

D and f block elements

Transition elements: (group 3 to 12)

These elements have properties which are intermediate between those of s and p block elements

A transition element is defined as the one which has incompletely filled d orbitals in its ground state or in any one of its oxidation states.

These are placed in the middle part of the periodic table (between s and p)

There are 4 series of elements:

First series : Sc to Zn (At. no. 21 to 30)

Second series: Y to Cd (At. no. 39 to 48)

Third series: La, Hf to Hg (At. no. 57, 72 to 80)

Fourth series: Ac, Rf to Cn (At. no. 89, 104 to 112)

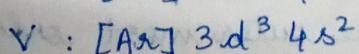
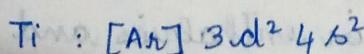
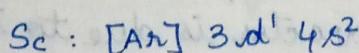
Configurations of d block elements:

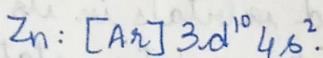
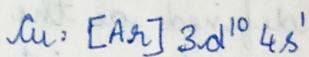
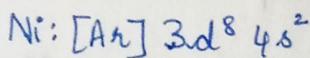
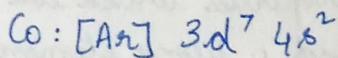
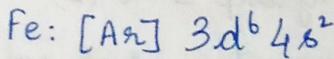
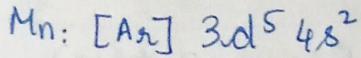
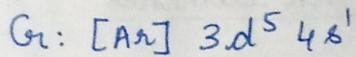
General configuration of d block elements is

$$(n-1) d^{1-10} n s^{1-2}$$

The inner d orbital is being filled with increase in atomic number.

There are 4 different transition series. The electronic configuration of first d series is as follows:





Special configurations of Cr and Cu is due to the extra stability of half filled and fully filled orbitals (d^5 and d^{10}) also the energy difference between 3d and 4s is not very large.

General Characteristics:

- Almost all transition elements show typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.
- Zn, Cd and Hg are considered as non-transition elements ~~as~~ these elements have completely filled ~~d~~ orbitals (d^{10}).
- Metallic Character

Except mercury, which is a liquid, all transition elements have typical metallic structure. Metallic character is due to their relatively low ionisation enthalpies and one or two electrons in the outer most orbit.

These elements are electropositive.

Melting point and boiling point:

Melting and boiling points of transition elements depends on the no. of unpaired electrons. Greater the no. of unpaired electrons, stronger is the metallic bonding, and hence high melting points.

- In a particular series, melting point increases upto the middle and then decreases with decrease in no. of unpaired electrons. So, Zn, Cd and Hg have low melting and boiling points.
- There is a dip in melting points of Mn and Tc as Mn has stable configuration and electrons are held more tightly by Mn atoms. This reduces the delocalisation of electrons resulting in weaker metallic bondings.
- Transition elements have high enthalpies of atomisation due to the overlap of unpaired electrons between the atoms resulting in strong metallic bonding.
- Zn, Cd, Hg have low enthalpies of atomisation as there are no unpaired electrons.

For graph: Refer fig. 8.1.

- Atomic size and Ionic size
- sizes of transition elements are intermediate between s and p block
- The atomic size first decreases with increase in atomic no. due to increase in nuclear charge, but low shielding effect.
- Atomic size becomes almost steady towards the middle of the series because of filling of d orbitals which screens outer shell electrons.
So increase in nuclear charge is partly cancelled by increase in screening effect.
- Towards the end of the series, there is a slight increase in size due to the increased repulsion between electrons in the same orbital.
- Atomic size of second transition series are found to be larger than first series
- Ionic sizes of Lanthanoids also follow the same order as that of the atomic size.
- ~~Ionic radii are different in different oxidation states due to increase in effective nuclear charge. So M^{3+} cations are smaller than M^{2+}~~
- Atomic sizes of 3rd transition series are found to be almost same as the 2nd series. This is explained as lanthanoid contraction

- steady decrease in atomic size of lanthanoids due to poor shielding effect of 4f electrons is called lanthanoid contraction.
- As shielding effect is less, nuclear charge increases along the series and hence size decreases.

Consequences:

- Similarity in size of Zr and Hf is due to lanthanoid contractions.
- Difficulty in separation of lanthanoids in pure state - since the change in ionic size of lanthanoids is small, their chemical properties are similar. This makes the separation of lanthanoids difficult in pure state
- Basic strength of lanthanoid hydroxides decreases from ~~La³⁺~~ to Lu³⁺, which is due to increase in covalent character of hydroxides. So La(OH)₃ is more basic than Lu(OH)₃
- Ionic size of lanthanoids follows the same order as that of atomic size.
Ionic radii are different in different oxidation states due to increase in effective nuclear charge. Hence M³⁺ cations are smaller than M²⁺ cations.

DENSITY:

Density of transition elements increase along the series due to decrease in atomic size and increase in nuclear charge (atomic volume decreases and atomic mass increases).

Ionisation Enthalpies:

- The first ionisation enthalpy of d block elements are higher than s and p block elements. This is due to increase in nuclear charge and poor shielding effect of 'd' electrons.
- Increase in ionisation enthalpy is not regular. This is because removal of one electron alters the relative energies of $4s$ and $3d$ orbitals, so there is reorganisation of energy accompanying ionisation.
- First ionisation enthalpy of Zn is found to be lower. This is because after the removal of one electron from Zn^{2+} it attains stable $3d^{10}$ configuration.
- Cr and Cu have exceptionally high IE_2 (second IE) than the neighbouring elements due to the stability of half-filled and fully filled configuration respectively ($3d^5$ and $3d^{10}$)
- Third IE of Zn^{2+} and Mn^{2+} is very high due to stability of $3d^{10}$ and $3d^5$ configuration.
- Very high values of third IE of Cu, Zn, Ni, indicate that it is difficult to show +3 oxidation state for these elements.
- The first IE of third transition series is very high. This is due to the poor shielding effect of $4f$ electrons. So outer electrons are attracted by the nucleus with a greater force.
- Ni^{2+} compounds are well-known but Pt^{2+} compounds are rare. This is because the first two ionisation enthalpies of Ni are lower

than Platinum. ($IE_1 + IE_2$)

Pt⁴⁺ compounds are well-known but Ni⁴⁺ compounds are rare. This is because the first ^{four} ionisation enthalpies of Ni are lower than that of Ni.

($IE_1 + IE_2 + IE_3 + IE_4$). That is, $K_2[PtCl_6]$ is available but $K_2[NiCl_6]$ is not known.

In $K_2[PtCl_6]$ Pt is +4.

In $K_2[NiCl_6]$ Ni is +4.

Oxidation States:

Transition elements exhibit variable oxidation state. This is due to the participation of electrons in the ns and (n-1) level which are ~~norms~~ of almost same energy. Also incomplete d orbitals both ns and (n-1)d orbitals involve in bonding.

Stability of a particular oxidation state depends on the nature of the element with which the element is combined. The highest oxidation states are found in fluorides and oxides because of their high electronegativity and small size.

- Out of fluorides and oxides, stability of higher oxidation states of oxides are more than fluorides due to multiple bonding of oxygen with metals (oxy anions).
- So highest fluorides of Mn is MnF_4 but oxide is Mn_2O_7 .
- Maximum number of oxidation states are shown by elements which are present almost middle of the series.
- Transition elements show oxidation states from +1 to +7. +8 is shown by Rh and Os (Rhodium and osmium).

- Except Sc all other elements from the first transition series show +2 oxidation state.
- Sc is the element which shows only one oxidation state, i.e; +3 and is the stable oxidation state. (Refer table 8.3 in book)
- The lowest oxidation states correspond to the number of ns electrons.
eg: Cu. it shows +1 oxidation state. For others it is +2.
- The highest oxidation is equal to the sum of ns and unpaired (n-1) electrons.
- In the first series highest oxidation state and maximum number of oxidation states are shown by Mn.
The highest oxidation state is +7 and others +2, +3, +4, +5, +6.
- Ti^{4+} is more stable than Ti^{2+} and Ti^{3+} because Ti^{4+} is $3d^0 4s^0$.
- For Zn, Zn^{2+} is the most stable configuration as Zn^{2+} is $3d^{10} 4s^0$.
- Some elements show zero oxidation state in compounds. eg. Ni, Fe; $[Ni(CO)_4]$, $[Fe(CO)_5]$
- In P block elements, higher oxidation states are stable for lighter elements. Eg. Tl^{+1} is more stable than Tl^{3+} due to inert pair effect. Also, Pb^{2+} , Sn^{2+} , etc are stable than Pb^{4+} and Sn^{4+} .
- For transition elements heavier elements show more stable higher oxidation state. Eg. Mn^{6+} , W^{6+} , etc are more stable than Cr^{+6} . So Cr^{+6} act as oxidising agent. Eg. $K_2Cr_2O_7$ is a powerful oxidising agent. But WO_3 and MoO_3

are not oxidising agents.

+2 and +3 oxidation states are shown generally by ionic compounds and in higher oxidation states the compounds are covalent in nature.

→ Standard Electrode Potential:

- The stability of a particular oxidation state in aqueous solution depends on ionisation enthalpy, sublimation enthalpy and hydration enthalpy.

$$\Delta H = \Delta_{\text{sub}} H + IE + \Delta_{\text{Hyd}} H$$

- Smaller the value of ΔH for a particular oxidation state, greater will be the stability of that oxidation state.
- E° values of first row transition elements are irregular. This is explained with the irregular variation in ionisation enthalpy ($IE_1 + IE_2$) and sublimation enthalpies, which are very less for Manganese and Vanadium.

→ Trends in oxidation state (M^{2+}/M)

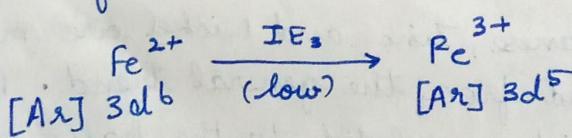
- The general trend towards less negative E° values across the series is related to increase in the sum of IE_1 and IE_2 .
- E° of manganese, Zinc and Nickel are more -ve than expected from the general trend. For Mn and Zn, it is related to the half-filled d^5 and fully filled d^{10} state respectively. The exceptional behaviour of Nickel towards E° is due to its high negative hydration enthalpies: $Mn^{2+} d^5$, $Zn^{2+} d^{10}$.
- In has low enthalpy of atomisation and high hydration enthalpy but it has low reduction

potential due to high IE ($IE_1 + IE_2$)

- Copper has positive value of E° which shows that it is the least reactive metal among the first series.
- This unique behaviour is responsible for the inability of copper to release H^+ from acids. The very high IE is not balanced by its hydration enthalpy.

Trends in oxidation state M^{3+}/M^{2+} :

- Except Cu and Zn, all elements show +3 oxidation state.
- Very low value of E° shows that Sc is highly stable.
- Highest E° value of Zn is due to its stable configuration in Zn^{2+} state. It is difficult to remove e^- from d^{10} configuration to change into +3 state.
- Highest value of E° for Mn is due to half filled stability of Mn^{2+} .
- Comparatively low value of E° is due to extra stability of d^5 state. It has low value of 3rd IE.



- $E^\circ_{V^{3+}/V^{2+}}$: low value of E° for Vanadium is related to half filled t_{2g}^3 configuration

1st row transition elements except copper are more reactive than other series.

These metals are oxidised by acids, but titanium and vanadium are passive to non-~~metals~~ oxidising acids.

E° value shows that Mn^{3+} and Co^{3+} are strong OA in aq. solⁿ whereas Ti^{2+} , V^{2+} , Cr^{2+} are strong reducing agents and liberate H_2 from dilute acids.

Stability of higher oxidation state - Halides:

Metal halides:

The reactivity order of Halogen with metal is :



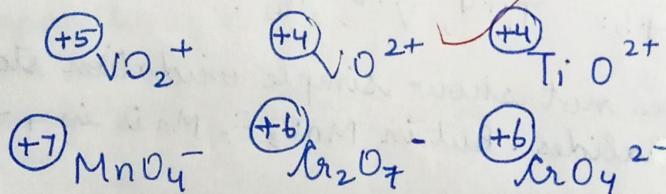
- Transition metals show highest oxidation state in Fluorides as it has high lattice enthalpies, High EN or high bond enthalpies.
- ~~CoF_3 is stable due to its high lattice enthalpy. But VF_5 and CrF_6 are stable due to high bond enthalpies (covalent bonds)~~
- Highest oxidation state in halides vary from +4 to +6: Ti^{+4} , V^{+5} , Cr^{+6} .
- Mn does not show simple oxidation state with +7 in halides. But in MnO_3F , Mn is in +7 oxidation state.
- In the first Transition series beyond Mn, no element shows OA more than +3.
- Fe and Co form trihalides ($FeCl_3$, CoF_3)
- Vanadium shows +5 oxidation state only in VF_5 , But other halides undergoes hydrolysis to give VOX_3 (oxo halides) in which V is in +5 oxidation state.

- In lower oxidation states, Fluorides are unstable.
 - Cu^{2+} halides are known, but Cu^+ halides are unstable in aqueous solⁿ as in disproportionation.
- $$2 \text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}^0.$$
- Cu^{2+} is more stable than Cu^+ . This is due to much more negative ΔHydH for Cu^{2+} than Cu^+ , which compensates the high IE_2 of copper.
 - Cu I_2 is not known as Cu^{2+} oxidises I^- to I_2 .



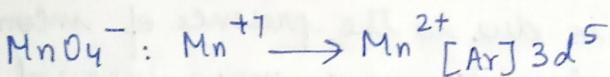
Metal Oxides:

- The ability of oxygen to stabilise highest oxidation state is more than fluorine, as it can form multiple bonds with metals.
- The highest O.S. is same as that of group no. upto group 7. Beyond group 7, max. O.S is +3. Higher O.S. are seen in oxo cations and oxo anions.



- Among halides, highest halides are with O.no. +4 but in oxides, Mn shows highest O.S. of +7.
- e.g. Highest fluoride of Mn = MnF_4
 Highest oxide of Mn = Mn_2O_7 .

order of increasing oxidation power in the first series: VO_2^+ < $\text{Cr}_2\text{O}_7^{2-}$ < MnO_4^- are explained with increasing stability of the lowest species to which it is reduced.

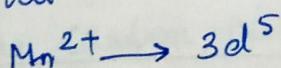
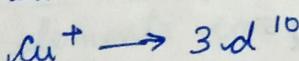
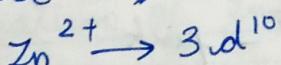
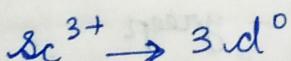


Paramagnetic substances: attracted in mag. field. These substances have one or more unpaired electrons. Most of the transition elements are paramagnetic in nature and are attracted in magnetic field.

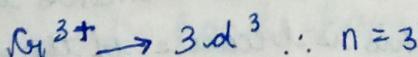
This is due to the presence of unpaired e^- s in their metal ions and in their compounds.

Magnetic properties are expressed in terms of magnetic moment in Bohr magneton units (BM)

Formula for calculations of "spin only" mag. moment is $\mu = \sqrt{n(n+2)}$ where $n = \text{no. of unpaired } e^-$ s.



$$\therefore n = 5 \quad \therefore \mu = \sqrt{5(5+2)} = \sqrt{35} \text{ BM} \\ \approx 5.9 \text{ BM}$$



$$\mu = \sqrt{3(3+2)} = \sqrt{15} \approx 3.8 \text{ BM}$$

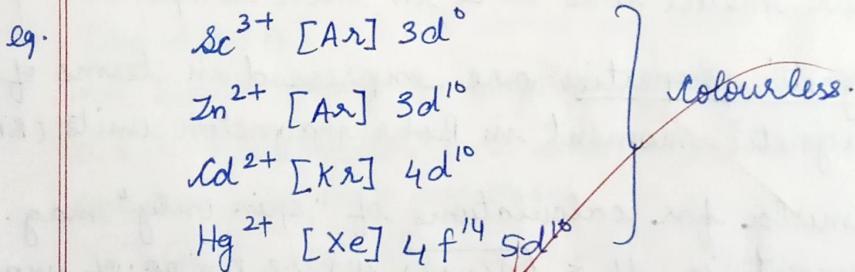
$$\text{Fe}^{2+} : 3d^6 \therefore n=4 \therefore \mu = \sqrt{4(4+2)} \\ \approx 4.9 \text{ BM}$$

$$\text{Co}^{2+} \Rightarrow 3d^7 \therefore n=3 \therefore 3.8 \text{ BM}$$

Table 8.7

- Most of the transition metal compounds are coloured, both in solid and aqueous state. Colour is due to the presence of incomplete d orbitals with one or more unpaired e^- s. Transition of e^- from lower energy d orbital to higher energy d orbital (d-d transition) occur and the energy of excitation corresponds to frequency of light.

This frequency lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed.



$\text{Fe}^{2+} [\text{Ar}] 3d^6$ - green

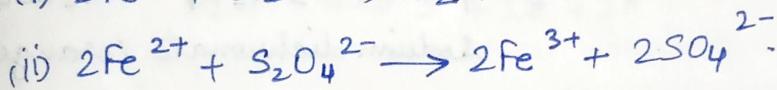
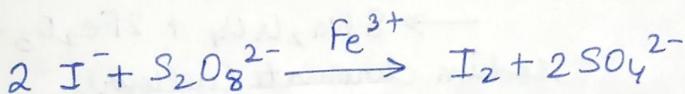
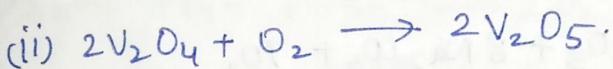
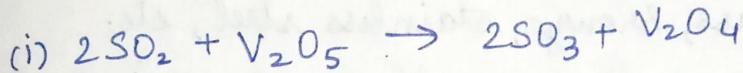
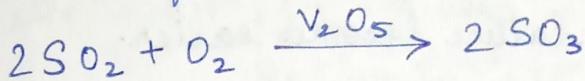
$\text{Mn}^{2+} [\text{Ar}] 3d^5$ - pink

$\text{Fe}^{3+} [\text{Ar}] 3d^5$

Formation of complex compounds:

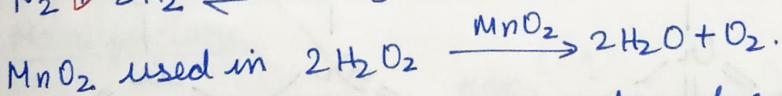
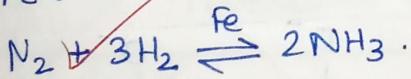
Most of the transition elements are taken as catalysts. This is because of the ability of transition elements to adopt multiple O.S.,

and to form complexes or intermediate compounds of variable oxidation state. Most of these metals are in solid state and hence it can provide enough surface area for the intermediate formation.



- Ni, Pd, Pt are used in Hydrogenation and reduction reactions.

- ~~Fe (metal)~~ is used in Haber's process,



↓ Fe and MnO₂ provide surface for adsorption.

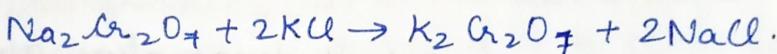
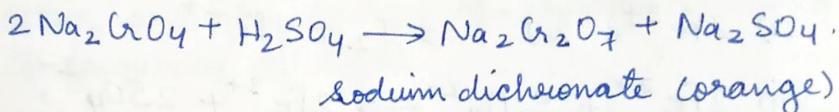
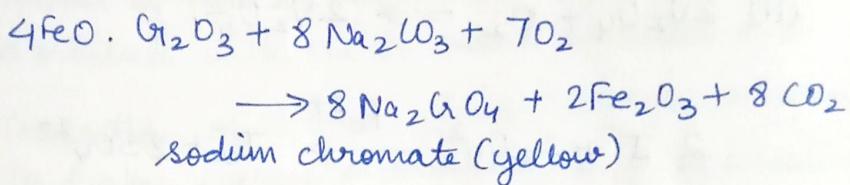
Formation of Interstitial compounds

Transition elements can trap some smaller atoms like carbon, Nitrogen, Hydrogen inside the crystal lattices of the metals. These compounds are non-stoichiometric in nature, chemically inert, hard, have high melting point, retain metallic conductivity

Alloy Formation :

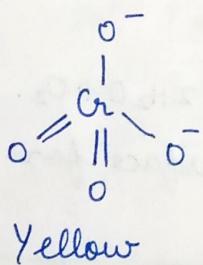
Transition elements form homogenous solid solutions or alloys as these metals have similarity in size and characteristics. So substitution of one metal by the other in its crystal lattice becomes easier.

e.g. Brass, Bronze, stainless steel, etc.

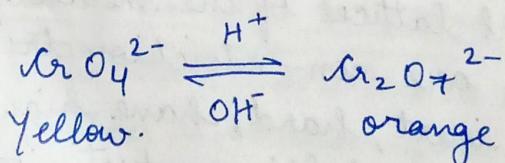
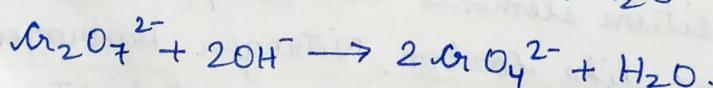
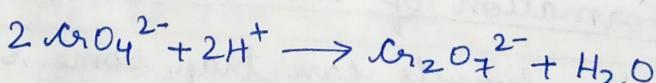
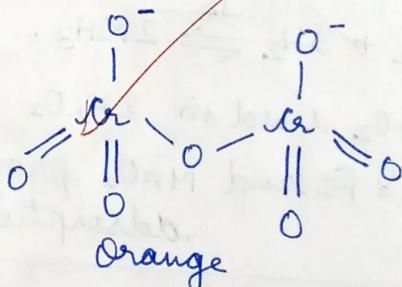


Structure:

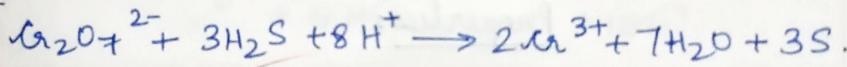
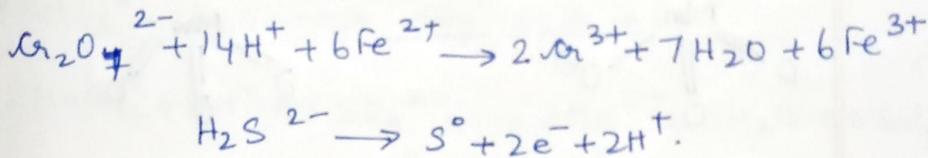
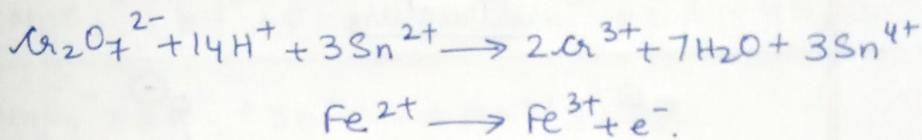
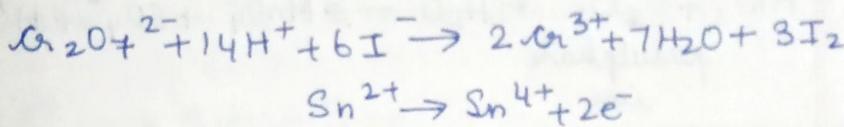
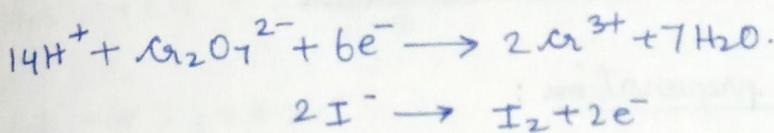
Chromate



Dichromate

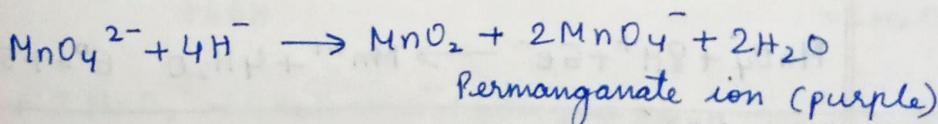
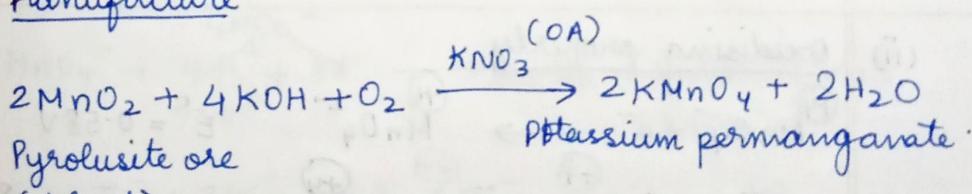


Oxidising property:

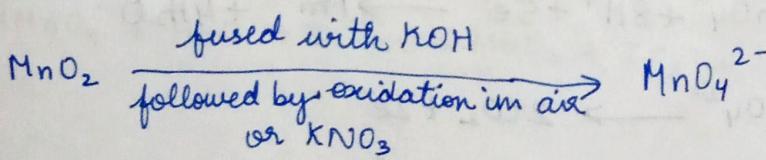


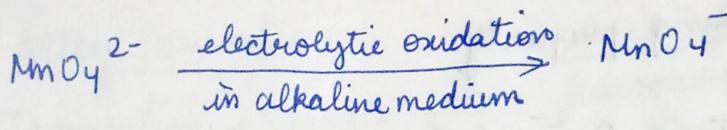
Potassium Permanganate

Manufacture

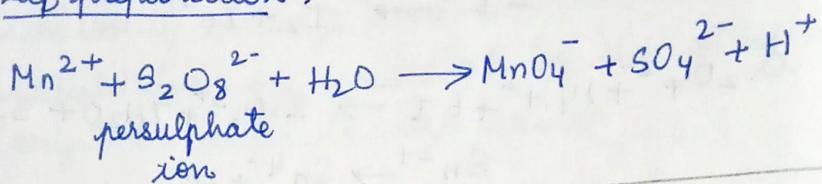


Commercial

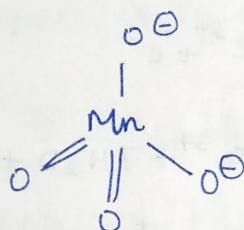




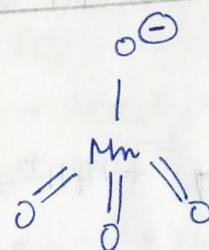
Lab preparation:



Structure



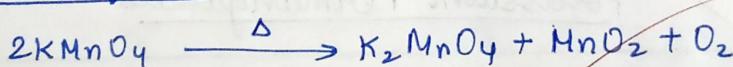
green
Manganate ion



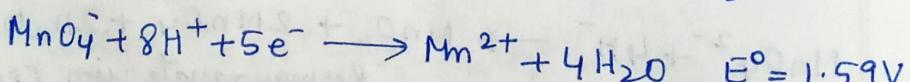
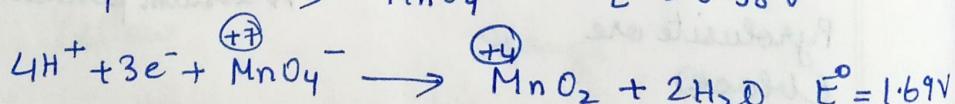
Purple
permanganate ion

Properties:

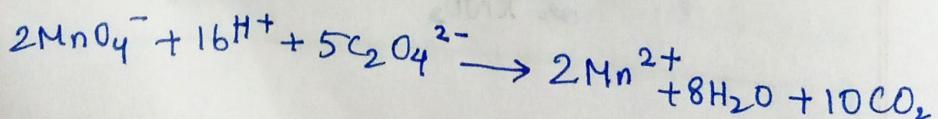
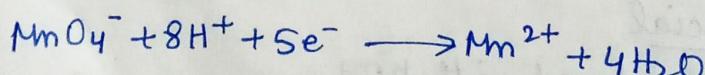
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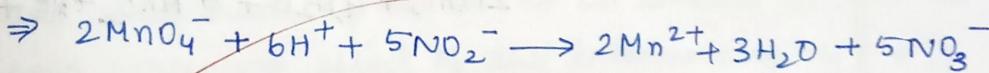
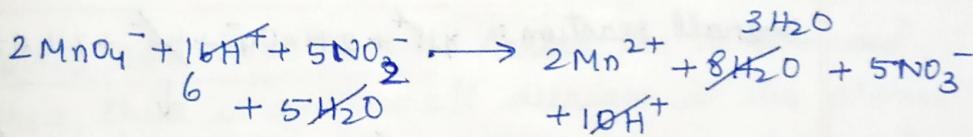
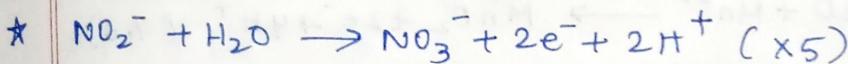
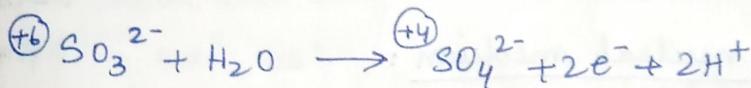
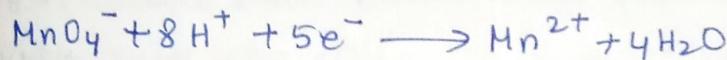
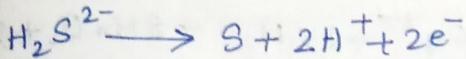
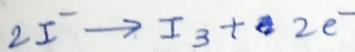
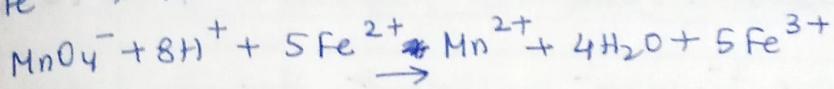
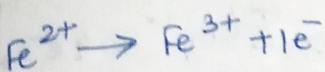


(ii) Oxidising property

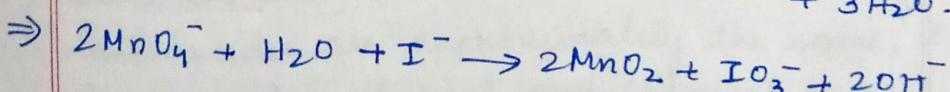
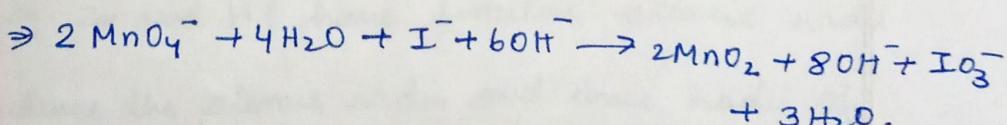
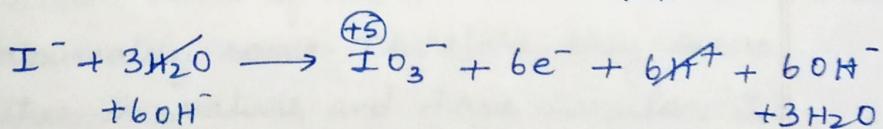
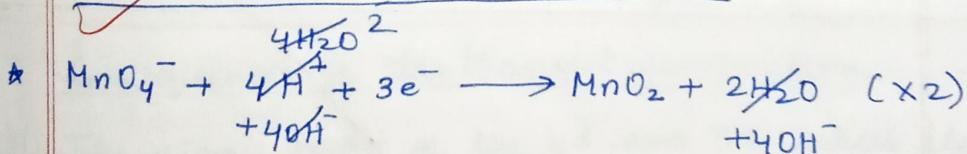


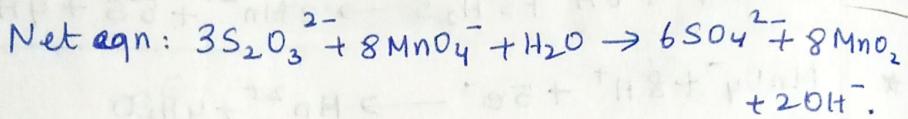
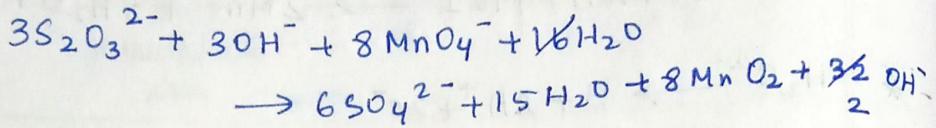
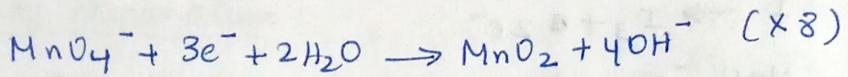
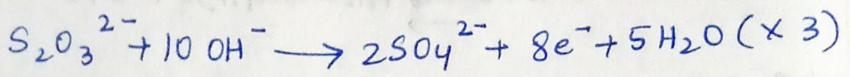
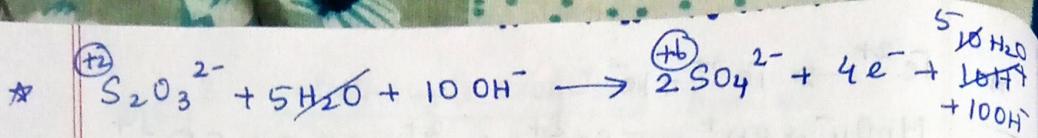
In acidic medium:



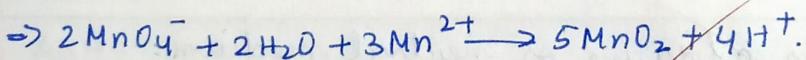
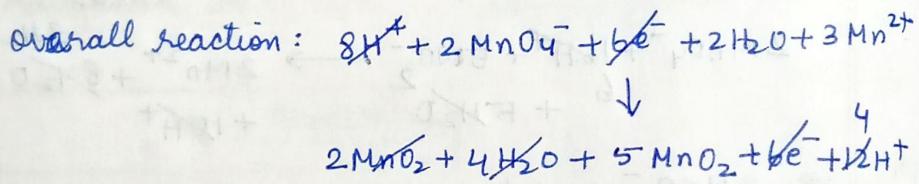
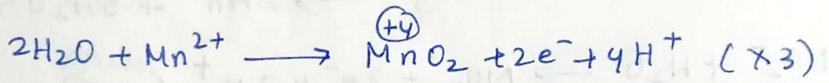
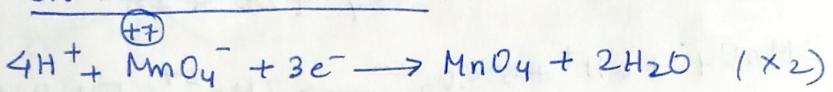


In alkaline or neutral medium:





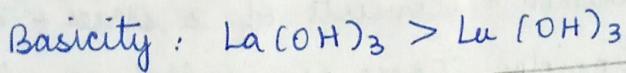
In neutral medium:



Inner transition Elements (F block)

- f block elements consists of 2 series - Lanthanides and actinides. These are called as inner-transition series as the valence e⁻s enter the antipenultimate (n-2) f orbital.
- Electronic configuration : $(n-2)f^{1-10}(n-1)d^{0-1}ns^2$
- The valence e⁻ in lanthanides enters the 4f orbital. Their outer elec. conf. can be given as :
 $4f^{1-14} 5d^{0-1} 6s^2$.
- The Valence e⁻ in actinides enter the 5f orbital. Their outer elec. conf. can be given as :
 $5f^{1-14} 6d^{0-1} 7s^2$.
- Atomic and ionic radii : Across the lanthanoid series, there is an overall decrease in the atomic and ionic radii from La to Lu which is due to poor screening effect of the intervening 4f e⁻s. This is termed as lanthanoid contraction.
- Consequences of lanthanoid contraction :
 - (i) The atomic radii of the 4d and 5d series elements approximately same. Therefore they occur together in nature and have similar IE.
eg. Zr and Hf have similar atomic radii
 - (ii) Since the atomic radii and ionic radii of lanthanides are approximately the same, they have similar physical and chemical properties. Hence they occur together and their separation becomes difficult.

(iii) The basic character of hydroxides decreases across the lanthanoid series.



- Actinoid contraction : Just like lanthanoids, in actinoids too there is a gradual decrease in atomic and ionic radii which is due to the poor screening effect of the intervening of e^- s. This is termed as actinoid contraction.

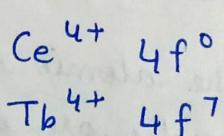
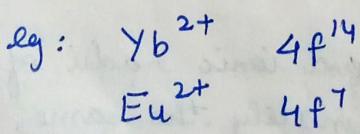
Actinoid contraction is greater than lanthanoid contraction. This is because the screening effect of $5f$ is poorer than $4f$ e^- s.

- Oxidation states :

Lanthanoids and actinoids show variable OS due to low energy difference between $(n-2)f$, $(n-1)d$ and $n s$ electrons.

(i) Lanthanoids :

- Due to low energy difference between $4f$, $5d$ and $6s$ e^- s, they show ~~variable~~ OS.
- The common OS is +3. However, certain elements exhibit +2 and +4 OS. also due to relative stability of the electronic conf.



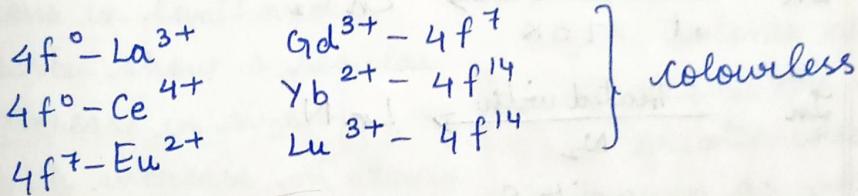
Actinoids:

Actinoids show a general OS of +3.

Other OS are +4 in Th, +5 in Pa, +6 in U and +7 in Np.

Actinoids show a wider OS when compared to lanthanoids because the 5f, 6d and 7s orbitals are more diffused and have very low energy difference.

Colour: Lanthanoids form coloured ions due to the presence of unpaired e^- resulting in f-f transition for which the light is absorbed from the visible region. Ions having conf. $4f^0, 4f^7, 4f^{14}$ are colourless



Magnetic property:

Lanthanoids and actinoids show paramagnetic behaviour due to the presence of unpaired e^- s in f orbitals.

The lanthanoid ions other than f^0 (La^{3+} and Ce^{3+}) and f^{14} (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism rises to maximum in Neodymium. Lanthanoid complexes are used in MRI (Magnetic resonance imaging).

Chemical Reactivity :

The first few members of lanthanides are quite reactive and show chemical behaviour similar to that of La. The standard electrode potentials of Ln^{3+}/Ln couple indicate that all lanthanides are more reactive than Al.

- $\text{Ln} \xrightarrow{\text{burns in O}_2} \text{Ln}_2\text{O}_3$
- $\text{Ln} \xrightarrow{\text{halogens}} \text{LnX}_3$
- $\text{Ln} \xrightarrow{\text{H}_2\text{O}} \text{Ln(OH)}_3 + \text{H}_2 \uparrow$
- $\text{Ln} \xrightarrow{\text{Acids}} \text{H}_2 \uparrow$
- $\text{Ln} \xrightarrow[\text{at } 273\text{K}]{\text{with C}} \text{LnC}_2$
- $\text{Ln} \xrightarrow[\text{N}_2]{\text{Heated with}} \text{LnN}$
- $\text{Ln} \xrightarrow{\Delta \text{ with S}} \text{Ln}_2\text{S}_3$

Chemical reactivity of Actinides:

Actinides are highly reactive metals especially when finely divided. However the chemistry of Actinides is more complex than lanthanides because of their ability to show a wider range of os.

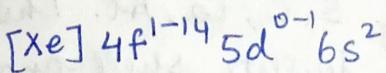
Moreover, many of these elements are radioactive which make their study difficult.

Comparison of Lanthanides and Actinides

LANTHANIDES

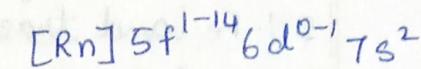
ACTINOIDES

a) Electronic configuration:



b) Oxidation state:

They show +3 O.S only except in few cases where it is +2 or +4. They never show +4 O.S



c) Atomic and Ionic size:

The ionic radii of M^{3+} ions in lanthanoid series show a regular decrease in size of ions with increase in atomic number. This decrease is known as lanthanoid contraction.

They show higher O.S such as +4, +5, +6, +7 also in addition to +3 O.S

There is a greater and gradual decrease in size of atoms or M^{3+} ions across the series. This greater decrease is known as actinoid contraction.

d) Chemical reactivity

These are less reactive metals and form oxides, nitrides, sulphides, hydroxides, halides, etc. These also form Hydrogen with acids. They show a lesser tendency for complex formation

These are highly reactive metals, especially in finely divided state, they form a mixture of oxides and hydride by action of boiling water. They combine with non-metals even at moderate temp. They show a greater tendency for complex formation.

Uses of Lanthanides :

(i) Misch Metal:

It is an alloy which consists of 95% Zn and 5% Fe and traces of S, C, Ca, Al. This alloy is used to produce bullets, shell and lighter flint.

(ii) Mixed oxides of lanthanides are used as catalysts in petroleum cracking.

(iii) Some individual lanthanoid oxides are used as catalysts phosphors in TV screens.
(Europium Eu is used to produce blue, red and white radiations)

Uses of Actinoids :

Most of them are radioactive like Uranium, Thorium etc and are used to generate nuclear power.