# THE D-AND F-BLOCK ELEMENTS

# GENERAL PROPERTIES OF THE TRANSITION ELEMENTS (d-Block)

*	CHARACTERISTIC PROPERTIES OF TRANSITION ELEMENTS:											
	<b>(a)</b> Variab	le oxidati	on state		(b) Coloured ions							
	(c)Paramagnetic properties					(d) Catalytic properties						
	(e) Formation of alloys					mat	tion o	of int	erstit	ial co	ompounds	
	<b>(g)</b> Forma	tion of co	mplexes.									
(a)	<b>Variable V</b> They exhi	<b>n Stat</b> invol	æ <b>s</b> vemer	nt of	f (ns)	) and	(n-1	) d-e	lectrons. Due			
	to less ene	ergy differ	ence between the	ese ele	ectron	s.						
(b)	The oxida	tion states	s of all transition (	eleme	ents of	'3d	' seri	es ar	e as f	ollov	vs –	
	Element	Conf.	Conf. Outer electronic			Oxidation states						
			configuration	n								
	Sc	3d14s2	<b>↑</b>	₽				+3				
			3d 4	4s								
	Ti	3d24s2	<b>↑ ↑</b>	₽	-	+2		+3		+4		
	V	3d34s2		₽	-	+2		+3		+4	+5	
	Cr	3d54s1	$\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$	1	-	+1	+2	+3	+4	+5	+6	
	Mn	3d54s2	$\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$	₽	-	+2	+3	+4	+5	+6	+7	
	Fe	3d64s2	$\uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow$	₽	-	+2	+3	+4		+6		
	Со	3d <sup>7</sup> 4s <sup>2</sup>	$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow$	₽	-	+2	+3	+4				
	Ni	3d84s2	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow$	₽	-	+2	+3	+4				

**↑** 

₽

+1

+2

+2

 $3d^{10}4s^{2} \qquad \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$ 

Cu

Zn

- (c) Highest oxidation state of transition elements can be calculated by n + 2 where (n = number of unpaired electrons) It is not applied for Cr and Cu.
- (d) The transition metal ions having stable configuration like  $d^0 d^5$  or  $d^{10}$  are more stable.
- **Ex.** Sc+3, Ti+4, V+5 Fe+3, Mn+2, Zn+2 etc.
- (e) In aqueous medium  $Cr^{+3}$  is stable.
- (f)  $Co^{+3}$  and  $Ni^{+2}$  is stable in complexes.
- (g) In aqueous medium due to disproportionation Cu<sup>+1</sup> is less stable than Cu<sup>+2</sup> while its configuration is 3d<sup>10</sup>
- (h) Most common oxidation state among the transition elements is +2.
- (i) Highest oxidation state shown by transition elements of '4d' and '5d' series is +8 by Ru (44) and Os (76).
- (j) The common oxidation state shown by elements of IIIB i.e., Sc, Y, La and Ac is +3 as their divalent compounds are highly unstable.
- (k) In lower oxidation state transition elements form ionic compounds and in higher oxidation state their compounds are covalent.
- (I) They also shows zero oxidation state in their carbonyl compounds like Ni(CO)<sub>4</sub>.
- (m) Usually transition metal ions in their lower oxidation state act as reducing agents and in higher oxidation state they are oxidising agents.
- **Ex.** Sc+2, Ti+2, V+2, Fe+2, Co+2 etc are reducing agents

Cr+6, Mn+7, Mn+6, Mn+5, Mn+4 etc are oxidising agents.

## **Standard Electrode Potentials**

The magnitude of ionization enthalpy gives the amount of energy required to remove electrons to form a particular oxidation state of the metal in a compound. Thus, the value of ionisation enthalpies gives information regarding the thermodynamic stability of the transition metal compounds in different oxidation states. Smaller the ionisation enthalpy of the metal, the stable is its compound. For example, the first four ionisation enthalpies of nickel and platinum are given below:

Ionisation enthalpies	Ni	Pt
$IE^1 + IE^2$	2.49×10 <sup>3</sup> Kj mol <sup>-1</sup>	2.66×10 <sup>3</sup> Kj mol <sup>-1</sup>
$IE^3 + IE^4$	8.8 ×10 <sup>3</sup> Kj mol <sup>-1</sup>	6.70×10 <sup>3</sup> Kj mol <sup>-1</sup>
Total	11.29 ×10 <sup>3</sup> Kj mol <sup>-1</sup>	9.36×10 <sup>3</sup> Kj mol <sup>-1</sup>

It is clear from the above table that the sum of first two ionization enthalpies is less for nickel than for platinum.

Ni 
$$\longrightarrow$$
 Ni<sup>2+</sup> + 2e<sup>-</sup>  
Pt  $\longrightarrow$  Pt<sup>2+</sup> + 2e<sup>-</sup>  
I.E. = 2.49 × 10<sup>3</sup> kJ mol<sup>-1</sup>  
I.E. = 2.66 × 10<sup>3</sup> kJ mol<sup>-1</sup>

Therefore, ionization of nickel to  $Ni^{2+}$  is energetically favorable as compared to that of platinum. Thus, the nickel (II) compounds are thermodynamically more stable than platinum (II) compounds. On the other hand, the sum of first four ionisation enthalpies is less for platinum than for nickel as:

Ni 
$$\longrightarrow$$
 Ni<sup>4+</sup> + 2e<sup>-</sup>  
Pt  $\longrightarrow$  Pt<sup>4+</sup> + 2e<sup>-</sup>  
I.E. = 11.29 × 10<sup>3</sup> kJ mol<sup>-1</sup>  
I.E. = 9.36 × 10<sup>3</sup> kJ mol<sup>-1</sup>

Thus, the platinum (IV) compounds are relatively more stable than nickel (IV) compounds. Therefore, K<sub>2</sub>PtCl<sub>6</sub> [having Pt (IV)] is a well-known compound whereas the corresponding nickel compound is not known.

However, in solutions the stability of the compounds depends upon electrode potentials.

#### **Electrode potentials:**

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:

$$M(s) \longrightarrow M^+(aq) + e^-$$

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

#### Class-12<sup>th</sup>



(i) 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.

 $M(s) \longrightarrow M^+(g)$  Enthalpy of sublimation,  $\Delta_{sub} H^{\Theta}$ 

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

$$M(s) \longrightarrow M^+(g) + e^-$$
 Ionisation enthalpy, IE

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

 $M^+(g) + nH_20 \longrightarrow M^+(aq)$  Enthalpy of hydration,  $\Delta_{hyd}H$ 

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

$$\Delta H = \Delta_{sub} H^{\Theta} + IE + \Delta_{hvd} H$$

Thus,  $\Delta H$  gives the enthalpy change required to bring the solid metal, M to the monovalent ion in aqueous medium, M<sup>+</sup> (aq). An exactly similar cycle may be constructed for the formation of an anion in solution except that the ionization enthalpy may be replaced by electron gain enthalpy when the gaseous atom goes to gaseous anion.  $\Delta H$  helps to predict the stability of a particular oxidation state. The smaller the values of total energy change for a particular oxidation state in aqueous solution, greater will be the stability of that oxidation state. The electrode potentials are a measure of total energy change. Qualitative, the stability of the transition metal ions in different oxidation states can be determined on the basis of electrode

potential data. The lower the electrode potential i.e., more negative the standard reduction potential of the electrode, the more stable is the oxidation state of the transition metal in the aqueous solution.

The electrode potentials of different metals can also be measured by forming the cell with standard hydrogen electrode. For the measurement of electrode potential of  $M^{2+}$  | 1M, the e.m.f. of the cell in which the following reaction occurs is measured:

$$2H^+(aq) + M(s) \rightleftharpoons M^{2+}(aq) + H_2(g)$$

Knowing the potential of  $2H^+(aq) | H_2(g)$ , it is possible to determine the potential of  $M^{2+}(aq) | M$ . For the first transition series, the  $E^{\Theta}$  values of  $M^{2+}(aq) | M$  are given below:

The observed values of  $E^{\Theta}$  and those calculated using the data are compared in the following figure.



Thermochemical data (kJ mol<sup>-1</sup>) for the first row Transition Elements and the Standard Electrode potentials for the Reduction of MII to M

Element (M)	$\Delta_{a}H_{q}(M)$	$\Delta_{f}H_{1}^{\theta}$	$\Delta_{f}H_{2}^{\theta}$	$\Delta_{hyd} H^{\theta} (M^{2+})$	$E^{\theta}/V$
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18

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Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Со	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	0.34
Zn	130	908	1730	-2059	-0.76

The results lead to the following conclusions:

- (i) There is no regular trend in these values. This is attributed to the irregular variation of ionisation enthalpies ( $IE_1 + IE_2$ ) and the sublimation energies in the period.
- (ii) It may be noted that the electrode potentials of transition metals are low in comparison to elements of group 2 (e.g., Ca = -2.87 V). Compared to group 2 elements, the transition elements have fairly large ionisation enthalpies and very large enthalpies of atomization. These reduce their electrode potentials though their hydration enthalpies are large.
- (iii) Zinc has low enthalpy of atomization and fairly large hydration energy. But it has also low electrode potential (-0.76 V) because of its very high ionisation enthalpy (IE<sub>1</sub> + IE<sub>2</sub>).
- (iv) It is clear from above table and figure that copper has positive reduction potential,  $E^{\Theta}$  (0.34 V) and this shows that copper is least reactive metal out of the first transition series. This unique behavior (+ve) E value of copper) also accounts for its inability to liberate H<sub>2</sub> from acids. It has been observed that only oxidizing acids (such as nitric acid and hot concentrated sulphuric acid) react with copper in which the acids are reduced. The high energy required to convert Cu(s) to Cu<sup>2+</sup> (aq) is not balanced by its hydration enthalpy.
- (v) In general, the value becomes, less negative across the series. This is related to the general increase in the sum of first and second ionisation enthalpies. It is interesting to note that the values of  $E^{\circ}$  of Mn, Ni and Zn are more negative than expected from the general trend. The relatively more negative values of  $E^{\Theta}$  for Mn and Zn are due to stability of half-filled d-sub-shell in Mn<sup>2+</sup> (3d<sup>5</sup>) and the completely filled (3d<sup>10</sup>)

configuration in  $Zn^{2+}$ . The exceptionally high  $E^{\Theta}$  value of Ni from regular trend is related to the highest negative enthalpy of hydration of Ni<sup>2+</sup> ion.

Trends in the  $M^{3+}$  |  $M^{2+}$  Standard Electrode Potentials

Except copper and zinc, all other elements of first transition series show +3 oxidation states also to form  $M^{3+}$  ions in aqueous solutions. The standard reduction potentials for  $M^{3+} \mid M^{2+}$  redox couple are given below :

	Ti	V	Cr	Mn	Fe	Со
$E^{\Theta}(M^{3+}(aq)   M^{2+}(aq)$ (in Volt)	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97

These values reveal the following facts:

- (i) The low value of scandium reflects the stability of  $Sc^{3+}$  which has a noble gas configuration.
- (ii) The comparatively high value for Mn shows that  $Mn^{2+}$  (d<sup>5</sup> configuration) is particularly stable. On the other hand comparatively low value for Fe shows the extra stability of Fe<sup>3+</sup> (d<sup>5</sup> configuration).
- (iii) The comparatively low value of V is related to the stability of  $V^{2+}$  (due to half-filled  $t_{2g}^{3}$  energy level of 3d orbitals in octahedral crystal field spitting).
- (iv) The  $E^{\Theta}$  value for  $Mn^{3+}/Mn^{2+}$  couple much more positive than for  $Cr^{3+}/Cr^{2+}$  or  $Fe^{3+}/Fe^{2+}$ . This is because of the much larger III<sup>rd</sup> ionisation energy of Mn (removal of electron from d<sup>5</sup> configuration).

## Trends in Stability of Higher Oxidation States

Standard electrode potential data provide valuable information about the stabilities of different oxidation states shown by an element. The highest oxidation states are shown generally among halides and oxides.

1. 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;  $F_2 > Cl_2 > Br_2 > I_2$ 

Oxidation	Sc	Ti	V	Cr	Min	Fe	Со	Ni	Cu	Zn
Number										
+6				CrF <sub>6</sub>						
+5			VF <sub>5</sub>	CrF <sub>5</sub>						
+4		TiX4	$VX_4^a$	CrF <sub>4</sub>	MnF <sub>4</sub>					
+3	ScX <sub>3</sub>	TiX <sub>3</sub>	VX <sub>3</sub>	CrF <sub>3</sub>	$MnF_3$	FeX <sup>a</sup> 3	CoF <sub>3</sub>			
+2		TiX <sub>2</sub>	VX <sub>2</sub> c	CrF <sub>2</sub>	MnX <sub>2</sub>	FeX <sub>2</sub>	CoF <sub>2</sub>	NiX <sub>2</sub>	CuX <sub>2</sub> <sup>b</sup>	ZnX <sub>2</sub>
+1									CuXc	
	wher	where $X = F$ , Cl, Br, I, $X^a = F$ , Cl, Br, $X^b = F$ , Cl, $X^c = Cl$ , Br, I								

#### Halides of first transition series

Within each of the transition groups 3 - 12, there is a difference in the stability of the various oxidation states. In general, the second and third transition series elements exhibit higher coordination number and their higher oxidation states are more stable than the corresponding first transition series elements. The following trends are observed from table regarding transition metal halides:

- (i) 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.
- (ii) 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<sub>5</sub> and CrF<sub>6</sub>.
- (iii) 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.
- (iv) After Mn, the tendency to show higher oxidation states with halogens are uncommon.Iron and cobalt form trihalides FeX<sub>3</sub> (X = F, Cl or Br) and CoF<sub>3</sub>.
- (v) The tendency of fluorine to stabilize the highest oxidation state is due to either higher lattice enthalpy as in case of CoF<sub>3</sub> or higher bond enthalpy due to higher covalent bonds e.g., VF<sub>5</sub> and CrF<sub>6</sub>.
- (vi) V(V) is shown by VF<sub>5</sub> only. However, the other halides undergo hydrolysis to form oxyhalides, VOX<sub>3</sub>.

(vii) 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,  $Cu^{2+}$  oxidizes I<sup>-</sup> to I<sub>2</sub>.

$$2Cu^{2+} + 4I^{-} \longrightarrow Cu_2I_2(s) + I_2$$

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 :

$$2Cu^+ \longrightarrow Cu^{2+} + Cu$$

Copper in +2 oxidation state is more stable than in +1 oxidation state. This can be explained on the basis of much larger negative hydration enthalpy ( $\Delta_{hyd}H^{\Theta}$ ) of Cu<sup>2+</sup> (aq) than Cu<sup>+</sup>, which is much more than compensates for the large energy required to remove the second electron i.e., second ionisation enthalpy of copper.

Oxidation	Sc	Ti	V	Cr	Min	Fe	Со	Ni	Cu	Zn
Number										
+7					Mn <sub>2</sub> O <sub>7</sub>					
+6				CrO <sub>3</sub>						
+5			<b>V</b> <sub>2</sub>							
			05							
+4		TiO <sub>2</sub>	<b>V</b> <sub>2</sub>	CrO <sub>2</sub>	MnO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>				
			04							
+3	Sc <sub>2</sub> O <sub>3</sub>	TiO <sub>3</sub>	<b>V</b> <sub>2</sub>	$Cr_2O_3$	$Mn_2O_3$	FeO	CoO	NiO	Cu0	Zn0
			03							
+2		TiO	VO	(Cr0)	Mn0				CuO	
+1										
Mixed oxides					Mn <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub>	Co <sub>3</sub> O <sub>4</sub>			

#### 2. In metal oxides and oxo cations.

The ability of oxygen to stabilize the highest oxidation state is demonstrated in their oxides. The highest oxidation states in their oxides coincides with the group number.

For example, the highest oxidation state of scandium of group 3 is +3 in its oxides,  $Sc_2O_3$  whereas the highest oxidation state of manganese of group 7 is +7, in  $Mn_2O_7$ . However, beyond group 7, no higher oxides of iron above  $Fe_2O_3$  are known. Although higher oxidation state such as +6 is shown in ferrates such as  $FeO_4^{2-}$  in alkaline medium, but they readily decompose to  $Fe_2O_3$  and  $O_2$ . Besides the oxides, oxidation of the metals also stabilizes higher oxidation states. For example, VV as  $VO_2^+$ ,  $V^{IV}$  as  $VO_2^+$  and Ti<sup>IV</sup> as TiO<sup>2+</sup>. It may be noted that the ability of oxygen to stabilize these high oxidation states exceeds that of fluorine. For example, manganese forms highest fluoride as  $MnF_4$  whereas the highest oxide is  $Mn_2O_7$ . This is due to the fact that oxygen has great ability to form multiple bonds to metals. In the covalent oxide.  $Mn_2O_7$ , each Mn is tetrahedrally surrounded by oxygen atoms and has Mn-O-Mn bridge. The tetrahedral  $[MO_4]^{n-}$  ions are also known for vanadium (V), chromium (VI), manganese (VII) 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  $MnO_4^-$  all bonds are covalent. As the oxidation number of a metal increases, the ionic character of their oxides decreases. For example, in case of Mn,  $Mn_2O_7$  is a covalent green oil. In these higher oxides the acidic character is predominant. Thus,  $CrO_3$  gives  $H_2CrO_4$  and  $H_2Cr_2O_7$  and  $Mn_2O_7$  gives  $HMnO_4$ .  $V_2O_5$  is, however amphoteric though mainly acidic and with alkalies as well as acids gives  $VO_4^{3-}$  and  $VO_2^+$ respectively.

#### The relative stability of various oxidation states

- (a) The relative stabilities of various oxidation states of 3d-series element can be correlated with the extra stability of  $3d^{\circ}$ ,  $3d^{5} \& 3d^{10}$  configuration to some extent.
- **Ex.** Stability of  $Ti^{4+}(3d^{0}) > Ti^{3+}(3d^{1}) Mn^{2+}(3d^{5}) > Mn^{3+}(3d^{4})$
- (b) The higher oxidation state of 4d and 5d series element are generally more stable than the elements of 3d series.

Ex. (i) (oxidation state of Mo is +6), (4d series) &(5d series) are more stable due to their maximum oxidation state.

(ii) & (3d-series) are strong oxidizing agents.

(c) Strongly reducing states probably do not form fluorides or oxides, but may well form the heavier halides Conversely, strong oxidizing state form oxides & fluoride, but not Bromide and lodide.

Ex.

- (i) V (Vanadium) react with halogens to form VF5 VCl5, VBr3, but doesn't form VBr5 or VI5 because in + 5 oxidation state Vanadium is strong oxidizing agent thus convert Br & I- to Br2 & I2 respectively, So VBr3 &VI3 are formed but not VBr5 & VI5.
- (ii) On the other hand VF<sub>5</sub> is formed because  $V^{5+}$  ion unable to oxidize highly electronegative & small anion F<sup>-</sup>
- (iii) Similarly, highly electronegative and small  $O^2$  ion formed oxides
- **Ex.** VO<sub>4</sub> <sup>3</sup> <sup>-</sup>, CrO<sub>4</sub><sup>2</sup><sup>-</sup> & MnO<sub>4</sub><sup>-</sup> etc.

## Different oxidation state of chloride & oxides compound

	+2	+3	+4	+5	+6	+7
	TiCl <sub>2</sub>	TiCl <sub>3</sub>	TiCl <sub>4</sub>			
	VCl <sub>2</sub> (Ionic, basic)	VCl <sub>3</sub> Less ionic (Amphoteric)	VCl <sub>4</sub> Covalen (Strong	VOCl <sub>3</sub> t and Acidic lewis acid)		
(d)	TiO	$Ti_2O_3$	TiO <sub>2</sub>			
	VO	$V_2O_3$		$V_2O_5$		
	CrO	$Cr_2O_3$		Cr	03	
	MnO	Mn <sub>2</sub> O <sub>3</sub>	MnO <sub>2</sub>	M	nO <sub>3</sub>	Mn <sub>2</sub> O <sub>7</sub>
	Ionic, basic	Less Ionic (A	mphoteric)		Acidic, co	valent

Such compounds are expected to be unstable except in case where vacant d-orbitals are used for accepting lone-pair from  $\pi$ -bonding ligand.

**Ex.** [Ni(CO)<sub>4</sub>], [Ag(CN)<sub>2</sub>]<sup>-</sup>, [Ag)(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>

## **Colour Property**

- (a) Most of the transition metal ions exhibit colour property.
- (b) This is due to d-d transition of unpaired electrons in their  $t_{2g}$  and  $e_g$  sets of 'd' orbitals.
- (c) They require less amount of energy to undergo excitation of electrons. Hence, they absorb visible region of light exhibiting colour.
- **Ex.**  $Sc^{+2} : [Ar]3d^1$ ,  $Ti^{+2} : [Ar]3d^2$ ,  $V^{+2} : [Ar]3d^3$
- (d) Transition metal ions which do not have any unpaired electrons in their 'd' orbitals like 3d<sup>0</sup> and 3d<sup>10</sup> configurations, do not exhibit any colour property.
- **Ex.**  $Sc^{+3}$ : [Ar]3d<sup>0</sup>, Cu<sup>+1</sup>: [Ar]3d<sup>10</sup>, Ti<sup>+4</sup>: [Ar]3d<sup>0</sup> etc are colourless ions.
- (e) A transition metal ion absorbs a part of visible region of light and emits rest of the colours, the combination of which, is the colour of emitted light. The colour of metal ion is the colour of the emitted light.
- (f) In transition metal ion the 'd' orbitals split into lower energy set  $t_{2g}$  orbitals and higher energy set  $e_g$  orbitals. The electrons from  $t_{2g}$  set get excited to higher energy



set e.g., set. This excitation of electrons is called as 'd-d' transition. Due to this 'd -d' transition the transition metal ions exhibit colour property.

## Factors affecting the colour of complex

The colour of a transition metal complex depends on-

- (a) The magnitude of energy difference between the two d-levels ( $\Delta 0$ ),
- (b) An increase in the magnitude of  $\Delta_0$  decreases the wave length (  $\lambda$ ) of the light absorbed by the complexes.

$$\Delta_0 \propto \frac{1}{\lambda(\text{Wavelength of light absorb})}$$

(c) Thus, with a decrease in the  $\lambda$  the colour of complex changes from Red to Violet.

Ex.	Complex ions	[Co(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>		[Co(NH3)6] <sup>3+</sup>		[Co(CN)6] <sup>3-</sup>
	Ligand field strength	H <sub>2</sub> 0	<	NH <sub>3</sub>	<	CN-
	Magnitude of $\Delta_0$	∆ <sub>0</sub> (H <sub>2</sub> 0)	<	$\Delta_0(NH_3)$	<	$\Delta_0(CN^-)$
	Magnitude of $\lambda$	λ(H <sub>2</sub> 0)	<	$\lambda(NH_3)$	<	λ(CN <sup>-</sup> )
	Colour of the transmitted	orange		Green-blue		violet
	Colour of absorbed light	Green-blue		Orange	Yellov	w greenlight
	(i.e., colour of the complex					

(d) KMnO4 (dark pink), K2Cr2O7 (orange) having d° configuration but they are coloured due to charge transfer spectrum and charge is transferred from anion to cation.

Ti <sup>+3</sup>	Purple	Mn <sup>+2</sup>	Light pink
Fe <sup>+3</sup>	Yellow	Ni <sup>+2</sup>	Green
Sc <sup>3+</sup>	Colourless	Ti <sup>3+</sup>	Purple
V <sup>3+</sup>	Green	Cr <sup>2+</sup>	Blue
Mn <sup>3+</sup>	Violet	Fe <sup>2+</sup>	Green(light)
Co <sup>2+</sup>	Pink	Zn <sup>2+</sup>	Colourless
Cr <sup>+3</sup>	Green	Fe <sup>+2</sup>	Green
Co+3	Pink	Cu <sup>+2</sup>	Blue
Ti <sup>4+</sup>	Colourless	V <sup>4+</sup>	Blue

Example of Some coloured metal ions :

#### Chemistry

V <sup>2+</sup>	Violet	Cr <sup>3+</sup>	Green
Mn <sup>2+</sup>	Pink	Fe <sup>3+</sup>	Yellow
Ni <sup>2+</sup>	Blue		

- **Ex.** Explain the blue colour of CuSO<sub>4</sub>.5H<sub>2</sub>O.
- **Sol.** Cu<sup>2+</sup> ion (3d<sup>9</sup>) absorbs red light from the visible region, for the promotion of 3d electrons, the ions reflect blue light and appear blue.

#### **Magnetic Properties**

- (a) Generally, transition elements exhibit the magnetic property. A paramagnetic substance is one which is attracted into a magnetic field. Para magnetism is mainly due to the presence of unpaired electrons in atoms or ions or molecules. It varies inversely with temperatures.
- (b) Diamagnetic substance is one which is slightly repelled by a magnetic field. It's independent of temperature.
- (c) As is evident most of the transition metal ions have unpaired electrons in their 'd' orbitals. Hence most of the transition metal ions are paramagnetic in nature.

**Ex.** Ti+2 [Ar]3d<sup>2</sup>, Ti+3 [Ar]3d<sup>1</sup>. V+2[Ar]3d<sup>3</sup>, Cr+3[Ar]3d<sup>3</sup>

- (d) Transition metal ions having  $3d^0$  and  $3d^{10}$  configuration exhibit diamagnetic nature.
- (e) The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons.
- (f) The magnetic moment (μ) created due to spinning of unpaired electrons can be calculated by using

$$\mu = \sqrt{n(n+2)}$$

Where - 'n' is the number of unpaired electrons in the metal ion.

 $\mu$  = Magnetic moment in Bohr Magnetons (B.M.)

- (g) The magnetic moment of diamagnetic substances will be zero.
- **(h)** Transition metal ions having d<sup>5</sup> configuration will have maximum number of unpaired electrons therefore they will be maximum paramagnetic in nature.

## **Catalytic Property**

- (a) Transition elements and their compounds exhibit catalytic properties. This is due to their variable valency as well as due to the free valencies on their surface.
- (b) When transition elements and their compounds are in powdered state, their catalytic properties exhibited will be to a greater extent. This is due to greater surface area available in the powdered state.
- (c) Transition metals and their compounds exhibiting catalytic properties in various processes are -

Catalyst	Used
TiCl <sub>3</sub>	Used as the Ziegler-Natta catalyst in the production of polythene.
MnO <sub>2</sub>	Used as a catalyst to decompose $KClO_3$ to give $O_2$
Fe	Promoted iron is used in the Haber-Bosch process for making NH <sub>3</sub>
FeCl <sub>3</sub>	Used in the production of $CCl_4$ from CS and $Cl_2$
$FeSO_4$ and $H_2O_2$	Used as Fenton's reagent for oxidizing alcohols to aldehydes.
PdCl <sub>2</sub>	Wacker process for converting C <sub>2</sub> H <sub>4</sub> +H <sub>2</sub> O+PdCl <sub>2</sub> to CH <sub>3</sub> CHO+2HCl+Pb.
pd	Used for hydrogenation (e.g., phenol to cyclohexanone).
Pt/pt0	Adams catalyst, used for reductions.
Pt	Formerly used for $SO_2 \rightarrow SO_3$ in the contact process for making $H_2SO_4$
Pt/Rh	Formerly used in the Ostwald process for making $HNO_3$ to $NO$
Cu	Is used in the direct process for manufacture of (CH <sub>3</sub> )2SiCl <sub>2</sub> used to make silicones.

# Chemistry

Cu/V	Oxidation of cyclohexanol/cyclohexanone mixture to adipic acid which is used to make nylone-66
CuCl	Decon process of making Cl from HCl
Ni	Raney nickel, numerous reduction processes (e.g., manufacture of hexamethylenediamine, production of H <sub>2</sub> from NH <sub>3</sub> reducing anthraquinone to anthraquinol in the production of H <sub>2</sub> O <sub>2</sub> )