

d-Block

Transition Elements

General introduction electronic configuration, 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 $K_2Cr_2O_7$ & $KMnO_4$

- * The elements in which the differentiating electron enters into d-orbital are called d-block elements.
- * The elements having partially filled d-orbitals in elemental state or in the stable ionic state are called transition elements.
- * d-block is positioned between “s” and “p” blocks.
- * Zn, Cd, Hg possess d^{10} configuration both in their atomic states and their most stable ‘+2’ state, hence they are not transition elements.
- * The d-block in the periodic table consists of four transition series, namely 3d series (first transition series), 4d series (second transition series), 5d series (third transition series) and 6d series (fourth transition series). The ‘6d’ series is incomplete series. The 3d, 4d, 5d series contain 10 elements each.
- * 3d series Sc ($z = 21$) to Zn ($z = 30$)
4d series Y ($z = 39$) to Cd ($z = 48$)
5d series La ($z = 57$) to Hg ($z = 30$)
- * In transition elements the differentiating electron enters into $(n - 1)$ d level. i.e. penultimate shell d-orbitals.

- * Transition metals are placed in IIIB, IVB, VB, VIB, VIIB, VIII and IB groups in the periodic table.
- * There is a gradual change in properties from s-block metals to p-block non metals through transitional elements hence they are called so.
- * The transition metals are less electro positive than s-block metals.
- * The transition metals are less reactive than s-block metals.
- * Transition metals are more malleable and ductile.
- * Transition metals are harder than s-block metals.
- * Certain transition metals show anomalous configuration for extra stability through coulomb exchange energies;

Cr: $3d^5 4s^1$, Mn: $3d^5 4s^1$, W: $5d^5 6s^1$.

Cu: $3d^{10} 4s^1$, Ag: $4d^{10} 5s^1$, Au: $6d^{10} 7s^1$

Pd: $4d^{10} 5s^0$

- * Transition elements possess greater melting and boiling points due to strong binding forces in crystals due to partially filled d-orbitals.
- * The m.pt & B. pts are highest in VB group.
- * Zn, Cd and Hg have very low m.pt and B.pt due to non involvement of d^{10} configuration in metallic bonding.
- * Conductivities of transition elements are very high. 'Ag' is the best conductor.
- * Densities of transition metals are very high due to their low atomic volumes.
- * VIII group elements possess maximum densities.

Highest density: Os: 22.57×10^{-3} kg/cc

Ir: 22.61×10^{-3} kg/cc

Among '3d' elements 'Cu' has maximum density.

- * Atomic sizes of transition elements do not differ much because the increase in nuclear charge and shielding effect go hand in hand. Atomic radius is minimum in VIII group.
- * IP of '3d' transition metals increases from Sc to Fe then decreases to Ni and increases in Cu & Zn.
- * IP values of transition elements are high and they have low heat of hydration. Hence transition elements are less reactive than s-block elements. The least reactive metals are Pt, Ir, and Au
- * d-block elements form ionic bonds in lower oxidation states and covalent bonds in higher oxidation states.
- * Transition elements show characteristic properties like
 - a) Variable oxidation states
 - b) Magnetic properties
 - c) Colored compounds
 - d) Alloy formation
 - e) Catalytic properties
 - f) Complex compound formation
- * Variable oxidation states:
 - a) Transition metals make use of their ns and (n-1) d electrons for bonding as their energies are close.
 - b) Most common oxidation state is +2
 - c) Highest common oxidation state is + 2
 - d) Highest oxidation state shown in 4d series is +8 by Ruthenium (less stable).
 - e) Highest oxidation state shown in 5d series is +8 by osmium (more stable).
 - f) The ions with d^5 and d^{10} configurations are relatively more stable.
 - g) Cu^+ (d^{10}) is less stable in aqueous medium than Cu^{+2} (d^9) because of high extent of hydration of Cu^{+2} .

h) The difference in successive oxidation states exhibited by a given transition element is one unit, whereas in p-block, it is two units.

Colours of transition metal ions

- * Many compounds of transition metals are coloured and the compounds of s-block and p-block elements are almost colourless.
- * The Transition Metal Ions with Unpaired d-electrons absorb characteristic coloured light from the visible region and transmit its complementary colour in the same region. This is responsible for the colour of the ion.
Ex: i) Hydrated Titanium ions (one 3d-electron) absorbs green light from visible region and transmits the purple light (pink)
ii) Hydrated Cu^{+2} ions absorb red colour and transmit blue colour.
iii) Mn^{2+} ion transmits pink colour
- * According to crystal field theory, the d-orbitals of transition metal ions split into two groups when ligands or counter ions or solvent molecules attack on them. This is known as d-orbital splitting (or) crystal field splitting.
- * In presence of other ions or molecules five d-orbitals lose their degeneracy and split into two groups namely e_g of slightly different energies.
- * As the energy difference between two groups e_g & t_{2g} is small, the energy from visible light is sufficient for the excitation of electrons.
- * The colour of the transition metal ion depends on the number of electrons undergoing the d-d transition and the energy difference between these d-orbitals.
- * The transition metal ions with empty d-orbitals (or) completely filled d-orbitals are colourless.
Eg: Sc^{+3} ; Cu^+ ; Zn^{+2} etc
- * The metal ions may exhibit different colours in different oxidation states.

Anhydrous CuSO_4 is almost colourless. But hydrated CuSO_4 is blue in colour. This is because of the absence of water molecules (ligands), there is no splitting of d-orbitals in anhydrous CuSO_4 .

- * The Cr (+6) and Mn (+7) have empty d-orbitals but their compounds are coloured.
- * The colours of oxoions like CrO_4^{2-} and MnO_4^- can be explained by charge transfer phenomenon.

Magnetic property of transition metals

- * The substances which are attracted into the magnetic field when they kept in higher magnetic field are called paramagnetic substances (weaker field to stronger field).
- * The substances which are repelled by the magnetic field when they kept in higher magnetic field are called diamagnetic substances (stronger to weaker field.)
- * Diamagnetic substances exhibit decrease in weight in the presence of magnetic field.
- * Ferromagnetic substances are considered as a special case of paramagnetic substances.
- * Paramagnetic substances contain **unpaired electron spins** or unpaired electrons.
Ex: $\text{K}_3[\text{Fe}(\text{CN})_6]$, Sc^{2+} , Cr^{3+} etc
- * In paramagnetic substances the magnetic field of the substance (B) is more than the applied magnetic field strength (H).
- * For paramagnetic substances $B > H$.
- * Diamagnetic substances contain electron pairs with opposite spins.
- * They move from a stronger part of the magnetic field to a weaker part of the magnetic field.
- * It is hard for magnetic lines to pass through a diamagnetic substance than in vacuum.
- * If Magnetic field in the substance (B) is less than external magnetic field (H), then they are said to be diamagnetic.
EX: Ti^{+4} , V^{+5} , Sc^{3+} , Zn, Hg, Cd etc
- * For diamagnetic substances $B < H$.

- * Ferromagnetic substances are those in which there are large no. of electrons with unpaired spins and whose magnetic moments are aligned in the same direction.
- * For Ferromagnetic substances
- * Iron, Cobalt and Nickel are best examples for ferromagnetic substances.
- * Ferromagnetism disappears in the aqueous solution of the substance
- * Para magnetism of substances (molecules, atoms or ions) is due to the spins of the unpaired electrons and also due to angular orbital momentum.
- * The magnetic moment of transition metal ions exhibiting paramagnetism is calculated by the formula. $\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)} \text{ BM}$

Where S = Sum of the spin quantum numbers

L = Sum of the orbital angular momentum quantum numbers.

- * For an electron, spin quantum numbers

$$s = \pm \frac{1}{2} \quad S = s \times n$$

Where n = number of unpaired electrons.

- * The unit of magnetic moment is Bohr Magneton (BM)

$$1 \text{ BM} = \frac{eh}{4\pi mc}$$

Where e = electron charge; h = Planck's constant, m = mass of electron, c = velocity of light.

$$1 \text{ BM} = 9.273 \times 10^{-24} \text{ Joule / Tesla.}$$

$$= 9.273 \times 10^{-21} \text{ erg / Gauss}$$

- * The contribution of orbital angular quantum number towards magnetic moment is low and hence it can be neglected [$L = 0$] for 3d series.

But in some cases μ_{exp} is higher than μ_{calc}

e.g. Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+}

Interstitial compounds

- * Compound formed when atoms with small atomic size like H, B, C and N are trapped in the holes of transition metals are called interstitial compounds. The components are not in definite ratios in them. So such compounds are also known as non stoichiometric compounds.
- * They have metallic nature, hard and brittle with high MP and B.P.
- * The density of these compounds is less than that of metals due to expansion of lattice.
- * Ti, Zr, Hf, V, Nb, Ta form such compounds.
- * Hydrogen occupies always smaller tetrahedral holes while C and N occupy larger octahedral holes.
- * Oxides and sulphides of T.E with more than one oxidation state form these compounds.

Ex: 1) $Fe_{0.82}O$ to $Fe_{0.94}O$

2) $WO_{2.88}$ to $WO_{2.92}$

3) $Fe_{0.89}S$ to $Fe_{0.96}S$

- * A stoichiometric compound may become non stoichiometric compound at high temperature.
- * ZnO is white when cold and yellow when hot, because stoichiometric ZnO changes to non-stoichiometric ZnO, when heated.
- * **Alloys**
 - a) A mixture of two or more metals, with or without a non metal, showing metallic properties is called an alloy.
 - b) The transition metals form large number of alloys due to their comparable atomic sizes.
 - c) The alloys with iron are called Ferro alloys. E.g.: Invar, Nichrome etc.

d) The alloys without iron are called non ferro alloys. E.g.: German silver, Bell metal Bronze etc.

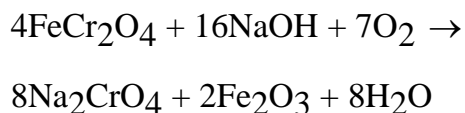
* **Catalytic properties**

- The transition metals and the ions show catalytic properties to a great extent.
- These metals and ions show catalytic properties either by adsorption of substrates or by a mechanism through the formation of low energy activated complexes.

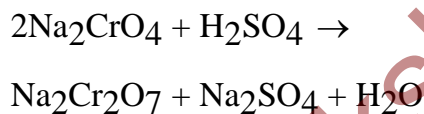
Compounds of Transition Elements

1. Potassium dichromate is prepared from chromite ore FeCr_2O_4 as follows:

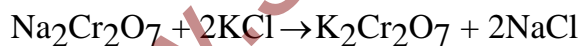
The chromite ore is fused with molten alkali in presence of air to form chromate.



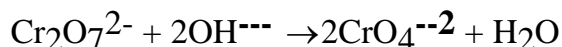
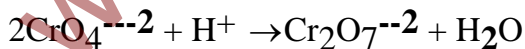
The solution containing sodium chromate is filtered and the filtrate is then acidified with dilute H_2SO_4 to obtain sodium dichromate, lanthanide.



The solution of sodium dichromate is then treated with potassium chloride when orange crystals of $\text{K}_2\text{Cr}_2\text{O}_7$ are obtained.



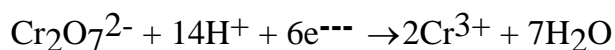
2. The chromates and dichromates can be inter-converted to each other in aqueous solution by altering the pH of the solution.



- In acidic medium i.e., when the pH of the solution is less than 7, the colour of the solution is orange due to the conversion of CrO_4^{2-} ions to $\text{Cr}_2\text{O}_7^{2-}$ ions.

- In alkaline medium i.e., when the pH of the solution is greater than 7, the colour of the solution is yellow due to the conversion of $\text{Cr}_2\text{O}_7^{2-}$ ions to yellow chromate CrO_4^{2-} ions.

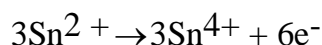
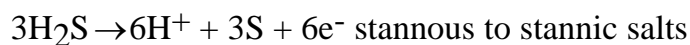
3. In acidic medium potassium dichromate acts as an oxidizing agent.



It oxidizes

(a) Iodide to iodine $6\text{I}^- \rightarrow 3\text{I}_2 + 6\text{e}^-$

(b) Hydrogen sulphide to sulphur.



(c) Iron (II) to iron (III) salts.

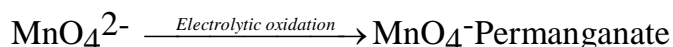
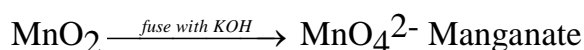


II. Potassium permanganate, KMnO_4

1. Potassium Permanganate is prepared by the fusion of MnO_2 (pyrolusite) with potassium hydroxide and an oxidizing agent such as KNO_3 to form potassium manganate which disproportionate in a neutral or acidic solution to form permanganate.

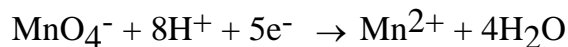


On a large scale, it is prepared by the alkaline oxidative fusion of MnO_2 to form potassium manganate. The electrolytic oxidation of potassium manganate in alkaline solution produces KMnO_4 at the anode.

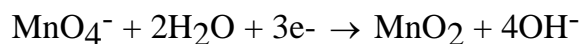


2. Potassium permanganate acts as an oxidizing agent both in acidic and alkaline media.

Acidic solution:

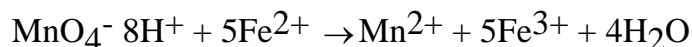


Alkaline solution:

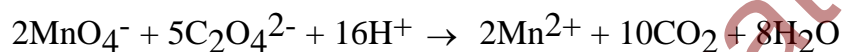


3. In acidic medium, potassium permanganate oxidises

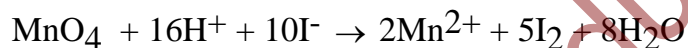
a) Iron (II) salts to iron (III) salts.



b) Oxalate to carbon dioxide.



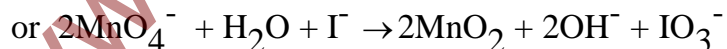
c) Iodide to iodine.



d) Nitrites to nitrates.



4. Alkaline potassium permanganate oxidizes iodide to iodate.



f-Block Elements

Lanthanides

- The f'- block consists of the two series of inner transition elements.
- a) Lanthanides(The fourteen elements following Lanthanum)
- b) Actinides (The fourteen elements following Actinium)
- Lanthanides are also called "rare earth elements"
- Lanthanum closely resembles the Lanthanides, Actinium closely resembles Actinides, hence these are usually included in any discussion of Lanthanides and Actinides.
- The Lanthanides resemble one another more closely because they exhibit a common stable oxidation state like transition elements.

Electronic Configuration

- The general electronic configuration of f-block elements is $(n - 2) f^{1-14} (n - 1) d^{0,1} ns^2$

Elements	Symbol	At. No	Configuration
Lanthanum	La	57	[Xe] 5d ¹ 6s ²
Cerium	Ce	58	[Xe] 4f ¹ 5d ¹ 6s ²
Praseodymium	Pr	59	[Xe] 4f ³ 6s ²
Neodymium	Nd	60	[Xe] 4f ⁴ 6s ²
Promethium	Pm	61	[Xe] 4f ⁵ 6s ²
Samarium	Sm	62	[Xe] 4f ⁶ 6s ²
Europium	Eu	63	[Xe] 4f ⁷ 6s ²
Gadolinium	Gd	64	[Xe] 4f ⁷ 5d ¹ 6s ²

Terbium	Tb	65	[Xe] 4f ⁹ 6s ²
Dysprosium	Dy	66	[Xe] 4f ¹⁰ 6s ²
Holmium	Ho	67	[Xe] 4f ¹¹ 6s ²
Erbium	Er	68	[Xe] 4f ¹² 6s ²
Thulium	Tm	69	[Xe] 4f ¹³ 6s ²
Ytterbium	Yb	70	[Xe] 4f ¹⁴ 6s ²
Lutetium	Lu	71	[Xe] 4f ¹⁴ 5d ¹ 6s ²

- The Lanthanides occur as orthophosphates in monazite sand.
- The Monazite sand contains 30% Thorium phosphate, 60% La, Ce, Pr, Nb phosphates and 10% Y and other heavy lanthanide phosphates.

Physical Properties

Density

- Lanthanides have densities ranging between 6.77 to 9.74g cm⁻³
- Densities in general increases with increase in atomic number.

Melting Point & Boiling Points

- Lanthanides have fairly high melting points however no definite trend is observed.

Electropositive Character

- Lanthanide metals are highly electropositive due to their low ionisation energy.

Ionisation Energy

- Lanthanides have fairly low ionisation energies. The IE₁ & IE₂ values are quite comparable to those of alkaline earth metals particularly calcium. (IE₁ 600 KJ/mole, IE₂ 1200 KJ/mole) La, Gd, Lu have low values due to empty, half filled and completely filled f orbitals respectively

Magnetic Behaviour

- Lanthanide ions (M³⁺) generally show paramagnetism due to the unpaired electrons in f-orbitals.

- Lanthanide ions like (configuration) (f^{14} configuration) are diamagnetic.
- The paramagnetism is maximum in Neodymium.
- Magnetic susceptibility of Actinides is relatively higher than those of Lanthanides of same electronic configuration.

Colour

- Many of the Lanthanide ions are coloured in solid state as well as in solutions.
- The colour is attributed to f-f transitions since they have partly filled f-orbitals. (Absorption bands are narrow probably because of the excitation within f-level)
- Ions with f^0 , f^{14} configuration are colourless.
- Ex :- $\text{La}^{+3}(4f^0)\text{Lu}^{+3}(4f^{14})$ are colourless
- The Lanthanide ion with configuration and configuration have same colour.

Ex (1):- and have same colour (pink)

Ex (2):- and have same colour (yellow)

Radioactivity

- All Lanthanides except promethium and samarium are non-radioactive

Oxidation States

- The common oxidation state exhibited by
- Lanthanides is + 3.
- Lanthanides can also exhibit occasionally +2 and +4 ions in solution or in their solid compounds.
- Irregularities arise mainly from the extra stability of empty, half filled or fully filled f-sub shell.
- +3 oxidation state in Lanthanum, Gadolinium and Lutetium are especially stable because +3 ions of these elements have an empty (f^0), a half filled [f^7] and completely filled (f^{14}] configurations.
- Cerium, Terbium also exhibit oxidation state of +4 because Ce^{+4} has configuration

(4f⁰), Tb⁺⁴ has the configuration (4f⁷)

- Pr, Nd, Dy also exhibit +4 state in their oxides only.
- Europium, Ytterbium can show +2 oxidation state due to configuration respectively.

Chemical Reactivity of Lanthanides

- The lanthanides have very close similarity. The separation of lanthanides from one another is very difficult.
- Lanthanides can be separated by ion exchange method
- Monazite is the starting material for the preparation lanthanides.
- The lanthanides are separated from monazite and are converted into chlorides (or) oxides.
- The lanthanides are obtained by the electrolysis of their molten chlorides.
- The lanthanides are obtained by the reduction of their anhydrous halides with electro positive metals like Na, Mg.
- The lanthanides slowly react with cold water and quickly react with hot water.
- $2M + 6H_2O \rightarrow 2M(OH)_3 + 3H_2$
- As the size of M⁺³ ion decreases the covalent character in M-OH bond and their basic strength in their hydroxides decreases gradually from La(OH)₃ to Lu(OH)₃. This is due to Lanthanide contraction
- Lanthanides form oxides of the type M₂O₃ (or) MO₂. These oxides are ionic in nature.
- Lanthanide ions cannot easily form co-ordinate compounds because of their large size.
- Lanthanide ions can form complexes with chelating ligands.

Lanthanide Contraction

- The decrease in atomic radii (derived from the structures of metals) is not quite regular but it is regular in their M^{+3} ions.
- As atomic number increases in Lanthanides series, for every proton added to the nucleus, the extra electron goes to fill 4f - orbitals. The 4f- electrons constitute inner shells and are rather ineffective in screening the nuclear charge. Gradual increase in the effective nuclear charge is responsible for decrease in size of Lanthanides. This phenomenon is called Lanthanide contraction.

Consequences

- The similarities between 4d & 5d series elements are closer than 3d & 4d elements.
- The atomic sizes of Zr & Hf, Nb & Ta, Mo & W are almost same.
- The separation of lanthanides is very difficult due to closer atomic radii.
- Inert pair effect.

Uses Of Lanthanides

- Lanthanides form alloys easily with Iron.
- Misch-metal is an alloy containing Lanthanide metals 94-95%, Fe 5% and traces of S, C, Ca, Al.
- Pyrophosphoric alloy contains Ce 40.5%, La & Nd 44%, Fe 4.5%, Al - 0.5% and other elements are C, Si, and Ca.
- Pyrophosphoric alloy is used in ignition devices such as tracer bullets, shells and flints for lighters.
- Mixed oxides of lanthanides are used as catalyst in petroleum cracking.

Actinides

Elements	Symbol	At. No	Configuration
Actinium	Ac	89	[Rn] $6d^1 7s^2$
Thorium	Th	90	[Rn] $6d^2 7s^2$

Protactinium	Pa	91	[Rn] 5f ² 6d ¹ 7s ²
Uranium	U	92	[Rn] 5f ³ 6d ¹ 7s ²
Neptunium	Np	93	[Rn] 5f ⁴ 6d ¹ 7s ²
Plutonium	Pu	94	[Rn] 5f ⁶ 7s ²
Americium	Am	95	[Rn] 5f ⁷ 7s ²
Curium	Cm	96	[Rn] 5f ⁷ 6d ¹ 7s ²
Berkelium	Bk	97	[Rn] 5f ⁹ 7s ²
Californium	Cf	98	[Rn] 5f ¹⁰ 7s ²
Einsteinium	Es	99	[Rn] 5f ¹¹ 7s ²
Fermium	Fm	100	[Rn] 5f ¹² 7s ²
Mendelevium	Md	101	[Rn] 5f ¹³ 7s ²
Nobelium	No	102	[Rn] 5f ¹⁴ 7s ²
Lawrencium	Lr	103	[Rn] 5f ¹⁴ 6d ¹ 7s ²

- The elements in which the last electron enters into 5f-orbital are called Actinides.
- Actinide series includes 15 elements. i.e.
- All these elements are radioactive.
- Except, the remaining elements are synthetic elements.
- Elements after Uranium are called transuranic elements.
- The common oxidation number is +3 and they also exhibit +4, +5, +6, oxidation numbers.
- Actinide contraction is due to poor shielding of 5f electrons.
- Except Thorium, Americium (Am) all the actinides have high densities.
- Most of the ions of actinides are coloured
- Their compounds are basic in nature.
- Actinides have weak tendency of complex formation.

- Actinides form oxocations. Ex: etc.,
- The ions of actinides are paramagnetic due to unpaired electrons.
- Actinides have high m.p's and b.p's
- Actinides have low I.P. values.
- All the actinides are highly electropositive.

Uses

- Uranium is used as nuclear fuel.
- Uranium salts are used in glass industry, textile industry, in medicines.
- Plutonium is used in atomic reactors.

www.sakshieducation.com