

# D & F BLOCK ELEMENTS

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# Transition elements

A transition element may be defined as an element whose atom in the ground state or ion in common oxidation state has ***incomplete sub-shell, has electron 1 to 9***. It is called transition element due to fact that it is lying between most electropositive (*s*-block) and most electronegative (*p*-block) elements and represent a transition from them. The ***general electronic configuration*** of these element is  $(n-1)^{1\text{ to }10} ns^{0\text{ to }2}$ .

Four series of elements are formed by filling the 3d, 4d, 5d and 6d subshells of electrons. Collectively these comprise the d-block elements. They are often called as 'transition elements' because their position in periodic table is between the s-block and p-block elements. Their properties are transitional between the highly reactive metallic elements of s-block (which form ionic compounds) and the elements of p-block (which are largely covalent). Typically the transition elements have an incompletely filled d level.

# Transition series

I<sup>st</sup> transition series or 3d series corresponding to filling of 3d sub-shell consists of the following 10 elements of 4<sup>th</sup> period.

$_{21}\text{Sc}$ , Ti, V, Cr, Mn, Fe, Co, Ni, Cu and  $_{30}\text{Zn}$ .

II<sup>nd</sup> transition series or 4d series corresponding to filling of 4d sub-shell consists of the following 10 elements of 5<sup>th</sup> period.

$_{39}\text{Y}$ , Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag and  $_{48}\text{Cd}$ .

III<sup>rd</sup> transition series or 5d series corresponding to filling of 5d sub-shell consists of following 10 elements of 6<sup>th</sup> period.

$_{57}\text{La}$ ,  $_{72}\text{Hf}$ , Ta, W, Re, Os, Ir, Pt, Au and  $_{80}\text{Hg}$ .

IV<sup>th</sup> transition series or 6d series corresponding to the filling of 6d sub-shell starts with  $_{89}\text{Ac}$  followed by elements with atomic number 104 onwards.

# Element and their configuration of 3d series

Element	Symbol	At. No.	Electronic configuration
Scandium	<i>Sc</i>	21	$[Ar] 3d4s$
Titanium	<i>Ti</i>	22	$[Ar] 3d4s$
Vanadium	<i>V</i>	23	$[Ar] 3d4s$
Chromium	<i>Cr</i>	24	$[Ar] 3d4s$
Manganese	<i>Mn</i>	25	$[Ar] 3d4s$
Iron	<i>Fe</i>	26	$[Ar] 3d4s$
Cobalt	<i>Co</i>	27	$[Ar] 3d4s$
Nickel	<i>Ni</i>	28	$[Ar] 3d4s$
Copper	<i>Cu</i>	29	$[Ar] 3d4s$
Zinc	<i>Zn</i>	30	$[Ar] 3d4s$

# Element and their configuration of 4d series

Element	Symbol	At. No.	Electronic configuration
Yttrium	<i>Y</i>	39	$[Kr] 4d^1 5s^2$
Zirconium	<i>Zr</i>	40	$[Kr] 4d^2 5s^2$
Niobium	<i>Nb</i>	41	$[Kr] 4d^4 5s^1$
Molybdenum	<i>Mo</i>	42	$[Kr] 4d^5 5s^1$
Technetium	<i>Tc</i>	43	$[Kr] 4d^5 5s^2$
Ruthenium	<i>Ru</i>	44	$[Kr] 4d^7 5s^1$
Rhodium	<i>Rh</i>	45	$[Kr] 4d^8 5s^1$
Palladium	<i>Pd</i>	46	$[Kr] 4d^{10}$
Silver	<i>Ag</i>	47	$[Kr] 4d^9 5s^1$
Cadmium	<i>Cd</i>	48	$[Kr] 4d^{10} 5s^2$

4d-orbitals are filled up

# Element and their configuration of 5d series

Element	Symbol	At. No.	Electronic configuration
Lanthanum	<i>La</i>	57	$[Xe] 5d6s$
Hafnium	<i>Hf</i>	72	$[Xe] 4f5d6s$
Tantalum	<i>Ta</i>	73	$[Xe] 4f5d6s$
Tungsten	<i>W</i>	74	$[Xe] 4f5d6s$
Rhenium	<i>Re</i>	75	$[Xe] 4f5d6s$
Osmium	<i>Os</i>	76	$[Xe] 4f5d6s$
Iridium	<i>Ir</i>	77	$[Xe] 4f5d6s$
Platinum	<i>Pt</i>	78	$[Xe] 4f5d6s$
Gold	<i>Au</i>	79	$[Xe] 4f5d6s$
Mercury	<i>Hg</i>	80	$[Xe] 4f5d6s$

5d-orbitals are filled up

# Element and their configuration of 6d series

Element	Symbol	At. No.	Electronic configuration
Actinium	<i>Ac</i>	89	$[Rn] 6d7s$
Rutherfordium	<i>Rf</i>	104	$[Rn] 5f6d7s$
Hahnium	<i>Ha</i>	105	$[Rn] 5f6d7s$
Seaborgium	<i>Sg</i>	106	$[Rn] 5f6d7s$
Bohrium	<i>Bh</i>	107	$[Rn] 5f6d7s$
Hassium	<i>Hs</i>	108	$[Rn] 5f6d7s$
Meitnerium	<i>Mt</i>	109	$[Rn] 5f6d7s$
Ununnilium	<i>Uun</i>	110	$[Rn] 5f6d7s$
Unununium	<i>Uuu</i>	111	$[Rn] 5f6d7s$
Unubium	<i>Uub</i>	112	$[Rn] 5f6d7s$

6d-orbitals are filled up ↓

# Physico Chemical properties of d block

## Atomic Radius

The atomic radii of the transition metals lie in-between those of s- and p-block elements. The covalent radii of the elements decreases from left to right across a row in the transition series, until near the end when the size increases slightly. The decrease in size is small after mid way. In the beginning, the atomic radius decreases with the increase in nuclear charge (as atomic number increases), where as the shielding effect of d-electrons is small. After mid way as the electrons enters the last but one shell, the added d-electron shields the outer most electrons. Hence with the increase in the d-electrons screening effect increases. This counter balances the increased nuclear charge. As a result, the atomic radii remain practically same after chromium.

Near the end of the series, the increased electron repulsions between the added electrons in the same orbitals are greater than the attractive forces. This results in the expansion of the electron cloud and thus atomic radius increases.

The atomic radii, in general, increase down the group. The atomic radii of second series are larger than those of first transition series. In the atoms of the second transition series, the number of shells are more than those of the 1st transition series. As a result, the atoms of 2nd transition series are larger than those of the elements of the first transition series. But the atomic radii of the second and third transition series are almost the same.



# Continue..

- Lanthanoid Contraction

This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called **Lanthanoid contraction** which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d-series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship.

## Melting and boiling points

The melting and boiling points of the transition series elements are generally very high. The melting points of the transition elements rise to a maximum and then fall as the atomic number increases. Manganese and technetium have abnormally low melting points. Strong metallic bonds between the atoms of these elements attribute to their high melting and boiling points. In a particular series, the metallic strength increases upto the middle with increasing number of unpaired electrons i.e up to  $d^5$ . After chromium, the number of unpaired electrons goes on decreasing. Accordingly, the melting points decrease after middle (Cr) because of increasing pairing of electrons.

# Continue..

★ The dip in melting points of Mn and Tc can be attributed to their stable electronic configurations (half filled  $3d^5$  and fully filled  $4s^2$ ). Due to this stable electronic configuration, the delocalisation of electrons may be less and thus the metallic bond is much weaker than preceding elements.

- Density

The atomic volumes of the transition elements are low compared with the elements of group 1 and 2. This is because the increased nuclear charge is poorly screened and so attracts all the electrons more strongly. In addition, the extra electrons added occupy inner orbitals. Consequently the densities of the transition metals are high. The densities of the second row are high and third row values are even higher. Elements with the highest densities are osmium  $22.57 \text{ g cm}^{-3}$  and irridium  $22.61 \text{ g cm}^{-3}$ .

★ Across a period from left to right atomic volumes decrease and atomic masses increase. Hence the densities also increase across a period.

★ The last element zinc is an exception, having large atomic volume and hence lower density.

# Ionisation Energy

The first ionisation energies of d-block elements are intermediate between those of the s- and p-blocks. This suggests that the transition elements are less electropositive than groups 1 and 2 and may form either ionic or covalent bonds depending on the conditions. Generally, the lower valent states are ionic and the higher valent states are covalent. Across a period from left to right ionisation energies gradually increase with increase in atomic number. This is because the nuclear charge increases and the atomic size decreases with increase in atomic number along the period. Consequently making the removal of outer electron difficult.

In a given series, the difference in the ionisation energies between any two successive d-block elements is very much less than the difference in case of successive s-block or p-block elements. The effect of increased nuclear charge and screening effect of the added d-electrons tend to oppose each other. Hence due to these two counter effects, the difference in the ionisation energies of two successive transition elements is very small on moving across a period.

The first ionisation energy of Zn, Cd, and Hg are very high because of their fully filled  $(n-1) d^{10} ns^2$  configuration.

# Continue..

II<sup>nd</sup> and III<sup>rd</sup> ionisation energies also increase along a period.

II<sup>nd</sup> ionisation energy of Cr > Mn and Cu > Zn

This is because after the removal of I<sup>st</sup> electron Cr and Cu acquire stable configurations (d<sup>5</sup> & d<sup>10</sup>) and the removal of II<sup>nd</sup> electron thus become very difficult.

Similarly the IE<sub>2</sub> of  ${}_{23}\text{V} < {}_{24}\text{Cr} > {}_{25}\text{Mn}$  and  ${}_{28}\text{Ni} < {}_{29}\text{Cu} > {}_{30}\text{Zn}$

The third ionization energy of Mn is very high because the third electron has to be removed from the stable half-filled 3d orbital.

# Oxidation state

The transition metals exhibit a large number of oxidation states. With the exception of a few elements, most of these show variable oxidation states. These different oxidation states are related to the electronic configuration of their atoms.

The existence of the transition elements in different oxidation states means that their atoms can lose different number of electrons. This is due to the participation of inner  $(n - 1)$  d-electrons in addition to outer ns-electrons because, the energies of the ns and  $(n - 1)$  d-sub-shells are nearly same. For example, scandium has the outer electronic configuration  $3d^1 4s^2$ . It exhibits an oxidation state of +2 when it uses both of its 4s-electrons for bonding but it can also show oxidation state of +3 when it uses its two s-electrons and one d-electron. Similarly, the other atoms can show oxidation states equal to ns-and  $(n - 1)$  d-electrons.

# Oxidation state of 3d elements

Element	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+3
Ti	$3d^2 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+2, +3, (+4), (+5), +6
Mn	$3d^5 4s^2$	+2, +3, +4, (+5), +6, +7
Fe	$3d^6 4s^2$	+2, +3, (+4), (+5), (+6)
Co	$3d^7 4s^2$	+2, +3, (+4)
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

# Oxidation state of 4d elements

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3	(+3)	(+2)	+2	+2	+2	+2	+2	+1	+2
	+4	(+3)	+3	(+4)	+3	+3	(+3)	(+2)	
		(+4)	+4	(+5)	+4	+4	+4	(+3)	
		+5	+5		(+5)	(+6)			
			+6		(+6)				
					(+7)				
					(+8)				

Oxidation states given in parenthesis are unstable.

# Oxidation state of 5d elements

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+3	(+3)	(+2)	+2	(-1)	+2	+2	+2	+1	+1
	+4	(+3)	(+3)	(+1)	+3	+3	(+3)	+3	+2
		(+4)	+4	(+2)	+4	+4	+4		
		+5	+5	+3	+6	(+6)	(+5)		
			+6	+4	+8		(+6)		
				+5					
				(+6)					
				+7					

It may be noted that the stability of a given oxidation state depends upon the nature of the elements with which the metal is combined. The highest oxidation states are found in compounds of fluorides and oxides because fluorine and oxygen are most electronegative elements.



# Important Points

The variable oxidation states of transition metals are due to participation of inner  $(n - 1)d$  and outer  $ns$ -electrons. The lowest oxidation state corresponds to the number of  $ns$ -electrons. For example, in the first transition series, the lowest oxidation states of Cr ( $3d^5 4s^1$ ) and Cu ( $3d^{10} 4s^1$ ) are +1 while for others, it is +2 ( $3d^{1-10} 4s^2$ ).

Except scandium, the most common oxidation state of the first row transition elements is +2 which arises due to loss of two  $4s$ -electrons. This means that after scandium  $3d$ -orbitals become more stable and, therefore, are lower in energy than the  $4s$ -orbitals. As a result, electrons are first removed from  $4s$ -orbitals.

The elements which show the greater number of oxidation states occur in or near the middle of the series. For example, in the first transition series, manganese exhibits all the oxidation states from +2 to +7. The lesser number of oxidation states in the beginning of series can be due to the presence of smaller number of electrons to lose or share (Sc, Ti). On the other hand, at the extreme right hand side end (Cu, Zn), lesser number of oxidation state is due to large number of  $d$  electrons so that only a few orbitals are available in which the electron can share with other for higher valence. The highest oxidation state shown by any transition metal is +8.

In the +2 and +3 oxidation states, the bonds formed are mostly ionic. In the compounds of higher oxidation states (generally formed with oxygen and fluorine), the bonds are essentially covalent. Thus, the bonds in +2 and +3 oxidation states are generally formed by the loss of two or three electrons respectively while the bonds in higher oxidation states are formed by sharing of  $d$ -electrons. For example, in  $MnO_4^-$  (Mn in +7 state) all the bonds are covalent.

# Continue..

Within a group, the maximum oxidation state increase with atomic number. For example, iron (group 8) shows common oxidation states of +2 and +3 but ruthenium and osmium in the same group form compounds in the +4, +6 and +8 oxidation states.

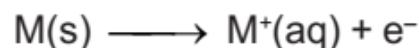
Transition metals also form compounds in low oxidation states such as +1 and 0 or negative. The common examples are  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Fe}(\text{CO})_5]$  in which nickel and iron are in zero oxidation state.

The variability of oxidation states in transition elements arises because of incomplete filling of the d-orbitals in such a way that their oxidation states differ by unity such as  $\text{V}^{\text{II}}$ ,  $\text{V}^{\text{III}}$ ,  $\text{V}^{\text{IV}}$  and  $\text{V}^{\text{V}}$ . This behaviour is in contrast with the variability of oxidation states of non-transition elements (p-block elements), where oxidation states normally differ by a unit of two such as  $\text{Sn}^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{In}^+$ ,  $\text{In}^{3+}$ , etc.

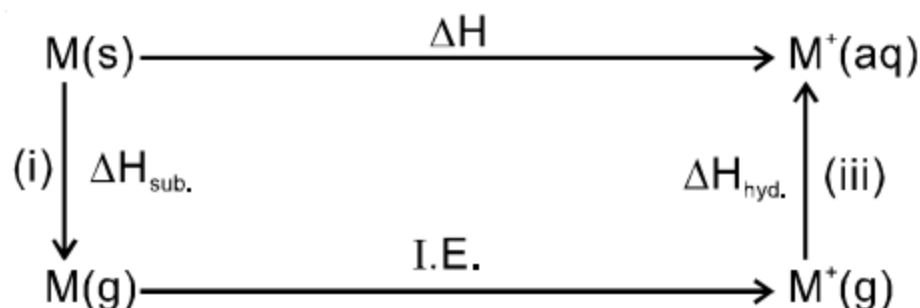
Unlike p-block elements where the lower oxidation states are favoured by heavier members (due to inert pair effect), the higher oxidation states are more stable in heavier transition elements. For example, in group 6, Mo (VI) and W (VI) are found to be more stable than Cr (VI). Therefore, Cr (VI) in the form of dichromate in acidic medium is a strong oxidising agent whereas  $\text{MoO}_3$  and  $\text{WO}_3$  are not.

# Electrode Potential

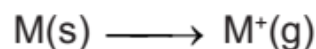
In addition to ionisation enthalpy, the other factors such as enthalpy of sublimation, hydration enthalpy, ionisation enthalpy etc. determine the stability of a particular oxidation state in solution. This can be explained in terms of their electrode potential values. The oxidation potential of a metal involves the following process:



This process actually takes place in the following three steps as given in following flowchart :



In the first step, the atoms get isolated from one another and become independent in the gaseous state. This converts solid metal to the gaseous state. The energy needed for this step is known as enthalpy of sublimation.



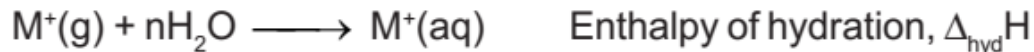
Enthalpy of sublimation,  $\Delta_{\text{sub}} H^\ominus$

# Continue..

In the second step, the outer electron is removed from the isolated atom. The energy required for this change is ionisation enthalpy.



In the third step the gaseous ion gets hydrated. In this process, energy known as hydration enthalpy, is liberated.



The oxidation potential which gives the tendency of the overall change to occur, depends upon the net effect of these three steps. The overall energy change is

$$\Delta\text{H} = \Delta_{\text{sub}}\text{H}^{\ominus} + \text{IE} + \Delta_{\text{hyd}}\text{H}$$

# Metal Halide

**In metal halides.** The transition elements react with halogens at high temperatures to form transition metal halides. These reactions have very high heat of reaction. But once the reaction starts, the heat of reaction is sufficient to continue the reaction. The halogens react in the following decreasing order ;  $F_2 > Cl_2 > Br_2 > I_2$ . In general, the elements of first transition series tend to exist in low oxidation states. Chromium to zinc form stable difluorides and the other chlorides are also known.

Since fluorine is the most electronegative element, the transition metals show highest oxidation states with fluorine. The highest oxidation states are found in  $TiX_4$  (tetrahalides,  $X = F, Cl, Br$  and  $I$ ),  $VF_5$  and  $CrF_6$ .

The +7 oxidation state for Mn is not shown by simple halides. However,  $MnO_3F$  is known in which the oxidation state of Mn is +7.

After Mn, the tendency to show higher oxidation states with halogens are uncommon. Iron and cobalt form trihalides  $FeX_3$  ( $X = F, Cl$  or  $Br$ ) and  $CoF_3$ .

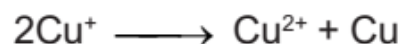
The tendency of fluorine to stabilise the highest oxidation state is due to either higher lattice enthalpy as in case of  $CoF_3$  or higher bond enthalpy due to higher covalent bonds e.g.,  $VF_5$  and  $CrF_6$ .

V(V) is shown by  $VF_5$  only. However, the other halides undergo hydrolysis to form oxohalides,  $VOX_3$ .

Fluorides are relatively unstable in their low oxidation states. For example, vanadium form only  $VX_2$  ( $X = Cl, Br$  or  $I$ ) and copper can form  $CuX$  ( $X = Cl, I$ ). All copper (II) halides are known except the iodide. This is because,  $Cu^{2+}$  oxidises  $I^-$  to  $I_2$ .



It has been observed that many copper (I) compounds are unstable in aqueous solution and they undergo disproportionation to Cu(II) and Cu(0) as :





# Metal Oxide and Oxocation

The ability of oxygen to stabilize the highest oxidation state is demonstrated in their oxides. The highest oxidation states in their oxides coincide with the group number. For example, the highest oxidation state of scandium of group 3 is +3 in its oxides,  $\text{Sc}_2\text{O}_3$  whereas the highest oxidation state of manganese of group 7 is +7, in  $\text{Mn}_2\text{O}_7$ . However beyond group 7, no higher oxides of iron above  $\text{Fe}_2\text{O}_3$  are known. Although higher oxidation state such as +6 is shown in ferrates such as  $\text{FeO}_4^{2-}$  in alkaline medium, but they readily decompose to  $\text{Fe}_2\text{O}_3$  and  $\text{O}_2$ . Besides the oxides, oxocation of the metals also stabilise higher oxidation states. For example,  $\text{V}^{\text{V}}$  as  $\text{VO}_2^+$ ,  $\text{V}^{\text{IV}}$  as  $\text{VO}^{2+}$  and  $\text{Ti}^{\text{IV}}$  as  $\text{TiO}^{2+}$ . It may be noted that the ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. For example, manganese forms highest fluoride as  $\text{MnF}_4$  whereas the highest oxide is  $\text{Mn}_2\text{O}_7$ . This is due to the fact that oxygen has great ability to form multiple bonds to metals. In the covalent oxide,  $\text{Mn}_2\text{O}_7$ , each Mn is tetrahedrally surrounded by oxygen atoms and has Mn–O–Mn bridge. The tetrahedral  $[\text{MO}_4]^{n-}$  ions are also known for vanadium (V), chromium (VI), manganese (VI) and manganese (VII).

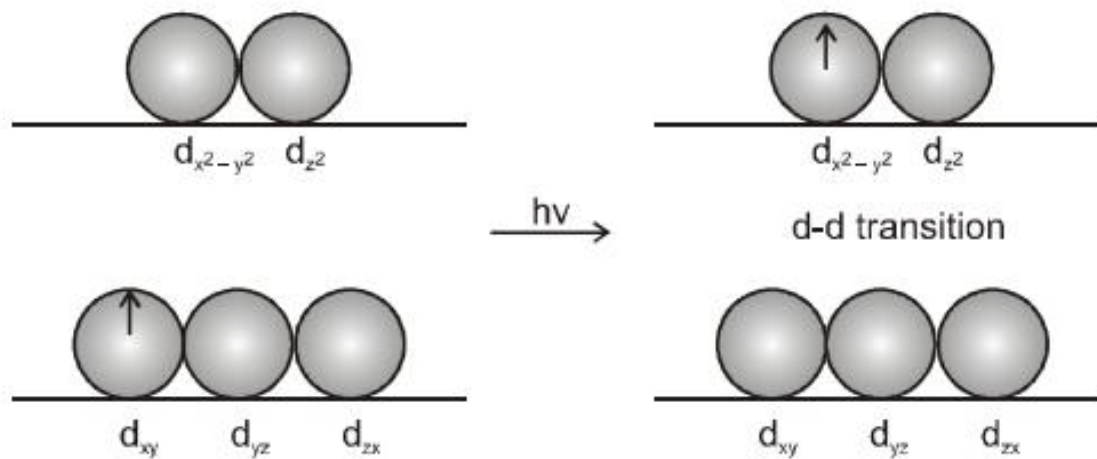
The transition elements in the +2 and +3 oxidation states mostly form ionic bonds whereas with higher oxidation states, the bonds are essentially covalent e.g., in  $\text{MnO}_4^-$  all bonds are covalent. As the oxidation number of a metal increases, the ionic character of their oxides decrease. For example, in case of Mn,  $\text{Mn}_2\text{O}_7$  is a covalent green oil. In these higher oxides the acidic character is predominant. Thus  $\text{CrO}_3$  gives  $\text{H}_2\text{CrO}_4$  and  $\text{H}_2\text{Cr}_2\text{O}_7$  and  $\text{Mn}_2\text{O}_7$  gives  $\text{HMnO}_4$ .  $\text{V}_2\text{O}_5$  is, however amphoteric though mainly acidic and with alkalis as well as acids gives  $\text{VO}_4^{3-}$  and  $\text{VO}_2^+$  respectively.

# Formation of coloured Ions

Most of the compounds of transition metals are coloured in the solid form or solution form. The colour of the compounds of transition metals may be attributed to the presence of incomplete  $(n - 1)$  d-sub-shell. In the case of compounds of transition metals, the energies of the five d-orbitals in the same sub-shell do not remain equal. Under the influence of approaching ions towards the central metal ion, the d-orbitals of the central metal split into different energy levels. This phenomenon is called **crystal field splitting**. For example, when the six ions or molecules approach the metal ion (called octahedral field), the five d-orbitals split up into two sets : one set consisting of two d-orbitals ( $d_{x^2-y^2}$ ,  $d_{z^2}$ ) of higher energies and the other set consisting of three d-orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ) of lower energies.

In the case of the transition metal ions, the electron can be easily promoted from one energy level to another in the same d-sub-shell. These are called **d-d transitions**. The amount of energy required to excite some of the electrons to higher energy states within the same d-sub-shell corresponds to energy of certain colours of visible light. Therefore, when white light falls on a transition metal compound, some of its energy corresponding to a certain colour, is absorbed and the electron gets raised from lower energy set of orbitals to higher energy set of orbitals as shown below :

# Continue..





# Colour of Metal ions

Ion	Outer Configuration	Colour of the ion
Sc (III), Ti (IV)	$3d^0$	Colourless
Ti (III)	$3d^1$	Purple
V (IV)	$3d^1$	Blue
V (III)	$3d^2$	Green
Cr (III)	$3d^3$	Green
Mn (III)	$3d^4$	Violet
Cr (II)	$3d^4$	Blue
Mn (II)	$3d^5$	Pink
Fe (III)	$3d^5$	Yellow
Fe (II)	$3d^6$	Green
Co (III)	$3d^6$	Blue
Co (II)	$3d^7$	Pink
Ni (II)	$3d^8$	Green
Cu (II)	$3d^9$	Blue
Cu (I)	$3d^{10}$	Colourless
Zn (II)	$3d^{10}$	Colourless

# Magnetic Behaviour

It is interesting to note that when the various substances are placed in a magnetic field, they do not behave in a similar way i.e., they show different behaviour which are known as magnetic behaviour.

These are classified as :

**Paramagnetic substances.** The substances which are attracted by magnetic field are called paramagnetic substances and this character arises due to the presence of unpaired electrons in the atomic orbitals.

**Diamagnetic substances.** The substances which are repelled by magnetic field are called diamagnetic substances and this character arises due to the presence of paired electrons in the atomic orbitals.

Most of the compounds of transition elements are paramagnetic in nature and are attracted by the magnetic field. The transition elements involve the partial filling of d-sub-shells. Most of the transition metal ions or their compounds have unpaired electrons in d-sub-shell (from configuration  $d^1$  to  $d^9$ ) and therefore, they give rise to paramagnetic character. The magnetic character is expressed in terms of magnetic moment. The larger the number of unpaired electrons in a substance, the greater is the paramagnetic character and larger is the magnetic moment. The magnetic moment is expressed in Bohr magnetons abbreviated as B.M.

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

where  $n$  is the number of unpaired electrons and  $\mu$  is magnetic moment in Bohr magneton (BM) units.

In addition to paramagnetic and diamagnetic substances, there are a **few** substances such as iron metal, iron oxide which are highly magnetic (about 1000 times more than ordinary metals). These are very strongly attracted by applied magnetic field and retained their magnetism when removed from the field are called **ferromagnetic substances**.

# Question

Determine the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

The metal having atomic number 25 has electron configuration  $[\text{Ar}]^{18} 3d^5 4s^2$ . So its divalent ion in aqueous solution will have electron configuration  $[\text{Ar}]^{18} 3d^5 4s^0$ . Thus it has five unpaired electrons.

So  $\mu_{(\text{spin})} = \sqrt{5(5+2)} = 5.92 \text{ BM}$ .

# Formation of complex compound

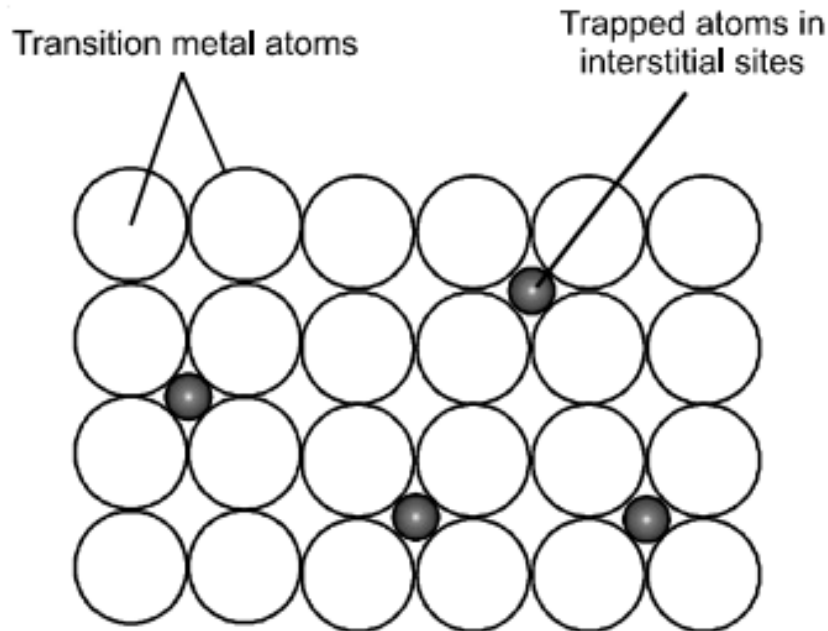
The great tendency of transition metal ions to form complexes is due to :

(i) small size of the atoms and ions, (ii) high nuclear charge and (iii) availability of vacant d-orbitals of suitable energy to accept lone pairs of electrons donated by ligands.

In contrast to representative elements, the transition elements form a large number of coordination complexes. The transition metal ions bind to a number of anions or neutral molecules in these complexes. The common examples are  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , etc.

# Formation of Interstitial compound

Transition metals form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N, etc.) get trapped in vacant spaces of the lattices of the transition metal atoms as shown below.



They are generally non-stoichiometric and are neither typically ionic nor covalent. The common examples of interstitial compounds of transition metals are  $\text{TiC}$ ,  $\text{Mn}_4\text{N}$ ,  $\text{Fe}_3\text{H}$ ,  $\text{TiH}_2$  etc. It may be noted that these formula do not correspond to any normal oxidation state of the metal. Generally, the nonstoichiometric materials are obtained having the composition as  $\text{TiH}_{1.7}$ ,  $\text{VH}_{0.56}$ , etc. Because of the nature of their composition, these compounds are referred to as **interstitial compounds**.

# Continue..

The general characteristic physical and chemical properties of these compounds are

- (i) They have high melting points which are higher than those of pure metals.
- (ii) They retain metallic conductivity i.e. of pure metals.
- (iii) They are very hard and some borides have hardness as that of diamond.
- (iv) They are chemically inert.

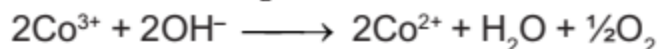
## **Catalytic properties**

Many transition metals and their compounds act as good catalysts for various reactions. Of these, the use of Fe, Co, Ni, V, Cr, Mn, Pt, etc. are very common.

The catalytic property of transition metals is due to their tendency to form reaction intermediates with suitable reactants. These intermediates give reaction paths of lower activation energy and, therefore increase the rate of the reaction.

These reaction intermediates readily decompose yielding the products and regenerating the original substance. The transition metals form these reaction intermediates due to the presence of vacant orbitals or their tendency to form variable oxidation states.

In some cases, the transition metal ions can change their oxidation states and become more effective as catalysts. For example, cobalt salts catalyse decomposition of bleaching powder as cobalt can easily change oxidation state from +2 to +3 as :

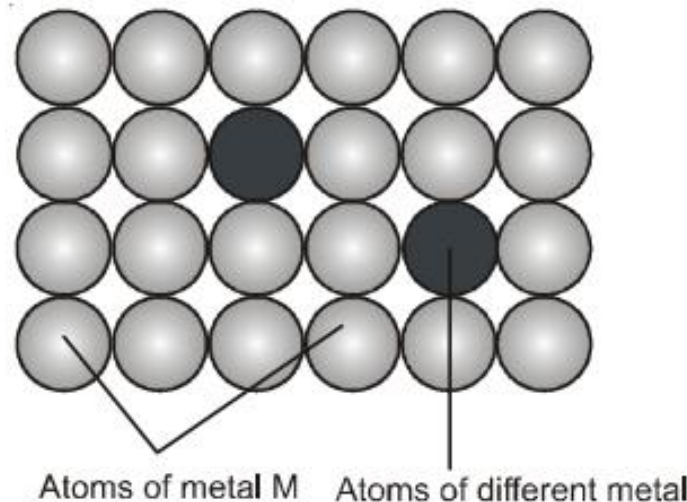


Iron (III) also catalyses the reaction between iodide and persulphate ions ( $\text{S}_2\text{O}_8^{2-}$ ).

# Alloy Formation

Alloys are homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other metal. The alloys are generally formed by those atoms which have metallic radii within about 15% of each other. Transition metals form a large number of alloys. The transition metals are quite similar in size and, therefore, the atoms of one metal can substitute the atoms of other metal in its crystal lattice. Thus, on cooling a mixture solution of two or more transition metals, solid alloys are formed. Such alloys are hard, have high melting points and are more resistant to corrosion than parent metals.

For example, the most common known alloys are ferrous alloys. Chromium, manganese, vanadium, tungsten, molybdenum etc. are used to produce variety of steels and stainless steel. Alloys of transition metals with non-transition metals such as bronze (copper-tin), brass (copper-zinc) are also industrially important alloys.



# Chemical property

## (b) Chemical :

- (i) On exposure to atmosphere, it turns brownish-yellow due to the formation of basic ferric sulphate.



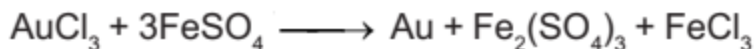
- (ii) Aqueous solution is acidic due to hydrolysis.



- (iii) 
$$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{140^\circ\text{C}} \text{FeSO}_4 \cdot \text{H}_2\text{O} \xrightarrow{300^\circ\text{C}} 2\text{FeSO}_4 \xrightarrow[\text{Temp.}]{\text{High}} \text{Fe}_2\text{O}_3 + \text{SO}_2 \uparrow + \text{SO}_3 \uparrow$$

- (iv) 
$$\text{FeSO}_4 + 6\text{KCN} \longrightarrow \text{K}_4[\text{Fe(CN)}_6] + \text{K}_2\text{SO}_4$$

- (v) It acts as reducing agent.





# Important Compound

## PREPARATIONS AND PROPERTIES OF SOME IMPORTANT d-BLOCK METAL COMPOUNDS

### COMPOUNDS OF IRON :

**Ferrous Sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Green vitriol)**

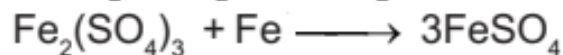
It is commonly known as harakasis

- **Preparation**

(i) By iron scrap :



(ii) From kipp's waste :



(iii)  $\text{FeCO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{FeSO}_4 + \text{H}_2\text{O} + \text{CO}_2$

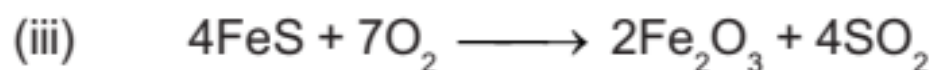
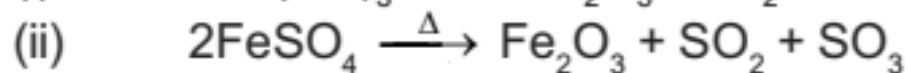
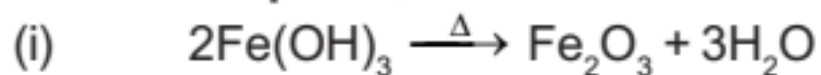
- **Properties**

**(a) Physical :** Hydrated ferrous sulphate is a green crystalline compound, effloresces on exposure to air.  
Anhydrous  $\text{FeSO}_4$  is colourless.

# Continue..

**Ferric Oxide,  $\text{Fe}_2\text{O}_3$  :**

● **Preparation :**

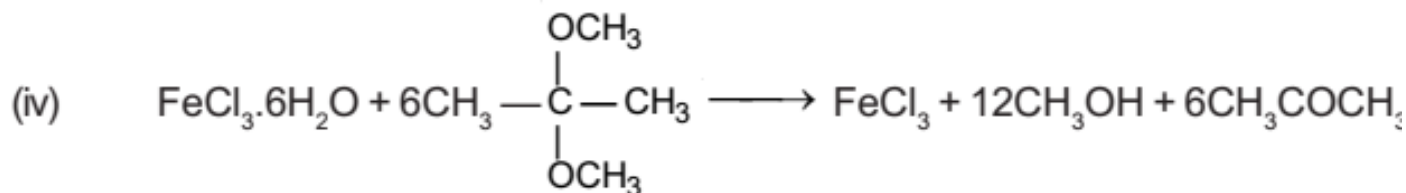
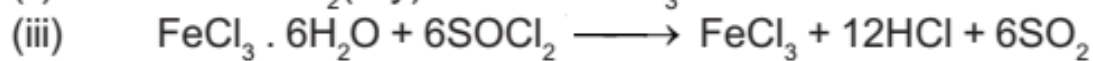
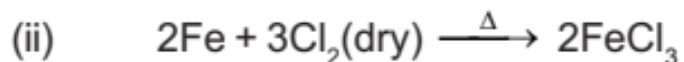
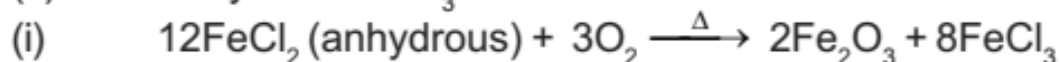


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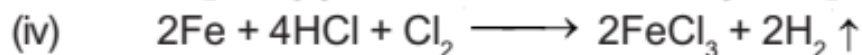
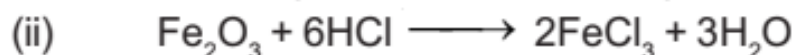
## Ferric Chloride, $\text{FeCl}_3$ :

### ● Preparation :

(a) Anhydrous  $\text{FeCl}_3$  :



(b) Hydrated  $\text{FeCl}_3$  :

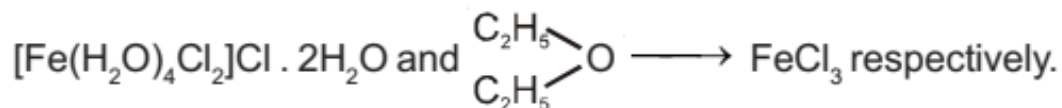


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## ● Properties

### (a) Physical :

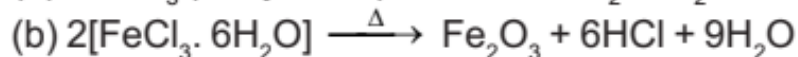
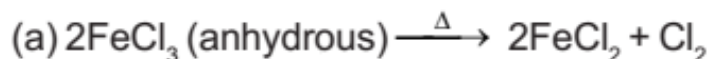
Anhydrous ferric chloride is dark black solid while hydrated salt,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  is yellowish-brown deliquescent crystalline solid. Both are soluble in water as well as in ether forming solvated species,



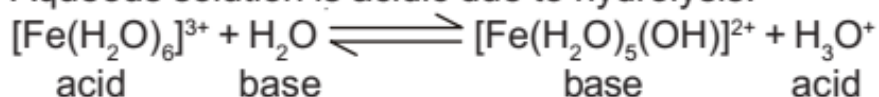
It is sublimed at  $300^\circ\text{C}$  giving a dimeric gas,  $\begin{array}{c} \text{Cl} \quad \quad \text{Cl} \\ \diagdown \quad \diagup \\ \text{Fe} \quad \quad \text{Fe} \\ \diagup \quad \diagdown \\ \text{Cl} \quad \quad \text{Cl} \end{array}$

### Chemical :

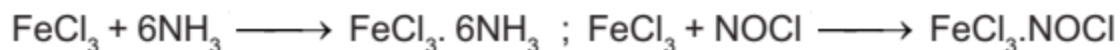
Action of heat :



Aqueous solution is acidic due to hydrolysis.



Formation of addition compounds :



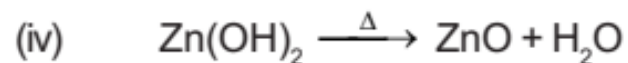
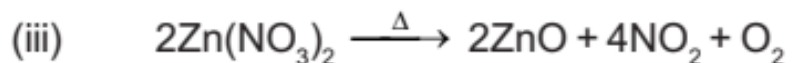
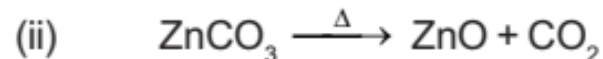
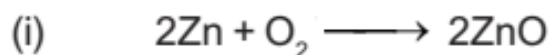
# Continue..

## COMPOUNDS OF ZINC :

Zinc oxide, ZnO (Chinese white or philosopher's wool)

It is found in nature as zincite or red zinc ore.

### ● Preparation :



# Continue..

## Zinc Sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (White vitriol)

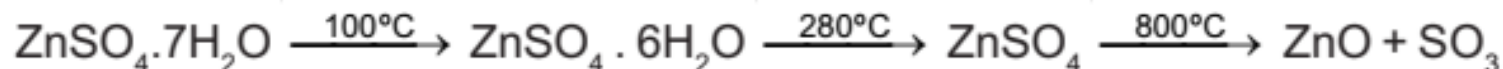
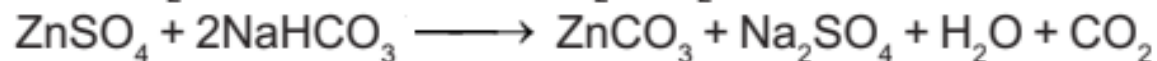
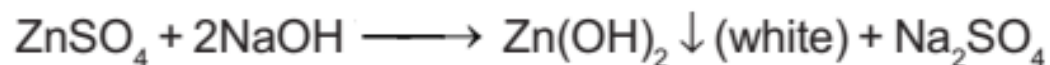
### ● Preparation :

- (i)  $\text{Zn} + \text{H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{H}_2$
- (ii)  $\text{ZnO} + \text{H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{H}_2\text{O}$
- (iii)  $\text{ZnCO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{H}_2\text{O} + \text{CO}_2$

### ● Properties :

- (a) **Physical :** It is a colourless, crystalline solid soluble in water. It slowly effloresces when exposed to air.  
It is isomorphous with Epsom salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ )

### Chemical :



# Continue..

## Zinc Chloride $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$

### ● Preparation :

It is prepared by dissolving zinc oxide, carbonate or hydroxide in dilute hydrochloric acid



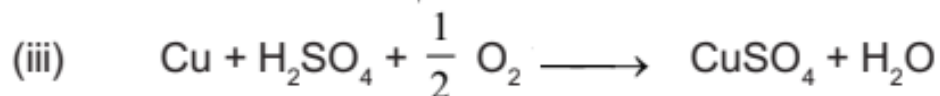
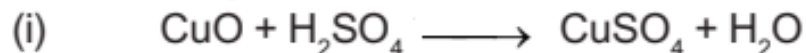
The solution so obtained on concentration and cooling gives the crystals of  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ .

Anhydrous zinc chloride cannot be prepared merely by heating the crystals of  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$  because a basic chloride  $\text{Zn(OH)Cl}$  is formed during decomposition which on further heating gives  $\text{ZnO}$ .

## Copper Sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Blue Vitriol)

It is also called 'Nilathotha'.

### ● Preparation :



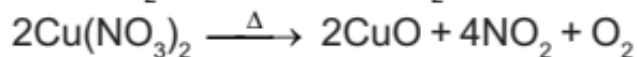
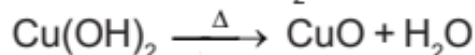
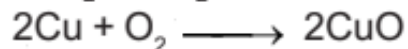
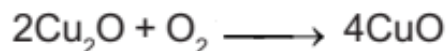
# Continue..

## Cupric Oxide, CuO

It is called black oxide of copper and is found in nature as tenorite.

**Preparation :** It is prepared

By heating  $\text{Cu}_2\text{O}$  in air or by heating copper for a long time in air (the temperature should not exceed above  $1100^\circ\text{C}$ )



On a commercial scale, it is obtained by heating/calcination of malachite which is found in nature.

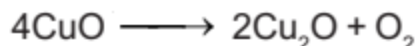


## Properties

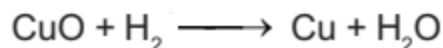
The oxide dissolves in acids  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  forming corresponding salts.



When heated to  $1100 - 1200^\circ\text{C}$ , it is converted into cuprous oxide with evolution of oxygen.



It is reduced to metallic copper by reducing agents like hydrogen, carbon and carbon monoxide.





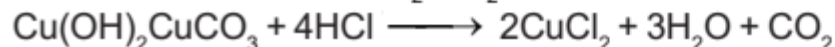
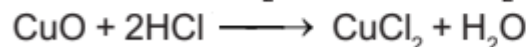
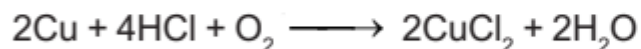
# Continue..

## Cupric Chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

### Preparation :

The metal or cupric oxide or cupric hydroxide or copper carbonate is dissolved in concentrated HCl.

The resulting solution on crystallisation gives green crystals of hydrated cupric chloride.



## Silver Nitrate, $\text{AgNO}_3$ (Lunar caustic) :

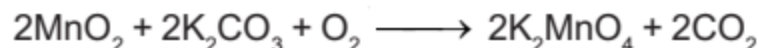
It is prepared by heating silver with dilute nitric acid. The solution is concentrated and cooled when the crystals of silver nitrate separate out.



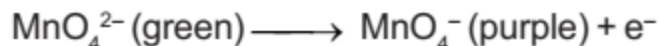
# POTASSIUM PERMANGANATE ( $\text{KMnO}_4$ ) :

## Preparation

This is the most important and well known salt of permanganic acid and is prepared from the pyrolusite ore. It is prepared by fusing pyrolusite ore either with  $\text{KOH}$  or  $\text{K}_2\text{CO}_3$  in presence of atmospheric oxygen or any other oxidising agent such as  $\text{KNO}_3$ . The fused mass turns green with the formation of potassium manganate,  $\text{K}_2\text{MnO}_4$ .



The fused mass is extracted with water and the solution is now treated with a current of chlorine or ozone or carbon dioxide to convert manganate into permanganate.



# Continue..

- **Properties**

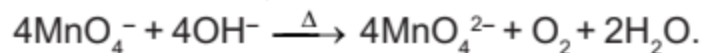
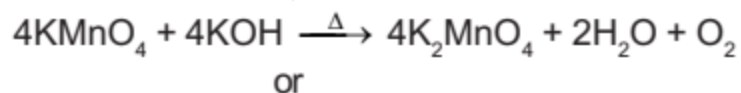
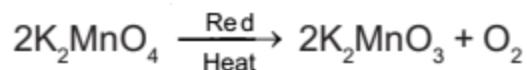
**(a) Physical :**

It is purple coloured crystalline compound. It is moderately soluble in water at room temperature.

**(b) Chemical :**

(i) Effect of heating

When heated alone or with an alkali, it decomposes evolving oxygen.

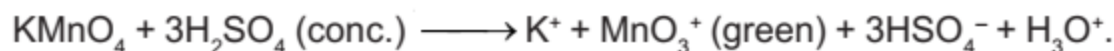
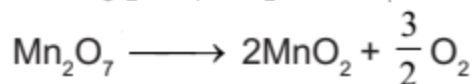


$\text{MnO}_4^{2-}$  in dilute alkaline, water and acidic solutions is unstable and disproportionates to give  $\text{MnO}_4^-$  and  $\text{MnO}_2$ .



# Continue..

On treatment with concentrated  $\text{H}_2\text{SO}_4$  ( $\text{KMnO}_4$  is taken in excess), it forms manganese heptoxide via permanganyl sulphate which decomposes explosively on heating.

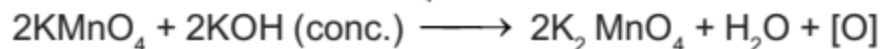


Potassium permanganate is a powerful oxidising agent.

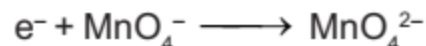
Potassium permanganate acts as an oxidising agent in alkaline, neutral or acidic solutions.

## In alkaline & neutral medium :

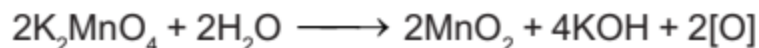
In strongly alkaline medium  $\text{KMnO}_4$  is reduced to manganate.



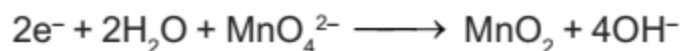
or



However if solution is dilute then  $\text{K}_2\text{MnO}_4$  is converted in to  $\text{MnO}_2$  which appears as a brownish precipitate.

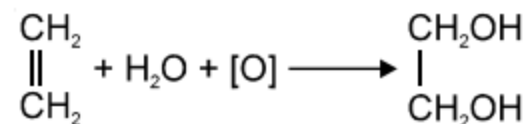


or



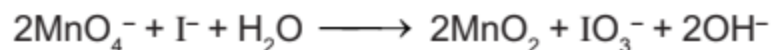
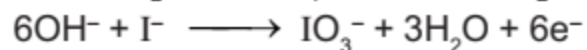
# Continue..

(a) It oxidises ethene to glycol.



In alkaline medium  $\text{KMnO}_4$  solution is also known as Bayer's reagent (1% alkaline  $\text{KMnO}_4$  solution).

(b) It oxidises iodide into iodate.



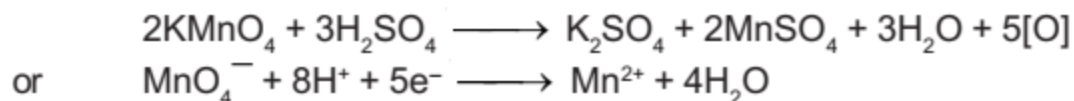
(c)  $\text{H}_2\text{S}$  is oxidised into sulphur :



# Continue..

**In acidic medium (in presence of dilute  $\text{H}_2\text{SO}_4$ ) :**

Manganous sulphate is formed. The solution becomes colourless.



This medium is used in quantitative (volumetric) estimations. The equivalent mass of  $\text{KMnO}_4$  in

acidic medium is =  $\frac{\text{Molecular mass}}{5}$  .

$\text{SO}_2$  is oxidised to  $\text{H}_2\text{SO}_4$  :



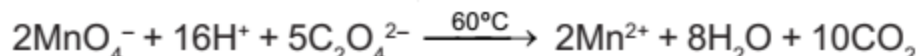
Nitrites are oxidised to nitrates :



Oxalic acid is oxidised to  $\text{CO}_2$  :

This reaction is slow at room temperature, but is rapid at  $60^\circ\text{C}$ .

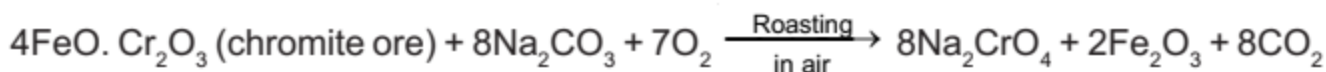
$\text{Mn(II)}$  ions produced catalyse the reaction; thus the reaction is autocatalytic



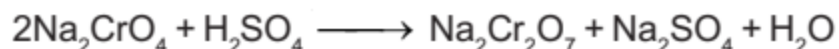
# POTASSIUM DICHROMATE ( $K_2Cr_2O_7$ )

- **Preparation :**

The chromite ore is roasted with sodium carbonate in presence of air in a reverberatory furnace



The roasted mass is extracted with water when  $Na_2CrO_4$  goes into the solution leaving behind insoluble  $Fe_2O_3$ . The solution is then treated with calculated amount of  $H_2SO_4$ .



The solution is concentrated when less soluble  $Na_2SO_4$  crystallises out. The solution is further concentrated when crystals of  $Na_2Cr_2O_7$  are obtained. Hot saturated solution of  $Na_2Cr_2O_7$  is then treated with KCl when orange red crystals of  $K_2Cr_2O_7$  are obtained on crystallisation.



$K_2Cr_2O_7$  is preferred over  $Na_2Cr_2O_7$  as a primary standard in volumetric estimation because  $Na_2Cr_2O_7$  is hygroscopic in nature but  $K_2Cr_2O_7$  is not.

# Continue..

- **Properties**

**(a) Physical :**

It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398°C.

**(b) Chemical :**

(i) Effect of heating :

On heating strongly, it decomposes liberating oxygen.



On heating with alkalies, it is converted to chromate, i.e., the colour changes from orange to yellow.

On acidifying, yellow colour again changes to orange.



Orange

Yellow



Yellow

Orange

Thus  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  exist in equilibrium and are interconvertable by altering the pH of solution.





# Continue..

In alkaline solution, chromate ions are present while in acidic solution, dichromate ions are present.

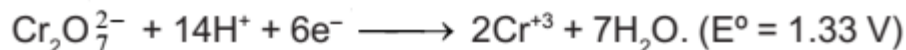


Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution reacts with  $\text{H}_2\text{O}_2$  to give a deep blue solution due to the formation of  $\text{CrO}_5$ .



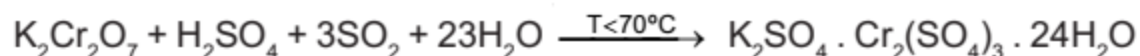
Blue colour in aqueous solution fades away slowly due to the decomposition of  $\text{CrO}_5$  to  $\text{Cr}^{3+}$  ions and oxygen. In less acidic solution  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{O}_2$  give salt which is violet coloured and diamagnetic due to the formation of  $[\text{CrO}(\text{O}_2)(\text{OH})]^-$ . In alkaline medium with 30%  $\text{H}_2\text{O}_2$ , a red-brown  $\text{K}_3\text{CrO}_8$  (diperoxo) is formed. It is tetra peroxospecies  $[\text{Cr}(\text{O}_2)_4]^{3-}$  and thus the Cr is in +V oxidation state. In ammonical solution a dark red-brown compound,  $(\text{NH}_3)_3\text{CrO}_4$  - diperoxo compound with Cr(IV) is formed.

It acts as a powerful oxidising agent in acidic medium (dilute  $\text{H}_2\text{SO}_4$ )



# Continue..

Chrome alum is obtained when acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is saturated with  $\text{SO}_2$ .



It oxidises ethylalcohol to acetaldehyde and acetaldehyde to acetic acid

