

d-BLOCK ELEMENTS & THEIR COMPOUNDS

The general electronic configuration of d-block elements is $(n-1)d^{1-10}ns^{0-2}$, where n is the outer most shell.

GENERAL TRENDS IN THE CHEMISTRY OF TRANSITION ELEMENTS.

Metallic character :

Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre. With the exceptions of Zn, Cd, Hg and Mn, they have one or more typical metallic structures at normal temperatures.

The transition elements (with the exception of Zn, Cd and Hg) are very much hard and have low volatility.

Melting and boiling points :

The melting and boiling points of the transition series elements are generally very high.

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 the transition metals are high.

Oxidation states :

Most of transition elements show variable oxidation states. Participation of inner $(n-1)$ d-electrons in addition to outer ns -electrons because, the energies of the ns and $(n-1)$ d-subshells are nearly same.

Different oxidation states of first transition series.

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

Characteristics of Oxides and Some Ions of V and Cr

O.S.	Oxide/ Hydroxide	Behaviour	Ion	Name of Ion	Colour of ion
+2	VO	basic	V^{2+}	vanadium (II) (vanadous)	violet
+3	V_2O_5	basic	V^{3+}	vanadium (III) (vanadic)	green
+4	VO_2	amphoteric	VO^{2+}	oxovanadium (IV) (vanadyl)	blue
			$V_4O_9^{2-}$	hypovanadate (vanadite)	brown
+5	V_2O_5	amphoteric	VO_2^+	dioxovanadium (V)	yellow
			VO_4^{3-}	orthovanadate	colourless
+2	CrO $\left[Cr(OH)_2 \right]$	basic	Cr^{2+}	chromium (II) (chromous)	light blue
+2	CrO $\left[Cr(OH)_2 \right]$	basic	Cr^{2+}	chromium (II) (chromous)	light blue
+3	Cr_2O_3 $\left[Cr(OH)_3 \right]$	amphoteric	Cr^{3+}	chromium (III)	violet
			$Cr(OH)^-$	chromic chromite	green
+5	CrO_3 $\left[CrO_2(OH)_2 \right]$ $H_2Cr_2O_7$	acidic	CrO_4^{2-}	chromate	yellow
			$Cr_2O_7^{2-}$	dichromate	orange

Standard electrode potentials :

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.

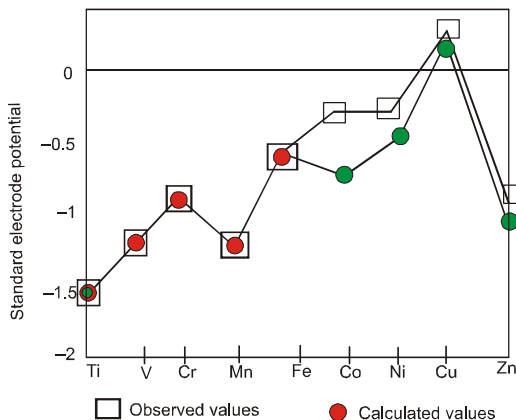
Electrode potentials :

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.

The overall energy change is

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

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.

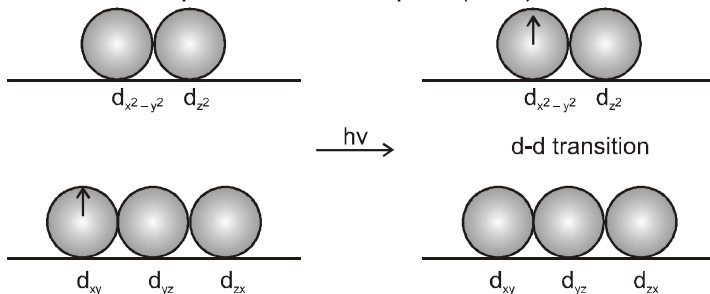


Thermochemical data (kJ mol^{-1}) for the first row Transition Elements and the Standard Electrode potentials for the Reduction of M^{II} to M

Element (M)	$\Delta_a H_q^\ominus$ (M)	$\Delta_f H_1^\ominus$	$\Delta_f H_2^\ominus$	$\Delta_{\text{hyd}} H^\ominus (\text{M}^{2+})$	E^\ominus / V
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	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

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-subshell.



The excess of other colours constituting white light are transmitted and the compound appears coloured. The observed colour of a substance is always complementary colour of the colour which is absorbed by the substance.

Magnetic Properties :

- (i) **Paramagnetic substances :** The substances which are attracted by magnetic field are called paramagnetic substances.
- (ii) **Diamagnetic substances :** The substances which are repelled by magnetic field are called diamagnetic substances. The 'spin only' magnetic moment can be calculated from the relation :

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

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

The paramagnetism first increases in any transition series and then decreases. The maximum paramagnetism is observed around the middle of the series (as contains maximum number of unpaired electrons).

Formation of Interstitial Compounds :

Transition metals form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen.

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.

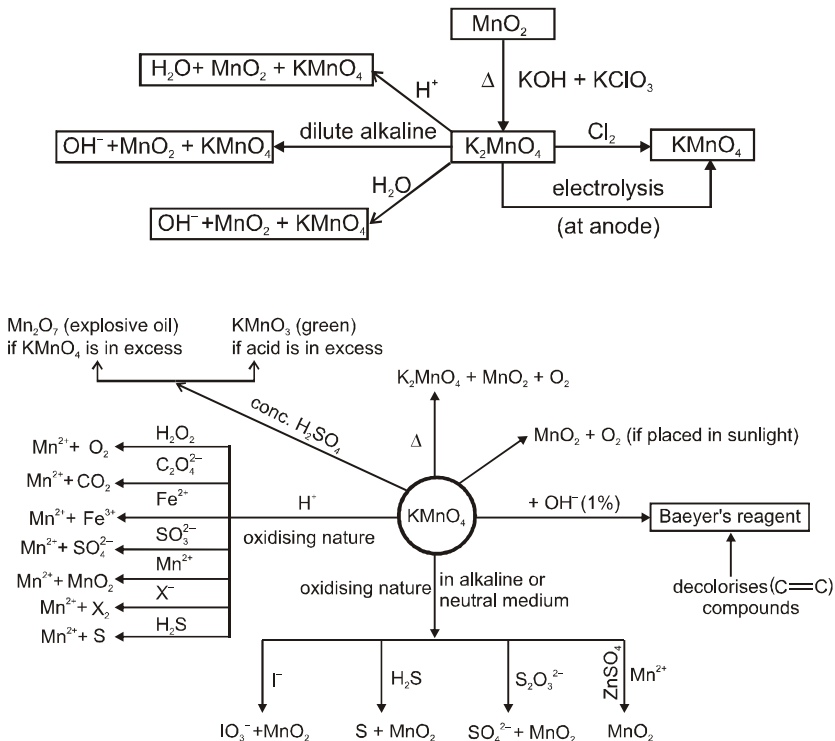
- (i) The catalytic property of transition metals is due to their tendency to form reaction intermediates with suitable reactants. These intermediates give reaction paths of lower activation energy and, therefore, increase the rate of the reaction.
- (ii) In some cases, the transition metal catalysts provide a suitable large surface area for the adsorption of the reactant. This increases the concentration of the reactants at the catalyst surface and also weakens the bonds in the reactant molecules. Consequently, the activation energy gets lowered.
- (iii) In some cases, the transition metal ions can change their oxidation states and become more effective as catalysts.

Alloy Formation :

Alloys are hard, have high melting points and are more resistant to corrosion than parent metals.

d-BLOCK METAL COMPOUNDS :

1. Potassium permanganate (KMnO_4) :



2. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) :

