d –Block elements and transition metals (Chapter 8)

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The elements lying in the middle of periodic table belonging to groups 3 to 12 are known as *d* – block elements.

Features of d-block elements:

- The general electronic configuration of *d*-block elements is $(n-1)\ d^{1-10}\ ns^{1-2}$, where $(n-1)$ stands for the inner d orbitals.
- In *d*-block, each horizontal row consists of ten elements as *d*-subshell can accommodate a maximum of 10 electrons.
- The *d*-block elements having incompletely filled *d*-subshell are called transition metals.
- Zinc, cadmium, mercury having the general electronic configuration as $(n-1)d^{10}\ ns^2$, are not regarded as transition metals due to completely filled *d* – orbital.
- There are mainly three series of the transition metals:

- 3*d* series starts with Sc (Z = 21) and ends with Zn (Z = 30)
- 4*d* series starts with Y (Z = 39) and ends with Cd (Z = 48)
- 5*d* series starts with La (Z = 57) and ends with Hg (Z = 80)

General General Properties of transition elements:

Metallic character

Almost all the transition elements display metallic properties such as metallic luster, high tensile strength, ductility, malleability and high thermal and electrical conductivity.

In any row, the melting point of these metals rises to a maximum at d^5 and after that as the electrons start pairing up so the melting point decreases regularly as the atomic number increases with an excepyion of Mn and Tc are exception.

Atomic and ionic radii

Due to the addition of new electron to a *d*-orbital each time the effective nuclear charge increases which causes the atomic radii to decrease in a series of transition elements. However, the atomic size of Fe, Co, Ni is almost the same because the attraction due to increase in nuclear charge is cancelled by the repulsion because of increased in shielding effect. The size of the 4*d* series elements is almost the same as the size of the 5*d* series elements. This phenomenon is associated with the intervention of the 4*f* orbitals which must be filled before the filling starts in 5*d* subshell.

Lanthanoid contraction

The filling of the 4*f* before the 5*d* orbital results in a regular decrease in size called lanthanoid contraction. This compensates for the expected increase in the atomic size with increasing atomic number. The net result of the lanthanoid contraction is is that the 4*d* and 5*d* series elements exhibit similar radii and show similarity in their physical and chemical properties.

Melting point

Due to the strong interatomic bonding which involves both $(n-1)d$ and ns electrons participation, transition metals have high melting points.

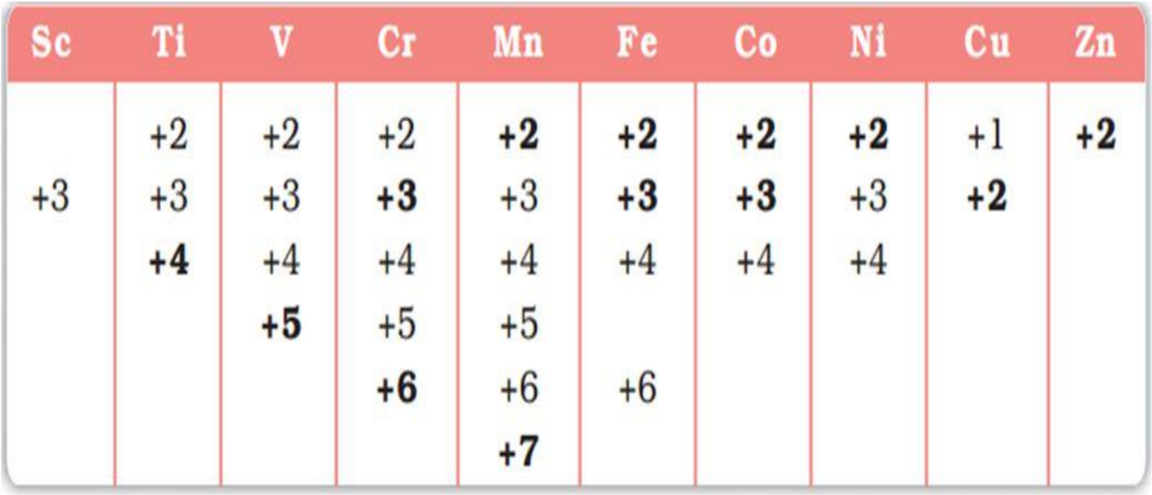
Ionization enthalpy

In a particular transition series, there is an increase in ionization enthalpy from left to right which is due to the increase in effective nuclear charge along a series. But the trend is not very regular. The exceptions are chromium and copper which have notably larger ionization enthalpy than their neighbours. These exceptions are due to the extra stability associated with the half-filled and fully-filled set of *d*-orbitals.

Oxidation States

Transition metals show variable oxidation states due to tendency of $(n\text{-}1)d$ as well as *ns* electrons to take part in bond formation.

For example:- Oxidation states of the first row transition metals are:



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	+1	**+2**
+3	+3	+3	**+3**	+3	**+3**	**+3**	+3	**+2**	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

Enthalpy of atomization

The transition elements have high enthalpy of atomization which is due to the presence of strong metallic bonding. The elements with highest enthalpy of atomization tend to be noble metals. The elements of 4*d* and 5*d* series have greater enthalpies of atomization than the elements of 3*d* series. That's why the elements of 4*d* and 5*d* series have more frequent metal-metal bonding in their compounds.

Reactivity

The metals of the 3*d* series are more reactive than the elements of the 4*d* or 5*d* series. All 3*d* series elements with the exception of Cu are highly reactive and are oxidized by 1 M H^+. The tendency to form divalent cation decreases along the 3*d* series as indicated by their

$E°_{(M^{2+}/M)}$ values. The E° value does not follow a regular trend. This is due to irregularity in IE and the heat of atomisation.

Magnetic properties

Most of transition metals are paramagnetic in nature due to the presence of unpaired electrons. It increases from Sc to Mn due to the increased number of unpaired electrons and then starts decreasing as the number of unpaired electrons decreases.

Formation of complexes

The transition metals form a large number of complexes. This is due to their Comparatively small sizes of the metal ions.
High ionic charges.
Availability of vacant d atomic orbitals

Formation of coloured compounds

Transition metals and their compounds show colour. The colour is due to the excitation of electron from one *d* atomic orbital to higher energy *d* atomic orbital in the same subshell. The frequency of the light absorbed generally lies in the visible region. The colour observed is due to the colour of the complementary light. The colour is due to the presence of unpaired electrons. All Zn^{2+} compounds are white.

Formation of interstitial compounds

Transition metals have lattice structure in which the unoccupied space is called void or hole or interstices. Transition metals entrap smaller but highly electronegative elements in these interstices and results in the formation of interstitial compounds. Interstitial com-pounds have high melting points, hardness and retain metallic conductivity. The interstitial compounds are chemically inert. Examples are TiC, steel.

Formation of alloys

Alloy is a homogeneous mixture of two or more metals. Due to the comparable size of transition metals, one metal can displace other metal in the crystal lattice and this results in the alloy formation. The alloys so formed are hard and have high melting points. The best known are ferrous alloys; chromium, vanadium, tungsten, manganese are used for the production of variety of steels and stainless steels.

Catalytic properties

Most of transition metals are used as catalysts.

This is due to the

(i) presence of incomplete or empty *d*-orbitals,
(ii) large surface area and

(iii) variable oxidation state. For example Fe, Ni, V_2O_3, Pt, Mo, Co, etc., are used as catalyst.

Formation of oxides

Transition metals form oxides on reaction with oxygen at elevated temperature. Transition metal form oxide in oxidation state of + 1 (in Ag_2O) to + 7 (Mn_2O_7) to + 8 (in OsO_4). As the oxidation number increases in case of same elements,

(a) The covalent character of oxides increases.

(b) The acidic strength of the oxides increases.

(c) The oxidizing power of oxides increases.

For example, Cr_2O_3 is amphoteric while CrO is basic and CrO_3 is acidic.

Some Important Compounds of Transition Elements

Potassium dichromate, $K_2Cr_2O_7$

Preparation:

It is prepared by fusion of chromate ore (FeCr2O4) with sodium carbonate in excess of air.

$$8Na_2CO_3 + 4FeCr_2O_4 + 7O_2 \rightarrow \underset{\text{Yellow}}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$$

Na_2CrO_4 produced in the above reaction is then acidified to get sodium dichromate, $Na_2Cr_2O_7$

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$$2Na_2CrO_4 + H_2SO_4 \rightarrow \underset{\text{Orange}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

Solution of sodium dichromate treated with potassium chloride to get the final product, $K_2Cr_2O_7$.

$$Na_2Cr_2O_7 + 2KCl \rightarrow \underset{\text{Orange Crystals}}{K_2Cr_2O_7} + 2NaCl$$

Structures of CrO_4^{2-} and $Cr_2O_7^{2-}$ ions:

Uses:

Potassium dichromate is used as a primary standard in volumetric analysis and as an oxidizing agent. In acidic medium, the oxidation state of Cr changes from + 6 in $Cr_2O_7^{2-}$ to + 3 in Cr^{3+}.

$$Cr_2O_7^{2-} + 14\,H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Potassium permanganate, $KMnO_4$

Preparation:

It is prepared by fusion of MnO_4 with alkali metal hydroxide (KOH) in presence of O_2 or oxidising agent like KNO_3. It produces dark green coloured compound , K_2MnO_4 which undergoes oxidation as well as reduction in neutral or acidic solution to give permanganate.

Commercially it is prepared by the alkaline oxidative fusion of MnO2 followed by the electrolytic oxidation of manganate (Vl).

Uses:

Potassium permanganate acts as a strong oxidizing agent in acidic, neutral or faintly basic medium.

In acidic medium:

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4\ H_2O$

Oxidises Fe^{2+} to Fe^{3+}:

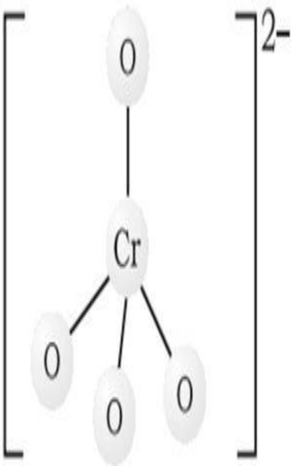
$Fe^{2+} \rightarrow Fe^{3+} + e^-$

In an alkaline medium:

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

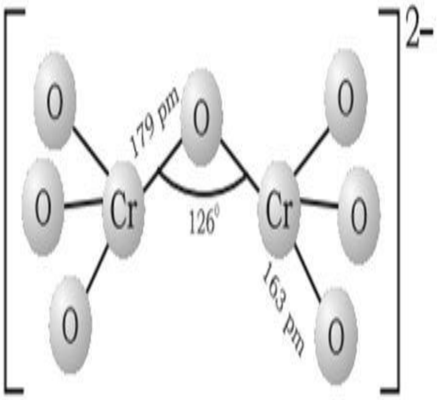
Oxidises I^- to iodate IO_3^-:

$6OH^- + I^- \rightarrow IO_3^- + 6e^- + 3H_2O$



Chromate ion

(Tetrahedral)



Dichromate ion

(Double tetrahedral)