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TRANSITION METALS or d – Block and f – Block elements

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[B.SC – II (HONS)]

d – Block and f – block element

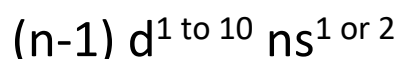
d – block element

or

Transition metals

Definition:- Those elements are called as d – block elements whose last electron enters into d – orbital.

General electronic configuration of valance electron (V.E):-



Here, n = outermost orbit number.

There are four series of transition metals:-

(1) 3d – series:-

Those transition metals are placed in 3d – series whose last electron enters into 3d – orbital.

Ex:- Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn

Here total 10 elements are found.

(2) 4d – series:-

Those transition metals are placed in 4d – series whose last electron enters into 4d – series whose last electron enters into 4d – orbital. Here also 10 elements are found.

Ex:- Y to Cd – 10 elements.

(3) 5d – series:-

Those transition metals are placed in 5d – series whose last electron enters into 5d – orbital.

Ex:- La to Hg – 10 elements.

(4) 6d – series:-

Those transition metals are placed in 6d – series whose last

electron enters in 6d – series whose last electron enters into 6d – orbital. This is incomplete series.

Ex:- Ac, Uuq, Uup, Uuh, Uus, Uuo.

Also those elements are called as transition metals in which incomplete d – orbitals are found.

(Q) Why Zn, Cd, Hg, Cu, Ag, Au, are placed in transition metals?

Ans:- Some properties of those elements (for ex- complex formation) resemble with transition metals. Also, for convenience these metals are placed with transition metals although most of the properties of these metals are different from transition metals.

Characteristisc of Transition metals:-

(1) Metallic character:-

- (a) All elements of transition elements are metals because in the outermost orbit of transition metals only one or two electrons are found, that can be easily lost.
- (b) These elements are called as transition elements because the properties of these elements are in between S – block and P – block elements.
- (c) Since from left to right of transition metals in a period the value of IP increases, the electropositive character decreases.
- (d) The strength of metallic bond of transition metals are very high due to high effective nuclear charge and large number of valence electrons.

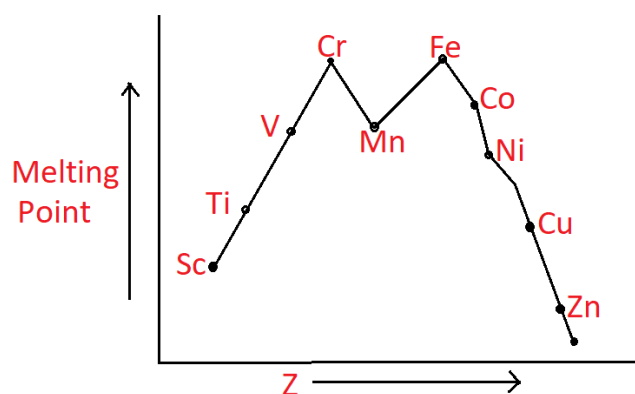
- (e) Due to above reason transition metals are very hard and possess high density.
- (f) Most of transition metals have density 5gm/cm^3 O.S being a transition metal have highest density 22.6gm/cm^3 .

(2) Melting point and Boiling point:-

(Q) Why melting point and boiling point of transition metals are very high?

Ans:- Since in transition metals incomplete d – orbitals are found, the number of V.E (valence electron) in these metals are larger. So, these metals also form covalent bond with its own atom. That is why the interparticle attractive forces in transition metals are very high. Thus, melting point and boiling point of transition metals are high.

(Q) Why from left to right in a period of transition metals melting point first increases and then decreases.



Since in transition series first there is increase of number of unpaired electron and then after there is decrease of no. of unpaired electron. Hence due to presence of increasing no. of unpaired electron there is increase in number of covalent bonds formed by similar atoms of transition metals at first and then due

to decrease of number of unpaired electron, there is also decrease of number of covalent bond between similar atoms of transition metals. So, in a series of transition metals at first there is increase of melting point and then there is decrease of melting point.

Note:- Mn and Tc have abnormally low melting point.

(3) Ionisation energy:-

(Q) Why in a series of Transition metals from left to right in a period there is slow increase of ionisation potential to S, P – block element?

Ans:- From left to right in a transition series there is increase of inner d – orbitals. Hence there is increase of screening effect of outer electrons by inner d – electrons. Thus, the energy required to remove from outer most orbit will not increase so much from left to right in a d – series as it is in S and P – block elements. So, IP of transition metals increase very slowly from left to right in a series.

Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

IP – 6.6, 6.8, 6.7, 6.8, 7.4, 7.9, 7.9, 7.6, 7.7, 9.4

(Q) Why IP is 5d – series elements are greater than 3d and 4d – series elements?

Ans:- Since in 5d – series elements 4f orbital are fulfilled which have got lesser screening effect, this increases the effective nuclear charge of 5d – series. This is why IP of 5d – series are greater than 4d and 3d – series elements.

(Q) Why Ni^{2+} compounds are more stable than Pt^{2+} compounds?

Ans:- Sum of the value of $IP_1 + IP_2$ of Ni = 2.49×10^3 kJ/mole and $IP_1 + IP_2$ of Pt = 2.66×10^3 kJ/mole. So, Ni^{+2} is more stable than Pt^{+2} compounds.

(Q) Why $K_2[Pt^{+4}Cl_6]$ is well known complex while $K_2[Ni^{+4}Cl_6]$ complex is not found?

Ans:- The sum of the value of $I.P_1 + I.P_2 + I.P_3 + I.P_4$ of Ni = 11.29×10^3 kJ/mole

and $I.P_1 + I.P_2 + I.P_3 + I.P_4$ of Pt = 9.36×10^3 kJ/mole

Since the sum of the values of four successive IP of Pt is lower than Ni. So, Pt can form Pt^{+4} ion but Ni cannot form Ni^{+4} ion. So, $K_2[PtCl_6]$ is found but $K_2[NiCl_6]$ is not found.

(Q) What are features which determine the stability of particular oxidation state?

Ans:- Following features determine the stability of particular oxidation state of transition metals.

(a) Enthalpy of sublimation [$\Delta H_S^{(+)}$]

(b) Ionisation potential [$\Delta H^{(+)}$]

(c) Hydration energy [$\Delta H^{(-)}$]

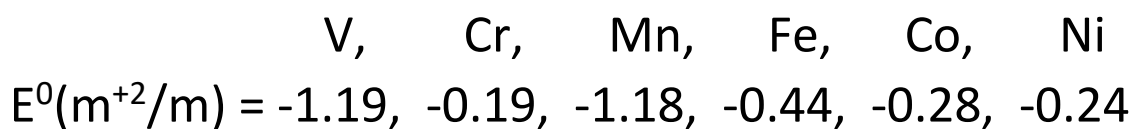
Lower the value of sum of the above parameters for a transition metal higher will be the stability of oxidation state.

$$\Delta H_T = \Delta H_S + \Delta H_{I.P} + \Delta H_{Hydrate}$$

(Q) How stability of oxidation state is explained on the basis of electrode potential?

Ans:- Electrode potential is the measure of ΔH_T and hence the stability of particular oxidation state. Lower the value of electrode potential larger will be the stability of the particular

oxidation state.



In the above example it is clear that +2 state of V is most stable.

(4) Atomic and Ionic Radii:-

(Q) Why atomic radii of transition metals first decrease till middle than almost become constant and towards the end it increases?

Ans:- From left to right in a transition series there is successive increase in the 3d – electrons and hence increase of screening effect due to this 3d – electrons. Up to middle transition metal nuclear charge exceeds over screening effect and hence there is decrease of radii. But after the middle of a transition series, the screening effect of d – orbitals just counterbalance the nuclear charge and hence there is not any measurable change in atomic radii.

But towards the end d – orbitals are fulfilled and due to this strong repulsion between d – orbitals and outermost ns electrons. So, now there is increase of atomic radius.

(Q) Why elements of second and third transition series belonging to particular group have almost equal atomic radii?

Ans:- In third transition series (5d – series) 4f – orbitals are fulfilled. Due to very small screening effect of 4f – orbitals there is Lanthanide contraction. So, in a particular group of second and third transition series there is not any increase in atomic radii.

(5) Oxidation state:-

Transition metals show variable oxidation state due to presence of incomplete d – orbitals.

The following points may be noted regarding the oxidation state of transition metals.

(i). From beginning to the middle of a transition series (Ex:- Sc, to Mn) the minimum oxidation states are equal to +2 and maximum oxidation states are equal to total number of valence electron.

Example:-

<u>Elements</u>	<u>Oxidation states</u>
Sc ($3d^14s^2$)	+2, +3
Ti ($3d^24s^2$)	+2, +3, +4
V ($3d^34s^2$)	+2, +3, +4, +5
Cr ($3d^54s^1$)	+2, +3, +4, +5, +6 ($K_2Cr_2^{+6}O_7$).
Mn ($3d^54s^2$)	+2, +3, +4, +5, +6, +7 ($KMn^{+7}O_4$).

(ii). The most common oxidation state of transition metals is (+2).

(iii). But in case of Fe, Co, Ni, Cu, Zn (these are more than half fulfilled 3d - subshells), the minimum oxidation states are (+2) where as the maximum oxidation states are not equal to the total number of valence electron rather the maximum oxidation states are less than total number of valence electron.

Examples:-

<u>Elements</u>	<u>Oxidation state</u>
(a). Fe ($3d^64s^2$)	+2, +3 It forms +4, +5, +6 oxidation states in rare cases +8 O.S of Fe is not found.
(b). Co ($3d^74s^2$)	+2, +3, +4

(c). Ni ($3d^14s^2$) +2, +3, +4

(d). Cu ($3d^14s^2$) +1, +2

(e). Zn ($3d^14s^2$) +2

(iv). Highest oxidation states shown by transition metals is +8.

Ex:- Os and Ru

(v). Some transition metals show 0 oxidation states.

Ex:- $[\text{Fe}^0(\text{Co})_5]$ $[\text{Ni}^0(\text{Co})_5]$

(6) Complex formation:-

Transition metals form complexes due to the following reasons:-

(a) Due to small size and high charge density of metal ions.

(b) Due to presence of vacant d – orbitals.

(7) Magnetic property:-

In transition metals or ions there are good number of unpaired electrons due to presence of incomplete d – orbitals.

Paramagnetic:- Those substance are called as paramagnetic in which unpaired electrons are present.

The unpaired electrons present in transition metals and ions create net magnetic moment.

Origin of paramagnetic:-

Paramagnetic character develops in substance due to presence of unpaired electrons. These unpaired electrons produce net magnetic moment due to orbital angular momentum and spin angular momentum.

Here for convenience orbital angular momentum is not taken. For the calculation of magnetic moment of a substance but with the help of spin angular momentum magnetic

moment is calculated which gives the following relationship of magnetic moment with unpaired electron.

$$M_{\text{eff}} = \sqrt{n(n + 2)} \text{ B.M}$$

Here n = Number of unpaired electrons

M_{eff} = Effective magnetic field

B.M = Bohr magneton

$$\text{B.M} = \frac{eh}{4\pi mc}$$

Here, e = Charge of electron

h = Planck's constant

m = Mass of electron

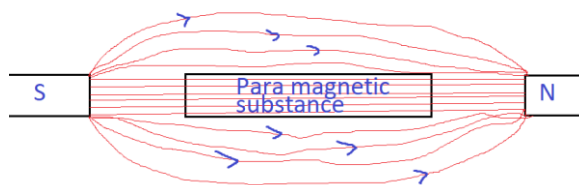
c = Velocity of light

Ex:-	Unpaired electron	Configuration	Magnetic Momentum (experiment)	Theoretical
Sc ⁺³	0	3d ⁰	0	0
Ti ⁺³	1	3d ¹	1.73 B.M	1.732 B.M
Ti ⁺²	2	3d ²	2.84 B.M	2.828 B.M

From above examples it is clear that, there is some difference between experimental and theoretical value of magnetic moment of a species. This is due to the fact that in theoretical value magnetic moment due to orbital angular momentum has been neglected.

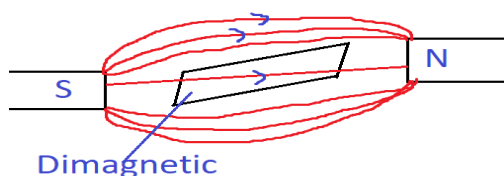
Characteristics of Paramagnetic substance:-

- (a) When paramagnetic substance is placed in a magnetic, field the magnetic lines of force go through the paramagnetic substance pass with greater density than in vacuum.



(b) Due to the interaction of external magnetic field and magnetic field due to the paramagnetic substance, an attractive force develops between magnet and paramagnetic substance.

Dimagnetic:- The substance which when placed in a magnetic field decreases the intensity of magnetic field than in vacuum are called as dimagnetic substance. The property due to which they show this behavior is called as dimagnetism.



The magnetic lines of force tend to avoid to pass through such substances and as such dimagnetic substances are repelled by the magnetic field. And set themselves at right angles to the magnetic field.

(8) Coloured compounds:-

Most of the transition metal ions or compounds are coloured due to the presence of incomplete d – orbitals.

But S and P – block elements generally do not form coloured compounds because S and P – orbitals do not split by the absorption of energy.

Those transition metal ions are not coloured in which d – subshell is completely filled or empty.

Ex:- $Zn^{2+} (3d^{10}) = \text{colourless}$

$Cu^{+1} (3d^{10}) = \text{colourless}$

$\text{Sc}^{3+} (3d^0) = \text{colourless}$

$\text{Ti}^{4+} (3d^0) = \text{colourless}$

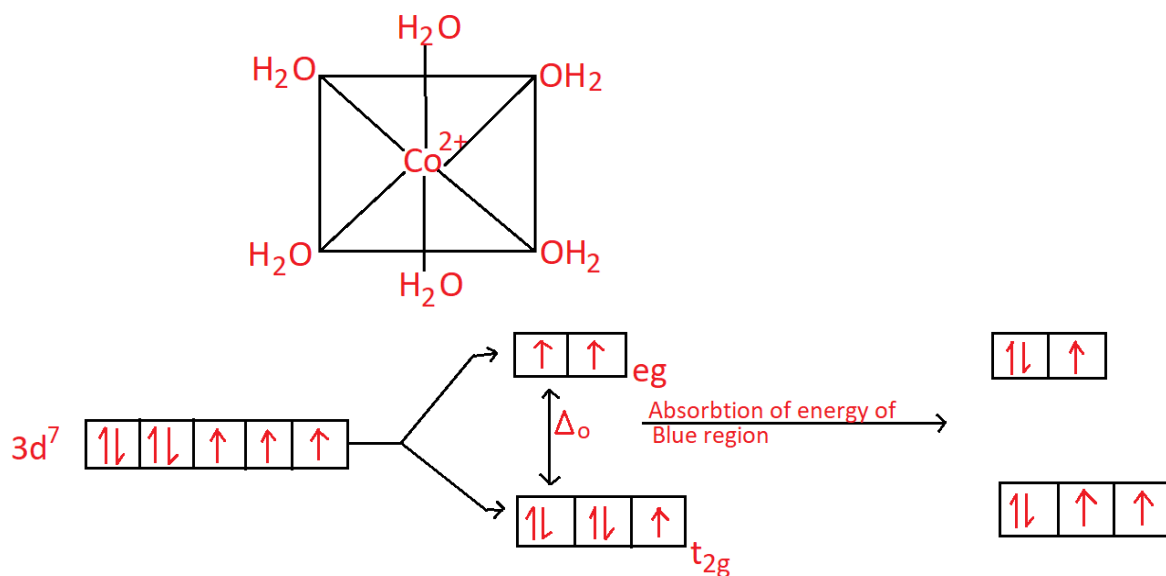
But in those transition metal ions in which incomplete d – subshells are present show colour due to d -d transition.

d – d transition:-

(a) Let us take an example to explain the d – d transition for colouration $[\text{Co}^{2+}(\text{H}_2\text{O})_6]^{2+}$. Here Co is found in oxidation state = +2.

$\text{Co}^{2+} (25) : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^0$

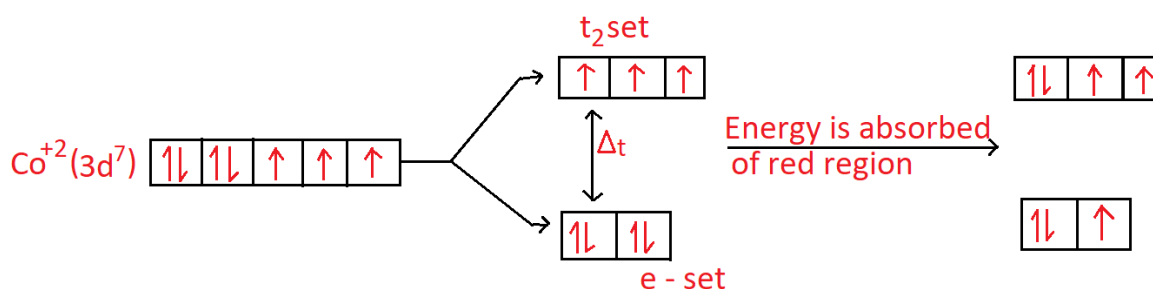
Now, here 3d – subshell splits up in to t_{2g} and eg set in the presence of octahedral legand field.



This complex requires high energy for excitation of electron from t_{2g} set to eg set so it absorbs energy of blue radiation. And the complementary colour of blue radiation is red. So, this complex emits red colour that's why the colour of this complex is red.

(b) The tetrahedral cobalt (+2) complexes of type $[\text{CoX}_4]^{2-}$ need smaller energy for the excitation because $\Delta_t < \Delta_o$. So, it absorbs red colour and emits its complementary blue colour.

Actually in tetrahedral field d – subshell split in to e and t₂ set. e set has lower energy than t₂ set.



(9) Catalytic property:-

Transition metals and their some compounds show catalytic behavior due to their variable valency.

Example:-

- Fe behaves as catalyst in the manufacture of NH₃ gas by Haber process.
- V₂O₅ behaves as catalyst in the conversion of SO₂ in to SO₃ in the following ways.



(10) Formation of Alloys:-

Transition metals form Alloys very often because their sizes are almost the same. So, they can interchange their atoms by another transition metals.

Ex:- Brass = Cu + Zn

Moneel metal = Cu + Fe + Ni

(11) Interstitial compounds:-

Transition metals form interstitial compounds. In the interstitial sites of transition metals some foreign elements are trapped

which makes the metal less malleable, ductile and more tensile and hard.

General properties of 1st row of Transition metals (3d - series):-

(1) Oxides:-

- (a) Transition metals form basic Amphoteric and acidic oxides.
- (b) Generally in lower oxidation state they form basic oxides.

Ex:- Mn^{+2}O , Mn_2^{+3} , $\text{V}_2^{+3}\text{O}_3$, Cr^{+2}O , Fe^{+2}O , Co^{+2}O , Ni^{+2}O , Cu_2^{+1}O .

- (c) Generally in the intermediate oxidation state they form amphoteric oxides.

Ex:- Mn_3O_4 , Mn^{+4}O_2 , Cu^{+2}O , Zn^{+2}O , Fe_2O_3 , MnO_2 , CrO_2 , Cr_2O_3 , VO_2 , TiO_2 .

- (d) Generally in higher oxidation states they form acidic oxides.

Ex:- V_2O_5 , CrO_3 , $\text{Mn}_2^{+7}\text{O}_7$ etc.

(2) Halides:-

- (a) Transition metals react with halogens at high temperature to give metallic halides.
- (b) The order of reactivity is as under.



Due to difference of electronegativity and size.

- (c) Fluorides of transition metals form ionic compounds. While chlorides Bromides and Iodides of transition metals are covalent.

Ex:- CuF_2 is ionic, CuCl_2 is covalent, CuBr is covalent.

- (d) Halides of transition metals in higher oxidation state are relatively unstable and get hydrolysed easily.

(3) Sulphides:-

- (a) Sulphides of transition metals are prepared by heating them with sulphur or reaction with H_2S or Na_2S .
- (b) In sulphides the oxidation states of transition metals are low because of E.N of S atom is low.

Ex:- Fe^{+2}S , Ni^{+2}S , Zn^{+2}S , Mn^{+}S .

- (c) Sulphides of transition metals are coloured or black.

Ex:- (i) NiS , CoS , CuS , ZnS = Black

(ii). MnS , CdS , etc. = coloured

(iii). MnS = Pink

(iv). CdS = Yellow

- (d) They are insoluble in water.

Group trends in the chemistry transitions metals:-

(A) Group 4 – elements:-

- (i) In this group Ti, Zr and Hf are found.
- (ii) Ti is strong, has high melting point and is resistant to corrosion.
- (iii) Zr and Hf are silvery white metals.
- (iv) The most stable oxidation state of this group is +4.
Oxides of Ti – Rutile, Ilmenite [FeTiO_3]
- (v) ZrO_2 is a refractory material.

(Q) Why atomic radii of Zr (160 pm) and Hf (159 pm) are almost equal?

Ans:- Due to Lanthanide contraction it happens.

- (vi) Zr and Hf are important for the nuclear energy.

(B) Group 5 – elements:-

- (i) This group consists of V, Nb, Ta, Db.

- (ii) The most important oxidation state is +5.
- (iii) Vd is used as additive to steel.
- (iv) V_2O_5 is used as catalyst.
- (v) Nb alloys are used in jet engines.
- (vi) Ta is very resistant to corrosion and is used for making apparatuses in chemical plants.
- (vii) Ta is used in surgery and also bone pins.

(C) Group 6 – elements:-

- (i) It consists of Cr, Mo, W.
- (ii) The most important oxidation states of Cr are +3, +6.
- (iii) The most important oxidation states of Mo and W are +5 and +6.
- (iv) In $Cr(CO)_6$ the oxidation state of Cr is 0.
- (v) W has the highest melting point.
- (vi) Cr is used for electroplating of Iron to prevent rusting.
- (vii) The ore of Cr is chromite – $FeCr_2O_4$.
- (viii) The ore of Mo is molybdenite – MoS_2 .
- (ix) The ore of W is wolframite – $FeWO_4$.
- (x) Mo and W form very hard alloys with Fe and are used for cutting purposes.
- (xi) W is used as filament in electric bulbs.
- (xii) MoS_2 acts as a lubricant.

(D) Group 7 – elements:-

- (i) It consists of Mn, Tc and Re.
- (ii) Most stable oxidation states of Mn are +2, +4 and +7.
- (iii) Most stable oxidation states of Tc and Re are +4 and +7.

- (iv) Mn is found in ores – named pyrolucite – MnO_2 , Braunitz – Mn_2O_3 , Hausmanite – Mn_3O_4 .
- (v) Tc does not occur in nature. It is first man – made element. It is Radioactive.
- (vi) Re is a rare element and occurs in ore of Mo.
- (vii) Ferromanganese Alloy – Fe + Mn. Manganese Bronze – Mn + Cu + Zn.
- (viii) Re is used as electronic filament.

(E) Group 8, 9 and 10 – elements:-

- (i) Fe, Co, Ni are ferromagnetic substances.

Ferromagnetic:- Those substance are called as ferromagnetic in which paramagnetic property is found in large amount. This is because the unpaired electrons in these elements have get magnetic filed in the same direction. So, the net magnetic filed becomes. Very larger

Ferromagnetic elements can be magnetized and hence magnets are formed. With the help of these elements.

- (ii) Fe has oxidation state +2 and +3.
- (iii) Co shows +2 oxidation state.
- (iv) Ni shows +2 oxidation state.
- (v) After Al, Fe is the most abundant metal.
- (vi) Rest metals of these groups are inert.

(F) Group 11 – elements:-

- (i) This group includes Cu, Ag and Au.
- (ii) These metals are known as coinage metals.
- (iii) The most stable state of Cu is +2.

- (iv) The most stable state of Ag and Au is +1.
- (v) The metals of this group have highest thermal and electrical conductivity.
- (vi) Metals of this group are found in free state and combined state.

(G) Group 12 – elements:-

- (i) It consists of Zn, Cd and Hg.
- (ii) These metals do not show characteristics of transition metals.
- (iii) These metals do not show oxidation state more than +2.
- (iv) Hg is found in Liquid state.

Iron metal:-

Important ores:-

- (a) Haematite (Red oxide of Fe) – Fe_2O_3 .
- (b) Magnetite (Magnetic oxide of Fe) Fe_3O_4 .
- (c) Limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$).
- (d) Siderite – FeCO_3 .
- (e) Iron pyrite – FeS_2 .

Types of Iron:- There are three types of iron-

- (a) **Cast iron or pig iron:-** In this iron carbon (2 – 5%), Silicon P, Mn etc, impurities are present in large amount. It contracts when it is heated. Belding of cast Iron is not possible. It is resistance to corrossion.
- (b) **Wrought Iron:-** (Maleable Iron) In this iron only carbon Impurity (0.2%) is present. It can be changed in to rod sheat etc. it can not be magnetised permantly.

(c) **Steal:-** In this iron C, Si, P, Mn etc. impurities are present in very small amount.

Extraction of cast Iron:-

Cast iron is mainly extracted from Haemotite (Fe_2O_3) or iron pyrite. This is performed in the following steps.

(A) Concentration of ores:-

Haemotite cast iron pyrite are is concentrated by washing or magnetic separation process.

(B) Calcination:-

Here concentrated ore is calcinated in a furance. Due to this proccess following changes take place-

- (i) C impurities is changed into CO_2 .
- (ii) H_2O changes into water vapour.
- (iii) S change into SO_2 ↑.
- (iv) FeS_2 changes into Fe_2O_3 .

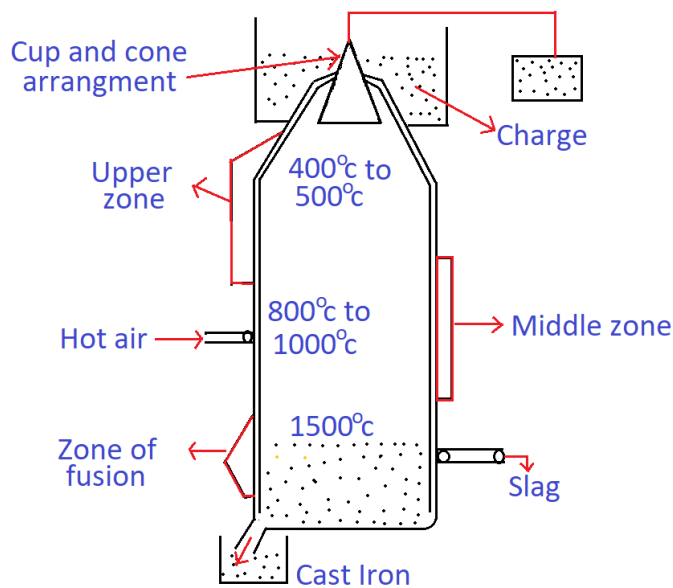


In this way after this process we get Fe_2O_3 (Porous).

(C) Reducing or Smelting:-

Calcinated ore is mixed with coke, and CaCO_3 and then it is taken in a blast furnace.

Blast furnace:- Its length is about 50 to 100 fit and breadth is about 15 to 20 fit. When charge (C + CaCO_3 + calcinated ore) is dropped through cup and cone arrangement following reactions take place and altimately cast iron is obtained.



(a) Zone of fusion (Lower zone):-

The temperature of this zone is 1500⁰c. Here very small amount of iron is obtained and mainly CO₂ gas is formed.



(b) Middle zone or zone of Heat absorption:-

The temperature of this zone is 800⁰c to 1000⁰c. Here mainly CO gas is formed and also formation of slag takes place here.



(c) Upper zone or zone of Reduction:-

The temperature of this zone is 400⁰c to 500⁰c. Here mainly Iron is obtained by the reduction of Fe₂O₃. Here only reduction takes place

