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

$Ag^{2+} \rightarrow 5s, 4d^9$

In Ag^{2+}, Ag has incompletely filled d orbitals hence is considered as transition element.

Q→ ~~Zinc~~, Zn, Cd, Hg are not considered as transition element. Why?

$Zn \rightarrow 30$

$[Ar]\ 4s^2, 3d^{10}$

Zn^{2+}

$[Ar]\ 4s, 3d^{10}$

$Xe \rightarrow 54$

Elements which have exceptional electronic configuration. (for 58-71)

Ce [58] [Xe] $6s^2, 5d^1, 4f^1$
Gd [64] [Xe] $6s^2, 5d^1, 4f^7$
Lu [71] [Xe] $6s^2, 5d^1 4f^{17}$

{ only these elements have d^1 config.

Use 6s, 5d, 4f for elements from 58 → 71

Tb (65) → [Xe] 6s [illegible] $4f^8$

Rn → 86

from 90 → 103

$[Rn]\,7s^2, 6d^2, 5f$ [illegible]

103
−89
14

exceptional

Pa (91) $[Rn]\,7s^2, 6d^1, 5f^2$
U (92) $[Rn]\,7s^2, 6d^1, 5f^3$
Np (93) $[Rn]\,7s^2, 6d^1, 5f^4$
Cm (96) $[Rn]\,7s^2, 6d^1, 5f^7$
Lr (103) $[Rn]\,7s^2, 6d^1, 5f^{14}$

Only these elements have d^1

Es (99) $[Rn]\,7s^2, 6d^0, 5f^{11}$

Physical Properties

1) Metallic Properties
2) High Melting and Boiling Point
3) less Valatile

Q→ enthalpy of atomisation =>

~~Copper~~

$$Cu(s) \xrightarrow[\Delta_{sublim}]{\Delta_a H^\circ} Cu(g)$$

Energy required to convert one mole of solid element to gas is called enthalpy of atomisation. (sublimation)

Q→ There is much more frequent metal bonding in compound of heavy transition metal. Why?

It is due to the metals of 2nd and 3rd series have greater enthapies of atomisation than corresponding elements of 1st series.

Atomic Size

Irregular variation of transition metals atomic size

The size diffrence between transition metal is quite strong.

Generally decreases.

Zn ⇒ 30

[Ar] $4s^2, 3d^{10}$

Sc ⇒ 21

[Ar] $4s^2, 3d^1$

Sc^{2+}

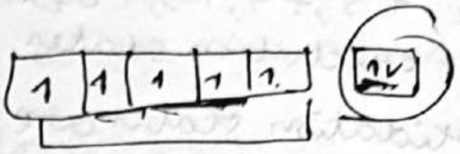
[Ar] $4s^0, 3d^1$

Sc^{3+}

[Ar] $4s^0, 3d^0$

Mg ⇒ 25

[Ar] $4s^2, 3d^5$

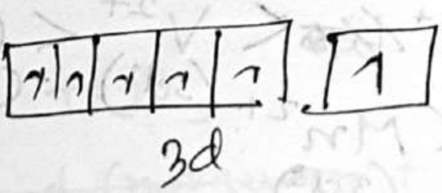


5 unpair elect

Mn^{+2} (4s)

+3
+4
+5
+6
+7

24 Cr



Q1 → Name an element of 3d transition series which show +1 oxidation state.

→ Cu ⇒ 29

[Ar] $4s^1, 3d^{10}$

~~Q2~~

4.13 How is variability in oxidation states of transition metals different from that of non transition metals? Illustrate with ~~expt~~ examples?

Transition element	S-block	P-block
They show variable oxidation state. for example → Mn shows +2, +3, +4, +5, +6 & +7 oxidation states. oxidation states are differed by 1.	They show fixed oxidation state Group 1 shows +1 oxidation state.	They show variable oxidation state. For e.g → Al, Ga, etc shows +1 & +3 oxidation state oxidation states are differed by 2.

9.3 explain briefly how +2 state becomes more and more ~~bor~~ stable in first half of the first row transition elements with increasing atomic number?

A→

First Half	Second Half
$Ti^{2+} < V^{2+} < Cr^{2+} < Mn^{2+}$ $(3d^2)$ $(3d^3)$ $(3d^4)$ $(3d^5)$	$Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$ $(3d^6)$ $(3d^7)$ $(3d^8)$ $(3d^9)$ $(3d^{10})$
They are approaching half filled stable configuration.	They are approaching d^{10} fully filled d^{10} configuration

4.2 Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?

$$\underset{(3d^5)}{Mn^{2+}} \rightarrow \underset{(3d^4)}{Mn^{3+}}$$

Due to half filled (d^5) stable configuration

& $$\underset{(3d^6)}{Fe^{2+}} \rightarrow \underset{(3d^5)}{Fe^{3+}}$$

of Mn^{2+}, it is more stable.

Q.4 To what extent do the electronic configuration decide the stability of oxidation state in first series of transition elements? Illustrate your answer with examples.

A→ Mn^{2+} ($3d^5$) half filled configuration

Cr^{3+} ($3d^0$) stable noble gas configuration

Zn^{2+} ($3d^{10}$) fully filled stable configuration

Eg

Q.5 What may be the stable oxidation state of transition element with the following ~~states~~ d electron configurations in ground state of their atoms: $3d^3$, $3d^5$, $3d^8$, $3d^4$?

A→ $3d^3$ (~~vanadium~~) +5

$4s^2 3d^5$ (~~Manganese~~) ~~and Cromium~~ +2, ~~+4~~, +7

$4s^1 3d^5$ (~~Chromium~~) ~~+3~~, +6

$3d^8$ (~~Nickel~~) +2

$3d^4$ +3, +6

Na => 11

(Ne) $3s^1$

4.6 Name the oxometal anions of first series of transition metals in which metal exhibits oxidation state equal to its group ~~member~~ number.

A → MnO_4^-

$Cr_2O_7^{2-}$

Eq.

$x + (-2 \times 4) = -1$

$x = 7$

$2x + (-2 \times 7) = -2$

$2x - 14 = -2$

$2x = 12$

$x = 6$

⇒ VO_5

Mn_2O_7

$x + (-5) = 0 \Rightarrow x$

$2x - 14 = 0$

$x = 7$

Q→ d^1 configuration in ion is very unstable. Why?

A→ Because the single electron in the (n-1) d orbital can easily be lost to achieve a stable empty d-orbital (d^0) configuration

$_{21}Sc$ [Ar] $4s^2 3d^1$

$$\boxed{Sc^{2+} = 4s^0 3d^1} \xrightarrow{\text{unstable}} Sc^{3+}$$

Q→ ~~Cobalt~~ Co^{2+} is stable in aqueous sol. but in the presence of complexing reagent, it is easily oxidised, Why?

→ Co^{2+} is readily oxidised to Co^{3+} in the presence of strong filled ligand like CN^-, NH_3, en because the resulting Co^{3+} complex achieve a much more low spin electronic configuration with high crytal field stabalization energy.

Q→ In what way is the electronic configuration of transition element different from non transition elements.

A→

Transition element	Non transition element	
$(n-1)d^{1-10} ns^{1-2}$	s-block	p-block
	ns^{1-2}	$ns^2 np^{1-6}$

E° value depends on following factors →

1) ~~Ent~~ Enthalpy of atomisation

$(Cu(s) \xrightarrow{\Delta_a H^\circ} Cu(g))$ $\Delta_a H^\circ > 0$

2) Ionisation enthalpy

$Cu(g) \xrightarrow{I.E} Cu^{2+}(g)$ $I.E > 0$

3) Hydration enthalpy

$Cu^{2+}(g) + H_2O \xrightarrow{\Delta_{hyd}H^\circ} Cu^{2+}(aq)$

$\Delta_{hyd}H^\circ < 0$

$\Delta_a H^\circ \to \Delta_{sub} H^\circ$

$Mn^{3+} \longrightarrow Mn^{2+}$
(O.A)
$3d^4 \longrightarrow 3d^5$

25
Mn $[Ar]\ 4s^2, 3d^5$
Mn^{3+} $[Ar]\ 4s^0, 3d^4$
Mn^{2+} $[Ar]\ 4s^0, 3d^5$

$Cr^{2+} \longrightarrow Cr^{3+}$
R.A
$3d^4$ $3d^3$

24
Cr $[Ar]\ 4s^1, 3d^5$
Cr^{2+} $[Ar]\ 4s^0, 3d^4$
Cr^{3+} $[Ar]\ 4s^0, 3d^3$

$Cu^+ \longrightarrow Cu^{2+} + Cu$

1) $Cu(s) \to Cu(g)$
2) $Cu(g) \to Cu^+(g)$
3) $Cu^+(g) + H_2O \to Cu^+$

1) $Cu(s) \to Cu(g)$
2) $Cu(g) \to Cu^{2+}(g)$
3) $Cu^{2+} + H_2O \to Cu^{2+}(aq)$

Q→ Name a compound which is more stable in +1 state for copper.

A→ $2Cu^{2+} + 4I^- \longrightarrow \underline{Cu_2I_2} + I_2$

Cu_2I_2

$2x + (\overset{-1}{-1 \times 2}) = 0$

$2x - 2 = 0$

$2x = 2$

$x = 1$

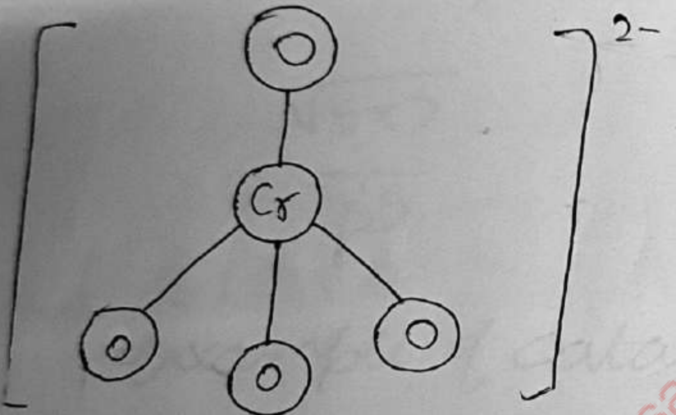
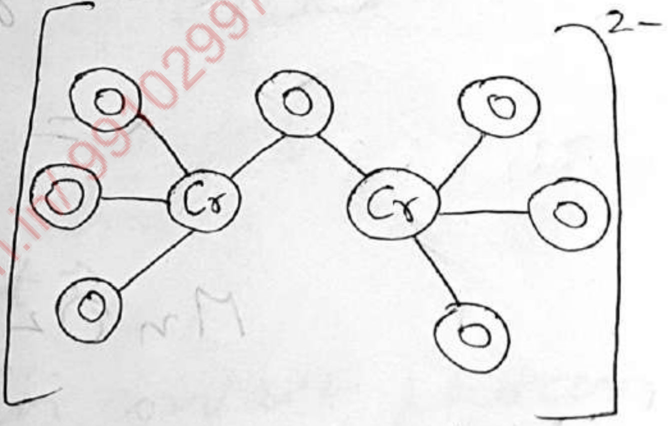
~~Q→~~

Q→ $E^\circ(M^{2+}/M)$ value for 1st row transition element is irregular. Why?

A→ $E^\circ(M^{2+}/M)$ values are not regular which can be explained from irregular variation of ionisation enthalpies ($\Delta_i H_1 + \Delta_i H_2$) and sublimation ethalpies which are relatively much less for manganese and vanadium.

and ather characteristic perperty. They have ability to form alloy.

Structure and colour of chromate and dichromate ion ⇒

Chromate ion	Dichromate ion
CrO_4^{2-}	$Cr_2O_7^{2-}$
	
Tetrahedral	2-tetrahedral sharing 1 corner with Cr – O – Cr bond
Yellow colour	Bright orange

Preparation of potassium dichromate from chromite ore ($FeCr_2O_4$)

Step 1 → $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

Step 2 → $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

Step 3 → $Na_2Cr_2O_7 + 2KCl \rightleftharpoons K_2Cr_2O_7 + 2NaCl$

Note → $K_2Cr_2O_7$ is used in leather industry, oxidising agent and preparation of many azo compounds.

Oxidiseds of transition metals ⇒

1) Except Sc, all metals form MO oxides (CrO, MnO)

2) Scandium forms Sc_2O_3

3) Higher the oxidation no., higher the ionic character.

4) Mn_2O_7 is covalent green oil.

Examples →

Acidic	Basic	Amphoteric
$\overset{+7}{Mn_2O_7} \xrightarrow{H_2O} HMnO_4$ higher oxidation state. $\overset{+6}{CrO_3} \xrightarrow{H_2O} H_2CrO_4 + H_2Cr_2O_7$	CrO, MnO	V_2O_5 (but more acidic) $V_2O_5 \xrightarrow{acid} VO_4^{3-} + VO_2^+$ $V_2O_4 \xrightarrow{acid} VO^{2+}$

$V_2O_3 < V_2O_4 < V_2O_5$

Basic character

Preparation of patassium permagnate =>

From fusion of MnO_2, KOH (or KNO_3)

1) $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

2) $MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + Mn_2O_4 + 2H_2O$

Q→ What is the effect of increase in pH values on sodium dichromate sol.?

A→ $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

dichromate ion

Chromate ion

Na

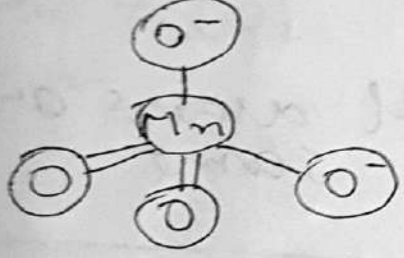
In Acidic medium

$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

Structure and colour of manganate ion and permagnate ion.

MnO_4^{2-}

Manganate



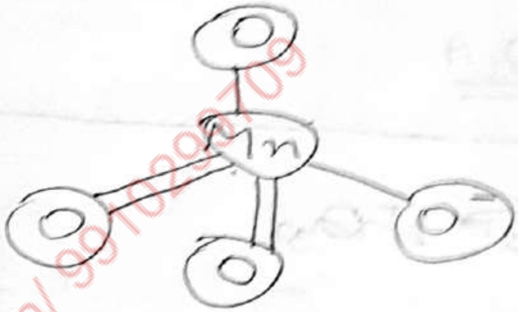
tetrahedral

Green colour

Paramagnetic due to presence of one unpair electron.

MnO_4^-

Permanganate



tetrahedral

Purple colour

Diamagnetic due to absence of unpair electron

Colour is due to (LMCT) that is ligand to metal charge transfer

Reactions of transition elements

Acidic

$MnO_4^- \to Mn^{2+}$

O.A

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

O.A

~~$I_2\ 2IO_3$~~

$I^- \to I_2$

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

$C_2O_4^{2-} \to CO_2$

$S^{2-} \to S$

$(H_2S \to 2H^+ + S^{2-})$

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

$NO_2^- \to NO_3^-$

$SN^{2+} \to SN^{4+}$

Faintly alkaline / neutral

$MnO_4^- \to MnO_2$

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

$MnO_4^- + Mn^{2+} \to MnO_2$

All others are same

Inner Transition Elements (F-block elements

- Ce (58)

[Xe] $6s^2, 5d^1, 4f^1$

$2n^2$ n = orbit no.

Mn (25)

[Ar] $4s^2, 3d^5$

$$\underbrace{(n-2)f^{0-14}\ (n-1)^{0-1}\ ns^2\ (n-1)d^0}_{\downarrow}$$

e^- config. of f block

Q → The chemistry of actinoids are more complicated than Langthanoids. Why?

A → It is due to actinoids are radio active and show wide range of oxidation state.

Q→ We study chemistry of Lanthanum with Langthanoids and actinium with actinoids Why?

Ln → Langthanoid
An → Acticinium

A→ Because Ln resemblems with La and An resembles with Ac

Q→

A→ 58

Ce $[Xe]6s^2$, ~~[illegible]~~ $5d^1, 4f^1$

{/}

NOTE → Ce^{4+} and Pr^{4+} (+4 oxidation state)

Sm^{2+}, ~~and~~ Eu^{2+}, Yb^{2+}, Tm^{2+} (+2 oxid ...)

Q → Ce^{4+} is strong oxidising agent why?

A→ because it has tendency to reduce itself in most common oxidation state +3.

Q → Yb^{2+} is strong reducing agent

A→ has tendency to reduce itself in most " " " +3.

Q→ Physical Properties of Lanthanoids.

A→ 1) Silvery white

2) Tarnish rapidly in air

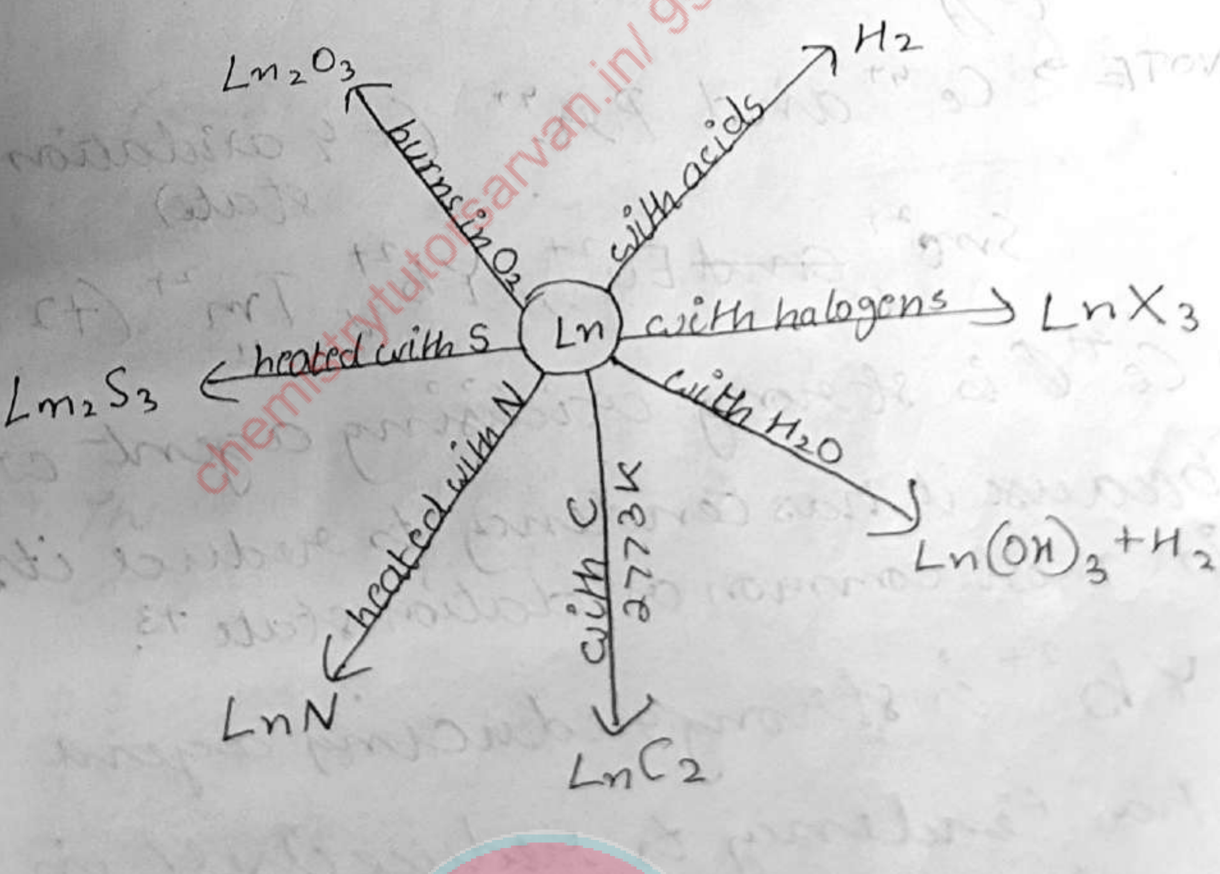
3) Hardness increases with increase in atomic number

4) samarium is steel hard.

5). Density and other properties changes smoothly except Eu & Eb.

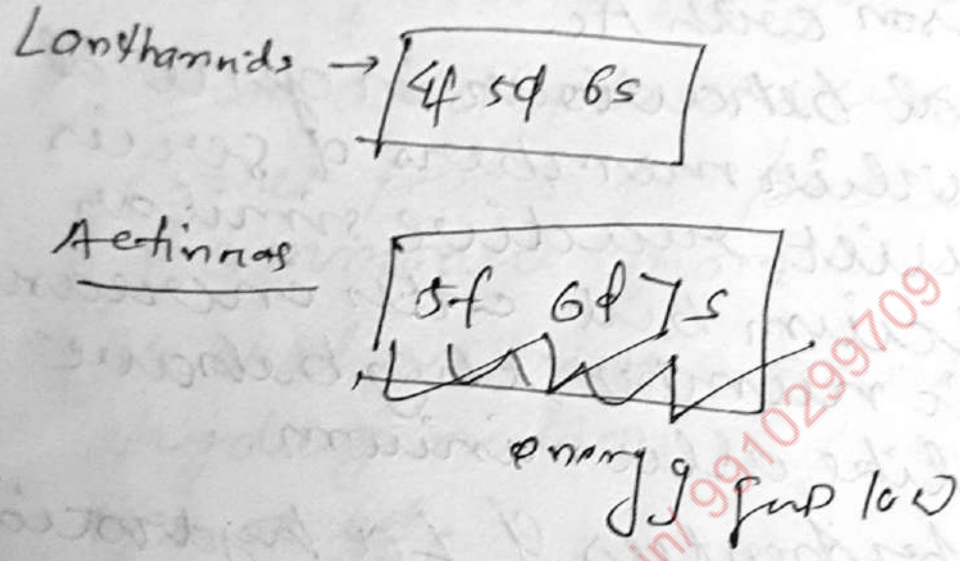
Q→ Reactions of d-block elements.

A→



Q→ Actinoid contraction is greater from element to element than Lanthanoid contraction. Why?

A→ It is due to poor shielding effect of 5f electrons.



NOTE # Np and Pu show greatest range of oxidation in actinoids (+3 to +7)

Actinoids also show +3 common oxidation state.

Comparison b/w Lanthanoid and actinoid

1) Magnetic properties of La are more complex than those of Ac.

2) The ionisation enthalpies of early

actinoids are lower than early lathanoids because 5f e^- is more effectively shielded from nuclear change than 4f electron.

NOTE

The 2nd ionisation enthalpy of La is comparison with Ac.

chemical behaviour in general the earlier members of series are quiet reactive similar to calcium but with increasing atomic number, they behave more like alluminium.

Basic properties of La hydroxide decreases from $La(OH)_3$ to $Lu(OH)_3$

Q→ Application of d and F block elements

A→ 1) TiO for pigment industry

2) MnO_2 for use ~~of~~ in dry battery cells

3) Group 11 are still worthy of being called the coinage metals

4) copper coins are copper coated steel.

5) Silver UK coins are Cu/Ni alloy

6) V_2O_5 catalyses the oxidation of SO_2 in manufacture of sulphuric acid

7) $TiCl_4$ with $Al(CH_3)_3$ forms basis of Ziegler catalysts used to manufacture polyethene.

8) Iron catalysts are used in Haber process for production of ammonia from N_2/H_2 mixture

9) Nickel catalysts enable the hydrogenation of fats to proceed.

10) In Wacker process, the oxidation of ethyne to ethanal is catalysed by $PdCl_2$. ~~Nickel~~

11) Photographic industry relies on special light sensetive prop. of $AgBr$