# d & f-Block Elements

The elemnts in which the last electron (or differentiating electron) enters (n - 1) d-subshell are known as d-Block elements. Their outer two shell are incompletely filled with electrons. Their general outer electronic configuration is $(n - 1)\ d^{1-10}\ ns^{1-2}$. In the long form of periodic table, d-Block elements are placed between s-and p-Block elements in the middle of the periodic table.

Technically, transition elements may be defined "as elements which have incompletely filled d-orbitals in atomic form or in some of their common oxidation states.

- Some of the typical properties of transition elements like paramagnetic or ferromagnetic behaviour, formation of coloured salts, high melting and boiling points (due to strong metallic bonds) are due to incompletely filled d-orbitals.

  There are four series of transition elements in the periodic table :

  (i) First transition series :
  or 3d-series : $_{21}$Sc..........................$_{30}$Zn
  (ii) Second transition series :
  or 4d-series : $_{39}$Y...........................$_{48}$Cd
  (iii) Third transition series :
  or 5d-series : $_{57}$La, $_{72}$Hf..........................$_{80}$Hg
  (iv) Fourth transition series : (Incomplete filled series)
  or 6d-series : $_{80}$Ac, $_{104}$Z.........................$_{112}$Z

- Group 12 elements Zinc (Z = 30), Cadmium (Z = 48) and Mercury (Z = 80) are not regarded as transition elements because their (n – 1) d sub-shell are fully filled with electrons, i.e., they have $(n - 1)\ d^{10}$ configuration in elemental as well as in ionic forms. Their d-electrons do not take part in bond formation. Hence, many of the properties of transition elements are not shown by these elements. Even then they are included in the series of transition elements because their last electron enters the (n – 1) d-sub-shell.
- Copper ($3d^{10}\ 4s^1$), Silver ($4d^{10}\ 5s^1$) and Gold ($5d^{10}\ 6s^1$) are transition elements although their (n-1) d-sub-shell are completely filled with electrons. It is due to the fact that their (n – 1) d-electrons participate in bond formation $Cu^{2+}$ ($d^9$), $Ag^{2+}$ ($d^9$) and $Au^{3+}$ ($d^8$). They show all the characteristics of transition elements.
- Group 3 elements (Sc, Y and La) form only tripositive ions with noble gas configuration. Their properties are quite different than that of other transition elements, e.g., their compounds are colourless and diamagnetic. These do not show variable oxidation states. But these elements have incompletely filled d-subshell in their elemental form, these are considered as transition elements.
- Group 3 (Sc, Y and La) and group 12 (Zn, Cd and Hg) are sometimes referred to as 'non-typical' transition elements.
- All transition elements are d-block elements but all d-block elements are not transition elements

## General Characteristics

- Transiton elements resemble in their physical and chemical properties as they have similar $ns^2$ configuration in their outermost energy shell. They are hard metals, have high tensile strength, ductility, malleability and are good conductors of heat and electricity. They have high M.P. and B.P. and form alloys with other metals. Their reactivity decreases with the increase in their atomic number.
  - Metallic character : All the transition elements are metals - They exhibit all the three types of structure hcp, bcc and ccp.
  - Metallic bonding is due to $ns^1$ or $ns^2$ and unpaired electrons of $(n-1)d^x$.

- Cr, Mo and W have max. number of unpaired (n–1)d electrons and they are hard where as Zn, Cd and Hg are soft as they do not have any unpaired electrons.
- Atomic radii - Smaller than s-block and larger than p-block elements of corresponding period. The atomic radii of the elemenets of a given series are decrease with increase in atomic no. but this decrease becomes smaller after mid way. This is due to screening effect and nuclear charge effect which oppose eachother.
- The value of atomic radii at the end of each series ae bit higher. This is due to electron-electron repulsions among (n–1)d electrons. These repulsions become predominant at the end of each series and thus size increases.
- In the vertical column atomic radii increase down the group from 1st transition series to the second transition series but the similarity in the atomic radii of the elements of 2nd and 3rd transiton series is due to lanthanoid contraction.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $Se_{21}$ | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | $Zn_{30}$ |
| 1.44 A | 1.32 | 1.22 | 1.18 | 1.17 | 1.17 | 1.16 | 1.15 | 1.17 | 1.25 |
| $Y_{39}$ | Zr | Pb | Mo | Tc | Ru | Rh | Pd | Ag | $Cd_{48}$ |
| 1.62 Å | 1.45 | 1.34 | 1.30 | - | 1.25 | 1.25 | 1.28 | 1.34 | 1.48 |
| La | $H^{+}$ | Ta | W | Re | Os | Ir | Pt | Au | Hg |
| 1.68Å | 1.44 | 1.34 | 1.30 | 1.28 | 1.26 | 1.26 | 1.29 | 1.34 | 1.49 |

Ionic Radii : Ionic radii follow the same trend as the atomic radii. In the same oxidation state the ionic radii generally decreases as the atomic number increases in a particular series.

| Ion | $Sc^{2+}$ | $Ti^{2+}$ | $V^{2+}$ | $Cr^{2+}$ | $Mn^{2+}$ | $Fe^{2+}$ | $Co^{2+}$ | $Ni^{2+}$ | $Cu^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ionic radii | 0.95 | 0.90 | 0.88 | 0.84 | 0.80 | 0.76 | 0.74 | 0.72 | 0.69 |

- Ionic radii decreases with increase in charge on the ion.

$${}^{r}Fe^{3+} < {}^{r}Fe^{2+},\ {}^{r}Ni^{3+} < {}^{r}Ni^{2+},\ {}^{r}Mn^{3+} < {}^{r}Mn^{2+}$$

Density : Except last two elements density increases from left to right in the series due to increases in atomic mass and decrease in atomic radii

- $\rho_{Ir} = 22.61\,gr/cc$ and $\rho_{Os} = 22.57\,gr/c.c.$, $\rho_{Sc}$ is lowest (3.1 gm/cc) an transition elements.
- except Sc, Ti and Y all transiton elements have densities greater than 5gm/c.c.

M.P. and B.P. - have high M.P. and B.P. due to strong metallic bonding

- In each series, the melting point and B.P. of these metals rise to a maximum value and then decrease with increase in atomic number.
- Mn and Tc have abnormally low melting points.
- Tungesten (W) has the highest M.P. amongst transition elements.
- Zn, Cd and Hg have low M.P. as they do not contain unpaired electrons.
- Ionisation enthalpies - Lie in between s and p-block elements
- Transiton elements do not form ionic compounds so readily as s and p-block elements do. Generally in oxidation state, compounds are ionic whereas in higher oxidation state compounds are covalent.
- Ionisation potential values increase in a period from left to right the increase however is not regular.
- $I.E_2$ For Cu and Cr are sufficiently higher than those of neighbouring elements.

  This is due to completely filled and half filled configuration of 3d-subsehll.
- In vertical columns i.e. In groups, Ionisation potential decreases from first member to 2nd member in most of the cases as expected however, the third member has the higher value than 2nd member. This is due to lanthanoid contraction.

### Variable oxidation states :

The characteristic property of transitional elements is to show several oxidation states. This is because both (n – 1) d and ns electrons can take part in bond formation due to small energy difference between them.

- The maximum variation in oxidation state is observed when the electronic configuration is $(n-1)\,d^5ns^2$.
- The highest oxidation states are found in the compounds with fluorine and oxygen since they are highly electronegative elements. The highest oxidation state shown by the transition metal is eight, e.g., $OsO_4$.
- The relative stability of different oxidation states w.r.t. oxidation can be determined with the help of standard electrode potential data. For example, E° values for couples $Cr^{+3}/Cr^{+2} = -0.41$ V and $Mn^{+3}/Mn^{+2} = +1.51$ V. These values suggest that $Cr^{+2}$ get easily oxidised to $Cr^{+3}$ while $Mn^{+3}$ gets easily reduced to more stable $Mn^{+2}$ in aqueous solutions. Similarly, $Fe^{+2}$ is unstable in aerated water and gets oxidised to $Fe^{+3}$.
- The common oxidation state of elements of 3d-series is +2 (Scandium is an exception) but $Cr^{+2}$ (Chromous ion) is unstable in water with respect to oxidation.
- In the +2 and +3 oxidation states, bonds formed are electrovalent. As the oxidation state of the transitional element increases, the covalent nature of the bond also increases. For example, in $MnO_4^-$ ion, all the Mn—O bonds are covalent.
- Within a group, the maximum oxidation state increases with atomic numbers. For example, iron shows the common oxidation state of +2 and +3 in its compounds but ruthenium and osmium in the same group give compounds in +4, +6 and +8 oxidation states.
- Transitional metals also form compounds in low oxidation states like zero and +1. For example, in metal carbonyls $M(CO)_n$, the metal M is in zero oxidation state, e.g., $Ni(CO)_4$, $Fe(CO)_5$, etc.

### Oxidation states :

### Colour :-

Most of the compounds of transition metals are coloured in solid state or in solution states. This is due to the presence of incompletely filled d-orbitals.

- Colour is due to d- d transiton.
- $Sc^{3+}$, $Ti^{4+}$, $V^{5+}$ are colourless as they have 3d° configuration.
- $Cu^+$, $Ag^+$, $Au^+$, $Zn^{2+}$, $Cd^{2+}$, $Hg^{2+}$ are colourless because they have completely filled d-orbitals.
- Colours of $Cr_2O_7^{2-}$, $CrO_4^{2-}$, $MnO_4^-, MnO_4^{2-}$ are due to charge transfer.
- Compounds of s and p-block elements are generally colourless as high energy is requried for promotion of eleectrons which is not available in visible region. The required energy is available in u-v region.
- Magnetic properties - Majority of substances show paramagnetic nature.

  Transition Metal compounds are paramagnetic due to presence of unpaired electron in (n–1) d subshell.

  Transition metal compounds are diamagnetic due to absence of unpaired electron in (n–1) d-subshell.
- Magnetic Moment : (μ) is given as

$$\mu = \sqrt{n(n+2)}\ \text{B.M.} \qquad 1\ \text{B.M} = \frac{eh}{4\pi mc}$$

### Complex formation :-

Transition metals form a large no. of complexes due to (a) small size (b) high charge and (c) presence of vacant d-orbitals in their outermost cells.

Alloy formation :- transiton metals form large number of alloys since they are similar insize.

Alloys containing Hg are called amalgams. Elements of (VIII) group do not form amalgam.

Catalytic property :- d-block elements and their compounds act as catalyst in various reaction due to utilisation of (n–1) orbtials or formation of interstitial compound.

## Inner-transiton elements

- Element having Z = 58 to Z = 71 are lanthanides or Lonthanoes or lanthanoids i.e. Lanthanides are $Ce_{58}$ to $Lu_{71}$.
- $Th_{90}$ to $Lw_{103}$ are Actinides or actinones or actinoids.
- Lanthanides mostly form ionic compounds in +3 oxidation state.

## Atomic and Ionic size

The ionic radii of lanthanoids show a progressive decrease with increasing atomic number. The decrease in size of $Ln^{3+}$ is known as Lantanoid contraction.

- Due to Lanthaide contraction, the elements of 4d and 5d transtion series resemble each other much more closely than do the elements of 3d and 4d series.
- Oxidation states - The common oxidation states of al the lanthanides is +3.

Other oxidation states are +2 and +4 in particular.

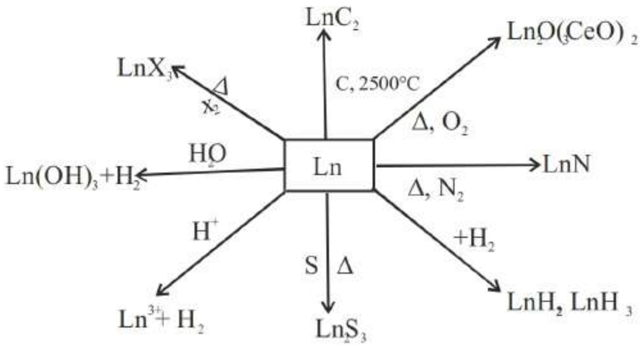
| La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| +3 | +3 | +3 | +2 | +3 | +2 | +2 | +3 | +3 | +3 | +3 | +3 | +2 | +2 | +3 |
|  | +4 | +4 | +3 |  |  | +3 | +4 |  |  |  |  | +3 | +3 |  |
|  |  |  | +4 |  | +3 |  |  | +4 | +4 |  |  |  |  |  |

- Colours of ions - Ions of lanthanides are coloured in the solid state as well as in aqueous solution (except – $La^{3+}$, $Ce^{3+}$, $Gd^{3+}$, $Yb^{3+}$ and $Lu^{3+}$)

Colour of these ions are due to f-f-transition.

- Magnetic properties - Ions having $4f^0$ ($La^{3+}$, $Ce^{4+}$) and $4f^{14}$ ($Yb^{2+}$ and $Lu^{3+}$) are diamagnetic and having other configuration are paramagnetic.

## Chemical reactivity :



## ACTIONOIDS

- have three shell (n–2), (n–1) and n shell incompletely filled and differentiating electron enters into 5f-orbital.
- G.E.C. $[Rn]5f^{1-14}\ 6d^{0-1}\ 7s^2$.
- The variation in the electronic configuration of the actionoids like those of lanthanoids is due to extra stabilities of $f^0, f^7$ and $f^{14}$ electronic configuration of the 5f orbitals.
- All actionoids are radioactive and are $\alpha$ – ray emitters.
- Atomic and Ionic Size :- The ionic radii for the $M^{3+}$ and $M^{4+}$ ions contract slightly with increasing atomic number. The decrase in size of $An^{3+}$ is known as actinoide contraction.
- Oxidation states :- The actinide in general show +3 oxidation stole. There is also a greater range of oxidation states due to comparable energies of 5f, 6d and 7s.
- The actinoids resemble the lanthanoids in having more compounds in +3 state than in +4 state but they tend ot hydrolyse.

- $U^{3+}$ in aqueous solution evolves $H_2$ on standing.
  Aq. solution of $Np^{3+}$ and $Pu^{3+}$ are stbale but are easily oxidised to $Np^{4+}$ and $Pu^{4+}$.
- $U^{4+}$ and $Np^{4+}$ are stable to water but are slowly oxidised by air to $UO_2^{2+}$ and $NpO_2^{2+}$
- $Pu^{4+}$ disproportionates to $Pu^{3+}$ and $Pu_2^{2+}$ when solutin is strongly acidic.
- $LiO_2^{+}$ disproportionates to $Li^{4+}$ and $LiO_2^{2+}$.
- Ionisation energy of the early actinoids are smaller than those of early lanthanoids.

## IMPORTANT COMPOUNDS

### 1. Copper sulphate (Blue vitriol), $CuSO_4.5H_2O$ -

(i) Preparation - By dissolving CuO or $CuCO_3$ or malachite in dil. $H_2SO_4$ and evaporating the solution to crystalization point.

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + H_2O + CO_2$$

(ii) Properties -

(a) Blue crystalline solid, soluble in water.

(b) Action of heat :

$$\begin{tikzcd}
CuSO_4.5H_2O \arrow[r, "373\ K"] & CuSO_4.H_2O \arrow[d, "423\ K"] \\
SO_3 + CuO & \underset{\substack{\text{White} \\ \text{(anhydrous salt)}}}{CuSO_4} \arrow[l, "773\ K"']
\end{tikzcd}$$

(iii) Uses -

(a) Used in copper refining, electroplating, dying, calico printing and Fehling's solution.

(b) Also used in the preparation of Bordeaux mixture (a mixture of $CuSO_4$ solution + lime), used as a fungicide for fruit trees, grapes, and vine plants.

(a) Action of $NH_4OH$ :
With ammonia solution; it forms the soluble blue complex. First it forms a precipitate of $Cu(OH)_2$ which dissolves in excess of ammonia solution.

$$CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2\ ppt \downarrow + (NH_4)_2SO_4$$

$$Cu(OH)_2 + 2NH_4OH + (NH_4)_2SO_4 \longrightarrow \underset{\substack{\text{Tetrammine cupric} \\ \text{sulphate}}}{[Cu(NH_3)_4]SO_4} + 4H_2O$$

$[Cu(NH_3)_4]SO_4$ is known as Schwizer's reagent

(b) Action of alkalies :
Alkalies form a pale blue precipitate of copper hydroxide.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 \downarrow + Na_2SO_4$$

(c) Action of potassium iodide :

First of all cupric iodide is formed which decomposes to give white cuprous iodide and iodine.

$$[CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4] \times 2$$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

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$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

(d) Action of potassium cyanide :

First of all cupric cyanide is formed which decomposes to give cuprous cyanide and cyanogen gas. Cuprous cyanide dissolves in excess of potassium cyanide to form a complex, potassium cupro cyanide $K_3[Cu(CN)_4]$.

$$2CuSO_4 + 10KCN \longrightarrow 2K_3[Cu(CN)_4] + 2K_2SO_4 + (CN)_2$$

(e) Action of potassium ferrocyanide :

Reddish brown precipitate of cupric ferrocyanide is formed. (test of $Cu^{2+}$ ion)

$$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow Cu_2[Fe(CN)_6] + 2K_2SO_4$$

(f) Addition of electropositive metals :

$$CuSO_4(aq) + Fe \longrightarrow Cu + FeSO_4$$

$$CuSO_4(aq) + Zn \longrightarrow Cu + ZnSO_4$$

(g) Action of $H_2S$ :

When $H_2S$ is passed into copper sulphate solution, a black precipitate of copper sulphide is formed.

$$CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4$$

The black precipitate dissolves in conc. $HNO_3$

$$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$$

(h) Action of potassium sulphocyanide :

Cupric sulphocyanide is formed.

$$2CuSO_4 + 2KCNS + SO_2 + 2H_2O \longrightarrow Cu_2(CNS)_2 + K_2SO_4 + 2H_2SO_4$$

(i) Double sulphates :

Copper sulphate forms double salts with alkali sulphate $K_2SO_4$. $CuSO_4$. $6H_2O$ and with ammonium sulphate as $(NH_4)_2SO_4CuSO_4.6H_2O$.

(j) Action of sodium thiosulphate :

Sodium thiosulphate reacts with copper sulphate to form cupric thiosulphate which is reduced by sodium thiosulphate. The cuprous compound thus formed dissolves in excess of sodium thiosulphate to form a sodium cuprothiosulphate

$$CuSO_4 + Na_2S_2O_3 \longrightarrow CuS_2O_3 + Na_2SO_4$$

$$2CuS_2O_3 + Na_2S_2O_3 \longrightarrow Cu_2S_2O_3 + Na_2S_4O_6$$

$$3Cu_2S_2O_3 + 2Na_2S_2O_3 \longrightarrow \underset{\text{Sodium cuprothiosulphate}}{Na_4[Cu_6(S_2O_3)_5]}$$

## 2. Mercurous Chloride ($Hg_2Cl_2$ - Calomel) :

Methods of preparation : (i) $Hg_2Cl_2$ (calomel) is formed as white precipitate when soluble chloride (say NaCl) is added to soluble mercurous salt (say $Hg_2(NO_3)_2$ :

$$Hg(NO_3)_2 + 2NaCl \longrightarrow Hg_2Cl_2 \downarrow + 2NaNO_3$$

(ii) $Hg_2Cl_2$ is also formed when aq $HgCl_2$ and aq. $SnCl_2$ are mixed in 1 : 1 molar ratio or $HgCl_2$ is reduced by Hg.

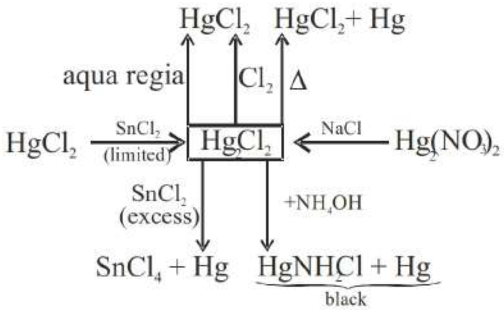
$$2\ HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

Excess of $SnCl_2$ would reduce $Hg_2Cl_2$ to Hg :

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

(iii) $$HgCl_2 + Hg \xrightarrow[\text{in iron tank}]{\Delta} Hg_2Cl_2$$

Properties of $Hg_2Cl_2$ : It is an amosphous, tasteless, odourless, non-poisonous, white power which is sparingly soluble in water.



- Mercurous ion is diamagnetic; this indicates that there is no unpaired electron, hence mercurous ion is not $Hg^+$ but $Hg_2^{2+}$:

## 3. Mercuric Chloride ($HgCl_2$ - Corrosive Sublimate)

Preparation :

(i) It is prepared by heating a mixture of mercuric sulphate with common salt, in presence of a little manganese dioxide (was to prevent the formation of any mercurous chloride). Mercuric chloride sublimes off and condenses on the cooler parts of the vessel.

$$HgSO_4 + 2NaCl \longrightarrow HgCl_2 + Na_2SO_4$$

(ii) By heating the Hg in a current of chlorine.

$$Hg + Cl_2 \longrightarrow HgCl_2$$

(iii) It can be prepared by dissolving mercuric oxide in hydrochloric acid.

$$HgO + 2HCl \longrightarrow HgCl_2 + H_2O$$

(iv) It can also be prepared by dissolving Hg or $Hg_2Cl_2$ in aqua-regia.

$$3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2Cl$$

$$Hg + 2Cl \longrightarrow HgCl_2$$

$$Hg_2Cl_2 + 2Cl \longrightarrow 2HgCl_2$$

Properties :

(i) It is a white crystalline compound having highly poisonous nature. It is less soluble in cold water but more soluble in hot water. It behaves like a covalent compound as it is soluble in organic solvents and very slightly ionised in water.

(ii) It is reduced by stannous chloride first into mercurous chloride (white) and then into mercury (black)

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{White}}{Hg_2Cl_2} + SnCl_2$$

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{Black}}{2Hg} + SnCl_2$$

(iii) Potassium iodide forms a scarlet precipitate of mercuric iodide when added to $HgCl_2$ solution.

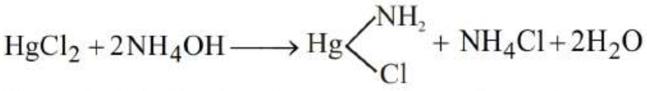
$$HgCl_2 + 2NaOH \longrightarrow HgO + 2NaCl + H_2O$$

$$HgCl_2 + 2KI \longrightarrow 2KCl + HgI_2$$

$$HgI_2 + 2KI \longrightarrow K_2HgI_4$$

The precipitate of mercuric iodide dissolves in excess of potassium iodide forming a complex, $K_2HgI_4$. The alkaline solution of $K_2HgI_4$ is known as Nessler's reagent. This reagent is used for testing ammonia.

(iv) When aqueous ammonia is added to the solution of mercuric chloride, a white precipitate of mercuric amino chloride is formed.



$$HgCl_2 + 2NH_4OH \longrightarrow Hg\begin{matrix} NH_2 \\ Cl \end{matrix} + NH_4Cl + 2H_2O$$

(v) Mercuric chloride absorbs gaseous ammonia and forms an addition compound.

$$HgCl_2 + 2NH_3 \longrightarrow HgCl_2.2NH_3$$

(vi) When $H_2S$ is passed into its solution, it forms a black precipitate of mercuric sulphide.

$$HgCl_2 + H_2S \longrightarrow \underset{\text{black}}{HgS\downarrow} + 2HCl$$

(vii) When heated with sodium carbonate or sodium hydroxide in solution, a yellow precipitate of mercuric oxide is formed.

$$HgCl_2 + Na_2CO_3 \longrightarrow HgO + 2NaCl + CO_2$$

### 4. Potassium dichromate :

A. Preparation. It is obtained from chromite ($FeO.Cr_2O_3$) by the following steps :-

(a) Fusion of ore with caustic soda -

$$4(FeOCr_2O_3) + 16NaOH + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$$

(b) Acidification of extract

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

(c) Conversion into Pot. dichromate -

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2\ NaCl$$

B. Properties.-

(a) Pot. dichromate exists as orange crystals which are soluble in water.

(b) On strong heating $K_2Cr_2O_7$ decomposes to evolve oxygen -

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2Cr_2O_4 + 2Cr_2O_3 + 3O_2$$

(c) When alkali is added, orange red solution of dichromate changes into yellow solution of chromate. The dichromate and chromate ions exist in equilibrium as under :

$$2CrO_4^{2-} \underset{\text{alkali}}{\overset{\text{Acid}}{\rightleftharpoons}} Cr_2O_7^{2-} + H_2O$$

(d) (i) Cold, conc. $H_2SO_4$ converts dichromate into red crystals of chromic anhydride

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2CrO_3 + 2KHSO_4 + H_2O$$

(ii) With hot conc. $H_2SO_4$, oxygen gas is evolved.

$$2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

(iii) It acts as a strong oxidising agent and oxidises $I^-$ to $I_2$, $Fe^{2+}$ to $Fe^{3+}$, $H_2S$ to S, $NO_2^-$ to $NO_3^-$, $SO_3^{2-}$ to $SO_4^{2-}$, $Sn^{2+}$ to $Sn^{4+}$, $Cl^-$ to $Cl_2$, alcohols to aldehydes and finally acids.

(f) It gives chromyl chloride when heated with concentration $H_2SO_4$ and a chloride.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

In acidic medium with $H_2O_2$ it gives deep blue colour due to the formation of $CrO_5$. This compound finally decomposes to $Cr^{3+}$.

(c) Uses - Potassium dichromate is used

(a) for cleaning glassware by making chromic acid

(b) in chrome tanning in leather industry

(c) as a laboratory reagent

(d) as a strong oxidising agent

(e) for the preparation of large number of important compounds like chrome alum $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$, Chrome yellow ($PbCrO_4$) and Chrome red ($PbCrO_4.PbO$) etc.

(d) Structure - Chromate ion is tetrahedral in geometry while dichromate ion is formed by the linking of two chromate ions through one O-atom.

## 5. Potassium permanganate :

A. Preparation - It is prepared from pyrolusite ($MnO_2$) by the following stages :

(a) Conversion of pyrolusite to potassium manganate by the action of KOH in the presence of oxygen.

$$2KMnO_4 + 4KOH + O_2 \xrightarrow{\text{Heat}} K_2MnO_4 + 2H_2O$$

(b) Conversion of potassium manganate to potassium permanganate by passing ozone or chlorine or carbon dioxide or by electrolysis.

$$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$$

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

(ii) Properties -

(a) Pot. permanganate exists in the form of dark purple coloured prism like crystals. These crystals become dull in air due to the reduction on surface.

(b) This is soluble in water but solubility is much more in hot water.

(c) Action of heat

$$2KMnO_4 \xrightarrow{Heat} K_2MnO_4 + MnO_2 + O_2$$

(d) Action of conc. $H_2SO_4$

With cold $H_2SO_4$, it makes $Mn_2O_7$ which on heating changes into $MnO_2$

$$2KMnO_4 + 2H_2SO_4 \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

$$2Mn_2O_7 \xrightarrow{\Delta} 4MnO_2 + 3O_2$$

When heated with conc. $H_2SO_4$, oxygen gas is evolved.

$$4KMnO_4 + 6H_2SO_4 \longrightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2$$

It acts as a strong oxidising agent in all the three media acidic, alkaline and neutral. The reactions in different media are :

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \text{ (In acidic medium)}$$

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O] \text{ (In alkaline medium)}$$

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O] \text{ (In neutral medium)}$$

In acidic medium $KMnO_4$ oxidises $I^-$ to $I_2$, $SO_3^{2-}$ to $SO_4^{2-}$, $C_2O_4^{2-}$ to $CO_2$, $Fe^{2+}$ to $Fe^{3+}$, alcohols to aldehydes and finally acids. In alkaline medium it oxidises $I^-$ to $IO_3^-$, toluene to benzoic acid.

(iii) Structure - Permanganate ion is tetrahedral in geometry due to $sp^3$ hybridised manganese.

(iv) Uses - Potassium permanganate is used :

  (a) As an oxidising agent in different media (acidic, alkaline as well as neutral).

  (b) As water purifier particularly for tank water and stinking wells.

  (c) As a laboratory reagent for various types of redox titrations and testing various anions.

## IRON

Symbol : Fe, At. Number : 26 At. mass : 55.847, Elect. conf. : $[Ar]3d^64s^2$, Oxid. states : +2, +3, Position in the periodic table : Belongs to group 8, period 4

1. Occurrence :

Iron is the fourth most abundant element and second most abundant metal (next to aluminium) occurring in the Earth's crust. Iron is rarely found in native state. In the combined form, it is generally found as oxides and carbonates as -

(i) Haematite (red haematite), $Fe_2O_3$
(ii) Limonite (Brown haematite), $Fe_2O_3.3H_2O$
(iii) Magnetite, $Fe_3O_4$
(iv) Siderite, $FeCO_3$
(v) Iron pyrites, $FeS_2$
(vi) Copper pyrites, $CuFeS_2$

2. Extraction :

The following steps are involved in the extraction of cast iron from haematite ore :

(i) Concentration : The ore is crushed and concentrated by levigation in a steam of water and by electromagnetic separation.

(ii) Roasting : The concentrated ore is roasted in air to remove moisture, volatile impurities such as S, As etc. and to convert any lower oxide like FeO or $Fe_3O_4$ to more porous $Fe_2O_3$ which can be easily reduced.

$$Fe_2O_3 \cdot 3H_2O \longrightarrow Fe_2O_3 + 3H_2O$$

$$2FeCO_3 \longrightarrow 2FeO + 2CO_2$$

$$S + O_2 \longrightarrow SO_2$$

$$4As + 3O_2 \longrightarrow 2As_2O_3$$

$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

(iii) Smelting (Reduction) : The roasted ore is mixed with coke (reducing agent) and limestone (flux).In the ratio of 8 : 4 : 1 and introduced into a blast furnace for smelting. The following reaction take place in the blast furnace in different zone as

(a) Combustion zone lowest part of the furnace above earth)

$$\underset{\text{Coke}}{C} + \underset{\text{Hot air}}{O_2} \longrightarrow CO_2 + \text{Heat}$$

$$CO_2(g) + \underset{\text{Coke}}{C} \longrightarrow 2CO(g)$$

Reduction Zone : (Uppermost part of the furnace) :

$$3Fe_2O_3 + CO \xrightarrow{300^\circ - 400^\circ} 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \xrightarrow{500-600^\circ} 3FeO + CO_2$$

$$FeO + CO \xrightarrow{700-600^\circ} \underset{\text{spongy iron}}{Fe} + CO_2$$

(c) Slag formation : Central Zone

$$CaCO_3 \xrightarrow{1073\text{ K}} CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow \underset{(\text{slag})}{CaSiO_3}$$

(d) Zone of fusion :

The molten slag is lighter than molten iron and thus floats on the molten iron. The molten iron tapped off from the blast furnace is called pig iron the pig iron is remelted and cast into moulds. This is known as cast iron.

3. Various forms of Iron :

(i) Cast Iron : It is the most impure form of iron and contains 2.5% to 5% carbon as the main impurity with traces of sulphur, phsophorus and manganese. It is hard and brittle.

(a) White Cast Iron : In white cast iron carbon is present form of cementite ($Fe_3C$). It is obtained when molten pig iron is cooled once.

(b) Grey Cast iron : In the grey cast iron carbon is present in the form of graphite. It It is obtained when molten pig iron is cooled slowly and slowly.

(ii) Wrought Iron or Malleable Iron : It is is the purest form of iron and contains minimum amount of carbon (0.1 to 0.25%). It is soft ductile and malleable.

(iii) Steel : The percentage of carbon contained in steel is (0.25 to 2%) intermediate between that in wrought iron and cast iron. It is the most important form of iron and have extensive applications.

4. Manufacture of Steel :

Steel is manufactured from cast iron by various processes viz:

(i) Bessemer's process
(ii) L.D. (Linz Donawitz) process
(iii) Open Hearth process or Siemins - Martin process
(iv) Electric Furnace process
(v) Duplex process etc.

Note : Spiegeleisen (an alloy of Fe, Mn and C) is added during manufacture of steel. Mn and C serve as deoxidiser and reduce FeO (if any) and the rest dissolves in molten steel. Mn makes steel harder and increases its tensile strength.

5. Heat Treatment of Steel :

The properties of steel such as hardness, toughness and tensile strength can be controlled to a great extent by proper heat treatment. Various methods of heat treatment are :

(i) Annealing : It is the process of heating steel to bright redness and then cooling it slowly. By annealing, steel becomes soft and pilable.

(ii) Hardening : It is the process of heating steel to bright redness and then cooling suddenly by plunging in oil or water (quenching). The resultant steel is hard and brittle.

(iii) Tempering : It is the process of heating the hardened steel to a temperature much below redness and then cooling it slowly. The resultant steel retains its hardness but brittleness disappears.

(iv) Case hardening : It is a process of giving a thin coating of hardened steel to a mild steel by heating it in contact with charcoal followed by quenching it in oil. Thus, due to hardened surface layer it can bear wears and tears. The inside, being still mild steel, can withstand shock. Locomotive axles are made of case hardened mild steel.

(v) Nitriding : It is a process of heating steel in an atmosphere of dry ammonia at 500°C to 600°C to 4 days. This process imparts a hard coating of iron nitride on the surface of steel.

Types of Steel :- The properties of steel depends upon its carbon content. With the increase in carbon content, the hardness of steel increases while its ductileness decreases. Based upon the percentage of carbon, steel may be classified as under :-

(i) Soft Steel - Contains less percentage of carbon (0.25%)
(ii) Mild Steel - Contains medium percentage of carbon (0.25 – 0.25%)
(iii) Hard Steel - Contains high percentage of carbon (0.5 – 1.5%)

(iv) Alloy Steels or Special Steels - Very useful and valuable properties may be imparted to steel by alloying it with other metals e.g. Ni, Co, Cr, W, V etc. All these alloy of steels are called alloy steels.

## COPPER

Symbol : Cu, At. No.: 29, At. mass : 63.546, Elect. conf.: $[Ar]3d^{10}4s^1$, Oxid. states : +1, +2; Position in the periodic table : Belongs to group 11, period 4

1. Occurrence :

Copper occurs in native as well as in combined state. In combined state it is found as -

(i) Copper pyrites (Charcopyrites), $CuFeS_2$
(ii) Copper glance (Charcocite), $Cu_2S$

(iii) Malachite, $CuCO_3Cu(OH)_2$
(iv) Azurite, $2CuCO_3.Cu(OH)_2$
(v) Cuprite or ruby copper, $Cu_2O$ etc.

2. Extraction :

Copper is generally extracted from copper pyrites. There are two processes for the extraction of copper based on concentration of copper in the ore (i) Pyrometallurgical (smelting) process employed in case of Cu rich ore, (ii) Hydrometallurgical process employed in case of Cu Poorer ore.

Pyrometallurgical Process :

It involves the following steps :

(i) Concentration : The powdered ore is concentrated by froth floatation process.

(ii) Roasting : The concentrated ore is heated strongly in the presence of air in reverberatory furnace.

$$S + O_2 \longrightarrow SO_2$$

$$4As + 3O_2 \longrightarrow 2As_2O_3$$

$$4Sb + 3O_2 \longrightarrow 2Sb_2O_3$$

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

(iii) Smelting : The roasted ore is mixed with sand (flux) and coke (fuel) and heated strongly in a blast furnace. The smelted ore contains mainly $Cu_2S$ and a little FeS and FeO. It is called as matte.

$$FeS + Cu_2O \longrightarrow FeO + Cu_2S$$

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

(iv) Bessemerisation : Molten matter is heated with a little sand in a Bessemer converter. The ferrous sulphide (FeS) undergoes oxidation first and is removed as a slag, then part of the cuprous sulphide ($Cu_2S$) is converted into cuprous oxide which react with unchanged sulphide to give the molten metal called as blister copper (contains 98% Cu and 2% impurities of Fe, S, Ag, Au etc).

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$Cu_2S + 2Cu_2O \longrightarrow \underset{\text{blister copper}}{6Cu} + SO_2$$

(v) Refining : The blister copper is refined either by fire refining (poiling) or by electrolysis.

(a) Refining (Poiling) : Blister copper is melted on the hearth of a furnace and stirred with logs of green wood. The hydrocarbons liberated by the decomposition of wood reduce any $Cu_2O$ to copper.
Note : Poling of copper is a reduction process.

(b) Electrolytic refining : A cell is constructed using following components :

Electrolyte : $CuSO_4$ + dil.$H_2SO_4$
Anode : Block of impure copper
Cathode : Thin strip of pure copper

On passing current, pure Cu (99.99% Pure) gets transferred from anode to cathode which gradually grows in size. The impurities settle down below the anode as anodic mud. (Anode mud contains Ag, Au and Pt)

# SILVER

Symbol : Ag, At. No. : 47, At. mass No. : 107.8682, Elect. conf. $[Kr]4d^{10}5s^1$,
Oxid. state : +1, Position in the periodic table : Belongs to group 11, period 5

1. Occurrence :

It is found both in free and combined state as -
(i) Horn silver (Chlorargyrite), AgCl
(ii) Argentite (Silver glance), $Ag_2S$
(iii) Pyrargyrite, (Ruby silver) $3Ag_2S.Sb_2S_3$
(iv) Silver copper glance, $(Cu, Ag)_2S$

2. Extraction :

The principal methods used for the extraction of silver are :

(i) Extraction from silver ores (Mac Arthur-Forest Cyanide Process) :
This is the most modern and widely used method for the extraction of Ag from argentite, $Ag_2S$. It involves the following steps :

(a) Concentration : The ore is crushed and concentrated by forth floatation process.

(b) Cyanidation : The concentrated ore is treated with a dilue solution (0.5%) on NaCN in the presence of air. The silver ions are changed into sodium argentocyanide, $Na[Ag(CN)_2]$.

$$Ag_2S + 4NaCN \rightleftharpoons 2Na\left[Ag(CN)_2\right] + Na_2S$$

The air also oxidises $Na_2S$ to free sulphur and thus enables the forward reaction to proceed for completion.

$$Na_2S + H_2O + ½O_2 \longrightarrow 2NaOH + S\downarrow$$

(c) Recovery of silver : The silver complex thus obtained is treated with zinc dust to precipitate out Ag.

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

(d) Refining : Impure silver is refined electrolytically. (Anode : Block of impure Ag. Cathode: Thin strip of pure Ag. Electrolyte : $AgNO_3$ + dil. $HNO_3$). On passing electric current pure Ag is transferred from anode to cathode.

(ii) Extraction of Ag from Argentiferous lead (separation of Ag from lead containing silver) - Mainly three methods are used. These are :

(a) Cupellation process
(b) Pattinson's process
(c) Parke's process

(iii) Extraction of Ag from coins ornaments (Alloy of Ag and Cu) : The coins or ornaments are dissolved in $HNO_3$. The solution is boiled to remove $HNO_3$ and then treated with HCl. AgCl is precipitated out while Cu remains in solution. AgCl is filtered and reduced to Ag.

Extraction of silver from coins :

A silver coin is an alloy of silver and copper. The alloy is heated with dilute $HNO_3$. It is dissolved forming silver and copper nitrates.

$$3Cu + \underset{\text{dil.}}{8HNO_3} \rightarrow 3Cu(NO_3)_2(aq) + 2NO + 4H_2O$$

$$3Ag + \underset{\text{dil.}}{4HNO_3} \rightarrow 3AgNO_3(aq) + NO + 2H_2O$$

The solution so obtained is treated with HCl when a white ppt. of AgCl is formed. It is separated by filtration. AgCl is converted into metallic silver by

(a) Strongly heating it with $Na_2CO_3$ :

$$4AgCl(s) + 2Na_2CO_3 \xrightarrow{\text{Strong heating}} 4Ag + 4NaCl + 2CO_2 + O_2$$

(b) Dissolving AgCl in KCN and adding zinc :

$$AgCl + 2KCN(aq) \rightarrow K\left[Ag(CN)_2\right](aq) + KCl$$

$$2K\left[Ag(CN)_2\right] + Zn \rightarrow K_2\left[Zn(CN)_4\right] + 2Ag\downarrow$$

## MERCURY

Symbol : Hg, At. No. : 80, At. mass : 200.59, Elect. conf.: [Xe] $5d^{10}6s^2$, Oxid. states : +1, +2, Position in the periodic table : Belongs to group 12, period 6

1. Occurrence :

It is rarely found in native state. The chief source of Hg is Cinnabar, HgS ore.

Recovery of mercury :

Ore is powdered and concentrated by froth floatation process. Then it is roasted at 570K to 580 K in excess of air to form HgO which then decomposes to Hg vapours and $O_2$. Hg vapours are condensed and refined.

$$2HgS + 3O_2 \rightarrow 2HgO + 2SO_2$$

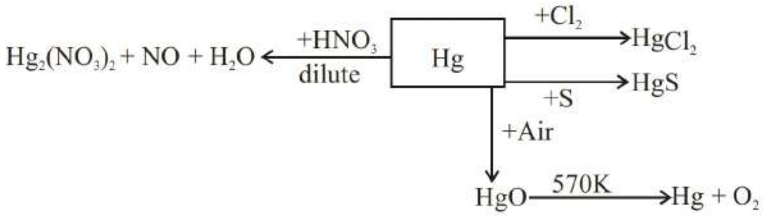
$$2HgO \rightarrow 2Hg\uparrow + O_2\uparrow$$

Refining of mercury :

Impure mercury is filtered through thick canvass or chamios leather. Then it is dropped into 5% $HNO_3$ to remove metallic impurities like Fe, Cu, Zn, Pb etc.(as their soluble nitrates) This mercury is further refined by distillation under reduced pressure.

4. Properties of Hg :

At room temperature, it is a lustrous, silvery white heavy liquid (density 13.6 g $cm^{-3}$). It freezes at 234.13 K and boils at 630 K. Its vapours are monoatomic and poisonous.



5. Amalgams :

Almost all metals (except Fe and Pt) are known to dissolve in mercury. The alloys of Hg with metal(s) are known as amalgams.

Note :

(i) Due to insolubility of Fe in Hg, mercury is transported in iron containers.

(ii) Dental alloy : An amalgam of Ag, Sn, Zn and Hg is used for filling of teeth.

(iii) Mercury tree : When a little mercury is poured into a $AgNO_3$ solution, a tree like growth of silver amalgam is produced, known as mercury tree.

(iv) Ammonium amalgam (Mercury butter) : When Na-Hg amalgam is kept in conc. solution of $NH_4Cl$, mercury undergoes swelling upto the extent of nearly three times of its original volume and forms a butter like mass of soluble mercury which is known as ammonium amalgam or mercury butter.

5. Uses of Mercury :
   - (i) It is used in scientific equipment such as thermometers, barometers and high vacuum pumps.
   - (ii) It is also used in mercury vapour lamps and rectifiers.
   - (iii) Certain compounds of Hg like Mercurochrome etc., are extensively used as antiseptic and germicide.
   - (iv) Amalgamated zinc plates are used in galvenic batteries.
   - (v) Sodium amalgam is used as a reducing agent.

## ZINC

Symbol : Zn, At. number : 30, At. mass : 65.37, Elect. conf. : $[Ar]3d^{10}4s^2$,
Oxid. state : +2, Position in the periodic table : Belongs to group 12, period 4.

1. Occurrence : Zinc is usually found in the combined state as :
   - (i) Zinc blende (Sphalerite), ZnS
   - (ii) Calamine (Smith stone or zinc spar), $ZnCO_3$
   - (iii) Zincite (Red zinc), ZnO
   - (iv) Silicious zinc, $Zn_2SiO_4.H_2O$
   - (v) Franklinite, $ZnO.Fe_2O_3$

2. Extraction :

Zinc is mainly extracted from zinc blende and calamine. It extraction of zinc from zinc blends occurs in the following steps :

(i) Concentration of ore :

The powdered ore is concentrated by froth floatation process.

(ii) Roasting :

The concentrated ore is strongly heated in the presence of excess of air. By roasting, ZnS is changed into zinc oxide and $SO_2$.

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

$$ZnS + 2O_2 \xrightarrow{\Delta} ZnSO_4$$

$$2ZnSO_4 \xrightarrow{\Delta} 2ZnO + 2SO_2 + O_2$$

(iii) Reduction :

The roasted ore is heated with coke at 1473 K so that oxide is converted into metal.

$$ZnO + C \xrightarrow{1400^\circ C - 1500^\circ C} Zn + CO$$

(iv) Purification :

Impure zinc, known as spelter is purified by electrolysis. Electrolysis is carried out in a cell having acidified $ZnSO_4$ and dilute $H_2SO_4$ as electrolyte. The anode is of impure zinc while cathode is pure zinc plate.

3. Properties of Zinc :

It is bluish white, lustrous metal (m.p. 692 K, b.p. 1180 K, density 7.14 g $cm^{-3}$). It is brittle at ordinary temperature, malleable and ductile at 410-430 K and again become brittle at 493 K. This is due to its different allotropic forms. It is a good conductor of electricity.

4. Uses of Zinc :

It is extensively used for galvanizing iron to prevent it from rusting. It is used as a reducing agent in dry cells, extraction of Au and silver. Various alloys of zinc like German silver (Cu, Zn and Ni), Brass (Cu and Zn), gun metal (Sn, Zn and Cu) are commercially important.