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TG ← 19/11/18

Agnive

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

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

- 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.

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 Lr ($Z=103$)

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 Lr³⁺ (5f¹⁴) are colourless].

Important Compounds of d-block Elements			
	Preparation	Properties	Uses
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 oxidizing agent. 	<ul style="list-style-type: none"> In chrome tanning in leather industry In calico printing and dyeing In photography and in hardening gelatine film.
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 oxidizing agent 	<ul style="list-style-type: none"> Baeyer's reagent (alkaline $KMnO_4$) to test unsaturation in organic compounds. As a disinfectant and germicide for bleaching of wool, cotton, silk and other textile fibres and also for dechlorination of oils.

Uses

Lanthanides

- Form alloys like mischmetal and pyrophoric alloys
- Used in making magnetic and electronic devices.
- Oxides are used in glass industry and their mixed oxides are used as catalysts in petroleum cracking
- Recently used in lasers.

Actinides

- 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

- 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).
- 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.
- Melting and boiling points:** All transition metals have generally very high melting and boiling points.
- These high values are due to strong interatomic metallic bonding and the number of unpaired d-electrons leading to covalent bonding.
- Ionisation Energy:**

see → Next page

- Alkaline metals - Li, Na and K
- Alkaline earth metals - Be, Ca and Ba
- Ferrous metals - Fe, Co and Ni
- Heavier metals - Os and Ir
- Werner metal - Ti*
- Liquid metal - Se
- Most abundant transition metal - Fe.

some more

• They also act as catalysts.
 $(\% 10-15) Cu + Zn (\% 40-52) \text{ as copper in zinc, } (\% 10-12) + Cu (\% 60-68) \text{ as copper in zinc, } (\% 10-12) \text{ as copper in zinc, } (\% 60-68) \text{ as copper in zinc, } (\% 10-12)$

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've 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 vapourisation 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	Y (At. no. 39) 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 Krb (At. no. 112).

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The group in a series, 5d series have high ionisation enthalpy 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 decreases). 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 electron 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.

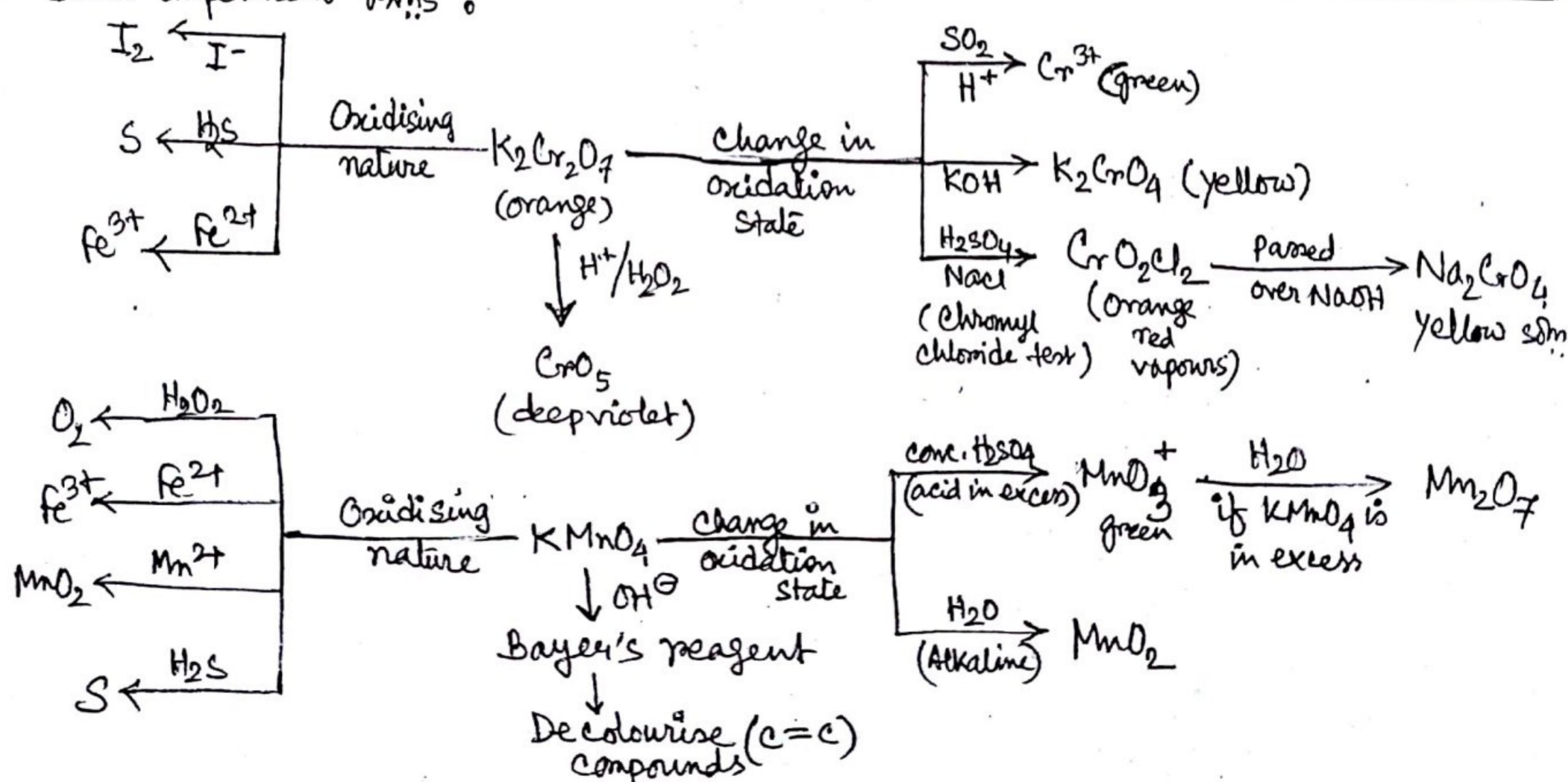
D Coloured ions: Most of the transition metal compounds (ionic as well as covalent) are coloured in their solid or solution form. Coloured ions are formed due to presence of vacant d-subshell. When visible light falls on transition metal compound the transition metal absorbs some radiation of white light 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.

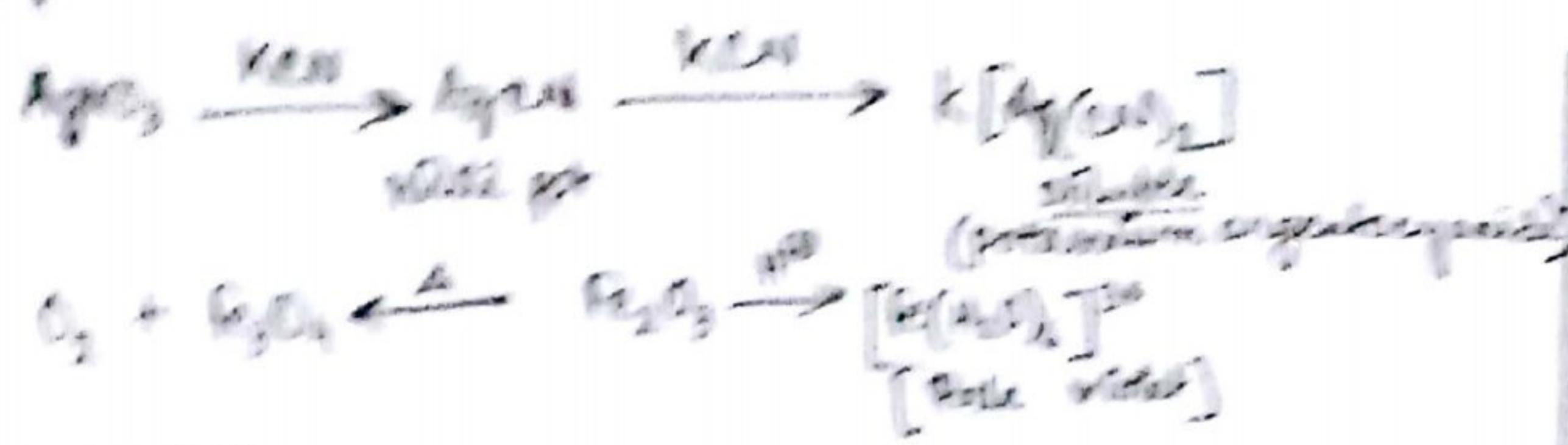
Some important compounds of d-block elements.

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, Baeyer'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 <u>Nessler's reagent</u>	to prepare Nessler's reagent, for making ointments for treating skin infections.

Some important tests:



Q. 10.



Key points

- In first transition series $\text{Cr}(3d^5 4s^1)$ and $\text{Cu}(3d^9 4s^1)$ have exceptions electronic configurations.

Large the number of unpaired electrons, charge in 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 last synthetic transition element was $_{43}\text{Te}$.

Characteristic properties of Lanthanoids

- Oxidation states: All the lanthanoids exhibit a common stable oxidation state of +3. In addition, some lanthanoids other than oxidation states are generally shown by these elements which by losing or gaining the stable f^0 , f^1 or f^2 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 important 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) showing 5f orbital belong to f-block. They don't have any 4f electrons after $\text{La}(5f^1)$ from $\text{Ce}(5f^2)$, $\left[(n-2)f^{14}(n-1)f^6\right]$ or d^1 in $\text{Lu}(7f^1)$. 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 of both 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.

Lanthanoids	Actinoids
III	Ce
IV	Pr
V	Nd
VI	Pm
VII	Eu
VIII	Gd
IX	Tb
X	Dy
XI	Ho
XII	Er
XIII	Tm
XIV	Yb
XV	Lu

ACTINOIDS

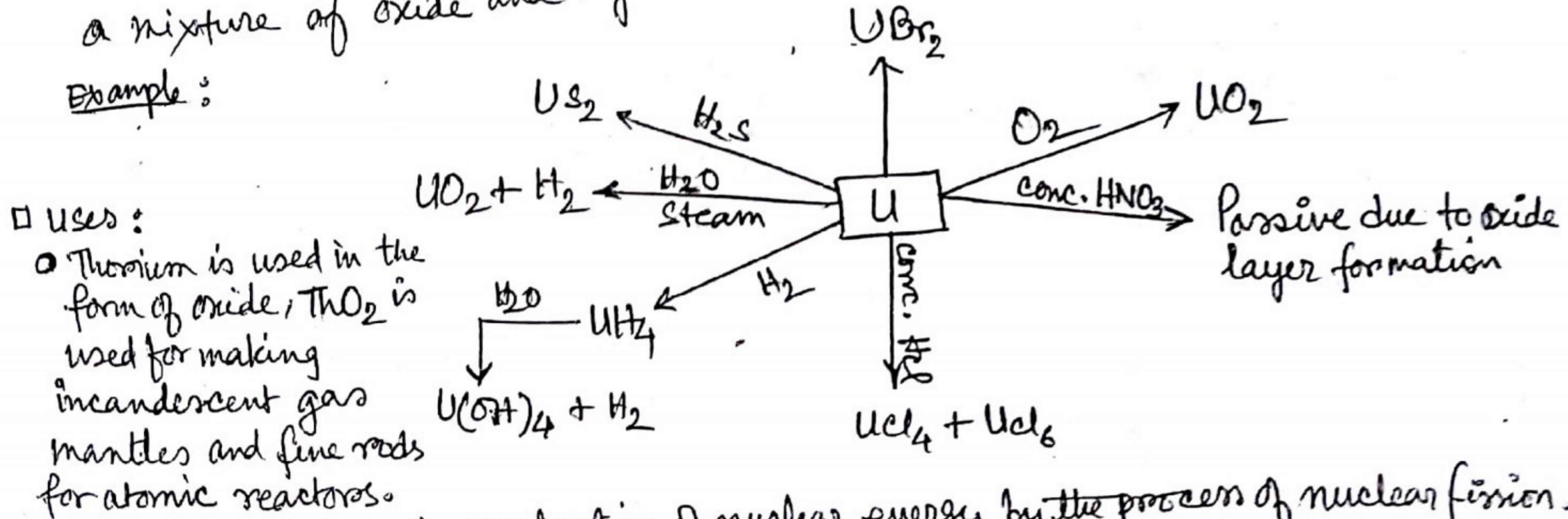
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- The elements in which the last 'e' enters one of the 5f orbital are called - actinoids or antinones or 5f-block elements or second inner transition series. It also includes 14 elements from Th (At. no. 90) to Lr (At. no. 103).

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.

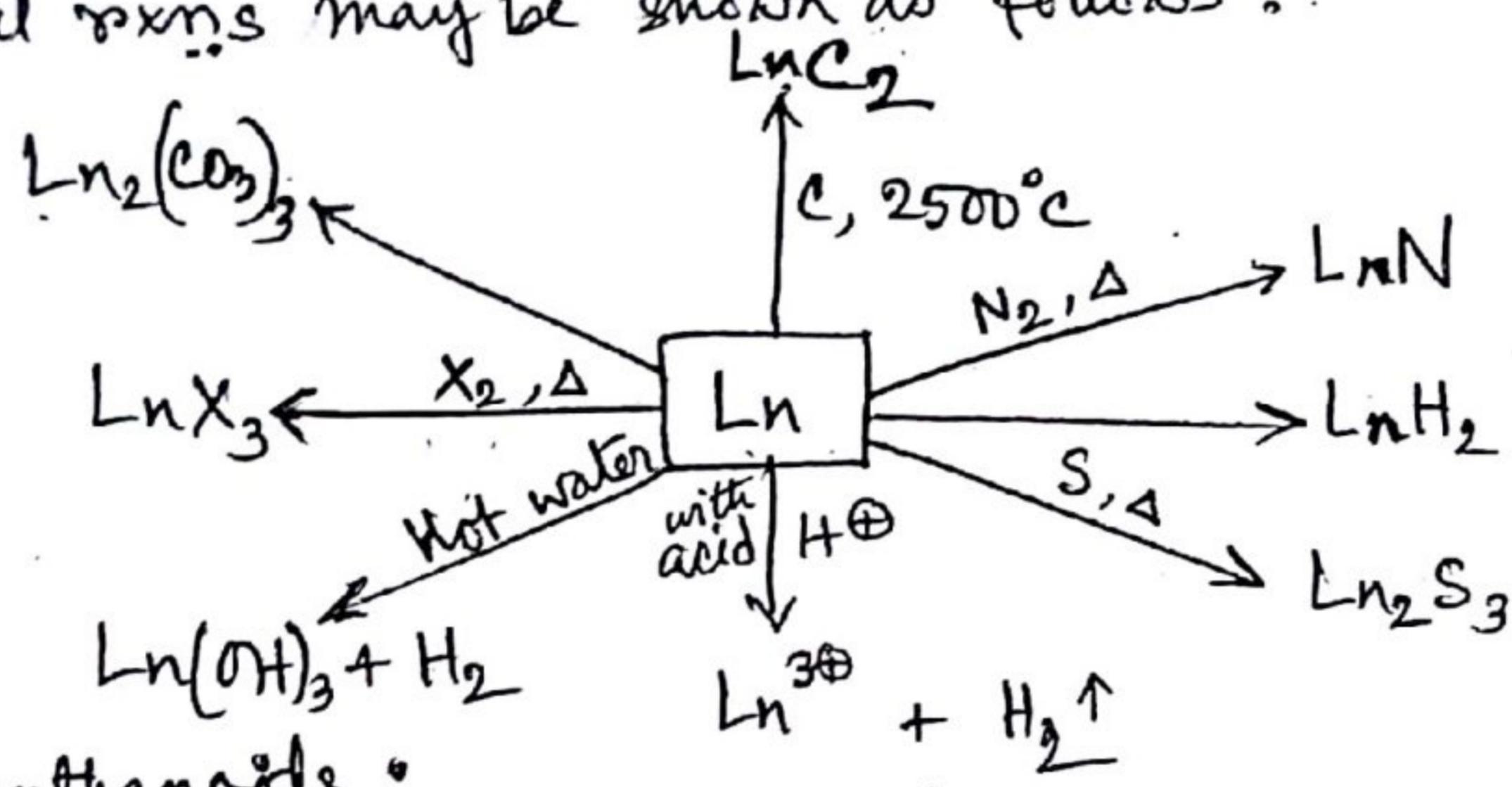
- Uranium is used in the production of nuclear energy by the process of nuclear fission.
- Uranium salts are used in textiles and ceramic industry.
- Plutonium is fissionable material & is used for fueling atomic reactors.

Key points : • Actinoids form oxo-ions such as UO_2^+ , PuO_2^{2+} , UO_4^- , UO_2^{4-} 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 $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.
- 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:

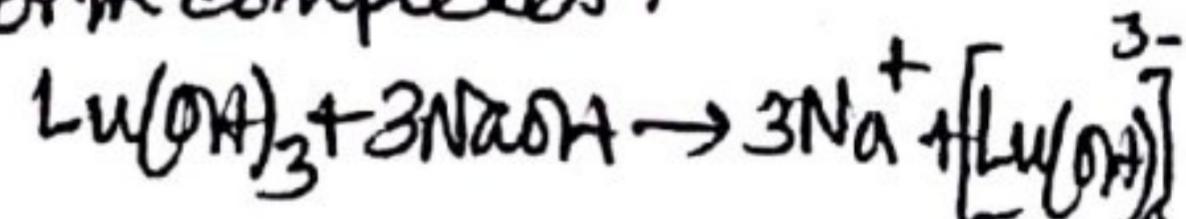


Uses of Lanthanoids:

- 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.

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 $Ce(OH)_3 > Pr(OH)_3 > Nd(OH)_3 \dots$ $\dots Tm(OH)_3 > \cancel{Dy(OH)_3} > \cancel{Yb(OH)_3} > Lu(OH)_3$

The hydroxides react with concentrated alkali to form complexes.



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.

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

- They've general electronic configuration of $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.
- 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.

f-Block Elements (Inner-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

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

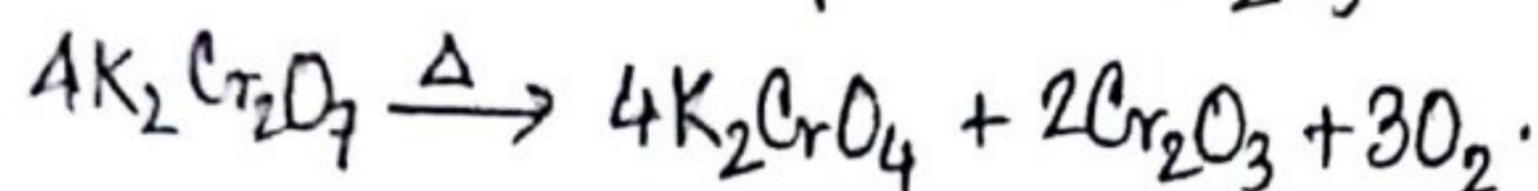
- Reactivity**

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

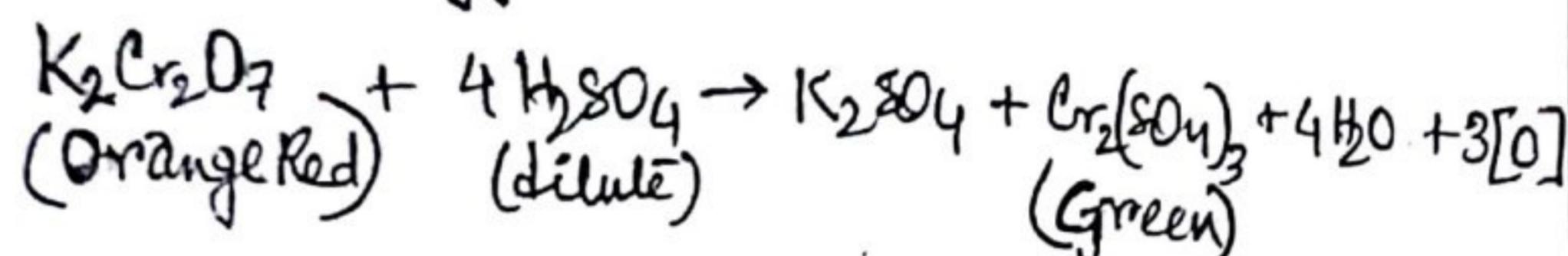
SOME IMPORTANT COMPOUNDS OF d-BLOCK ELEMENTS

a) Potassium Dichromate ($K_2Cr_2O_7$)

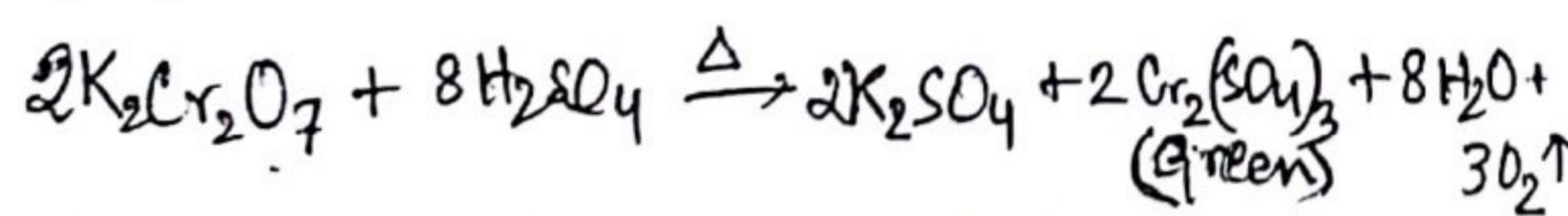
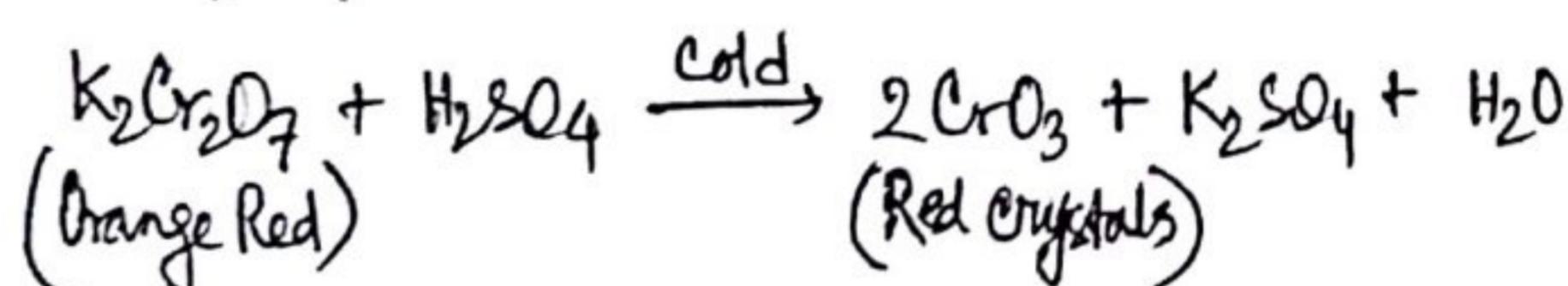
- It is an orange red prismatic crystal that is moderately soluble in H_2O but highly soluble in hot water.
 - It is manufactured from chromite ore, $FeO \cdot Cr_2O_3$.
 - When heated, it is decomposed to Cr_2O_3 .



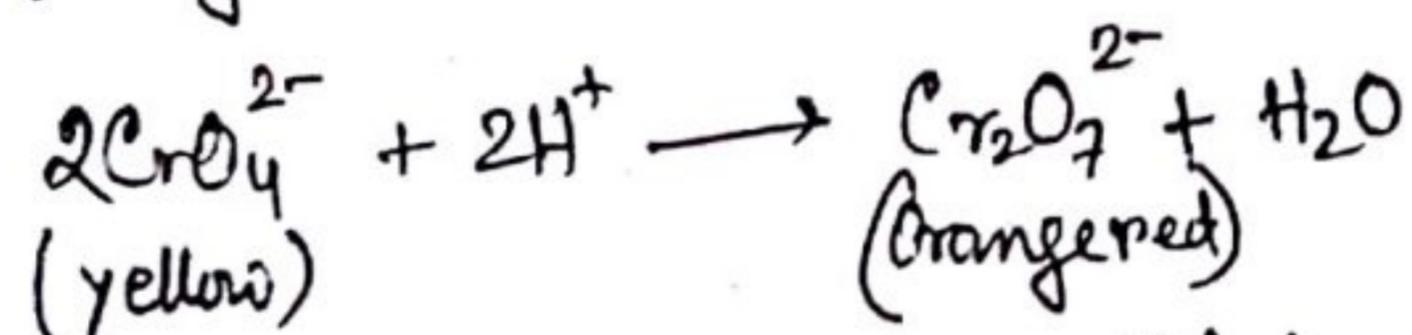
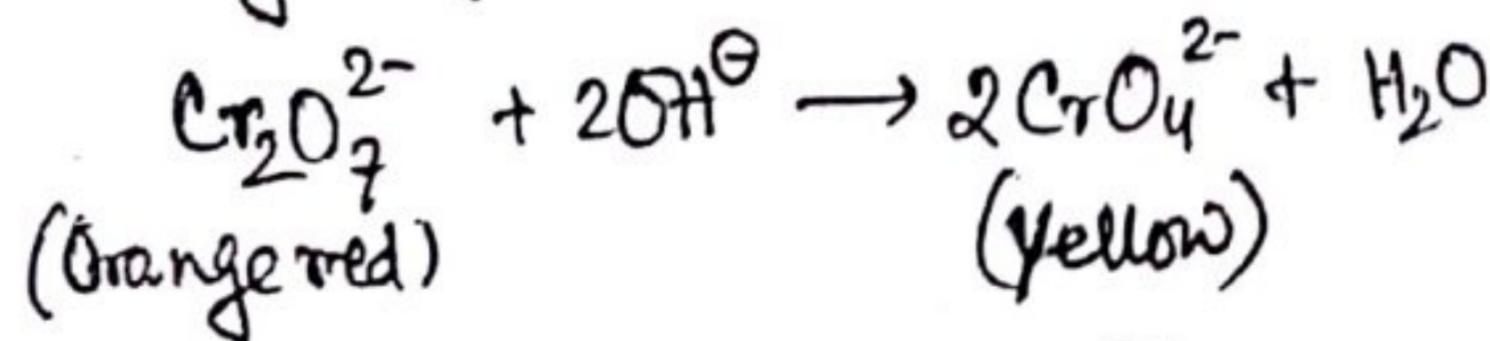
- It acts as a strong oxidising agent in the presence of dilute H_2SO_4 due to the formation of nascent Oxygen.



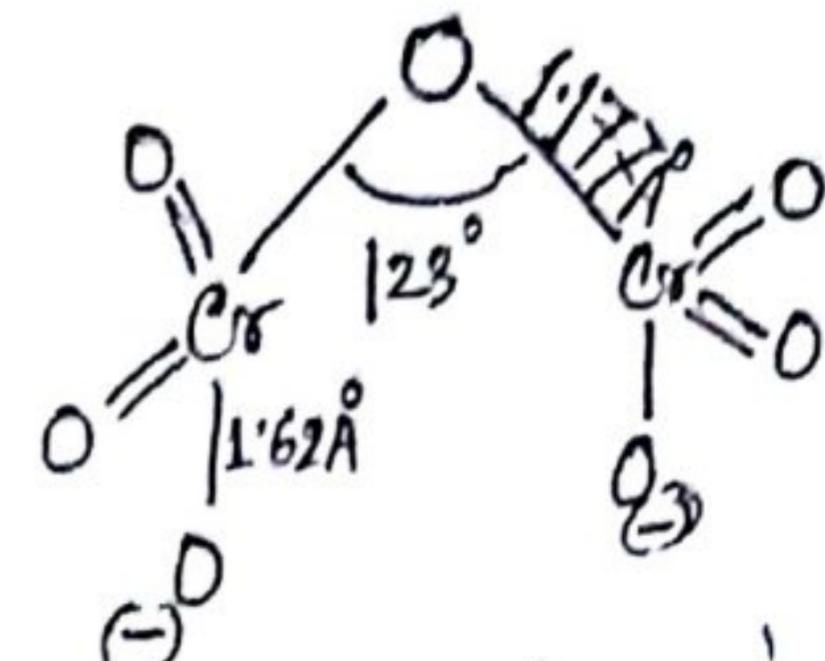
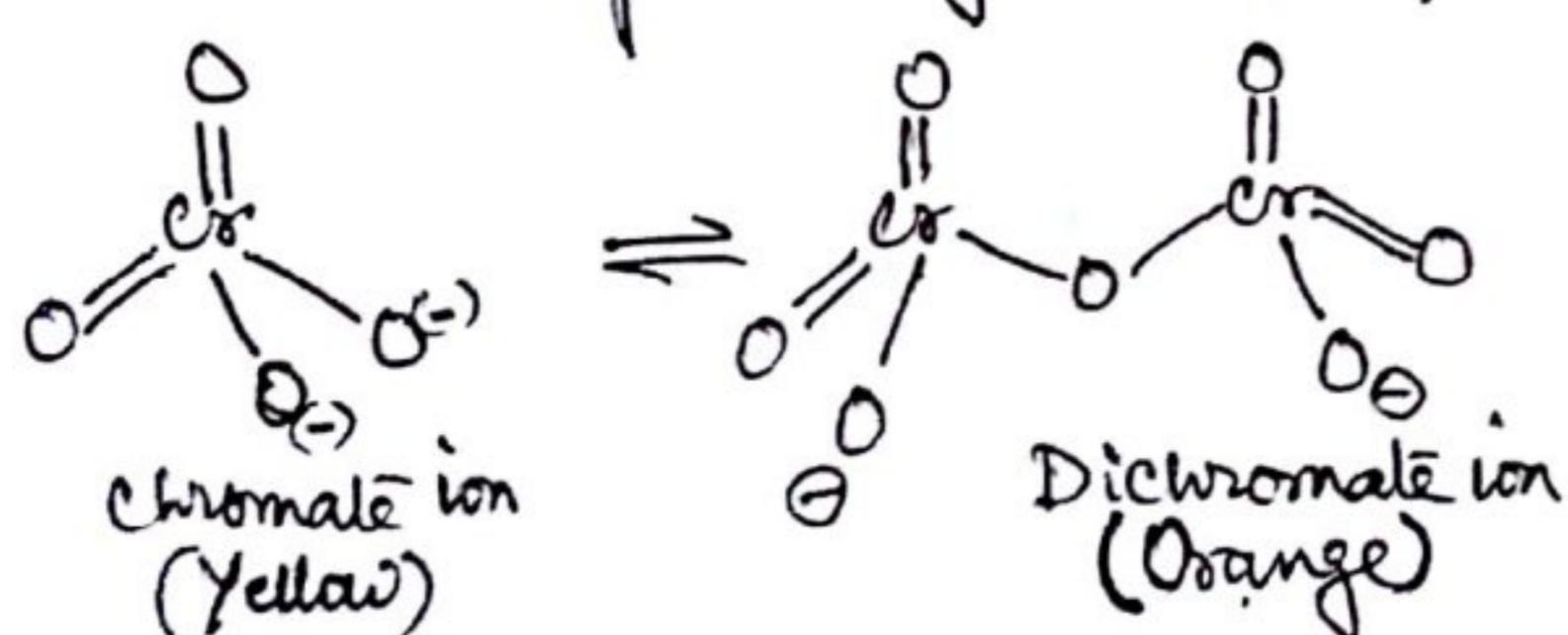
- It oxidises KI , $FeSO_4$ and H_2S to I_2 , $Fe(SO_4)_3$ and S respectively.
 - It reacts differently in different react conditions with H_2SO_4 .



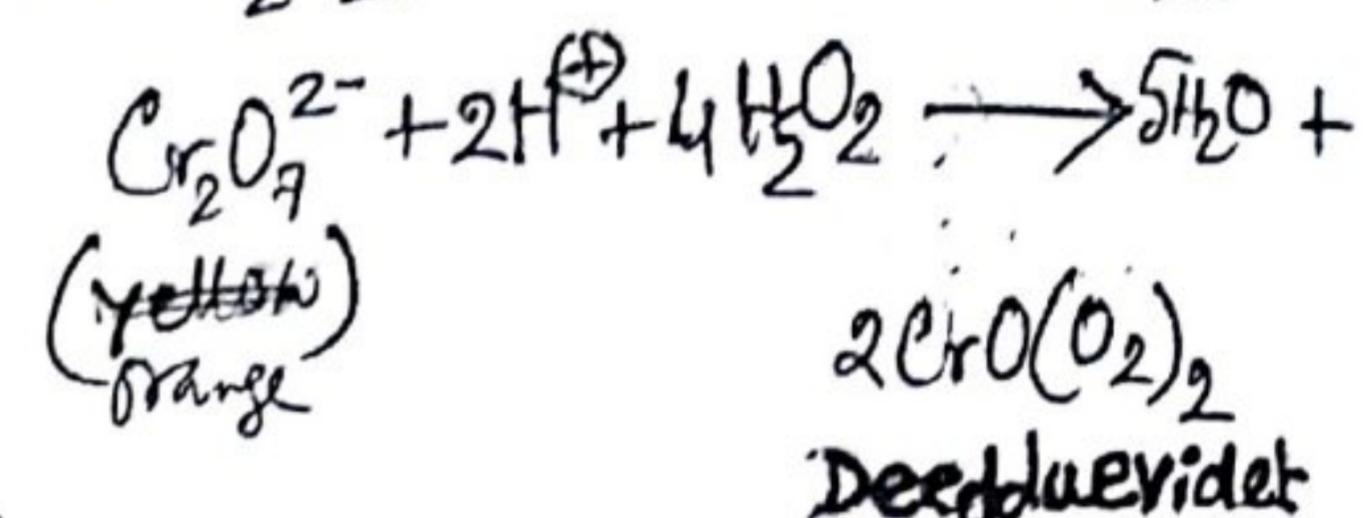
- When heated, it is decomposed to Cr_2O_3 .
 - In acidic and basic mediums, it reacts in the following ways :



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.

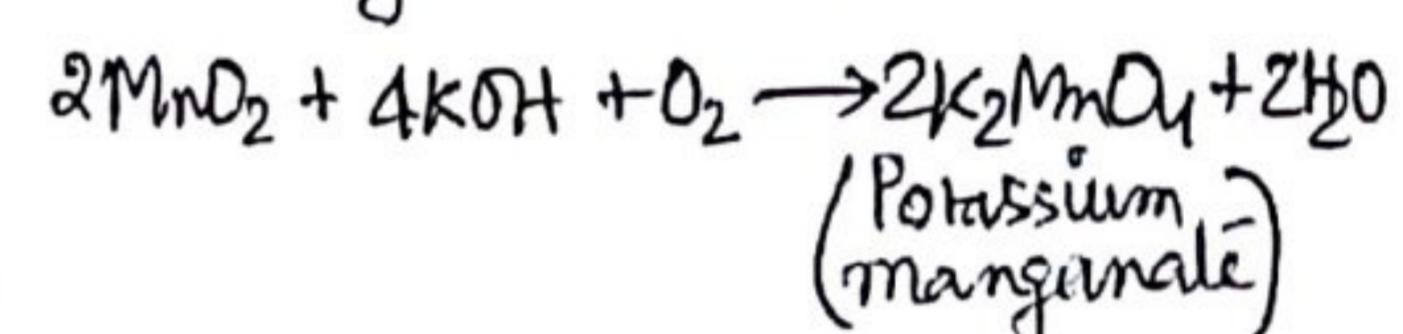


- Acidified solution of $K_2Cr_2O_7$ reacts with H_2O_2 producing $CrO(O_2)_2$.



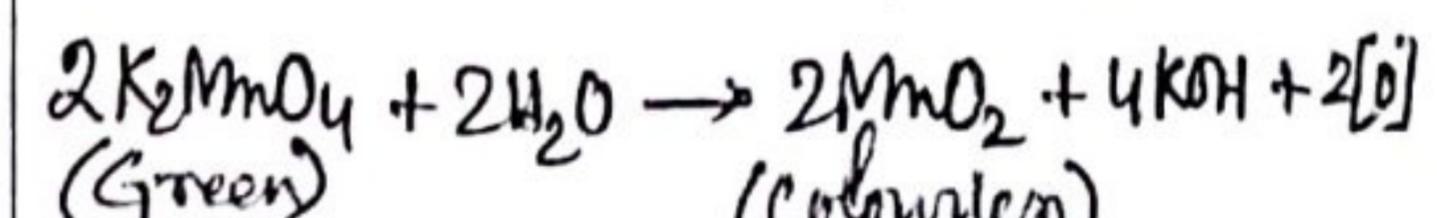
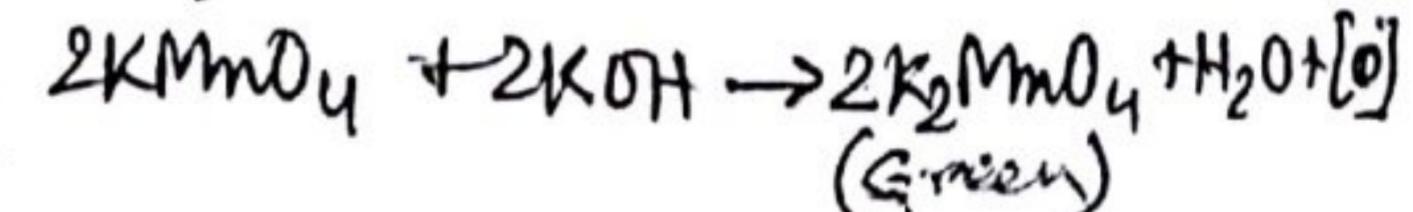
b) Potassium Permanganate ($KMnO_4$)

- 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 $KMnO_4$.

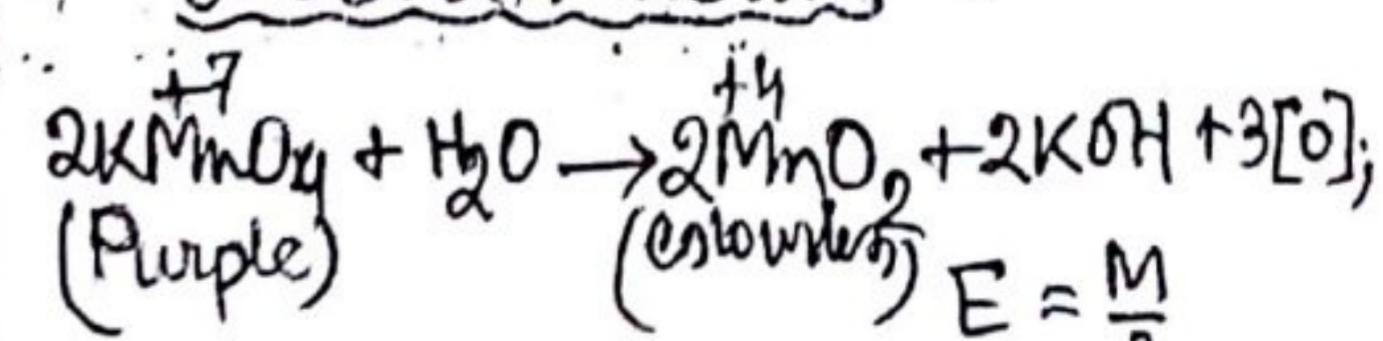


KMnO₄ is a good oxidising agent but the products formed depend on whether the reaction is carried out in acidic, alkaline or neutral medium.

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



Overall reaction

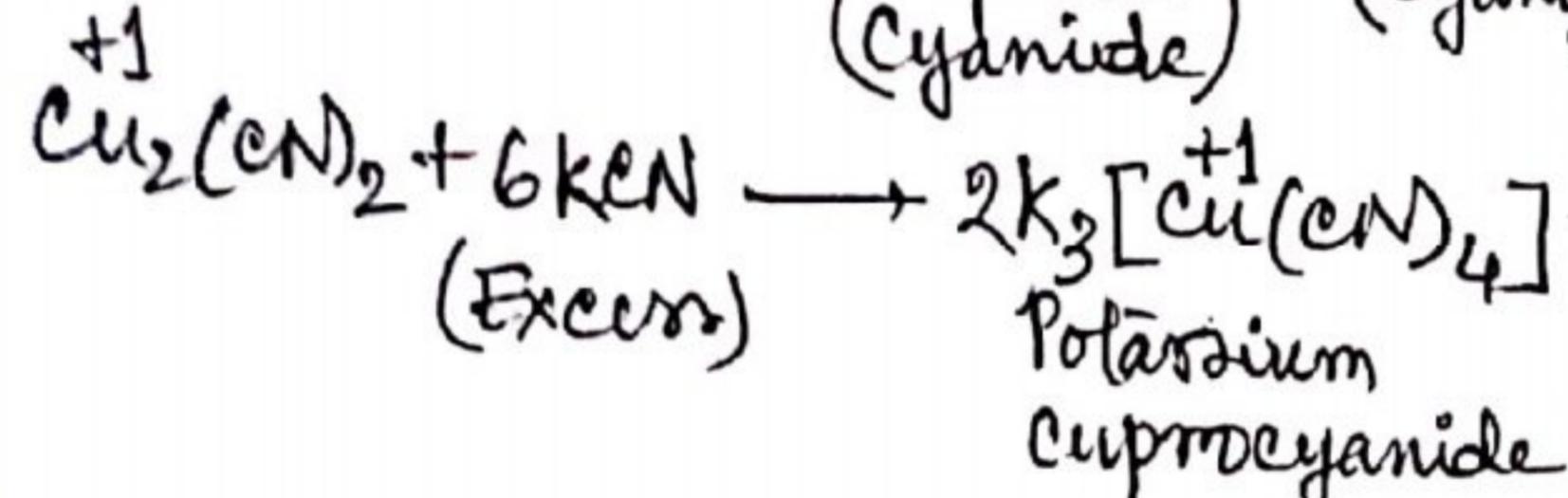
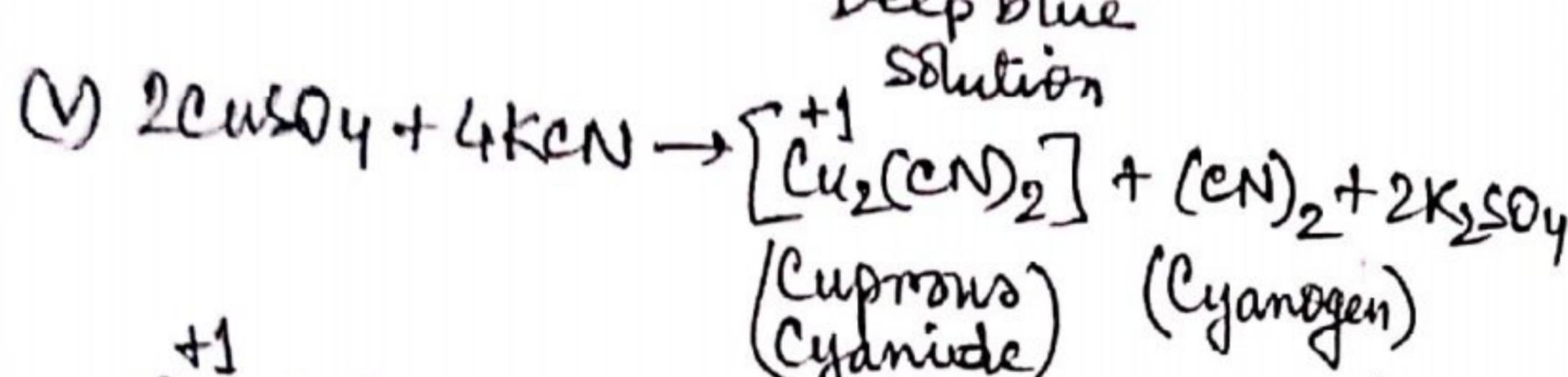
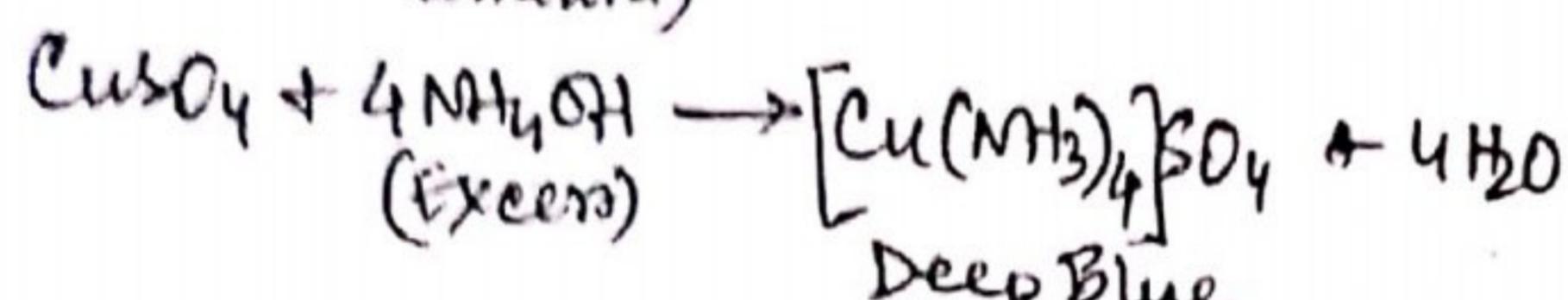
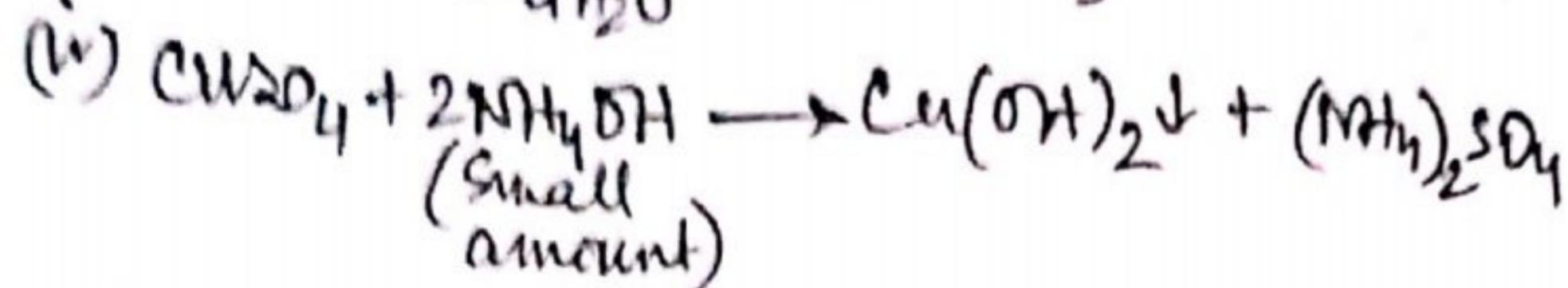
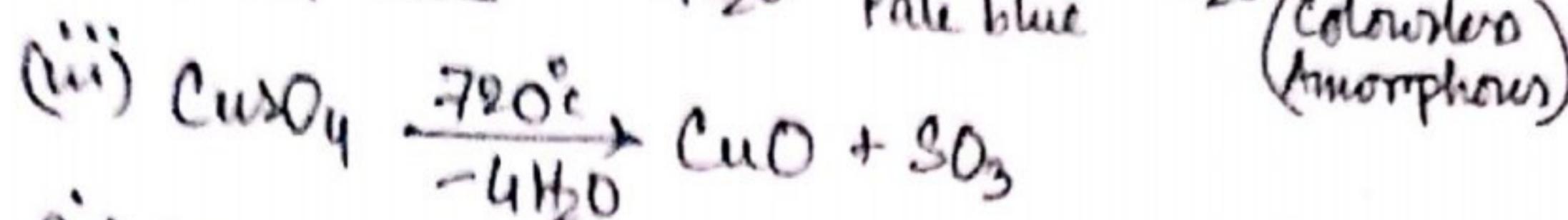
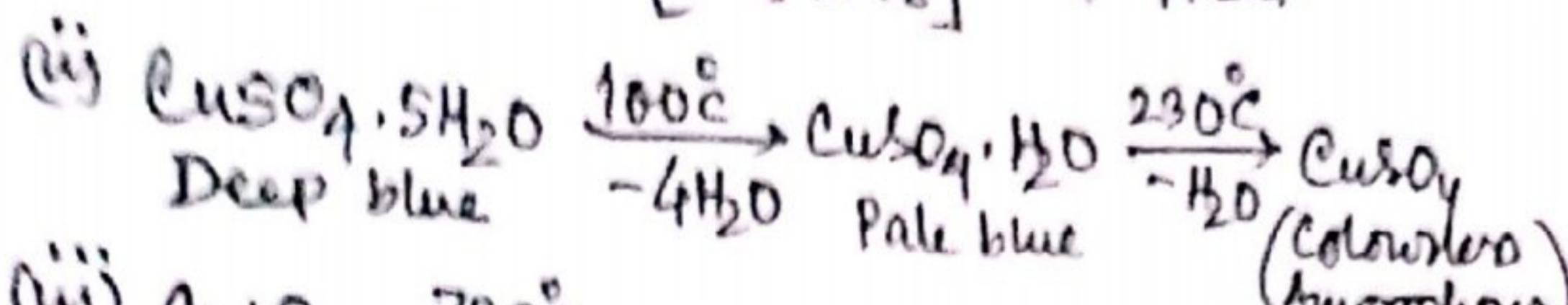
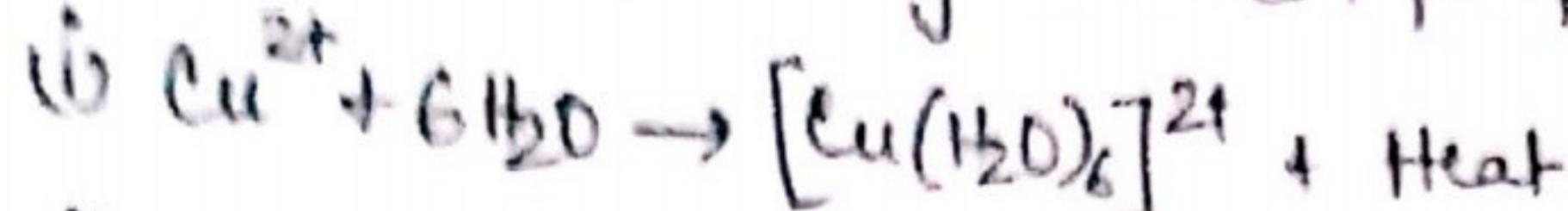


In alkaline medium, it oxidises I,
 NH_3 , nitrotoluene etc. to IO_3^- , N_2 ,
 nitrobenzoic acid etc. respectively.

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 .
- $\text{Cu} + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$
- It is a blue coloured crystal and paramagnetic (when hydrated)

It shows the following chemical properties.



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

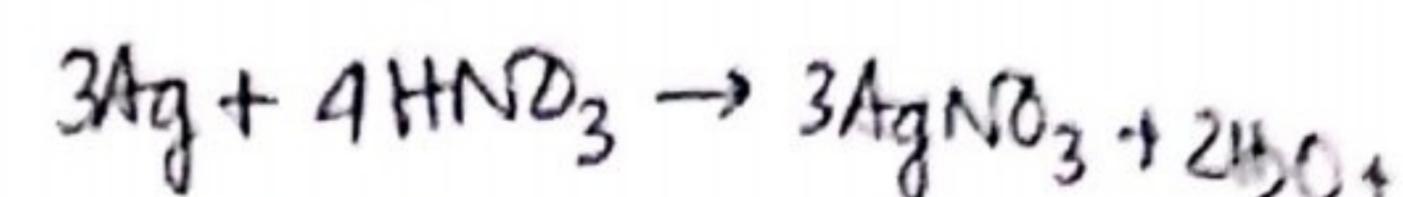
- It is also a component in Fehling's solution and Benedict's solution to test for reducing sugars in which CuSO_4 is reduced to insoluble Cu_2O .

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

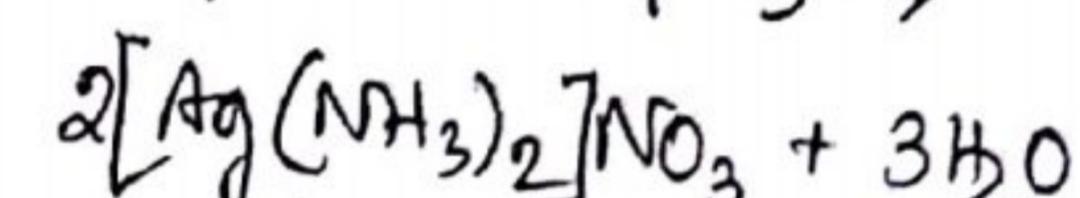
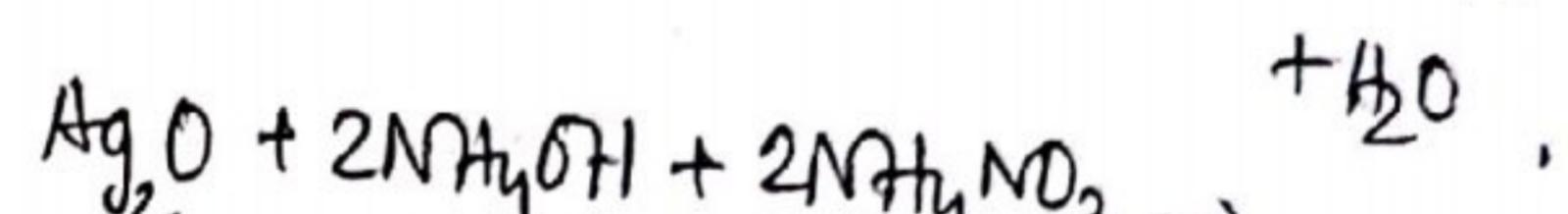
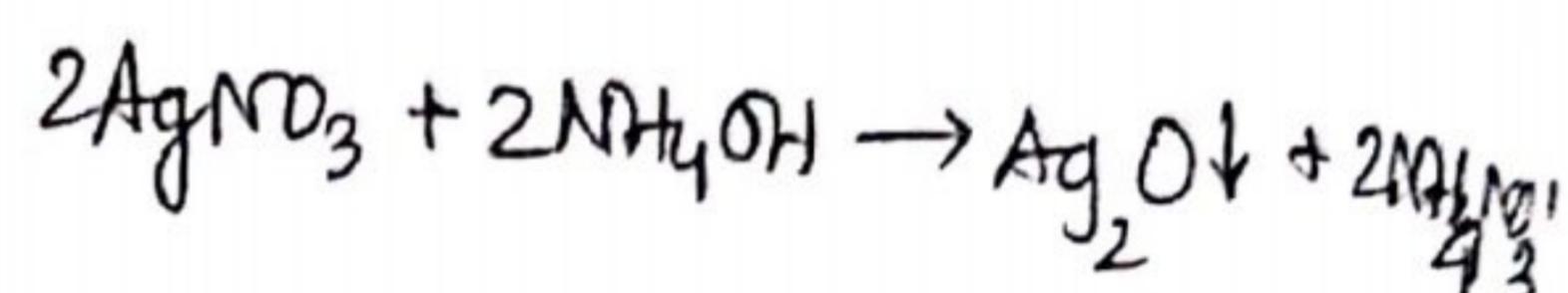
- It is prepared by treating metallic Zn with dil. H_2SO_4 .
- It is a colourless, crystalline solid and soluble in water.
- It decomposes to ZnO and SO_3 when heated above 300°C .
- It is isomorphous with $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4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

f) Silver Nitrate or Lunac Carbie

- 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,

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

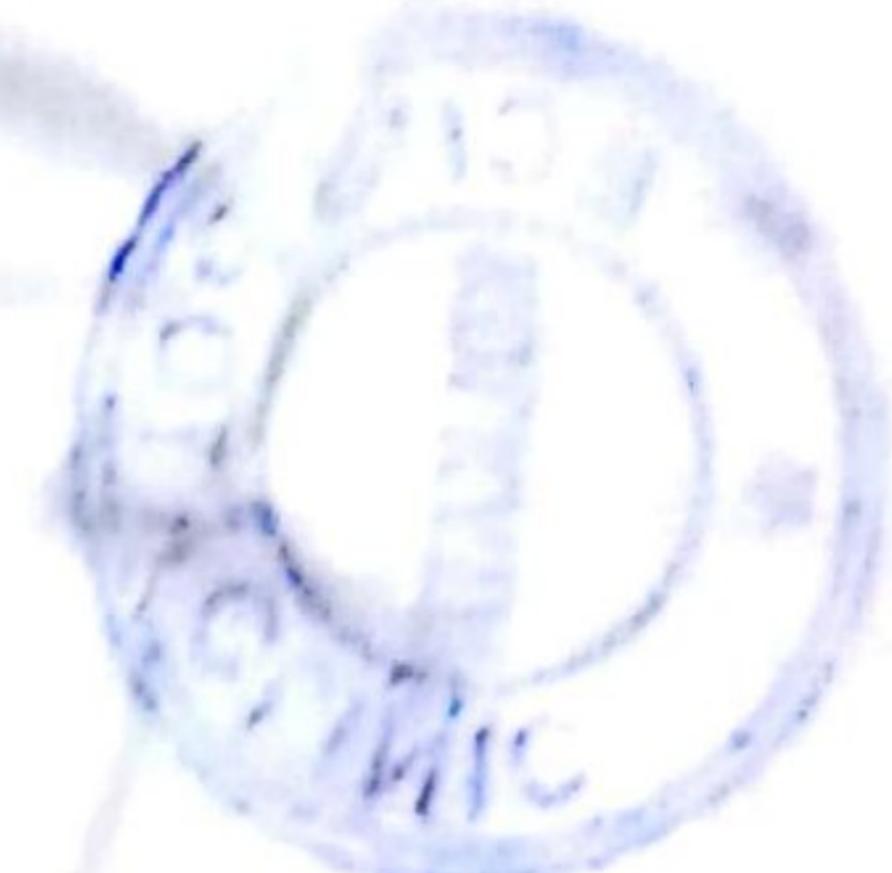
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Dr. GIRIDESH D. P.
MEDICINE RESIDENT

ECGS POLYCLINIC
KOLKATA
MONDAYS / THURSDAYS

ELECTRONIC CONFIGURATIONS OF THE *d*-BLOCK ELEMENTS

General E.C. of the *d*-block element is as

For 3*d* series $3d^1 - 10 \quad 4s^1 - 2$

For 4*d* series $4d^1 - 10 \quad 5s^0 - 2$

For 5*d* series $5d^1 - 10 \quad 6s^1 - 2$

For 6*d* series $6d^1 - 10 \quad 7s^1 - 2$

Overall
 $(n-1)d^{1-10} ns^{0-2}$

Outer Electronic Configurations of the Transition Elements (ground state)

1st Series										
Z	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
21	22	23	24	25	26	27	28	29	30	
2	2	2	1	2	2	2	2	1	2	
1	2	3	5	5	6	7	8	10	10	

2nd Series										
Z	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
39	40	41	42	43	44	45	46	47	48	
2	2	1	1	2	1	1	0	1	2	
1	2	4	5	6	7	8	10	10	10	

3rd Series										
Z	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
57	72	73	74	75	76	77	78	79	80	
2	2	2	2	2	2	2	1	1	2	
1	2	3	4	5	6	7	9	10	10	

4th Series										
Z	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
89	104	105	106	107	108	109	110	111	112	
2	2	2	2	2	2	2	2	1	2	
1	2	3	4	5	6	7	8	10	10	

However, this generalisation has several exceptions because of very little energy difference between $(n-1)d$ and ns orbitals. Furthermore half filled and fully filled sets of orbitals are relatively more stable. Apart from it as Z^* increases energy gap between $(n-1)d$ and ns decreases, which is small enough to prevent electron entering in $(n-1)d$ before completely filling of ns .

The *d* orbitals of the transition element project to the periphery of an atom more than the other orbitals (*s* and *p*). Hence, they are more influenced by the surrounding as well as affecting the atoms or molecules surrounding them.

Example 1 : On what ground can we say that Sc($Z = 21$) is a transition element while Zn($Z = 30$) is not?

Solution : E.C. of $_{21}Sc = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$. In this E.C. $3d$ orbital have one electron in its ground state. That is why it is regarded as a transition element.

E.C. of $Zn = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

Zn does not have partly filled d orbital in its ground state or in its excited state that is why it is not considered as a typical transition element.

Example 2 : Copper atom has completely filled d orbitals ($4d^{10}$) in its ground state. How can we say that it is a transition element?

Solution : Transition element is defined as the one which has incompletely filled d orbitals in its ground state or in their most common oxidation state. Cu in its +2 oxidation state exhibit $4d^9$ E.C. That is why it is considered as a transition element.

Note :

As per rule (Aufbau Rule) last electron is filled in $3d$ after filling of $4s$ in Fe. But during removal last electron is removed from ultimate shell that is $(4s)$ and hence E.C. of Fe^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.

Aufbau Rule or $(n + l)$ Rule is only valid for unfilled orbital. After filling of the electron in E.C. higher will be value of n higher will be energy and if value of n is same then higher will be value of l higher will be energy.

For s orbital, $l = 0$

p, $l = 1$

d, $l = 2$

f, $l = 3$

Try Yourself

1. Write the electronic configuration of given atoms/ions.

(i) Cr (ii) Mn^{3+} (iii) Fe^{3+} (iv) W (v) Pd^{2+} (vi) Pd

GENERAL PROPERTIES OF THE TRANSITION ELEMENTS (d-BLOCK)**Physical Properties**

Nearly all the transition elements display metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.

Note : Except Zn, Cd, Hg and Mn, other metals have one or more typical metallic structure at normal temperature.

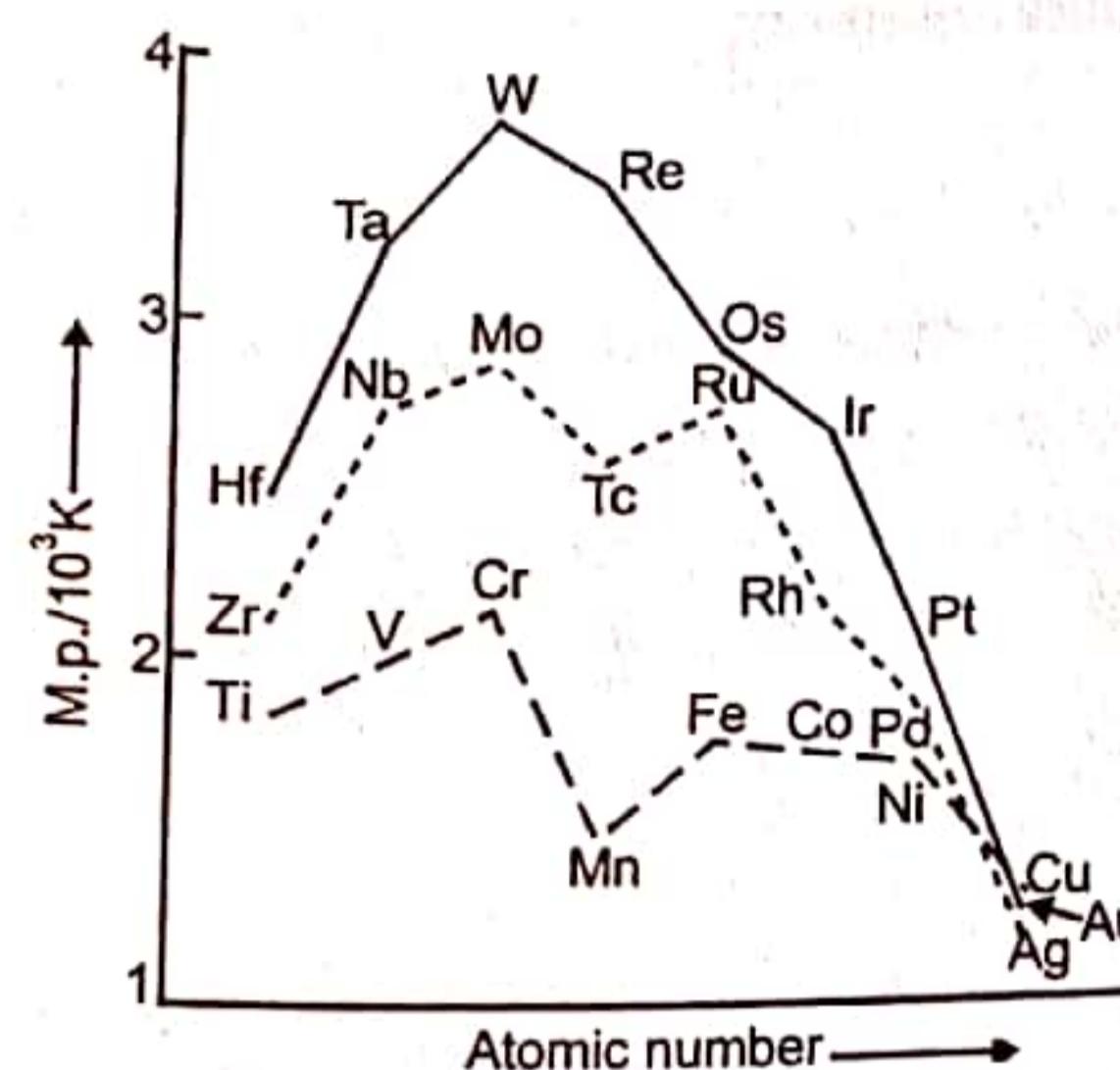
Lattice Structures of Transition Metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
hcp (bcc)	hcp (bcc)	bcc	bcc (bcc, ccp)	X (hcp)	bcc (hcp)	ccp	ccp	ccp	X (hcp)
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
hcp (bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X (hcp)
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
hcp 'ccp,bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X

(bcc = body centred cubic; hcp = hexagonal close packed; ccp = cubic close packed; X = a typical metal structure).

The transition metals (with the exception of Zn, Cd, Hg) are very much harder and have low volatility. Their melting points and boiling points are high.

The high melting points of these metals are attributed to involvement of greater number of electrons $(n-1)d$ in the addition to ns electrons in the interatomic metallic bonding. In any row the melting points of these metals rise to maximum at d^5 except for anomalous behaviour of Tc and fall regularly as the atomic number increases. They have high enthalpies of atomisation which is shown in figure.



Trends in melting points of transition elements

In general greater the number of valence electrons, stronger is the resultant bonding. Since enthalpy of atomisation is an important factor in determining the standard electrode potential of a metal, metals with very high enthalpy of atomisation i.e., very high boiling point tend to be noble in their reactions.

Another generalisation that may be drawn that metals of the 2nd and 3rd series have greater enthalpies of atomisation than the corresponding elements of 1st series. This is an important factor in accounting for the occurrence of much more frequent metal-metal bonding in compounds of heavy transition metals.

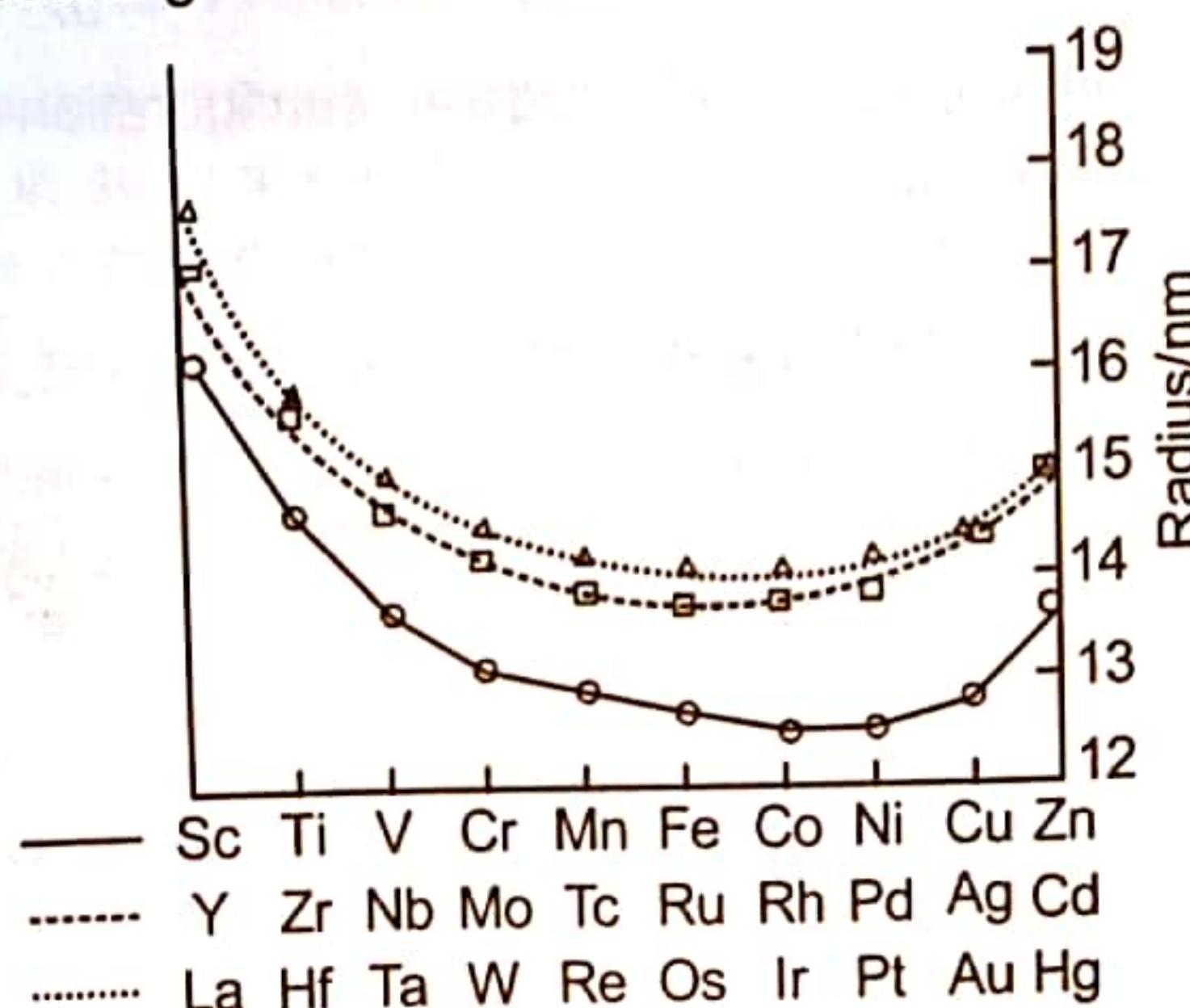
Electronic Configurations and some other Properties of the First Series of Transition Elements

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Atomic number	21	22	23	24	25	26	27	28	29	30	
Electronic configuration											
M	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^4 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$	
M^+	$3d^1 4s^1$	$3d^2 4s^1$	$3d^3 4s^1$	$3d^5$	$3d^5 4s^1$	$3d^6 4s^1$	$3d^7 4s^1$	$3d^8 4s^1$	$3d^{10}$	$3d^{10} 4s^1$	
M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$	
M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	—	—	
Enthalpy of atomisation, $\Delta_a H^\ominus$ kJ mol ⁻¹	326	473	515	397	281	416	425	430	339	126	
Ionisation enthalpy/ $\Delta_i H^\ominus$ kJ mol ⁻¹											
$\Delta_i H^\ominus$ I	631	656	650	653	717	762	758	736	745	906	
$\Delta_i H^\ominus$ II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734	
$\Delta_i H^\ominus$ III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829	
Metallic/ionic radii/pm	M	164	147	135	129	137	126	125	125	137	
M ²⁺	—	—	79	82	82	77	74	70	73	75	
M ³⁺	73	67	64	62	65	65	61	60	—	—	
Standard electrode potential E [⊖] /V	M ²⁺ /M	—	-1.63	-1.18	-0.90	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76
M ³⁺ /M ²⁺	—	—	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	—	—	—
Density/g cm ⁻³	3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1	

Atomic and Ionic Size

In general, ions of the same charge in given series show progressive decrease in radius with increasing atomic number. This is because the new electron enters a *d* orbital each time the nuclear charge increases by unity and shielding effect of *d* electron is not effective hence net electrostatic attraction between the nuclear charge and outer most electron increases and the ionic radius decreases.

This same trend is observed in the atomic radii of a given series. However the variation within a series is quite small. Elements of 4*d* series have larger size than 3*d* but size of 4*d* and 5*d* elements is nearly same in a group. This is due to poor screening of 4*f* electrons.



Trends in atomic radii of transition elements

The filling of 4*f* before 5*d* orbitals results in regular decrease in atomic radii called **Lanthanoid contraction** which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the **Lanthanoid contraction** is that the 4*d* and 5*d* series exhibit similar radii and have very similar physical and chemical properties much more than the expected on the usual family relationship.

Density : The decrease in metallic radius coupled with increase in mass results in a general increase in the density of these elements. Thus from Ti to Cu the significant increase in density may be noted.

Note :

- Sc, Ti and Y have density less than 5 g/cm^3 while other elements have density greater than 5 g/cm^3 .
- Densities of the 2nd row are high and third row values are even higher.
- Density of Os = 22.57 g/cm^3
- Density of Ir = 22.61 g/cm^3

Ionisation Enthalpy

Due to increase in nuclear charge which accompanies the filling of the inner *d* orbitals there is an increase in ionisation enthalpy along each series of the transition elements from left to right. However many small variations occur.

The values for the first three ionisation enthalpies of the first row elements are given in table on previous page. These values show that successive enthalpies of these elements do not increase as steeply as in main group elements. Although the 1st ionisation enthalpy, in general, increases, the magnitude of the increase in the 2nd and 3rd ionisation enthalpy for the successive elements, in general, is much higher.

The irregular trend in the 1st ionisation enthalpy of the 3*d* metals though of little chemical significance can be accounted for by considering that removal of one electron alters the relative energies of 4*s* and 3*d* orbitals. So the unipositive ions have d^n configuration with no 4*s* electrons. There is thus a reorganisation energy accompanying ionisation with some gains in exchange energy as the number of electrons increase and from the transference of *s* electron into *d* orbital. There is generally expected increasing trend in the values as the

effective nuclear charge increases. However, the value of Cr is lower because of the absence of any charge in the d configuration and the value for Zn higher because it represents an ionisation from 4s level.

The lowest common oxidation state of these elements is +2 (except Sc and Cu). To form the +2 ion from the gaseous atoms the sum of 1st and 2nd ionisation energy is required in addition to enthalpy of atomisation for each element.

The trend in the third ionisation enthalpies is not complicated by the 4s orbital factor and shows the greatest difficulty in removing an electron from the d^6 and d^{10} configurations.

Example 3 : Why Cr and Cu have abnormally higher 2nd ionisation energy?

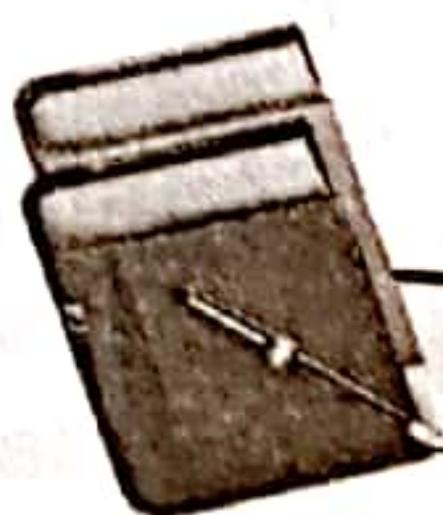
Solution : This is due to half filled and fully filled electronic configuration of Cr^+ and Cu^+ respectively which are considered as very stable.

Example 4 : In 3d series, the enthalpy of atomisation of zinc is the lowest. Why?

Solution : Enthalpy of atomisation depends on number of unpaired electrons. In Zn there is no unpaired electron. As a result, metallic bonding is weak so that enthalpy of atomisation is low.

Example 5 : Why Cu, Ni and Zn generally do not show oxidation state greater than 2?

Solution : IE_3 for Cu, Ni and Zn is generally very high. That is why it does not show oxidation state of +3.



Try Yourself

2. Out of Mn and Fe which has higher IE_3 and why?
3. In 3d series which element has highest IE_3 ?
4. In 3d, 4d and 5d series which element is expected to have highest IE_1 ?

Note :

Out of 4d and 5d series element, element of 5d series have higher IE_1 , because of poor screening of 4f orbital called Lanthanoid contraction. Hg has highest IE_1 (1007 kJ/mol) and La has lowest IE_1 (540 kJ/mol).

Oxidation State

One of the notable features of a transition element is the great variety of oxidation states it may show in compounds.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2 +3 +4	+2 +3 +4 +5	+2 +3 +4 +5 +6 +7	+2 +3 +4 +5 +6 +7	+2 +3 +4 +5 +6	+2 +3 +4	+2 +3 +4	+1 +2	+2

The elements which give the greatest number of oxidation states occur in or near the middle of series. It exhibits all oxidation states from +2 to +7.

- Note :**
- Sc does not exhibit oxidation state of +2.
 - Ti(IV) is more stable than Ti(III) and Ti(II).
 - After middle as we approach from left to right, higher oxidation state becomes less stable.
 - Fe(II, III), Co (II, III), Ni(II), Cu(I, II) are typical species.

Example 6 : How can we show that change in oxidation state is different from variable oxidation state for non transition element?

Solution : The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of *d*-orbitals in such a way that their oxidation states differ from each other by unity e.g., V^{II}, V^{III}, V^{IV}, V^V. This is in contrast with the variability of oxidation states of non-transition elements where oxidation states normally differ by a unit of two.

Example 7 : How would you account for the increasing oxidising power in the series $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$?

Solution : This is due to increasing stability of the lower species to which they are reduced.

Formulas of Halides of 3d Metals

Oxidation Number						
+6				CrF ₆		
+5		VF ₅		CrF ₅		
+4	TiX ₄	VX ₄ ^I	CrX ₄	MnF ₄		
+3	TiX ₃	VX ₃	CrX ₃	MnF ₃	FeX ₃ ^I	CoF ₃
+2	TiX ₂ ^{III}	VX ₂	CrX ₂	MnX ₂	FeX ₂	CoX ₂ NiX ₂ CuX ₂ ^{II} ZnX ₂
+1						CuX ^{III}

Key : X = F → I; X^I = F → Br; X^{II} = F, Cl; X^{III} = Cl → I

Oxides of 3d Metals

Oxidation Number	3	4	5	6	7	8	9	10	11	12	Groups
+7					Mn ₂ O ₇						
+6					CrO ₃						
+5			V ₂ O ₅								
+4		TiO ₂	V ₂ O ₄	CrO ₂	MnO ₂						
+3	Sc ₂ O ₃	Ti ₂ O ₃	V ₂ O ₃	Cr ₂ O ₃	Mn ₂ O ₃	Fe ₂ O ₃					
					Mn ₃ O ₄ *	Fe ₃ O ₄ *	Co ₃ O ₄ *				
+2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO	
+1									Cu ₂ O		

* Mixed oxides



Try Yourself

5. MnF_7 is not stable while Mn_2O_7 is stable.
6. What is the hybridisation of Mn in K_2MnO_4 ?
7. Why is FeI_3 not stable?

Example 8 : Name the transition element which does not exhibit variable oxidation states.

Solution : Sc ($Z = 21$) does not exhibit variable oxidation states.

Example 9 : Name any two transition metals which exhibit oxidation state of +8.

Solution : Ru and Os exhibit +8 oxidation states.

Example 10 : Calculate the oxidation state of Fe in $\text{Fe}(\text{CO})_5$.

Solution : Zero.

Example 11 : In 3d series Mn shows highest oxidation state. Why?

Solution : The maximum oxidation states of reasonable stability corresponds in value to the sum of s and 'd' electrons up to manganese. Total 7 electrons are present in 3d and 4s in Mn and hence it can exhibit maximum oxidation state of +7.

Example 12 : For the first row transition metals the E^\ominus values are :

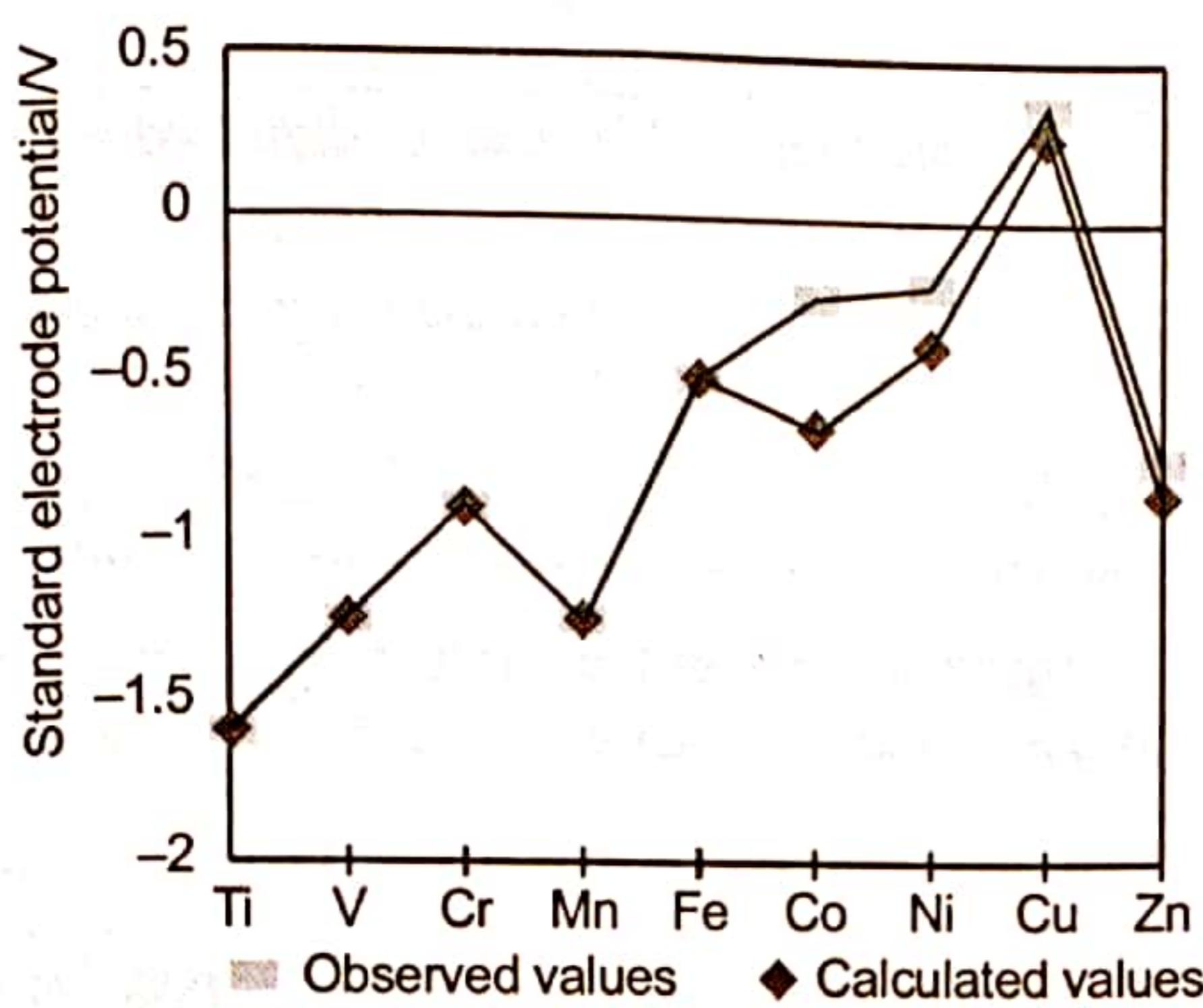
E^\ominus	V	Cr	Mn	Fe	Co	Ni	Cu
(M^{2+}/M)	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

Explain the irregularity in the above values.

Solution : The $E^\ominus (\text{M}^{2+}/\text{M})$ values are not regular which can be explained from the irregular variation of ionisation enthalpies ($\Delta_i \text{H}_1 + \Delta_i \text{H}_2$) and also the sublimation enthalpies which are relatively much less for manganese and vanadium.

Example 13 : Why is the E^\ominus value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$? Explain.

Solution : Much larger third ionisation energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.

Trends in the M^{2+}/M Standard Electrode Potentials

Observed and calculated values for the standard electrode potentials
 $M^{2+} \rightarrow {}^{\circ}M$ of the elements Ti to Zn

Thermochemical data (kJ mol^{-1}) for the first row Transition Elements and the Standard Electrode Potentials for the Reduction of M^{II} to M

Element (M)	$\Delta_a H^\ominus (M)$	$\Delta_i H_1^\ominus$	$\Delta_i H_2^\ominus$	$\Delta_{hyd} H^\ominus (M^{2+})$	E^\ominus / V
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	0.34
Zn	130	908	1730	-2059	-0.76

The stability of the half-filled d sub-shell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+} are related to their E^\ominus values, whereas E^\ominus for Ni is related to the highest negative $\Delta_{hyd} H^\ominus$.

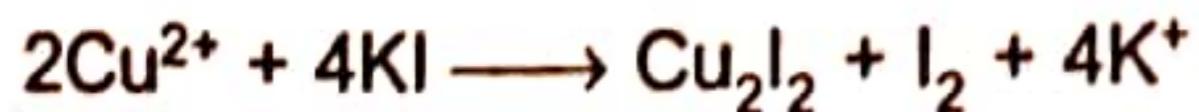
Table contains the thermochemical parameters related to the transformation of the solid metal atoms to M^{2+} ion in solution and their standard electrode potential.

The unique behaviour of Cu having a positive E^\ominus , accounts for its trend in M^{3+}/M^{2+} standard electrode potential. An examination of the $E^\ominus(M^{3+}/M^{2+})$ values show varying trend. The low value for Sc reflects that Sc in +3 have noble gas E.C. The highest value for Zn is due to the removal of an electron from the stable d^{10} configuration of Zn^{2+} . The comparatively high values for Mn shows that $Mn^{2+}(d^5)$ is especially more stable.

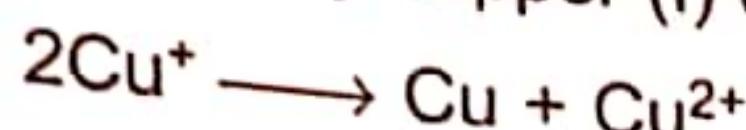
Trend in stability of higher oxidation state

Higher oxidation states are stable with F and O while lower oxidation states are stable with I.

V^{IV} is represented only by VF_5 , the other halide however, undergo hydrolysis to give oxohalides VOX_3 . Another feature of fluorides is their instability in the low oxidation state e.g., VX_2 (X – Cl, Br, I) and same applies to CuX. On the other hand, all Cu^{2+} halides are known except the iodide. In this case Cu^{2+} oxidises I^- to I_2 .



However, many copper (I) compound show disproportionation reaction in aq. medium



Now, in aq. medium Cu^{2+} is more stable than Cu^+ due to its high hydration energy than Cu^+ which compensates IE_2 .

The highest oxidation number in the oxides coincides with the group number and is attained in Sc_2O_3 , Mn_2O_7 .

Example 14 : Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4 configuration?

Solution : Cr^{2+} is reducing as its configuration changes from d^4 to d^3 having half filled t_2 g level. On the other hand, the change from Mn^{3+} to Mn^{2+} result in the half filled d^5 configuration which has extra stability.

Example 15 : The $E^\circ(M^{2+}/M)$ value for copper is positive (0.34 volt). What is possible reason for this?

Solution : Reduction potential will depend on

- (i) $\text{Cu(s)} \longrightarrow \text{Cu(g)}$; ΔH (atomisation)
- (ii) $\text{Cu(g)} \longrightarrow \text{Cu}^{2+}$; ($\text{IE}_1 + \text{IE}_2$)
- (iii) $\text{Cu}^{2+} \xrightarrow{\text{H}_2\text{O}} \text{Cu}^{2+}$; (ΔH_{Hyd})

Due to high enthalpy of atomisation and low $\Delta H_{\text{hydration}}$ energy $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ is high.

Example 16 : Which is stronger reducing agent $\text{Cr}^{2(+)}$ or Fe^{2+} and why?

Solution : By using table Cr^{2+}/Cr (-0.90) and Fe^{2+}/Fe (-0.44) we can say that Cr^{2+}/Cr is stronger reducing agent.



Try Yourself

8. Why highest oxidation state are stable with F and O?
9. Why IE_3 of Mn is high?

Chemical Reactivity and E° Values

Transition metals vary widely in their chemical reactivity. Many of them are sufficiently electropositive to dissolve in mineral acid although a few are noble, it means these do not react with single acid.

The metal of 3d series except Cu are relatively more reactive and are oxidised by 1M H^+ though the actual rate at which these metals react with oxidising agents like hydrogen ion (H^+) is some time slow.

For example Ti and V are passive to dilute non oxidising acids at room temperature. Increase in reduction potential M^{2+}/M from left to right indicate decreasing tendency to form divalent cation along the series.

Note :

- E° value of Mn^{2+}/Mn , Ni^{2+}/Ni and Zn^{2+}/Zn are more negative than expected. This is due to half filled and full filled E.C. for Mn^{2+} and Zn^{2+} respectively while for Ni^{2+} . This is because of high enthalpy of hydration.
- Higher will be M^{3+}/M^{2+} stronger will be oxidising agent. That is why Mn^{3+} and Co^{3+} are strongest oxidising agent in aqueous solutions?
- Ti^{2+} , V^{2+} and Cr^{2+} are strong reducing agents and liberate hydrogen from a dilute acid

$$2Cr^{2+} + 2H^+ \longrightarrow Cr^{3+} + H_2$$
- The trend of reduction potential is not regular because trend of enthalpies of atomisation and $(IE_1 + IE_2)$ is not regular.

Magnetic Properties

When magnetic field is applied to substance. Mainly two types of magnetic behaviour are observed : diamagnetism and paramagnetism. Diamagnetic substance contain no unpaired electron and repelled by magnet while paramagnetic substances are attracted and contain one or more unpaired electron. The substance which are strongly attracted by magnet are said to be ferromagnetic. Paramagnetism arises due to presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the 1st series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. That is why for these element spin only moment i.e., μ is calculated.

$$\mu = \sqrt{n(n+2)} BM \text{ where } n \text{ is number of unpaired electron and } BM\text{-Bohr magneton.}$$

Calculated and Observed Magnetic Moments (BM)

Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Tl^{2+}	$3d^2$	2	2.84	2.76
V^{2+}	$3d^3$	3	3.87	3.86
Cr^{2+}	$3d^4$	4	4.90	4.80
Mn^{2+}	$3d^5$	5	5.92	5.96
Fe^{2+}	$3d^6$	4	4.90	5.3 – 5.5
Co^{2+}	$3d^7$	3	3.87	4.4 – 5.2
Ni^{2+}	$3d^8$	2	2.84	2.9 – 3, 4
Cu^{2+}	$3d^9$	1	1.73	1.8 – 2.2
Zn^{2+}	$3d^{10}$	0	0	

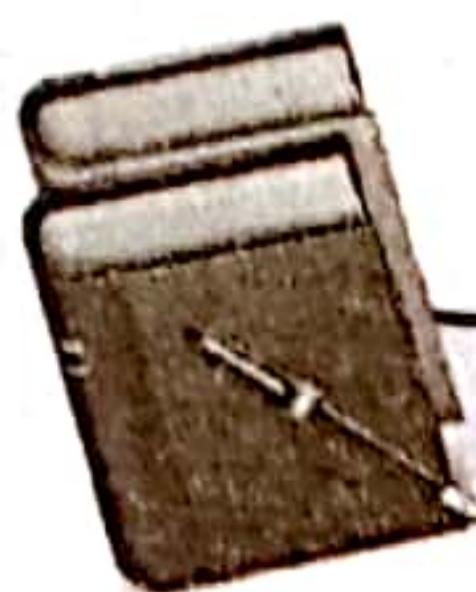
Note : The experimental data are mainly for hydrated ions in solution or in solid state.

Example 17 : Calculate the spin only moment of a divalent ion in aq. solution of atomic number 25.

Solution : E.C. of $Mn^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Number of unpaired electron = 5.

$$\mu = \sqrt{5(5+2)} BM = \sqrt{35} BM$$



Try Yourself

10. Calculate spin only moment of given ions.

- (i) Cu^{2+}
- (ii) Cr^{2+}
- (iii) Fe^{3+}
- (iv) Ni^{2+}

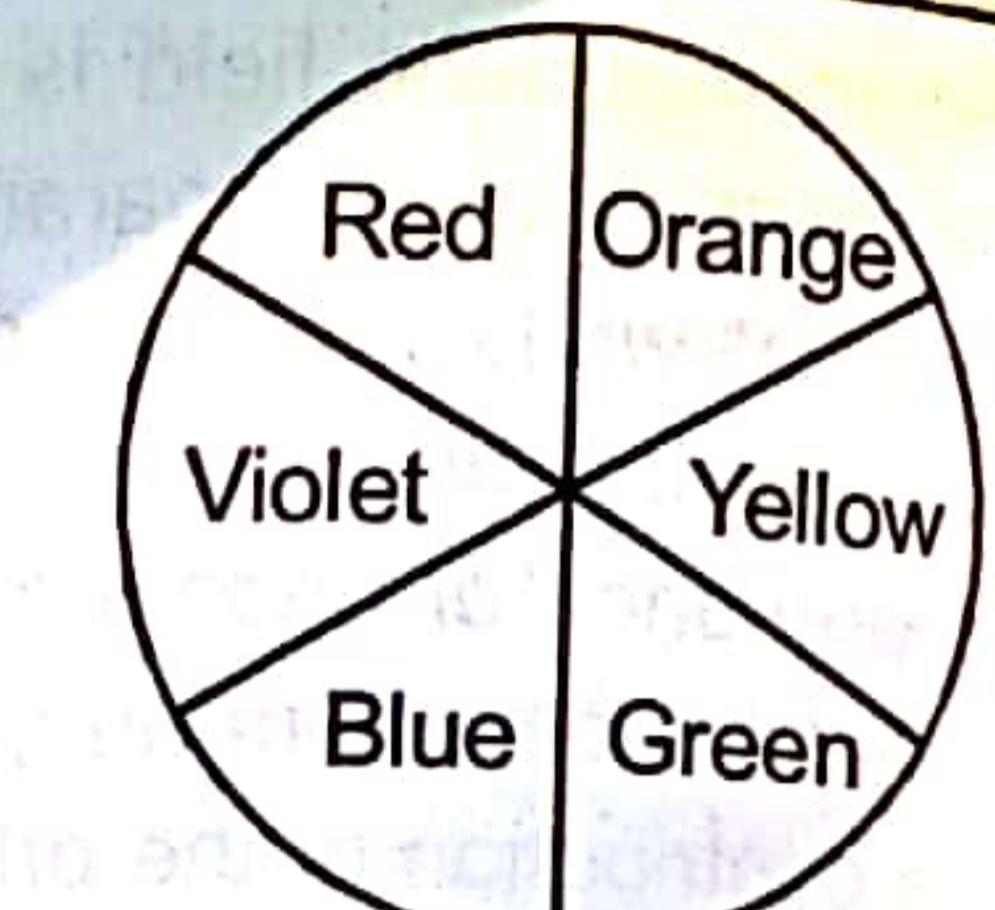
Formation of Coloured Ions

When an electron from a lower energy *d* orbital is excited to higher energy *d* orbital, the energy of excitation corresponds to the frequency of light absorbed. This frequency absorbed generally lies in the visible region. The colour observed corresponds to the complementary colour of light absorbed.

The frequency of light that is absorbed is determined by

- (i) Nature of ligand
- (ii) Size of metal ion
- (iii) Oxidation state of metal

Complementary Colours

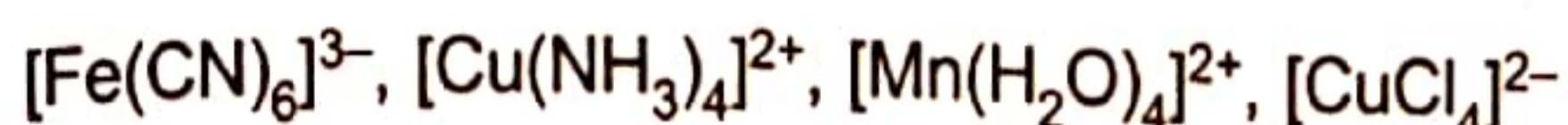


Colours of Some of the First Row (aquated) Transition Metal Ions

Configuration	Example	Colour
$3d^0$	Sc^{3+}	colourless
$3d^0$	Ti^{4+}	colourless
$3d^1$	Ti^{3+}	purple
$3d^1$	V^{4+}	blue
$3d^2$	V^{3+}	green
$3d^3$	V^{2+}	violet
$3d^3$	Cr^{3+}	violet
$3d^4$	Mn^{3+}	violet
$3d^4$	Cr^{2+}	blue
$3d^5$	Mn^{2+}	pink
$3d^5$	Fe^{3+}	yellow
$3d^6$	Fe^{2+}	green
$3d^6, 3d^7$	$\text{Co}^{3+}, \text{Co}^{2+}$	bluepink
$3d^8$	Ni^{2+}	green
$3d^9$	Cu^{2+}	blue
$3d^{10}$	Zn^{2+}	colourless

Formation of Complex Compound

Due to smaller size of the metal ions high ionic charges and the availability of *d* orbitals for bond formation, transition elements form a number of complex compounds. Example of some complex compounds/ions are

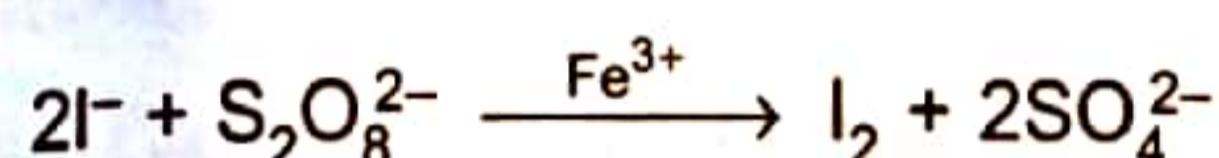


Catalytic Properties

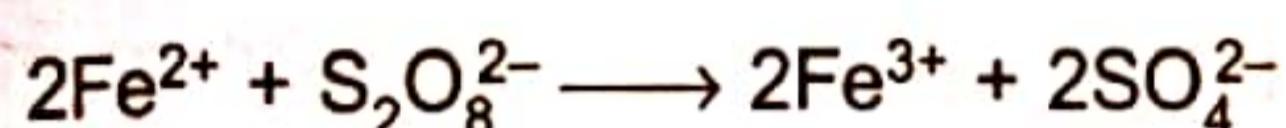
The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to them due to their ability

1. To adopt multiple oxidation states
2. To form complexes

Catalyst at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of catalyst. This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowered). Also because transition metal ions can change their oxidation states, they become more effective as catalyst. For example Fe(III) catalyses the reaction between I^- and $\text{S}_2\text{O}_8^{2-}$.



Mechanism :



So actually Fe^{3+} oxidise I^- to I_2 .

Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattice of metals. These are usually non stoichiometric and are neither typically ionic nor covalent. For example, TiC , Mn_4N , Fe_3H , $\text{VH}_{0.56}$ and $\text{TiH}_{1.7}$ etc. The formulas quoted do not of course correspond to any normal oxidation state of metal. Because of the nature of their composition, these compounds are referred to as interstitial compounds.

The principle physical and chemical characteristics of these compounds are :

1. They have high melting point, higher than those of pure metal.
2. These are very hard.
3. They retain metallic conductivity.
4. They are chemically inert.

Alloy Formation

Alloy may be homogeneous solid solution in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals alloys are readily formed by these metals. The alloys so formed are hard and have often high melting point. The best known are ferrous alloys. Cr, V, W, Mo and Mn are used for the production of a variety of steels and stainless steel.

Alloys of transition metals with non transition metals such as brass ($\text{Cu} - \text{Zn}$) and bronze ($\text{Cu} - \text{Sn}$) are also of considerable industrial importance.

Other examples are:

German Silver: 50-60% Cu, 10-30% Ni, 20-30% Zn

Bell Metal: 80% Cu, 20% Sn

Gun Metal: 80% Cu, 10% Sn, 2% Zn



Try Yourself

11. Explain why Cu^+ ion is not stable in aq. solution.
12. Write the disproportionation reaction of MnO_4^{2-} .

EXERCISE

1. $(n-1)d^{10}ns^2$ is the general electronic configuration of

(1) Fe, Co, Ni	(2) Cu, Ag, Au
(3) Zn, Cd, Hg	(4) Se, Y, La
2. The lowest melting point metals among d-block metals belongs to

(1) Group 3	(2) Group 11
(3) Group 6	(4) Group 12
3. Cu^+ ion in aqueous medium undergoes

(1) Oxidation only	(2) Reduction only
(3) Neither oxidation nor reduction	(4) Disproportionation
4. Which of the following oxide is least basic?

(1) CrO	(2) Cr_2O_3
(3) CrO_3	(4) Cr_2O_4
5. Which metal is not present in german silver?

(1) Cu	(2) Ag
(3) Ni	(4) All are present
6. d-block elements have tendency for complex formation because of

(1) Small size of metal ions	(2) High ionic charges
(3) Availability of vacant d-orbitals	(4) All of these
7. Incorrect order is

(1) $\text{Mn} > \text{Fe}$ (IIIrd ionisation energy)	(2) $\text{Cr} > \text{Mn}$ (IIInd ionisation energy)
(3) $\text{Cu}^{1+}(\text{aq}) > \text{Cu}^{2+}(\text{aq})$ (stability order)	(4) All of these

8. Hardness of transition metals is due to
- Large atomic size
 - Metallic bonding
 - Ionic bond
 - High ionization energy
9. Zn and Hg do not form coloured ions because
- They are soft
 - Their inner d-orbitals are completely filled
 - They have only 2-electrons in the outer most shell
 - None of these
10. The most abundant transition metal is
- Iron
 - Copper
 - Aluminium
 - Zinc

SOME IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

Oxide and Oxoanions of Metals

These oxides are generally formed by the reaction of metals with oxygen at high temperature. All the metals except Sc form metal oxide which are ionic.

As the oxidation number of metal increases, ionic character decreases. In the case of Mn, Mn_2O_7 is a covalent green oil. Even CrO_3 and V_2O_5 have low melting points. In these higher oxides the acidic character is predominant.

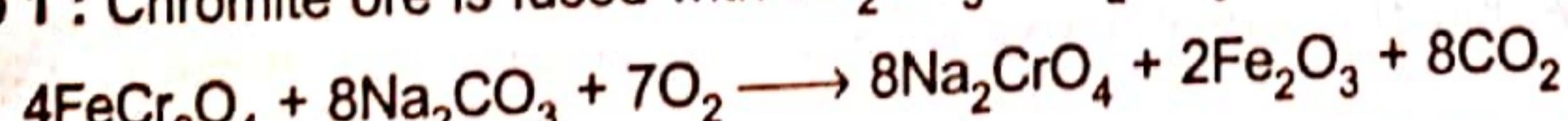
Thus, Mn_2O_7 gives $HMnO_4$ and CrO_3 gives H_2CrO_4 and $H_2Cr_2O_7$. V_2O_5 is however amphoteric though mainly acidic and it gives VO_4^{3-} as well as VO_2^+ salt. V_2O_5 reacts with alkalies as well as acids to give VO_4^{3-} and VO_2^+ respectively. The well characterised CrO is basic but Cr_2O_3 is amphoteric.

Potassium Dichromate $K_2Cr_2O_7$

It is an important chemical used in leather industry and an oxidant for preparation of many azo compounds.

It is prepared from chromite ore ($FeCr_2O_4$)

Step 1 : Chromite ore is fused with Na_2CO_3 or K_2CO_3 in excess air.

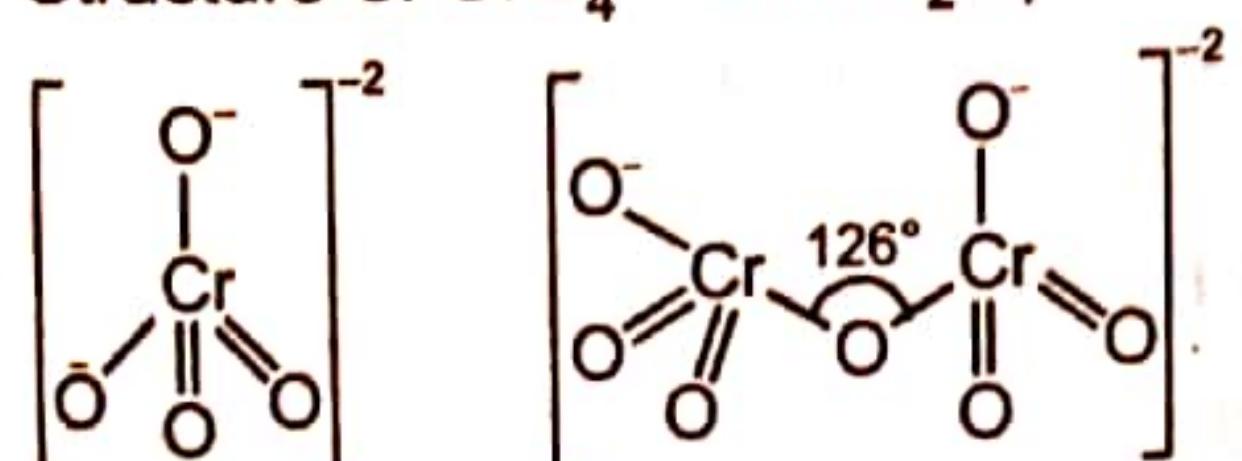


Yellow solution of Na_2CrO_4 is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate $Na_2Cr_2O_7 \cdot 2H_2O$ is crystallised.

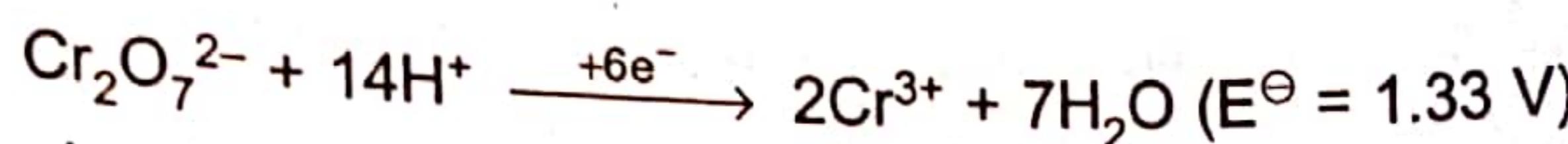
Note : $Na_2Cr_2O_7$ is more soluble than $K_2Cr_2O_7$



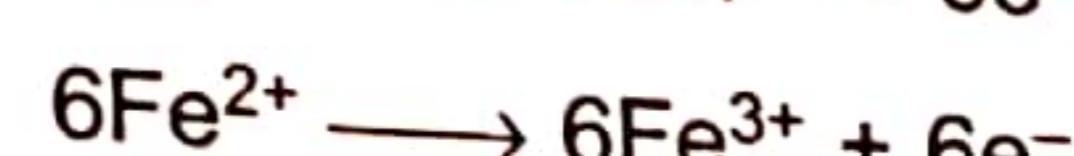
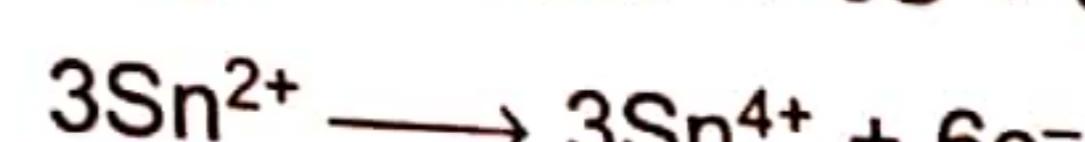
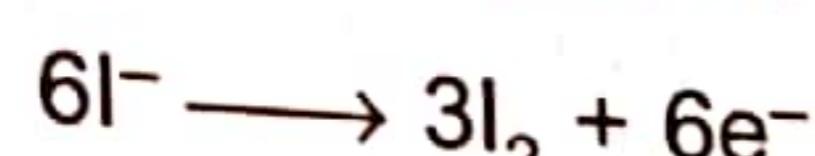
Structure of CrO_4^{2-} and $Cr_2O_7^{2-}$



Sodium and potassium dichromate are good oxidising agent. But potassium dichromate is used as primary standard in volumetric analysis.

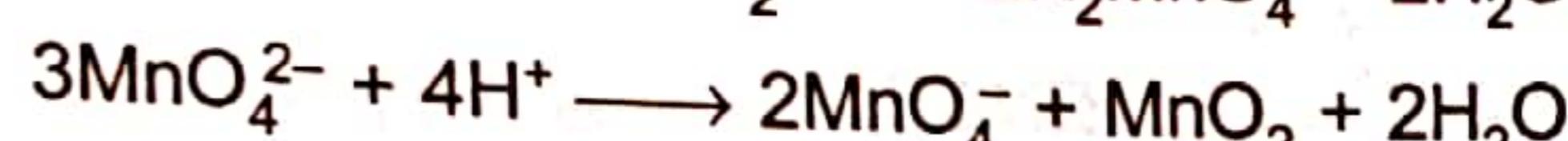
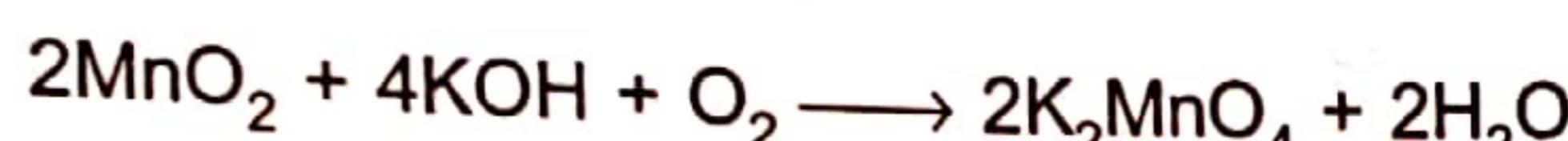


Example of reaction involving oxidation by $\text{Cr}_2\text{O}_7^{2-}$

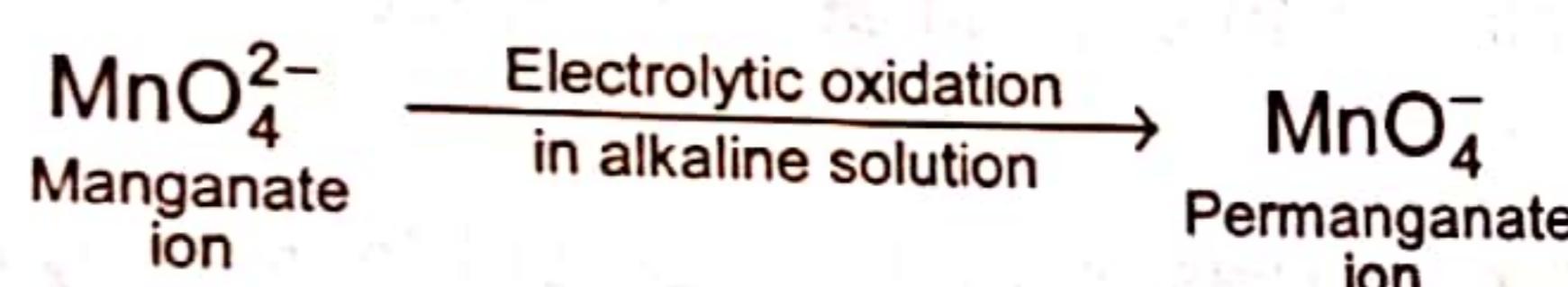


Potassium Permanganate KMnO_4

Preparation : KMnO_4 is prepared by fusion of MnO_2 with an alkali metal hydroxides and an oxidising agent like KNO_3 . This produces dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.



Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (VI).

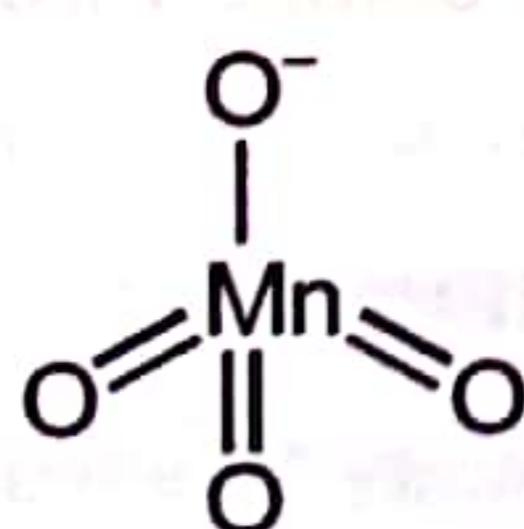


Laboratory preparation : In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.



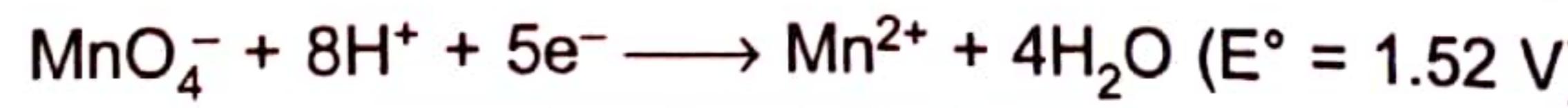
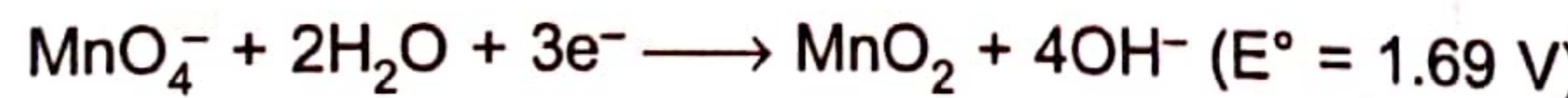
Characteristic properties

1. KMnO_4 forms dark purple (almost black) crystals which are isostructural with those of KClO_4 . The salt is not very soluble in water. (6.4 g/100 g of water at 293 K).
2. It has intense colour and weak temperature dependent paramagnetism.
3. Green manganate ion is paramagnetic while permanganate ion is diamagnetic.
4. π bonding takes place by overlap of p orbital of oxygen with d orbitals of manganese.
5. Structure :



6. KMnO_4 is a good oxidising agent in acidic, basic, or neutral medium.

7. Half cell reaction of KMnO_4 in different medium



We can very well see that the hydrogen ion concentration of the solution play an important part in influencing the reaction. Although reactions can be understood by consideration of redox potential, kinetics of the reaction is also an important factor.

Important oxidising reactions of KMnO_4

1. In acidic medium

- (i) $10\text{I}^- + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{I}_2$
- (ii) $5\text{Fe}^{2+} \text{ (Green)} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} \text{ (Yellow)} + 4\text{H}_2\text{O}$
- (iii) $5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$
- (iv) $5\text{S}^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{S}$
- (v) $5\text{SO}_3^{2-} + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{SO}_4^{2-}$
- (vi) $5\text{NO}_2^- + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{NO}_3^-$

2. In neutral or faintly alkaline solutions

- (i) $2\text{MnO}_4^- + \text{H}_2\text{O} + \text{I}^- \rightarrow 2\text{MnO}_2 + 2\text{OH}^- + \text{IO}_3^-$
- (ii) $8\text{MnO}_4^- + \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + 2\text{OH}^-$
- (iii) $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \xrightarrow{\text{Zn}} 5\text{MnO}_2 + 4\text{H}^+$

Example 18 : Why permanganate titrations in presence of hydrochloric acid are unsatisfactory?

Solution : Because hydrochloric acid is oxidised to chlorine (Cl_2).

EXERCISE

11. Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ on reaction with hydrogen peroxide give deep blue solution due to formation of

- | | |
|----------------------------------|-----------------------------|
| (1) $\text{Cr}_2(\text{SO}_4)_3$ | (2) CrO_5 |
| (3) CrO_4^{2-} | (4) Cr_2O_3 |

12. Hybridisation of chromium ions in chromate and dichromate ions is respectively

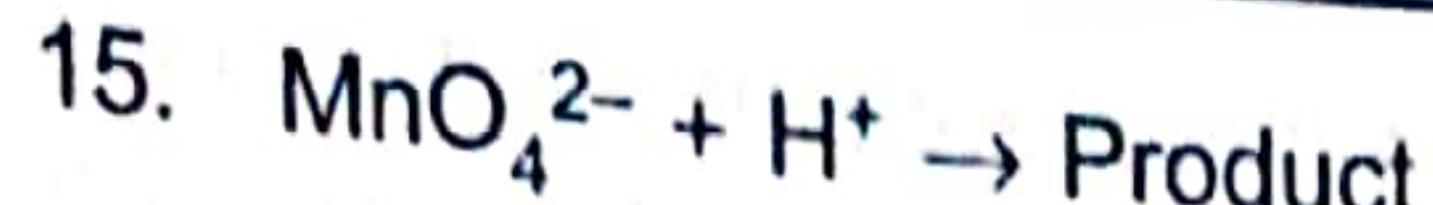
- | |
|-----------------------|
| (1) sp^2 and sp^2 |
| (2) sp^2 and sp^3 |
| (3) sp^3 and sp^2 |
| (4) sp^3 and sp^3 |

13. Equivalent weight of Baeyer's reagent is

- | | |
|----------|------------------|
| (1) 158 | (2) 31.6 |
| (3) 52.6 | (4) All of these |

14. On oxidation with KMnO_4 in acidic medium, SO_2 is oxidised to

- | | |
|------------------------|-----------------------------|
| (1) SO_2 | (2) H_2SO_4 |
| (3) SO_3^{2-} | (4) H_2S |



Product formed is

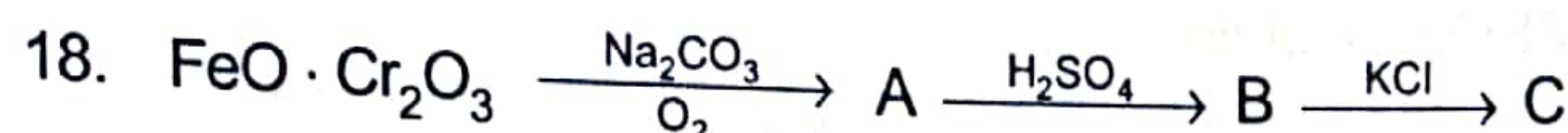
- (1) MnO_4^-
- (2) MnO_2
- (3) Mn
- (4) Both (1) & (2)

16. Which is coloured because of *d-d* transition?

- (1) KMnO_4
- (2) K_2CrO_4
- (3) CoCl_3
- (4) All of these

17. When ferric chloride is added to potassium ferrocyanide there is formation of

- (1) Prussian blue
- (2) Nitroprusside ion
- (3) Coloured ring
- (4) Ferrous nitrate



The hybridisation of compound C and colour of its crystal is

- (1) sp^3 , orange red
- (2) sp^3 , yellow
- (3) sp^2 , orange red
- (4) sp^2 , yellow

19. Number of moles of ferrous sulphate oxidised by 1 mole of potassium permanganate in acidic medium is

- (1) $\frac{2}{5}$
- (2) $\frac{5}{2}$
- (3) $\frac{1}{5}$
- (4) 5

20. When NaCl is heated with $\text{K}_2\text{Cr}_2\text{O}_7$ in sulphuric acid, the red vapours formed is because of

- (1) CrO_5
- (2) CrO_4^{2-}
- (3) CrO_2Cl_2
- (4) Cr_2O_3

THE INNER TRANSITION ELEMENTS

The *f* block consists of two series lanthanoids and actinoids. Lanthanum closely resembles the lanthanoids, it is usually included in any discussion of the lanthanoids for which the general symbol Ln is often used. Similarly a discussion of the actinoids includes actinium besides the fourteen elements constituting the series.

Lanthanoids resemble one another more closely than do the members of ordinary transition elements in any series. They have only one stable oxidation state and their chemistry provides an excellent opportunity to examine the effect of small size and nuclear charge along a series of otherwise similar elements.

THE LANTHANOIDS**Electronic Configuration**

It may be noted that the atoms of these elements have electronic configuration as $6s^2 5d^0$ or $1\ 4f^{1-14}$.

Electronic Configurations and Radii of Lanthanum and Lanthanoids

Atomic Number	Name	Symbol	Electronic configurations*				Radius/pm	
			Ln	Ln ²⁺	Ln ³⁺	Ln ⁴⁺	Ln	Ln ³⁺
57	Lanthanum	La	5d ¹ 6s ²	5d ¹	4f ⁰		187	106
58	Cerium	Ce	4f ¹ 5d ¹ 6s ²	4f ²	4f ¹	4f ⁰	183	103
59	Praseodymium	Pr	4f ² 6s ²	4f ³	4f ²	4f ¹	182	101
60	Neodymium	Nd	4f ³ 6s ²	4f ⁴	4f ³	4f ²	181	99
61	Promethium	Pm	4f ⁴ 6s ²	4f ⁵	4f ⁴		181	98
62	Samarium	Sm	4f ⁵ 6s ²	4f ⁶	4f ⁵		180	96
63	Europium	Eu	4f ⁶ 6s ²	4f ⁷	4f ⁶		199	95
64	Gadolinium	Gd	4f ⁷ 5d ¹ 6s ²	4f ⁷ 5d ¹	4f ⁷		180	94
65	Terbium	Tb	4f ⁹ 6s ²	4f ⁹	4f ⁸	4f ⁷	178	92
66	Dysprosium	Dy	4f ¹⁰ 6s ²	4f ¹⁰	4f ⁹	4f ⁸	177	91
67	Holmium	Ho	4f ¹¹ 6s ²	4f ¹¹	4f ¹⁰		176	89
68	Erbium	Er	4f ¹² 6s ²	4f ¹²	4f ¹¹		175	88
69	Thulium	Tm	4f ¹³ 6s ²	4f ¹³	4f ¹²		174	87
70	Ytterbium	Yb	4f ¹⁴ 6s ²	4f ¹⁴	4f ¹³		173	86
71	Lutetium	Lu	4f ¹⁴ 5d ¹ 6s ²	4f ¹⁴ 5d ¹	4f ¹⁴	-	-	-

Atomic Size and Ionic Size

Decrease in size from La to Lu is a unique feature in chemistry of lanthanoids. This is due to lanthanoid contraction. The decrease in atomic radii is not quite regular as it is regular in M^{3+} ion. This contraction is similar to that observed in an ordinary transition series and is attributed to same cause, the imperfect shielding of one electron by another in the same sub-shell. However, shielding of one 4f electron by another is less than one d electron by another with the increase in nuclear charge along the series.

Oxidation State

In the lanthanoids, Ln(III) compounds are predominant. However some element may show oxidation state of II and IV. Pr, Nd, Tb and Dy can exhibit +4 O.S. only in MO_3 oxide.

Eu^{2+} is formed by losing the two s-electron and its f E.C. accounts for the formation of this ion. However Eu^{2+} is a strong reducing agent changing to the common +3 state. Tb^{IV} has half filled f orbital and is an oxidant. Sm also exhibit +2 oxidation state.

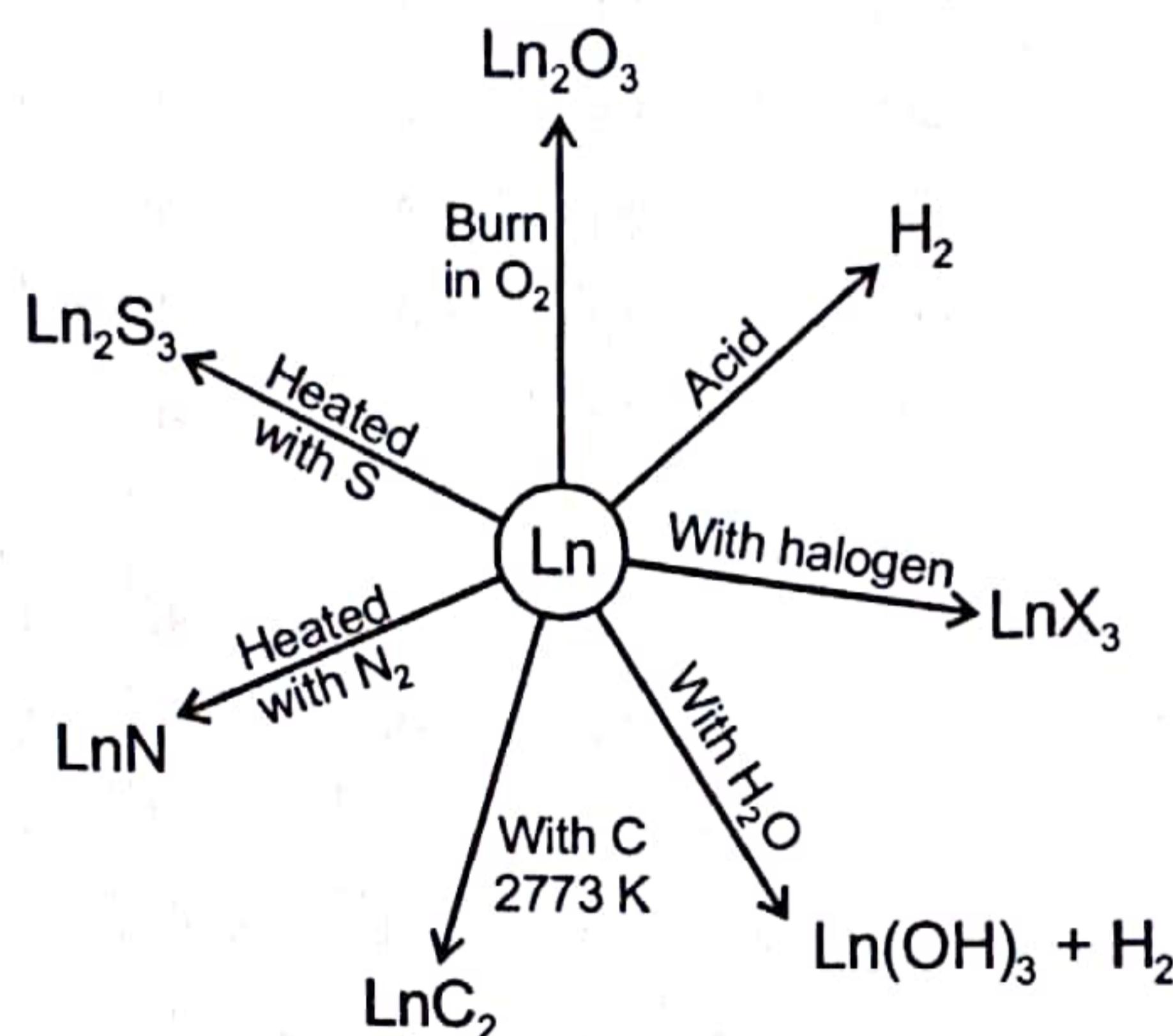
General Characteristics

1. All the lanthanoids are silvery white soft metals and tarnish rapidly.
2. Hardness increases with increasing atomic number, samarium (Sm) being steel hard.
3. These are good conductor of electricity.
4. Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.

5. Many trivalent lanthanoid ions are coloured both in solid state and in aq. solution. Colour of these ions may be attributed to the presence of f electrons.
- For M^{3+} ion, species having same unpaired electrons have nearly same colour.
 - Colour of f block ions are generally not affected by ligands.
6. IE_1 of the lanthanoids are around 600 kJ/mole and IE_2 is about 1200 kJ/mole comparable with those of Ca. A detailed discussion of IE_3 's variation indicates that the exchange enthalpy considerations (as in $3d$ orbitals of the first transition series) appear to impart a certain degree of stability to empty, half filled and completely filled orbitals of f level. This is indicated from the abnormally low value of the IE_3 of La, Gd and Lu.

Note : In chemical behaviour in general, the earlier members of the series are quite reactive similar to calcium but with increasing atomic number, they behave more like aluminium.

Reaction :



Uses

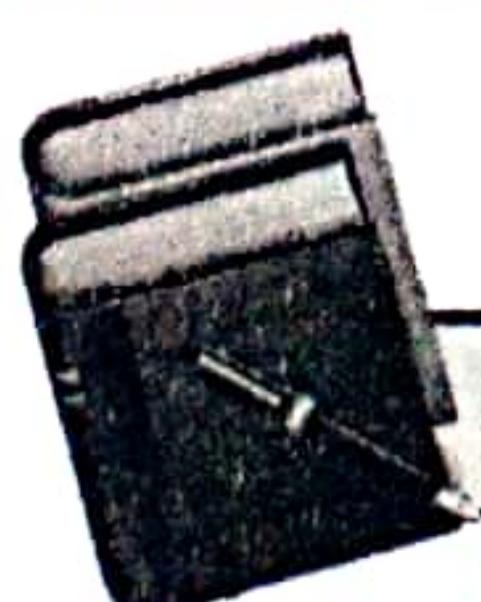
- Best use of the lanthanoids is for the production of alloy steels for plate and pipe.
- A well known Mischmetal consists of a lanthanoid metal (~95%) and iron (~5%) and traces of S, C, Ca and Al. It is used in Mg-based alloy to form bullets.
- Mixed oxide of lanthanoids are employed as catalysts in petroleum cracking.
- Some individual lanthanoid oxide are used in television screen and similar fluorescing surfaces.

Example 19 : Why Ce^{4+} is a good oxidising agent?

Solution : Due to high reduction potential of Ce^{4+}/Ce^{3+} is 1.74 V.

Example 20 : Out of following which is more basic $Lu(OH)_3$ and $Ce(OH)_3$.

Solution : $Ce(OH)_3$



Try Yourself

- Why $Ce(OH)_3$ is more basic than $Lu(OH)_3$?
- Which have maximum paramagnetism in M^{3+} ion for Lanthanoid (spin only)?

THE ACTINIODS

Actinoids include the fourteen elements from Th to Lr. The name symbol and some properties of these elements are shown as

Atomic Number	Name	Symbol	Electronic configurations*			Radii/pm	
			M	M ³⁺	M ⁴⁺	M ³⁺	M ⁴⁺
89	Actinium	Ac	6d ¹ 7s ²	5f ⁰		111	
90	Thorium	Th	6d ² 7s ²	5f ¹	5f ⁰	99	
91	Protactinium	Pa	5f ² 6d ¹ 7s ²	5f ²	5f ¹	96	
92	Uranium	U	5f ³ 6d ¹ 7s ²	5f ³	5f ²	103	93
93	Neptunium	Np	5f ⁴ 6d ¹ 7s ²	5f ⁴	5f ³	101	92
94	Plutonium	Pu	5f ⁶ 7s ²	5f ⁵	5f ⁴	100	90
95	Americium	Am	5f ⁷ 7s ²	5f ⁶	5f ⁵	99	89
96	Curium	Cm	5f ⁷ 6d ¹ 7s ²	5f ⁷	5f ⁷	99	88
97	Berkelium	Bk	5f ⁹ 7s ²	5f ⁸	5f ⁷	98	87
98	Californium	Cf	5f ¹⁰ 7s ²	5f ⁹	5f ⁸	98	86
99	Einstenium	Es	5f ¹¹ 7s ²	5f ¹⁰	5f ⁹	—	—
100	Fermium	Fm	5f ¹² 7s ²	5f ¹¹	5f ¹⁰	—	—
101	Mendelevium	Md	5f ¹³ 7s ²	5f ¹²	5f ¹¹	—	—
102	Nobelium	No	5f ¹⁴ 7s ²	5f ¹³	5f ¹²	—	—
103	Lawrencium	Lr	5f ¹⁴ 6d ¹ 7s ²	5f ¹⁴	5f ¹³	—	—

The actinoids are radioactive elements and the earlier members have relatively long half life, the latter ones have half life values ranging from a day to 3 minute for Lawrencium (Z-103).

Electronic Configurations

General electronic configuration of all elements can be consulted from table. The fourteen electrons are formally added to 5f though not in thorium (Z-90) but from Pa onward the 5f orbitals are complete at element 103. The irregularities in the electronic configurations of the actinoids like those in the Lanthanoids are related to the stabilities of the f⁰, f⁷, f¹⁴ occupancies of the 5f orbitals.

Note : Although the 5f orbitals resemble with the 4f orbitals in their angular part of the wave function, they are not as buried as 4f orbital and hence 5f electrons can participate in bonding to a far greater extent.

Ionic Sizes

There is gradual decrease in the size of atoms or M³⁺ ions across the series. This is referred to as actinoid contraction which is greater than lanthanoid contraction.

Oxidation States

There is greater range of oxidation states which is in part attributed to the fact that the 5f, 6d and 7s level are of comparable energies.

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3		3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

The elements, in first half of actinoids frequently exhibit higher oxidation states. However, +3 and +4 ions tend to hydrolyse because the distribution of oxidation states among the actinoids is so uneven and so different for the former and later elements, it is unsatisfactory to review their chemistry in terms of oxidation states.

General Characteristics

1. All are silvery in appearance but display a variety of structure. This is due to irregularity in metallic radii.
2. These are highly reactive metal.
3. HCl react with all actinoids.
4. Most of them are slightly affected by HNO_3 owing to the formation of protective oxide layer. However, alkalies have no action.
5. Magnetic properties of the actinoids are more complex than those of lanthanoid.
6. Actinoids compound or their ions are coloured most probably due to charge transfer or *f-f* transition.

Differences

Lanthanides	Actinides
<ol style="list-style-type: none"> 1. In addition to +3 oxidation state, they exhibit +2 and +4 oxidation states only. 2. Most of their ions are colourless 3. They do not form complexes easily. 4. They do not form oxo cations. 5. Their compounds are less basic 6. Except promethium, they are non-radioactive. 7. Their magnetic properties can be easily explained. 	<ol style="list-style-type: none"> 1. In addition to +3 oxidation state, they show +4, +5, +6 and +7 oxidation states. 2. Most of their ions are coloured. 3. They have much greater tendency to form complexes. 4. They form oxocations such as UO_2^{2+}, PuO_2^{2+} and UO^+. 5. Their compounds are more basic. 6. They are radioactive. 7. Their magnetic properties can not be easily explained.

SOME APPLICATIONS OF *d* & *f*-BLOCK ELEMENTS

1. Iron and steels are the most important construction material. Their production is based on reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals like Cr, Mn and Ni.
2. Some compounds are manufactured for special purpose such as TiO for the pigment industry and MnO_2 for use in dry cell along with use of Zn.
3. Many of the elements or compounds of this block elements are important catalyst.
4. AgBr is an important chemical used in photography. Along with AgBr , Ag and AgI can also be used.
5. Some compounds like MnO_4^- , CrO_4^{2-} are good oxidising agents.

Example 21 : Why actinoid contraction is more than lanthanoid contraction?
This is due to poor screening of 5f orbital.

This is due to poor screening of $5f$ orbital.

Q2 : Which element show highest oxidation state in actinoid?

Example 22: Np and Pu exhibit +7 oxidation state.

Try Yourself

15. Discuss the effect of pH on CrO_4^{2-} .

EXERCISE

21. In blue vitriol, number of water molecules joined by co-ordinate bonds with copper and by hydrogen bond is respectively
(1) 3, 2 (2) 2, 3
(3) 4, 1 (4) 5, 0

22. Correct electronic configuration of lanthanum is
(1) $[\text{Xe}]5d^16s^2$ (2) $[\text{Xe}]4d^15s^2$
(3) $[\text{Xe}]4f^15s^2$ (4) $[\text{Xe}]5f^16s^2$

23. General electronic configuration of actinides can be shown as
(1) $(6-2)f^{1-14}(6-1)d^{1-10}6s^2$ (2) $(6-2)f^{1-14}(6-1)d^{0-1}6s^2$
(3) $(7-2)f^{1-14}(7-1)d^{1-10}7s^2$ (4) $(7-2)f^{1-14}(7-1)d^{0-1}7s^2$

24. First synthetic elements is
(1) Tc (2) La
(3) Po (4) Y

25. Which is correct?
(1) Ce(OH)_3 is weaker base than Lu(OH)_3
(2) $E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}}$ is more positive than $\text{Fe}^{3+}/\text{Fe}^{2+}$
(3) $\text{Ti} > \text{Zr} > \text{Hf}$ (Group 4 atomic radii)
(4) Lanthanides are not separated by ion exchange method

26. Lanthanides and Actinides are similar in
(1) Oxoion formation (2) Radioactive nature
(3) Tendency towards complex formation (4) Electronic configuration

27. The basic nature of the Lanthanide hydroxides decreases from Ce(OH)_3 to Lu(OH)_3 . This is due to
(1) Decrease in ionic radius (2) Due to lanthanoid contraction
(3) Increase in metallic character (4) All of these

