

Intext Question

8.8 Calculate the 'spin only' magnetic moment of $M^{2+}_{(aq)}$ ion ($Z = 27$).

8.3.10 Formation of Coloured Ions

When an electron from a lower energy d orbital is excited to a higher energy d orbital, the energy of excitation corresponds to the frequency of light absorbed (Unit 9). This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand. In aqueous solutions where water molecules are the ligands, the colours of the ions observed are listed in Table 8.8. A few coloured solutions of d -block elements are illustrated in Fig. 8.5.



Fig. 8.5: Colours of some of the first row transition metal ions in aqueous solutions. From left to right: V^{4+} , V^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} .

Table 8.8: Colours of Some of the First Row (aquated) Transition Metal Ions

Configuration	Example	Colour
$3d^0$	Sc^{3+}	colourless
$3d^0$	Ti^{4+}	colourless
$3d^1$	Ti^{3+}	purple
$3d^1$	V^{4+}	blue
$3d^2$	V^{3+}	green
$3d^3$	V^{2+}	violet
$3d^3$	Cr^{3+}	violet
$3d^4$	Mn^{3+}	violet
$3d^4$	Cr^{2+}	blue
$3d^5$	Mn^{2+}	pink
$3d^5$	Fe^{3+}	yellow
$3d^6$	Fe^{2+}	green
$3d^63d^7$	$Co^{3+}Co^{2+}$	bluepink
$3d^8$	Ni^{2+}	green
$3d^9$	Cu^{2+}	blue
$3d^{10}$	Zn^{2+}	colourless

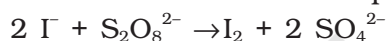
8.3.11 Formation of Complex Compounds

Complex compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species with characteristic properties. A few examples are: $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$. (The chemistry of complex compounds is

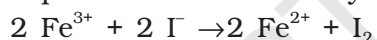
dealt with in detail in Unit 9). The transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of *d* orbitals for bond formation.

8.3.12 Catalytic Properties

The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in Catalytic Hydrogenation) are some of the examples. Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3*d* and 4*s* electrons for bonding). This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering). Also because the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulphate ions.



An explanation of this catalytic action can be given as:



8.3.13 Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn₄N, Fe₃H, VH_{0.56} and TiH_{1.7}, etc. The formulas quoted do not, of course, correspond to any normal oxidation state of the metal. Because of the nature of their composition, these compounds are referred to as *interstitial* compounds. The principal physical and chemical characteristics of these compounds are as follows:

- (i) They have high melting points, higher than those of pure metals.
- (ii) They are very hard, some borides approach diamond in hardness.
- (iii) They retain metallic conductivity.
- (iv) They are chemically inert.

8.3.14 Alloy Formation

An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.

Example 8.9 What is meant by 'disproportionation' of an oxidation state? Give an example.

Solution When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation. For example, manganese (VI) becomes unstable relative to manganese(VII) and manganese (IV) in acidic solution.



Intext Question

8.9 Explain why Cu^+ ion is not stable in aqueous solutions?

8.4 Some Important Compounds of Transition Elements

8.4.1 Oxides and Oxoanions of Metals

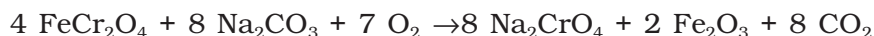
These oxides are generally formed by the reaction of metals with oxygen at high temperatures. All the metals except scandium form MO oxides which are ionic. The highest oxidation number in the oxides, coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7 . Beyond group 7, no higher oxides of iron above Fe_2O_3 are known. Besides the oxides, the oxocations stabilise V^{V} as VO_2^+ , V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+} .

As the oxidation number of a metal increases, ionic character decreases. In the case of Mn, Mn_2O_7 is a covalent green oil. Even CrO_3 and V_2O_5 have low melting points. In these higher oxides, the acidic character is predominant.

Thus, Mn_2O_7 gives HMnO_4 and CrO_3 gives H_2CrO_4 and $\text{H}_2\text{Cr}_2\text{O}_7$. V_2O_5 is, however, amphoteric though mainly acidic and it gives VO_4^{3-} as well as VO_2^+ salts. In vanadium there is gradual change from the basic V_2O_3 to less basic V_2O_4 and to amphoteric V_2O_5 . V_2O_4 dissolves in acids to give VO^{2+} salts. Similarly, V_2O_5 reacts with alkalis as well as acids to give VO_4^{3-} and VO_4^+ respectively. The well characterised CrO is basic but Cr_2O_3 is amphoteric.

Potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$

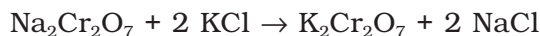
Potassium dichromate is a very important chemical used in leather industry and as an oxidant for preparation of many azo compounds. Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore (FeCr_2O_4) with sodium or potassium carbonate in free access of air. The reaction with sodium carbonate occurs as follows:



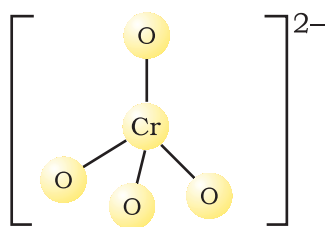
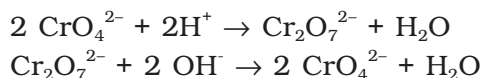
The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ can be crystallised.



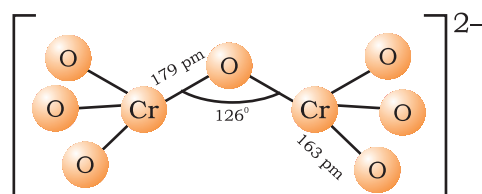
Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.



Orange crystals of potassium dichromate crystallise out. The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.



Chromate ion



Dichromate ion

The structures of chromate ion, CrO_4^{2-} and the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$ are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126° .

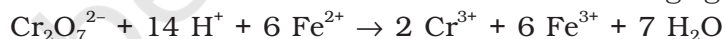
Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:



Thus, acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:

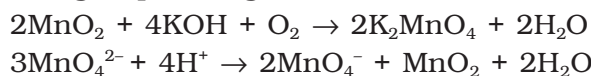


The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,

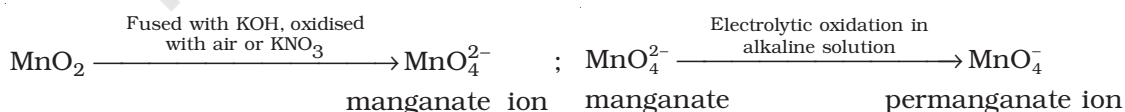


Potassium permanganate KMnO_4

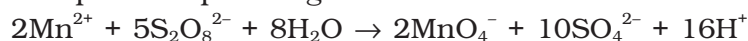
Potassium permanganate is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3 . This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.



Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (VI).



In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.



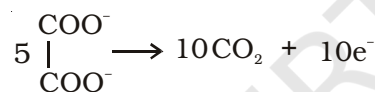
Potassium permanganate forms dark purple (almost black) crystals which are isostructural with those of KClO_4 . The salt is not very soluble in water (6.4 g/100 g of water at 293 K), but when heated it decomposes at 513 K.



It has two physical properties of considerable interest: its intense colour and its diamagnetism along with temperature-dependent weak paramagnetism. These can be explained by the use of molecular orbital theory which is beyond the present scope.

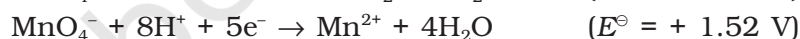
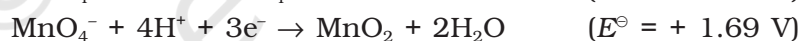
The manganate and permanganate ions are tetrahedral; the π -bonding takes place by overlap of p orbitals of oxygen with d orbitals of manganese. The green manganate is paramagnetic because of one unpaired electron but the permanganate is diamagnetic due to the absence of unpaired electron.

Acidified permanganate solution oxidises oxalates to carbon dioxide, iron(II) to iron(III), nitrites to nitrates and iodides to free iodine. The half-reactions of reductants are:



The full reaction can be written by adding the half-reaction for KMnO_4 to the half-reaction of the reducing agent, balancing wherever necessary.

If we represent the reduction of permanganate to manganate, manganese dioxide and manganese(II) salt by half-reactions,

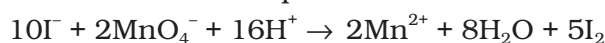


We can very well see that the hydrogen ion concentration of the solution plays an important part in influencing the reaction. Although many reactions can be understood by consideration of redox potential, kinetics of the reaction is also an important factor. Permanganate at $[\text{H}^+] = 1$ should oxidise water but in practice the reaction is extremely slow unless either manganese(II) ions are present or the temperature is raised.

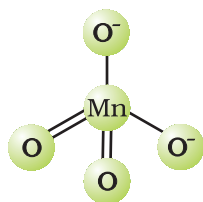
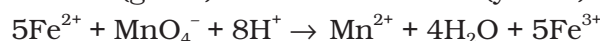
A few important oxidising reactions of KMnO_4 are given below:

1. In acid solutions:

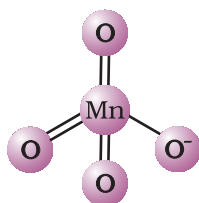
(a) Iodine is liberated from potassium iodide :



(b) Fe^{2+} ion (green) is converted to Fe^{3+} (yellow):



Tetrahedral manganate ion (green)



Tetrahedral permanganate ion (purple)

- (c) Oxalate ion or oxalic acid is oxidised at 333 K:

$$5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$$
- (d) Hydrogen sulphide is oxidised, sulphur being precipitated:

$$\text{H}_2\text{S} \longrightarrow 2\text{H}^+ + \text{S}^{2-}$$

$$5\text{S}^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{S}$$
- (e) Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:

$$5\text{SO}_3^{2-} + 2\text{MnO}_4^- + 6\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{SO}_4^{2-}$$
- (f) Nitrite is oxidised to nitrate:

$$5\text{NO}_2^- + 2\text{MnO}_4^- + 6\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 5\text{NO}_3^- + 3\text{H}_2\text{O}$$

2. In neutral or faintly alkaline solutions:

- (a) A notable reaction is the oxidation of iodide to iodate:

$$2\text{MnO}_4^- + \text{H}_2\text{O} + \text{I}^- \longrightarrow 2\text{MnO}_2 + 2\text{OH}^- + \text{IO}_3^-$$
- (b) Thiosulphate is oxidised almost quantitatively to sulphate:

$$8\text{MnO}_4^- + 3\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \longrightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + 2\text{OH}^-$$
- (c) Manganous salt is oxidised to MnO_2 ; the presence of zinc sulphate or zinc oxide catalyses the oxidation:

$$2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \longrightarrow 5\text{MnO}_2 + 4\text{H}^+$$

Note: Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

Uses: Besides its use in analytical chemistry, potassium permanganate is used as a favourite oxidant in preparative organic chemistry. Its uses for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.

THE INNER TRANSITION ELEMENTS (*f*-BLOCK)

The *f*-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium). Because lanthanum closely resembles the lanthanoids, it is usually included in any discussion of the lanthanoids for which the general symbol Ln is often used. Similarly, a discussion of the actinoids includes actinium besides the fourteen elements constituting the series. The lanthanoids resemble one another more closely than do the members of ordinary transition elements in any series. They have only one stable oxidation state and their chemistry provides an excellent opportunity to examine the effect of small changes in size and nuclear charge along a series of otherwise similar elements. The chemistry of the actinoids is, on the other hand, much more complicated. The complication arises partly owing to the occurrence of a wide range of oxidation states in these elements and partly because their radioactivity creates special problems in their study; the two series will be considered separately here.

8.5 The Lanthanoids

The names, symbols, electronic configurations of atomic and some ionic states and atomic and ionic radii of lanthanum and lanthanoids (for which the general symbol Ln is used) are given in Table 8.9.