Transition Metals

- d-block elements: d subshell is filled from d^1 to d^{10}
- Transition Metals are d-block elements but with **partially filled** d subshells

Physical Properties

- Refer to Atomic Structure and Chemical Bonding Masterclass for Atomic Radii, Ionisation Energy, MP, Density of Transition Metals

Chemical Properties

Variable oxidation States

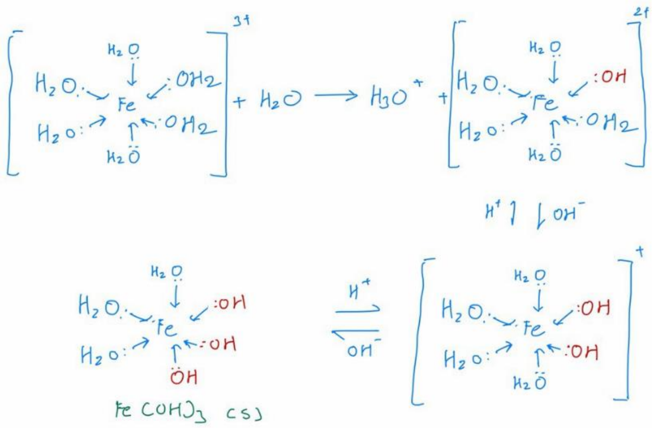
- TMs possess variable O.S. due to small energy level differences btwn 3d and 4s orbitals
- Diff no. of 3d and 4s e^- can be lost to form stable ions, or utilized in bonding to form compounds of different O.S.
- S block elements are restricted to +1 and +2
    - Further removal of inner shell e^- requires too much energy

Predicting O.S.

- Max O.S. of TM: No. of 4s e^- + No. of unpaired 3d e^-

Hydrolysis for TMs

- Some TM cations can undergo hydrolysis in water to form acidic solutions
    - Due to smaller cationic size
    - Large positive charge
    - Higher charge density and higher polarizing power to draw e^- to itself from O atom of neighbouring water molecules
    - Polarizes O-H bonds, weakening the bonds and making them easier to break to form H^+



Relative stability of O.S.

- In period 4 TMs, stability of +2 OS relative to +3 OS increases across series

E° (M^{2+} (aq)| M(s))

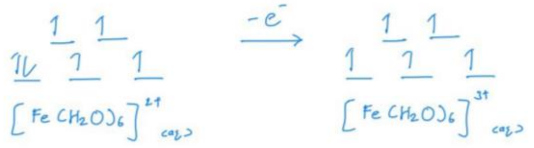
- Look at E°, it is negative
    - Except for Cu^{2+}, M^{2+} is more stable relative to M(s)
    - Since E°(M^{2+} (aq)| M(s)) more negative than E°(H^+ (aq)| H_2(g)), all metals except Cu expected to react with aqueous acids to give M^{2+} (even though M^{2+} can undergo further oxidation)
    - Generally E°(M^{2+} (aq)| M(s)) becomes less negative across the period
        - Oxidation of M to M^{2+} less likely to occur across the period

E° (M^{3+} (aq)| M(s))

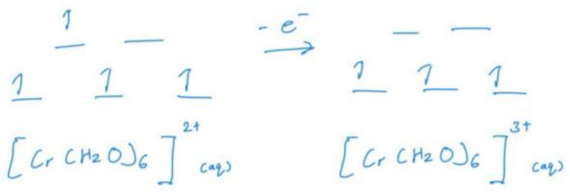
- Look at E°
- E° (M^{3+} (aq)| M(s)) for Co^{3+} and Ni^{3+} is +ve
    - The ions more likely to be reduced
- E° (M^{3+} (aq)| M(s)) for other TMs is -ve
- Generally E° (M^{3+} (aq)| M(s)) becomes less negative across the period
    - Oxidation of M to M^{3+} less likely to occur across the period
    - M^{3+} increasingly less stable relative to M across the period

E° (M^{3+} (aq)| M^{2+}(aq))

- Both M^{2+} and M^{3+} decrease in stabiulity across series
- Look at E°(M^{3+} (aq)| M^{2+}(aq))
    - Increases across period
    - M^{3+} more likely to reduce to M^{2+} across period
    - M^{3+} decreases in stability more than M^{2+} across the period
    - Note: Reason similar to 3rd I.E. across the period
        - Nuclear charge increase
        - Shielding effect relatively same
        - Effective nuclear charge increases
        - EFOA btwn nucleus and outermost shell e^- increases
        - Increasingly difficult to remove e^- from M^{2+} to form M^{3+}
    - Exceptions: Drop in E°(M^{3+} (aq)| M^{2+}(aq)) from Mn to Fe
        - Inter-electronic repulsion in d^6
        - Hint: similar to explanation in I.E



- Exceptions: E°(M^{3+} (aq)| M^{2+}(aq)) more negative for Cr compared to V
    - In d^4, one e^- is in a higher d orbital group, so more easily lost
    - Obs: Cr^{2+} is a stronger reducing agent than expected



Overall takeaway: Always look at the E° to tell which is more stable/more easily oxidised/reduced or which species is the stronger reducing/oxidising agent

Formation of Complexes

Complex: A central metal atom/ion surrounded by other ions or molecules called ligands bonded to the central atom/ion by dative covalent bonds

d-block elements have very high tendency to form complexes as:

- Relatively small size and high charge
- High charge density
- High polarising power to attract ligands
- TM also have low-lying vacant d-orbitals
    - Able to accept lone pairs of e^- on ligands via dative covalent bonds

s-block elements are larger, have lower polarising power -> tend to be involved in ion-dipole attraction instead

2 important feature of complexes

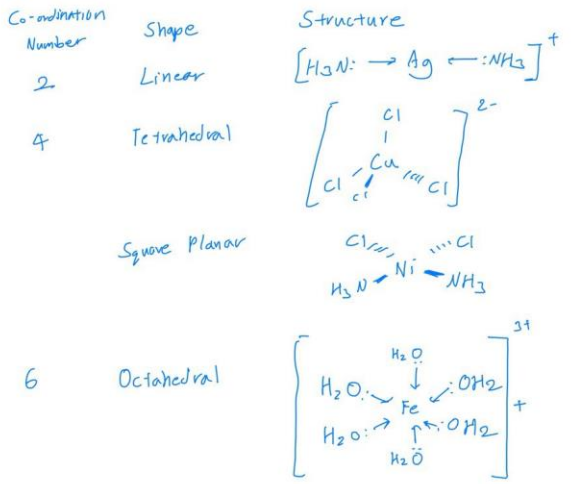
1. Net charge
2. Co-ordination number
    a. No. of ligand grps
    b. 4,6
    c. Point 2 is quite important in Copper (I) and Silver (I) compounds

Ligand: A neutral molecule or anion that contains at least one atom bearing a lone pair of e^- to be used in dative bonding with a metal ion/atom

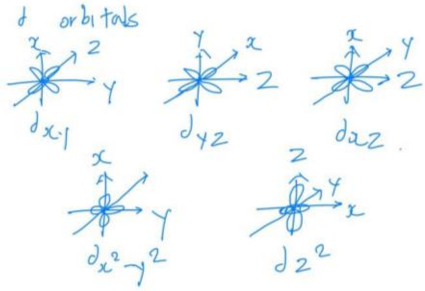
- All ligands are lewis bases
- Denticity of ligand: no. of dative bonds formed per ligand
- If ligands have denticity >= 2
    - Complexes: chelates
    - Interacting w metal atom/ion: chelating

E.g. Bidentate Ligand.

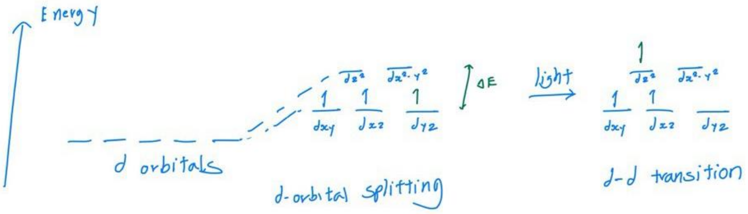
Shapes of Complexes



Colour of TM ions & Complexes



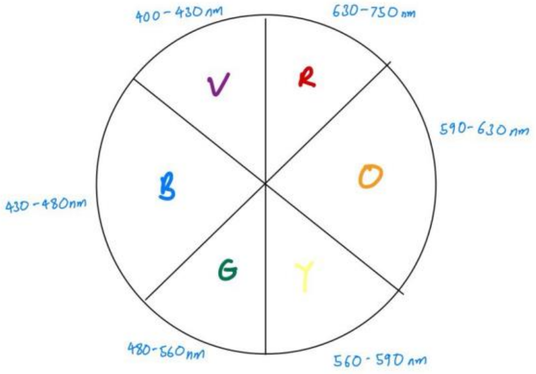
- Each ligand forms a dative bond with the TM ion via a lone pair of e^- along x,y,z axis
- When ligands approach the TM ion along axis, there is inter-electronic repulsion between the lone pair of e^- to form the donor atom of ligand & the e^- in the d orbital of the TM ion
    - Thus, energies of d electrons increase
- When ligands approach the x, y, z axis, e^- in the d_{x2-y2} and d_{z2} orbitals experience greater repulsion than those in the 3 other orbitals
- Hence, the 5 d orbitals split into 2 energy lvls with d_{x2-y2} and d_{z2} orbitals at higher energies
- Splitting of d-orbitals explains the colour, stability and magnetic properties of TM complexes



d-d transition

- Colours due to the d-d transition!
- In a complex, presence of ligands split the d orbitals of TM atom/iion into 2 diff energy levels -> d-orbital splitting
    - (Explained above)
- A d electron in the lower energy d orbital will absorb a specific wavelength of light from the visible light region of EM spectrum, and is promoted to higher energy d-orbital -> d-d transition
- Reamining wavelegnths of light transmitted -> complementary colour observed
- **For d-d transition to occur, d subshell must not be fully filled or fully empty** -> Sc (III), Cu (I), Zn (II) not coloured

Determination of colour



$\Delta E \propto \frac{1}{\lambda}$

- Large ΔE: short λ absorbed, long λ transmitted
- Small ΔE: Long λ absorbed, short λ transmitted

Example Answering technique

Why is $[Cu(H_2O)_6]^{2+}$ blue?

- Cu^{2+} has incomplete d-subshell
- In $[Cu(H_2O)_6]^{2+}$, the presence of H_2O ligands splits the 3d orbitals of the Cu^{2+} metal ion into 2 energy levels
- A 3d e^- in the lower energy d- orbital absorbs light energy corresponding to the wavelengths

- for orange light and is promoted to a higher energy 3d orbital (d-d transition)
- Remaining wavelengths transmitted, complementary blue colour is observed

Factors affecting ΔE

1. Nature of TM and its O.S.
    a. ΔE increase with O.S
    b. Increase charge density, increase attraction for ligands, increase repulsion, larger ΔE
    c. For same O.S., variation in ΔE is irregular
2. Shape of Complex
    a. Shape affects no. of ligands and position relative to orientation of d orbitals
    b. Results in different extent of interactions btwn the lone pairs of e^- on ligands and d orbitals, thus different magnitudes of ΔE
3. Nature of Ligands (Crystal Field)
    a. Magnitude of ΔE changes as strength of repulsion between d electrons and point charges changes -> ΔE measures strength of crystal field
        i. Weak field ligands -> Small ΔE
        ii. Strong Field Ligands-> Large ΔE
    b. Weak field ligands -> weaker metal-ligand bonds
    c. Strong field ligands -> stronger metal-ligand bonds

Example Answering Technique:

Explain why a solution of $[Fe(H_2O)_6]^{2+}$ is pale green, while a solution of $[Fe(CN)_6]^{4-}$ is yellow

- H_2O is a weak field ligand which causes smaller d orbital splitting and results in a smaller ΔE
- Red light of longer λ absorbed and the green light of shorter λ transmitted
- Thus, solution of $[Fe(H_2O)_6]^{2+}$ appears pale green
- CN^- is a strong field ligands that causes a larger d orbital splitting and results in a larger ΔE
- Violet light of shorter λ is absorbed and yellow light of longer λ is transmitted
- Thus, solution of $[Fe(CN)_6]^{4-}$ is yellow

Ligand Exchange

- Usually results in a change of colour

1. Strength of ligand
    a. Stronger ligands replace weaker ions in a complex ion
    b. Example: $[Cu(H_2O)_6]^{2+}$ -> $[Cu(NH_3)_4]^{2+}$

Light Blue   Dark Blue

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)} + 4H_2O_{(aq)}$$

    - Since Reaction is reversible, able to obtain $[Cu(H_2O)_6]^{2+}$ by removing NH_3 ligands
    - Neutralisation using dilute sulfuric acid
    - When H_2SO_4 added, $[NH_3]$ decreases, POE shifts left to reform $[Cu(H_2O)_6]^{2+}$. Solution turns back to light blue.

2. Conc. of ligands

- Large conc. of a different ligands can cause ligand exchange reaction.
- Example: $[Cu(H_2O)_6]^{2+}$ -> $[CuCl_4]^{2-}$

Light Blue   Yellow

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons [CuCl_4]^{2-}_{(aq)} + 6H_2O_{(l)}$$

- When conc. HCL added, $[Cl^-]$ increases. POE shifts right to form $[CuCl_4]^{2-}$
- Presence of both blue $[Cu(H_2O)_6]^{2+}$ and yellow $[CuCl_4]^{2-}$ causes solution to appear yellow-green.
- NOTE: Reaction is reversible
    - If solution is diluted, POE shifts left to reform $[Cu(H_2O)_6]^{2+}$. Solution turns light blue.

Examples in which a compound that is insoluble in water is made soluble through conversion to a complex

$$\underset{\text{green}}{Cr^{3+}_{(aq)}} \xrightarrow{NaOH_{(aq)}} \underset{\text{grey-green ppt}}{Cr(OH)_{3\,(s)}} \xrightarrow{\text{Excess } NaOH_{(aq)}} \underset{\text{dark-green}}{[Cr(OH)_6]^{3-}_{(aq)}}$$

$$\underset{\text{Colourless}}{Zn^{2+}_{(aq)}} \xrightarrow{NaOH_{(aq)}} \underset{\text{white ppt}}{Zn(OH)_2} \xrightarrow{\text{Excess } NaOH_{(aq)}} \underset{\text{Colourless}}{[Zn(OH)_4]^{2-}_{(aq)}}$$

$$\underset{\text{Colourless}}{Zn^{2+}_{(aq)}} \xrightarrow{NaOH_{(aq)}} \underset{\text{white ppt}}{Zn(OH)_2} \xrightarrow{\text{Excess } NH_{3(aq)}} \underset{\text{Colourless}}{[Zn(NH_3)_4]^{2+}_{(aq)}}$$

$$\underset{\text{Light Blue}}{Cu^{2+}_{(aq)}} \xrightarrow{NH_{3(aq)}} \underset{\text{Blue ppt}}{Cu(OH)_{2\,(s)}} \xrightarrow{\text{Excess } NH_{3(aq)}} \underset{\text{Dark blue}}{[Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)}}$$

$$\underset{\text{Pink}}{Co^{2+}_{(aq)}} \xrightarrow{NH_{3(aq)}} \underset{\text{Blue ppt}}{Co(OH)_{2\,(s)}} \xrightarrow{\text{Excess } NH_{3(aq)}} \underset{\text{Pale brown}}{[Co(NH_3)_6]^{2+}_{(aq)}}$$

$$\underset{\text{Green}}{Ni^{2+}_{(aq)}} \xrightarrow{NH_{3(aq)}} \underset{\text{Green ppt}}{Ni(OH)_{2\,(s)}} \xrightarrow{\text{Excess } NH_{3(aq)}} \underset{\text{Dark-Blue}}{[Ni(NH_3)_6]^{2+}_{(aq)}}$$

CO/O_2 exchange in haemoglobin

- Haemoglobin consists of 4 subunits
    - Each subunit is composed of a protein chain tightly associated with a non-protein prosthetic haem group
    - Haem group consists of Fe (II), and exhibits hexa-coordination, 5 sites occupied by N
- O_2 may become reversibly bonded at the 6th site to allow haemoglobin to transport O_2

If H_2O bound : Haemoglobin

$$H_2O \uparrow\downarrow O_2$$

If O_2 bound : Oxyhaemoglobin

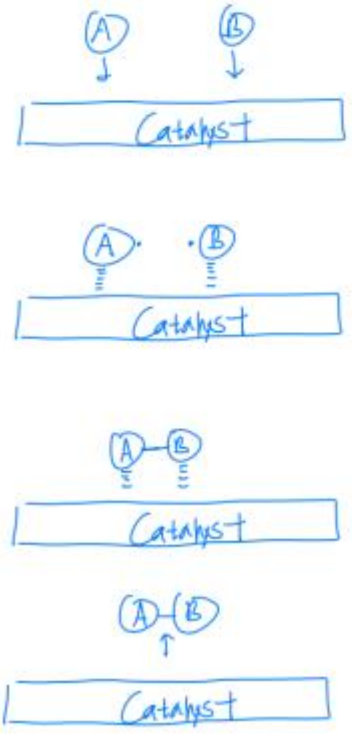
$$O_2 \uparrow\downarrow CO$$

If CO bound : Carboxyhaemoglobin

- CO binds to haemoglobin at the same site as O_2, but about 210 times more tightly to give carboxyhaemoglobin
- Leads to gradual suffocation
- Because CO is a stronger field ligand than O_2
- Ligands such as CN^- also strongly bind to this site

Catalytic Activity

- TM ions are effective heterogeneous catalysts because they have partially filled 3d orbitals which allow for reactant particles to be adsorbed onto surface
    - d electrons can be used to form bonds -with reactant molecules
    - Energetically accessible and available orbitals can be used to accommodate lone pairs of e^- from reactant molecules to form bonds
- Mechanism: Refer to Reaction Kinetics Masterclass



Homogenous catalyst

- TM ions are effective homogenous catalysts because they can exist in different O.S. and undergo conversion from one O.S to another relatively easily
- Mechanism: Refer to Reaction Kinetics Masterclass

Colours of Common Transition Metal Complexes

Transition Metal	O.S of Transition Metal	Formula	Colour
Vanadium	+2	$[V(H_2O)_6]^{2+}$	Violet
	+3	$[V(H_2O)_6]^{3+}$	Green
	+4	$[VO(H_2O)_5]^{2+}$	Blue
	+5	$[VO_2(H_2O)_5]^{+}$	Yellow
Chromium	+2	$[Cr(H_2O)_6]^{2+}$	Blue
	+3	$[Cr(H_2O)_6]^{3+}$	Purple
		$[Cr(OH)_6]^{3-}$	Dark Green
		$[Cr(NH_3)_6]^{3+}$	Purple
	+6	CrO_4^{2-}	Yellow
		$Cr_2O_7^{2-}$	Orange
Manganese	+2	$[Mn(H_2O)_6]^{2+}$	Pale Pink/Colourless
	+3	$[Mn(H_2O)_6]^{3+}$	Red
	+4	MnO_2	Brown Solid
	+5	MnO_4^{3-}	Deep Blue
	+6	MnO_4^{2-}	Dark Green
	+7	MnO_4^{-}	Purple
Fe	+2	$[Fe(H_2O)_6]^{2+}$	Pale Green
		$[Fe(CN)_6]^{4-}$	Yellow
	+3	$[Fe(H_2O)_6]^{3+}$	Violet (Yellow due to hydrolysis)
		$[Fe(CN)_6]^{3-}$	Orange-Red
		$[Fe(H_2O)_5(SCN)]^{2+}$	Deep Red
	+6	FeO_4^{3-}	Red-Purple
Co	+2	$[Co(H_2O)_6]^{2+}$	Pink
		$[Co(NH_3)_6]^{2+}$	Pale Brown
		$[CoCl_4]^{2-}$	Blue
	+3	$[Co(H_2O)_6]^{3+}$	Blue Green
		$[Co(NH_3)_6]^{3+}$	Brown
Ni	+2	$[Ni(H_2O)_6]^{2+}$	Green
		$[Ni(NH_3)_6]^{2+}$	Blue
		$[Ni(CN)_6]^{4-}$	Yellow
Cu	+1	CuI	White Solid
		Cu_2O	Brick-Red Solid
	+2	$[Cu(H_2O)_6]^{2+}$	Blue
		$[Cu(NH_3)_4(H_2O)_2]^{2+}$	Dark Blue
		$[CuCl_4]^{-}$	Yellow
Ag	+1	$[Ag(NH_3)_2]^{+}$	Colourless