

ST. LAWRENCE HIGH SCHOOL A JESUIT CHRISTIAN MINORITY INSTITUTION STUDY MATERIAL FOR CHEMISTRY (CLASS-12) <u>TOPIC-</u> d and f-BLOCK ELEMENTS <u>PREPARED BY</u>: MR. ARNAB PAUL CHOWDHURY SET NUMBER-11 DATE: 30.11.2020



The d-block of the Periodic Table contains the elements of the groups 3-12 in which the d·orbitals are progressively filled. There are mainly three series of the elements, 3d-series (Sc to Zn) 4d-series (Y to Cd) and 5d-series (La to Hg omitting Ce to Lu). The fourth 6d-series which begins with Ac is still incomplete.

Transition Elements

Elements having partially filled d-orbitals in ground state or in excited state, are known as transition elements. They have been placed in the centre of the Periodic Table between s-block and p-block elements.

Iron is the most abundant and widely used transition metal.

General Electronic Configuration of Transition Elements

Transition elements have the electronic configuration $(n - 1)d^{1-10} ns^{o-2}$, Zn, Cd, Hg, the end members of first three series have general electronic configuration (n - 1)d10ns2. These elements do not show properties of transition elements to any extent and are called nontypical transition elements.

Electronic Configuration of Transition Elements

3d-Series			4d-Series			5d-Series			
At. no.	Element	Electronic configuration	At. no.	Element	Electronic configura- tion	At. no.	Element	Electronic configura- tion	
21	Sc	[Ari3d* 4s ²	39	Y	[Kr]4 d ³ 5s ²	57	La	[Xe]5d ¹ 6s ²	
22	Ti	$[Ar]3o^2 4s^2$	40	Zr	$[Kr]4 d^2 5s^2$	72	Hf	$[Xe]4t^{14}5d^26s^2$	
23	V S	[Ar]3d ³ 4s ²	41	Nb	[Kr]4 d ⁴ 5s ¹	73	Та	[Xe]4 ¹⁴ 5d ³ 6s ²	
24	Ci I	[Ar]3d ⁻⁵ 4s ¹	42	Mo	[Kr]4 d ⁵ 5s ¹	74	: W	LXe]41 ¹⁴ 5d ⁴ 6s ²	
25	Mл	[Ari3d ⁵ 4s ²	4.3	Te	[Kr]4 d ⁵ 5s ²	75	Re	[Xe]4 ¹⁴ 5d ⁵ 6 s ²	
26	Fe	(Ar)30 ⁶ 4s ²	44	Ru	[Kr]4 d ⁷ 5s ¹	76	Os	 [Xe]4/ ¹⁴ 5d ⁶ 5s ²	
27	Co	(Ar,3d ⁷ 4s ²	45	Rh	[Kri4 d ⁸ 5s ¹	77]•	[Xe]4/ ¹⁴ 5d ⁷ 5 s ²	
28	Ni	LA1.3d ⁻⁸ 4s ²	46	Pd	[Kr]4 d ¹⁰ 5s ⁰	78	Pţ	[Xe]4/14 5d 96 s ¹	
39	Cu	[Ar]3d ¹⁰ 4s ¹	17	Ag	[Kr]4 d ¹⁰ 5s ¹	79	Au	[Xe]4/ ¹⁴ 50 ¹⁰ 6 s ¹	
30	Zn	[Ar]3d ¹⁰ 4s ²	48	Cd	$[Kr]4 d^{10} 5s^2$	80	Hg	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²	

General Physical Properties of Transition Elements

(i) **Atomic and ionic size** lons of the same charge in a given series exhibit regular decrease in radius with increasing atomic number, because the new electron enters in a d – orbital and nuclear charge increases by unity.

In last of the series, a small increase in size is observed due to electron-electron repulsion.

(Atomic and ionic radii increase from 3d-series to 4d-series but the radii of the third (Sd) series elements are virtually the same as those of the corresponding member of the second series. It can be explained on the basis of lanthanoid contraction [poor shielding of 4f].

Due to lanthanide contraction Zr and Hf Have almost similar radii.

(ii) **Ionisation enthalpies** In a series as we move from left to right, ionization enthalpy increases due to increase in nuclear charge but not in regular trend.

The irregular trend in the first ionisation enthalpy of the 3d metals, though of little chemical significance, can be accounted by considering that the removal of one electron alters the relative energies of 4s and 3d-orbitals.

(iii) **Oxidation states** Transition metals show variable oxidation state due to two incomplete outermost shells. Only stable oxidation states of the first row transition metals are Sc(+3), Ti(+4). V(+5), Cr(+3, +6), Mn(+2, +7), Fe(+2. +3). Co(+2, +3). Ni(+2), Cu(+2), Zn(+2).

The transition elements in their lower oxidation states (+2 and +3) usually forms ionic compounds. In higher oxidation state compounds are normally covalent.

Only Os and Ru show +8 oxidation states in fluorides and oxides. Ni and Fe in Ni(CO)₄ and Fe(CO)₅ show zero oxidation state.

(iv) **Enthalpy of atomisation** Transition elements exhibit higher enthalpies of atomization. Because of the presence of a large number of unpaired electrons in their atoms, they have stronger interatomic interactions and hence, stronger bond.

(v) Trends in the M²⁺ / M standard electrode potentials

 $E_{M}^{o_{2^{+}}/M}$ is governed by three factors. Enthalpy of sublimation, enthalpy of ionisation and enthalpy of hydration.

The irregular trend in 3d series is due to irregular variation in ionisation enthalpy and heat of sublimation.

Except copper 3d – elements are good reducing agents.

[If sum of the first and second ionisation enthalpies is greater than hydration enthalpy standard potential $(E_{M}^{o^{2+}}/M)$ will be positive and reactivity will be lower and vice-versa.]

(vi) **Melting and boiling point** Due to strong metallic bond, they have high m.p. and b.p. The m.p. of these elements becomes maximum and then decreases with the increase in atomic number.

Manganese and technetium show abnormal values in the trend. Tungsten has the highest m.p. (3410°C).

Mercury is liquid at room temperature (m.p. -38.9° C) due to absence of unpaired electrons, and weak metallic bonding.

(vii) **Density** d-block elements have high density because of their small atomic size and strong metallic bonding.

Density	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
g/cm ³	3.0	4.54	6.12	7.19	7.40	7.87	8.74	8.90	8.92	7.13

Osmium has slightly lower density (22.52 g cm⁻³) as compared to iridium (22.61 g cm⁻²). Thus, iridium has the highest density among transition metals.

(viii) Atomic volume Atomic volume decreases along the period due to decrease in atomic size.(ix) Reactivity d-block elements are less reactive due to high ionisation energies. Some are

almost inert and known as noble metals, e.g., Au; Pt, Os, Ir, etc

(xii) **Complex formation** They are well known to form a large number of complex compounds mainly due to

(a) small atomic size and high nuclear charge

(b) presence of partly filled or vacant d-orbitals, e.g., K₄[Fe(CN)₆]

(xiii) **Coloured ions** Colour exhibited by transition metal ions is due to the presence of unpaired electrons in d-orbitals and is due to the d-d transitions of electrons, when invisible light is incident on the ion.

Colour of a complex depends on the metal, its oxidation state and its ligands, e.g., $[Cu(H_2O)_4]^{2+}$ is pale blue while $[Cu(NH_3)_4]^{2+}$ is dark blue. $CuSO_4 \cdot 5H_2O$ is blue in colour and anhydrous $CuSO_4$ is colourless.

Charge transfer also give intense colour e.g., MnO_4^- ion does not contain any unpaired delectron. Its purple colour is due to charge transfer from O to MD, thus O^{-2} change to O^- and Mn(VII) to Mn(VI). Charge transfer is possible only when the energy levels on the two different atoms involved are fairly close.

(xiv) Magnetic properties

(a) **Paramagnetic** nature is due to the presence of unpaired electrons in d-orbitals. Paramagnetic character increases with increase in the number of unpaired electrons and highest for Mn(II) [among 3d-series].

(b) Diamagnetic substances are repelled by applied magnetic field and have no unpaired electron.

(c) In ferromagnetism, permanent magnetic character is acquired by substance e.g., Fe.

Magnetic moment is given by

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

Where, n = number of unpaired electrons and BM = Bohr magneton (unit of magnetic moment).

(xv) **Catalytic properties** The transition metals anti their compounds behave like catalyst due to (a) the presence of partly filled d-orbitals resulting in variable oxidation states.

(b) formation of intermediate complex with reactants by lowering the energy of activation.

(c) their rough surface area which provides active sites for adsorption of reactant molecules.

Iron in the preparation of NH₃ (Haber's process), finely divided nickel for hydrogenation, Pt in the preparation of nitric acid (Ostwald's process) Some important catalysts having transition metals are

- 1. Ziegler Natta catalyst : $TiCI_4 + (C_2H_5)_3 AI$
- 2. Lindlar's catalyst : Pd / BaSO₄
- 3. Wilkinson's catalyst : [Ph₃P₃RhCl
- 4. Adam's catalyst : Pt / PtO

5. Brown's catalyst or P-2 catalyst: Nickel boride

(xiv) **Formation of alloys** d-block elements have a strong tendency to form alloys, because their atomic :;ires are Vel')' similar and in the crystal lattice one metal can be readily replaced by another. Alloys so formed have high m.p.. The metals Mo, W, Cr, Ni, and V are used for the production of stainless steel.

Amalgam is an alloy formed by mercury with other metals, Iron and platinum do not form any alloy with mercury.

List of Alloys

	Alloy	Composition (%)	Uses
1.	Stainless	Fe = 73, Cr = 18, NI = 8, C (traces)	Cutlery, machine parts
2.	Coinage alloy or Coinage silver	Ag = 92.5, Cu = 7.5	Coins, Jewellery
3	Dental alloy	Ag = 33, $Hg = 52$, $Sn = 12.5$, Cu = 2, $Zn = 0.5$	For filling teeth
4	Brass	Cu = 80, Zn = 20	Utensils, condenser tubes
5.	Bronze	Cu = 80, Sn = 20	Utensils, statues, coins
6.	Gun metal	Cu = 87, Sn = 10, Zn = 3	Gun, gears
7.	Bell metal	Cu = 80, Sn = 20	Bells, Gongs
8.	German silver	Cu = 60, Zn = 20, Ni = 20	Cutlery, resistant wires
9.	Duralumin	Al = 95, Cu = 4, Mg and Mn : 1%	Air ships
10.	Misch metal	Ce(25%) + lanthanide metals + 5% Fe + traces of S, C, Si, Ca, Al	Lighter flints

(xv) **Interstitial compounds** The vacant space present in a crystal lattice is known as interstitial site or void. The non-metal atoms (e.g., H, N, C, etc.) due to their small size when occupy such place, the resulting compound is known as interstitial compound. Such compounds are hard and rigid, e.g., cast iron and steel.

(xvi) **Non-stoichiometric compounds** The compounds not navm the elements in the exact ratio as in the ideal crystal are known non-stoichiometric compounds e.g., in $Fe_{0.94}O_1$ the Fe : O is approx 0.94 : 1 and not exactly 1 : 1. It is due to the variability of Oxidation state in the transition metal. These elements form such compound by trapping H, B, C and N etc. (xvii) **Spinel** These are the mixed oxides in which oxygen atoms constitute a fcc lattice e.g., $ZnFe_2O_4$ It is a normal spinel in which the trivalent ions occupy the octahedral holes and divalent ions occupy the tetrahedral holes.

In inverse spinel, the trivalent ion occupy the tetrahedral holes and divalent ion occupy the octahedral holes. e.g., $FeFe_2O_4$ or Fe_3O_4 .

Some important reagents having transition metals

1. Baeyer's reagent Dilute alkaline KMnO₄ used to test the presence of unsaturation.

2. **Tollen's reagent** Ammoniacal solution of $AgNO_3$, i.e., $[Ag(NH_3)_2]OH$. used to test the aldehyde group.

3. Nessler's reagent Alkaline solution of K_2HgI_{43} (g) and NH: .

4. **Benedict's solution** CuSO₄ solution + sodium citrate + Na₂CO₃, used to test the aldehyde group.

5. Lucas reagent HCl (cone.) + anhydrous $ZnCl_2$, used to distinguish between 1°, 2° and 3° alcohols.

Applications of transition elements

1. A mixture of TiO_2 and $BaSO_4$ is called titanox and a mixture of $ZnS + BaSO_4$ is called lithopone.

2. TiCl₂ and TiO₂ are used in smoke screens. TiO₂ is also used as white pigment of paints.

3. Tantalum is used in surgical venables and analytical weights.

4. Chromium is used in stainless steel and chrome plating.

5. Mo is used in X-rays tubes. Pt is used in resistance thermometers.

6. Cd is used for making joints in jewellery.

7. Ce is used as a scavenger of oxygen and sulphur in many metals-

8. Alkaline solution of K_2HgI_4 is called Nessler's reagent and is used to test the presence of ammonium ion (NH_4^+) .

1. Potassium Dichromate (K₂ Cr₂ O₇) Ore Ferrochrome or chromite (FeO· Cr₂O₃) or (FeCr₂O₄) Preparation $4FeO \cdot Cr_2O_3 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ yellow $2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$ orange $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

Sodium dichromate is more soluble than potassium dichromate.

Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solutions.



Properties Sodium and potassium dichromates are strong oxidising agents, thus, acidified K_2Cr_{27} will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).

$$\begin{array}{rcl} \mathrm{Cr}_{2}\mathrm{O}_{7}^{2-} + 14\mathrm{H}^{+} + 6\mathrm{I}^{-} &\longrightarrow & 2\mathrm{Cr}^{3+} + 7\mathrm{H}_{2}\mathrm{O} + 3\mathrm{I}_{2} \\ \mathrm{Cr}_{2}\mathrm{O}_{7}^{2-} + 3\mathrm{H}_{2}\mathrm{S} + 8\mathrm{H}^{+} &\longrightarrow & 2\mathrm{Cr}^{3+} + 3\mathrm{S} + 7\mathrm{H}_{2}\mathrm{O} \\ \mathrm{Cr}_{2}\mathrm{O}_{7}^{2-} + 14\mathrm{H}^{+} + 3\mathrm{Sn}^{2+} &\longrightarrow & 3\mathrm{Sn}^{4+} + 2\mathrm{Cr}^{3+} + 7\mathrm{H}_{2}\mathrm{O} \end{array}$$

Uses

1. K_2Cr_{27} is used as oxidising agent in volumetric analysis.

2. It is used in mordant dyes, leather industry, photography (for hardening of film).

3. It is used in chromyl chloride test.

4. It is used in cleaning glassware.

2. Potassium Permanganate (KMnO ₄) Ore Pyrolusite (MnO₂) Preparation

 $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$ green

$$3MnO_4^2 + 4H^+ \longrightarrow 2MnO_4^- + MnO_9 + 2H_9O_9$$

Commercial preparation



Properties KMnO₄ acts as strong oxidising agent.

1. In the presence of dilute H_2SO_4 , $KMnO_4$ is reduced to manganous salt.

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

Acidic $KMnO_4$ solution oxidises oxalates to CO_2 , iron(II) to iron (III), nitrites to nitrates and iodides to iodine. The half-reactions of reductants are

 $\begin{array}{rcl} 5\mathrm{C}_{2}\mathrm{O}_{4}^{2-} &\longrightarrow & 10\mathrm{CO}_{2} + 10e^{-} \\ & & 5\mathrm{Fe}^{2+} &\longrightarrow & 5\mathrm{Fe}^{3+} + 5e^{-} \\ \\ 5\mathrm{NO}_{2}^{-} + 5\mathrm{H}_{2}\mathrm{O} &\longrightarrow & 5\mathrm{NO}_{3}^{-} + 10\mathrm{H}^{+} + 10e^{-} \\ & & 10\mathrm{I}^{-} &\longrightarrow & 5\mathrm{I}_{2} + 10e^{-} \end{array}$

To acidify $KMnO_4$, only H_2SO_4 is used and not HCI or HNO_3 because HCI reacts with $KMnO_4$ and produce Cl_2 while HNO_3 , itself acts as oxidising agent.

2. In alkaline medium, $KMnO_4$ is reduced to insoluble MnO_2 .

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

Alkaline or neutral KMnO₄ solution oxidises I⁻ to IO⁻³, S₂O^{2⁻₃ to SO^{2⁻₄</sub>, Mn²⁺ to MnO₂, etc. Aqueous KMnO₄, reacts with NH\$ to liberate N₂ gas.}}

 $2KMnO_4 + 2NH_3 \rightarrow 2KOH + 2MnO_2 + N_2 + 2H_2O$

Uses

KMnO₄ is used

(i) in laboratory preparation of CI_2 .

(ii) as an oxidising agent and disinfectant.

(iii) in making Baeyer's reagent.

Structures



3. **Copper Sulphate** (CUSO₄ \cdot 5H₂O) It is also known as blue vitriol.

Method of preparation It is obtained by the action of dil H_2SO_4 on copper scrap in the presence of air.

$$2\mathrm{Cu} + 2\mathrm{H}_2\mathrm{SO}_4 + \mathrm{O}_2 \longrightarrow \mathrm{CuSO}_4 + 2\mathrm{H}_2\mathrm{O}_4$$

Properties

1. On heating it turns white due to loss of water of crystallisation.

At 1000 K, CuSO₄ decomposes into CuO and So₃

$$CuSO_4 \xrightarrow{1000 \text{ K}} CuO + SO_3$$

2. It gives blue solution with NH_4OH and white ppt of Cu_2I_2 with KI.

Uses It 1S used in electroplating, as mordant in dyeing, in making bordeaux mixture [(Ca(OH) $_2$ + CuSO₄)], etc.

4. Silver Nitrate (AgNO₃)

It is also called Lunar caustic.

Method of preparation It is prepared by heating silver with dilute nitric acid



Properties

1. It is colourless, crystalline compound which blackens when comes in contact of organic substances (skin, cloth, etc.)

2. With potassium dichromate, it gives red ppt of Ag₂CrO₄.

3. On strong heating, it decomposes to metallic silver.

$$2 \operatorname{AgNO}_{3}(s) \xrightarrow{\Delta} 2 \operatorname{Ag}(s) + 2 \operatorname{NO}_{2}(g) + \operatorname{O}_{2}(g)$$

4. Ammoniacal solution of silver nitrate is known as Tollen's reagent.

Uses It is used as laboratory reagent, in silvering of mirror, in the preparation of inks and hair dyes, etc.

Inner-Transition Elements

The elements in which the filling of atomic orbitals by electrons take place in {-subshells, two levels inside the outer subshell, are known as inner-transition elements. They are also known as f-block elements

Classification of f-block Elements

They have been classified into two series.

(a) **4f-series (first inner-transition series)** The last electron enters in 4f-orbital. The elements belonging to this series are also known as **lanthanoids.**

(b) **5f-series (second inner-transition series)** The last electron enters in 5f-orbital. The elements belonging to this series are also known as **actinides**.

Lanthanides

The fifteen elements from lanthanum (at. no. 57) to lutetium (at. no. 71) are known as lanthanides or rare earths. Their properties are as follows :

1. Electronic configuration

The general electronic configuration of these elements is $[Xe]4f^{0-14} 5d^{0-1} 6s^2$. The lanthanum, electronic configuration $[Xe]4f^0 5d^1 6s^2$ and lutetium, electronic configuration $[Xe]4f^{14} 5d^1 6s^2$, have no partially filled 4f-orbital in their ground state, are considered as lanthanides due to their properties close to these elements.

2. Oxidation state

The most common and most stable oxidation state of lanthanides is +3 but some elements also exhibit +2 and +4 oxidation states in which they leave behind stable ions, e.g.,

$$Eu^{2+} = [Xe]4f^7$$
, $Yb^{2+} = [Xe]4f^{14}$
 $Ce^{4+} = [Xe]4f^0$, $Tb^{4+} = [Xe]4f^7$

An aqueous solution of Ce⁴⁺ is a good oxidising agent. The Eu²⁺ and Yb²⁺ can exist in aqueous solution and are good reducing agents. But there are exceptions also e.g.,

$$Sm^{2+} = [Xe]4f^6$$
 $Tm^{2+} = [Xe]4f^{13}$
 $Pr^{4+} = [Xe]4f^1$

3. Magnetic properties

Magnetic properties have spin and orbit contributions. Hence, magnetic moments are given by the formula

 $\mu = \sqrt{4S(S + 1)} + L(L + 1)$

Where, L = orbital quantum number, S = spin quantum number

All lanthanide ions with the exception of La^{3+} , Lu^{3+} and Ce^{4+} , are paramagnetic in nature.

4. Lanthanoid contraction

Steady decrease in the atomic and ionic (Ln³⁺) radii as the atomic Dumber of the lanthanide elements increases is called lanthanide contraction. This is because the additional electron goes to 4f-subshell and 4f-orbitals being large and diffuse, have poor shielding effect. The effective nuclear charge increases which causes the contraction in the size of electron charge cloud. This contraction in size is quite regular and is known as lanthanoid contraction.

The f- f transitions are possible due to absorption of light from the visible region.

Consequences of lanthanoid contraction

(i) Covalent character of cations increase.

(ii) The electronegativity of trivalent ions increases slightly.

(iii) There is decrease in basic strength of oxides and hydroxides from La to Lu.

(iv) There is small increase in standard electrode potential values.

(v) Sizes of Zr and Hf; Nb and Ta are similar, so they are called chemical twins.

5. Colour

The species containing unpaired electrons are coloured and so on in the case of lanthanide ions.

6. Melting and boiling pOints

Lanthanides have high melting and boiling points but there is no regular trend.

7. Density

Lanthanides have densities varying . from 6.67 to 9.7 g cm⁻³, but there IS no regular trend for these values.

8. Electronegativity

For lanthanides the electronegativity values are almost same as that of \$-block elements. Lanthanides form ionic compounds.

9. Ionisation energies

The ionisation energy values of lanthanoids are not very high due to their large size and comparable with those of alkaline earth metals.

10. Complex compound

Due to their large ionic SIze, they have little tendency to form complexes.

11. Reactivity

Due to their low values of ionisation energies, the lanthanides are very reactive.

12. Alloys

They form alloy especially with iron e.g., misch metal rare earths 94 $_$ 95%, iron \sim 5% and S, C, Ca and AI in traces. Mg mixed with 3% misch metal is used for making jet engine parts.

Actinides

The fifteen elements from actinium (at. no. 89) to lawrencium (at. no. 103) are known as actinides and constitute the 5f series. From neptunium to onwards the elements are man-made (artificially prepared) and also known as transuranic elements.

1. Electronic configuration

The last electron in such elements enters in the 5f atomic orbital.

Their general electronic configuration is

[Rn]5 $f^{0-14} 6d^{0-17s^2}$

There is not much difference between the energies of 5f and 6d, so it is difficult to predict whether the electron has entered in 5f or 6d.

2. Oxidation state

The common oxidation state is +3 but other oxidation states are also exhibited by actinides upto the maximum being +7.

3. Magnetic properties

The magnetic moments of actinide ions are smaller than theoretical values. It is hard to interpret due to large spin orbit coupling.

4. Actinide contraction

It is similar to lanthanide contraction due to poor shielding or 5f – electrons

5. Melting and boiling points

They have high values for melting and boiling points but there is no regular trend.

6. Density

The value of density vary from 7.0 gcm⁻³ to 20 gcm⁻³. Again there is no regular trend in density.

7. Reducing character

They are strong reducing agents as they have high E° values approximately 2.0 V.

8. Reactivity

Actinide are very reactive in nature and combine with oxygen and halogens like lanthanoids.

9. Coloured ions

Actinide ions are coloured due to the presence of unpaired electrons and f-f transitions.

10. Complex formation

They have higher tendency to form complex compounds.

PREPARED BY: MR. ARNAB PAUL CHOWDHURY