

d and *f*-Block Elements

[TOPIC 1] *d*-Block Elements and their Compounds

1.1 *d*-Block Element

When differentiating electron of an element enters in *d*-subshell, element is said to be a *d*-block element. The *d*-block elements lying in the middle of the periodic table belonging to groups 3-12 in which the *d*-orbitals are progressively filled in each of the four long periods are known as transition elements because their properties are intermediate between those of *s*- and *p*-block elements.

For an element to be a transition element, it should have incompletely filled *d*-orbital in its ground state or in its most common oxidation state.

Series of Transition Metals

There are mainly three series of the transition metals, i.e. 3*d*-series (Sc to Zn), 4*d*-series (Y to Cd) and 5*d*-series (La to Hg, omitting Ce to Lu).

General Configuration

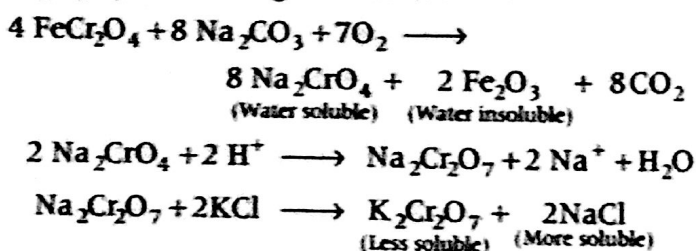
General electronic configuration of transition metals is $(n-1)d^{1-10}ns^{1-2}$. Some of the exceptions are observed in electronic configuration due to very little energy difference between $(n-1)d$ and ns orbital such as Cr: $3d^54s^1$; Cu: $3d^{10}4s^1$. However, zinc (Zn), cadmium (Cd), mercury (Hg) are represented by a general formula $(n-1)d^{10}ns^2$. These are not regarded as transition metals due to completely filled *d*-orbitals.

Properties of *d*-Block Elements

- (i) Nearly, all the transition elements exhibit metallic properties. They (except Zn, Cd and Hg) are very much hard and have low volatility. Their melting and boiling points are high due to strong metallic bonding. Greater the number of valence electrons, stronger is the resultant bonding. They have high enthalpy of atomisation.
- (ii) From Sc to Cr, atomic radii decreases because effective nuclear charge increases. The atomic sizes of Fe, Co and Ni are almost same because pairing of electrons in *d*-orbitals causes repulsion and hence, effective nuclear charge does not increase appreciably.
- (iii) Density of the transition metals from Sc to Cu increases due to high atomic mass and small atomic volume.
- (iv) Ionisation enthalpy increases with increase in nuclear charge along each series. However, the first ionisation energy of Cr is low because loss of one electron gives stable configuration and the value for Zn is higher because it represents an ionisation from the completely filled 4*s* level.
- (v) Transition metals show variable oxidation states due to the participation of (*n* - 1) *d* as well as *ns* electrons in bond formation. The maximum oxidation states are shown by Mn, i.e. from +2 to +7 (in first series). Sc shows only +3 oxidation state. High oxidation state is shown by their fluorides and oxides because fluorine and oxygen are strong oxidising agents.
- (vi) The electrode potentials of first row of transition elements generally show an increase with increasing atomic numbers. Electrode potential M^{2+}/M of a metal is dependent upon three parameters viz. enthalpy of atomisation, enthalpy of ionisation and enthalpy of hydration of M^{2+} .
- (vii) Cu^{2+} is more stable than Cu^+ due to lower reduction potential which is due to higher hydration energy. Cu^+ compounds are unstable in aqueous solution and undergo disproportionation.
- $$2\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + \text{Cu}$$
- (viii) Most of the transition metals are paramagnetic due to the presence of unpaired electrons (as paramagnetic character \propto number of unpaired electrons). The species having all paired electrons are diamagnetic in nature.
- (ix) The magnetic moment is determined by the formula, $\mu = \sqrt{n(n+2)}$ BM where, *n* is the number of unpaired electrons and BM is Bohr Magneton (unit of magnetic moment).
- (x) Most of the transition metals and their compounds are used as catalyst because they show variable oxidation states and have ability to form complexes, e.g. finely divided iron in Haber's process, V_2O_5 in contact process, etc.
- (xi) Transition elements form coloured ions due to the presence of unpaired electrons in *d*-orbitals as they can undergo *d-d* transition by absorbing colour from visible region and radiating complementary colour.
- (xii) Transition elements form complexes due to smaller size, higher charge on cations and presence of vacant *d*-orbitals, e.g. $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ etc.
- (xiii) Transition elements have lower value of reduction potential and there is irregular variation in reduction potential due to irregular variation in ionisation energy, hydration energy, etc.
- (xiv) Transition elements form interstitial compounds which are non-stoichiometric (e.g. Mn_4N , $\text{TiH}_{1.7}$, TiC, etc). They also form alloy due to similar size.
- Alloys are formed by the atoms with metallic radii differ for about 15 per cent from each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals.
- (xv) Transition metal oxides in lowest oxidation state are basic, in intermediate oxidation state are amphoteric and in highest oxidation state are acidic.
- (xvi) Transition metal halides in lower oxidation state are ionic and in higher oxidation state are covalent. Mostly fluorides are ionic and chlorides and bromides are covalent.

1.2 Potassium Dichromate

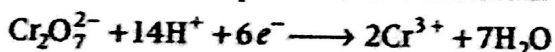
Potassium dichromate ($K_2Cr_2O_7$) is an acidic compound in which Cr is present in +6 oxidation state. Potassium dichromate is prepared from sodium chromate, which is obtained by fusion of chromite ore ($FeCr_2O_4$) with sodium carbonate in excess of air, which on acidification with sulphuric acid give orange sodium dichromate solution $Na_2Cr_2O_7$, this formed $Na_2Cr_2O_7$ then reacts with KCl to give potassium dichromate ($K_2Cr_2O_7$). It is orange coloured solid.



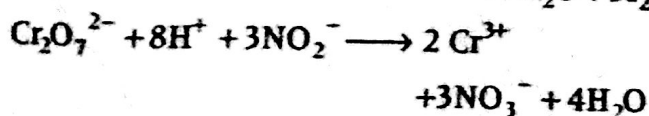
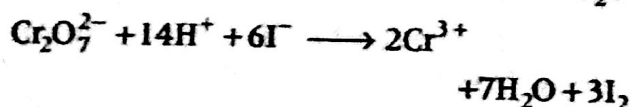
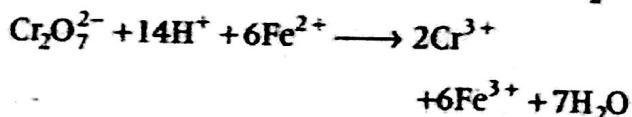
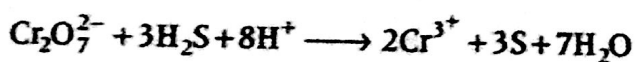
- (i) Its colour depends upon the pH of the solution. In acidic pH, it is orange (exists as dichromate ions) while in basic pH, it is yellow (exists as chromate ions). The oxidation state of chromium in chromate and dichromate is same.



- (ii) It is used as primary standard solution in volumetric analysis in acidic medium.

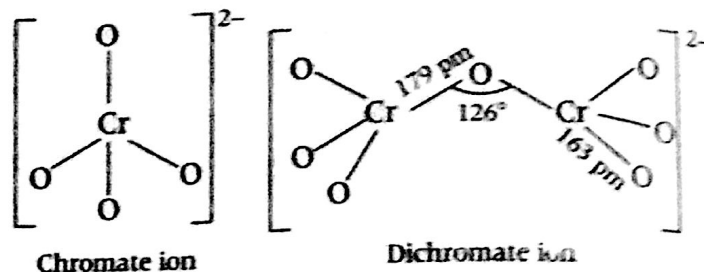


- (iii) It acts as a strong oxidising agent. Thus, acidified $K_2Cr_2O_7$ oxidises sulphides to sulphur, Fe(II) salts to Fe(III), iodides to iodine and nitrites to nitrates.



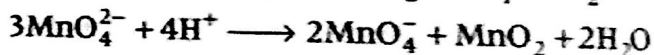
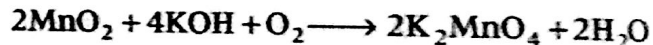
Structure of Chromate and Dichromate Ion

The structure of chromate ion is tetrahedral and dichromate ion consists of two tetrahedra sharing one corner with Cr—O—Cr bond angle of 126° .

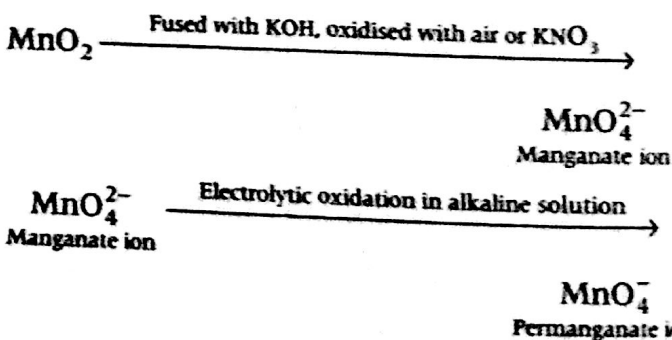


1.3 Potassium Permanganate

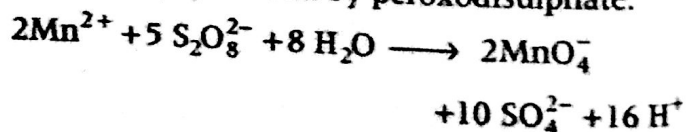
Potassium permanganate ($KMnO_4$) is also an acidic compound in which Mn is present in +7 oxidation state. Potassium permanganate is prepared by fusion of pyrolusite ore (MnO_2) with alkali metal hydroxide in the presence of O_2 . It is dark purple coloured crystalline solid.



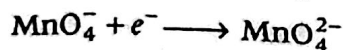
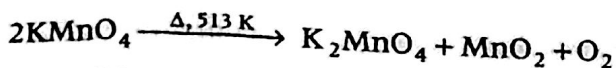
It is prepared by alkaline oxidative fusion of MnO_2 followed by electrolytic oxidation of manganate ion.



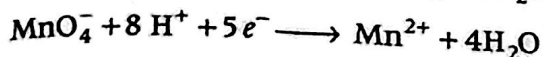
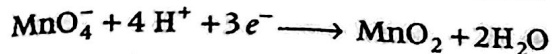
In laboratory it can be prepared by oxidation of manganese (II) ion salt by peroxodisulphate.



$KMnO_4$ decomposes to gives K_2MnO_4 and MnO_2 on heating and evolves O_2 .

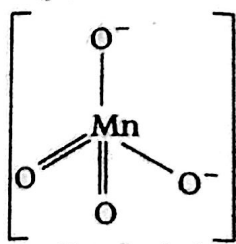


KMnO_4 acts as an oxidising agent in all the three mediums i.e. acidic, alkaline and neutral.

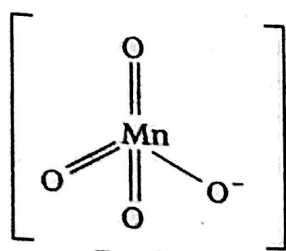


Structure of Manganate and Permanganate Ion

The manganate (MnO_4^{2-}) and permanganate (MnO_4^-) ions are tetrahedral.



Tetrahedral
manganate ion
(Paramagnetic)

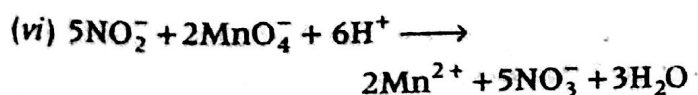
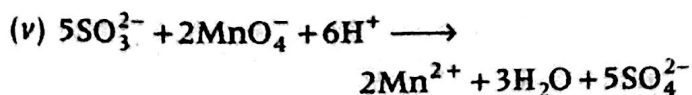
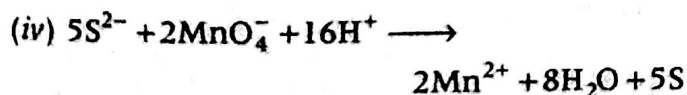
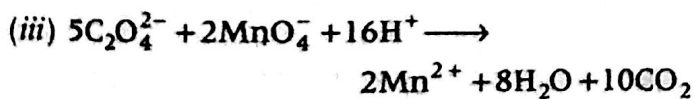
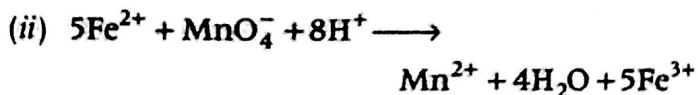
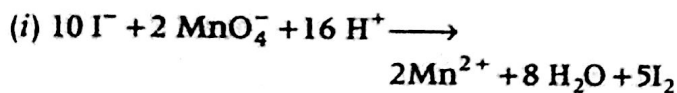


Tetrahedral
permanganate ion
(Diamagnetic)

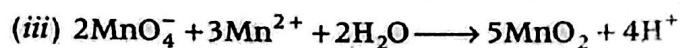
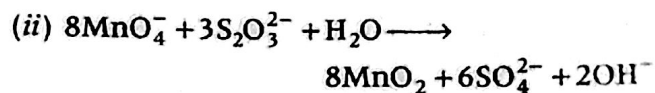
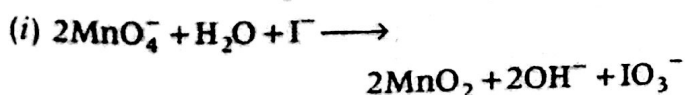
Reactions of KMnO_4

Important oxidising reactions of KMnO_4 are:

In acidic solutions



In neutral or faintly alkaline solutions



[TOPIC 2] *f*-Block Elements (Lanthanoids and Actinoids)

Elements in which differentiating electron enters in *f*-subshell are called *f*-block elements. There are two series, which constitute *f*-block. These are lanthanoids and actinoids.

2.1 Lanthanoids

1. The 14 elements after lanthanum are called **lanthanoids** in which 4 *f*-orbitals are progressively filled. General configuration of lanthanoids is $4f^{1-14}5d^{0-1}6s^2$.
2. Most common oxidation state of lanthanoid is +3. However, Ce shows +4, Eu and Yb show +2 oxidation state because they acquire stable configuration. Hence, Ce^{4+} act as an oxidising agent, Eu^{2+} , Yb^{2+} act as strong reducing agents.
3. There is steady decrease in the atomic and ionic radii of lanthanoids with increase in atomic number due to lanthanoid contraction. It is a unique feature in the chemistry of the lanthanoids. It is due to poor shielding effect of *f*-electrons.
4. The radii of members of 5*d*-series are similar to those of corresponding members of the 4*d*-series due to lanthanoid contraction, e.g. Zr and Hf have almost same radii and due to identical radii, they have similar physical and chemical properties. Also the basic character of decreases from $La(OH)_3$ to $Lu(OH)_3$ due to lanthanoid contraction.
5. Most of the lanthanoids are coloured and paramagnetic in nature due to the presence of unpaired electrons.
6. Lanthanoids show magnetic properties. La^{3+} , Lu^{3+} are diamagnetic in nature

whereas trivalent ions of other lanthanoids are paramagnetic.

7. Lanthanoids are highly electropositive and reactive metals.
8. They easily form alloys with other metals mainly iron. e.g. Mischmetal, an alloy of lanthanoids metal (~95%) with iron (~45%) and traces of S, C, Ca and Al, used to make lighter flints, bullets, shells etc.

2.2 Actinoids

1. The 14 elements after actinium are called actinoids in which 5 *f*-orbitals are progressively filled. General configuration of actinoids is $5f^{1-14}6d^{0-1}7s^2$.
2. In general, actinoids show +3 oxidation state. These resemble the lanthanoids in having more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse.
3. There is a greater range of oxidation states in actinoids. It is due to the fact that 5*f*, 6*d* and 7*s* levels are of comparable energies.
4. The steady decrease in atomic and ionic size along actinoid series is called **actinoid contraction** and it is due to poor shielding effect of 5*f*-electrons which results in increase in effective nuclear charge.
5. They show less tendency to form complexes but greater than lanthanoids.
6. They tarnish rapidly in air forming coating of oxide and thus, are not attacked by alkalis.
7. They are strongly paramagnetic, have low ionisation energies.