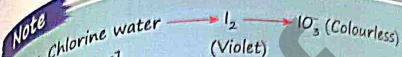


A brown colouration in the organic layer confirms the presence of bromide ion.



A violet colour appears in the organic layer

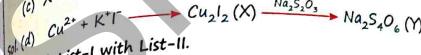
### Note



When chlorine water is added to a solution containing both Br<sup>-</sup> and I<sup>-</sup> ions, the iodide is first oxidized to iodine, which forms a violet colored layer in the organic solvent. Then Br<sup>-</sup> oxidises to bromine, which forms an orange-yellow layer in the organic solvent.

17. When Cu<sup>2+</sup> 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<sub>2</sub> Y = Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  
(b) X = CuI<sub>2</sub> Y = Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub>  
(c) X = Cu<sub>2</sub>I<sub>2</sub> Y = Na<sub>2</sub>S<sub>4</sub>O<sub>5</sub>  
(d) X = Cu<sub>2</sub>I<sub>2</sub> Y = Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub>



18. Match List-I with List-II.

| List - I (Anion)                  | List - II (Gas evolved on reaction with dil. H <sub>2</sub> SO <sub>4</sub> )       |
|-----------------------------------|-------------------------------------------------------------------------------------|
| (A) CO <sub>3</sub> <sup>2-</sup> | (I) Colourless gas which turns lead acetate paper black.                            |
| (B) S <sup>2-</sup>               | (II) Colourless gas which turns acidified potassium dichromate solution green.      |
| (C) SO <sub>3</sub> <sup>2-</sup> | (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. |

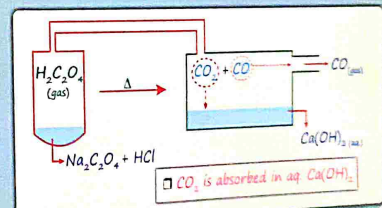
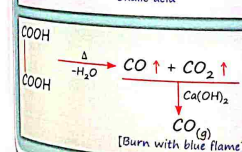
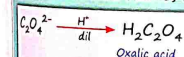
Choose the correct answer from the options given below:

- (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

(JEE Mains 2022)

### Note

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.



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# 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.

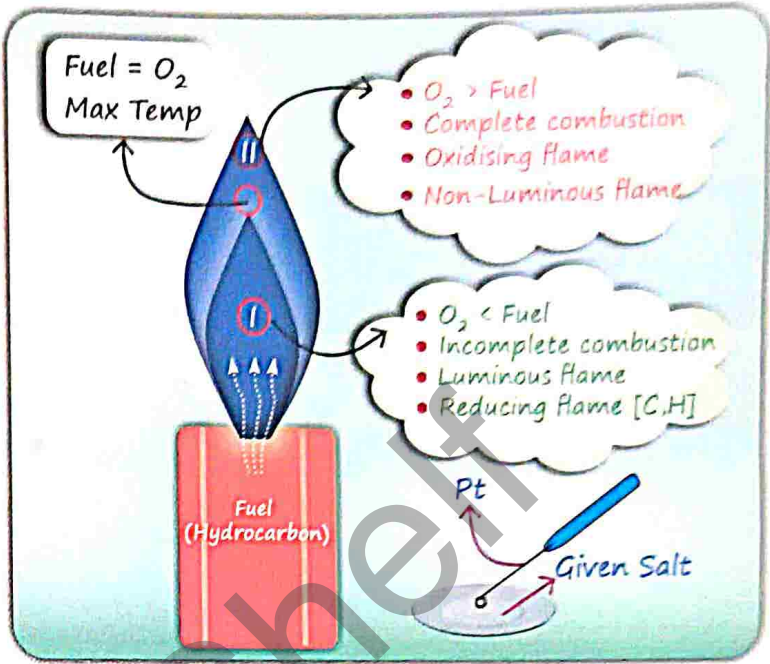
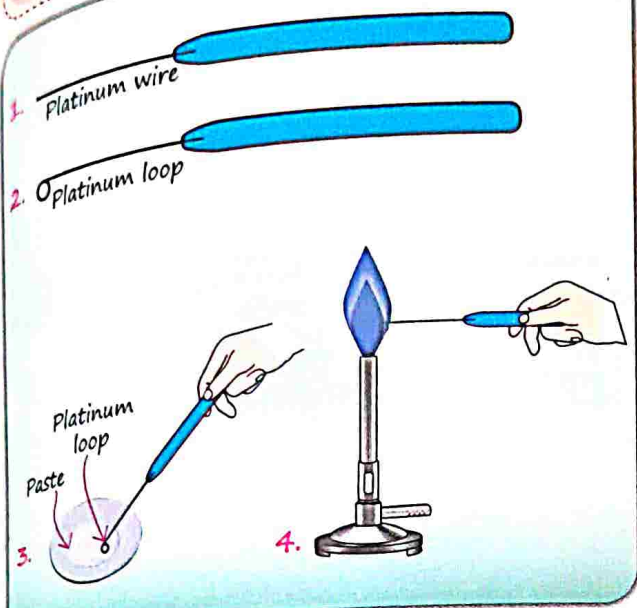
| Colour                     | Cations Indicated                   |
|----------------------------|-------------------------------------|
| Light green, Yellow, Brown | $\text{Fe}^{2+}$ , $\text{Fe}^{3+}$ |
| Blue                       | $\text{Cu}^{2+}$                    |
| Bright green               | $\text{Ni}^{2+}$                    |
| Blue, Red, Violet, Pink    | $\text{Co}^{2+}$                    |
| Light pink                 | $\text{Mn}^{2+}$                    |

### 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                 | $\text{Cu}^{2+}$ |
| Green            | Dirty white or yellow | $\text{Fe}^{2+}$ |
| White            | Yellow                | $\text{Zn}^{2+}$ |
| Pink             | Blue                  | $\text{Co}^{2+}$ |

# Flame Test

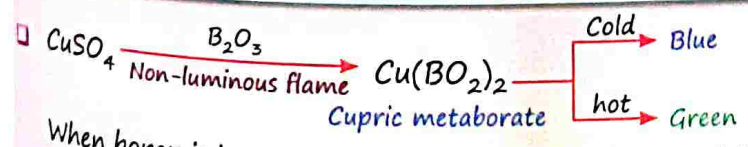
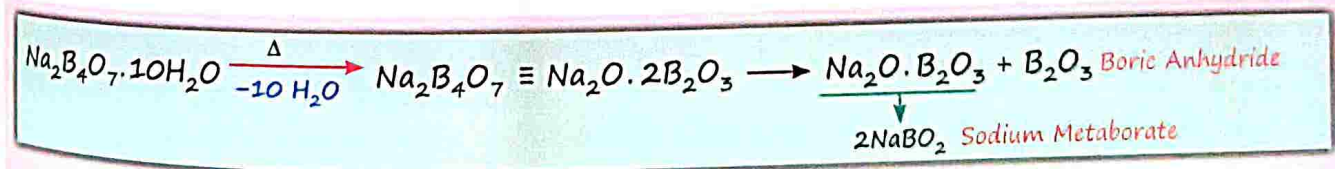


| Colour of the flame observed by naked eye | Colour of the flame observed through blue glass | Inference |
|-------------------------------------------|-------------------------------------------------|-----------|
| Green flame with blue centre              | Same colour as observed without glass           | $Cu^{2+}$ |
| Crimson red                               | Purple                                          | $Sr^{2+}$ |
| Apple green                               | Emerald 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?  
(a)  $Cu^{2+}$  (b)  $Sr^{2+}$  (c)  $Ba^{2+}$  (d)  $Ca^{2+}$   
[24 Jan, 2022 (Shift-II)]  
Sol. (a)

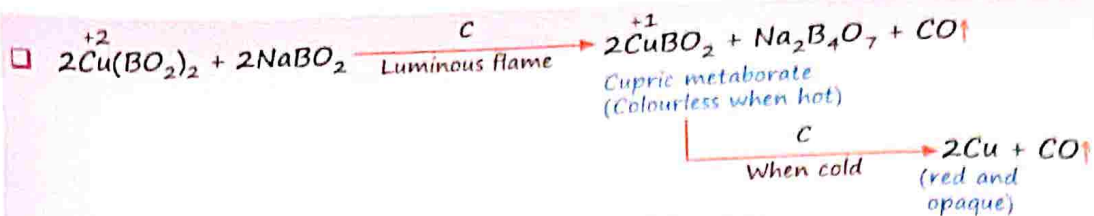
## Borax Bead Test → Identification of d block metals (like Cr, Co, Cu)

- 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).



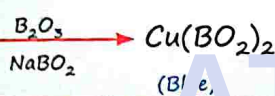
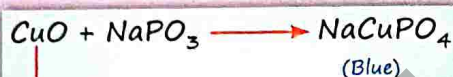
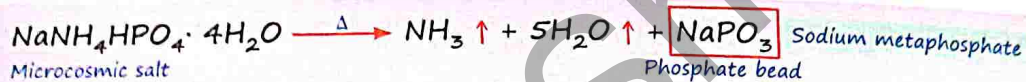
When borax is heated in a Bunsen burner flame with  $CuO$  on a loop of platinum wire, a blue coloured  $Cu(BO_2)_2$  bead is formed.



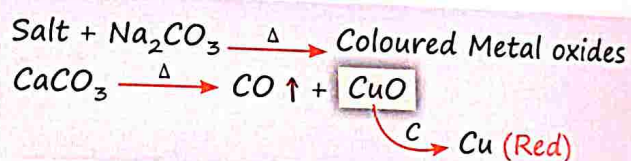
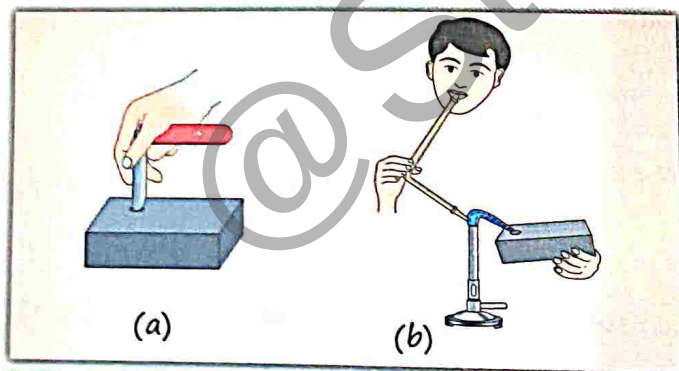


| Heating in oxidising (non-luminous) flame |                 | Heating in reducing (luminous) flame |            | Inference        |
|-------------------------------------------|-----------------|--------------------------------------|------------|------------------|
| Colour of the salt bead                   |                 | Colour of the salt bead              |            |                  |
| In cold                                   | In hot          | In cold                              | In hot     |                  |
| Blue                                      | Green           | Red opaque                           | Colourless | $\text{Cu}^{2+}$ |
| Reddish brown                             | Violet          | Grey                                 | Grey       | $\text{Ni}^{2+}$ |
| Light violet                              | Light violet    | Colourless                           | Colourless | $\text{Mn}^{2+}$ |
| Yellow                                    | Yellowish brown | Green                                | Green      | $\text{Fe}^{3+}$ |

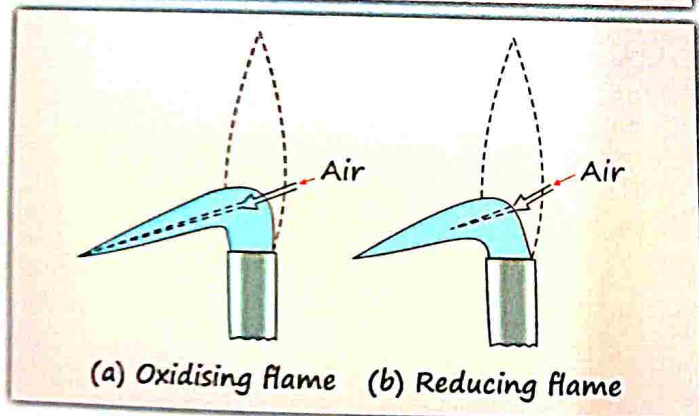
### Phosphate Bead Test



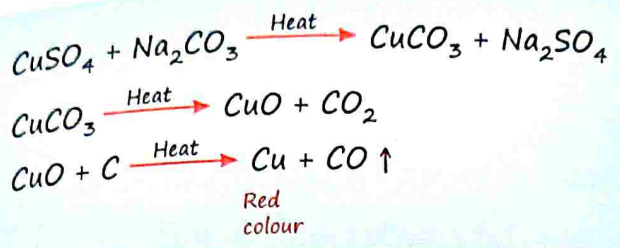
### Charcoal Cavity Test



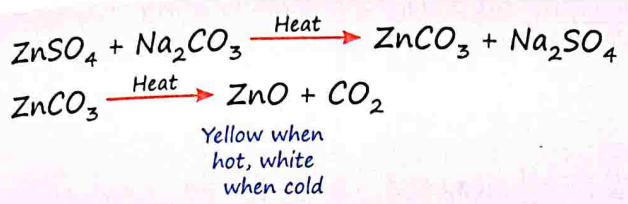
| Colour of oxides (cold) |                      |
|-------------------------|----------------------|
| $\text{Pb}^{2+}$        | Grey                 |
| $\text{Cd}^{2+}$        | Brown                |
| $\text{As}^{3+}$        | White (garlic odour) |
| $\text{Zn}^{2+}$        | White                |



When test is performed with  $\text{CuSO}_4$ , the following change occurs:



In case of  $\text{ZnSO}_4$ :



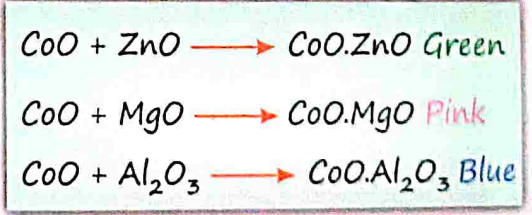
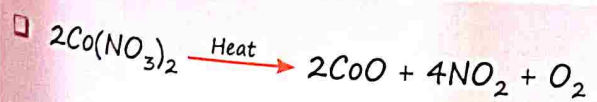
| Observations                                     | Inference        |
|--------------------------------------------------|------------------|
| Yellow residue when hot and grey metal when cold | $\text{Pb}^{2+}$ |
| White residue with the odour of garlic           | $\text{As}^{3+}$ |
| Brown residue                                    | $\text{Cd}^{2+}$ |
| Yellow residue when hot and white when cold      | $\text{Zn}^{2+}$ |

### 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.





## 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<sub>3</sub> 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 <sup>2+</sup> Hg <sub>2</sub> <sup>2+</sup> Ag <sup>+</sup><br><i>Aaj ka Hoga Prabhu</i>                                                     | dil. Cl                                                              |
| II.   | IIA Pb <sup>2+</sup> Cu <sup>2+</sup> Hg <sup>2+</sup> Cd <sup>2+</sup> Bi <sup>3+</sup> [Cu group]<br><i>Prabhu, Cadbury Kaju Bimar Hogayi</i> | H <sub>2</sub> S gas + HCl → less [S <sup>2-</sup> ]                 |
|       | IIB As <sup>3+</sup> As <sup>5+</sup> Sb <sup>3+</sup> Sb <sup>5+</sup> Sn <sup>2+</sup> Sn <sup>4+</sup> [As group]<br><i>Aas Sab Suno</i>     |                                                                      |
| III.  | Al <sup>3+</sup> Cr <sup>3+</sup> Fe <sup>3+</sup><br><i>Aloo Feka Kro</i>                                                                      | NH <sub>4</sub> OH + NH <sub>4</sub> Cl → less [OH <sup>-</sup> ]    |
| IV.   | Ni <sup>2+</sup> Co <sup>2+</sup> Mn <sup>2+</sup> Zn <sup>2+</sup><br><i>Co nahi Man Zinda</i>                                                 | H <sub>2</sub> S gas + NH <sub>4</sub> OH → more [S <sup>2-</sup> ]  |
| V.    | Ba <sup>2+</sup> Sr <sup>2+</sup> Ca <sup>2+</sup><br><i>Bharat Sar-kar</i>                                                                     | (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> + NH <sub>4</sub> OH |
| VI.   | Na <sup>+</sup> K <sup>+</sup> Mg <sup>2+</sup>                                                                                                 | Na <sub>2</sub> HPO <sub>4</sub> + NH <sub>4</sub> OH                |

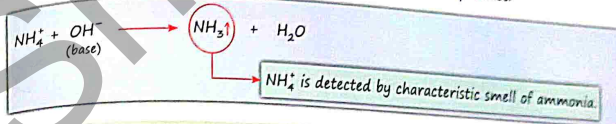
This table is based on K<sub>sp</sub> values –  
 K<sub>sp</sub> : I < II < III < IV < V < VI

For example → K<sub>sp</sub> : Na<sub>2</sub>S > ZnS > CuS  
 : CdS < NiS

## TEST FOR GROUP-0 CATION : NH<sub>4</sub><sup>+</sup>

Group Reagent: Aq. NaOH, KOH

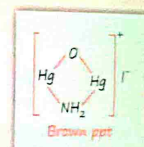
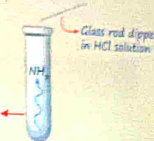
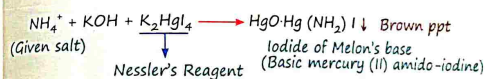
- Zero group test is performed before group analysis begins.
- Reasons Why NH<sub>4</sub><sup>+</sup> Is Not in the Table of Cations in Salt Analysis:
  - NH<sub>4</sub><sup>+</sup> doesn't form characteristic precipitates with group reagents like HCl, H<sub>2</sub>S, NH<sub>4</sub>OH.
  - NH<sub>4</sub><sup>+</sup> is already present in the form of group reagent, so group reagent can not be used for identification of NH<sub>4</sub><sup>+</sup>.
  - NH<sub>4</sub><sup>+</sup> cation is the only cation which is identified by its volatile product.



### Detection of NH<sub>3</sub> & NH<sub>4</sub><sup>+</sup>

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 mouth of the test tube, dense fumes form.  
 $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$



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<sub>3</sub> and Y = HgO
- (b) X = NH<sub>3</sub> and Y = K<sub>2</sub>HgI<sub>4</sub> + KOH
- (c) X = NH<sub>4</sub>Cl and Y = KOH
- (d) X = HCl and Y = NH<sub>4</sub>Cl

Sol. (b)

21. Formulae of Nessler's Reagent is

- (a) KHg<sub>2</sub>I<sub>2</sub>
- (b) KHgI<sub>3</sub>
- (c) K<sub>2</sub>HgI<sub>4</sub>
- (d) HgI<sub>2</sub>

Sol. (c)

(JEE Mains 2023)

Salt Analysis

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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)  $\text{Fe}^{3+}$  (b)  $\text{Zn}^{2+}$  (c)  $\text{Co}^{2+}$  (d)  $\text{Ni}^{2+}$

Sol. (a)

23. Match column-I with column-II:

| Column - I (Metal ion) | Column - II (Group in Qualitative Analysis) |
|------------------------|---------------------------------------------|
| (A) $\text{Mn}^{2+}$   | (I) Group -III                              |
| (B) $\text{As}^{3+}$   | (II) Group -II A                            |
| (C) $\text{Cu}^{2+}$   | (III) Group -IV                             |
| (D) $\text{Al}^{3+}$   | (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 (Group reaction)                                              |
|--------------------------------------|-------------------------------------------------------------------------|
| (A) $\text{Pb}^{2+}, \text{Cu}^{2+}$ | (I) $\text{H}_2\text{S}$ gas in presence of dilute HCl                  |
| (B) $\text{Al}^{3+}, \text{Fe}^{3+}$ | (II) $(\text{NH}_4)_2\text{CO}_3$ in presence of $\text{NH}_4\text{OH}$ |
| (C) $\text{Co}^{2+}, \text{Ni}^{2+}$ | (III) $\text{NH}_4\text{OH}$ in presence of $\text{NH}_4\text{Cl}$      |
| (D) $\text{Ba}^{2+}, \text{Ca}^{2+}$ | (IV) $\text{H}_2\text{S}$ in presence of $\text{NH}_4\text{OH}$         |

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  $\text{H}_2\text{S}$  gas into a mixture of  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}_2^{2+}$  ions in an acidified aqueous solution precipitates [06 April, 2023 (Shift-II)]

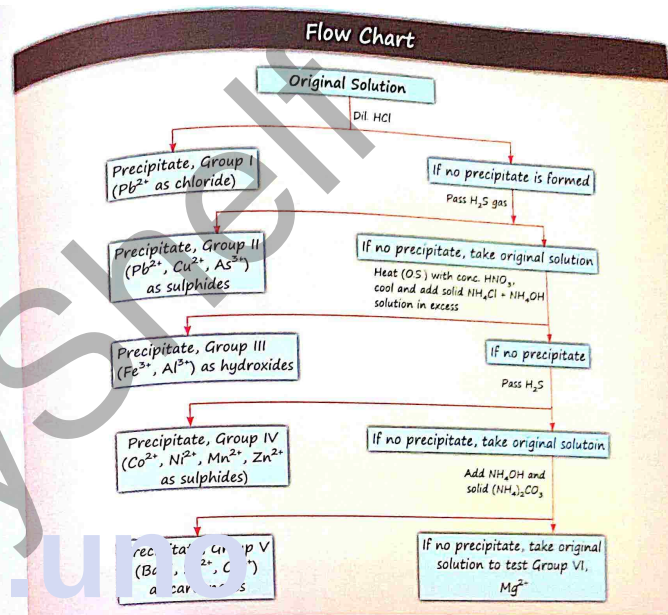
- (a)  $\text{CuS}$  and  $\text{HgS}$  (b)  $\text{MnS}$  and  $\text{CuS}$  (c)  $\text{MnS}$  and  $\text{NiS}$  (d)  $\text{NiS}$  and  $\text{HgS}$

Sol. (a)

26. Upon treatment with ammoniacal  $\text{H}_2\text{S}$ , the metal ion that precipitates as a sulphide is

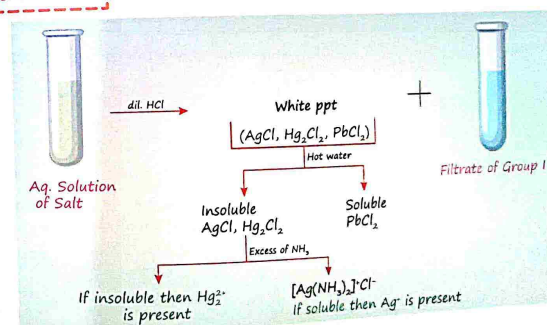
- (a)  $\text{Fe}$  (III) (b)  $\text{Al}$  (III) (c)  $\text{Mg}$  (II) (d)  $\text{Zn}$  (II)

Sol. (d)



### TEST FOR GROUP-1 CATION ( $\text{Ag}^+, \text{Hg}_2^{2+}, \text{Pb}^{2+}$ )

Group reagent : dil. HCl

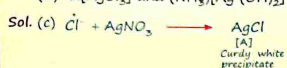


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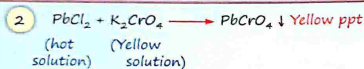
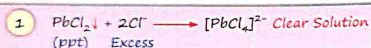


27. A chloride salt solution acidified with dil.  $\text{HNO}_3$  gives a curdy white precipitate. [A], on addition of  $\text{AgNO}_3$ , [A] on treatment with  $\text{NH}_4\text{OH}$  gives a clear solution, B. A and B are respectively  
 (JEE Mains 2023)

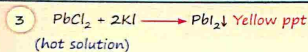
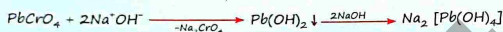
- (a)  $\text{AgCl}$  and  $(\text{NH}_4)[\text{Ag}(\text{OH})_2]$   
 (b)  $\text{H}[\text{AgCl}_2]$  and  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$   
 (c)  $\text{AgCl}$  and  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$   
 (d)  $\text{H}[\text{AgCl}_2]$  and  $(\text{NH}_3)[\text{Ag}(\text{OH})_2]$



### Test for $\text{Pb}^{2+}$

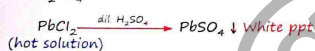


The yellow precipitate ( $\text{PbCrO}_4$ ) is soluble in hot  $\text{NaOH}$  solution.

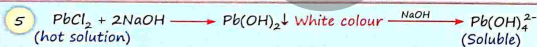


Yellow precipitate ( $\text{PbI}_2$ ) is soluble in boiling water and reappears on cooling as shining crystals.

4 A white precipitate of lead sulphate ( $\text{PbSO}_4$ ) is formed on addition of alcohol followed by dil.  $\text{H}_2\text{SO}_4$ .



Lead sulphate is soluble in ammonium acetate solution due to the formation of tetraacetoplumbate ( $\text{II}$ ) ions. This reaction may be promoted by addition of few drops of acetic acid.



28. The reaction of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{NaCl}$  in water produces a precipitates that dissolves upon the addition of  $\text{HCl}$  of appropriate concentration. The dissolution of the precipitate is due to the formation of:  
 (JEE Adv. 2022)

- (a)  $\text{PbCl}_2$   
 (b)  $\text{PbCl}_4$   
 (c)  $[\text{PbCl}_4]^{2-}$   
 (d)  $[\text{PbCl}_4]^{2-}$

Sol. (c)  $\text{Pb}(\text{NO}_3)_2 + 2\text{NaCl} \rightarrow \text{PbCl}_2 \downarrow + 2\text{NaNO}_3$   
 A colourless aqueous solution contains nitrates of two metals, X and Y. When it was added to an aqueous solution of  $\text{NaCl}$ , 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  $\text{NH}_3$  and also in excess sodium thiosulphate. The hot solution Q gave a yellow precipitate with  $\text{KI}$ . The metals X and Y, respectively, are  
 (JEE Adv.)

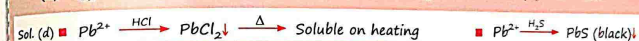
- (a) Ag and Pb  
 (b) Ag and Cd  
 (c) Cd and Pb  
 (d) Cd and Zn

Sol. (a) Aqueous solution of  $\text{AgNO}_3 / \text{Pb}(\text{NO}_3)_2 \xrightarrow{\text{Cl}^-} \text{AgCl} \downarrow / \text{PbCl}_2 \downarrow$  White ppt  
 Hot water  $\rightarrow$  Q (Solution)  $\rightarrow \text{PbCl}_2$  is soluble in hot water  
 P (Residue)  $\rightarrow \text{AgCl}$  is insoluble in hot water

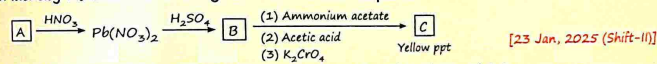


30. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a  
 (JEE Adv. 2018)

- (a)  $\text{Hg}_2^{2+}$  salt  
 (b)  $\text{Cr}^{2+}$  salt  
 (c)  $\text{Ag}^+$  salt  
 (d)  $\text{Pb}^{2+}$  salt



31. Identify A, B and C in the given below reaction sequence



- (a)  $\text{PbCl}_2$ ,  $\text{Pb}(\text{SO}_4)_2$ ,  $\text{PbCrO}_4$   
 (b)  $\text{PbS}$ ,  $\text{PbSO}_4$ ,  $\text{PbCrO}_4$   
 (c)  $\text{PbS}$ ,  $\text{PbSO}_4$ ,  $\text{Pb}(\text{CH}_3\text{COO})_2$   
 (d)  $\text{PbCl}_2$ ,  $\text{PbSO}_4$ ,  $\text{PbCrO}_4$

Sol. (b)

32. Formation of which complex, among the following, is not a confirmatory test of  $\text{Pb}^{2+}$  ions  
 [6 April, 2023 (Shift-II)]

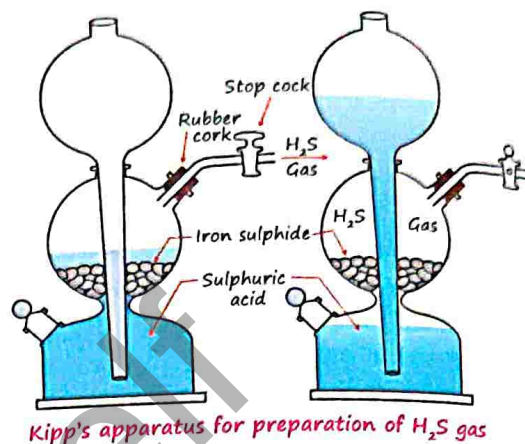
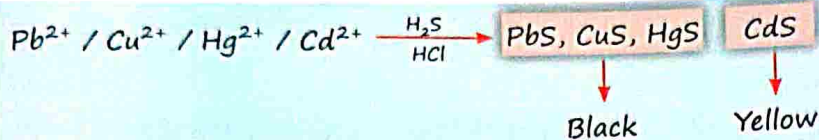
- (a) Lead chromate  
 (b) Lead iodide  
 (c) Lead nitrate  
 (d) Lead sulphate

Sol. (c)  $\text{Pb}(\text{NO}_3)_2$  is soluble in water but others are ppt.

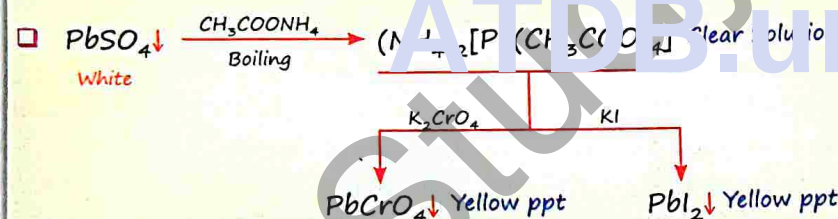
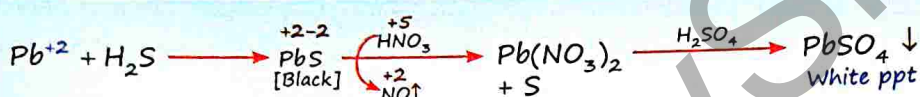
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## TEST FOR GROUP-II A ( $\text{Pb}^{+2}$ , $\text{Cu}^{+2}$ , $\text{Hg}^{+2}$ , $\text{Cd}^{+2}$ , $\text{Bi}^{+3}$ )

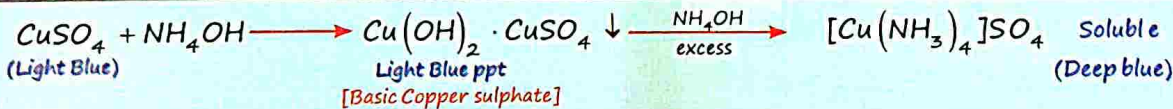
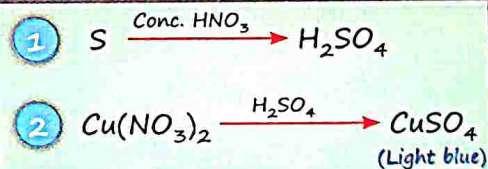
Group reagent :  $\text{H}_2\text{S}$  gas +  $\text{HCl}$



### Test for $\text{Pb}^{2+}$

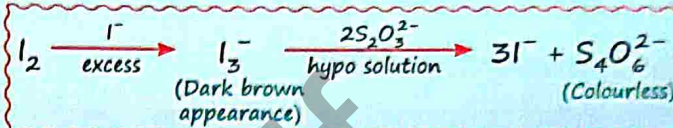
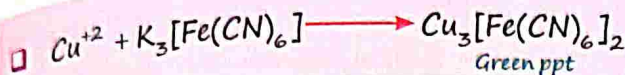
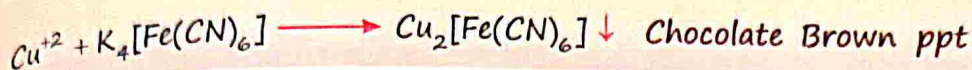
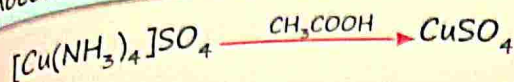


### Test for $\text{Cu}^{2+}$

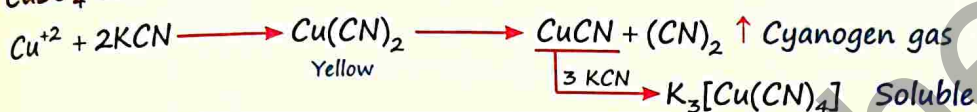




The blue solution on acidification with acetic acid and then adding  $K_4[Fe(CN)_6]$  solution gives a chocolate colouration due to the formation of copper ferrocyanide.



$CuSO_4$  decolourises on addition of KCN.



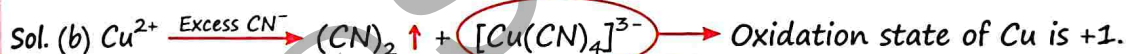
33. The pair(s) of ions where both the ions are precipitated upon passing  $H_2S$  gas in presence of dilute  $HCl$ , is (are) [JEE Adv. 2015]

- (a)  $Ba^{2+}, Zn^{2+}$  (b)  $Bi^{3+}, Fe^{3+}$  (c)  $Cu^{2+}, Pb^{2+}$  (d)  $Hg^{2+}, Bi^{3+}$

Sol. (c) and (d)

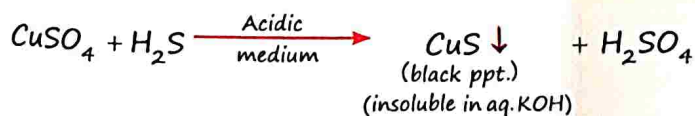
34.  $CuSO_4$  decolourises on addition of KCN, the product is [JEE Adv. 2006]

- (a)  $[Cu(CN)_4]^{2-}$  (b)  $Cu^{2+}$  get reduced to form  $[Cu(CN)_4]^{3-}$   
(c)  $Cu(CN)_2$  (d)  $CuCN$



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.



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  $I_2$ .



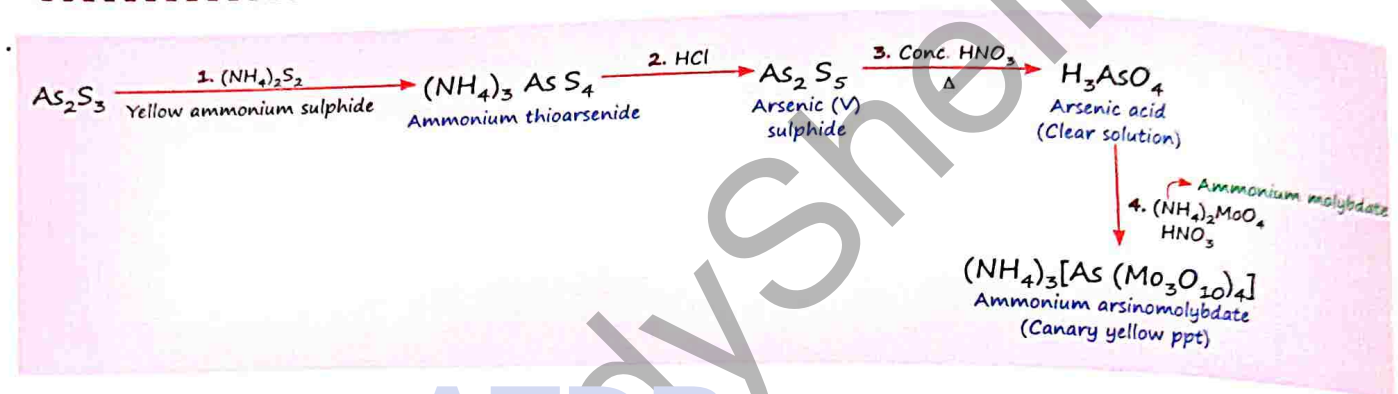


II<sup>nd</sup> GROUP (Hg<sup>2+</sup>, Pb<sup>2+</sup>, Bi<sup>3+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, As<sup>3+</sup>, Sb<sup>3+</sup>, Sn<sup>2+</sup>)

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:

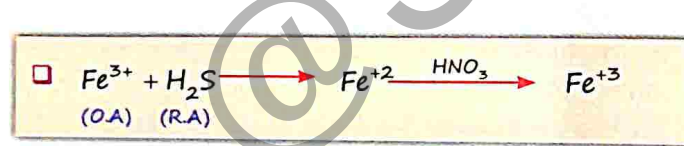
| IIA                                                                                                                     | IIB                                                                                                                                                                  |
|-------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| HgS, PbS, CuS, Bi <sub>2</sub> S <sub>3</sub> , all black but CdS is yellow. All insoluble in yellow ammonium sulphide. | SnS <sub>2</sub> , As <sub>2</sub> S <sub>3</sub> are yellow, Sb <sub>2</sub> S <sub>5</sub> is orange & SnS is dark brown. All soluble in yellow ammonium sulphide. |

TEST FOR GROUP-II B (As<sup>3+</sup>)



TEST FOR GROUP-III (Fe<sup>3+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup>)

Group reagent  $\rightarrow NH_4OH + NH_4Cl$  : Less [OH<sup>-</sup>]



Before performing the test of III<sup>rd</sup> group cation, boil II<sup>nd</sup> group filtrate to remove H<sub>2</sub>S gas. After this add few drops of conc. HNO<sub>3</sub> to oxidise Fe<sup>2+</sup> ion (which was obtain after reduction of Fe<sup>3+</sup> ion) into Fe<sup>3+</sup>.

Filtrate of Group-2

(1) Boil to remove H<sub>2</sub>S gas

(2) Add few drops of HNO<sub>3</sub>

(3) NH<sub>4</sub>OH + NH<sub>4</sub>Cl

Al<sup>3+</sup>

Al(OH)<sub>3</sub>↓

White Gelatinous ppt

Cr<sup>3+</sup>

Cr(OH)<sub>3</sub>↓

Green - yellow ppt

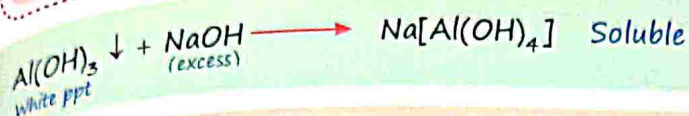
Fe<sup>3+</sup>

Fe(OH)<sub>3</sub>↓

Red Brown ppt



## Test for $Al^{+3}$



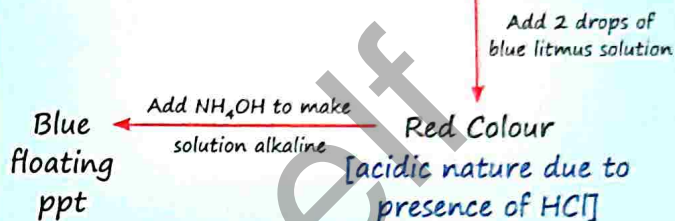
### Lake Test

□ The lake test is confirmatory test used to detect the presence of  $Al^{3+}$  in a solution.

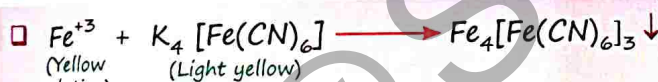
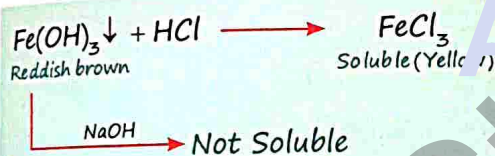


#### □ Principle for this test:

$Al(OH)_3$  is a good adsorbent, and therefore it adsorbs the blue litmus solution and gives this blue lake test.



## Test for $Fe^{+3}$



Prussian Blue (ppt)



Soluble Prussian Blue (Colloidal Solution)  
[can not be filtered.]



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]

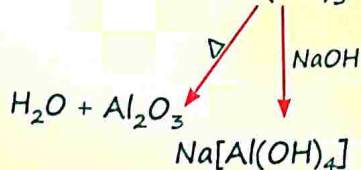
(a) Zn

(b) Ca

(c) Al

(d) Fe

Sol. (c)



Salt Analysis

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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-II)]

(a)  $KFe[Fe(CN)_6]$  (b)  $K_5Fe[Fe(CN)_6]_2$  (c)  $Fe_4[Fe(CN)_6]_3$  (d)  $HFe[Fe(CN)_6]$

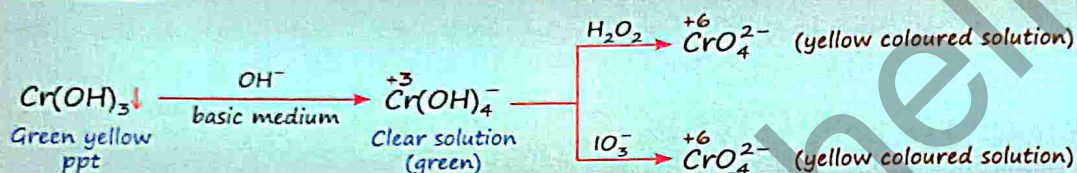
**Sol. (a)**

38. A solution of  $\text{FeCl}_3$  when treated with  $\text{K}_4[\text{Fe}(\text{CN})_6]$  gives a prussian 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)  $Fe_4[Fe(CN)_6]_3$

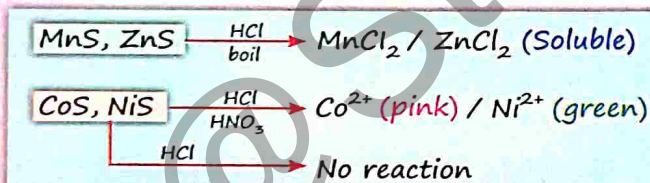
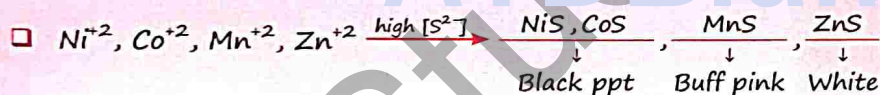
**Sol. (d)**

### Note



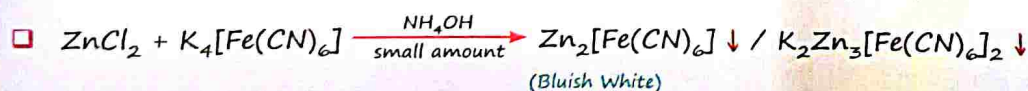
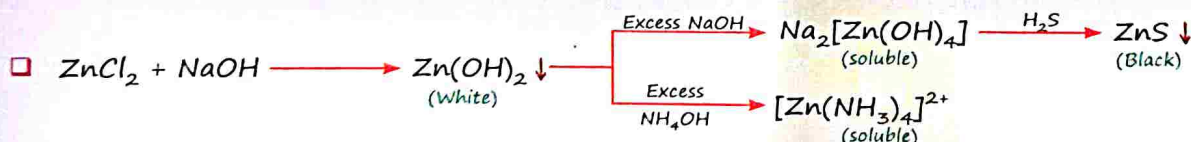
**TEST FOR GROUP -IV ( $\text{Ni}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Mn}^{+2}$ ,  $\text{Zn}^{+2}$ )**

**Group Reagent:**  $\text{NH}_4\text{OH} + \text{H}_2\text{S}$



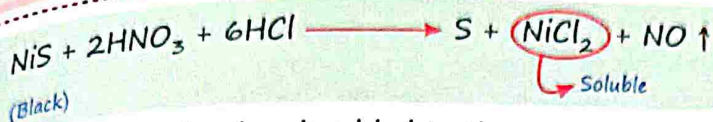
$\text{Zn}_2 [\text{Fe}(\text{CN})_6]$  Bluish white ppt  
 $\text{Cu}_2 [\text{Fe}(\text{CN})_6]$  Chocolate brown ppt  
 $\text{Fe}_4 [\text{Fe}(\text{CN})_6]_3$  Prussian blue ppt  
 $\text{K}_4 [\text{Fe}(\text{CN})_6]$  Light yellow solution.  
 $\text{K}_3 [\text{Fe}(\text{CN})_6]$  Orange-red

### Test for $Zn^{+2}$

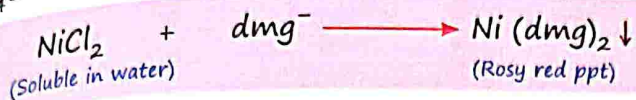




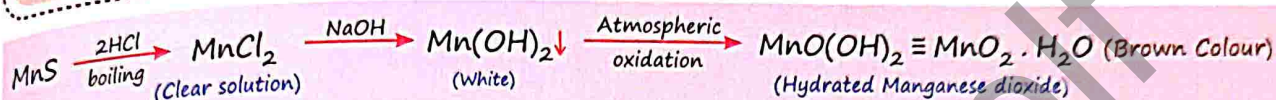
### Test for Ni<sup>+2</sup>



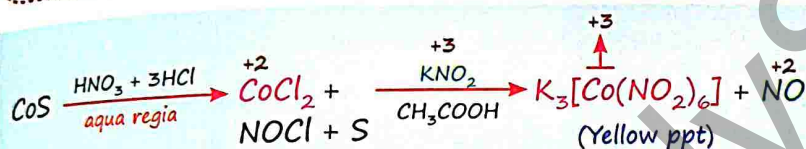
- When dimethyl glyoxime is added to the aqueous solution of nickel chloride, made alkaline, by adding NH<sub>4</sub>OH solution, a brilliant red precipitate is obtained.



### Test for Mn<sup>2+</sup>

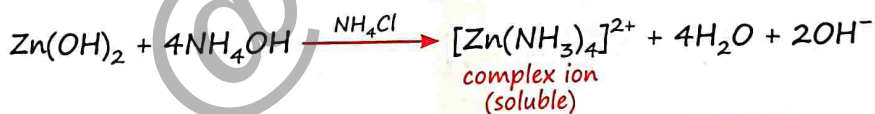


### Test for Co<sup>2+</sup>



39. A solution when diluted with H<sub>2</sub>O and boiled, it gives a white precipitate. On addition of excess NH<sub>4</sub>Cl / NH<sub>4</sub>OH, the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in NH<sub>4</sub>Cl / NH<sub>4</sub>OH : [JEE Adv. 2006]

- (a) Zn(OH)<sub>2</sub>      (b) Al(OH)<sub>3</sub>      (c) Mg(OH)<sub>2</sub>      (d) Ca(OH)<sub>2</sub>



40. An ammoniacal metal salt solution gives a brilliant red precipitate on addition of dimethylglyoxime. The metal ion is [JEE Mains 2023]

- (a) Ni<sup>2+</sup>      (b) Cu<sup>2+</sup>      (c) Fe<sup>2+</sup>      (d) Co<sup>2+</sup>

Sol. (a)

41. During the qualitative analysis of salt with cation (Y<sup>2+</sup>), addition of a reagent (X) to alkaline solution of the salt gives a bright red precipitate. The reagent (X) and the cation (Y<sup>2+</sup>) present respectively are: [24 Jan 2022, (Shift-I)]

- (a) Dimethylglyoxime and Ni<sup>2+</sup>      (b) Dimethylglyoxime and Co<sup>2+</sup>  
(c) Nessler's reagent and Hg<sup>2+</sup>      (d) Nessler's reagent and Ni<sup>2+</sup>

Sol. (a)



## TEST FOR GROUP-V ( $\text{Ba}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ca}^{2+}$ )

Group Reagent:  $(\text{NH}_4)_2\text{CO}_3$  in presence of  $\text{NH}_4\text{OH}$

Original Solution  $\xrightarrow[\text{NH}_4\text{OH}]{\text{NH}_4\text{Cl}}$   $\xrightarrow{(\text{NH}_4)_2\text{CO}_3}$   $\xrightarrow{\text{CH}_3\text{COOH}}$  Divide in 3 parts

White ppt  $\downarrow$   
 $\text{BaCO}_3 \downarrow, \text{SrCO}_3 \downarrow, \text{CaCO}_3 \downarrow$

$\text{Ba}(\text{CH}_3\text{COO})_2$   
or  
 $\text{Sr}(\text{CH}_3\text{COO})_2$   
or  
 $\text{Ca}(\text{CH}_3\text{COO})_2$   $\rightarrow$  Soluble

Preserve a small amount of the precipitate for flame test.

Part (1)  $\xrightarrow{\text{K}_2\text{CrO}_4}$  Yellow ppt of  $\text{BaCrO}_4$

$\text{Ba}^{2+} \rightarrow \text{CrO}_4^{2-} / \text{SO}_4^{2-} / \text{C}_2\text{O}_4^{2-}$  Insoluble

Part (2)  $\xrightarrow{(\text{NH}_4)_2\text{SO}_4}$  White ppt of  $\text{SrSO}_4$

$\text{Sr}^{2+} \rightarrow \text{SO}_4^{2-} / \text{C}_2\text{O}_4^{2-}$  Insoluble

Part (3)  $\xrightarrow{(\text{NH}_4)_2\text{C}_2\text{O}_4}$  White ppt of  $\text{CaC}_2\text{O}_4$

$\text{Ca}^{2+} \rightarrow \text{C}_2\text{O}_4^{2-}$  Insoluble

- $\text{Ba}(\text{CH}_3\text{COO})_2 + \text{K}_2\text{CrO}_4 \rightarrow \text{BaCrO}_4 \downarrow$  Yellow ppt (soluble) (soluble)
- $\text{Sr}(\text{CH}_3\text{COO})_2 + (\text{NH}_4)_2\text{SO}_4 \rightarrow \text{SrSO}_4 \downarrow$  White
- $\text{Ca}(\text{CH}_3\text{COO})_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{CaC}_2\text{O}_4 \downarrow$  White

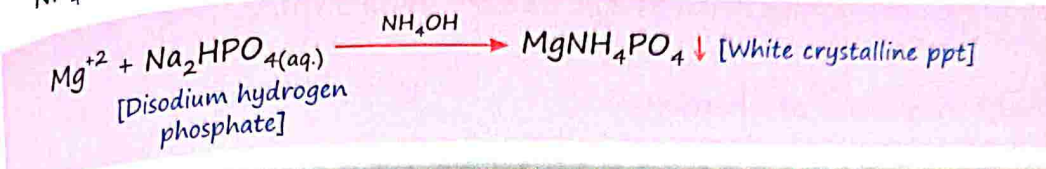
| $\text{Ba}^{2+}$ ions                                                                                                                                                                | $\text{Sr}^{2+}$ ions                                                                                                                                                                                                                                                                                                                        | $\text{Ca}^{2+}$ ions                                                                                                                                                                                                                                                                                                                                                        |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (a) To the first part add potassium chromate solution. A yellow precipitate appears.<br>(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.<br>(b) Perform the flame test with the preserved precipitate. A <b>crimson-red</b> flame confirms the presence of $\text{Sr}^{2+}$ 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.<br>(b) Perform the flame test with the preserved precipitate. A <b>brick red flame</b> , which looks greenish-yellow through blue glass, confirms the presence of $\text{Ca}^{2+}$ 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.

$$NH_4^+ + CO_3^{2-} \rightleftharpoons NH_3 + HCO_3^-$$


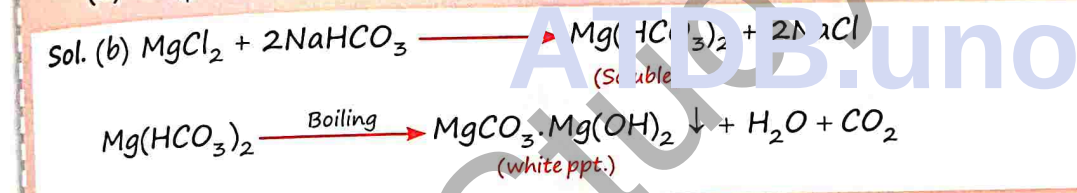
42.  $MgSO_4$  on reaction with  $NH_4OH$  and  $Na_2HPO_4$  forms a white crystalline precipitate. What is its formula? [JEE Adv. 2018]

(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)  $NO_3^-$



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  $Cu^{2+}$ . [11 April, 2023 (Shift-I)]

46. The complex that dissolves in water is

(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:

- (a)  $\text{Zn(OH)}_2$  (b)  $\text{ZnO}$  (c)  $[\text{Zn(OH)}_4]^{2-}$

[29 July, 2022 (Shift-I)]  
 (d)  $[\text{ZnO}_2]^{2-}$

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

- (a)  $\text{NO}_3^-$  only (b)  $\text{K}^+$  only (c)  $\text{Ag}^+$  and  $\text{I}^-$  both (d)  $\text{I}^-$  only

Sol. (c) Major quantity of  $\text{Ag}^+$  and  $\text{I}^-$  precipitate down as  $\text{AgI}$ . So very small quantity of  $\text{Ag}^+$  and  $\text{I}^-$  will be there in solution.

49. Choose the correct tests with respective observations.

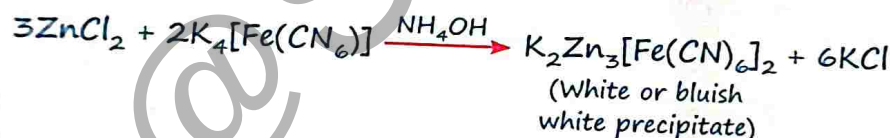
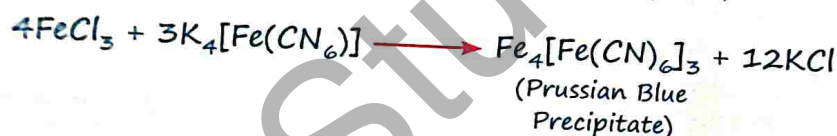
- (A)  $\text{CuSO}_4$  (acidified with acetic acid) +  $\text{K}_4[\text{Fe(CN)}_6]$  → Chocolate brown precipitate.  
 (B)  $\text{FeCl}_3$  +  $\text{K}_4[\text{Fe(CN)}_6]$  → Prussian blue precipitate.  
 (C)  $\text{ZnCl}_2$  +  $\text{K}_4[\text{Fe(CN)}_6]$ , neutralised with  $\text{NH}_4\text{OH}$  → White or bluish white precipitate.  
 (D)  $\text{MgCl}_2$  +  $\text{K}_4[\text{Fe(CN)}_6]$  → Blue precipitate.  
 (E)  $\text{BaCl}_2$  +  $\text{K}_4[\text{Fe(CN)}_6]$ , neutralised with  $\text{NaOH}$  → White precipitate.

Choose the correct answer from the options given below:

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

[02 April, 2025 (Shift-I)]

Sol. (c)

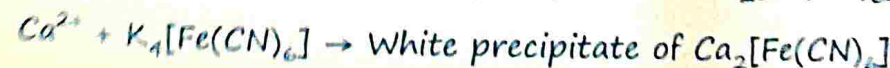
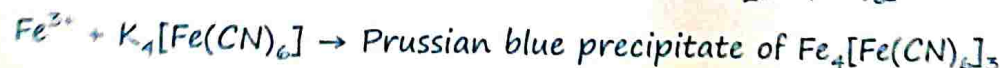


50. Among the following cations, the number of cations which will give characteristic precipitate in their identification tests with  $\text{K}_4[\text{Fe(CN)}_6]$  is \_\_\_\_.

[24 Jan, 2025 (Shift-I)]

$\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$

Sol. [4]

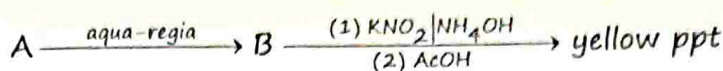


NTA Ans key : 3



51. Find the compound 'A' from the following reaction sequences.

[24 Jan, 2025 (Shift-I)]



(a) NiS

(b) MnS

(c) CoS

(d) ZnS

Sol. (c)

52. Identify the inorganic sulphides that are yellow in colour:

(A)  $(\text{NH}_4)_2\text{S}$

(B) PbS

(C) CuS

(D)  $\text{As}_2\text{S}_3$

(E)  $\text{As}_2\text{S}_5$

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  $(\text{NH}_4)_2\text{S}$ ,  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{S}_5$  are yellow in color.

53. The number of white coloured salts among the following is .....

[01 Feb, 2024 (Shift-I)]

(A)  $\text{SrSO}_4$

(B)  $\text{Mg}(\text{NH}_4)\text{PO}_4$

(C)  $\text{BaCrO}_4$

(D)  $\text{Mn}(\text{OH})_2$

(E)  $\text{PbSO}_4$

(F)  $\text{PbCrO}_4$

(G) AgBr

(H)  $\text{PbI}_2$

(I)  $\text{CaC}_2\text{O}_4$

(J)  $[\text{Fe}(\text{OH})_2(\text{CH}_3\text{COO})]$

Sol. [5]  $\text{SrSO}_4$  - white,  $\text{Mg}(\text{NH}_4)\text{PO}_4$  - white,  $\text{BaCrO}_4$  - yellow,  $\text{Mn}(\text{OH})_2$  - white,  $\text{PbSO}_4$  - white,  $\text{PbCrO}_4$  - yellow, AgBr - pale yellow,  $\text{PbI}_2$  - yellow,  $\text{CaC}_2\text{O}_4$  - white,  $[\text{Fe}(\text{OH})_2(\text{CH}_3\text{COO})]$  - 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.                                   | $\text{MCO}_3 \rightarrow \text{MO} \xrightarrow[+\Delta]{\text{Co}(\text{NO}_3)_2} \text{CoO} \cdot \text{MO}$                            |
| B.                        | Charcoal cavity test | II.                                  | $\text{MCO}_3 \rightarrow \text{MCl}_2 \rightarrow \text{M}^{2+}$                                                                          |
| C.                        | Cobalt nitrate test  | III.                                 | $\text{MSO}_4 \xrightarrow[\Delta]{\text{Na}_2\text{B}_4\text{O}_7} \text{M}(\text{BO}_2)_2 \rightarrow \text{MBO}_2 \rightarrow \text{M}$ |
| D.                        | Flame test           | IV.                                  | $\text{MSO}_4 \xrightarrow[\Delta]{\text{Na}_2\text{CO}_3} \text{MCO}_3 \rightarrow \text{MO} \rightarrow \text{M}$                        |

Choose the correct answer from the option below:

[08 April, 2024 (Shift-I)]

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

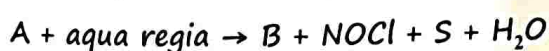
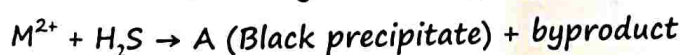
(b) A-III, B-II, C-IV, D-I

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

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

Sol. (d)

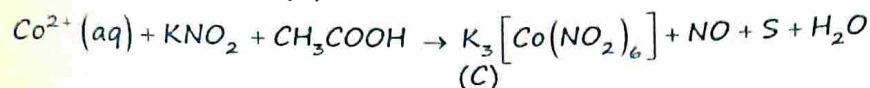
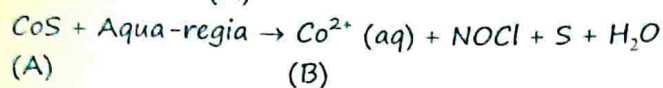
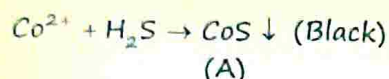
55. Consider the following test for a group-IV cation.



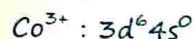
The spin only magnetic moment value of the metal complex C is \_\_\_\_ BM. (Nearest integer)

[09 April, 2024 (Shift-II)]

Sol. [0]



In  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ , Co is in  $\text{Co}^{3+}$  oxidation state.



Hence, it has  $d^2sp^3$  hybridisation. Number of unpaired  $e^- = 0$

Hence, Magnetic moment,  $\mu = \sqrt{n(n+2)} = 0 \text{ B.M}$

56. Consider the sulphides  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{CuS}$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{As}_2\text{S}_3$  and  $\text{CdS}$ . Number of these sulphides soluble in 50%  $\text{HNO}_3$  is \_\_\_\_\_. [31 Aug, 2021 (Shift-I)]

Sol. [4] Out of the given sulphides, only  $\text{CdS}$ ,  $\text{PbS}$ ,  $\text{As}_2\text{S}_3$  &  $\text{CuS}$  are soluble in 50%  $\text{HNO}_3$  but  $\text{Sb}_2\text{S}_3$  &  $\text{HgS}$  are not soluble.

57. Upon treatment with ammoniacal  $\text{H}_2\text{S}$ , the metal ion that precipitates as a sulphide is

(JEE Adv. 2013)

(a)  $\text{Fe (III)}$

(b)  $\text{Al (III)}$

(c)  $\text{Mg (II)}$

(d)  $\text{Zn(II)}$

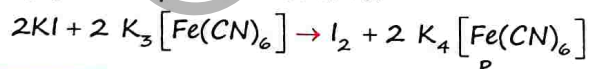
Sol. (d)

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)

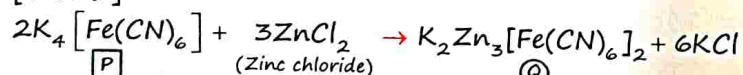
Sol. [2] We require 2 mol of KI.



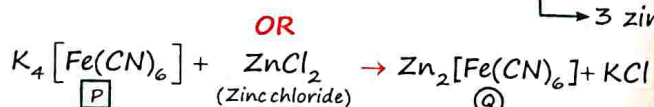
(ii) The number of zinc ions present in the molecular formula of Q is \_\_\_\_.

(JEE Adv. 2024)

Sol. [3 or 2]



→ 3 zinc ions are present



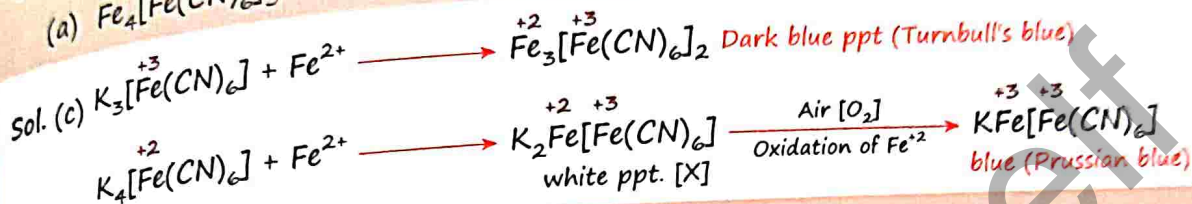
→ 2 zinc ions are present



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)  $KFe[Fe(CN)_6]$



- (ii) Among the following, the brown ring is due to the formation of  
 (a)  $[Fe(NO)_2(SO_4)_2]^{2-}$  (b)  $[Fe(NO)_2(H_2O)_4]^{3+}$  (c)  $[Fe(NO)_4(SO_4)_2]$  (d)  $[Fe(NO)(H_2O)_5]^{2+}$

(JEE Adv. 2021)

Sol. (d)

60. **Statement-I:** A very dilute acidic solution of  $Cd^{2+}$  and  $Ni^{2+}$  gives yellow precipitate of  $CdS$  on passing  $H_2S$

**Statement-II:** Solubility product of  $CdS$  is not more than that of  $NiS$ . (IIT JEE 1989)

- (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



$Cd^{2+}$  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)

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Salt A...



2.  $\text{HgCl}_2$  and  $\text{I}_2$  both when dissolved in water containing  $\text{I}^-$  ions, the pair of species formed is: [NEET 2017-Delhi]
- (a)  $\text{Hg}_2\text{I}_2, \text{I}^-$  (b)  $\text{HgI}_2, \text{I}_3^-$  (c)  $\text{HgI}_2, \text{I}^-$  (d)  $\text{HgI}_4^{2-}, \text{I}_3^-$

Sol. (d)

3. Match List-I with List-II:

[NEET 2024 Re]

| List-I: Solid salt treated with dil. $\text{H}_2\text{SO}_4$ |                                 | List-II: Anion detected |                    |
|--------------------------------------------------------------|---------------------------------|-------------------------|--------------------|
| A.                                                           | effervescence of colourless gas | I.                      | $\text{NO}_2^-$    |
| B.                                                           | gas with smell of rotten egg    | II.                     | $\text{CO}_3^{2-}$ |
| C.                                                           | gas with pungent smell          | III.                    | $\text{S}^{2-}$    |
| D.                                                           | brown fumes                     | IV.                     | $\text{SO}_3^{2-}$ |

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)

4. Match List-I with List-II

[NEET 2025]

| List-I: Ion |                  | List-II: Group Number in Cation Analysis |           |
|-------------|------------------|------------------------------------------|-----------|
| A.          | $\text{Co}^{2+}$ | I.                                       | Group-I   |
| B.          | $\text{Mg}^{2+}$ | II.                                      | Group-III |
| C.          | $\text{Pb}^{2+}$ | III.                                     | Group-IV  |
| D.          | $\text{Al}^{3+}$ | 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)

5. Match List-I with List-II:

[NEET 2024 Re]

| List-I: Test/reagent |                         | List-II: Radical identified |                  |
|----------------------|-------------------------|-----------------------------|------------------|
| A.                   | Lake Test               | I.                          | $\text{NO}_3^-$  |
| B.                   | Nessler's Reagent       | II.                         | $\text{Fe}^{3+}$ |
| C.                   | Potassium sulphocyanide | III.                        | $\text{Al}^{3+}$ |
| D.                   | Brown Ring Test         | IV.                         | $\text{NH}_4^+$  |

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

Sol. (d)

6. Given below are certain cations. Using inorganic qualitative analysis, arrange them in increasing group number from 0 to VI.

[NEET 2024]

- A.  $\text{Al}^{3+}$  B.  $\text{Cu}^{2+}$  C.  $\text{Ba}^{2+}$  D.  $\text{Co}^{2+}$  E.  $\text{Mg}^{2+}$

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

Sol. (c)

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