

General Characteristics of *d*-Block Elements

- Nearly all transition elements show metallic properties except mercury which is a liquid.
- They are electropositive in nature.
- Most of them form coloured compounds.
- They have good tendency to form complexes.
- They show variable oxidation states.
- Their compounds are generally paramagnetic in nature.
- They form alloys with other metals.
- A number of these transition metals and their compounds show catalytic properties.
- They have high melting and boiling points and have higher heat of vaporisation than non-transition elements.

General Trends in the Chemistry of *d*-Block Elements

- **Atomic and ionic radii** : The atomic radii of *d*-block elements are intermediate between those of *s*- and *p*-block. The following trends in atomic radii have been observed.
 - The atomic radii in a series decrease with increase in atomic number but the decrease in atomic radius becomes small after midway.
 - At end of each period, there is slight increase in the atomic radii.
 - The atomic radii increase while going down the group.
- **Ionisation enthalpies** : Ionisation enthalpies of *d*-block elements lie in between those of *s*- and *p*-block elements. They are less electropositive than *s*-block elements and more electropositive than *p*-block elements. Ionisation enthalpies increase along a given transition series due to increased nuclear charge. Ionisation enthalpies also increase down the group in a series. 5*d* series have higher ionisation enthalpy than 3*d* and 4*d* series but irregularity has been seen in ionisation enthalpies of 3*d* and 4*d* series.
- **Metallic character** : Except mercury, all transition elements have typical metallic structure (*hcp*, *ccp* or *bcc*) and show all the properties of metals. The metallic character is due to low ionisation enthalpies and number of vacant orbitals in the outermost shell. Greater the number of unpaired *d*-electrons, greater is the number of bonds and therefore greater is the strength of these bonds, so hardness and enthalpy of atomization increase with increase in number of unpaired electrons. As we move from left to right in a particular *d*-series, number of unpaired electrons increase from 1 to 6 and then decreases to 0.
- **Density** : All *d*-block elements have high density. Within a period, the densities vary inversely with the atomic radii. As we move in a period, the density increases (as the radii decrease). The density increases while descending a group.
- **Standard electrode potential (E°) and chemical reactivity**: Thermodynamic stability of transition elements can be evaluated in terms of magnitude of ionisation enthalpies. Smaller the ionisation enthalpy, more stable is its compound. More positive value of electrode potential

refers to strong oxidising action while more negative value of electrode potential indicates strong reducing action.

- **Oxidation states** : *d*-block elements show variable oxidation states because both *ns* and $(n - 1)d$ electrons take part in bond formation. Oxidation states of transition elements are related to their electronic configuration. Minimum oxidation state exhibited by transition elements is equal to number of *ns*-electrons. While generally maximum oxidation state refers to number of *ns*-electrons in addition to unpaired *d*-electrons which participate in bond formation. In general, the maximum oxidation state increases with atomic number within a group.
- **Coloured ions** : Most of the transition metal compounds (ionic as well as covalent) are coloured in their solid or solution form. Coloured ions are formed due to presence of vacant *d*-subshell. When visible light falls on transition metal compound the transition metal absorbs some radiation of white light and undergoes *d-d* transition. The transmitted (unabsorbed) or reflected light appears coloured which is complementary to colour of absorbed radiation. Transition metal ions containing either completely filled or completely empty *d*-subshell appear colourless.
- **Complex formation** : Transition metal ions form a large number of complex compounds because they have small size, large effective nuclear charge and have vacant *d*-orbitals so that these orbitals can accept lone pairs of electrons donated by the ligands.

Magnetic Properties

- The transition metals generally contain one or more unpaired electrons in the $(n - 1)d$ orbital. Due to these unpaired electrons they behave as **paramagnetic substances**. These substances are attracted by the magnetic field.

The transition elements that contain paired electrons behave as **diamagnetic substances**. These substances are repelled by the magnetic field.

Magnetic character of a substance is measured in terms of magnetic moment

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

Where μ = magnetic moment, n = number of unpaired electrons.

Catalytic Property

- The transition elements exhibit catalytic properties due to their ability to show variable oxidation states as a result of which they can form complexes. Iron and vanadium are the most important catalysts.

<i>e.g.</i> ,	Catalyst	Process
	Iron	Manufacture of NH_3
	V_2O_5	Manufacture of H_2SO_4
	Ni	Hydrogenation of oils
	Co	Decomposition of CaOCl_2

Interstitial Compounds

- Transition metals form large number of interstitial compounds in which small sized non-metallic atoms like H, C and N occupy the interstitial sites in their lattices. Interstitial compounds are **non-stoichiometric** in nature. They have similar chemical properties as that of parent atom but differ in physical properties like they have high m.pt. and b.pt. than parent metal, show conductivity, etc, e.g. interstitial compounds of Fe and C are quite hard.

Alloy Formation

- Alloys are homogeneous mixtures of two or more elements in which at least one of elements is a metal. Since d-block elements have nearly same atomic sizes they can easily take up position of one another in crystal lattices and cause alloy formation.

Alloys containing mercury as one of the constituents are known as **amalgam**.

Chemical properties of constituents are retained in alloys but physical properties are improved appreciably.

e.g., **Composition**

	Alloy
Cu(60%) + Zn(40%)	Brass
Cu(90%) + Sn(10%)	Bronze
Steel + Cr(18%) + Ni(8%)	Stainless steel
Ag(50%) + Cu(40–50%) + Ni(5–10%)	Coinage silver

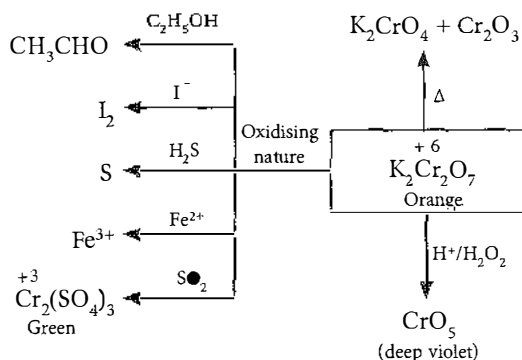
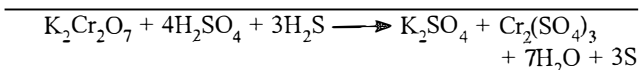
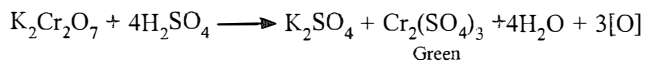


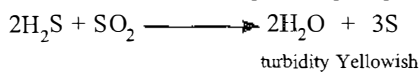
Illustration 1

Two gases 'A' and 'B' turns acidified $K_2Cr_2O_7$ green. When these gases are passed through water simultaneously, solution turns turbid yellow. What are the gases 'A' and 'B'?

Soln.:



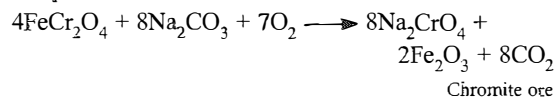
When both SO_2 and H_2S are passed simultaneously through water then colloidal sulphur is precipitated.



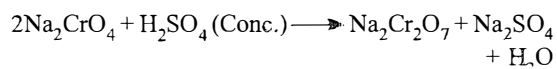
Potassium Dichromate ($K_2Cr_2O_7$)

- It is a very important compound of chromium. It is prepared from chromite ore or ferrochrome or chrome iron ($FeCr_2O_4$ or $FeO \cdot Cr_2O_3$). This preparation involves various steps:

> Preparation of sodium chromate :

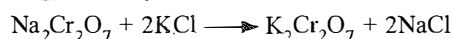


> Conversion of sodium chromate into sodium dichromate :



Sodium sulphate being less soluble on cooling separates as $Na_2SO_4 \cdot 10H_2O$ leaving sodium dichromate.

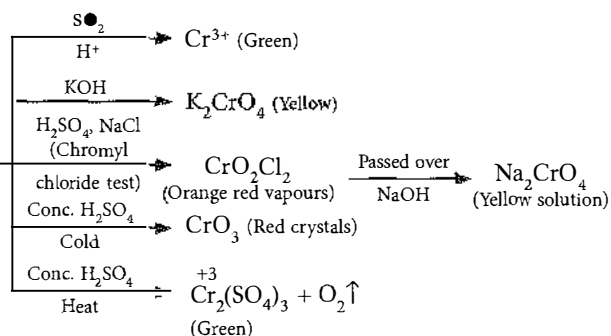
> Conversion of Sodium dichromate into potassium dichromate :



Potassium dichromate being less soluble crystallises out on cooling.

• Properties :

- > $K_2Cr_2O_7$ is soluble in hot water.
- > It is in the form of orange crystals which melt at $400^\circ C$.



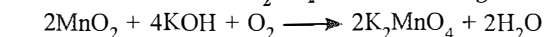
• Uses of $K_2Cr_2O_7$:

- > In photography, in hardening gelatine film.
- > In volumetric analysis for estimation of iron and iodine in redox titrations.
- > In chrome tanning in leather industry.

Potassium Permanganate ($KMnO_4$)

- It is the most important compound of manganese. It is prepared from the mineral pyrolusite (MnO_2). The preparation involves various steps:

> Conversion of MnO_2 to potassium manganate



> Oxidation of potassium manganate to potassium permanganate

Oxidation can be done in two ways, either chemical oxidation or electrolytic oxidation.

Chemical oxidation

- In this method potassium manganate is treated with chlorine or ozone or CO_2 to form potassium permanganate.