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 → Zn (Z = 21 to 30)

4d series : Y → Cd (Z = 39 to 48)

5d series : La, Hf → Hg (Z=57, 72-80)

6d series : Ac, Rf → Cn (incomplete)

IUPAC Definition

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

Zn, Cd, Hg, Cn → $3d^{10}\ 4s^2$.

\- NOT T.M. (full ← shell)

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

Electronic Configuration

General outer config :

$(n-1)\ d^{1-10}\ \ ns^{1-2}$ <- outer 2 <- orbitals

Anomalies (Cr & Cu)

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

Cr (Z=24) : $3d^5\ 4s^1$ not $3d^4\ 4s^2$

Cu (Z=29) : $3d^{10}\ 4s^1$ not $3d^9\ 4s^2$ *

Pd (Z=46) : $4d^{10}$ ~~5s2~~ $5s^0$ - unique

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^- => stronger M-M bonding => high D_a H.

$D_a H$ (Zn) = 126 kJ/mol (lowest)

<-no unpaired
<-e in 3d

2nd & 3rd series have greater D_a H than 1st series => 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 -> 4d : radii INCREASE (expected)
4d -> 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.

La^{3+} (106 pm) --> Lu^{3+} (85 pm)

<- shrinks <- 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. *

D_iH_1 < D_iH_2 < D_iH_3

<-always
<-increasing

Irregularity

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

~~D2H~~ D_iH_2 (Mn) is high : Mn^+ is $3d^5\ 4s^1$
Compare with Cr^+ which is $3d^5$. Removing 4s from Mn+ breaks d5 -> needs more energy.

D_iH_3 is very high for Zn : $3d^{10}$ is extra stable; explains why Zn(III) absent.

3rd IE high for Cu, Ni, Zn => 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 => +7 in MnO_4^-).

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

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

Standard Electrode Potentials

M2+ / M values - measure of reducing tendency of metal in aqueous medium.

Trend across 3d series

E° (M^{2+}/M) becomes less negative left -> right (D_i H1 + D_i H2 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° (Cu^{2+}/Cu) = +0.34 V

<-POSITIVE ?? <-noble-like

Cu cannot displace H2 from dilute HCl or H2SO4 (only oxidising acids attack it).

Reason : high D_a H + 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)] BM

<- n = no. of
<- unpaired e

m in Bohr Magnetons (BM)
1 unpaired e => m = 1.73 BM

Quick Table

Ti^{3+} (d^1) -> n=1 -> m = 1.73 BM
V^{3+} (d^2) -> n=2 -> m = 2.84 BM
Cr^{3+} (d^3) -> n=3 -> m = 3.87 BM
Mn^{2+} (d^5) -> n=5 -> m = 5.92 BM
Fe^{2+} (d^6) -> n=4 -> m = 4.90 BM
Zn^{2+} (d^{10}) -> n=0 -> m = 0 (diamag.)

Orbital contribution is quenched in 3d.

Coloured Ions

Colour due to d-d transition : . an electron from t2g --> eg on absorbing visible light. We see complementary colour.

| DE = h n = h c / l |

<-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+/M2+ 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 Cpds.

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 I^- + $S_2O_8^{2-}$

$2 Fe^{3+} + 2 I^- \rightarrow 2 Fe^{2+} + I_2$

$2 Fe^{2+} + S_2O_8^{2-} \rightarrow 2 Fe^{3+} + 2 SO_4^{2-}$

Industrial : V205 (Contact), Fe (Haber), Ni (hydrogenation), TiCl4 (Ziegler-Natta).

Interstitial Compounds

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

e.g. TiC, Mn_4N, Fe_3H, $VH_{0.56}$, $TiH_{1.7}$

(i) hard, high m.p.

(ii) retain metallic conductivity

(iii) chemically inert

Alloys e.g. ~~steat~~ steel (Fe + Cr/Ni/Mn)

Potassium Dichromate K2Cr2O7

Preparation (from chromite)

Step 1 : Chromite ore + Na2CO3 + O2

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

Step 2 : yellow chromate + H_2SO_4

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

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

(orange crystals).

Interconversion in solution

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

(yellow chromate -> orange dichromate).

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

As Oxidising Agent

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$ <-E = +1.33V

Oxidises :

* $I^- \rightarrow I_2$; $Sn^{2+} \rightarrow Sn^{4+}$
* $Fe^{2+} \rightarrow Fe^{3+}$; $H_2S \rightarrow S$

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

Potassium Permanganate $KMnO_4$

Preparation (from MnO_2)

Step 1 : Fusion with KOH + air / KNO_3

$$2\,MnO_2 + 4\,KOH + O_2 \rightarrow 2\,K_2MnO_4 + 2\,H_2O$$

(dark green manganate)

Step 2 : Electrolytic / disproportionation

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

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 :

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$ <- E = +1.52V

Neutral / faintly alkaline :

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$$ <- E = +1.69V

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

KMnO4 - Key Reactions

Acidic Medium (Mn $\rightarrow$ Mn2+)

(a) Iodide : $10\ I^- + 2\ MnO_4^- + 16\ H^+$
$\rightarrow 2\ Mn^{2+} + 5\ I_2 + 8\ H_2O$

(b) Fe^{2+} : $5\ Fe^{2+} + MnO_4^- + 8\ H^+$
$\rightarrow Mn^{2+} + 5\ Fe^{3+} + 4\ H_2O$

(c) Oxalate : $5\ C_2O_4^{2-} + 2\ MnO_4^- + 16\ H^+$
$\rightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$ (at 333 K

(d) H_2S : $5\ S^{2-} + 2\ MnO_4^- + 16\ H^+$
$\rightarrow 2\ Mn^{2+} + 5\ S + 8\ H_2O$

Neutral / Alkaline (Mn $\rightarrow$ MnO2)

(a) Iodide $\rightarrow$ iodate :
$2\ MnO_4^- + H_2O + I^- \rightarrow 2\ MnO_2 + 2\ OH^- + IO_3^-$

(b) Thiosulphate $\rightarrow$ sulphate :
$8\ MnO_4^- + 3\ S_2O_3^{2-} + H_2O$
$\rightarrow 8\ MnO_2 + 6\ SO_4^{2-} + 2\ OH^-$

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

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

Atomic / Ionic Sizes

Steady DECREASE in size from La to Lu :

La : 187 pm -> Lu : 173 pm

Ln <-contraction

La^{3+} (106 pm) --> 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 ~~d~~ 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) => effective nuclear charge on outer e rises => size decreases steadily.

Consequences

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

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

(iii) Basic strength of M(OH)3 decreases :

* $La(OH)_3 > \dots > Lu(OH)_3$

(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.

Config : $[Rn]\ 5f^{1-14}\ 6d^{0-1}\ 7s^2$

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) ; TiO_2 pigment ;
MnO_2 in dry cells ; AgBr in photography ;
mischmetall (95% Ln + 5% Fe) - flints.