

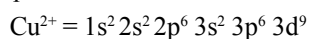
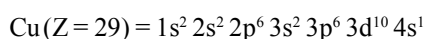
# d & f BLOCK ELEMENTS

## 1. INTRODUCTION

### 1.1 Definition

“The elements in which the last differentiating electron enters into the d-orbitals of the penultimate shell i.e. (n-1) d where n is the last shell are called d-block elements”.

A transition element may also be defined as the element which partially filled d-orbital in their ground state or most stable oxidation state.



(Cupric ion)

The properties of these elements are intermediate between the properties of s-block and p-block elements.

These elements represent a change or transition in properties from more electropositive elements (s-block) to less electropositive elements (p-block). Therefore these elements are called transition elements.

### Position in the periodic table

The position of d-block element has been shown in periodic table as follows :

|         |          |           |           |           |           |           |           |           |            |            |            |            |           |          |           |            |            |
|---------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|------------|------------|------------|------------|-----------|----------|-----------|------------|------------|
| IA<br>1 | IIA<br>2 | d-block   |           |           |           |           |           |           |            |            |            | IIIA<br>13 | IVA<br>14 | VA<br>15 | VIA<br>16 | VIIA<br>17 | Zero<br>18 |
|         |          | IIIB<br>3 | IVB<br>4  | VB<br>5   | VIB<br>6  | VII<br>7  | VIII<br>8 | VIII<br>9 | VIII<br>10 | IB<br>11   | IIB<br>12  |            |           |          |           |            |            |
|         |          | 21<br>Sc  | 22<br>Ti  | 23<br>V   | 24<br>Cr  | 25<br>Mn  | 26<br>Fe  | 27<br>Co  | 28<br>Ni   | 29<br>Cu   | 30<br>Zn   |            |           |          |           |            |            |
|         |          | 39<br>Y   | 40<br>Zr  | 41<br>Nb  | 42<br>Mo  | 43<br>Tc  | 44<br>Ru  | 45<br>Rh  | 46<br>Pd   | 47<br>Ag   | 48<br>Cd   |            |           |          |           |            |            |
|         |          | 57<br>La  | 72<br>Hf  | 73<br>Ta  | 74<br>W   | 75<br>Re  | 76<br>Os  | 77<br>Ir  | 78<br>Pt   | 79<br>Au   | 80<br>Hg   |            |           |          |           |            |            |
|         |          | 89<br>Ac  | 104<br>Rf | 105<br>Db | 106<br>Sg | 107<br>Bh | 108<br>Hs | 109<br>Mt | 110<br>Uun | 111<br>Uuu | 112<br>Uub |            |           |          |           |            |            |
|         |          | s-block   |           |           |           |           |           |           |            |            |            | p-block    |           |          |           |            |            |
|         |          | f-block   |           |           |           |           |           |           |            |            |            |            |           |          |           |            |            |

- d-block elements lie in between 's' and 'p' block elements, i.e. these elements are located in the middle of the periodic table.
- d-block elements are present in,
  - 4<sup>th</sup> period (<sub>21</sub>Sc to <sub>30</sub>Zn, 10 elements) → 1<sup>st</sup> Transition series.
  - 5<sup>th</sup> period (<sub>39</sub>Y to <sub>48</sub>Cd, 10 elements) → 2<sup>nd</sup> Transition series.
  - 6<sup>th</sup> period (<sub>51</sub>La, <sub>72</sub>Hf to <sub>80</sub>Hg, 10 elements) → 3<sup>rd</sup> Transition series.
  - 7<sup>th</sup> period (<sub>89</sub>Ac, <sub>104</sub>Rf to <sub>112</sub>Uub, 10 elements) → 4<sup>th</sup> Transition series.

## 1.2 Electronic configuration

- In d-block elements with increase in atomic number, the d-orbitals of penultimate shell i.e. (n-1) d are gradually filled by electrons. The general electronic configuration of d-block element is,  
(n-1) d<sup>1-10</sup>, ns<sup>0-2</sup>.
- Depending upon the d-orbitals of which penultimate shell i.e. n = 4, 5, 6, 7 are filled, four rows (called series) of ten elements each obtained. They correspond to 3d, 4d, 5d and 6d subshells.
- Energy of '(n-1)d' subshell is slightly greater than 'ns' subshell, hence orbital is filled first then (n-1) d orbitals.
- The general electronic configuration of d-block/d-series elements be shown as follows :

### 1. First (3d) Transition Series (Sc–Zn)

|         |  |    |    |    |    |    |    |    |    |    |
|---------|--|----|----|----|----|----|----|----|----|----|
| At. No. | 21   | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Element | Sc   | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| E.C.    | 3d <sup>1</sup> 4s <sup>2</sup> 3d <sup>2</sup> 4s <sup>2</sup> 3d <sup>3</sup> 4s <sup>2</sup> 3d <sup>4</sup> 4s <sup>1</sup> 3d <sup>5</sup> 4s <sup>1</sup> 3d <sup>6</sup> 4s <sup>2</sup> 3d <sup>7</sup> 4s <sup>2</sup> 3d <sup>8</sup> 4s <sup>2</sup> 3d <sup>9</sup> 4s <sup>1</sup> 3d <sup>10</sup> 4s <sup>2</sup> |    |    |    |    |    |    |    |    |    |

### 2. Second (4d) Transition Series (Y–Cd)

|         |  |    |    |    |     |    |    |    |    |    |
|---------|--|----|----|----|-----|----|----|----|----|----|
| At. No. | 39   | 40 | 41 | 42 | 43  | 44 | 45 | 46 | 47 | 48 |
| Element | Y  | Zr | Nb | Mo | Tc* | Ru | Rh | Pd | Ag | Cd |
| E.C.    | 4d <sup>1</sup> 5s <sup>2</sup> 4d <sup>2</sup> 5s <sup>2</sup> 4d <sup>3</sup> 5s <sup>1</sup> 4d <sup>4</sup> 5s <sup>1</sup> 4d <sup>5</sup> 5s <sup>1</sup> 4d <sup>6</sup> 5s <sup>1</sup> 4d <sup>7</sup> 5s <sup>1</sup> 4d <sup>8</sup> 5s <sup>1</sup> 4d <sup>9</sup> 5s <sup>1</sup> 4d <sup>10</sup> 5s <sup>2</sup> |    |    |    |     |    |    |    |    |    |

### 3. Third (5d) Transition Series (La–Hg)

|         |  |    |    |    |    |    |    |    |    |    |
|---------|--|----|----|----|----|----|----|----|----|----|
| At. No. | 57   | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 |
| Element | La   | Hf | Ta | W  | Re | Os | Ir | Pt | Au | Hg |
| E.C.    | 5d <sup>1</sup> 6s <sup>2</sup> 5d <sup>2</sup> 6s <sup>2</sup> 5d <sup>3</sup> 6s <sup>2</sup> 5d <sup>4</sup> 6s <sup>2</sup> 5d <sup>5</sup> 6s <sup>2</sup> 5d <sup>6</sup> 6s <sup>2</sup> 5d <sup>7</sup> 6s <sup>2</sup> 5d <sup>8</sup> 6s <sup>2</sup> 5d <sup>9</sup> 6s <sup>1</sup> 5d <sup>10</sup> 6s <sup>2</sup> |    |    |    |    |    |    |    |    |    |

### 4. Fourth (6d) Transition Series

|         |  |     |     |     |     |     |     |     |     |     |
|---------|--|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| At. No. | 89   | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 |
| Element | Ac   | Ku  | Ha  | Sg  | Bh  | Hs  | Mt  | Uun | Uuu | Uub |
|         | (Unh) (Uns) (Uno) (Une)  |     |     |     |     |     |     |     |     |     |
| E.C.    | 6d <sup>1</sup> 7s <sup>2</sup> 6d <sup>2</sup> 7s <sup>2</sup> 6d <sup>3</sup> 7s <sup>2</sup> 6d <sup>4</sup> 7s <sup>2</sup> 6d <sup>5</sup> 7s <sup>2</sup> 6d <sup>6</sup> 7s <sup>2</sup> 6d <sup>7</sup> 7s <sup>2</sup> 6d <sup>8</sup> 7s <sup>2</sup> 6d <sup>9</sup> 7s <sup>1</sup> 6d <sup>10</sup> 7s <sup>2</sup> |     |     |     |     |     |     |     |     |     |

**Exceptional configuration of Cr and Cu.** The exceptions observed in the first series are in case of electronic configurations of chromium (Z = 24) and copper (Z = 29). It may be noted that unlike other elements, chromium and copper have a single electron in the 4s-orbital. This is due to the gain of additional stability by the atom by either having half-filled configuration (i.e., containing 5 electrons in the d-sublevel) or completely filled configuration, (i.e., containing 10 electrons in the d-sublevel). The 3d-level in case of chromium gets exactly half-filled with configuration 3d<sup>5</sup> 4s<sup>1</sup> and that in case of copper, it gets completely filled with configuration 3d<sup>10</sup> 4s<sup>1</sup>. This can be explained on the basis of exchange energy

Thus, the electronic configuration of chromium ( $Z = 24$ ) and copper ( $Z = 29$ ) are  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$  and  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$  respectively.

### 1.3 Properties

#### 1. Atomic Radii

- (i) The atomic radii of the transition metals lie in-between those of s- and p-block elements.
- (ii) Generally the atomic radii of d-block elements in a series decrease with increase in atomic number but the decrease in atomic size is small after midway.

#### Explanation

The atomic radius decreases with the increase in atomic number as the nuclear charge increases whereas the shielding effect of d-electron is small. After midway, as the electrons enter the last but one (penultimate) shell, the added d-electron shields (screens) the outermost electron. Hence, with the increase in the d-electrons, screening effect increases. This counterbalances the increased nuclear charge due to increase in atomic number. As a result, the atomic radii remain practically same after chromium. For example in Fe, the two opposing tendencies almost counterbalance and there is no change in the size from Mn to Fe.

- (iii) At the end of the period, there is a slight increase in the atomic radii.

#### Explanation

Near the end of series, the increased electron-electron repulsions between added electrons in the same orbitals are greater than the attractive forces due to the increased nuclear charge. This results in the expansion of the electron cloud and thus the atomic radius increases.

- (iv) The atomic radii increase down the group. This means that the atomic radii of second series are larger than those of first transition series. But the atomic radii of the second and third transition series are almost the same.

The atomic radii of the elements of the second and third transition metals are nearly same due to lanthanide contraction (or also called lanthanoid contraction) discussed later.

### 1.4 Ionic radii

- (i) The trend followed by the ionic radii is the same as that followed by atomic radii.
- (ii) Ionic radii of transition metals are different in different oxidation states.
- (iii) The ionic radii of the transition metals are smaller than those of the representative elements belonging to the same period.

### 1.5 Metallic character

Except for mercury which is a liquid, all the transition elements have typical metallic structure. They exhibit all the characteristics of metals. ductile, have high melting and boiling points, high thermal and electrical conductivity and high tensile strength.

Transition elements have relatively low ionization energies and have one or two electrons in their outermost energy level ( $ns^1$  or  $ns^2$ ). As a result, metallic bonds are formed. Hence, they behave as metals. Greater the number of unpaired d electrons, stronger is the bonding due to the overlapping of unpaired electrons between different metal atoms.

### 1.6 Melting Point

Transition metals have high melting points which is due to their strong metallic bond. The metallic bond. The metallic bonding depends upon the number of unpaired  $e^-$ . The melting point first increases (Sc-Cr), reaches a maximum value (Cr) and then decreases (Fe-Zn)

- \* Tungsten (W) has the highest melting point.
- \* Mercury (Hg) has the lowest melting point.
- \* Mn has the lowest melting point in 3d series typical transition elements.

### 1.7 Ionisation energies or Ionisation enthalpies

- (i) The first ionisation enthalpies of d-block elements lie between s-block and p-block elements. They are higher than those of s-block elements and are lesser than those of p-block elements. The ionisation enthalpy gradually increases with increase in atomic number along a given transition series though some irregularities are observed

#### Explanation

- (i) The increasing ionization enthalpies are due to increased nuclear charge with increase in atomic number which reduces the size of the atom making the removal of outer electron difficult.
- (ii) In a given series, the difference in the ionisation enthalpies between any two successive d-block elements is very much less than the difference in case of successive s-block or p-block elements.

#### Explanation

The addition of d electrons in last but one  $[(n-1)]$  or penultimate shell with increase in atomic number provides a screening effect and thus shields the outer s electrons from inward nuclear pull. Thus, the effects of increased nuclear charge and addition of d electrons tend to oppose each other.

- (iii) The first ionization enthalpy of Zn, Cd and Hg are, however, very high because of the fully filled  $(n-1) d^{10} ns^2$  configuration.
- (iv) Although second and third ionization enthalpies also, in general, increase along a period, but the magnitude of increase for the successive elements is much higher.

- (v) The high values of 3rd ionization enthalpies for Cu, Ni and Zn explain why they show a maximum oxidation state of +2.
- (vi) The first ionisation enthalpies of 5d elements are higher as compared to those of 3d and 4d elements. This is because the weak shielding of nucleus by 4f electrons in 5d elements results in greater effective nuclear charge acting on the outer valence electrons.

### 1.8. Oxidation state

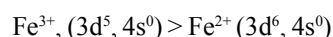
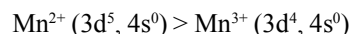
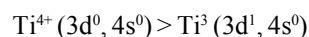
“The net numerical charge assigned to an atom of an element in its combined state is known as its Oxidation state or Oxidation number”.

- (1) With the exception of few elements, most of the d-block elements show more than one oxidation state i.e. they show variable oxidation states. The elements show variable oxidation state because of following reasons:
- (i) ‘(n-1) d’ and ‘ns’ orbitals in the atoms of d-block elements have almost same energies and therefore electron can be removed from ‘(n-1)d’ orbitals as easily as ‘s’ orbitals electrons.
- (ii) After removing ‘s’ electrons, the remainder is called Kernel of the metal cations. In d-block elements, the kernel is unstable and therefore it loses one or more electrons from (n – 1)d electrons. This results in formation of cations with different oxidation states.
- (2) All transition elements show variable oxidation state except last element in each series.
- (3) Minimum oxidation state = Total number of electrons in 4s lost. Maximum oxidation state = (Total number of electrons in 4s + number of unpaired electrons in 3d lost).

In ‘3d’ series all element contain 2 electrons in ‘4s’ and hence they all give a common minimum oxidation state of +2. (Except ‘Cr’ and ‘Cu’ where minimum oxidation state is +1.) The maximum oxidation state is given by Mn i.e.  $Mn^{+7}$  in which two electrons are removed from 4s and five unpaired electrons are removed from 3d orbitals.

- (4) The highest oxidation state is shown by Ruthenium (Ru) and Osmium (Os) i.e. +8.
- (5) Across the period oxidation state increases and it is maximum at the centre and then decreases even if atomic number increases. The element which shows highest oxidation state occur in the middle or near the middle of the series and then decreases.
- (6) Transition metals also show zero oxidation states in metal carbonyl complex. (Nickel tetracarbonyl).  
Example : Ni in  $Ni(CO)_4$  has zero oxidation state.
- (7) The bonding in the compounds of lower oxidation state (+2, +3) is mostly ionic and the bonding in the compounds of higher oxidation state is mostly covalent.
- (8) The relative stabilities of some oxidation states can be explained on the basis of rule extra stability, according to which  $d^0$ ,  $d^5$  and  $d^{10}$  are stable configurations.

For example, the stability order of some ions is as follows:



- (9)  $Cu^{+2}$  is more stable than  $Cu^{+1}$  even when  $Cu^{+1}$  is  $3d^{10}$  while  $Cu^{+2}$  is 3d due to high heat of hydration.

Variable oxidation states shown by 3d-series of d-block elements.

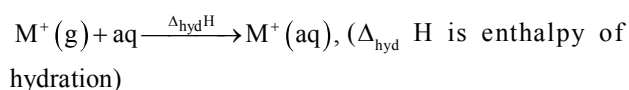
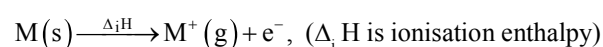
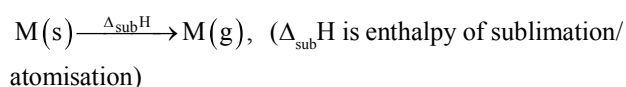
### Oxidation States

| ELECTRONIC CONFIGURATION | Sc       | Ti       | V        | Cr       | Mn       | Fe       | Co       | Ni       | Cu          | Zn          |
|--------------------------|----------|----------|----------|----------|----------|----------|----------|----------|-------------|-------------|
|                          | $d^1s^2$ | $d^2s^2$ | $d^3s^2$ | $d^4s^2$ | $d^5s^2$ | $d^6s^2$ | $d^7s^2$ | $d^8s^2$ | $d^9s^2$    | $d^{10}s^2$ |
|                          |          |          |          | $d^5s^1$ |          |          |          |          | $d^{10}s^1$ |             |
| OXIDATION STATES         |          |          |          | +1       |          |          |          |          | +1          |             |
|                          | +2       | +2       | +2       | +2       | +2       | +2       | +2       | +2       | +2          | +2          |
|                          | +3       | +3       | +3       | +3       | +3       | +3       | +3       | +3       | +3          |             |
|                          |          | +4       | +4       | +4       | +4       | +4       | +4       | +4       |             |             |
|                          |          |          | +5       | +5       | +5       | +5       | +5       |          |             |             |
|                          |          |          |          | +6       | +6       | +6       |          |          |             |             |
|                          |          |          |          |          | +7       |          |          |          |             |             |

### 1.9 Standard electrode potentials ( $E^\circ$ ) and chemical reactivity

Thermodynamic stability of the compounds of transition elements can be evaluated in terms of the magnitude of ionisation enthalpies of the metals — smaller the ionisation enthalpy of the metal, stabler is its compound.

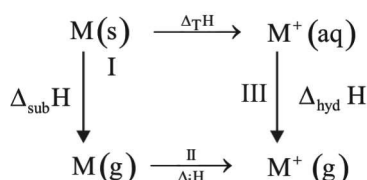
In solution, the stability of the compounds depends upon electrode potentials rather than ionization enthalpies. Electrode potential values depend upon factors such as enthalpy of sublimation (or atomisation) of the metal, the ionisation enthalpy and the hydration enthalpy, i.e.,



The total energy,  $\Delta_T H$ , for the process involving sublimation, ionisation and hydration simultaneously, i.e., for the process,  $M(s) \longrightarrow M^+(aq) + e^-$ , will be the sum of the three types of enthalpies, i.e.,

$$\Delta_T H = \Delta_{\text{sub}}H + \Delta_iH + \Delta_{\text{hyd}}H.$$

Thus,  $\Delta_T H$ , is the total enthalpy change when solid metal, M is brought in the aqueous medium in the form of monovalent ion,  $M^+(aq)$ .



#### Trends in the $M^{2+}/M$ Standard Electrode Potentials

- There is no regular trend in the  $E^\circ$  ( $M^{2+}/M$ ) values. This is because their ionization enthalpies ( $I_1 + IE_2$ ) and sublimation enthalpies do not show any regular trend.
- The general trend towards less negative  $E^\circ$  values along the series is due to the general increase in the sum of first and second ionization enthalpies.
- Copper shows a unique behaviour in the series as it is the only metal having positive value for  $E^\circ$ . This explains why it does not liberate  $H_2$  gas from acids. It reacts only with the oxidizing acids ( $HNO_3$  and  $H_2SO_4$ ) which are reduced. The reason for positive  $E^\circ$  value for copper is that the sum of enthalpies of sublimation and ionization is not balanced by hydration enthalpy.

- The values of  $E^\circ$  for Mn, Ni and Zn are more negative than expected from the general trend. This is due to greater stability of half-filled d-subshell ( $d^5$ ) in  $Mn^{2+}$ , and completely filled d-subshell ( $d^{10}$ ) in  $Zn^{2+}$ . The exceptional behaviour of Ni towards  $E^\circ$  value from the regular trend is due to its high negative enthalpy of hydration.

#### Trends in the $M^{3+}/M^{2+}$ Standard Electrode Potentials

- A very low value for  $E^\circ$  ( $Sc^{3+}/Sc^{2+}$ ) reflects the stability of  $Sc^{3+}$  ion which has a noble gas configuration.
- The highest value for Zn is on account of very high stability of  $Zn^{2+}$  ion with  $d^{10}$  configuration. It is difficult to remove an electron from it to change it into +3 state.
- The comparatively high value of  $E^\circ$  ( $Mn^{3+}/Mn^{2+}$ ) shows that  $Mn^{2+}$  is very stable which is on account of stable  $d^5$  configuration of  $Mn^{2+}$ .
- The comparatively low value of  $E^\circ$  ( $Fe^{3+}/Fe^{2+}$ ) is on account of extra stability of  $Fe^{3+}$  ( $d^5$ ), i.e., low third ionization enthalpy of Fe.
- The comparatively low value for V is on account of the stability of  $V^{2+}$  ion due to its half-filled  $t_{2g}^3$  configuration (discussed in unit 9).

**Chemical Reactivity and  $E^\circ$  Values.** The transition metals vary very widely in their chemical reactivity. Some of them are highly electropositive and dissolve in mineral acids whereas a few of them are 'noble', i.e., they do not react with simple acids. Some results of chemical reactivity of transition metals as related to their  $E^\circ$  values are given below :

- The metals of the first transition series (except copper) are relatively more reactive than the other series. Thus, they are oxidized by  $H^+$  ions though the actual rate is slow, e.g., Ti and V are passive to dilute non-oxidizing acids at room temperature.
- As already explained, less negative  $E^\circ$  values for  $M^{2+}/M$  along the series indicate a decreasing tendency to form divalent cations.
- More negative  $E^\circ$  values than expected for Mn, Ni and Zn show greater stability for  $Mn^{2+}$ ,  $Ni^{2+}$  and  $Zn^{2+}$ .
- $E^\circ$  values for the redox couple  $M^{3+}/M^{2+}$  indicate that  $Mn^{3+}$  and  $Co^{3+}$  ions are the strongest oxidizing agents in aqueous solution whereas  $Ti^{2+}$ ,  $V^{2+}$  and  $Cr^{2+}$  are strongest reducing agents and can liberate hydrogen from a dilute acid, e.g.,  $2 Cr^{2+}(aq) + 2 H^+(aq) \longrightarrow 2 Cr^{3+}(aq) + H_2(g)$

### 1.10 Catalytic Property

Most transition elements and their compounds have good catalytic properties because

- They possess variable oxidation state.

(b) They provide a large surface area for the reactant to be absorbed.

| Catalysts   | Uses   |
|---|--|
| $\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$ | Ziegler-Natta catalyst, used in polymerisation of ethylene |
| $\text{V}_2\text{O}_5$                              | Contact process $\text{SO}_2 \rightarrow \text{SO}_3$      |
| Fe  | Haber Bosch process  |
| $\text{PdCl}_2$                                     | Wacker's process for $\text{CH}_3\text{CHO}$ manufacturing |
| Pd  | Hydrogenation of alkene, alkyne etc                        |
| Pt/PtO  | Adam's catalyst for selective reduction                    |
| Pt  | Catalytic convertor, for cleaning car exhaust fumes        |
| Pt/Rh   | Ostwald's process : $\text{NH}_3 \rightarrow \text{NO}$    |
| Cu  | Oxidation of alcohols                                      |

### 1.11 Magnetic Behaviour

When a substance is placed in a magnetic field of strength  $H$ , the intensity of the magnetic field in the substance may be greater than or less than  $H$ . If the field in the substance is greater than  $H$ , the substance is a paramagnetic material and attracts line of force. If the field in the substance is less than  $H$ , the substance is diamagnetic. Diamagnetic materials tend to repel lines of force. The magnetic moment of a substance depends on the strength of magnetic field generated due to electronic spin, there is a change in electric flux which leads to induction of magnetic field. The electron is also under orbital angular momentum or orbital spin. It leads to generation of magnetic moment.

In first transition elements series the orbital angular magnetic moment is insignificant the orbital contribution is quenched by the electric fields of the surrounding atoms so magnetic moment is equal to the spin magnetic moment only.

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ BM}$$

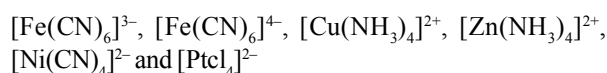
$n \rightarrow$  no. of unpaired electron.

Maximum transition elements and compounds are paramagnetic due to presence of unpaired electrons.

## 2. COMPLEX FORMATION

Transition metal ions form a large number of complex compounds. Complex compounds are those which have a metal ion linked to a number of negative ions (anions) or neutral molecules having lone pairs of electrons. These ions or molecules are called ligands. They donate lone pairs of electrons to the central transition metal ion forming coordinate bonds.

A few examples are given below :



Such complex compounds are not formed by s - and p - block elements.

**Explanation.** The transition elements form complexes because of the following reasons :

- Comparatively smaller size of their metal ions.
- Their high ionic charges.  
(Because of (i) and (ii), they have large charge/size ratio)
- Availability of vacant d-orbitals so that these orbitals can accept lone pairs of electrons donated by the ligands.

### 2.1 Interstitial Compounds

The transition metals form a large number of interstitial compounds in which small atoms such as hydrogen, carbon, boron and nitrogen occupy the empty spaces (interstitial sites) in their lattices (Fig.).

They are represented by formulae like  $\text{TiC}$ ,  $\text{TiH}_2$ ,  $\text{Mn}_4\text{N}$ ,  $\text{Fe}_3\text{H}$ ,  $\text{Fe}_3\text{C}$  etc. However, actually they are non-stoichiometric materials, e.g.,  $\text{TiH}_{1.7}$ ,  $\text{VH}_{0.56}$  etc. and the bonds present in them are neither typically ionic nor covalent. Some of their important characteristics are as follows:

- They are very hard and rigid, e.g., steel which is an interstitial compound of Fe and C is quite hard. Similarly, some borides are as hard as diamond.
- They have high melting points which are higher than those of the pure metals.
- They show conductivity like that of the pure metal.
- They acquire chemical inertness.

### 2.2 Alloy formation

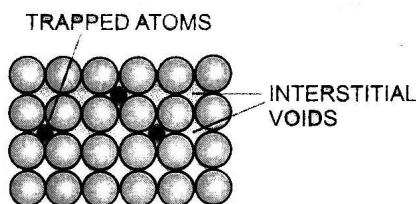
Alloys are homogeneous solid solutions of two or more metals obtained by melting the components and then cooling the melt. These are formed by metals whose atomic radii differ by not more than 15% so that the atoms of one metal can easily take up the positions in the crystal lattice of the other (Fig.)

Now, as transition metals have similar atomic radii and

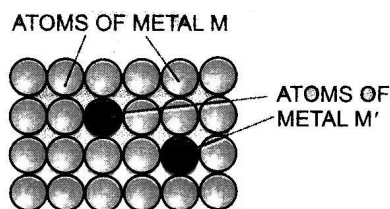


other characteristics, hence they form alloys very readily. Alloys are generally harder, have higher melting points and more resistant to corrosion than the individual metals.

The most commonly used are the ferrous alloys the metals chromium, vanadium, molybdenum, tungsten and manganese are used in the formation of alloy steels and stainless steels. Some alloys of transition metals with non-transition metals are also very common. e.g., brass (Cu + Zn) and bronze (Cu + Sn)



Formation of interstitial compounds.

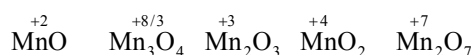


Formation of alloys.

### 3. COMPOUNDS OF TRANSITION ELEMENTS

#### 3.1 Oxides

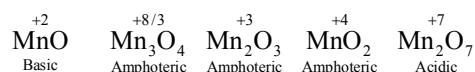
- The metals of the first transition series form oxides with oxygen at high temperature.
- The oxides are formed in the oxidation, states +1 to +7 (as given in Table 8.10, page 8/14).
- The highest oxidation state in the oxides of any transition metal is equal to its group number, e.g., 7 in  $\text{Mn}_2\text{O}_7$ . Beyond group 7, no higher oxides of iron above  $\text{Fe}_2\text{O}_3$  are known. Some metals in higher oxidation state stabilize by forming oxocations, e.g.,  $\text{V}^{\text{V}}$  as  $\text{VO}_2^+$ ,  $\text{V}^{\text{IV}}$  as  $\text{VO}^{2+}$  and  $\text{Ti}^{\text{IV}}$  as  $\text{TiO}^{2+}$ .
- All the metals except scandium form the oxides with the formula  $\text{MO}$  which are ionic in nature. As the oxidation number of the metal increases, ionic character decreases, e.g.,  $\text{Mn}_2\text{O}_7$  is a covalent green oil. Even  $\text{CrO}_3$  and  $\text{V}_2\text{O}_5$  have low melting points.



- In general, the oxides in the lower oxidation states of the metals are basic and in their higher oxidation states, they are acidic whereas in the intermediate oxidation state, the

oxides are amphoteric.

For example, the behaviour of the oxides of manganese may be represented as follows :

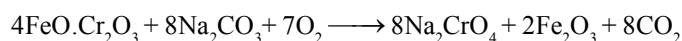


Thus,  $\text{Mn}_2\text{O}_7$  dissolves in water to give the acid  $\text{HMnO}_4$ .

#### 3.2 $\text{KMnO}_4$ Potassium permanganate

It is prepared from the ore called chromite or ferrochrome or chrome iron,  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ . The various steps involved are as follows :

- Preparation of sodium chromate. The ore is finely powdered, mixed with sodium carbonate and quick lime and then roasted, i.e., heated to redness in a reverberatory furnace with free exposure to air when sodium chromate (yellow in colour) is formed and carbon dioxide is evolved. Quick lime keeps the mass porous and thus facilitates oxidation.



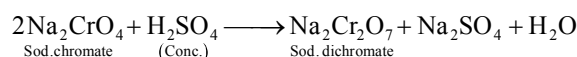
Chromite ore

Sod. chromate

Ferric oxide

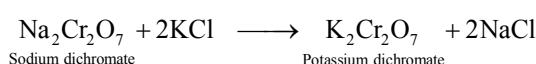
After the reaction, the roasted mass is extracted with water when sodium chromate is completely dissolved while ferric oxide is left behind. Ferric oxide is separated out by filtration.

- Conversion of sodium chromate into sodium dichromate. The filtrate containing sodium chromate solution is treated with concentrated sulphuric acid when sodium chromate is converted into sodium dichromate.



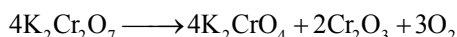
Sodium sulphate being less soluble crystallizes out as decahydrate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and is removed. The clear solution is then evaporated in iron pans to a specific gravity of 1.7 when a further crop of sodium sulphate is formed. It is removed and the solution is cooled when orange crystals of sodium dichromate,  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  separate on standing.

(iii) Conversion sodium dichromate into potassium dichromate. Hot concentrated solution of sodium dichromate is treated with calculated amount of potassium chloride when potassium dichromate, being much less soluble than sodium salt, crystallizes out on cooling as orange crystals.

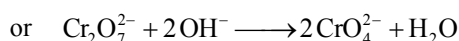
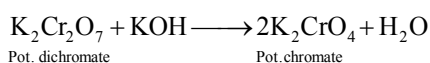


## 3.3 Properties

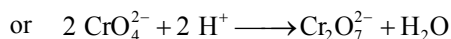
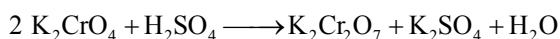
- Colour and Melting point.** It forms orange crystals which melt at 669 K.
- Solubility.** It is moderately soluble in cold water but freely soluble in hot water.
- Action of heat.** When heated to a white heat, it decomposes with the evolution of oxygen.



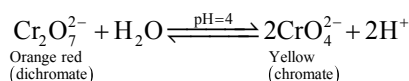
- Action of alkalis.** When an alkali is added to an orange red solution of dichromate, a yellow solution results due to the formation of chromate.



On acidifying, the colour again changes to orange red due to the reformation of dichromate.



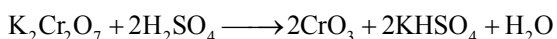
This interconversion is explained by the fact that in dichromate solution, the  $\text{Cr}_2\text{O}_7^{2-}$  ions are invariably in equilibrium with  $\text{CrO}_4^{2-}$  ions at  $\text{pH} = 4$ , i.e.,



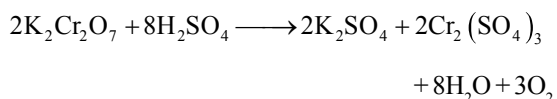
On adding an alkali (i.e., increasing the pH of the solution), the  $\text{H}^+$  ions are used up and according to the law of chemical equilibrium, the reaction proceeds in the forward direction producing yellow chromate solution. On the other hand, when an acid is added (i.e., pH of the solution is decreased), the concentration of  $\text{H}^+$  ions is increased and the reaction proceeds in the backward direction producing an orange red dichromate solution.

#### 5. Action of concentrated sulphuric acid

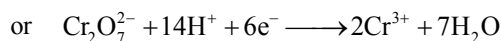
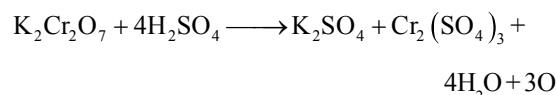
(a) In cold, red crystals of chromic anhydride (chromium trioxide) are formed.



(b) On heating the mixture, oxygen is evolved.

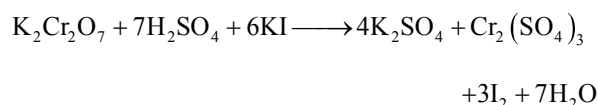


- Oxidising properties.** It is a powerful oxidising agent. In the presence of dilute sulphuric acid, one molecule of potassium dichromate furnishes 3 atoms of available oxygen as indicated by the equation :

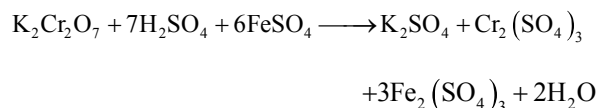


$$\therefore \text{Eq. wt. of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{\text{Mol. wt.}}{6} = \frac{294}{6} = 49$$

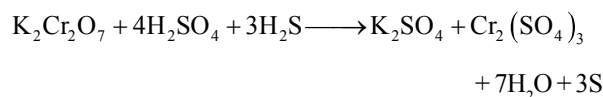
- It liberates  $\text{I}_2$  from KI



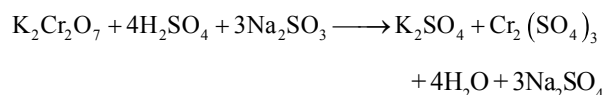
- It oxidises ferrous salts to ferric salts



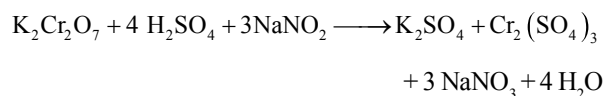
- It oxidises  $\text{H}_2\text{S}$  to sulphur



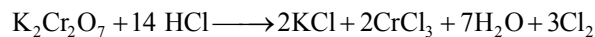
- It oxidises sulphites to sulphates and thiosulphates to sulphates and sulphur



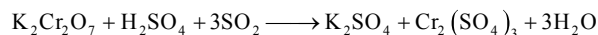
- It oxidises nitrites to nitrates



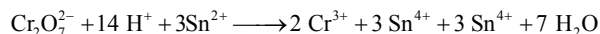
- It oxidises halogen acids to halogen



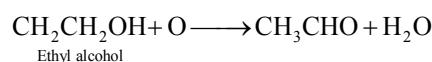
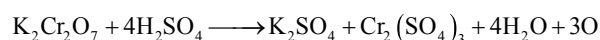
- It oxidises  $\text{SO}_2$  to sulphuric acid

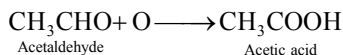


- It oxidises stannous salts to stannic salts



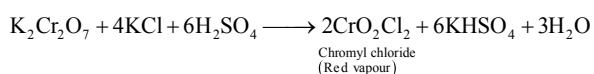
- It oxidises ethyl alcohol to acetaldehyde and acetic acid.



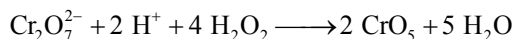


**Test for a drunken driver.** The above reaction helps to test whether a driver has consumed alcohol or not. he is asked to breathe into the acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution taken in a test tube. If the orange colour of the solution changes into green colour (due to  $\text{Cr}_2(\text{SO}_4)_3$  formed in the reaction), the driver is drunk, otherwise not.

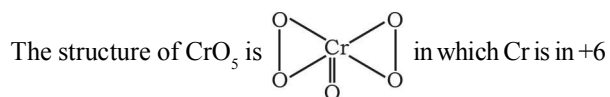
7. **Chromyl chloride test** (Reaction with a chloride and conc. sulphuric acid). When heated with concentrated hydrochloric acid or with a chloride and strong sulphuric acid, reddish brown vapours of chromyl chloride are obtained.



8. **Reaction with hydrogen peroxide.** Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution reacts with  $\text{H}_2\text{O}_2$  to give a deep blue solution due to the formation of peroxo compound,  $\text{CrO}(\text{O}_2)_2$ .



The blue colour fades away gradually due to the decomposition of  $\text{CrO}(\text{O}_2)_2$  into  $\text{Cr}^{3+}$  ions and oxygen.



oxidation state.

#### Uses.

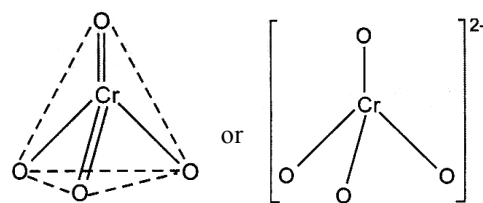
- (i) In volumetric analysis, it is used as a primary standard for the estimation of  $\text{Fe}^{2+}$  (ferrous ions) and  $\text{I}^-$  (iodides) in redox titrations.

#### Note

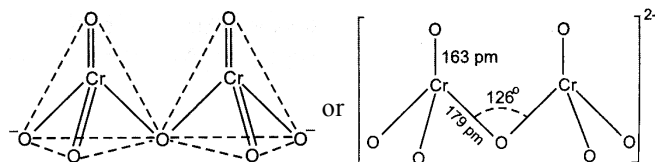
$\text{Na}_2\text{Cr}_2\text{O}_7$  is not used in volumetric analysis because it is deliquescent.

- (ii) In industry, it is used
- In chrome tanning in leather industry.
  - In the preparation of chrome alum  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  and other industrially important compounds such as  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_3$ ,  $\text{CrO}_2\text{Cl}_2$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{CrCl}_3$  etc.
  - In calico printing and dyeing.
  - In photography and in hardening gelatine film.
- (iii) In organic chemistry, it is used as an oxidising agent.

#### Structures of chromate and dichromate ions.



a Chromate ion-Tetrahedral structure



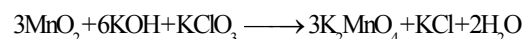
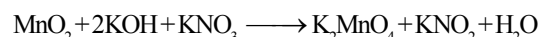
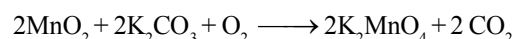
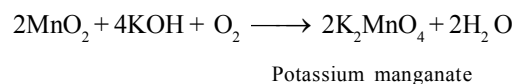
b Dichromate ion-Two tetrahedra sharing one oxygen atom at one corner

### 3.4 Potassium Permanganate ( $\text{KMnO}_4$ )

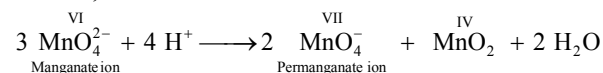
#### Preparation

On a large scale, it is prepared from the mineral, pyrolusite,  $\text{MnO}_2$ . The preparation involves the following two steps:

- (i) Conversion of  $\text{MnO}_2$  into potassium manganate. The finely powdered pyrolusite mineral is fused with potassium hydroxide or potassium carbonate in the presence of air or oxidising agent such as potassium nitrate or potassium chlorate when green coloured potassium manganate is formed.

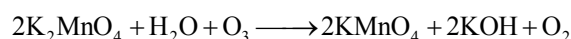
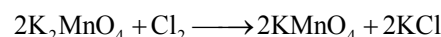


Potassium manganate thus formed undergoes disproportionation in the neutral or acidic solution as follows, if allowed to stand for some time :



- (ii) Oxidation of potassium manganate to potassium permanganate.

(a) Chemical oxidation. The fused mass is extracted with water and the solution after filtration is converted into potassium permanganate by bubbling carbon dioxide, chlorine or ozonised oxygen through the green solution.



The carbon dioxide process is uneconomical as one third of the original manganate is reconverted to manganese



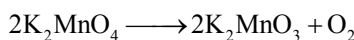
dioxide. However, this process has the advantage that the potassium carbonate formed as a by-product can be used for the oxidative fusion of manganese dioxide. In the chlorine process, potassium chloride obtained as a by-product is lost.

### PROPERTIES

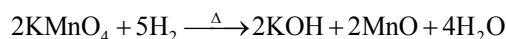
- 1. Colour.** Potassium permanganate exists as deep purple black prisms with a greenish lustre which become dull in air due to superficial reduction.
- 2. Solubility.** It is moderately soluble in water at room temperature and it is more soluble in hot water.
- 3. Action of heat.** When heated to 513 K, it readily decomposes giving oxygen.



At red heat, potassium manganate formed decomposes into potassium manganite ( $\text{K}_2\text{MnO}_3$ ) and oxygen.

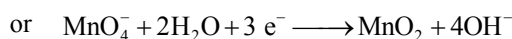
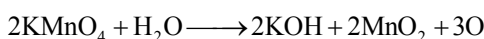


- 4. Action of heat in current of hydrogen.** When heated in a current of  $\text{H}_2$ , solid  $\text{KMnO}_4$  gives  $\text{KOH}$ ,  $\text{MnO}$  and water vapours.



- 5. Oxidising property.** Potassium permanganate is powerful oxidising agent. The actual course of reaction depends on the use of the permanganate in (a) neutral (b) alkaline or (c) acidic solution.

- (a) In neutral solution.** Potassium permanganate acts as a moderate oxidising agent in neutral aqueous solution because of the reaction :

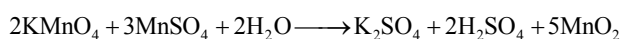


Thus,  $\text{MnO}_4^-$  ion gains 3 electrons. Also, according to the above equation, in neutral medium, from two moles of permanganate, three oxygen atoms are available. In fact, during the course of reaction, the alkali generated renders the medium alkaline even when we start with neutral solutions. Hence, Eq. wt. of  $\text{KMnO}_4$  in neutral or weakly alkaline medium

$$= \frac{\text{Mol. wt.}}{3} = \frac{158}{3} = 52.67$$

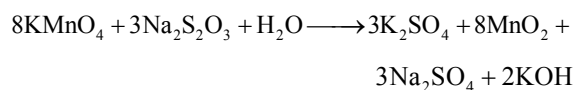
Some oxidizing properties of  $\text{KMnO}_4$  in the neutral medium. These are given below :

- (i)** It oxidises hot manganous sulphate to manganese dioxide.

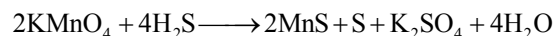


Presence of  $\text{ZnSO}_4$  or  $\text{ZnO}$  catalyses the oxidation.

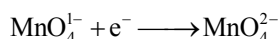
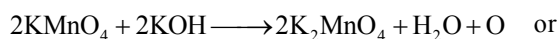
- (ii)** It oxidises sodium thiosulphate to sodium sulphate.



- (iii)** It oxidises hydrogen sulphide to sulphur.

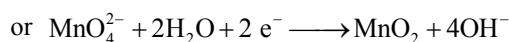
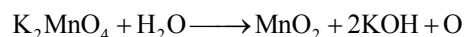


- (b) In alkaline solution.** In strongly alkaline solution,  $\text{MnO}_4^{2-}$  (manganate) ion is produced.

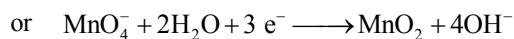
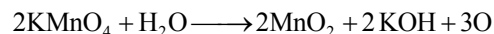


$$\therefore \text{Eq. wt. of } \text{KMnO}_4 = \frac{\text{Mol. wt.}}{1} = \frac{158}{1} = 158$$

Potassium manganate is also further reduced to  $\text{MnO}_2$  when a reducing agent is present.



So the complete reaction is :

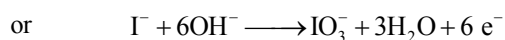
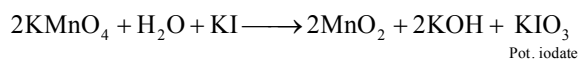


which is the same as that for neutral medium. Hence, equivalent weight of  $\text{KMnO}_4$  in weakly alkaline medium is same as that in the neutral medium, viz., 52.67

### Some oxidizing properties of $\text{KMnO}_4$ in the alkaline medium.

These are given below :

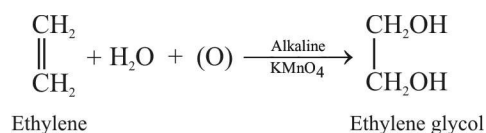
- (i)** It oxidises potassium iodide to potassium iodate.



In this case, iodine is not liberated unlike the case of acidic medium.

Similar reaction takes place with  $\text{KBr}$ .

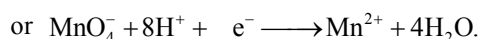
- (ii)** It oxidises olefinic compounds to glycols, i.e., when an olefinic compound is shaken with alkaline  $\text{KMnO}_4$ , pink colour of  $\text{KMnO}_4$  is discharged.



Alkaline  $\text{KMnO}_4$  used for this test is known as Baeyer's reagent. It is used for oxidation of a number of organic compounds.

**d & f BLOCK ELEMENTS**

- (c) **In acidic medium.** Potassium permanganate in the presence of dil. sulphuric acid, i.e., in acidic medium, acts as a strong oxidising agent because of the reaction



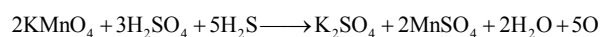
Since in the above reaction,  $\text{MnO}_4^-$  ion gains 5 electrons of five atoms of oxygen are available from two molecules of  $\text{KMnO}_4$ . Hence.

$$\text{Eq. wt. of } \text{KMnO}_4 = \frac{\text{Mol. wt.}}{5} = \frac{158}{5} = 31.6$$

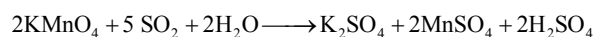
**Some oxidizing properties of  $\text{KMnO}_4$  in the acidic medium.**

These are given below :

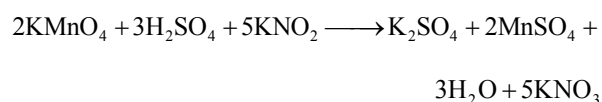
- (i) It oxidises  $\text{H}_2\text{S}$  to S.



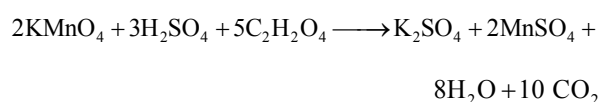
- (ii) It oxidises sulphur dioxide to sulphuric acid.



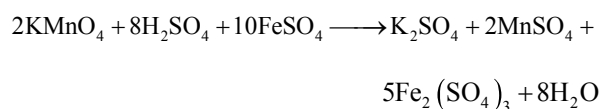
- (iii) It oxidises nitrites ( $\text{NO}_2^-$ ) to nitrates ( $\text{NO}_3^-$ ), arsenites ( $\text{AsO}_3^{3-}$ ) to arsenates ( $\text{AsO}_4^{3-}$ ) and sulphites and thiosulphates to sulphates.



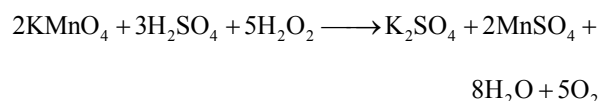
- (iv) It oxidises oxalates or oxalic acid to  $\text{CO}_2$



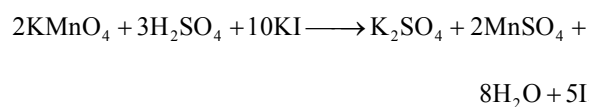
- (v) It oxidises ferrous sulphate to ferric sulphate (i.e., ferrous salt to ferric salt).



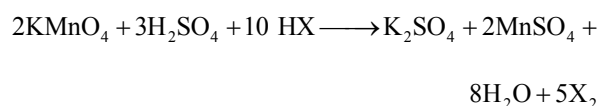
- (vi) It oxidises  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{O}$  and  $\text{O}_2$ . This is because acidified  $\text{KMnO}_4$  is a stronger oxidising agent than  $\text{H}_2\text{O}_2$ .



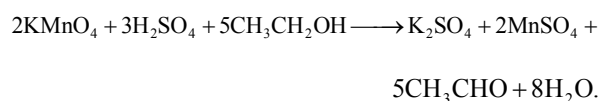
- (vii) It oxidises potassium iodide to iodine



- (viii) It oxidises  $\text{HX}$  (where  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) to  $\text{X}_2$



- (ix) It oxidises ethyl alcohol to acetaldehyde



**Uses.**

- (i) It is often used in volumetric analysis for the estimation of ferrous salts, oxalates, iodides and hydrogen peroxide. However, it is not a primary standard because it is difficult to obtain it in the pure state and free from traces of  $\text{MnO}_2$ . It is, therefore, always first standardised with a standard solution of oxalic acid.

**Remember that** volumetric titrations involving  $\text{KMnO}_4$  are carried out only in presence of dilute  $\text{H}_2\text{SO}_4$  but not in the presence of  $\text{HCl}$  or  $\text{HNO}_3$ . This is because oxygen produced from  $\text{KMnO}_4 + \text{dill. H}_2\text{SO}_4$  is used only for oxidizing the reducing agent. Moreover,  $\text{H}_2\text{SO}_4$  does not give any oxygen of its own to oxidize the reducing agent. In case  $\text{HCl}$  is used, the oxygen produced from  $\text{KMnO}_4 + \text{HCl}$  is partly used up to oxidize  $\text{HCl}$  to chlorine and in case  $\text{HNO}_3$  is used, it itself acts as oxidizing agent and partly oxidizes the reducing agent.

- (ii) It is used as a strong oxidising agent in the laboratory as well as in industry. It is a favourite and effective oxidising agent used in organic synthesis. Alkaline potassium permanganate is used for testing unsaturation in organic chemistry and is known as Baeyer's reagent.
- (iii) Potassium permanganate is also widely used as a disinfectant and germicide. A very dilute solution of permanganate is used for washing wounds and gargling for mouth sore. It is also used for purifying water of stinking wells.
- (iv) Because of its strong oxidizing power, it is also used for bleaching of wool, cotton, silk and other textile fibres and also for decolourisation of oils.

## THE LANTHANIDE SERIES

### 1. INTRODUCTION

These elements are classified by the filling up of the antipenultimate 4f energy levels.

### 2. PHYSICAL PROPERTIES

#### Electronic Configuration and oxidation states

| Element      |    | Electronic Configuration                              | Electronic Configuration of $M^{3+}$ | Oxidation States |
|--------------|----|---|--------------------------------------|------------------|
| Lanthanum    | La | [Xe] 5d <sup>1</sup> 6s <sup>2</sup>                  | [Xe]                                 | +3               |
| Cerium       | Ce | [Xe] 4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>  | [Xe] 4f <sup>1</sup>                 | +3 (+4)          |
| Praseodymium | Pr | [Xe] 4f <sup>3</sup> 6s <sup>2</sup>                  | [Xe] 4f <sup>2</sup>                 | +3 (+4)          |
| Neodymium    | Nd | [Xe] 4f <sup>4</sup> 6s <sup>2</sup>                  | [Xe] 4f <sup>3</sup>                 | (+2) +3          |
| Promethium   | Pm | [Xe] 4f 6s <sup>2</sup>                               | [Xe] 4f <sup>4</sup>                 | (+2) +3          |
| Samarium     | Sm | [Xe] 4f <sup>6</sup> 6s <sup>2</sup>                  | [Xe] 4f <sup>5</sup>                 | (+2) +3          |
| Europium     | Eu | [Xe] 4f <sup>7</sup> 6s <sup>2</sup>                  | [Xe] 4f <sup>6</sup>                 | (+2) +3          |
| Gadolinium   | Gd | [Xe] 4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>  | [Xe] 4f <sup>7</sup>                 | +3               |
| Terbium      | Tb | [Xe] 4f <sup>9</sup> 6s <sup>2</sup>                  | [Xe] 4f <sup>8</sup>                 | +3 (+4)          |
| Dysprosium   | Dy | [Xe] 4f <sup>10</sup> 6s <sup>2</sup>                 | [Xe] 4f <sup>9</sup>                 | +3 (+4)          |
| Holmium      | Ho | [Xe] 4f <sup>11</sup> 6s <sup>2</sup>                 | [Xe] 4f <sup>10</sup>                | +3               |
| Erbium       | Er | [Xe] 4f <sup>12</sup> 6s <sup>2</sup>                 | [Xe] 4f <sup>11</sup>                | +3               |
| Thulium      | Tm | [Xe] 4f <sup>13</sup> 6s <sup>2</sup>                 | [Xe] 4f <sup>12</sup>                | (+2) +3          |
| Ytterbium    | Yb | [Xe] 4f <sup>14</sup> 6s <sup>2</sup>                 | [Xe] 4f <sup>13</sup>                | (+2) +3          |
| Lutetium     | Lu | [Xe] 4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup> | [Xe] 4f <sup>14</sup>                | +3               |

#### 2.1 Oxidation state

The sum of the first three ionization energies for each element are low. Thus the oxidation state (+III) is ionic and  $\text{Ln}^{3+}$  dominates the chemistry of these elements. The  $\text{Ln}^{2+}$  and  $\text{Ln}^{4+}$  ions that do occur are always less stable than  $\text{Ln}^{3+}$ .

Oxidation numbers (+II) and (+IV) do occur, particularly when they lead to :

1. a noble gas configuration e.g.  $\text{Ce}^{4+}$  ( $f^0$ )
2. a half filled f shell, e.g.  $\text{Eu}^{2+}$  and  $\text{Tb}^{4+}$  ( $f^7$ )
3. a completely filled f level, e.g.  $\text{Yb}^{2+}$  ( $f^{14}$ ).

**NOTE**

The 4f electrons in the antipenultimate shell are very effectively shielded from their chemical environment outside the atom by the 5s and 5p electrons. Consequently the 4f electrons do not take part in bonding. They are neither removed to produce ions nor do they take any significant part in crystal field stabilization or complexes. Crystal field stabilization is very important with the d-block elements. The octahedral splitting of f orbitals  $\Delta_o$  is only about  $1\text{ kJ mol}^{-1}$ . Whether the f orbitals are filled or empty has little effect on the normal chemical properties. However, it does affect their spectra and their magnetic properties.

**2.2 Atomic radius**

In lanthanide series, with increasing atomic number, there is a progressive decrease in the atomic as well as ionic radii of trivalent ions from  $\text{La}^{3+}$  to  $\text{Lu}^{3+}$ . This regular decrease in the atomic and ionic radii with increasing atomic number is known as lanthanide contraction.

**Atomic and Ionic radii (pm) of lanthanum and lanthanoids.**

| Element                          | La  | Ce  | Pr  | Nd  | Pm  | Sm  | Eu  | Gd  | Tb  | Dy  | Ho  | Er  | Tm  | Yb  | Lu  |
|----------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Atomic Radii (Ln)                | 187 | 183 | 182 | 181 | 181 | 180 | 199 | 180 | 178 | 177 | 176 | 175 | 174 | 173 | 172 |
| Ionic Radii ( $\text{Ln}^{3+}$ ) | 106 | 103 | 101 | 99  | 98  | 96  | 95  | 94  | 92  | 91  | 90  | 89  | 88  | 87  | 86  |

**2.3 Magnetic behaviour**

Paramagnetism is shown by the positive ions of lanthanides except  $\text{La}^{3+}$  (lanthanum ion,  $f^0$ ) and  $\text{Lu}^{3+}$  (lutetium ion,  $f^{14}$ ). This property of the lanthanides is due to presence of unpaired electrons in the incomplete 4f subshell.

lanthanides differ from transition elements in the fact that their magnetic moments do not obey 'spin only' formula,

viz.,  $\mu_{\text{eff}} = \sqrt{n(n+2)}$  B.M. where n is the number of unpaired electrons. This because in case of transition elements, the orbital contribution is quenched by the electric field of the environment but in case of lanthanides, 4f orbitals lie too deep to be quenched. Hence, their magnetic moment is

As we move along the lanthanide series, the nuclear charge increases by one unit at each successive element. The new electron is added into the same subshell (viz., 4f). As a result, the attraction on the electrons by the nucleus increases and this tends to decrease the size. Further, as the new electron is added into the f-subshell, there is imperfect shielding of one electron by another in this subshell due to the shapes of these f-orbitals. This imperfect shielding is unable to counterbalance the effect of the increased nuclear charge. Hence, the net result is a contraction in the size though the decrease is very small. It is interesting to note that in lanthanides, the decrease in the atomic radius for 14 elements [Ce (58) to Lu (71)] is only 11 pm (from 183 to 172 pm). Similarly, decrease in ionic radii from  $\text{Ce}^{3+}$  to  $\text{Lu}^{3+}$  is only 17 pm (103 to 86 pm).

The contraction is similar to that observed in any transition series. The cause is also similar, just as in the transition series where the contraction is due to imperfect shielding of one d electron by another. But the shielding of one 4f electron by another is less than one d electron by another with increase in nuclear charge along the series.

calculated by considering spin as well as orbital contribution, i.e.,

$$\mu_{\text{eff}} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M.}$$

where S is spin quantum number and L is orbital quantum number.

**NOTE****Separation of the Lanthanide Elements**

Since the change in ionic radius is very small, the chemical properties are similar. This makes the separation of the element in pure state difficult. Separation is done by Ion Exchange methods which is based on the ionic size.

**2.4 Colour**

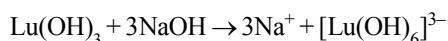
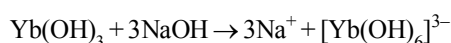
The Lanthanides are silvery white metals. However, most of the trivalent metal ions are coloured, both in the solid state and in aqueous solution. This is due to the partly filled-f-orbitals which permit f-f transition.

**NOTE**

Lanthanides ions with x f electrons have a similar colour to those with (14-x) f electrons e.g.,  $\text{La}^{3+}$  and  $\text{Lu}^{3+}$  are colourless,  $\text{Sm}^{3+}$  and  $\text{Dy}^{3+}$  are yellow and  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  are pink.

**2.5 Hydroxides**

The hydroxides  $\text{Ln}(\text{OH})_3$  are precipitated as gelatinous precipitates by the addition of  $\text{NH}_4\text{OH}$  to aqueous solutions. These hydroxides are ionic and basic. They are less basic than  $\text{Ca}(\text{OH})_2$  but more basic than  $\text{Al}(\text{OH})_3$  which is amphoteric. The metals, oxides and hydroxides all dissolve in dilute acids, forming salts.  $\text{Ln}(\text{OH})_3$  are sufficiently basic to absorb  $\text{CO}_2$  from the air and form carbonates. The basicity decreases as the ionic radius decreases from Ce to Lu. Thus  $\text{Ce}(\text{OH})_3$  is the most basic, and  $\text{Lu}(\text{OH})_3$ , which is the least basic, is intermediate between Scandium and Yttrium in basic strength. The decrease in basic properties is illustrated by the hydroxides of the later elements dissolving in hot concentrated  $\text{NaOH}$ , forming complexes.

**ACTINIDES SERIES****The elements and their Oxidation States**

| Atomic | Element      | Symbol | Outer electronic structure | Oxidation states* |
|--------|--------------|--------|----------------------------|-------------------|
| 89     | Actinium     | Ac     | $6d^1 7s^2$                | +3                |
| 90     | Thorium      | Th     | $6d^2 7s^2$                | +3, +4            |
| 91     | Protactinium | Pa     | $5f^2 6d^1 7s^2$           | +3, +4, +5        |
| 92     | Uranium      | U      | $5f^3 6d^1 7s^2$           | +3, +4, +5, +6    |

|     |               |    |                     |                    |
|-----|---------------|----|---------------------|--------------------|
| 93  | Neptunium     | Np | $5f^4 6d^1 7s^2$    | +3, +4, +5, +6, +7 |
| 94  | Plutonium     | Pu | $5f^6 7s^2$         | +3, +4, +5, +6, +7 |
| 95  | Americium     | Am | $5f^7 7s^2$         | +2, +3, +4, +5, +6 |
| 96  | Curium        | Cm | $5f^7 6d^1 7s^2$    | +3, +4             |
| 97  | Berkelium     | Bk | $5f^9 7s^2$         | +3, +4             |
| 98  | Californium   | Cf | $5f^{10} 7s^2$      | +2, +3             |
| 99  | Einsteinium   | Es | $5f^{11} 7s^2$      | +2, +3             |
| 100 | Fermium       | Fm | $5f^{12} 7s^2$      | +2, +3             |
| 101 | Mendelevium   | Md | $5f^{13} 7s^2$      | +2, +3             |
| 102 | Nobelium      | No | $5f^{14} 7s^2$      | +2, +3             |
| 103 | Lawrencium    | Lr | $5f^{14} 6d^1 7s^2$ | +3                 |
| 104 | Rutherfordium | Rf | $4f^{14} 6d^2 7s^2$ |                    |

**1. OXIDATION STATE**

Unlike Lanthanides, Actinides show a large number of oxidation states. This is because of very small energy gap between 5f, 6d and 7s subshells. Hence, all their electrons can take part in bond formation. The dominant oxidation state of these element is +3 (similar to Lanthanides). Besides +3 state, Actinides also exhibit an oxidation state of +4. Some Actinides show still higher oxidation states. The maximum oxidation state first increases upto the middle of the series and then decreases, e.g., it increases from +4 from Th to +5, +6, and +7 for Pa, U and Np but decreases in the succeeding elements.

The Actinides resemble Lanthanides in having more compounds in +3 state than in the +4 state. However, the compounds in the +3 and +4 state tend to undergo hydrolysis.

Further, it may be noted that in case of Actinides, the distribution of oxidation states is so uneven that it is of no use to discuss their chemistry in terms of their oxidation states.

**2. ATOMIC RADIUS**

The Actinides show Actinide contraction (very much like Lanthanide contraction) due to poor shielding effect of the 5f-electrons. As a result, the radii of the atoms or ions of these metals decrease regularly across the series. The contraction is greater from element to element in this series due to poorer shielding by 5f electrons. This is because 5f orbitals extend in space beyond 6s and 6p orbitals whereas 4f orbitals are buried deep inside the atom.



### 3. MAGNETIC BEHAVIOUR

Like Lanthanides, the Actinides elements are strongly paramagnetic. The variation in magnetic susceptibility of Actinides with the increasing number of unpaired electrons is similar to that of Lanthanides but the values are higher for the Actinides than the Lanthanides.

### 4. COLOUR

These metals are silvery white. However, Actinide cations are generally coloured. The colour of the cation depends upon the number of 5f-electrons. The cations containing no 5f-electron or having seven 5f-electrons (i.e., exactly half-filled f-subshell) are colourless. The cations containing 2 to 6 electrons in the 5f-subshell are coloured both in the crystalline state as well as in aqueous solution. The colour arises due to f-f transition e.g.  $\text{Ac}^{3+}$  ( $5f^0$ ) = colourless,  $\text{U}^{3+}$  ( $5f^3$ ) = Red,  $\text{Np}^{3+}$  ( $5f^4$ ) = Blue,  $\text{Pu}^{3+}$  ( $5f^5$ ) = Violet,  $\text{Am}^{3+}$  ( $5f^6$ ) = Pink,  $\text{Cm}^{3+}$  ( $5f^7$ ) = Colourless,  $\text{Th}^{3+}$  ( $5f^0$ ) = Colourless as so on.

#### COMPARISON OF LANTHANIDES AND ACTINIDES

##### Similarities :

As both Lanthanides and actinides involve filling of f-orbitals, they show similarities in many respects as follows :

- Both show mainly an oxidation state of +3.
- Both are electropositive and very reactive.
- Both exhibit magnetic and spectral properties.
- Actinides exhibit Actinide contraction like Lanthanide contraction shown by Lanthanides.

##### Differences :

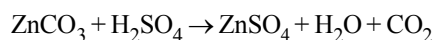
The show differences in some of their characteristics as follows :

| Lanthanides  | Actinides   |
|--|---|
| (i) Besides + 3 oxidation state they show + 2 and +4 oxidation states only in few cases. | (i) Besides +3 oxidation state, they show higher oxidation states of +4, +5, +6, +7 also. |
| (ii) Most of their ions are colourless   | (ii) Most of their ions are coloured  |
| (iii) They have less tendency towards complex formation                                  | (iii) They have greater tendency towards complex formation.                               |
| (iv) Lanthanides compounds are less basic.   | (iv) Actinides compounds are more basic   |
| (v) Do not form oxocation  | (v) Form oxocations e.g. $\text{UO}_2^{2+}$ , $\text{PuO}_2^{2+}$ and $\text{UO}^+$       |
| (vi) Except promethium, they are non-radioactive   | (vi) They are radioactive.  |
| (vii) Their magnetic properties can be explained easily.                                 | (vii) Their magnetic properties cannot be explained easily, as they are more complex.     |

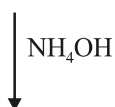
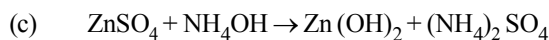
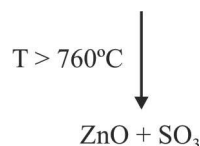
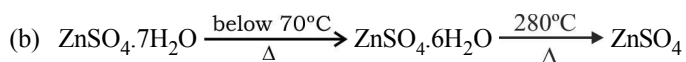
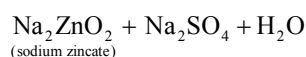
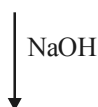
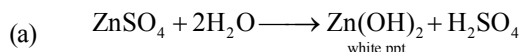
## IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

### 1. ZINC SULPHATE (ZnSO<sub>4</sub> · 7H<sub>2</sub>O - WHITE VITRIOL)

#### I. PREPARATION:



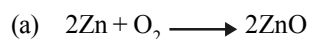
#### II. REACTIONS:



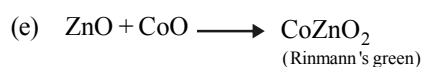
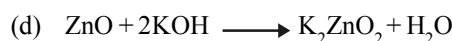
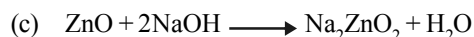
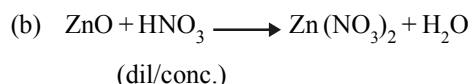
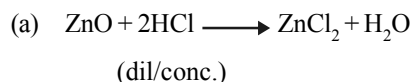
### 2. ZINC OXIDE, ZNO (CHINESE WHITE OR PHILOSPHER'S WOOL)

It found in nature as zincite or red zinc ore.

#### I. PREPARATION:



#### II. REACTIONS:



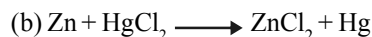
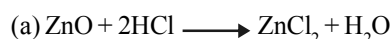
#### III. USES:

- (i) As a white paint (It does not get tranished even in presence of H<sub>2</sub>S because Zns is also white)
- (ii) For preparing Rinmann's green (Green Paint)
- (iii) As catalyst for preparation of methyl alcohol
- (iv) For making soft rubber
- (v) For making cosmetic powders, creams and in medicine

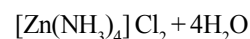
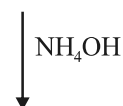
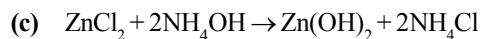
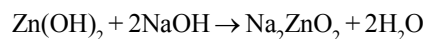
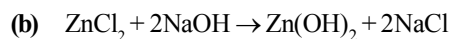
### 3. ZINC CHLORIDE ZnCl<sub>2</sub> · 2H<sub>2</sub>O

Anhydride of zinc chloride cannot be obtained by heating its aqueous salt.

#### I. PREPARATION:

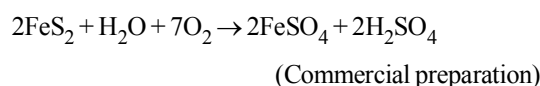
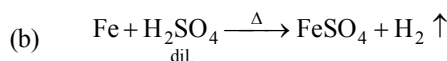
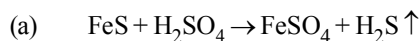


#### II. PROPERTIES:

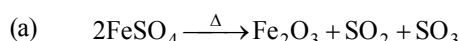


#### 4. FERROUS SULPHATE ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ - GREEN VITRIOL)

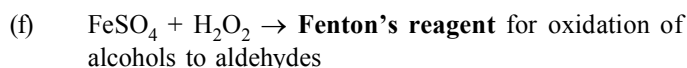
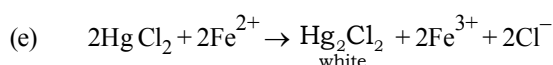
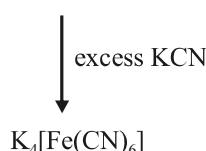
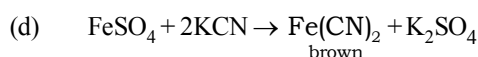
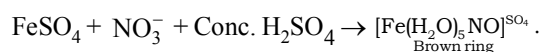
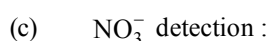
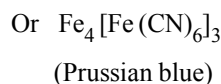
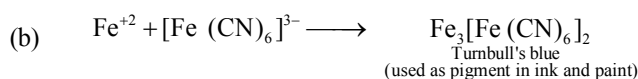
##### I. PREPARATION:



##### II. REACTIONS:



(light green) (brown)

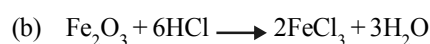
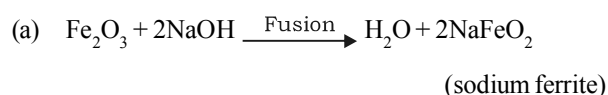


#### 5. FERRIC OXIDE, $\text{Fe}_2\text{O}_3$

##### I. PREPARATION:



##### II. REACTIONS:



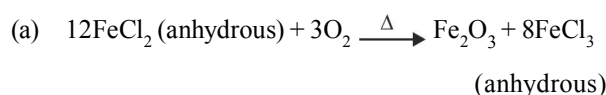
##### III. USES:

- (i) As a red pigment
- (ii) As abrasive polishing powder
- (iii) As catalyst

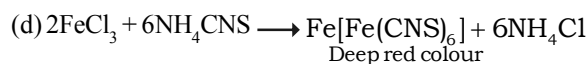
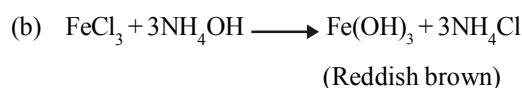
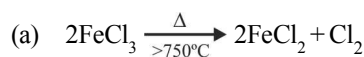
#### 6. FERRIC CHLORIDE, $\text{FeCl}_3$

It is known in anhydrous and hydrated form. It is a red deliquescent solid.

##### I. PREPARATION:

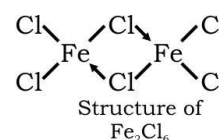


##### II. REACTIONS:



Deep red colouration is produced due to formation of complex.

(e) Till  $750^\circ\text{C}$  it exists as its dimer  $\text{Fe}_2\text{Cl}_6$ .

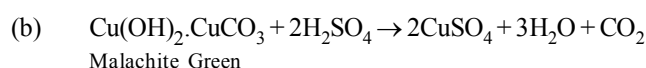


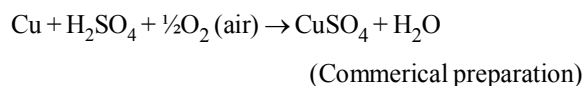
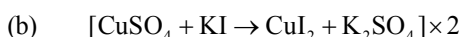
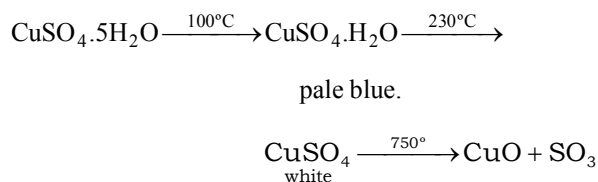
##### III. USES:

- (i) Its alcoholic solution is medicine, name (Tincture ferri perchloride)
- (ii) For detection of acetates and phenols
- (iii) For making prussian blue & as an oxidising agent

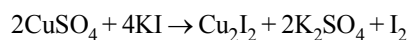
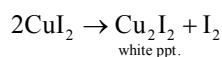
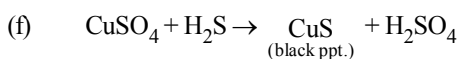
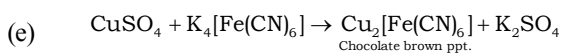
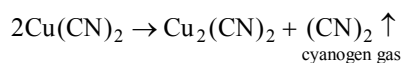
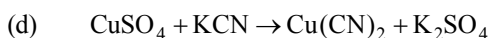
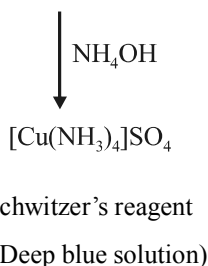
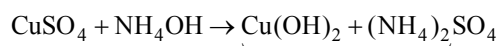
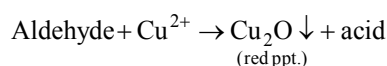
#### 7. COPPER SULPHATE ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ - BLUE VITRIOL)

##### I. PREPARATION:



**Copper scrape****II. REACTIONS :****(a) Effect of heat**

(Unstable  
dirty white)

**(c) Test of  $\text{Cu}^{2+}$** **(g) In Fehling's test & Benedict's test****III. USES :**

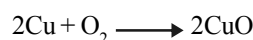
- (1) Bordeaux Mix  $\rightarrow \text{CuSO}_4 + \text{CaO}$   
(to kill fungi)

**8. CUPRIC OXIDE,  $\text{CuO}$** 

It is called black oxide of copper and is found in nature as tenorite.

**I. PREPARATION :**

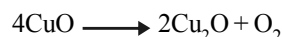
- (a) By heating  $\text{Cu}_2\text{O}$  in air or by heating copper for a long time in air (the temperature should not exceed above  $1100^\circ\text{C}$ )



- (c) On a commercial scale, it is obtained by heating malachite which is found in nature.

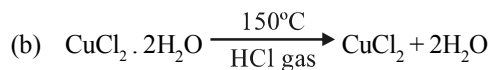
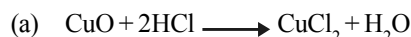
**II. REACTIONS :**

- (a) When heated to  $1100\text{--}1200^\circ\text{C}$ , it is converted into cuprous oxide with evolution of oxygen.

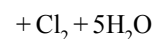
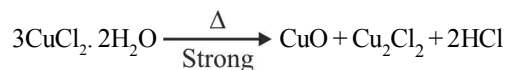


(Black)                      (Red)

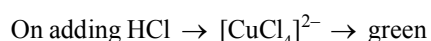
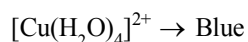
**Uses :** Used to impart blue and green colour to glazes and glass.

**9. CUPRIC CHLORIDE,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$** **I. PREPARATION :****II. REACTIONS :**

- (a) The anhydrous salt on heating forms  $\text{Cu}_2\text{Cl}_2$  and  $\text{Cl}_2$

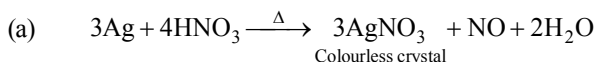


Dilute solution of  $\text{CuCl}_2$  is blue but concentrated solution is green. Its dilute solution on adding HCl becomes yellow.

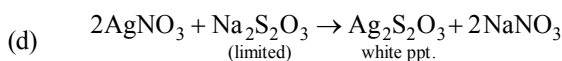
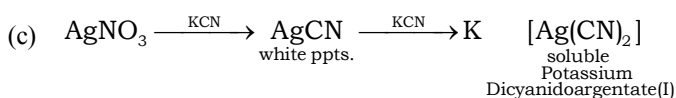
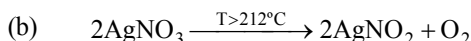
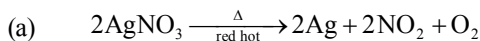


## 10. AgNO<sub>3</sub> (LUNAR CAUSTIC)

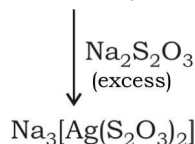
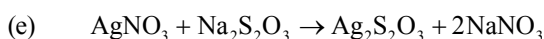
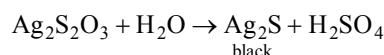
### I Preparation :



### II REACTION:

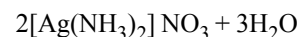
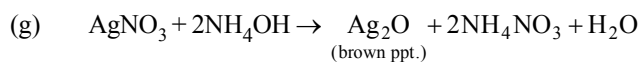
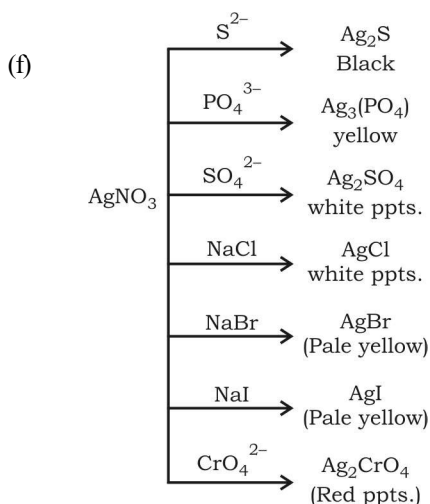


White ppt. of Ag<sub>2</sub>S<sub>2</sub>O<sub>3</sub> which gradually changes



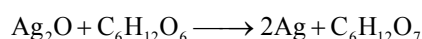
Sodium argentothio sulphate.

It is used in photography.

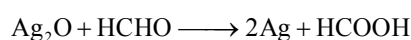


(h) Ammonical AgNO<sub>3</sub> → **Tollen's reagent** used to test aldehydes

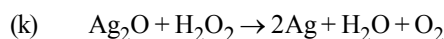
(i) It converts glucose to gluconic acid.



(j) It oxidises formaldehyde to formic acid



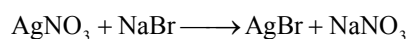
Very dilute solution of AgNO<sub>3</sub> is used as dental antiseptic.



## 11. SILVER BROMIDE, (AgBr)

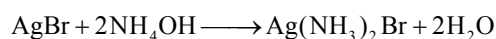
### I PREPARATION:

It is prepared by the reaction of silver nitrate with a soluble bromide.



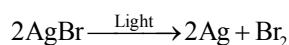
### II PROPERTIES

(a) It is a pale yellow solid. It is insoluble in water and concentrated acids. It is partially soluble in strong solution of ammonium hydroxide due to complex formation.

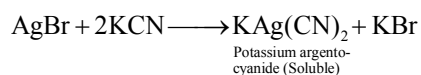


(b) On heating, it melts to a red liquid.

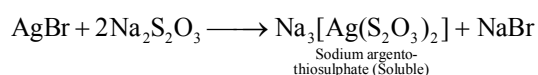
(c) It is most sensitive to light. It undergoes photoreduction.



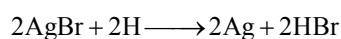
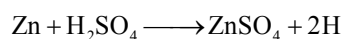
(d) It dissolves in potassium cyanide.



(e) It dissolves in sodium thiosulphate.



(f) AgBr is reduced to silver, when treated with zinc and dilute H<sub>2</sub>SO<sub>4</sub>.





All above reactions are also observed in the case of AgCl. However, it is white and fairly soluble in ammonium hydroxide. It is sensitive to light.

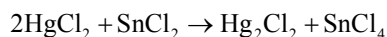
### III. USES :

It is used for making photographic films and plates because it is sensitive to light.

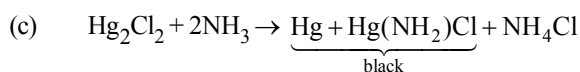
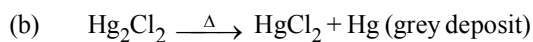
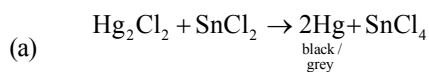
## 12. MERCURY CHLORIDES

### 12.1 Mercurous Chloride ( $\text{Hg}_2\text{Cl}_2$ - Calomel)

#### I. PREPARATION :



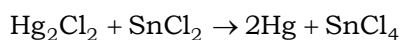
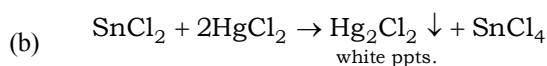
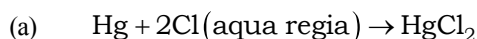
#### II. REACTIONS :



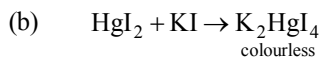
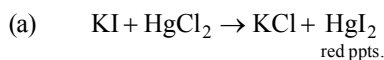
### 12.2 Mercuric Chloride ( $\text{HgCl}_2$ - Corrosive sublimate)

#### I. PREPARATION :

It is highly corrosive, poisonous and hence is called as corrosive sublimate.

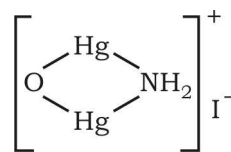
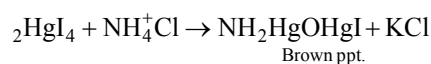


#### II. REACTION :



Basic solution of  $\text{K}_2\text{HgI}_4$  ( $\text{K}_2\text{HgI}_4 + \text{KOH}$ ) is called as Nessler's Reagent.

#### (c) Test for ammonium ion



#### Iodide of Millon's Base

