8. d and f BLOCK ELEMENTS

1.Magnetic properties

The magnetic moment of transition element is only determined by spin angular momentum, depending upon the number of unpaired electrons and is calculated by using the 'spin-only' formula, i.e.,

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

where n is the number of unpaired electrons ,
μ is the magnetic moment and unit is Bohr magneton (BM).

For example ,Ti $^{3+}$ [Ar]B $4s^0$ $3d^1$ One unpaired electron in d orbital So

Root 1(1+2) = root 3 = 1.73 BM

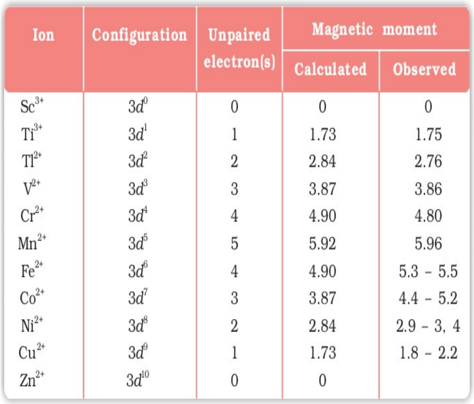
Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

For atomic number 25, electronic configuration is [Ar] $4s^2$ $3d^5$ the divalent ion in aqueous solution will have configuration [Ar]$4s^0$ $3d^5$
d^5 configuration (five unpaired electrons).

The magnetic moment, μ is

$$\mu = \sqrt{5(5+2)} = 5.92\,\text{BM}$$

Table 8.7: Calculated and Observed Magnetic Moments (BM)



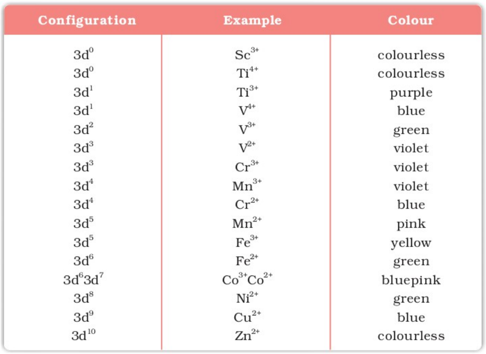
Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Tl^{2+}	$3d^2$	2	2.84	2.76
V^{2+}	$3d^3$	3	3.87	3.86
Cr^{2+}	$3d^4$	4	4.90	4.80
Mn^{2+}	$3d^5$	5	5.92	5.96
Fe^{2+}	$3d^6$	4	4.90	5.3 – 5.5
Co^{2+}	$3d^7$	3	3.87	4.4 – 5.2
Ni^{2+}	$3d^8$	2	2.84	2.9 – 3, 4
Cu^{2+}	$3d^9$	1	1.73	1.8 – 2.2
Zn^{2+}	$3d^{10}$	0	0	

2, Formation of Coloured Ions

Colour of transition metal is due to d-d transition

Ion with d^0 and d^{10} are colourless or white because no unpaired electrons are available for excitation

all other ions with d electrons 1 to 9 are having characteristic colour due to d-d transition



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
$3d^6 3d^7$	$Co^{3+} Co^{2+}$	bluepink
$3d^8$	Ni^{2+}	green
$3d^9$	Cu^{2+}	blue
$3d^{10}$	Zn^{2+}	colourless

3.Complex Formation

A few examples $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$ and $Fe(CO)_5$

Transition metals forms number of complex compounds. This is due to the comparatively

a)smaller sizes of the metal ions,
b)their high ionic charges and the
c)availability of d orbitals for bond formation.

4.Catalytic properties

Catalytic property of transition metals is due to their ability to adopt multiple oxidation states and to form complexes.

Examples for Catalysis:- Vanadium(V) oxide in Contact Process,
Finely divided iron in Haber's Process, and
Nickel in Catalytic Hydrogenation

5.Oxidation state ... shows variable valency

Transition elements show variable oxidation states because energies of ns sub level and (n-1)d sub level are almost equal.Highest oxidation state of transition metal is exhibited in its oxide or fluoride. Because of small size and high electronegativity, oxygen or fluorine can oxidise the metal to its highest oxidation state.

6.Hardness and Melting points

Except Zn, Cd and Hg transition metals are hard and they have high melting point. The high melting points of these metals are attributed to involvement of greater number of unpaired electrons. Greater the number of unpaired electrons stronger will be metallic bonding and higher will be melting points.

Among all transition elements W has highest melting point Zn, Cd and Hg do not contain unpaired electrons. Therefore, they are soft metals.

7.Alloy formation

Transition elements form alloys due to similar size e.g. Manganese steel

8. Formation of interstitial compounds

Transition metals forms interstitial compounds because small atoms like H, C or N are trapped inside the crystal lattices of transition metals . As a result they have high melting points than those of pure metals. They are very hard.

Some important compounds of Transition elements

1.POTASSIUM DICHROMATE $K_2Cr_2O_7$

9.Preparation

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:

$$4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7O_2 \rightarrow 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$$

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7.2H_2O$ can be crystallised after cooling.

$$2Na_2CrO_4 + 2\ H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

The solution of sodium dichromate Is treated with potassium chloride.

$$Na_2Cr_2O_7 + 2\ KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$$

Orange crystals of potassium dichromate crystallise out.

10.Properties of Potassium dichromate $K_2Cr_2O_7$

i) The chromates and dichromates are interconvertible

in aqueous solution depending upon pH of the solution.

$$2\ CrO_4^{2-}\ \text{(yellow)} + 2H^+ \rightarrow Cr_2O_7^{2-}\ \text{(orange)} + H_2O$$

$$Cr_2O_7^{2-}\ \text{(orange)} + 2\ OH^- \rightarrow 2\ CrO_4^{2-}\ \text{(yellow)} + H_2O$$

ii) Oxidising action

It acts as strong oxidizing agent in acidic medium

$$K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O + 3[O]$$

Therefore acidified $K_2Cr_2O_7$ oxidises

i)Potassium Iodide to Iodine

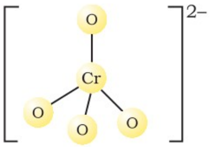
$$K_2CrO_7 + H_2SO_4 + KI \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O + I_2$$

ii)Hydrogen Sulphide to sulphur

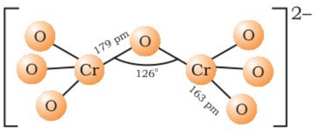
$$K_2Cr_2O_7 + H_2SO_4 + H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O + S$$

11. Structures of chromate ion, and dichromate ion,

CrO_4^{2-} $Cr_2O_7^{2-}$



Chromate ion



Dichromate ion

2. POTASSIUM PERMANGANATE $KMnO_4$

12.Preparation

Generally prepared From Pyrolusite ore (MnO_2)

Step 1 Pyrolusite is fused with KOH in presence of air and an oxidizing Agent

$$MnO_2 + KOH + O_2 \rightarrow K_2MnO_4 + H_2O$$

Step 2 The dark green coloured Potassium manganate (K_2MnO_4) Disproportionate in acidic medium giving permanganate

$$K_2MnO_4 + H^+ \rightarrow KMnO_4 + MnO_2 + H_2O$$

The purple solution obtained on evaporation gives crystal of potassium permanganate

Commercial method of preparation of Potassium permanganate

Step 1 Pyrolusite is fused with KOH in presence of air and an oxidizing Agent

$$MnO_2 + KOH + O_2 \rightarrow K_2MnO_4 + H_2O$$

Step 2 Electrolytic oxidation of Potassium manganate gives potassium permanganate

At anode, $MnO_4^{2-} \rightarrow MnO_4^- + e-$

At Cathode, $2H^+ + e- \rightarrow H_2$

Formed MnO_4^- reacts with K^+ to form $KMnO_4$

The purple solution obtained on evaporation gives crystal of potassium permanganate

13.Properties of Potassium Permanganate

Oxidising action

$KMnO_4$ acts as strong oxidizing agent in acidic medium

$$KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + H_20 + 5[O]$$

Therefore acidified $KMnO_4$ oxidises Many compounds

Acidified $KMnO_4$ oxidises

i)Ferrous ion to ferric ion

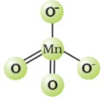
$$KMnO_4 + H_2SO_4 + Fe^{2+} \rightarrow K_2SO_4 + MnSO_4 + H_2O + Fe^{3+}$$

ii)Hydrogen sulphide in to sulphur

$$KMnO_4 + H_2SO_4 + H_2S \rightarrow K_2SO_4 + MnSO_4 + H_2O + S$$

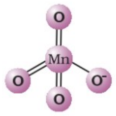
14.Structure of Manganate and permanganate ion

The structures of Manganate ion MnO_4^{2-}



Tetrahedral manganate ion (green)

The structures of Permanganate ion MnO_4^-



Tetrahedral permanganate ion (purple)

15. Lanthanoids

Lanthanoids are 14 elements coming after Lanthanum starting from Lutetium and ends in Lawrencium .In lanthanide filling of electron takes place in 4f sub shell before 5d orbitals. It belongs to sixth period.

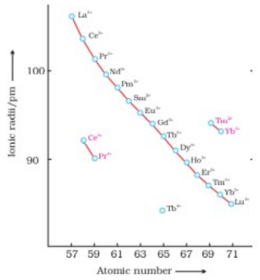
General electronic configuration is ns^2 $(n-1)d^{0,1}$ $(n-2)$ f^{1-14} .

The common oxidation state of lanthanoid is +3. Example La^{3+},Ce^{3+}......

16. Lanthanoid contraction --Atomic and ionic Radii

Steady and slow decreasing of atomic and ionic radii of lanthanoids from La^{3+} to Lu^{3+} is called as Lanthanoid contraction.

Reason for lanthanoid contraction



This is Because of ineffective shielding effect of 4f orbital due to its diffused shape, As a result , the shielding effect caused by one 4f electron by another is less than one d electrons by another with increasing nuclear charge along the series. As a result whole nuclear power reaches to outermost shell and size slowly decreases

Consequence of lanthanoid contraction

1. The radii of some elements of second transition series is similar to third transition series Eg:- Zr and Hf , Nb and Ta

2. Lanthanoids occur together in nature and separation become difficult

17. Use of lanthanoids

1. Misch metal is alloy of lanthanoids (about 95% lanthanoids, about 5% iron and traces of S,C, Ca and Al). Misch Metal is used in Mg based alloy to produce bullets, shell etc.
2. Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking.