ATOMIC ENERGY CENTRAL SCHOOL-3,TARAPUR

Module-1

Unit : d & f- block elements

Chapter: d-block elements

SYLLABUS

d and f Block Elements (Period 14) General introduction ,electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation. Preparation and properties of $K_2 Cr_2 O_7$ and $KMnO_4$.

INTRODUCTION

Elements in which last electron enters in the (n-1)d- subshell of their atoms are called as d- block elements.

For example : Cu, Ag, Au and Zn etc.

TRANSITION METALS

- Originally the name transition metals was derived from the fact that their chemical properties were transitional between those of *s* and *p*-block elements.

- Elements of d-block in which partially filled (n-1)d subshell is present in either their atomic state or any stable oxidation state.

  For ex: Cu, Ag, Au, Fe etc.

ELECTRONIC CONFIGURATION

- General electronic configuration of d-block elements :

  $(n-1)d^{1-10}ns^{1-2}$, where n is ultimate shell and (n-1) is penultimate shell.

- General electronic configuration of transition elements is :

  $(n-1)d^{1-10} ns^{1-2}$, where n is ultimate shell(outermost shell) and (n-1) is penultimate shell.

- **Scandium** is only the 50th most common element on Earth (35th most abundant in the crust), but it is the 23rd most common element in the Sun.

- **Copper** occurs combined in many minerals, such as chalcocite, chalcopyrite, bornite, cuprite, malachite, and azurite. It is present in the ashes of seaweeds, in many sea corals, in the human liver.

- Fe is rarely found uncombined in nature, it is found in combine state in minerals like hematite, limonite, siderite etc.

OCCURRENCE

General characteristics shown by transition metals are as follows:

- ❖ variability of oxidation states
- ❖ Formation of alloy
- ❖ Formation of interstitial compounds
- ❖ Formation of paramagnetic species.
- ❖ Formation of colured compounds
- ❖ Formation of complex compounds

CHARACTERISTICS

- One of the notable features of a transition elements is the great variety of oxidation states & valency these may show in their compounds. For example **Mn** shows +2, +3, +4, +5, +6, +7 oxidation states in its compounds.

- Although in the *p*–block the lower oxidation states are favoured by the heavier members (due to inert pair effect), the opposite is true in the groups of *d*-block. For example, in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidizing agent, whereas MoO_3 and WO_3 are not. Variability of oxidation states not shown by Zn and Sc in first transition series.

Reason : This is due to the closeness of energies of (n-1)d electrons and ns electrons due to this, along with outermost electrons, (n-1)d electrons are also participating in bond formation.

VARIABILITY OF OXIDATION STATES

- Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.

- **Reason** : Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals.

FORMATION OF ALLOY

- Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent,for example, TiC, Mn4N, Fe3H, VH0.56 and TiH1.7, etc.

- chemical characteristics of these compounds are as follows:

- (i) They have high melting points, higher than those of pure metals.

- (ii) They are very hard, some borides approach diamond in hardness.

- (iii) They retain metallic conductivity.

- (iv) They are chemically inert.

Reason : Small atoms like H, C or N are trapped inside the crystal lattices of these metals, due to that they can form interstitial compounds.

FORMATION OF INTERSTITIAL COMPOUNDS

- **Paramagnetism** arises from the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula, i.e., $\mu = n(n + 2)$ where n is the number of unpaired electrons and µ is the magnetic moment in units of Bohr magneton (BM). A single unpaired electron has a magnetic moment of 1.73 Bohr magnetons (BM). The magnetic moment increases with the increasing number of unpaired electrons. Thus, the observed magnetic moment gives a useful indication about the number of unpaired electrons present in the atom, molecule or ion.

Reason: Generally the atom, ions and compounds of transition elements are paramagnetic because of presence of unpaired electrons.

FORMATION OF PARAMAGNETIC SPECIES

When an electron from a lower energy d -orbital is excited to a higher energy d -orbital, the energy of excitation corresponds to the frequency of light absorbed. This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed.
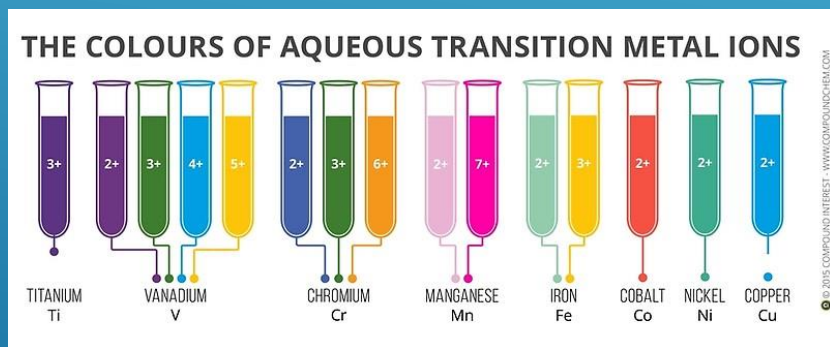
Reason : Generally ions and compounds of transition metals are coloured due to the presence of unpaired electron or electrons.

THE COLOURS OF AQUEOUS TRANSITION METAL IONS

| TITANIUM Ti | VANADIUM V | CHROMIUM Cr | MANGANESE Mn | IRON Fe | COBALT Co | NICKEL Ni | COPPER Cu |

FORMATION OF COLOURED SPECIES

Complex compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species

With characteristic properties.

A few examples are: $[Fe(CN)6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$.

<u>Reason</u> : The transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of d -orbitals for bond formation.

FORMATION OF COMPLEX COMPOUNDS

The transition metals and their compounds are known for their catalytic activity. Vanadium(V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in Catalytic Hydrogenation) are some of the examples. Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst .

For example, iron(III) catalyses the reaction between iodide and persulphate ions.

$2 I^- + S_2O_8^{2-} \text{----------}> I_2 + 2 SO_4^{2-}$

An explanation of this catalytic action can be given as:

$2 Fe^{3+} + 2 I^- \text{----------}> 2 Fe^{2+} + I_2$

$2 Fe^{2+} + S_2O_8^{\ 2-} \text{----->} 2 Fe^{3+} + 2SO_4^{2-}$

Reason : This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. First row transition metals utilise $3d$ and $4s$ electrons for bonding, this has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering). Also because the transition metal ions can change their oxidation states, they become more effective as catalysts.

CATALYTIC ACTIVITY

▶ <u>**Metallic character**</u> :

Metallic character of an **element** is defined as the easiness of its atom in losing electrons. Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.

GENERAL TRENDS IN PROPERTIES OF THE FIRST ROW TRANSITION METALS

- **<u>Ionization enthalpy</u>** : The irregular trend in the first ionisation enthalpy of the metals of 3d -series, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4*s* and 3d -orbitals. You have learnt that when d-block elements form ions, ns- electrons are lost before (n – 1) *d* electrons. As we move along the period in 3*d* series, we see that nuclear charge increases from scandium to zinc but electrons are added to the orbital of inner subshell, i.e., 3d orbitals. These 3d electrons shield the 4*s* electrons from the increasing nuclear charge somewhat more effectively than the outer shell electrons can shield one another. Therefore, the atomic radii decrease less rapidly. Thus, ionization energies increase only slightly along the 3d -series.

- The dominant term is the second ionization enthalpy which shows unusually high values for Cr and Cu where M^+ ions have the d^5 and d^{10} configurations respectively. The value for Zn is correspondingly low as the ionization causes the removal of 1s electron which results in the formation of stable d^{10} configuration.
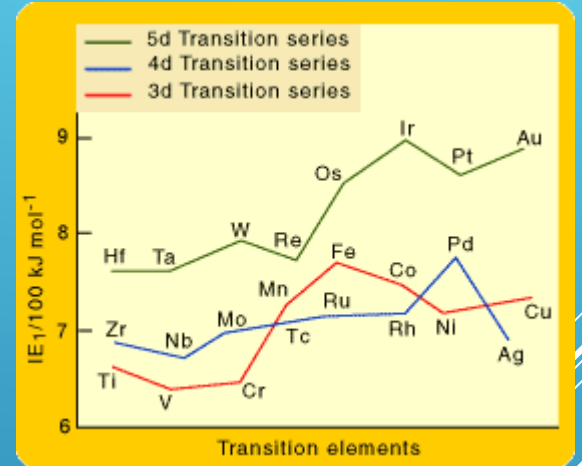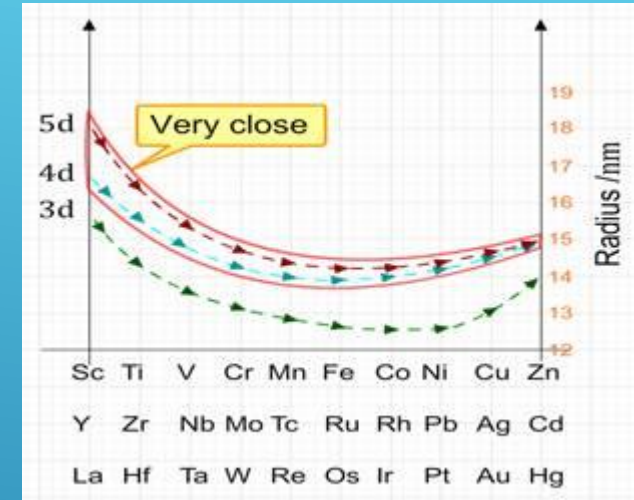
GENERAL TRENDS IN PROPERTIES OF THE FIRST ROW TRANSITION METALS

- **<u>Oxidation states</u>** : There are greater similarities in the properties of the transition elements of a horizontal row in contrast to the non-transition elements. However, some group similarities also exist. The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many d electrons (hence fewer orbitals available in which to share electrons with others) for higher valence (Cu, Zn). Thus, early in the series scandium(II) is virtually unknown and titanium (IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (no d electrons are involved). The maximum oxidation states of reasonable stability correspond in value to the sum of the s and d electrons upto manganese (Ti(IV)O_2, V(V)O_2^+, Cr(V1)O_4^{2-}, Mn(VII)O_4^-) followed by a rather abrupt decrease in stability of

  higher oxidation states, so that the typical species to follow are Fe(II,III), Co(II,III), Ni(II), Cu(I,II), Zn(II).

GENERAL TRENDS IN PROPERTIES OF THE FIRST ROW TRANSITION METALS

- **<u>Ionic radii</u>** : In general, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. This is because the new electron enters a *d* orbital each time the nuclear charge increases by unity. It may be recalled that the shielding effect of a *d* electron is not that effective, hence the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases. The same trend is observed in the atomic radii of a given series. However, the variation within a series is quite small.

GENERAL TRENDS IN PROPERTIES OF THE FIRST ROW TRANSITION METALS

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:

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

The yellow solution of sodium chromate is filtered and acidified

with sulphuric acid to give a solution from which orange sodium

dichromate, $Na_2Cr_2O_7$. 2H2O can be crystallised.

$2Na_2CrO_4 + 2\ H^+ ------> Na_2Cr_2O_7 + 2\ Na^+ + H_2O$

Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride. Orange crystals of potassium dichromate crystallise out.

$Na_2Cr_2O_7 + 2\ KCl ----> K_2Cr_2O_7 + 2\ NaCl$

POTASSIUM DICHROMATE ($K_2\ CR_2\ O_7$)

Properties : Potassium dichromate is a strong oxidising agent.

In acidic solution, its oxidising action can be represented as follows:

$Cr_2O_7^{2-} + 14H^+ + 6e^-$ ----------->$2Cr^{3+} + 7H_2O$ (E^0= 1.33V)

Thus, acidified potassium dichromate will oxidise iodide to iodine,

sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The

half-reactions are noted below:

$6 I^-$ -----------> $3I_2 + 6 e^-$; $3 Sn^{2+}$ ------> $3Sn^{4+} + 6 e^-$

$3 H_2S$ ----------> $6H^+ + 3S + 6e-$; $6 Fe^{2+}$ ----> $6Fe^{3+} + 6 e-$

The full ionic equation may be obtained by adding the half-reaction for

potassium dichromate to the half-reaction for the reducing agent,

for e.g.,

$Cr_2O_7^{2-} + 14 H^+ + 6 Fe^{2+}$ -------> $2 Cr^{3+} + 6 Fe^{3+} + 7 H_2O$
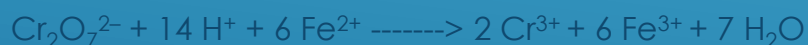
▸ The chromate and dichromate are inter convertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

$2 CrO_4^{2-} + 2H^+$ ----------> $Cr_2O_7^{2-} + H_2O$

$Cr_2O_7^{2-} + 2 OH^-$ ----------->$2 CrO_4^{2-} + H_2O$

POTASSIUM DICHROMATE(K_2 CR_2 O_7)

▸ Preparation :

Potassium permanganate is prepared by fusion of MnO_2 (which also occurs as the mineral <u>pyrolusite</u>) with an alkali metal hydroxide and an oxidising agent like KNO_3. This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.

$2MnO_2 + 4KOH + O_2 \text{------->} 2K_2MnO_4 + 2H_2O$

$3MnO_4^{2-} + 4H^+ \text{------>} 2MnO_4^- + MnO_2 + 2H_2O$

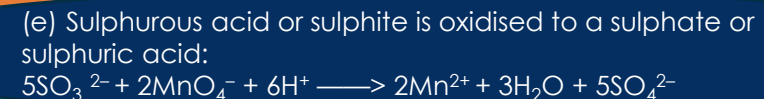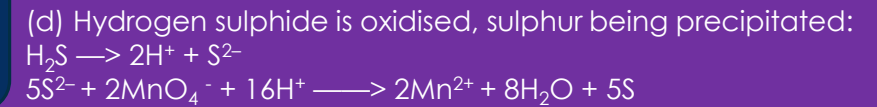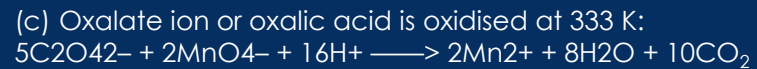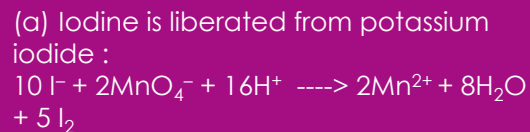POTASSIUM PERMANGANATE ($KMNO_4$)

▶ Properties :

Potassium permanganate forms dark purple (almost black) crystals which are isostructural with those of $KClO_4$.

▶ when heated it decomposes at 513 K.

$$2KMnO_4 \text{ ----------> } K_2MnO_4 + MnO_2 + O_2$$

▶ It has two physical properties of considerable interest: its intense colour and its diamagnetism.

▶ It is a strong oxidizing agent. A few important oxidising reactions of KMnO4 are given below:

(1). In acid solutions:

(c) Oxalate ion or oxalic acid is oxidised at 333 K:
$5C_2O4^{2-} + 2MnO4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H2O + 10CO_2$

(d) Hydrogen sulphide is oxidised, sulphur being precipitated:
$H_2S \longrightarrow 2H^+ + S^{2-}$
$5S^{2-} + 2MnO_4^{\,-} + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5S$

(a) Iodine is liberated from potassium iodide :
$10\,I^- + 2MnO_4^- + 16H^+ \text{ ----> } 2Mn^{2+} + 8H_2O + 5\,I_2$

(b) Fe^{2+} ion (green) is converted to Fe^{3+} (yellow):
$5Fe^{2+} + MnO_4^- + 8H^+ \text{ ------>} Mn^{2+} + 4H_2O + 5Fe^{3+}$

(e) Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:
$5SO_3^{\,2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$

POTASSIUM PERMANGANATE (KMNO$_4$)

(f) Nitrite is oxidised to nitrate:
$5NO^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

Properties :

Oxidising property :

(2) **In neutral or faintly alkaline solutions**:

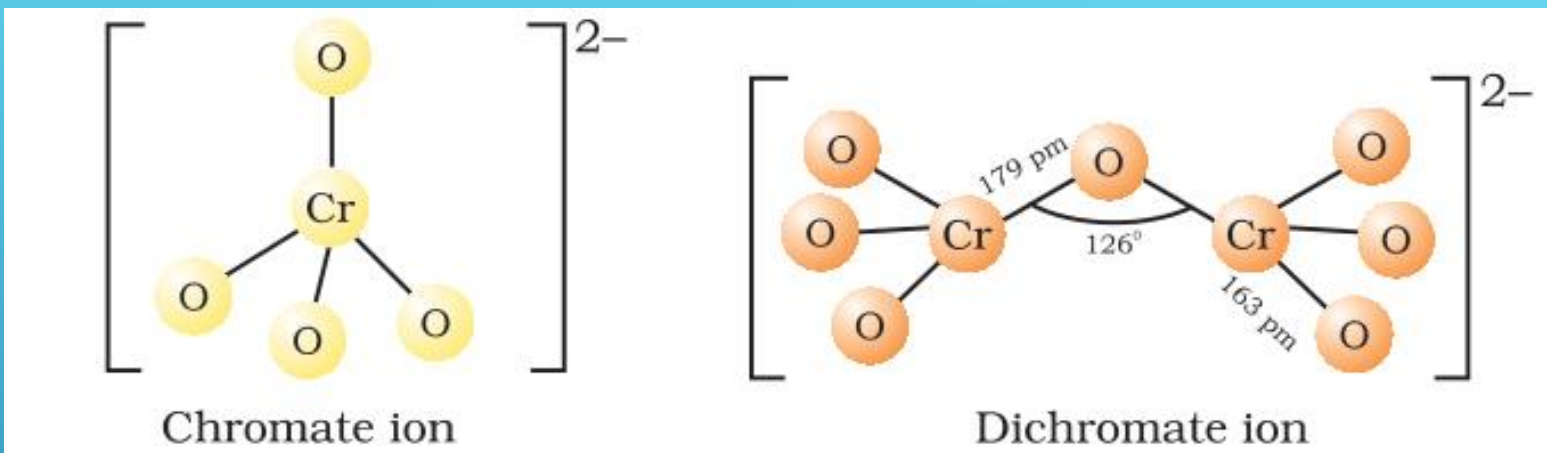(a) A notable reaction is the oxidation of iodide to iodate:

$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$

(b) Thiosulphate is oxidised almost quantitatively to sulphate:

$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

(c) Manganous salt is oxidised to MnO_2; the presence of zinc sulphate

or zinc oxide catalyses the oxidation:

$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

POTASSIUM PERMANGANATE (KMNO$_4$)

Chromate ion

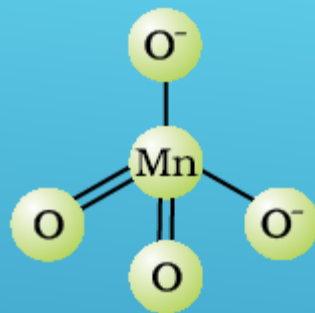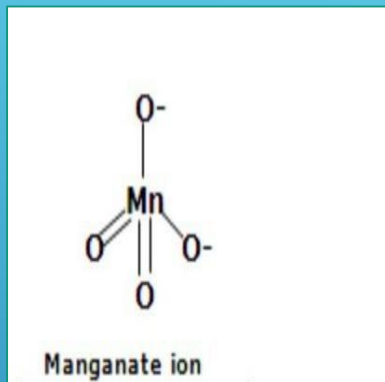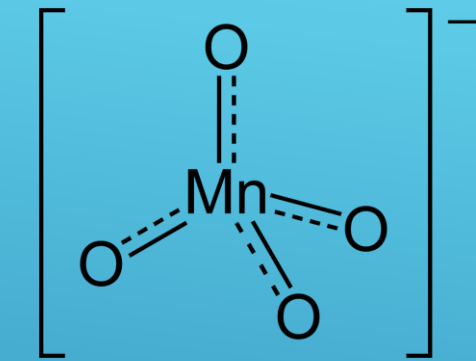Dichromate ion

The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedral sharing one corner with Cr–O–Cr bond angle of 126°.

STRUCTURES OF CHROMATE AND DICHROMATE IONS

Manganate ion

Tetrahedral manganate ion (green)

Permaganate ion

Tetrahedral permanganate ion (purple)

STRUCTURES OF MANGANATE AND PERMANGANATE IONS

THE –END