Chromium Group

Cr } 24
Mo } 42
W } 74

Oxd^{n} states ⇒

Cr :- electronic conf^{n} ⇒ $3d^5 4s^1$
Stable oxd^{n} states ⇒ Cr(II) ⇒ reducing
Cr(III) ⇒ stable
Cr(VI) ⇒ Oxidising

Other are +I

Mo :- electronic config^{n} ⇒ $4d^5 5s^1$
oxd^{n} state ⇒ +III ⇒ reducing
+VI ⇒ stable

others are +I, +II.

W :- electronic conf^{n} ⇒ $5d^4 6s^2$
oxd^{n} state ⇒ +III ⇒ reducing
+VI ⇒ stable

other are +II.

This shows the general trends of transition elements that higher oxd^{n} states are stable downwards a group.

General Properties ⇒ Metals are hard and have high melting points.

At low temperature, Cu forms a protective layer of oxide thus Cu remains unreactive at low temp. Due to this passive behaviour Cr is extensively used for electroplating onto iron or other metals.

Cr dissolves in acids like HCl and H_2SO_4 by forming Cr(II) ion and hydrogen gas.

Cr does not react with HNO_3 due to the formation of the protective layer.

Cr reacts with HCl vapour to form anhyd. $CrCl_2$ ~~wit~~ and H_2 gas.

Cr doesnot react with O_2 at low temp. but react with O_2 at high temp., forms green α-Cr_2O_3.

Cr(VI)

There are very few compounds known as Cr(VI) e.g. $[CrO_4]^{2-}$, $[Cr_2O_7]^{2-}$, CrO_3, CrO_2X_2, $CrOX_4$ etc.

Chromyl chloride test ⇒

$$Cr_2O_7^{2-} + Cl^- \xrightarrow[\text{warm}]{H_2SO_4} CrO_2Cl_2$$

reddish-brown

$\downarrow$ NaOH

Na_2CrO_4 Yellow soln.

~~$PbCrO_4\downarrow$ Yellow ppt. ← $(CH_3COO)_2Pb$~~

$\xrightarrow{(CH_3COO)_2Pb}$ $PbCrO_4\downarrow$ (yellow ppt)

d^3

Cr(III) → It is the most stable(*) oxd^n state of Cr. Cr(III) is highly stable in acidic soln. but it oxidizes to Cr(VI) in alkaline medium.

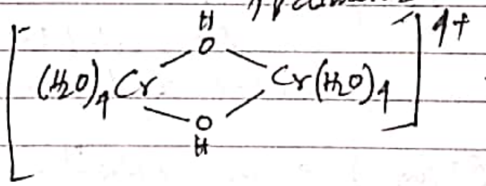
$$(NH_4)_2Cr_2O_7 \xrightarrow{heat} \underset{green}{Cr_2O_3} + N_2 + 4H_2O$$

Cr_2O_3 is used as pigment, as a catalyst in reactions like manufacture of polythene and butadiene.

The aq. soln. of Cr^{3+} contain $[Cr(H_2O)_6]^{3+}$ ions which is violet in colour. Aqua complex is acidic in nature, it releases H^+ ion by dissociation of one H_2O molecule.

$$[Cr(H_2O)_6]^{3+} \rightleftharpoons H^+ + [Cr(H_2O)_5(OH)]^{2+}$$

↓ dimerization



+ $2H_2O$

(*) The stability is due to the electronic configuration (d^3) that contain halffilled t_{2g} orbital.

The ~~well known Cr(III) oxide is Cr_2O_3~~, Cr_2O_3 is amphoteric in nature. It forms $[Cr(H_2O)_6]^{3+}$ in acids and $[Cr(OH)_5H_2O]^{2-}$ or $[Cr(OH)_6]^{3-}$ in alkaline solutions.

$[Cr(OH)_5H_2O]^{2-}$ ⇓ pH is moderate

$[Cr(OH)_6]^{3-}$ ⇓ pH is very high.

Reinecke's Salt ⇒ $NH_4[Cr(NH_3)_2(NCS)_4] \cdot H_2O$

08 it is used to precipitate large positive ions.
It is because when the site of +ve and -ve ions are
09 same then they separate out of the solution.

10 Addition of NaOH in Cr^{3+} doesnot precipitate
$Cr(OH)_3$ instead of that it precipitates as
11 hydrated oxide,

Cr_2O_3 + ~~H_2O~~ NaOH → $Cr(OH)_3$ → $Cr_2O_3(H_2O)_n$.

12

S.C. of ~~Chromium Acetate dihydrate~~ ⇒

01

02 Cr(II) ⇒ It gets stability in coordination compounds.

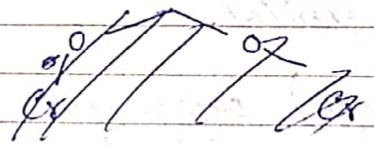
03 Most stable chromous compound is chromium acetate dihydrate

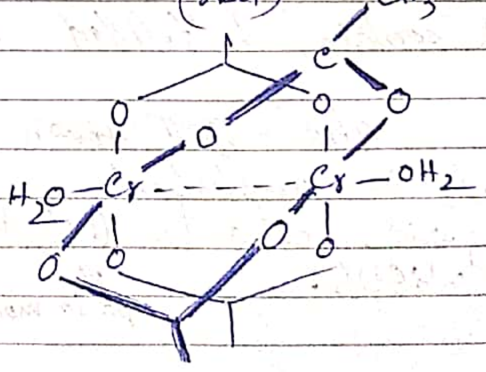
04

$$Cr^{2+}(aq.) + CH_3COONa \xrightarrow[atm.]{N_2} Cr_2(CH_3COO)_4 \cdot 2H_2O$$

05 (red)

06





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29	30	31											

Zero state ⇒ Metal Carbonyls & $[M(CO)_6]$
-I " ⇒ $[M_2(CO)_{10}]^{-2}$
-II " ⇒ $[M(CO)_5]^{-2}$

Chromates ⇒ ~~Chromium and~~ Anions of chromium and oxygen are known as chromates are highly oxidising agents.

On acidifying, chromates CrO_4^{2-} form $HCrO_4^-$ and orage-red & dichromates ~~or~~ $Cr_2O_7^{2-}$, in which two Td units join together. by ~~sharing the~~ ~~equilibrium exists as write~~

In acid medium

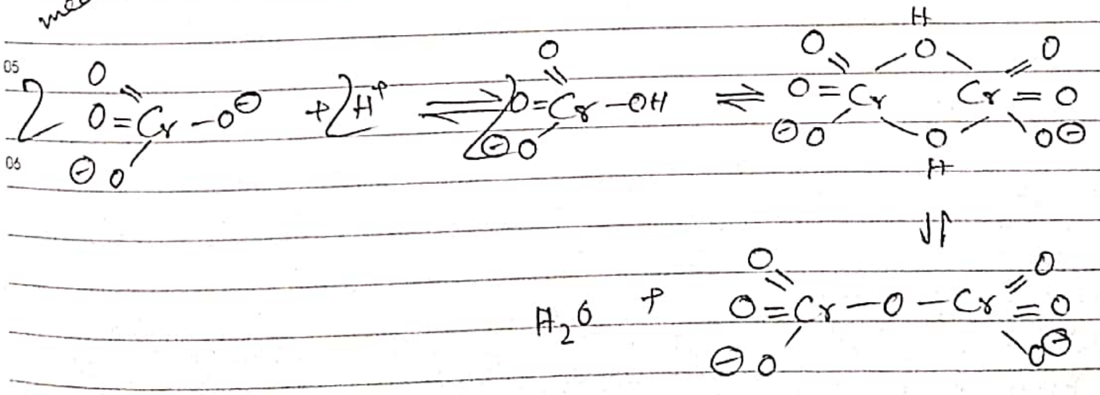
$$\begin{cases} H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \\ 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \\ HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \end{cases}$$

In acidic medium $Cr_2O_7^{2-}$ is main species.

Alkaline medium

$$\begin{cases} Cr_2O_7^{2-} + OH^- \rightleftharpoons CrO_4^{2-} + HCrO_4^- \\ HCrO_4^- + OH^- \rightleftharpoons CrO_4^{2-} + H_2O \end{cases}$$

In alkaline medium CrO_4^{2-} is main species.



(*) Metals like Ag^+, Pb^{2+} or Ba^{2+} quantitatively precipitate as chromates not as dichromates. Why?

(*) VO_4^{3-} forms several polymers but? CrO_4^{2-} condenses to form only $Cr_2O_7^{2-}$ - why?

(*) Why dichromates are more soluble than chromates?

Some important Salts ⇒

08 Chrome alum :- $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$

09 $aq. Cr_2(SO_4)_3 + K_2SO_4(aq.) \rightarrow K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$

violet deep purple ~~violet~~

10

[illegible].

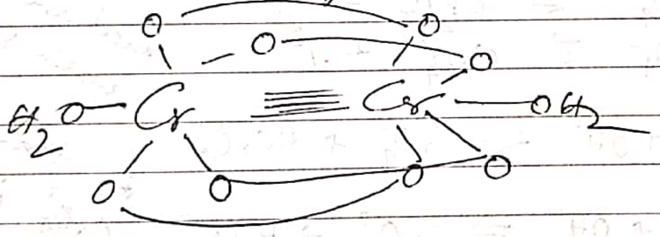
11 It is used ~~in~~ as dye in tanning of leather.

12

01 Chromium (II) acetate dihydrate ⇒

02

03



04

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Manganese

Highest oxidation state VII.

Mn has oxidation state ~~Ex~~ from -VII to +VII. The +II oxidation state is most stable and common.

In alkaline soln. Mn^{2+} oxidizes to MnO_2.

most stable
Mn(II) ⇒ MnO
Mn(III) ⇒ Mn_2O_3
Mn(IV) ⇒ MnO_2
Mn(V) ⇒ —
Mn(VI) ⇒ —
Mn(VII) ⇒ $KMnO_4$

Properties ⇒
- It reacts with H_2O slowly and forms H_2 gas.
- The finely divided particles react with air but massive metal does not react with air unless heated.
- Low oxidation states are basic and higher oxidation states are acidic in nature.
- On adding small amount of base in the soln., the solution turns to brown-black from pink gelatinous precipitate.

$$\underset{\text{(pale pink)}}{[Mn(H_2O)_6]^{2+}} + H_2O \rightarrow \underset{\text{(pale pink)}}{Mn(OH)_2} \xrightarrow[\text{black}]{\text{brown}} \underset{\text{(Black)}}{MnO_2}$$

- Half filled d-shell thus more stable than the other metals of the row.

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M	T	W	T	F	S	S	M	T	W	T	F	S	S
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$$[Mn(CN)_6]^{5-} \xleftarrow[red^n]{Zn} [Mn(CN)_6]^{4-} \xrightarrow[oxd^n]{air} [Mn(CN)_6]^{3-}$$

In all cases, d^5 ~~to~~ are not colourless, in lowspin complexes d^5 ~~g~~ shows colour as here d-d electronic transition is spin allowed.

$t_{2g}^3 e_g^2$ ⇒ high spin, spin forbidden, colourless

$t_{2g}^5 e_g^0$ ⇒ Low spin complex, spin allowed, strongly coloured.

(+IV)

MnO_2 is the main and ~~comm~~ commercially important oxide in the group. It is oxidising agent, thus not stable. It decomposes to Mn_3O_4 on heating ~~at~~ to 530°c. It is the main ore of Mn, named pyrolusite.

Simple

In laboratory it is prepared by permanganate titration in alkaline solution.

$$MnO_4^- + 2H_2O + 3e \longrightarrow MnO_2 + 4\,OH^-$$

On heating with NaOH, MnO_2 ~~gives~~ forms a dark green coloured compound, sodium manganate ~~of~~ $Na_2[MnO_2]$.

MnO_2 oxidises toluene to benzaldehyde, aniline to quinhydrone.

It is used in the prep^n of O_2 from $KClO_3$ by heating it.

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Mn(III)

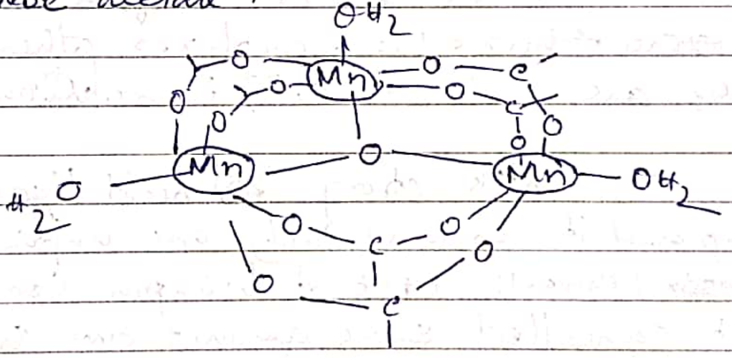
Mn_3O_4 is the most stable oxide at high temperature.

It has a normal spinel structure in which Mn(+III) is in oh holes and Mn(+II) in td holes.

[illegible]

(*) Why for the titration of permanganate

Basic Manganese acetate :=



The Formula is $[Mn_3O(CH_3COO)_6L_3]^+$ here L = ligand, may be water or other.

(*) Mn(III) and Mn(IV) are the two species that are involved in the production of O_2 in photosynthesis.

Mn(II) ⇒ It is the most stable oxd^n state. All the salts of Mn(II) are water soluble, forms hydrated ions. $Mn_3(PO_4)_2$, $MnCO_3$ are sparingly soluble.

In basic solution, Mn^{2+} precipitates as ~~[illegible]~~ a pale pink coloured gelatinous precipitate of $Mn(OH)_2$ which further oxidises to ~~[illegible]~~ brown-black coloured MnO_2.

⊛ Why the above phenomenon is not possible in acidic solution?.

~~Due~~

Due to d^5 configuration, CFSE of Mn^{2+} is zero thus the complexes other than chelate complexes are stable only in solutions.

With strong ~~[illegible]~~ field ligands, the electrons paired up and it contains only one unpaired electron. ~~[illegible]~~ Thus the CFSE of low spin complexes are greater but it cancelled some amount due to pairing energy. The low spin complexes are more reactive as removing one electron decreases the pairing energy and increases the CFSE.

$K_4[Mn(CN)_6]\cdot 3H_2O$, $[Mn(CNR)_6]^{2+}$, $[Mn(CN)_5;NO]^{3-}$ are some examples.

$$[Mn(CN)_6]^{4-} \xrightarrow{air} [Mn(CN)_6]^{5-}$$
$$\xrightarrow{Zn} [Mn(CN)_6]^{3-}$$

In, The low spin d^5 complexes, the d – d transitions are spin allowed thus they strongly coloured.