

Reaktion / Reaktion

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Agnivo

d-Block Elements

(Group 3-12)

Outer transition elements
E.C.: $(n-1)d^{1-10} ns^{0-2}$
Where, n is the outermost shell

Introduction

- Show transitional properties between s and p-block elements.
- All transition elements are d-block elements but all the d-block elements are not transition metals.
e.g., Zn, Cd, Hg and Cu [contain completely filled $(n-1)d$ orbitals] are not considered as transition metals

Classification

Series	Elements
First transition or 3d series	Sc ($Z=21$) to Zn ($Z=30$)
Second transition or 4d series	Y ($Z=39$) to Cd ($Z=48$)
Third transition or 5d series	La ($Z=57$), Hf ($Z=72$) to Hg ($Z=80$)
Fourth transition or 6d series	Ac ($Z=89$), Rf ($Z=104$) to Cn* ($Z=112$) Cn* = Copernicium

Trends and Characteristics

- Atomic radii decreases with increase in atomic number - Atomic radii of the pairs are almost same
- Show variable oxidation states [except 1st and last member of the series].
- Most common oxidn state of the first series is +2 [except Sc].
- Higher oxidn state shown by Ru and Os is +8
- Most of the metals exhibit paramagnetism (contains unpaired e⁻s) [except Zn, Cd, Hg, Zn²⁺, Cd²⁺, Hg²⁺, Cu⁺, Sc³⁺, Ti⁴⁺, V⁵⁺ which are diamagnetic].
- They form coloured compounds both in solids as well as in aqueous soln due to d-d transition (i.e. incomplete d-subshell) [Except Sc³⁺ (3d⁰), Ti⁴⁺ (3d⁰), Cu⁺ (3d¹⁰), Zn²⁺ (3d¹⁰) are colourless].
- They form complexes, interstitial compounds

Reactivity: The transition elements have less tendency to react due to their high ionisation energies and low heats of hydration.

f-Block Elements

Inner transition elements

E.C.: $(n-2)f^{1-14} (n-1)d^{0-1} ns^2$
Where, $n=6$ for Lanthanides
and $n=7$ for actinides

Introduction

- f-block elements are placed outside the periodic table.
- Elements after Uranium (U) are termed as "transuranic elements".
- Lanthanides along with La ($Z=57$), Y ($Z=39$) and Sc ($Z=21$) were originally called as 'rare earth elements' since their oxides (in earth) were rare

Classification

Series	Elements
Lanthanides or 4f series	Ce ($Z=58$) to Lu ($Z=71$)
Actinides or 5f series	Th ($Z=90$) to Ln ($Z=103$)

Trends and Characteristics of Lanthanides

- Show common stable oxidn state +3.
- Regular decrease in atomic and ionic rad with increase in atomic number is called "Lanthanide contraction".
- They have low I.E and high b.p and m.p.

Trends and Characteristics of Actinides

- All actinides show +3 oxidation state.
- They are highly reactive metals.
- All the metals are radioactive metals.
- They are generally coloured [except Ac³⁺ (5f⁰), Cm³⁺ (5f⁷) and Ln³⁺ (5f¹⁴) are colourless].

Important Compounds of d-block Elements		
	Preparation	Properties
Potassium dichromate ($K_2Cr_2O_7$)	From $Na_2Cr_2O_7$ - $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$	<ul style="list-style-type: none"> Orange crystalline solid, melting pt. = 669 K Moderately soluble in cold water but freely soluble in hot water Powerful oxidising agent.
Potassium permanganate ($KMnO_4$)	From potassium manganate $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$	<ul style="list-style-type: none"> Deep purple, melting point = 513 K. Moderately soluble in water at room temperature and more soluble in hot water. Powerful oxidising agent

Users
Lanthanides
<ul style="list-style-type: none"> Form alloys like mischmetal and pyrophoric alloys Used in making magnetic and electronic devices.
<ul style="list-style-type: none"> Oxides are used in glass industry and their mixed oxides are used as catalysts in petroleum cracking Recently used in lasers.
Actinides
<ul style="list-style-type: none"> ThO_2 - used for making incandescent gas mantles and fine rods for atomic reactors. Uranium - used in the production of nuclear energy. Plutonium - used for fuelling atomic reactors.

Properties of d-Block elements
<ul style="list-style-type: none"> Bonding: Strong metallic bonding due to greater nuclear charge and large number of valence electrons results in high density hard solids (except mercury which is liquid).
<ul style="list-style-type: none"> Presence of unpaired d-electrons favours covalent bond formation, hence greater the no. of unpaired d-electrons, more is the number of covalent bonds resulting in hard metals.
<ul style="list-style-type: none"> Melting and boiling points: All transition metals have generally very high melting and boiling points.
<ul style="list-style-type: none"> These high values are due to strong interatomic metallic bonding and the number of unpaired d-electrons leading to covalent bonding.
<ul style="list-style-type: none"> Ionisation Energy:

see →
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- Fusible metals - Zn, Cd and Hg
- Ceramic metals - Cu, Co and Au
- Ferromagnetic metals - Fe, Cr and Ni
- Heavier metals - Os and Ir
- Ward's metal - Pb *
- Liquid metal - Se
- Most abundant deoxidation metal - Fe.

Some useful facts

• Only also act as catalysts.
 + $Zn (40-90\%)$, Be and Al as deoxidizers.
 and Al (20-80%), Be and Al as deoxidizers of $Cu (60-80\%)$
 $(0.5-10\%)$, Be and Al as deoxidizers of $Cu (60-80\%)$

The d-block elements are also called as transition elements as they show transitional properties between s- and p-block elements. These elements are called d-block elements since in them $3d > 4d, 5d$ and $6d$ subshells are incomplete and the last electron enters the $(n-1)d$ orbitals i.e. penultimate shell. Their general electronic configuration is $(n-1)d^{1-10} ns^{0-2}$ where n is the outermost shell.

Classification of d-block elements : In the periodic table there are 4 main transition series of elements corresponding to filling of $3d$, $4d$, $5d$ and $6d$ subshells in 4th, 5th, 6th and 7th periods.

General characteristics of d-block elements:

- Nearly all transition elements show metallic properties except mercury is a liquid.
- They are electroactive in nature.
- Most of them form coloured compounds.
- They have good tendency to form complexes.
- They show variable oxidation states.
- A number of these transition metals and their compounds shows catalytic properties.
- They have high m.p. and b.p. and have higher heat of vaporisation than non-transitional elements.

General trends in the chemistry of d-block elements

Atomic and ionic radii : The atomic radii of d-block elements are intermediate between those of s- and p-block. The following trends in atomic radii have been observed.

- The atomic radii in a series decreases with increase in atomic number but the decrease in atomic radius becomes small after midway.
- At end of each period, there is slight increase in the atomic radii.
- The atomic radii increases while going down the group.

Ionisation enthalpies: Ionisation enthalpies of d-block elements lies in between those of s- and p-block elements. They are less electropositive than s-block elements and more electroactive than p-block elements.

Ionisation enthalpies increase along a given transition series due to increased nuclear charge. Ionisation enthalpies also increases down

Series	
First transition series or 3d series	Sc (At. No. 21) to Zn (At. No. 30)
Second transition Series or 4d series	Ti (At. no. 22) to Cd (At. no. 48)
Third transition Series or 5d series	La (At. no. 54), Hf (At. no. 72) to Hg (At. no. 80)
Fourth transition series or 6d series	Ac (At. no. 89), Rf (At. no. 104) to Lrb (At. no. 112).

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the group in a series. 5d series have high ionisation enthalpies than 3d and 4d series but irregularly have been seen in ionisation enthalpies of 3d and 4d series.

- **Metallic character:** Except Hg, all transition elements have typical metallic structure (hcp, ccp or bcc) and show all the properties of metal. The metallic character is due to low ionisation enthalpies and number of vacant orbitals in the outermost shell. Greater the no. of unpaired d-electrons, greater is the number of bonds and therefore greater is the strength of these bonds, so hardness and enthalpy of atomization increases with increase in number of unpaired electrons. As we move from left to right in a particular d-series number of unpaired electrons increases from 1 to 6 and then decreases to 0.
- **Density:** All d-block elements have high density. Within a period, the densities vary inversely with the atomic radii. As we move in a period, the density increases (as the radii decrease). The density increases while descending a group.
- **Standard electrode potential (E°) and chemical reactivity:** Thermodynamic stability of transition elements can be evaluated in terms of magnitude of ionisation enthalpies. Smaller the ionisation enthalpy, most stable is its compound. More positive value of electrode potential refers to strong oxidising action while more negative value of electrode potential indicates strong reducing action.
- **Oxidation states:** d-block elements show variable oxidation states both ns and (n-1)d electrons take part in bond formation. Oxidation states of transition elements are related to their electronic configuration. Minimum oxidn state exhibited by transition elements is equal to number of ns-electrons. While generally max. oxidation state refers to number of ns-electrons in addition to unpaired d-electrons which participate in bond formation. In general, the maximum oxidn state increases with atomic no. within a group.
- **Complex formation:** Transition metal ions form a large number of complex compds because they have small size, large effective nuclear charge and have vacant d-orbitals so that these orbitals can accept lone pairs of electrons donated by the ligands.
- **Oxides:**
 - General formula of oxides : MO , M_2O_3 , M_3O_4 , MO_2 , M_2O_5 and MO_3 .
 - In general, when the metal is in its high oxidation state, its oxide is acidic, for low oxidation state, its oxide is basic while for intermediate oxidation state the oxides show amphoteric behaviour.
 - When we move in a transition series, +2 oxidation state becomes more and more stable. Thus, their reducing character increases in a period. As we move down the group, the higher oxidn state becomes more stable.

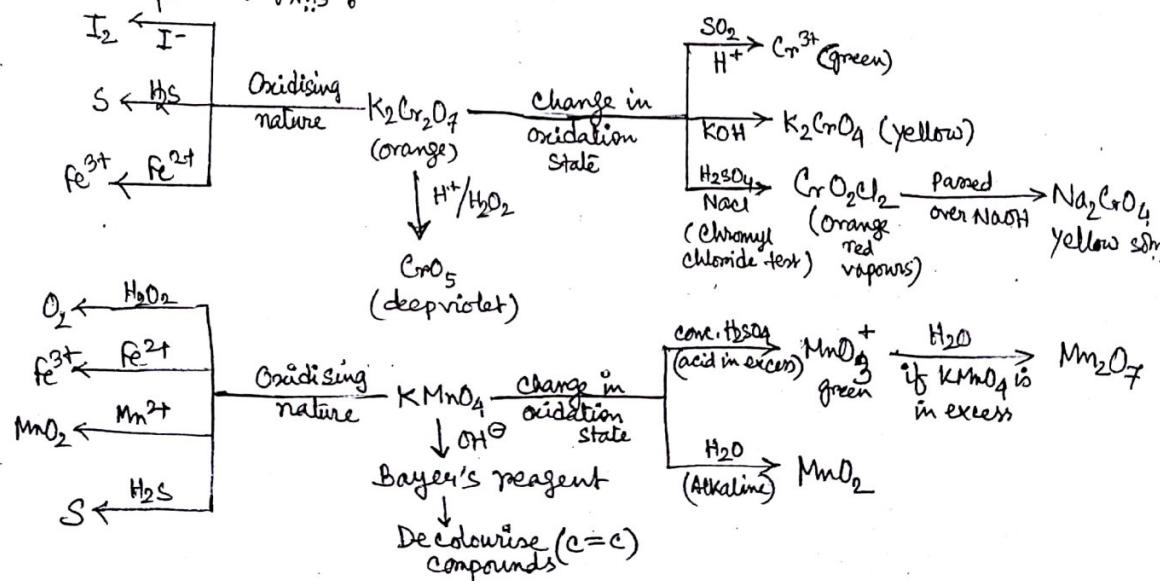
D) **Coloured ions:** Most of the transition metal compounds (ionic as well as covalent) are coloured in their solid or solution form. Coloured ions are formed due to presence of vacant d-subshell. When visible light falls on transition metal compound the transition metal absorbs some radiation of white light and undergoes d-d transition. The transmitted (unabsorbed) or reflected light appears coloured which is complementary to colour of absorbed radiation.

Transition metal ions containing either completely filled or completely empty d-subshell appear colourless.

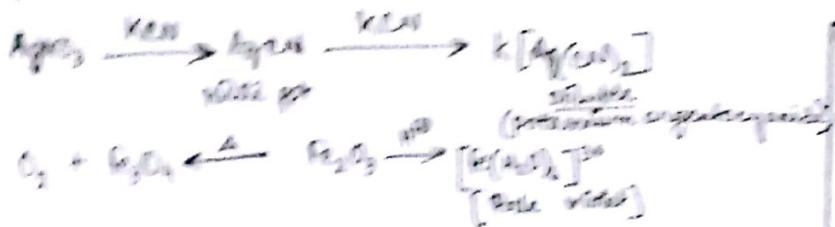
Some important compounds of d-block elements.

Compounds	Preparation	Physical properties	Uses
$K_2Cr_2O_7$	From $Na_2Cr_2O_7$ (obtained from chromite ore) $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$	Orange red, crystalline solid, oxidising agent, m.p. = $398^\circ C$	in dyeing, photography, leather industry
$KMnO_4$	From potassium manganate (K_2MnO_4): $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$	Dark violet, crystalline solid, oxidising agent, m.p. = $523K$	as disinfectant, germicide, Bayer's reagent (alkaline $KMnO_4$)
$CuSO_4 \cdot 5H_2O$ (blue vitriol)	From cupric oxide $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$	Blue (hydrated salt), ab 423K becomes anhydrous, readily dissolves in water.	as electrolyte, mordant, fungicide.
$AgNO_3$ (lunar caustic)	From silver metal $3Ag + 4HNO_3 \rightarrow AgNO_3 + NO \uparrow + H_2O$	White crystalline, decomposes to give Ag at high temp.	for making inks, hair dyes, photography, silvering of glass.
HgI_2	From mercuric chloride $HgCl_2 + 2KI \rightarrow HgI_2 + 2KCl$	It exists in 2 forms, i.e., red and yellow, dissolves in excess of KI to form a complex, called as Nessler's reagent	to prepare Nessler's reagent, for making ointments for treating skin infections.

□ Some important rxns:



Q. 10.



LANTHANIDES

- The elements in which the last electron enters one of the $4f$ orbital are called lanthanoids or lanthanides or f -block elements or first inner transition series elements. It includes 14 elements from Ce (At. no. 58) to Lu (At. no. 71).

Characteristic properties of Lanthanoids

- Oxidation states:** All the lanthanoids exhibit a common stable oxidation state of +3. In addition, some lanthanoids also show oxidation states like +2, +4, etc. These elements which by losing 3 electrons attain the stable f^0 configuration.
- Atomic and ionic radii (Lanthanoid contraction):**

In lanthanoids there is regular decrease in atomic and ionic radii with increase in atomic number from La to Lu. This regular decrease is known as Lanthanoid contraction.

- Cause of lanthanoid contraction:** As we move along the lanthanoid series, the nuclear charge increases by one unit at each successive element and a new electron enters the 4f subshell. Due to the peculiar shape of f-orbitals, there is inner shell shielding of 4f-electrons by other electrons from the nuclear attraction. As a result of this, the size of lanthanoid atoms keep on decreasing from La to Lu.

- Q. What do you mean by the term "Lanthanoid contraction"?**

Among Lanthanoids ($4f^{1-14}$) and Actinoids (Th to Lu) having 5f orbital belong to f-block. They don't have any 3f electrons after La ($5f^1$) from Ce ($5f^1$), $[(n-2)f^{1-14}(n-1)s^2p^6 \text{ or } d^2 n^4]$. 4f electron starts filling and ends in Lu ($7f^1$). These additional 14 inner electrons occupy the 4f subshell which is well buried within the inner core of 6s orbital. As we move from La to Lu the nuclear charge increases. The screening effect of 4f orbital being very poor, the outer electrons are drawn closer to the nucleus. These two combined effect, namely the increased nuclear charge and poor screening effect of the inner 4f electron, bring about a slow contraction b/w atomic & ionic radii of the lanthanoids. This phenomenon is known as "Lanthanide contraction".

- Melting and boiling points:** They've high melting and boiling points. However they don't exhibit any regular trend with rise in atomic number.
- Ionisation energy:** They've low ionisation energy which is quite comparable with that of alkaline earth metals. Hence these are highly reactive metals.

Key points

- In first transition series Cr ($3d^5 4s^1$) and Cu ($3d^9 4s^1$) have exceptional electronic configurations.

Large the number of unpaired electrons, stronger is the metallic bond and hence higher is the m.p.

- Titanium is the second most abundant metal occurring in earth's crust.

Lithopone ($\text{ZnS}\cdot\text{BaSO}_4$) is used as a white paint.

- The first synthetic transition element was $_{23}\text{Te}$.

Actinoids	Lanthanoids
$_{\text{Th}}$	$_{\text{Ce}}$
$_{\text{Pa}}$	$_{\text{Pr}}$
$_{\text{Am}}$	$_{\text{Nd}}$
$_{\text{Rf}}$	$_{\text{Pm}}$
$_{\text{Np}}$	$_{\text{Sm}}$
$_{\text{Bk}}$	$_{\text{Eu}}$
$_{\text{Cf}}$	$_{\text{Gd}}$
$_{\text{Es}}$	$_{\text{Tb}}$
$_{\text{Fm}}$	$_{\text{Dy}}$
$_{\text{Md}}$	$_{\text{Ho}}$
$_{\text{No}}$	$_{\text{Tb}}$
$_{\text{Lr}}$	$_{\text{Lu}}$

ACTINIDS

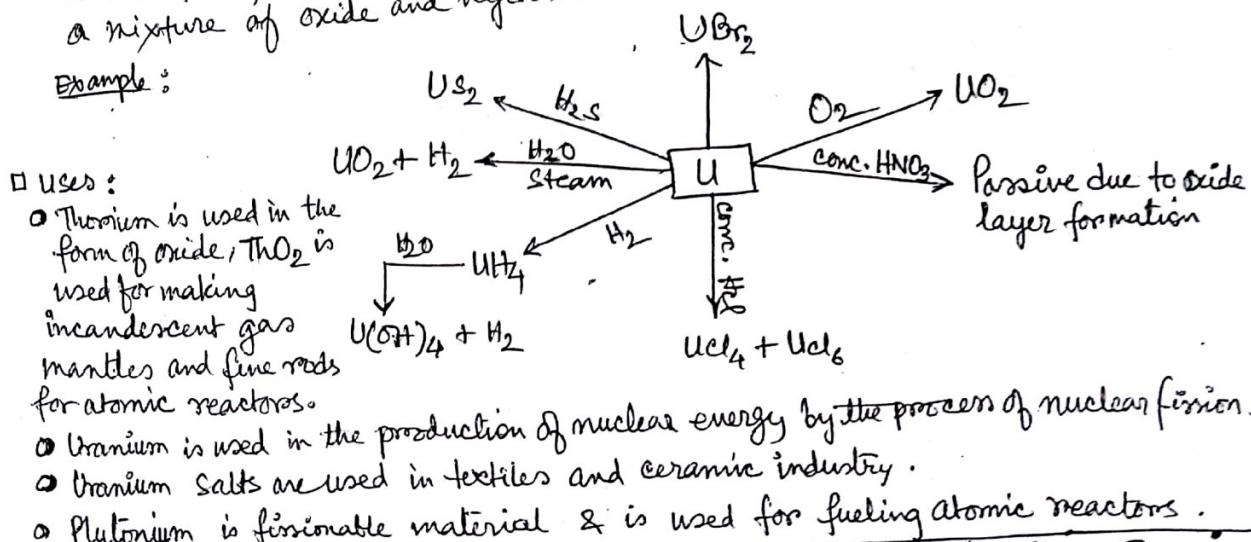
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- The elements in which the last 'e' enters only the 5f orbital are called - actinoids or antinones or 5f-block elements or second inner transition series. It also includes 14 elements from Th (At. no. 90) to Lr (At. no. 103).

Properties of actinoids

- Oxidation state : The most common & stable oxidation state of actinoids is +3. Actinoids also show oxidation state of +4 and even higher i.e. +5, +6 and +7. The maximum oxidation state first increases upto middle of the series and then decreases.
- Atomic and ionic radii (Actinoid contraction) : There is a gradual decrease in the size of atoms across the series. This is known as - actinoid contraction (very similar to lanthanoid contraction). The contraction is however greater from element to element in this series resulting from poor shielding by 5f-electrons.
- Ionisation enthalpies : The actinoids have low ionisation enthalpies.
- Density : All the actinoids except thorium and americium have high densities.
- Radioactivity : All of these elements are radioactive. The half-life periods of transuranic elements are so short that they don't occur in nature and have been prepared artificially (except ^{232}Th and ^{238}U).
- Reducing agents : All the actinoids are strong reducing agents.
- Coloured ions : Cations of actinoids with two or more 5f-electrons are coloured both in the crystalline state, as well as in their aqueous solution.
- Chemical reactivity : Actinoids are highly reactive metals especially in the finely divided state. They react with boiling water to give a mixture of oxide and hydride.

Example :



Uses :

- Thorium is used in the form of oxide, ThO_2 is used for making incandescent gas mantles and fine rods for atomic reactors.
- Uranium is used in the production of nuclear energy by the process of nuclear fission.
- Uranium salts are used in textiles and ceramic industry.
- Plutonium is fissionable material & is used for fueling atomic reactors.

Key points:

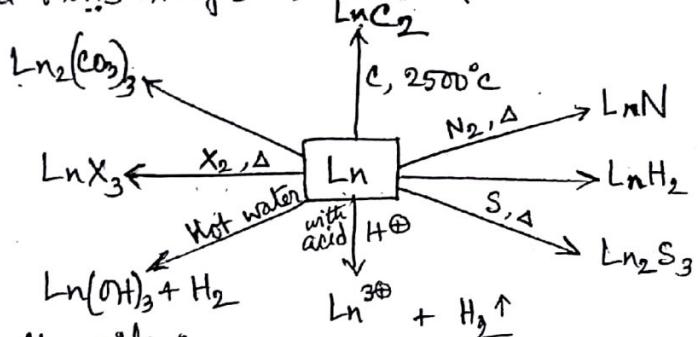
- Actinoids form oxo-ions such as UO_2^+ , PuO_2^{2+} , UO_4^+ , UO_4^{2-} etc. These ions are stable in acid and aqueous solutions while lanthanoids don't form oxo-ions.
- Elements with atomic no. > 92 (atomic no. of Uranium) are called transuranium elements. All these elements are man made.

f-Block Elements:

- The elements in which the last electron enters the $(n-2)f$ orbital are called f-block elements. They are also known as inner transition elements. The block consists of two series of elements known as Lanthanoids and actinoids.
- The general electronic configuration of the f-block elements is $(n-2)f^{1-14}(n-1)d^0-ns^2$.
- For lanthanoids, n is 6 while its value is 7 for actinoid series.

Complex formation: The lanthanoids don't have much tendency to form complexes due to low charge density because of their large size. The tendency to form complexes and their stability increases with increasing atomic number.

Chemical reactivity: Representing the lanthanoids by the general symbol Ln, the general rxns may be shown as follows:



Uses of Lanthanoids:

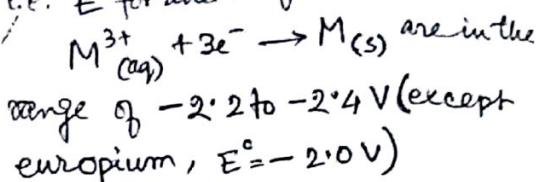
- They are used in the form of their alloys such as - misch metal or pyrophoric alloys
- Cerium salts are used for dyeing Cotton and also as catalyst.
- The compounds of lanthanoids are used in making magnetic and electronic devices.
- Their oxides are used in glass industry.
- Recently lanthanoids have been used in lasers.

Key points:

- Lanthanoids along with lanthanum ($Z=57$) and yttrium ($Z=39$) were originally called as rare earths, since their oxides (earths) were rare.
- Most of the trivalent lanthanoid ions are coloured. This is due to f-f transition.
- $La(OH)_3$ is most basic while $Lu(OH)_3$ is least basic.
- An alloy containing Mg and about 3% misch metal is used in jet engine parts.

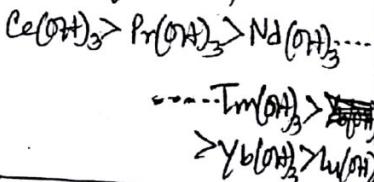
Magnetic behaviour: The lanthanoid ions other than f⁰ type (La^{3+} and Ce^{4+}) and f¹⁴ type (Yb^{2+} & Lu^{3+}) are paramagnetic due to presence of unpaired f electrons.

Standard reduction potential: Their standard reduction potential values i.e. E° for the half rxn

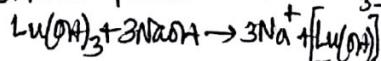


The hydrides of lanthanide are basic & the basicity decreases from left [$Ce(OH)_3$] to right [$Lu(OH)_3$] due

to decrease in ionic radius. Hence the order of basicity is



The hydroxides react with concentrated alkali to form complexes.



f-Block Elements (Inner-Transition Elements)

These are also called inner transition elements, as they lie inside d-block elements. They all belong to III B group in 6th (lanthanide series) and 7th (actinide series) period of periodic table.

- They've general electronic configuration of $(n-2)f^{1-14}(n-1)d^0-ns^n$.
- The f-block elements of 6th period belong to lanthanide series (or 4f series) and contains 14 elements from Ce to Lu.
- The f-block elements of 7th period belong to actinide series (or 5f series) and contains 14 elements from Th to Lr.

Lanthanide Contraction

Due to the addition of 14 f-block elements (lanthanides) from Ce to Lu in third group of 6th period, contraction in the size of transition elements (5d series) takes place from Hf to Hg. As a result, either a very small change (0.01 \AA) or almost no change in atomic radius is observed from 5th to 6th period. This contraction in the size of atomic radius due to addition of 14 lanthanide elements is called lanthanide contraction. The covalent radii of 5th and 6th period transition elements are given below:

5th period	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	1.62	1.45	1.34	1.29	1.27	1.24	1.25	1.28	1.34	1.41
6th period	La ³⁺	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	1.69	1.44	1.34	1.30	1.28	1.26	1.26	1.29	1.34	1.44

* Contraction in size of 6th period transition elements
* 14 lanthanide elements.

Due to lanthanide contraction, the size of 5th & 6th period transition elements are identical and hence, it becomes very difficult to separate these elements. Also due to lanthanide contraction, 5th and 6th period transition elements resemble each other more likely than 4th period transition elements.

Physical and Chemical Properties

- Atomic Radius: They've almost similar radius and it doesn't follow a regular trend due to lanthanide contraction.
- Due to their similarity in radius, the lanthanide series elements have almost similar physical and chemical properties. Hence it becomes very difficult to separate lanthanide series elements from each other. Ion exchange method and valence exchange methods are the most effective methods to separate them.
- Ionisation Enthalpy: They've low ionisation energy comparable to that of S-block elements and Al. Hence, they're more electropositive and highly reactive.
- Oxidation State: Lanthanides exhibit oxidation state of +2, +3 & +4 but +3 is the most stable one. Hence, they're primarily trivalent. Actinides, however show a variety of oxidation states from +2 to +7. Also their stability vary among different elements.
- Colour and Magnetic Behaviour: Both lanthanides and actinides form coloured complexes due to f-f transition of electrons.

All lanthanoids are coloured except La³⁺, Ce³⁺, Gd³⁺, Lu³⁺, Yb³⁺

Except Lu³⁺, Yb³⁺ and Ce⁴⁺, all other lanthanoids are paramagnetic.

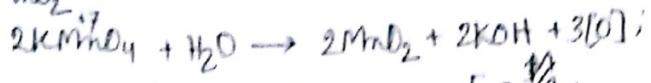
• During the calculation of magnetic moment for f-block elements, both spin quantum number(s) and orbital quantum (l) are considered. Hence

$$M_{eff} = \sqrt{4S(S+1) + l(l+1)} \text{ B.M}$$

e) Reactivity

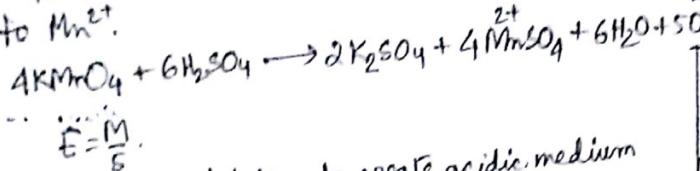
Due to low ionisation energy which is comparable with S-block elements, they're highly electrofue & hence more reactive.

(ii) In neutral medium : KMnO_4 indirectly reduced to MnO_2 .



In neutral medium, KMnO_4 , oxidises Mn^{2+} , $\text{Na}_2\text{S}_2\text{O}_3$, H_2S etc. to MnO_2 , $\text{Na}_2\text{S}_4\text{O}_6$, S , etc. respectively.

(iii) In acidic medium (H_2SO_4 and not HCl is used to create acidic medium) KMnO_4 is reduced to Mn^{2+} .



$$\bar{E} = \frac{M}{5}$$

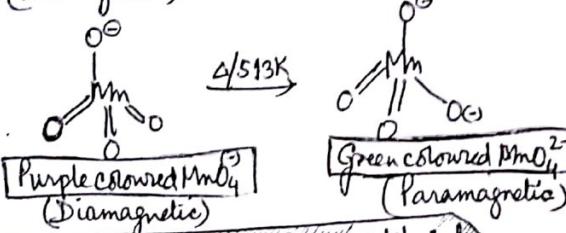
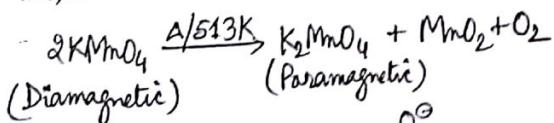
- Here HCl is not taken to create acidic medium because HCl is oxidised to chlorine by KMnO_4 .

In acidic medium it oxidises $\text{Fe}(\text{II})$ salt, $\text{H}_2\text{C}_2\text{D}_4$, H_2S , SO_2 , SO_3^{2-} , NO_2^- , I^- , H_2O_2 etc. to $\text{Fe}(\text{III})$ salt CO_2 , S , H_2SO_4 , SO_4^{2-} , NO_3^- , I_2 , O_2 etc. respectively.

Magnetic Behaviour of Manganate and Permanganate Ion

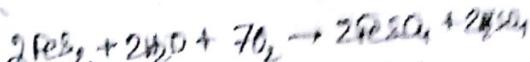
Although, the manganate (MnO_4^{2-}) and permanganate (MnO_4^-) ions have tetrahedral shape they've different colour and magnetic behaviour.

Green coloured MnO_4^{2-} ion is paramagnetic with one unpaired electron, whereas the purple coloured MnO_4^- ion is diamagnetic. MnO_4^- is decomposed to MnO_2 ion, when heated at 513 K.

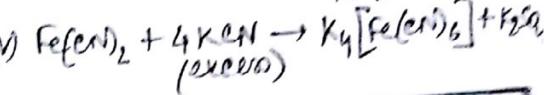
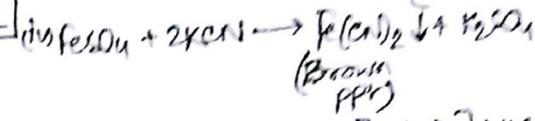
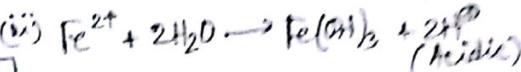
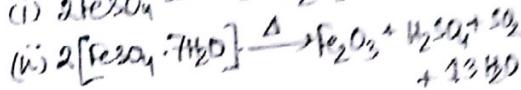


Ferrous Sulphate or Green Vitriol

- It is industrially prepared by slow oxidation of FeS_2 (iron pyrites) in presence of air. It is used in the treatment of iron deficiency and in different industries.

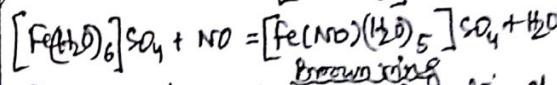
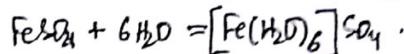
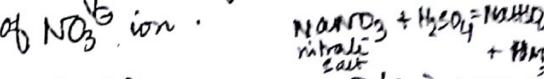


- It is used in the treatment of iron deficiency and in different industries
- It shows the following chemical properties:

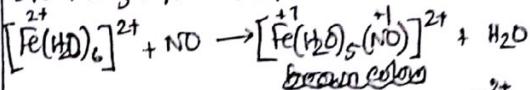
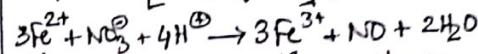


Brown Ring Test : A Test for NO_3^-

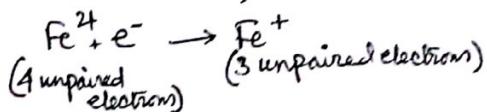
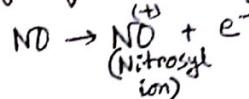
In brown ring test, FeSO₄ solution is added to aqueous solution of NO_3^- followed by the addition of conc. H_2SO_4 slowly. This results in the formation of a brown ring at the junction of the two layers, confirming the presence of NO_3^- ion.



The brown colour is due to the formation of complex ion $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$, as shown below:



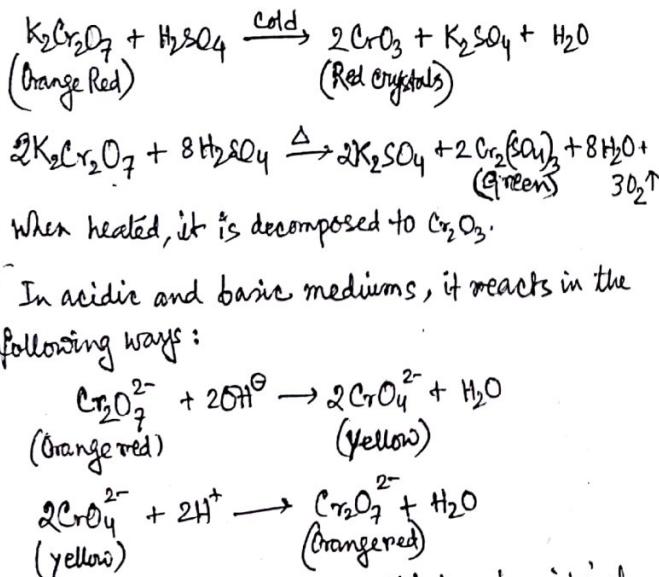
Here the brown colour of $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$ is due to transfer of an electron from NO to Fe^{2+} .



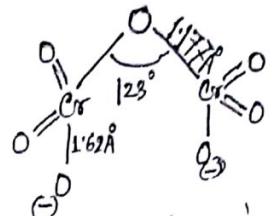
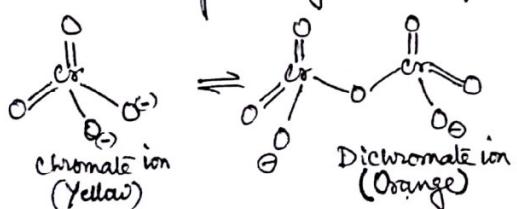
SOME IMPORTANT COMPOUNDS OF d-BLOCK ELEMENTS

- a) Potassium Dichromate ($K_2Cr_2O_7$)

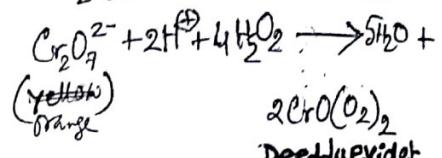
 - It is an orange red prismatic crystal that is moderately soluble in H_2O but highly soluble in hot water.
 - It is manufactured from chromite ore, $FeO \cdot Cr_2O_3$.
 - When heated, it is decomposed to Cr_2O_3 .
$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$
 - It acts as a strong oxidising agent in the presence of dilute H_2SO_4 due to the formation of nascent oxygen.
$$(Orange\ Red) \quad (dilute) \quad (Green)$$
 - It oxidises KI , Fe^{+2} and H_2S to I_2 , $\underset{[Fe^{+2}]}{Fe_2(SO_4)_3}$ and S respectively.
 - It reacts differently in different react conditions with H_2SO_4 .



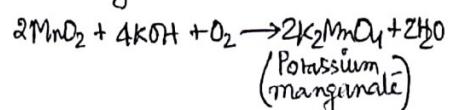
Hence, it is evident that an equilibrium is maintained between the concentration of $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} that can be altered by altering the pH of the solution.



- Acidified solution of $K_2Cr_2O_7$ reacts with H_2O_2 producing $CrO(O_2)_2$.

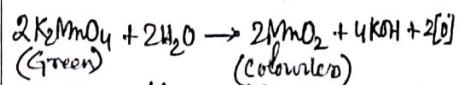
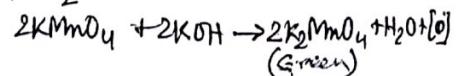


- b) Potassium Permanganate ($KMnO_4$)
 It is purple black prismatic crystal, when dissolved in water gives dense pink or purple colour solution. Commercially it is prepared from pyrolusite ore (MnO_2). Alkaline oxidative fusion of MnO_2 followed by electrolytic oxidation gives $KMnO_4$.

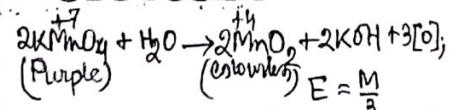


KMnO₄ is a good oxidising agent but the products formed depend on whether the reaction is carried out in acidic, alkaline or neutral medium.

- (i) In alkaline medium It is first converted to MnO_4^{2-} and finally to MnO_2 .



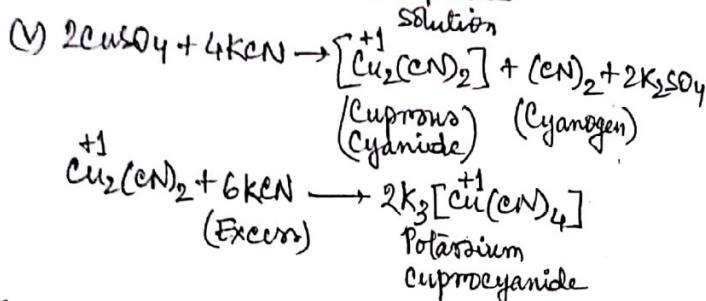
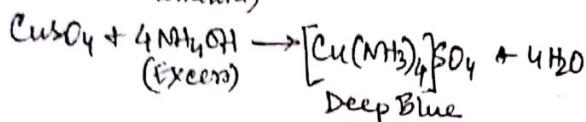
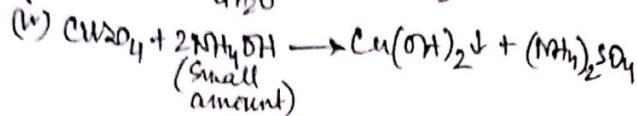
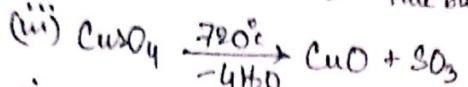
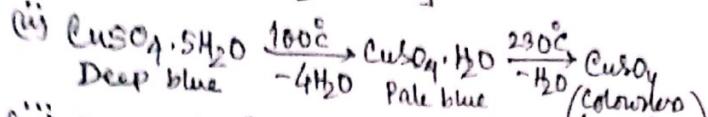
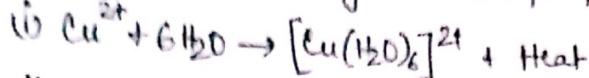
Overall reaction :-



In alkaline medium, it oxidises I⁻, NH₃, nitrotoluene etc. to IO₃²⁻, N₂, nitrobenzoic acid etc. respectively.

d) Cupric Sulphate or Blue Vitriol ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) P.①

- It is prepared industrially by boiling cut turnings in the presence of conc. H_2SO_4 .
- It is a blue coloured crystal and paramagnetic (when hydrated).
 $\text{Cu} + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$
- It shows the following chemical properties.



It is used as a pesticide (Bordeaux mixture) in inorganic synthesis as a dyeing agent, etc.

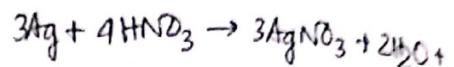
It is also a component in Fehling's solution and Benedict's solution to test for reducing sugars in which CuSO_4 is reduced to insoluble Cu_2O .

e) Zinc Sulphate or white vitriol ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)

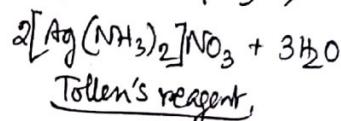
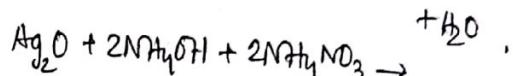
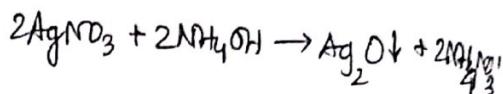
- It is prepared by treating metallic Zn with dil. H_2SO_4 .
- It is a colourless, crystalline solid and soluble in water.
- It decomposes to ZnO and SO_3 when heated above 300°C
- It is isomorphous with $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ etc.
- It is used for many purposes like the production of lithopone pigment, rayon fibre etc.

f) Silver Nitrate or Lunar Caustic

It is a colourless transparent rhombic crystal, which is prepared by dissolving Ag in hot dil. HNO_3 .



Ammoniacal solution of AgNO_3 is called Tollen's reagent, which is used to distinguish between aldehyde and Ketones through the following reactions :-



Tollen's reagent oxidises aldehyde to acid forming silver mirror (Ag), whereas Ketone doesn't react with Tollen's reagent.



29 MAR 2016



CARDIOLOGY O/P
CH (EC) KOLKATA
MONDAYS / THURSDAYS

DATE 31/03/16
TIME 11:00 AM
ROOM NO 182-04
BP - 120/70

29 MAR 2016



29 MAR 2016

pt planned for dental extraction

-Stop tlopipid

- CT Ecospirin
rest all

Dr. GIRIDESH D. P.
MEDICINE RESIDENT