ULTIMATE KCET

CRASH COURSE 2026

Chemistry | Lecture - 02

D and f block elements

By – Sreeja Ma'am

Recap *of previous lecture*

1. D and f block elements – part 1

Topics *to be covered*

1. D and f block elements –part 2

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Enthalpy of Atomisation:

→ atoms arrangement
→ 3d → unpaired e⁻
→ 3d–3d → Metallic bonding
atom = atom

- Minimum energy required to break the metallic lattice of crystalline metals into atoms is known as enthalpy of atomisation.
- In a series when we move from left to right enthalpy of Atomisation is first increases then start decreases.
- $\Delta_{atom}H^0 \propto$ interatomic interaction.

Sc Ti V Cr Mn Fe Co Ni Cu Zn

$3d^1$ $3d^2$ $3d^3$ $3d^5$ $3d^5$ $3d^6$ $3d^7$ $3d^8$ $3d^9$ $3d^{10}$

More metallic ↓ due to atoms arrangement

Mn: low enthalpy compared to chromium

Zn: lowest enthalpy of atomisation

lattice energy

atoms/ions → lattice

General properties of d & f block

Catalyst → variable oxidation state
→ large surface area in finely divided state.

HNO_3 → Oswald process
↳ Pt

H_2SO_4 → contact → V_2O_5

Haber's process

NH_3 → Fe/Mo

H_2/oil → Pt/Pd/Ni.

Wacker's process

$HC\equiv CH$ → aldehyde

↓ $PdCl_2$

$n(H_2C=CH_2) \xrightarrow{TiCl_4 + Al(CH_3)_3} -(H_2C-CH_2)_n-$

↓ Ziegler natta catalyst

$S_2O_8^{2-} + 2I^{\ominus} \xrightarrow{Fe^{3+}} 2SO_4^{2-} + I_2$.

Per oxo disulphate ion

$S_2O_8^{2-}$ ↓ oxidizing agent ↓ it accepts electron

Fe^{3+} ↓ catalyst

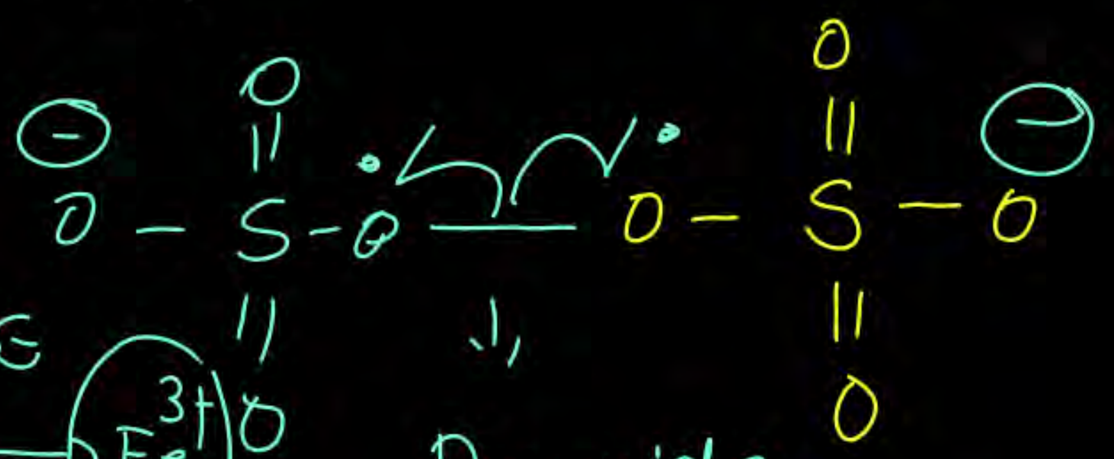
SO_4^{2-} ↓ sulphate ion.

$I^{\ominus}$

$2Fe^{3+} + 2e^{\ominus} \rightarrow 2Fe^{2+}$

$S_2O_8^{2-}$ — $2e^{\ominus}$ — Fe^{3+}

H_2SO_4



Peroxide
per oxo bond.

d block General property

- → Alloy formation → same size
  - Bronze → (Cu + Sn)
  - Brass (Cu + Zn)
  - Steel (C + Fe + Cr + Mn + Ni)
- → Interstitial comp.
  - → hard
  - → inert
  - → high m.p
- → Complex formation
  - → small size
  - → availability of empty d orbital
  - → variable oxidation state
  - → $\frac{\text{charge}}{\text{size}}$ = ratio is high

$K_2Cr_2O_7$ ⟶ $Cr_2O_7^{2-}$

Acidic medium

R.A ⟶ e⁻ donars

$Cr_2O_7^{2-}$ + S^{2-} (sulphide ⟶ $S\downarrow$

SO_2 ⟶ SO_4^{2-}

$S_2O_3^{2-}$ ⟶ Thiosulphate ion ⟶ SO_4^{2-}

Fe^{2+} ⟶ Fe^{3+}

I^{-} ⟶ I_2

$C_2O_4^{2-}$ ⟶ CO_2.

↓ O.A

R.A ⟶ Oxidizide state

↙ state where they have lost e⁻

$KMnO_4$ ⟶ MnO_4^{-}

Acidic medium

R.A.

MnO_4^{-} + { S^{2-} ⟶ S

SO_2 ⟶ SO_4^{2-}

$S_2O_3^{2-}$ ⟶ SO_4^{2-}

Fe^{2+} ⟶ Fe^{3+}

$C_2O_4^{2-}$ ⟶ CO_2

I^{-} ⟶ I_2. }

↓ purple ↓ O.A

$Cr_2O_7^{2-}$ < MnO_4^{-}

↳ strongest O.A ↓ accepts e⁻ more quickly

Potassium Dichromate

- Potassium dichromate is important chemical used in leather industry.
- It is prepared from chromite orle ($FeCr_2O_4$)

Preparation:

(i) $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

(Sodium chromate) → yellow colour Solution

(ii) $2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

(Sodium dichromate) → Orange colour

(iii) $Na_2CrO_2 + 2kCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

(potassium dichromate) → Orange colour

$\overset{+2\ -2}{FeO} + Cr_2O_3$

↓ +2 ↓ +3

$Cr^{+3}\ O^{-2}$

$Cr_2O_7^{2-}$ → orange

dichromate

CrO_4^{2-}

chromate

↓

yellow

Chromate ion

[redacted]

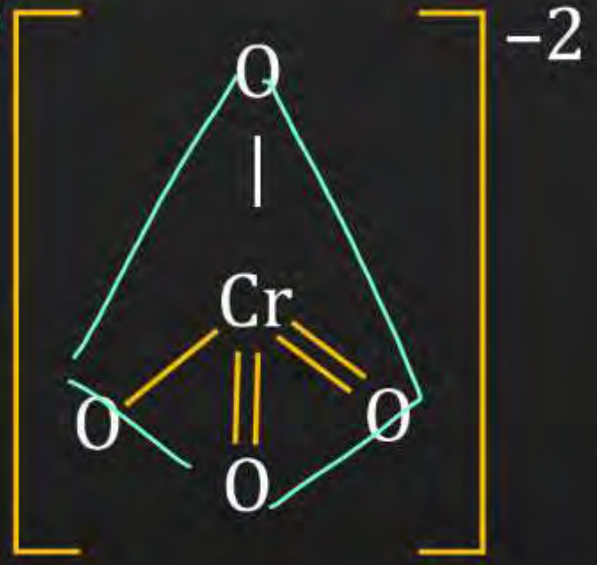
yellow colour

(Potassium Dichromate)

↓

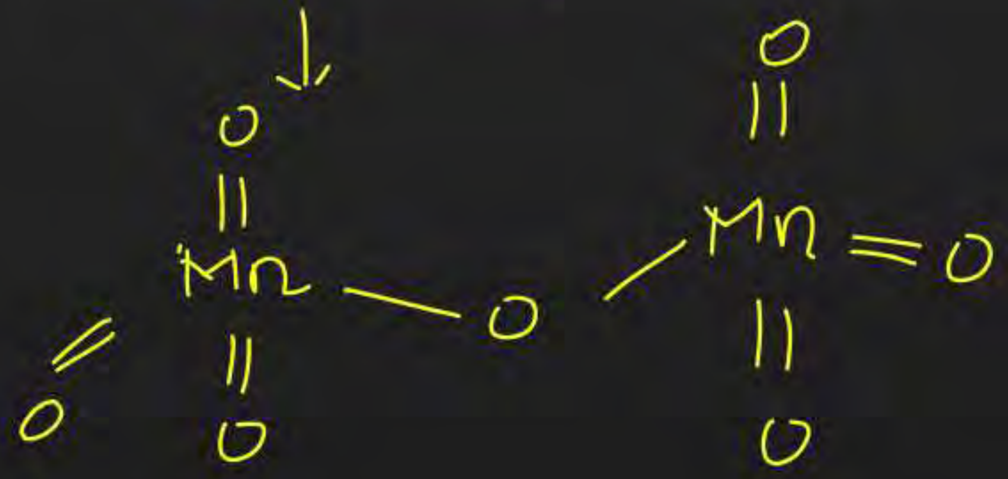
Orange colour

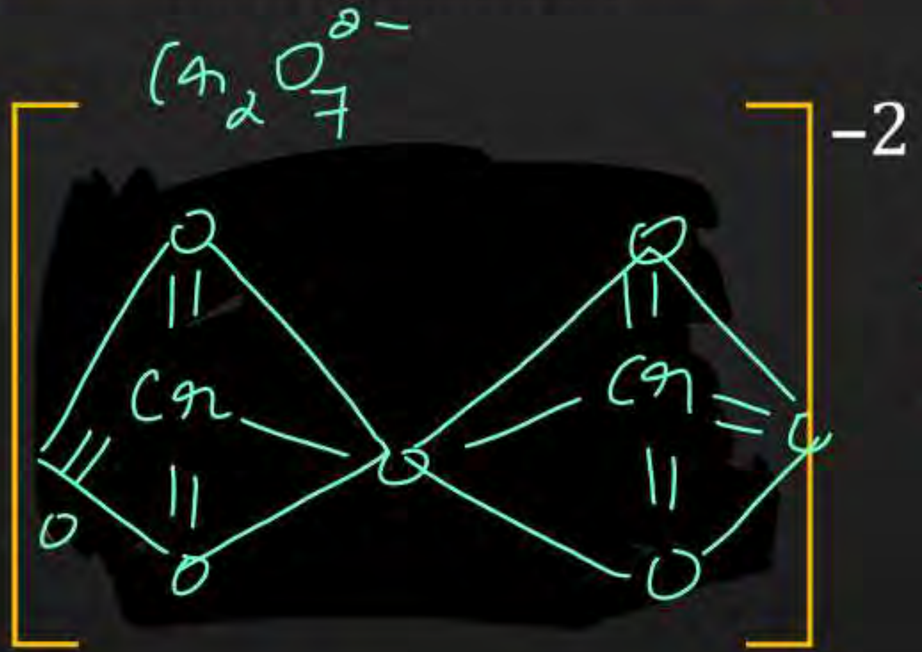
Mn_2O_7



Chromate ion

(CrO_4^{-2})





Tetrahedral

Dichromate ion

$(Cr_2O_7)^{2-}$)

Note: $Na_2Cr_2O_7$ is more soluble than $K_2Cr_2O_7$ because of small Size.

- ❖ $Na_2Cr_2O_7$ and $K_2Cr_2O_7$ are strong oxidising agents.
  (hygroscopic)
- ❖ Potassium dichromate will oxidise (in the presence of acidic medium)

$Cr_2O_7^{2-} \rightarrow Cr^{+3}$

[redacted]

$I^- \rightarrow I_2$

$H_2S \rightarrow S$

$Sn^{+2} \rightarrow Sn^{+4}$

$Fe^{+2} \rightarrow Fe^{+3}$

Some important Reactions:

(i) $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O + 3I_2$

2

+6 Oxidation

$$14H^+ + Cr_2O_7^{2-} + 6I^- \rightarrow 2Cr^{+3} + 3I_2^0 + 7H_2O$$

Reduction

6

(ii) $Cr_2O_7^{2-} + SO_2 \longrightarrow Cr^{+3} + SO_4^{-2}$

Oxidation

+4 2 +6

$$2H^+ + Cr_2O_7^{2-} + 3SO_2 \rightarrow 2Cr^{+3} + 3SO_4^{-2} + H_2O$$

6

Reduction

So final equation

$$H_2O + Cr_2O_7^{2-} + 3SO_2 \longrightarrow 2Cr^{+3} + 3SO_4^{-2} + 2H^+$$

(iii) $Cr_2O_7^{2-} + Fe^{+2} \longrightarrow Cr^{+3} + Fe^{+3}$

Oxidation

1

$$14H^+ + Cr_2O^{2-} + 6Fe^{+2} \rightarrow 2Cr^{+3} + 6Fe^{+3} + 7H_2O$$

6

Reduction

So final equation

$$14H^+ + Cr_2O^{2-} + 6Fe^{+2} \rightarrow 2Cr^{+3} + 6Fe^{+3} + 7H_2O$$

(iv) $Cr_2O_7^{2-} + H_2S \longrightarrow Cr^{+3} + S$

Oxidation

2

$$8H^+ + CH_2O_7^{2-} + 3H_2S \rightarrow 2Cr^{+3} + 3S + 7H_2O$$

6

Reduction

So final equation

$$8H^+ + CH_2O_7^{2-} + 3H_2S \rightarrow 2Cr^{+3} + 3S + 7H_2O$$

Reactions with Base (OH^-):

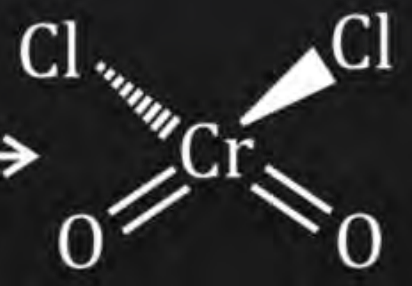
$$Cr_2O_7^{2-} \xrightarrow{OH^-} CrO_4^{2-}$$

$$K_2Cr_2O_7 + 2KOH \longrightarrow 2\,K_2CrO_4 + H_2O$$

(orange-red) (yellow)

Chromyl chloride

$CrO_2Cl_2 \longrightarrow$



Action of heat:

$$4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

(chromic oxide) → extra

[redacted]

Chromyl chloride test: (PYQ) → Extra

The below reaction is widely employed in the salt analysis of chloride ions.

$$K_2Cr_2O_7 + 4HCl + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 6KHSO_4 + 3H_2O$$

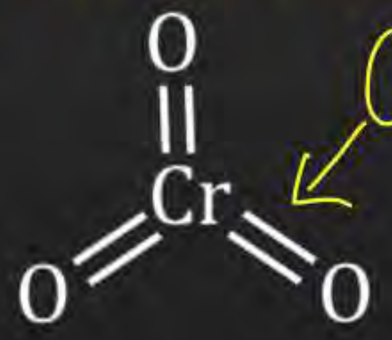
(chromyl chloride)

→ red colour vapour

↓ NaOH

yellow colour solution.

Important Reactions:



$K_2Cr_2O_7 + H_2SO_4 \longrightarrow CrO_3$

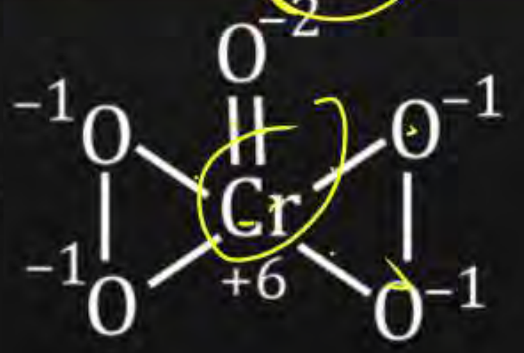
(cold) (chromic anhydride)

$K_2Cr_2O_7 + H_2SO_4(\text{ hot }) \longrightarrow Cr_2(SO_4)_3 + O_2 \uparrow$

$K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \rightarrow 2CrO_5 + K_2SO_4 + 5H_2O$

(chromic peroxide)

Butterfly Structure $\longrightarrow$



Potassium Permanganate ($KMnO_4$)

Preparation:

(i) $2MnO_2 + 4KOH + O_2 \longrightarrow K_2MnO_4 + 2H_2O$

Reddish Brown (dark green)

$3MnO_4^{-2} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

(manganate ion) (permanganate ion)

+6 +7 +4 O R

→ Vimp

→ disproportionation

(ii)

$MnO_2 \xrightarrow[\text{Oxidised with air, } KNO_3]{\text{Fused with KOH,}} MnO_4^{2-}$ Green colour

(magnate ion)

$MnO_4^{2-} \xrightarrow[\text{Oxidation in alkaline solution}]{\text{Elechrolytic}} MnO_4^-$

(manganate ion) (permagnate ion)

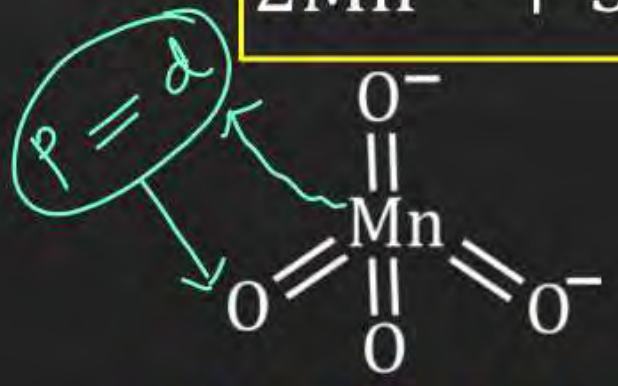
MnO_4^{2-}

$x + (-2 \times 4) = -2$

$x = +6$

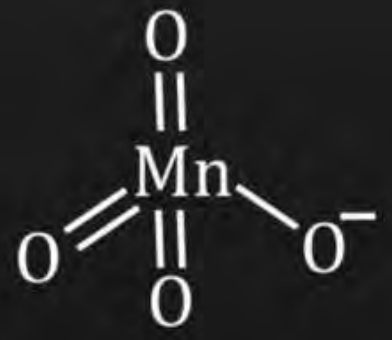
(iii) Laboratory preparation:

$$2Mn^{+2} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{-2} + 16H^+$$



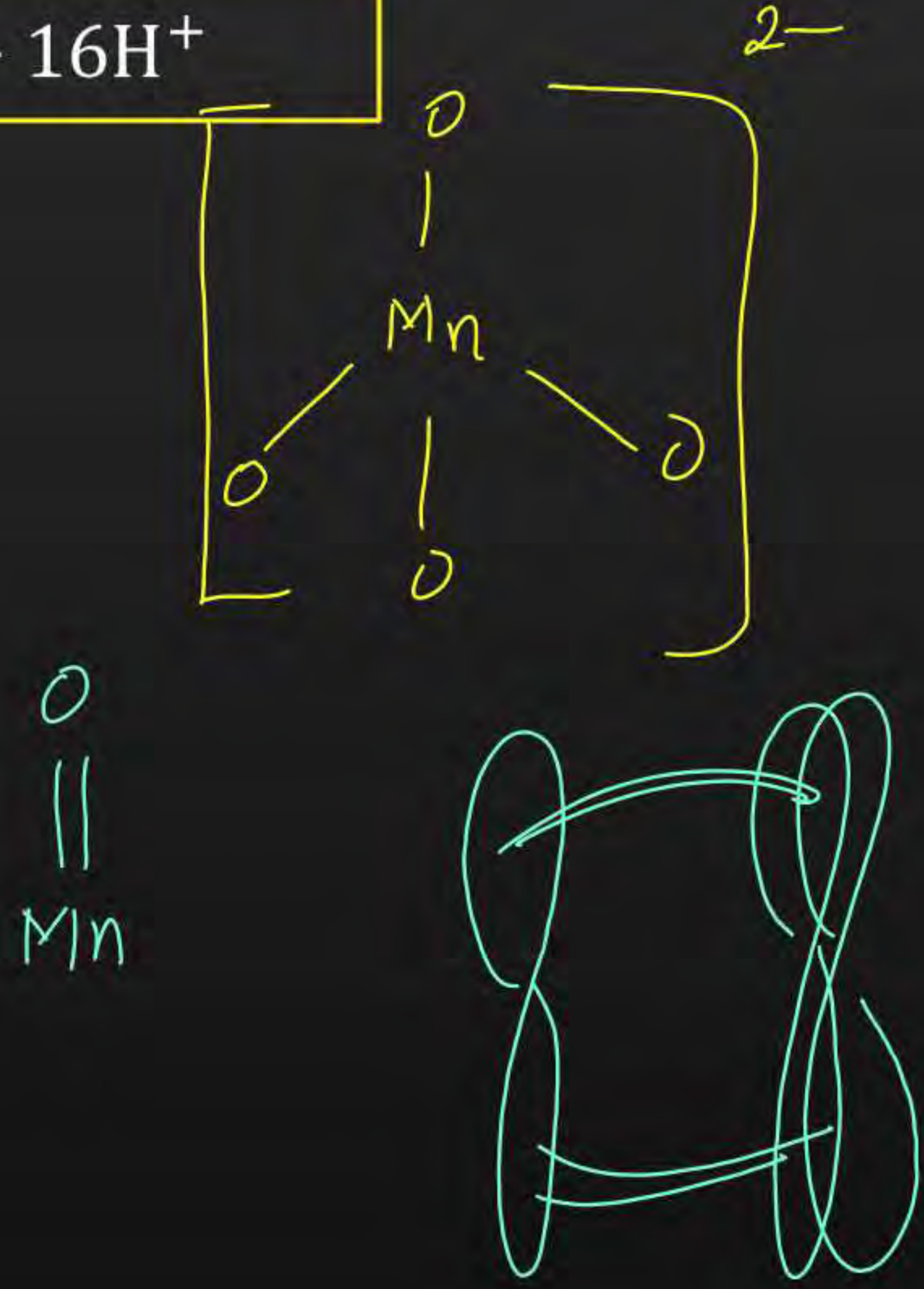
MnO_4^{2-}

Tetrahedral manganate → Paramagnetic (green) ion



$MnO_4^{(-)}$

Tetrahedral permanganate → Diamagnetic (purple) ion



The π bonding takes place by ovenlap of p olbitals of oxygen with d dibitals of manganese.

Acidified permanganate solution oxideses

$C_2O_4^{-2} \rightarrow CO_2$

$Fe^{+2} \rightarrow Fe^{+3}$

$I^- \rightarrow I_2$

$SO_3^{-2-} \rightarrow SO_4^{-2}$

sulphite — sulphate

$NO^-_2 \rightarrow NO^-_3$

Nitrite — Nitrate

$H_2S \rightarrow S$

$S^{2-} \rightarrow S$

$MnO_4^- + I^- + H_2O \rightarrow MnO_2 + IO_3^- + 2OH^-$

iodate.

$MnO_4^- + Br^- + H_2O \rightarrow MnO_2 + BrO_3^- + OH^-$

In the presence of Basic medum:

$I^- \rightarrow IO_3^-$

$S_2O_3^{-2} \rightarrow SO_4^{-2}$

Thiosulphate → sulphate

Chemical reactions: acidic medium

(i) $MnO_4^- + I^- \; Mn^{+2} + I_2$

Oxidation: 2×5

$\overset{+7}{MnO_4^-} + 2I^- \rightarrow Mn^{+2} + I_2$

Reduction: 5×2

$16H^+ + 2MnO_4^- + 10I^- \rightarrow 2Mn^{+2} + 15I_2 + 8H_2O$

Iodine gas is liberated

0 - Oxidation Reduction

A - Atoms Balance

C - Charge Galance

0 - Orygen Belance

H - Hydrogen bulance.

(ii) Fe^{+2} ion (green) is converted to Fe^{+3} (yellow):

$$Fe^{+2} + MnO_4^- \longrightarrow Mn^{+2} + Fe^{+3}$$

purple

$$8H^+ + 5Fe^{+2} + \overset{+7}{MnO_4^-} \rightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$$

1 × 5

5 × 1

(iii) Oxalate ion or oxalic acid is oxidised at 333 K:

$$C_2O_4^{-2} + MnO_4^- \longrightarrow Mn^{+2} + CO_2$$

5 × 2 $e^{(-)}$

$$C_2^{+3}O_4^{-2} + \overset{+7}{MnO_4^-} \longrightarrow 2Mn^{+2} + 2\overset{+4}{CO_2}$$

2 × 5 $e^{(-)}$

$$16H^+ + 5C_2O_4^{-2-} + 2MnO_4^- \longrightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$$

(iv) Hydrogen sulphide is oxidised; Sulphur being precipitated:

$$H_2S \longrightarrow 2H^+ + S^{-2}; \quad S^{-2} + MnO_4^- \longrightarrow Mn^{+2} + S$$

Reduction

5×2

$$16H^+ + 5S^{-2} + 2\overset{+7}{Mn}O_4^- \longrightarrow 2Mn^{+2} + 5S^0 + 8H_2O$$

2×5

Oxidation

sulphur.

(v) Sulphurous acid or sulphite is oxidised to a sulphate or? Sulphuric acid:

$$SO_3^{-2} + MnO_4^{-} \rightarrow Mn^{+2} + SO_4^{-2}$$

Oxidation

2 × 5

$$6H^{+} + 5\overset{+4}{S}O_3^{-2} + 2\overset{+7}{Mn}O_4^{-} \rightarrow 2Mn^{+2} + 5\overset{+6}{S}O_4^{+3} + 3H_2O$$

2 × 5

Reduction

(vi) Nitrite is oxidised to nitrate:

$$NO_2^- + MnO_4^- \rightarrow Mn^{+2} + NO_3^-$$

Reduction ($+7 \rightarrow +2$): 5×2

$$6H^+ + 5\overset{+3}{N}O_2^- + 2\overset{+7}{Mn}O_4^- \longrightarrow 2Mn^{+2} + 5\overset{+5}{N}O_3^- + 3H_2O$$

Oxidation ($+3 \rightarrow +5$): 2×5

Nitrite

Nitrate

In Basic solutions:

(i) Oxidation of iodide to iodate:

$$MnO_4^- + I^- \longrightarrow MnO_2 + IO_3^-$$

6

$$\overset{+7}{2MnO_4^-} + I^- \longrightarrow \overset{+4}{2MnO_2} + \overset{+5}{IO_3^-} + H_2O$$

3 × 2

$$2H_2O + 2MnO_4^- + I^- \longrightarrow 2MnO_2 + IO_3^- + 2OH^- + H_2O$$

$$MnO_4^- + I^- + H_2O \longrightarrow MnO_2 + IO_3^- + 2OH^-$$

Finally, $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + IO_3^- + 2OH^-$

(ii) Thiosulphate is oxidised almost quantitatively to sulphate:

$$MnO_4^- + S_2O_3^{-2} \longrightarrow MnO_2 + SO_4^{-2}$$

$$8\overset{+7}{Mn}O_4^- + 3\overset{+2}{S_2}O_3^{-2} \longrightarrow 8\overset{+4}{Mn}O_2 + 6\overset{+6}{S}O_4^{-2} + H_2O$$

8 × 3

3 × 8

$$2H_2 + 8MnO_4^- + 3\,S_2O_3^{-2} \rightarrow 8MnO_2 + 6SO_4^{-2} + H_2O + 2OH^-$$

Finally, $$8MnO_4^- + 3S_2O_3^{-2} + H_2O \rightarrow 8MnO_2 + 6SO_4^{-2} + 2OH^-$$

Some Important Reactions:

(i) $2KMnO_4 + KI + H_2O \longrightarrow 2MnO_2 + 2KOH + KIO_3^-$

(Basic medium)

(ii) $2KMnO_4 + 16HCl \longrightarrow 2MnCl_2 + 2KCl + 8H_2O + Cl_2$

(acidic)

(iii) $2KMnO_4 + H_2SO_4 \longrightarrow K_2SO_4 + Mn_2O_7 + H_2O$

Lanthanoids → 4f block → common oxidation state → +3

Ce → Lu
58 → 71

→ $_{58}Ce$

EC: $[Xe]_{54}\, 4f^1\, 5d^1\, 6s^2$

General E.C → $[\text{Noble gas}]\, 4f^{1-14}\, 5d^{0-1}\, 6s^2$

↿	↿	↿	↿	↿	↿	↿

$Ce^{+4} \rightarrow [Xe]\, 4f^0\, 5d^0\, 6s^0$

Lanthanoide contraction — 4d — atomic size — Zr 4d, Hf 5d

La [Ce — Lu] Hf —5d— Hg

5d 4f

size reduction → poor shielding

$Eu \rightarrow [Xe]\, 4f^7\, 5d^0\, 6s^2$

$Gd \rightarrow [Xe]\, 4f^7\, 5d^1\, 6s^2$

$Yb \rightarrow [Xe]\, 4f^{14}\, 5d^0\, 6s^2$

$Lu \rightarrow [Xe]\, 4f^{14}\, 5d^1\, 6s^2$

Atomic Number	Name	Symbol	Electronic configurations*			Radii/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	$4f^3 6s^2$	$4f^3$	$4f^2$	$4f^1$	182	101
60	Neodymium	Nd	$4f^4 6s^2$	$4f^4$	$4f^3$	$4f^2$	181	99
61	Promethium	Pm	$4f^5 6s^2$	$4f^5$	$4f^4$		181	98
62	Samarium	Sm	$4f^6 6s^2$	$4f^6$	$4f^5$		180	96
63	Europium	Eu	$4f^7 6s^2$	$4f^7$	$4f^6$		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	$4f^{14} 5d^1 6s^2$	$4f^{14} 5d^1$	$4f^{14}$	–	–	–

General Characteristics

All the lanthanoids are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number, samarium being steel hard. Their melting points range between 1000 to 1200 K but samarium melts at 1623 K. They have typical metallic structure and are good conductors of heat and electricity. Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.

Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of *f* electrons. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so. However, absorption bands are narrow, probably because of the excitation within *f* level. The lanthanoid ions other than the f^{0} type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic.

The first ionisation enthalpies of the lanthanoids are around 600 kJ mol^{-1}, the second about 1200 kJ mol^{-1} comparable with those of calcium. A detailed discussion of the variation of the third ionisation enthalpies indicates that the exchange enthalpy considerations (as in 3*d* orbitals of the first transition series), appear to impart a certain degree of stability to empty, half-filled and completely filled orbitals *f* level. This is indicated from the abnormally low value of the third ionisation enthalpy of lanthanum, gadolinium and lutetium.

In their 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. Values for E^{o} for the half-reaction:

$$Ln^{3+}(aq) + 3e^{-} \rightarrow Ln(s)$$

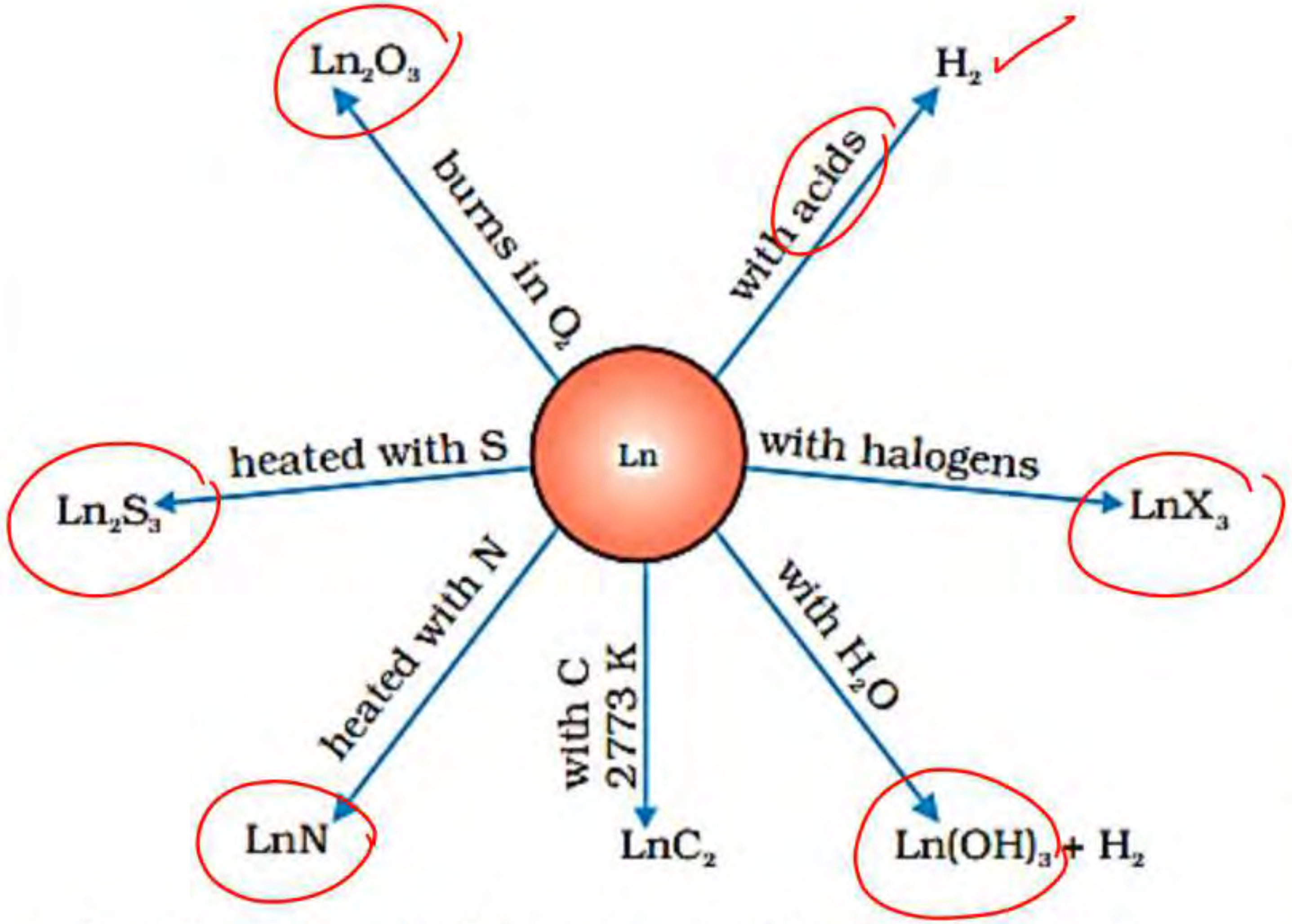


***Fig 4.7:** Chemical reactions of the lanthanoids.*

are in the range of –2.2 to –2.4 V except for Eu for which the value is –2.0 V. This is, of course, a small variation. The metals combine with hydrogen when gently heated in the gas. The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon. They liberate hydrogen from dilute acids and burn in halogens to form halides. They form oxides M_2O_3 and hydroxides $M(OH)_3$. The hydroxides are definite compounds, not just hydrated oxides. They are basic like alkaline earth metal oxides and hydroxides. Their general reactions are depicted in Fig. 4.7.

The best single use of the lanthanoids is for the production of alloy steels for plates and pipes. A well known alloy is *mischmetall* which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A good deal of **mischmetall** is used in Mg-based alloy to produce bullets, shell and lighter flint. Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking. Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

Actinoids → 5f block

→ $_{90}Th \longrightarrow {}_{103}Lr$

(Thorium) Lawrencium

→ $[_{86}Rn]\,5f^{1-14}\,6d^{0-1}\,7s^{2}$

$_{90}Th \longrightarrow [_{86}Rn]\,5f^{0}\,6d^{2}\,7s^{2}$

$_{95}Am \longrightarrow [Rn]\,5f^{7}\,6d^{0}\,7s^{2}$

$_{96}Cm \longrightarrow [Rn]\,5f^{7}\,6d^{1}\,7s^{2}$

$_{102}No \longrightarrow [Rn]\,5f^{14}\,6d^{0}\,7s^{2}$

$_{103}Lr \longrightarrow [Rn]\,5f^{14}\,6d^{1}\,7s^{2}$

$Th \longrightarrow Lr$

Actinoid contraction

$e^{\ominus}$ in 5f orbital act as poor shielder

Atomic Number	Name	Symbol	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	$5f^7 6d^1 7s^2$	$5f^7$	$5f^6$	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-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium ($Z=103$). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

4.6.1 Electronic Configurations

All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshells. The fourteen electrons are formally added to 5*f*, though not in thorium (Z = 90) but from Pa onwards the 5*f* 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 f^0, f^7 and f^{14} occupancies of the 5f orbitals. Thus, the configurations of Am and Cm are [Rn] $5f^7 7s^2$ and [Rn] $5f^7 6d^1 7s^2$. Although the 5*f* orbitals resemble the 4*f* orbitals in their angular part of the wave-function, they are not as buried as 4*f* orbitals and hence 5*f* electrons can participate in bonding to a far greater extent.

4.6.2 Ionic Sizes

The general trend in lanthanoids is observable in the actinoids as well. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the **actinoid contraction** (like lanthanoid contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5*f* electrons.

4.6.3 Oxidation States

There is a greater range of oxidation states, which is in part attributed to the fact that the 5*f*, 6*d* and 7*s* levels are of comparable energies. The known oxidation states of actinoids are listed in Table 4.11.

The actinoids show in general +3 oxidation state. The elements, in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements (Table 4.11). The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state. 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.

Table 4.11: Oxidation States of Actinium and Actinoids

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									

4.6.4 General Characteristics and Comparison with Lanthanoids

The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids.

The actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non metals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action.

The magnetic properties of the actinoids are more complex than those of the lanthanoids. Although the variation in the magnetic susceptibility of the actinoids with the number of unpaired 5 *f* electrons is roughly parallel to the corresponding results for the lanthanoids, the latter have higher values.

It is evident from the behaviour of the actinoids that the ionisation enthalpies of the early actinoids, though not accurately known, but are lower than for the early lanthanoids. This is quite reasonable since it is to be expected that when 5*f* orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5*f* electrons, will therefore, be more effectively shielded from the nuclear charge than the 4*f* electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

A comparison of the actinoids with the lanthanoids, with respect to different characteristics as discussed above, reveals that behaviour similar to that of the lanthanoids is not evident until the second half of the actinoid series. However, even the early actinoids resemble the lanthanoids in showing close similarities with each other and in gradual variation in properties which do not entail change in oxidation state. The lanthanoid and actinoid contractions, have extended effects on the sizes, and therefore, the properties of the elements succeeding them in their respective periods. The lanthanoid contraction is more important because the chemistry of elements succeeding the actinoids are much less known at the present time.

Some Applications of d- and f-Block Elements

Iron and steels are the most important construction materials. Their production is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals such as Cr, Mn and Ni. Some compounds are manufactured for special purposes such as TiO for the pigment industry and MnO_2 for use in dry battery cells. The battery industry also requires Zn and Ni/Cd. The elements of Group 11 are still worthy of being called the coinage metals, although Ag and Au

are restricted to collection items and the contemporary UK 'copper' coins are copper-coated steel. The 'silver' UK coins are a Cu/Ni alloy. Many of the metals and/or their compounds are essential catalysts in the chemical industry. V_2O_5 catalyses the oxidation of SO_2 in the manufacture of sulphuric acid. $TiCl_4$ with $Al(CH_3)_3$ forms the basis of the Ziegler catalysts used to manufacture polyethylene (polythene). Iron catalysts are used in the Haber process for the production of ammonia from N_2/H_2 mixtures. Nickel catalysts enable the hydrogenation of fats to proceed. In the Wacker process the oxidation of ethyne to ethanal is catalysed by $PdCl_2$. Nickel complexes are useful in the polymerisation of alkynes and other organic compounds such as benzene. The photographic industry relies on the special light-sensitive properties of AgBr.

Question

Incorrect statement with reference to Ce (Z = 58) is

(A) Ce^{4+} is a reducing agent.

(B) Ce in +3 oxidation state is more stable than in + 4

(C) Atomic size of Ce is more than that of Lu.

(D) Ce shows common oxidation states of + 3 and + 4

Question

$K_2Cr_2O_7 + HCl$ (or $NaCl$) $+ H_2SO_4 \longrightarrow CrO_2Cl_2 + KHSO_4$ ($NaHSO_4$) $+ H_2O$

A mixture of NaCl and $K_2Cr_2O_7$ is heated with conc. H_2SO_4 deep red vapours are formed. Which of the following statements is false?

(A) The vapours give a yellow solution with NaOH

(B) The vapours contain CrO_2Cl_2 only

(C) The vapours contain CrO_2Cl_2 and Cl_2

(D) The vapours when passed into lead acetate in acetic give a yellow precipitate

$CrO_2Cl_2 \rightarrow$ deep red vapour.

$CrO_2Cl_2 \xrightarrow{NaOH} Na_2CrO_4 \rightarrow$ sodium chromate.

$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4 \downarrow$

Question

The elements in which electrons are progressively filled in 4f-orbital are called

(A) actinoids (5f)

(B) transition elements

(C) lanthanoids 4f ✓

(D) halogens

Question

La → Lanthanum → 5d

Which of the following statement is wrong regarding lanthanoids?

(A) Ln(III) compounds are predominantly ionic in character.

Ce → Lu

atomic size ← more Ce ——— Lu ——→ covalent character
ionic ↳ atomic size

(B) Ln(Ill) compounds are generally colourless. ✗

↳ Exception Lu^{+3} → only this is colourless.

Ce^{+3} → ionic

(C) Ln(III) hydroxides are mainly basic in nature.

$Ce(OH)_3$, ——→ $Lu(OH)_3$ small atomic size
↳ basic nature less

$Ce(OH)_3$

(D) The ionic size of Ln(III) ions decreases with increasing atomic number

↳ Lanthanoid contraction

Question

The electronic configuration of Cu(II) is $3d^9$ whereas that of Cu(I) is $3d^{10}$. Which of the following is correct?

(A) Cu (II) is more stable.

(B) Cu(II) is less stable.

(C) Cu(I) and Cu(II) are equally stable.

(D) Stability of Cu(I) and Cu(II) depends on nature of copper salts.

Question

Metallic radii of some transition elements are given below. Which of these elements will have highest density?

Element	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

Ni & Cu → 8.9 g/cm³

(A) Fe

(B) Ni

(C) Co

(D) Cu

Question

Generally transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state ?

(A) Ag_2SO_4

(B) CuF_2

(C) ZnF_2

(D) Cu_2Cl_2

$Ag \rightarrow 4d^{10} 5s^1$

${}_{29}Cu \rightarrow 3d^{10} 4s^1$

$Ag_2SO_4 \rightarrow Ag^+ \; SO_4^{2-}$; $Ag^+ \rightarrow 4d^{10}$

$CuF_2 \rightarrow Cu^{+2} \; F^{-}$; $Cu^{+2} \rightarrow 3d^9 \rightarrow$ unpaired

$ZnF_2 \rightarrow Zn^{2+} \rightarrow 3d^{10} \rightarrow$ colourless

$Cu_2Cl_2 \rightarrow Cu^{+1} \rightarrow 3d^{10}$

$Cu^+ \rightarrow 3d^{10} 4s^0$

$Ag \rightarrow 4d \; 5s^1$

$Ag^+ \rightarrow 4d^{10} 5s^0$

↿⇂ | ↿⇂ | ↿⇂ | ↿⇂ | ↿ → unpaired → colours

Question

Extra

On addition of small amount of $KMnO_4$ to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.

(A) Mn_2O_7 → highly explosive

(B) MnO_2

(C) $MnSO_4$

(D) Mn_2O_3

Question

Which of the following reactions are disproportionation reactions?

(i) $2Cu^+ \longrightarrow Cu^{2+} + Cu$

(ii) $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

(iii) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

(iv) $2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

(A) (i), (ii)

(B) (i), (ii), (iii)

(C) (ii), (iii), (iv)

(D) (i), (iv)

MnO_4^-

$x + (-2\times4) = -1$

$x - 8 = -1$

$x = +7$

K_2MnO_4

$1\times2 + x + (-2\times4) = 6$

MnO_2

$x + (-2\times2) = 0$

$x - 4 = 0$

$x = +4$

Question

Which of the following are amphoteric oxides?

Mn_2O_7, CrO_3, Cr_2O_3, CrO, V_2O_5, V_2O_4

(A) V_2O_5, Cr_2O_3 ampho

(B) acidic Mn_2O_7, acidic CrO_3

(C) basic CrO, ampho V_2O_5

(D) ampho V_2O_5, less basic V_2O_4

Question

Gadolinium belongs to 4f series. It's atomic number is 64 . Which of the following is the correct electronic configuration of gadolinium?

A. $[Xe]4f^7 5d^1 6s^2$

B. $[Xe]4f^6 5d^2 6s^2$

C. $[Xe]4f^8 6s^2$

D. $[Xe]4f^9 5s^1$

$Eu \longrightarrow 4f^7 5d^0 6s^2$

$Gd \longrightarrow 4f^7 5d^1 6s^2$

Question

Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds?

(A) They have high melting points in comparison to pure metals.

(B) They are very hard.

(C) They retain metallic conductivity.

(D) They are chemically very reactive.

Question

The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion is

(A) 2.87 B.M

(B) 3.87 B.M

(C) 3.47 B.M

(D) 3.57 B.M

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

$Cr^{+3} \longrightarrow$

$_{24}Cr \longrightarrow 3d^5 4s^1$

$Cr^{+3} \longrightarrow 3d^3 4s^0$

$n = 3$

$\mu = \sqrt{3(3+2)}$

$\sqrt{3 \times 5} = \sqrt{15}$

↑	↑	↑		

$\sqrt{16} = 4$

Question

$KMnO_4$ acts as an oxidising agent in alkaline medium. When alkaline $KMnO_4$ is treated with KI, iodide ion is oxidised to

(A) I_2

(B) IO^-

(C) IO_3^-

(D) IO_4^-

Question

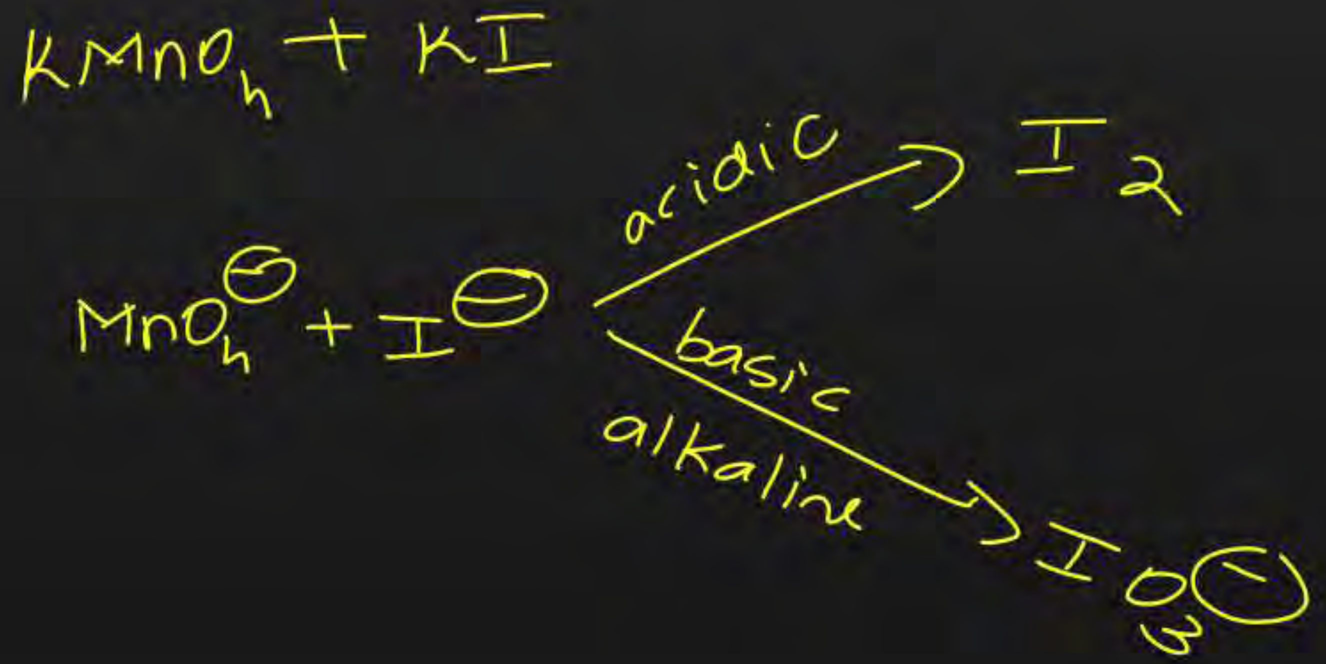
$KMnO_4$ acts as an oxidising agent in alkaline medium. When alkaline $KMnO_4$ is treated with KI, iodide ion is oxidised to

(A) I_2

(B) IO^-

(C) IO_3^- ✓

(D) IO_4^-



Question

Why is HCl not used to make the medium acidic in oxidation reactions of $KMnO_4$ if acidic medium?

A Both HCl and $KMnO_4$ act as oxidising agents

B $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidising agent

C $KMnO_4$ is a weaker oxidising agent than HCl

D $KMnO_4$ acts as a reducing agent in the presence of HCl

Question

In the form of dichromate, Cr(VI) is a strong oxidising agent in acidic medium but Mo(VI) in MoO_3 and W(VI) in WO_3 are not because

A Cr(VI) is more stable than Mo(VI) and W(VI).

B Mo(VI) and W(VI) are more stable than Cr(VI).

C Higher oxidation states of heavier members of group-6 of transition series are more stable.

D Lower oxidation states of heavier members of group-6 of transition series are more stable.

Question

Which of the following actinoids show oxidation states upto +7 ?

(A) Am

(B) Pu

(C) U

(D) Np

Question

Which of the following will not act as oxidising agents?

(A) CrO_3 → O.A

(B) MoO_3

(C) WO_3

(D) CrO_4^{2-} → O.A

Can you guess?

Question (2017)

Which of the following statement is wrong regarding lanthanoids ?

(A) Ln(III) compounds are predominantly ionic in character.

(B) Ln(III) compounds are generally colourless.

(C) Ln(III) hydroxides are mainly basic in nature.

(D) The ionic size of Ln(III) ions decreases with increasing atomic number.

Thank you.