B.Sc. Part-II (Sub), Paper-II, Group-B (Inorganic Chem)

Unit-2 General characteristics of Transition metals (d-block elements)

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⟹ Transition metals?

Those elements in which last or differentiating electron enters or occupies in penultimate, i.e. (n-1) d-orbitals are called d-block elements. d-block elements are called transition metals since properties of these elements are intermediate of that of s & p-block elements. These elements are placed between s & p-block elements in modern periodic table. d-block elements or, transition metals are 40 (4 series), and members of Gr. 3 to 12 of modern P.T

(i) 3d or, 1st transition series: Sc_{21} ($3d^14s^2$) to Zn_{30} ($3d^{10}4s^2$) (10 elements)

(ii) 4d or 2nd transition series: Y_{39} ($4d^15s^2$) to Cd_{48} ($4d^{10}5s^2$) (10 elements)

(iii) 5d or, 3rd transition series: La_{57} ($5d^16s^2$), Hf_{72} ($5d^26s^2$) to Hg_{80} ($5d^{10}6s^2$) (10 elements)

(iv) 6d or, 4th transition series: Ac_{89}, Rf_{104} to Cn_{112} (10 elements)

⟹ General characteristics of Transition metals?

1. Electronic Configuration: The general electronic configuration of transition metals is:

$$[\text{Noble gas}](n-1)d^{1-10}ns^{0,1 \text{ or } 2}$$

Outer electronic configuration: $(n-1)d^{1-10}ns^{0,1 \text{ or } 2}$ ($n = 4$ to 7)

* Electronic configuration of transition metals (except Gr. 12) have both inner, i.e. (n-1) d & outer ~~orbit~~ orbitals are incomplete. Gr. 12 elements have only outermost orbit incomplete like normal elements, and so they resemble more with them.

* Elements having d^5s^1 or d^5 and $d^{10}s^2$ or d^{10} conf. are extra stable due to symmetrical (half or fully occupy) conf. e.g; Cr_{24} shows ele. conf. $3d^54s^1$, not $3d^44s^2$ and Cu_{29} shows ele. conf. $3d^{10}4s^1$, not $3d^94s^2$.

2. Oxidation states: Transition metals generally show variable valencies or oxidation states, i.e; transition metals form compounds in different valencies/oxidation states. The various O. states of transition metals are related to their outer electronic configuration. O. states of transition metals of 3d series are given below:

Element	Outer electronic configuration	Oxidation states
Scandium (Sc_{21})	$3d^14s^2$ or, [↿│ │ │ │] [⇅] 3d 4s	(+2), +3
Titanium (Ti_{22})	$3d^24s^2$ or, [↿│↿│ │ │] [⇅] 3d 4s	(+2), +3, +4
Vanadium (V_{23})	$3d^34s^2$ or, [↿│↿│↿│ │] [⇅] 3d 4s	+2, +3, +4, +5
Chromium (Cr_{24})	$3d^54s^1$ or, [↿│↿│↿│↿│↿] [↿] 3d 4s	(+1), +2, +3, (+4), (+5), +6
Manganese (Mn_{25})	$3d^54s^2$ or, [↿│↿│↿│↿│↿] [⇅] 3d 4s	+2, +3, +4, (+5), +6, +7
Iron (Fe_{26})	$3d^64s^2$ or, [⇅│↿│↿│↿│↿] [⇅] 3d 4s	+2, +3, (+4), (+5), (+6)
Cobalt (Co_{27})	$3d^74s^2$ or, [⇅│⇅│↿│↿│↿] [⇅] 3d 4s	+2, +3, (+4)
Nickel (Ni_{28})	$3d^84s^2$ or, [⇅│⇅│⇅│↿│↿] [⇅] 3d 4s	+2, (+3), (+4)

Element	O. Electronic Configuration	Oxidation states
Copper (Cu_{29})	$3d^{10}4s^1$ or, $\underbrace{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}}_{3d}\ \underbrace{\boxed{\uparrow\downarrow}}_{4s}$	+1 , +2
Zinc (Zn_{30})	$3d^{10}4s^2$ or, $\underbrace{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}}_{3d}\ \underbrace{\boxed{\uparrow\downarrow}}_{4s}$	+2 (Constant)

* Oxidation states within small brackets ( ) are unstable and Circle are most stable, common and maximum. Os & Ru show maximum Oxidation state +8.

* Minimum or lowest Oxidation state shown by transition metal is equal to the number of ns electron(s). Lowest O. states for Cr, Cu are +1 while for other metals is +2 (3d-series)

* The common O. states are +2 or +3. The O. states higher than +3 are rarely known.

* Some transition metals forms compounds (Carbonyl, nitrosyl etc.) in zero O. state.

* O. states/ions having d^0, d^5 & d^{10} confs. are more stable. e.g. $Fe^{3+}(3d^5)$ is more stable than $Fe^{2+}(3d^6)$.

⇒ <u>Reason for variable O. states</u>? Transition metals show variable oxidation states/valencies due to presence of incompletely filled (n-1)d orbitals, electron(s) of which participate in bonding along with ns-electron(s). Since energies of (n-1)d & ns orbitals are comparable, i.e; quite close to each other.

⇒ <u>Colour of compds./ions</u>: Transition metal compounds/ions are generally coloured in solid state as well as in aqueous solution. Colour vary from metal to metal and also with the variation of oxidation states. The colours of important ions of 3d-series elements given below: $Ti^{3+}(3d^1)$: purple; $V^{3+}(3d^2)$: Green; V^{2+}, $Cr^{3+}(3d^3)$: Violet; $Mn^{3+}(3d^4)$: Violet; $Mn^{2+}(3d^5)$: light pink; $Fe^{3+}(3d^5)$: Yellow/yellowish brown; $Fe^{2+}(3d^6)$: Light green; $Co^{2+}(3d^7)$: Pink; $Ni^{2+}(3d^8)$: Bluish green; $Cu^{2+}(3d^9)$: Blue etc. Sc^{3+}, Ti^{4+}, $V^{5+}(3d^0)$ and Cu^+, $Zn^{2+}(3d^{10})$ are Colourless or white.

* Transition metal compounds/ions with d^{1-9} (incompletely filled) always show colours.

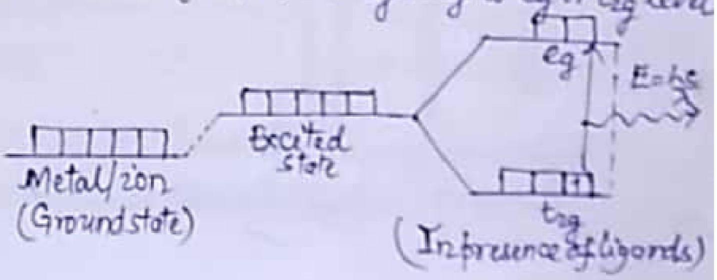
* Transition metal compds/ions with d^0 or d^{10} or Noble core are generally Colourless/white

Exceptions: $Hg^{2+}S$ (d^{10})- Red; $Cd^{2+}Cl_2$ (d^{10})- yellow; $Ag^{+}I$ (d^{10})- yellow; $Ag_2^{+}S$ (d^{10})- Black.

⇒ <u>Reason/Explanation of Colours of transition metal compds./ions</u>? Transition metal compounds/ions are coloured due to following reasons: (i) d-d transition (ii) Charge transf

(i) <u>d-d transition</u>: Colours of transition metal compds./ions. having partly/incompletely filled d-orbitals (d^1 to d^9) are due to d-d transition. Shifting of electron by exposure of light from one set of d-orbitals (t_{2g} or e_g) to another set of d-orbitals (e_g or t_{2g}) is called d-d transition. In transition metal atom/ion, all the five d-orbitals are degenerate (same energy), but as soon as neutral/anionic species (ligands) approach, they split into two sets of d-orbitals (t_{2g} & e_g), Called crystal field splitting. When Ordinary (white) light falls on such a transition metal Compound, radiations of Certain wave length (colour) absorbed and electron jumps from t_{2g} or e_g to e_g or t_{2g} level

During this electronic transition radiation of Characteristic wavelength (complementary of that absorbed) is emitted. The emitted colour depends upon the colour which is absorbed for electronic transition.



(ii) Charge transfer: Transition metal compounds/ions having completely filled d-orbitals (d^{10}) show colour due to charge transfer. In such cases, when visible light falls on the substance, electron cloud is shifted or transferred from anion to cation by taking up or absorbing some energy and emit/transmit the remaining one. The transmitted/emitted light has the complementary colour to that of absorbed light. For example, HgS is red coloured, due to electron shift/charge transfer from S^{2-} to Hg^{2+} by absorbing blue colour radiation, emitting radiation of characteristic wave length (red colour).

⇒ Magnetic properties: Transition metals/compounds/ions are generally paramagnetic. However, some are diamagnetic and a few are ferromagnetic/ferri/antiferromagnetic. A paramagnetic substance is one which attracted by the magnetic field and a diamagnetic substance is one which is repelled by magnetic field. Paramagnetic substances contain one or more unpaired electrons (d^1 to d^9 conf.) while diamagnetic substances contain only paired electrons/no unpaired electron (d^0 & d^{10} conf.). The magnetic character is expressed in terms of magnetic moment, which arises only from the spin of electrons. Magnetic moment $(\mu_s) = \sqrt{n(n+2)}$ BM

Paramagnetism $\propto \mu_s \propto n$ [where n = number of unpaired electron(s)]

e.g. Mn^{2+} : $[Ar]3d^5$, No. of unpaired electron (n) = 5; $\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.9$ BM.

Cr^{3+} : $[Ar]3d^3$, " " (n) = 3; $\mu_s = \sqrt{3(3+2)} = \sqrt{15} = 3.8$ BM.

Fe^{2+} : $[Ar]3d^4$, " " (n) = 4; $\mu_s = \sqrt{4(4+2)} = \sqrt{24} = 4.9$ BM.

Sc^{3+}, Ti^{4+} ($3d^0$), Cu^+, Zn^{2+} ($3d^{10}$) etc. are diamagnetic.

* Those substances which are strongly attracted by magnetic field or show permanent magnetism in absence of magnetic field are called ferromagnetic substances. It is special case of Paramagnetism. e.g., Fe, Co, Ni and their compounds/ions, CrO_2 etc. This property arises due to spontaneous alignment of magnetic moments of unpaired electrons in same directions.

* Those substances which are expected to posses paramagnetism/ferromagnetism on the basis of unpaired electrons but actually they possess zero magnetic moment are called antiferromagnetic substances. e.g. MnO. This is due to presence of equal number of magnetic moments in opposite directions.

* Those substances which are expected to possess large magnetism on the basis of unpaired electrons, but actually have small net magnetic moments are called ferrimagnetic substances. e.g. Fe_3O_4, MFe_2O_4 (ferrite), M = Mg, Cu, Zn etc. It's arises due to the unequal number of magnetic moments in opposite directions resulting in some net magnetic moment.

⇒ Reason/Explanation of Paramagnetism: Transition metals/ions/compounds are generally have incomplete d-orbitals (d^1 to d^9) and so have one or more unpaired electron(s). An electron (single/unpaired) is a charged particle, its orbital motion produces a small magnetic field along the spin axis. Thus, each electrons may considered as a tiny magnet having a resultant permanent magnetic moment and substances may be considered to contain a number of magnetic dipoles.

Diamagnetic substances/species have paired electrons. The magnetic moment possessed by an electron with spin in one direction is cancelled by that of opposite direction

⟹ <u>Complex forming ability</u>: Transition metals or ions have tendency or ability to form coordinate covalent bonds with ions or neutral molecules containing lone pair of electrons (ligands) i.e, transition metals/ions have tendency to form complex or coordination compounds/ions. Transition metals form complex compounds/ions in different oxidation states and different coordination numbers (4 or 6). They have different shapes and geometries or structures depending upon type of hybridisation of transition metal/ion. Stability of complexes increase with oxidation states and in the same oxidation state with the size of atom/ion. Transition metals generally form complexes with weaker ligands, e.g. F^-, H_2O, CO, C_2H_4 etc. in lower or zero oxidation states while with stronger ligands, e.g. CN^-, NH_3, Cl^- etc. in higher oxidation states. Some examples are $[Ni(CO)_4]$, $[Fe(H_2O)_5NO]^{2+}$, $[Cr(CN)_6]^{3-}$, $[Co(NH_3)_4(H_2O)_2]^{3+}$, $[Pd(NH_3)_4]^{2+}$ etc

⟹ <u>Reason for Complex forming ability</u>: Transition metals have a marked tendency to form complex compounds/ions due to following reasons: (i) High charge density or, smaller size & high nuclear charge (ii) Presence of vacant orbitals of comparable energies.

(i) <u>High charge density</u>: Transition metal ions have smaller size and high +ve charge, and therefore have high positive charge density (i.e, charge/size). This facilitates acceptance of lone pairs of electrons from ligands and thus coordinate covalent bond or coordination compounds formed.

(ii) <u>Presence of vacant orbitals</u>: Transition metals/ions have one or more vacant d-orbitals/hybrid orbitals to accept lone pairs of electrons donated by ligands and easily form coordination/complex compounds/ions.

complex forming ability of transition metals decrease downward in a group due to increase in ionic radii or size.

⟹ <u>Catalytic property</u>: Most of transition metals & some of their compounds act as catalysts in different chemical reactions, i.e, they have catalytic property. Some common examples are: (i) Pt metal used in manufacture of H_2SO_4 (ii) Ni metal used in the hydrogenation of oils/alkenes etc (iii) Fe & Mo metals used in manufacture of NH_3 (Haber's process) (iv) V_2O_5 used in oxidation of SO_2 during manufacture of H_2SO_4 by contact process (v) MnO_2 used in preparation of O_2 gas etc

⟹ <u>Reason/Explanation of catalytic property</u>: The catalytic property of transition metals/compds are due to following reasons: (i) Large surface area (ii) Presence of vacant d-orbitals

(i) <u>Large surface area</u>: Some transition metals/compounds provide large surface area for the reactants to be adsorbed and so come closer to one another making more effective collisions. They increase rate of reaction, and hence act as catalysts.

(ii) <u>Presence of vacant d-orbitals</u>: Some transition metals/compds have vacant (n-1)d-orbitals which can form intermediate compds. with reactants. Intermediate compounds being unstable, readily converted into products (stable) and so reaction rate increase, i.e, catalysis occurs.

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