

TEACHER ORIENTED

UNIT VIII d & f Block Elements (5 : MARKS)

- 1) Electronic configuration
- 2) Occurrence and General characteristics of transition elements
- 3) General trends in properties
- 4) Preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$
- 5) Lanthanoids
- 6) Actinoids

STUDENT ORIENTED

d & f Block Elements

CONCEPT DETAIL

UNIT 8 d and f Block elements (5: MARKS) .

The elements belonging to groups 3 to 12 of the extended form of the periodic table are called d-block elements. They are present between s and p block elements and belong to 4th, 5th, 6th and 7th periods of periodic table. They are also called transition elements (elements having incomplete (n-1)d orbital in their atoms or in their simple ions). Their general electronic configuration is



All transition elements are d block elements but all d block elements are not transition metals e.g. the elements of group 12, namely Zn, Cd, Hg and Uub, though belong to d block but aren't considered as transition metals due to partially filled (n-1)d sub shell either in ground state or in ion.

There are four transition series which involve filling of (n-1)d sub shell

First series (3d series)- Sc(21) to Zn(30)

Second series (4d series) – Y(39) to Cd(48)

Third series (5d series)-La(57) to Hg(80)

Fourth series (6d series) Ac(89) to Uub(112) All the transition elements are metals. Iron is the most abundant transition metal in the earth's crust.

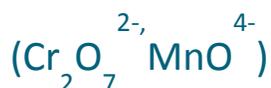
Technetium and all the members of fourth transition series are radioactive.

Tchnetium is the first synthetic element. The elements after uranium are termed transuranic elements, obtained artificially by nuclear transmutation. Transition elements have high density, hardness, high tensile strength, malleability, ductility, high thermal and electrical conductivity, high energy of atomisation, high melting and boiling points. Larger the number of unpaired electrons, stronger is the metallic bond and hence higher is the energy of atomisation and the melting point. All the transition elements are metals. Iron is the most abundant transition metal in the earth's crust. Tchnetium and all the members of fourth transition series are radioactive. Tchnetium is the first synthetic element. The elements after uranium are termed transuranic elements, obtained artificially by nuclear transmutation.

Transition elements have high density, hardness, high tensile strength, malleability, ductility, high thermal and electrical conductivity, high energy of atomisation, high melting and boiling points. Larger the number of unpaired electrons, stronger is the metallic bond and hence higher is the energy of atomisation and the melting point. The ionisation energy gradually increases with increase in atomic number along a given transition series. The ionisation energies of 3d and 4d elements are irregular. The first ionisation energy of 5d elements is higher than 3d and 4d elements belonging to same group due to lanthanide contraction. The ionisation energy gradually increases with increase in atomic number along a given transition series. The ionisation energies of 3d and 4d elements are irregular. The first ionisation energy of 5d elements is higher than 3d and 4d elements belonging to same group due to lanthanide contraction. The ionisation energy gradually increases with increase in atomic number along a given transition series. The ionisation energies of 3d and 4d elements are irregular. The first ionisation energy of 5d elements is higher than 3d and 4d elements belonging to same group due to lanthanide contraction. Transition metals show variable oxidation states (except first and last member of the

series). The most common oxidation state of the first transition series is +2 except scandium. The maximum oxidation state increases with atomic no up to Mn in the first transition series due to involvement of 4s electrons and unpaired electrons of 3d sub shell. Mn ($3d^5 4s^2$) shows maximum oxidation state of +7. Lower states are ionic while higher states are covalent.

The highest oxidation state shown by transition elements is +8 (by Ru and Os). Ions with the metal in high oxidation state tend to be good oxidising agents



and ions with the metal in low oxidising state are good reducing agents

($\text{V}^{2+}, \text{Cr}^{2+}$) Most of the transition metals and their compounds exhibit paramagnetism. Substances containing unpaired electrons are paramagnetic. Those containing no unpaired electrons are diamagnetic (Zn, Cd, Hg etc.)

Magnetic moment is given as $\mu = \sqrt{n(n+2)}$ BM

where n = number of unpaired electrons

In the first transition series Cr has maximum paramagnetism and amongst ions Mn^{2+} has maximum magnetic moment.

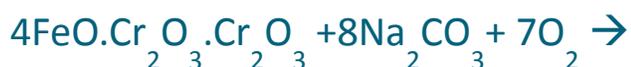
Most of the transition metal compounds (ionic as well as covalent) are coloured both in solid state and aqueous solution. Colour is due to the presence of incomplete d sub shell i.e. there is d-d transition. $\text{Sc}^{2+}, \text{Zn}^{2+}, \text{Cu}^+$ are colourless because they have either $3d^0$ or $3d^{10}$ configuration. Most of the transition metal compounds (ionic as well as covalent) are coloured both in solid state and aqueous solution. Colour is due to the presence of incomplete d sub shell i.e. there is d-d transition. $\text{Sc}^{2+}, \text{Zn}^{2+}, \text{Cu}^+$ are colourless because they have either $3d^0$ or $3d^{10}$ configuration. Colour is due to the presence of incomplete d sub shell i.e. there is d-d transition. $\text{Sc}^{2+}, \text{Zn}^{2+}, \text{Cu}^+$ are colourless because they have either $3d^0$ or $3d^{10}$ configuration.

Transition metals have a tendency to form complex compounds, interstitial compounds and alloys. They and their compounds act as good catalysts. Iron, cobalt and nickel are termed ferrous metals. Copper, silver and gold are called coinage metals. Zinc, cadmium and mercury are called zinc metals. The transition metals vary widely in their chemical behaviour. Many of them are sufficiently electropositive to dissolve in mineral acids though few are noble. Of the first series, with the exception of copper, all the metals are relatively reactive.

The transition metals react with a number of non metals like oxygen, sulphur, halogens etc to form binary compounds. The first series transition metal oxides are formed from the reactions of metals with oxygen at high temperatures. These oxides dissolve in acids and bases to form oxo-metallic salts. Potassium dichromate and potassium permanganate are common examples.

Preparation-

$K_2Cr_2O_7$ is prepared from the chromite ore. The finely powdered ore is mixed with sodium carbonate and the mixture is fused in reverberatory furnace in excess of air. The roasted mass is extracted with water and the solution is treated with conc. H_2SO_4 . $Na_2SO_4 \cdot 10H_2O$ being less soluble crystallises out and is filtered. Hot solution of $Na_2Cr_2O_7$ is treated with calculated amount of KCl when $K_2Cr_2O_7$ crystals are obtained.



$K_2Cr_2O_7$ is an orange crystalline compound. It decomposes on heating to give

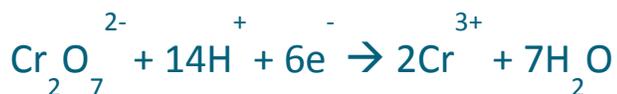


Its acidic solution contains dichromate ions while alkaline solution contains chromate ions. It is a strong oxidising agent. Acidified solution is used as a

primary standard in volumetric analysis for the estimation of reducing agents such as ferrous sulphate, oxalic acid, etc. On heating with a chloride (NaCl) and conc. H_2SO_4 , red vapours of CrO_2Cl_2 are evolved. Its equivalent mass in acidic medium is $\text{Mol. mass}/6 = 49$

Potassium dichromate acts as oxidising agent in acidic medium.

Acidic Solution-



NOTE- Ferrous salts are oxidised to ferric salts

Sulphites are oxidised to sulphates

Iodide is oxidised to iodine

In alkaline solution Chromate ions are present while in acidic solution dichromate ions are present. Both the ions are in equilibrium at pH=4



Preparation -

KMnO_4 is prepared from pyrolusite ore (MnO_2) fine. The finely powdered ore is fused with KOH or K_2CO_3 in presence of air or oxidising agent when K_2MnO_4 (manganate) is formed. It is oxidised chemically by using H_2SO_4 , CO_2 or Cl_2 or electrolytically.

It is a deep purple crystalline compound, moderately soluble in water. It decomposes when heated giving O_2 . It acts as a strong oxidising agent in neutral, alkaline and acidic medium. The acidified KMnO_4 (dil. H_2SO_4) is used as a volumetric reagent. It is not a primary standard i.e. it is first standardised and then used. Its equivalent mass in acidic medium is $\text{Mol. Mass}/5 = 31.6$

Alkaline KMnO_4 solution is called **Baeyer's reagent** used in organic analysis. It has tetrahedral structure.

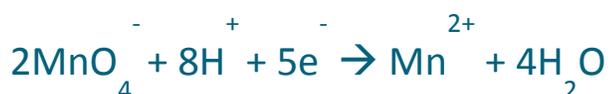
Potassium permanganate acts as oxidising agent in alkaline as well as acidic solution.

Alkaline Solution-

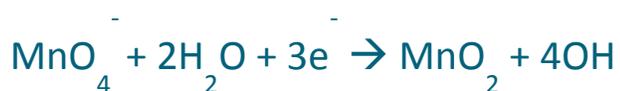


NOTE- Iodides are oxidised to Iodates

Acidic Solution-



Neutral Medium-



In MnO_4^- ion manganese is in +7 state with d^0 configuration. Hence, there is no d-d transition. The pink colour is due to charge transfer from oxygen to manganese atom.

There is gradual decrease in the atomic and ionic sizes of these metals along the series. These are called lanthanide contraction and actinide contractions.

Lanthanide contraction is responsible for various changes in chemical properties of the elements succeeding them.

All the lanthanides are rather soft white metals. They react easily with water to give solutions giving +3 ions. The principal oxidation state is +3 although +4, +2 oxidation states are also exhibited. Those having +2 change to +3 and act as reducing agents. Those having +4 tend to change to +3 and act as oxidising agents. The maximum oxidation state shown by actinides is +7. U, Np and Pu show oxidation state of +6. However, all the actinides also show +3 oxidation state.

Paramagnetism is shown by the positive ions of lanthanides except La^{3+} ($4f^0$) and Lu^{3+} ($4f^{14}$). Most of the trivalent lanthanide ions are coloured. This is due to f-f transition. Actinide cations are also generally coloured. The cations having $5f^7$ or $5f^{14}$ configuration are colourless. $\text{La}(\text{OH})_3$ is most basic while $\text{Lu}(\text{OH})_3$ is least acidic.

INSTANT DIAGNOSTIC QUESTIONS

1. Why do transition elements show variable oxidation states?
2. What are inner transition elements?
3. Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?
4. What are different oxidation states exhibited by Lanthanides?

LEVELWISE ASSIGNMENTS

LEVEL I : SLOW BLOOMERS

1. What are Transition elements ?
2. Why are transition elements coloured ?

LEVEL II : AVERAGE

1. Why are Mn^{2+} compounds more stable than Fe^{2+} compounds towards oxidation to +3 state?
- 2- (a) What is lanthanide contraction? What effect does it have on the chemistry of the elements, which follow lanthanoids?
(b) The chemistry of actinoid elements is not so much smooth as that of lanthanoids. Justify these
3. Why do Zr and Hf exhibit almost similar properties.
4. Why is $\text{La}(\text{OH})_3$ stronger base than $\text{Lu}(\text{OH})_3$.
5. The enthalpies of atomisation of the transition metals are high.
6. The transition metals generally form coloured compounds.
7. Transition metals and their many compounds act as good catalyst.
8. Transition metals have a strong tendency to form complexes

LEVEL III : BRIGHT LEARNER

- 1- (a) Describe the general trends in the following properties of the first series of the transition elements:- (i) Stability of +2-oxidation state (ii) Formation of oxometal ions
(b) Write steps involved in the preparation of KMnO_4 from K_2MnO_4
2. What is meant by disproportionation? Give two examples.

PROJECTS

Compare chemistry of Lanthanoids & actinoids.

Survey & Find out the commonly used lanthanoids.