

The d- and f-Block Elements

d-block : Groups 3 to 12 of the periodic table. Inner $(n-1)$ d orbitals are progressively filled. Also called transition metals.

f-block : 4f and 5f orbitals filled in.

Two series : lanthanoids (Ce - Lu) and actinoids (Th - Lr). Inner transition metals.

Series of transition metals

3d series : Sc \rightarrow Zn ($Z = 21$ to 30)

4d series : Y \rightarrow Cd ($Z = 39$ to 48)

5d series : La, Hf \rightarrow Hg ($Z = 57, 72-80$)

6d series : Ac, Rf \rightarrow Cn (incomplete)

IUPAC Definition

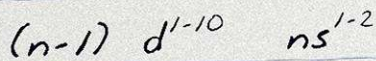
A transition metal has ~~complete~~ incomplete d-subshell in atom OR in its common ion.

Zn, Cd, Hg, Cn \rightarrow $3d^{10} 4s^2$ - NOT full T.M.
 ←-shell

But studied with T.M. as they are end members of 3d, 4d, 5d series respectively.

Electronic Configuration

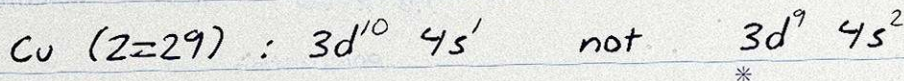
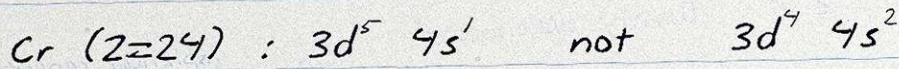
General outer config :



← outer 2
← orbitals

Anomalies (Cr & Cu)

Energy gap between $(n-1)d$ and ns is very small. Half / fully filled sets are extra stable.



Common features (partly filled d)

- (1) Variable oxidation states
- (2) Coloured ions in solution
- (3) Complex formation *
- (4) Paramagnetism
- (5) Catalytic activity
- (6) Interstitial cpds & alloys

Physical Properties

Typical metals : hard, ductile, malleable, high tensile strength, lustrous, good conductors of heat & electricity.

Exceptions : Zn, Cd, Hg, Mn (soft).

Melting / Boiling Points

High m.p. due to strong metallic bond from involvement of $(n-1)d + ns$ electrons in interatomic bonding.

Maxima at d^5 (one unpaired e per d-orbital)

Mn and Tc are anomalous (low m.p.).

Tungsten (W) has highest m.p. : 3683 K.

Enthalpy of Atomisation

More unpaired e⁻ \Rightarrow stronger M-M bonding \Rightarrow high $D_a H$.

$$D_a H (\text{Zn}) = 126 \text{ kJ/mol (lowest)}$$

\leftarrow no unpaired e⁻ in 3d

2nd & 3rd series have greater $D_a H$ than 1st series \Rightarrow frequent M-M bonding.

Atomic & Ionic Radii

Across a series - radii decrease as Z increases (poor d-shielding).

But variation is small - filling of inner d makes outer e relatively shielded.

Comparison of Series

3d \rightarrow 4d : radii INCREASE (expected)

4d \rightarrow 5d : radii ~~increase~~ almost SAME

Famous pair : Zr (160 pm) & Hf (159 pm).

Reason - Lanthanoid contraction.

Lanthanoid Contraction

Steady decrease in size of Ln & Ln³⁺ ions from La to Lu, due to imperfect shielding of one 4f electron by another.

La³⁺ (106 pm) \rightarrow Lu³⁺ (85 pm)

\leftarrow shrinks
 \leftarrow 21 pm

Consequences :

- (i) 4d / 5d series have similar radii
- (ii) Zr - Hf, Nb - Ta hard to separate.
- (iii) Basic character $M(OH)_3$ decreases.

Ionisation Enthalpies

I.E. of T.M. increases left to right
(nuclear charge increases).

But increase is less steep than in p-block
due to shielding by inner d-electrons.

*
Order of I.E.

$$DH_1 < DH_2 < DH_3$$

<-always
<-increasing

Irregularity

Exchange energy stabilises d^5 & d^{10}

~~2H~~ DH_2 (Mn) is high : Mn^+ is $3d^5 4s^1$
Compare with Cr^+ which is $3d^5$. Removing 4s
from Mn^+ breaks d^5 \rightarrow needs more energy.

DH_3 is very high for Zn : $3d^{10}$ is
extra stable; explains why Zn(III) absent.

3rd IE high for Cu, Ni, Zn \Rightarrow states
above +2 are difficult for these metals.

Oxidation States

T.M. show variety of O.S. - due to small energy gap between $(n-1)d$ and ns orbitals. Both can take part in bonding.

Key Examples (3d series)

Sc : +3 only

Ti : +2, +3, +4 (most stable = +4)

V : +2 to +5 (max = +5)

Cr : +2 to +6 (Cr^{3+} most stable)

Mn : +2 to ~~+8~~ +7. (all states ?)

Fe : +2, +3* (most stable = +3 in Fe^{3+})

Cu : +1, +2 ; Zn : +2 only

Trends in O.S.

Max O.S. = sum of $(n-1)d$ + ns electrons upto Mn ($3d^5 4s^2 \Rightarrow +7$ in MnO_4^-).

Beyond Mn - $3d$ electrons get paired, fewer e available for bonding \Rightarrow max O.S. decreases sharply.

Within group : $6d > 5d > 3d$ stability of higher O.S. (opposite to p-block).

Standard Electrode Potentials

M^{2+} / M values - measure of reducing tendency of metal in aqueous medium.

Trend across 3d series

$E^\circ (M^{2+}/M)$ becomes less negative left \rightarrow right ($D_{iH} + D_{iH_2}$ increases).

Anomalies : Mn, Ni, Zn more negative than expected.

*

* Mn : Mn^{2+} is d^5 (extra stable)

* Zn : Zn^{2+} is d^{10} (extra stable)

* Ni : highly negative $D_{hyd}H$

Cu - the odd one

$$E^\circ (Cu^{2+}/Cu) = +0.34 \text{ V}$$

<- POSITIVE ??
<- noble-like

Cu cannot displace H_2 from dilute HCl or H_2SO_4 (only oxidising acids attack it).

Reason : high D_{aH} + low $D_{hyd}H$ are not compensated.

Magnetic Properties

Diamagnetic *: repelled by mag. field
(all electrons paired).

Paramagnetic : attracted by mag. field
(unpaired electrons present).

Ferromagnetic : strongly attracted
(e.g. Fe, Co, Ni) - ~~para~~ extreme para.

Spin-only Formula *

$$m = \sqrt{n(n+2)} \text{ BM}$$

<- n = no. of
<- unpaired e

m in Bohr Magnetons (BM)

1 unpaired e $\Rightarrow m = 1.73 \text{ BM}$

Quick Table

Ti³⁺ (d¹) $\rightarrow n=1 \rightarrow m = 1.73 \text{ BM}$

V³⁺ (d²) $\rightarrow n=2 \rightarrow m = 2.84 \text{ BM}$

Cr³⁺ (d³) $\rightarrow n=3 \rightarrow m = 3.87 \text{ BM}$

Mn²⁺ (d⁵) $\rightarrow n=5 \rightarrow m = 5.92 \text{ BM}$

Fe²⁺ (d⁶) $\rightarrow n=4 \rightarrow m = 4.90 \text{ BM}$

Zn²⁺ (d¹⁰) $\rightarrow n=0 \rightarrow m = 0 \text{ (diamag.)}$

Orbital contribution is quenched in 3d.

Coloured Ions

Colour due to d-d transition : ∴ an electron from t_{2g} \rightarrow e_g on absorbing visible light. We see complementary colour.

$$\Delta E = h \nu = hc / \lambda$$

<- depends on
<- ligand

Examples (aq. ions)

Ti^{3+} (d^1) - purple ; V^{4+} - blue

Cr^{3+} (d^3) - violet ; Mn^{2+} - pink

Fe^{3+} - yellow ; Fe^{2+} - green

Co^{2+} - pink ; Ni^{2+} - green ; Cu^{2+} - blue

Sc^{3+} (d^0), Zn^{2+} (d^{10}) : colourless

Complex Formation

T.M. form many complexes due to :

(i) small size of M^+ / M^{2+} ions

(ii) high charge density

(iii) availability of vacant d orbitals

Examples : $[Fe(CN)_6]^{3-}$, $[Cu(NH_3)_4]^{2+}$
 $[PtCl_4]^{2-}$, $[Co(NH_3)_6]^{3+}$

Detailed in Unit 5 - Coordination Cpd.

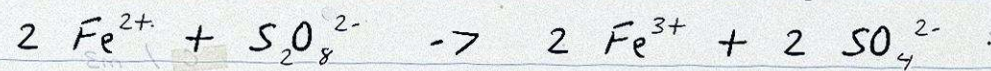
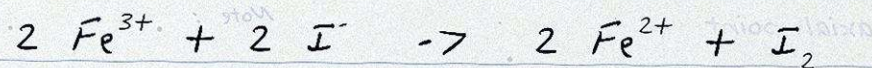
Catalysis & Interstitial

Catalytic Property

T.M. and compounds act as catalysts because of :

- (i) variable oxidation states
- (ii) large surface area (3d / 4s overlap)
- (iii) ability to form complexes

Example : Fe^{3+} catalyses $\text{I}^- + \text{S}_2\text{O}_8^{2-}$



Industrial : V_2O_5 (Contact), Fe (Haber),
 Ni (hydrogenation), TiCl_4 (Ziegler-Natta).

Interstitial Compounds

Small atoms H , C , N , B trapped in voids of metal lattice - non-stoich.

e.g. TiC , Mn_3N_2 , Fe_3H , $\text{VH}_{0.56}$, $\text{TiH}_{1.7}$

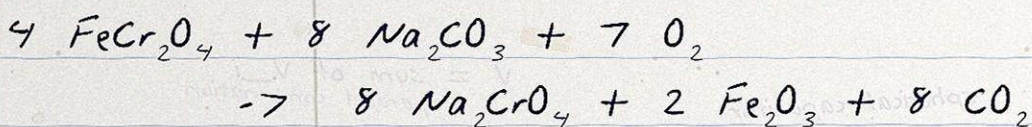
- (i) hard, high m.p.
- (ii) retain metallic conductivity
- (iii) chemically inert

Alloys e.g. ~~stee~~ steel ($\text{Fe} + \text{Cr}/\text{Ni}/\text{Mn}$)

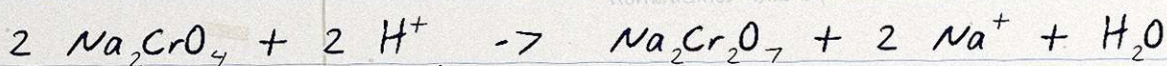
Potassium Dichromate $K_2Cr_2O_7$

Preparation (from chromite)

Step 1 : Chromite ore + Na_2CO_3 + O_2



Step 2 : yellow chromate + H_2SO_4



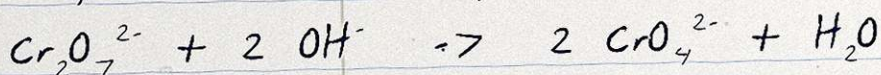
Step 3 : $Na_2Cr_2O_7 + 2 KCl \rightarrow K_2Cr_2O_7 + 2 NaCl$

(orange crystals).

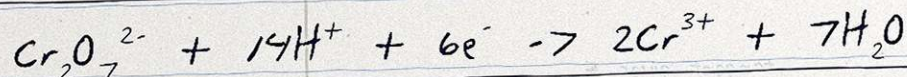
Interconversion in solution



(yellow chromate \rightarrow orange dichromate)

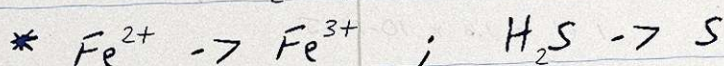
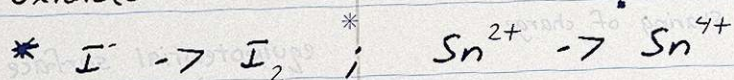


As Oxidising Agent



$\leftarrow E = +1.33V$

Oxidises :

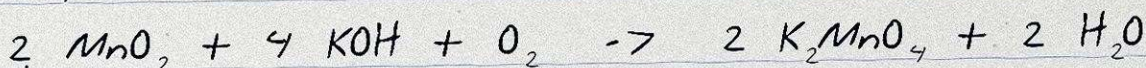


Cr-O-Cr angle (dichromate) = 126 deg.

Potassium Permanganate $KMnO_4$

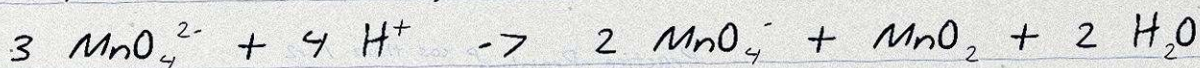
Preparation (from MnO_2)

Step 1 : Fusion with KOH + air / KNO_3



(dark green manganate)

Step 2 : Electrolytic / disproportionation



Structure & Properties

MnO_4^- ion : tetrahedral, diamagnetic

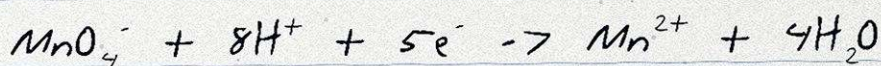
(no unpaired e on $Mn(VII)$, d^0).

MnO_4^{2-} : paramag. ($Mn(VI)$, d^1).

Dark ~~violet~~ purple crystals.

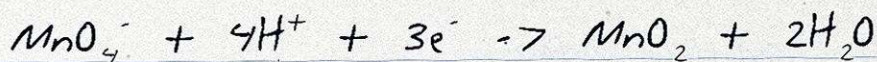
As Oxidising Agent

Acidic medium :



$\leftarrow E = +1.52V$

Neutral / faintly alkaline :

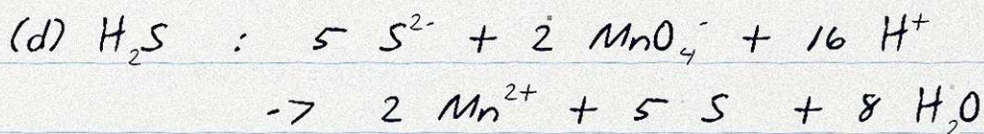
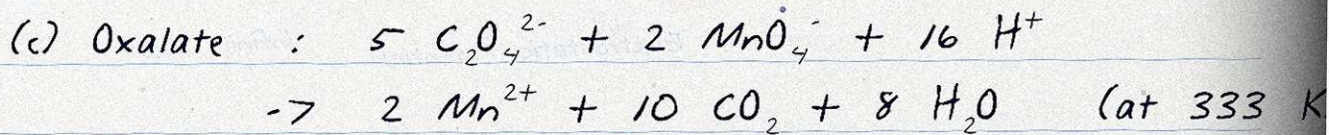
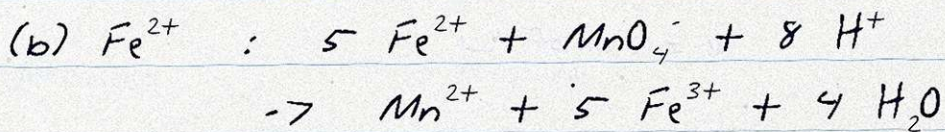
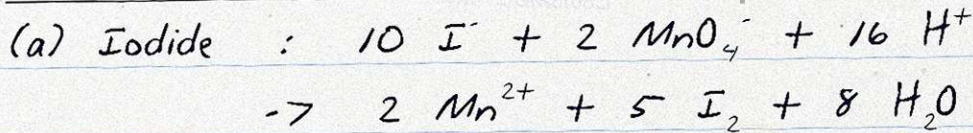


$\leftarrow E = +1.69V$

Cannot be used in HCl (Cl^- gets oxidised).

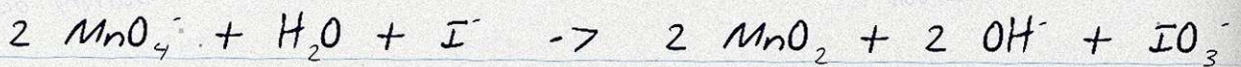
KMnO₄ - Key Reactions

Acidic Medium (Mn \rightarrow Mn²⁺)

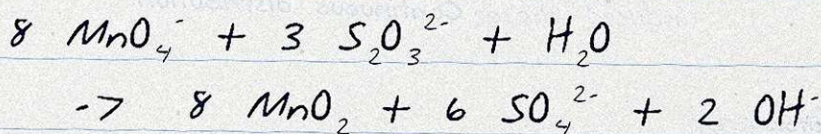


Neutral / Alkaline (Mn \rightarrow MnO₂)

(a) Iodide \rightarrow iodate :



(b) Thiosulphate \rightarrow sulphate :



Uses

Volumetric titrations, bleaching, oxidant
in org. synth., decolourising oils.

Lanthanoids (Ce - Lu)

Position & Configuration

14 elements following La ($Z = 58$ to 71)

General symbol : Ln

General config : $[Xe] 4f^{0-14} 5d^{0-1} 6s^2$

Ln^{3+} always $[Xe] 4f^n$ ($n = 0$ to 14)

Atomic / Ionic Sizes

Steady DECREASE in size from La to Lu :

La : 187 pm \rightarrow Lu : 173 pm f^{n-1}
 \leftarrow contraction

La^{3+} (106 pm) \rightarrow Lu^{3+} (85 pm)

Oxidation States

+3 is most common & stable for all.

Ce also shows +4 (Ce^{4+} is oxidant).

Eu also shows +2 (Eu^{2+} is reductant).

Yb^{2+} ($4f^{14}$) - reductant ; Tb^{4+} ($4f^7$) - oxidant

Reason : empty / half / full f shell stable

Colour & Magnetism

La^{3+} , Lu^{3+} : colourless ; others coloured

Ln Contraction (Causes & Effects)

Cause

Across Ln series, Z increases by 1 each

step but added e goes into INNER $4f$.

$4f$ shielding is poor (shape is diffuse) \Rightarrow

effective nuclear charge on outer e rises \Rightarrow

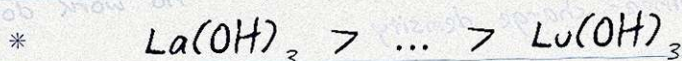
size decreases steadily.

Consequences

(i) Similar radii of $4d$ & $5d$ series.

(ii) Difficult to separate Zr/Hf , Mb/Ta .

(iii) Basic strength of $M(OH)_3$ decreases :



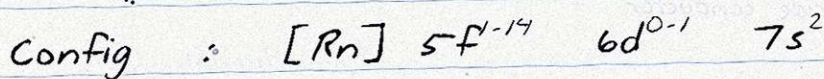
(iv) Increased density of $5d$ metals.

(v) Difficult separation of lanthanoids.

Actinoids (Th - Lr)

14 elements* after Ac ($Z = 90$ to 103).

All radioactive ; later ones synthetic.



Show more variable O.S. than Ln :

+3 most common ; also +4, +5, +6, +7

(e.g. Np shows max +7).

Lanthanoids vs Actinoids

Similarities

- * Both show +3 as principal O.S.
- * Both show contraction (Ln & An).
- * Both are highly electropositive.
- * Both have variable f electrons.

Differences

Lanthanoids :

- 4f electrons buried, do not bond
- mainly +3 ; rare +2, +4
- non-radioactive (Pm is)
- ions less complex-forming

*

Actinoids :

- 5f exposed, take part in bonding
- many states +3 to +7
- ALL radioactive
- greater complex tendency
- contraction is greater per step

Applications of d & f Block

Steel & alloys (Cr, Mn, Ni) ; TiO₂ pigment ;

MnO₂ in dry cells ; AgBr in photography ;

mischmetal (95% Ln + 5% Fe) . - flints.