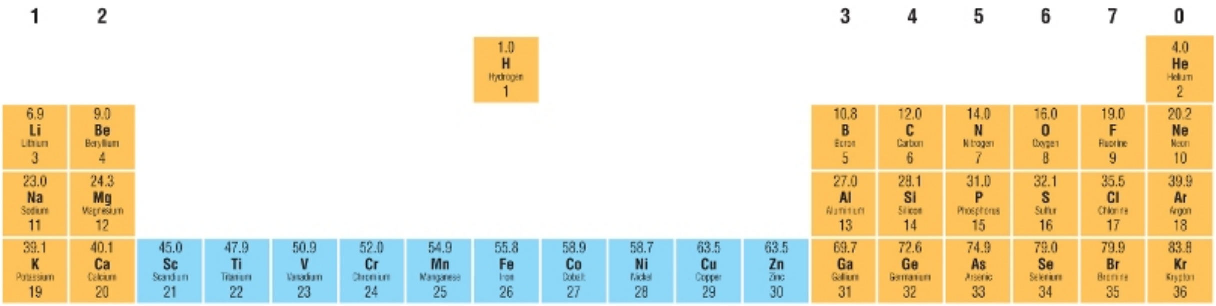
2.5 Transition metals



d – Block element:
Is found between Group 2 and Group 3 on the Periodic table.

Transition element:
A metal that that can form one or more stable ions with an incomplete d sub-level

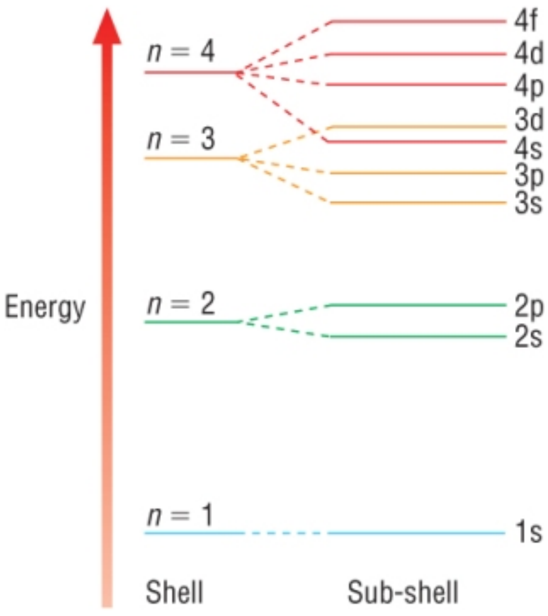
- This means that **Scandium** and **Zinc** are not Transition elements.

Sc $1s^22s^22p^63s^23p^63d^14s^2$ **Sc^{3+}** $1s^22s^22p^63s^23p^6$

Zn $1s^22s^22p^63s^23p^63d^{10}4s^2$ **Zn^{2+}** $1s^22s^22p^63s^23p^63d^{10}$

Electron configurations review:

- Fill from the lowest sub level up.
- 4s - sub shell fills before the 3d - sub shell
- Fill orbitals individually before pairing up (seats on a bus)



Element	Z	Electron configuration	Noble gas configuration	Electron in box diagram					
Scandium	21	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$	[Ar] $4s^2\ 3d^1$	↑↓	↑				
Titanium	22	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$	[Ar] $4s^2\ 3d^2$	↑↓	↑	↑			
Vanadium	23	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$	[Ar] $4s^2\ 3d^3$	↑↓	↑	↑	↑		
Chromium	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$	[Ar] $4s^1\ 3d^5$	↑	↑	↑	↑	↑	↑
Manganese	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$	[Ar] $4s^2\ 3d^5$	↑↓	↑	↑	↑	↑	↑
Iron	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$	[Ar] $4s^2\ 3d^6$	↑↓	↑↓	↑	↑	↑	↑
Cobalt	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$	[Ar] $4s^2\ 3d^7$	↑↓	↑↓	↑↓	↑	↑	↑
Nickel	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$	[Ar] $4s^2\ 3d^8$	↑↓	↑↓	↑↓	↑↓	↑	↑
Copper	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$	[Ar] $4s^1\ 3d^{10}$	↑	↑↓	↑↓	↑↓	↑↓	↑↓
Zinc	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$	[Ar] $4s^2\ 3d^{10}$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Chromium and copper:

- Chromium and Copper fills differently:

A half - filled or full d - sub shell offers more stability than a full s - sub shell.

The electron configurations of transition metal ions:

The 4s subshell fills first but also empties first when forming ions

- This seems a bit odd as the 4s fills first.
- When the orbitals have been filled the 4s and 3d sub shell levels swap over in the expected order.
- This happens because the energy levels are very close in the first place.
- The addition of electrons changes the energy levels slightly so they swap over.
- It is easier to do this if you write the electron configuration in electron shell order (number order):

Examples:

Fe	[Ar]$3d^6 4s^2$	Fe^{2+}	[Ar]$3d^6$	Fe^{3+}	[Ar]$3d^5$
Cu	[Ar]$3d^{10} 4s^1$	Cu^{1+}	[Ar]$3d^{10}$	Cu^{2+}	[Ar]$3d^9$

Questions:

1) Write electron configurations for the following atoms:

a) Sc
b) Mn
c) Co
d) Cu

e) V
f) Fe
g) Ni
h) Cr

2) Write electron configurations for the following ions:

a) Sc^{3+}
b) Mn^{2+}
c) Co^{2+}
d) Cu^+

e) V^{3+}
f) Cu^{2+}
g) Cr^{3+}
h) Ti^{3+}

Properties of transition metals

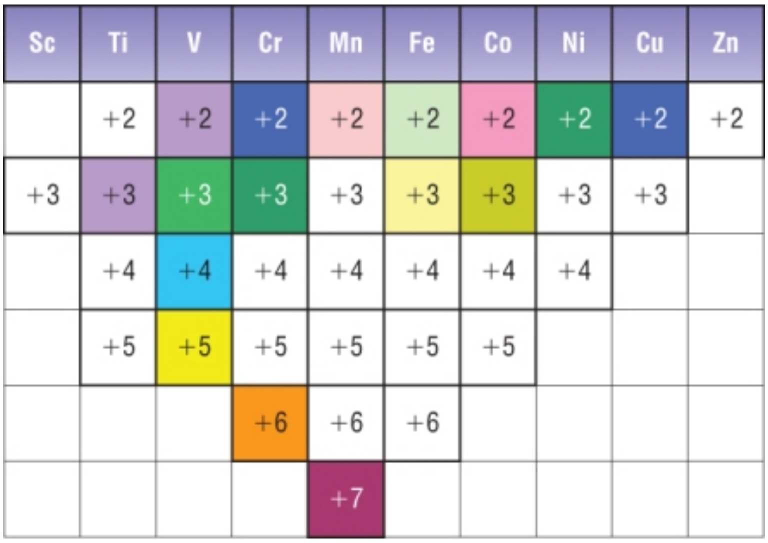
Physical properties - general metals

- Shiny
- High densities
- High melting points and boiling points
- Giant metallic structure
- Delocalised electrons - good conductors of electricity

Chemical properties - transition metals

- Form complex ions (later)
- Variable oxidation states
- Coloured ions
- Catalysts - due to d shell electrons

Variable oxidation states and colours



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
	+5	+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

- Transition elements can exist in multiple oxidation numbers.
- The most common is 2+ as the 4s electrons are usually the first to go.
- Because the 4s and 3d electrons are close in energy, the 3d electrons can be easily removed as well
- This means they can form several ions by losing different numbers of electrons, all of which are stable.
- Changes in oxidation states of the transition metals often give rise to colour changes during the reaction.

MAKE SURE YOU CAN WORK OUT OXIDATION STATES

- As Sc and Zn do not have an incomplete d sub-shell, they do not exhibit these Transition metal properties.

Complex ions

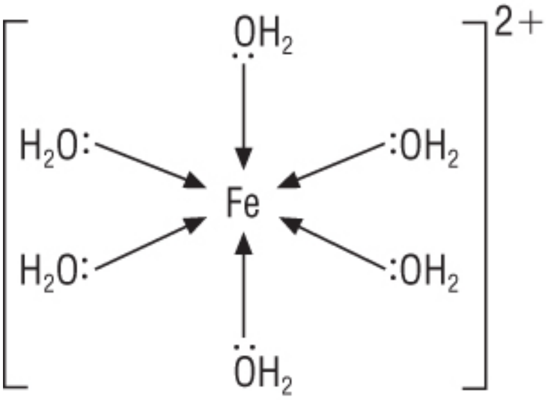
- A property of transition metals is their ability to form **complex ions:**

Complex ion:
A central metal ion surrounded by ligands

Ligand:
A molecule or ion that forms a dative covalent bond with a central metal ion by donating a pair of electrons

Dative covalent bond (co-ordinate bond)
A covalent bond where the pair of electrons have been donated by the same atom / molecule

Co-ordination number:
Is the number of dative (co-ordinate) bonds to the central metal ion



- **Fe $^{2+}$** is the **Transition metal ion**.
- **Ligands** are the **water** molecules.
- **Coordination number** is the number of coordinate bonds to the central metal ion **= 6**.
- **Square brackets** group the species and the **overall charge** is written outside the brackets.
- **Overall charge** is the sum of the charges of the metal ion and the ligands (if the ligands have a charge)

Monodentate ligands:

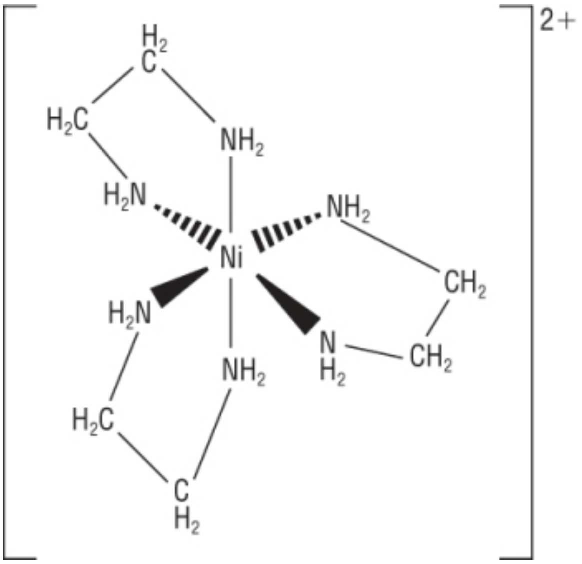
- Ligands have a **pair of electrons that donors** which is used to make a dative covalent bond to the central metal ion.
- All the ligands in the table have **1 lone pair** and can form **1 dative covalent bond** with the central metal ion.
- These types of ligands are called **monodentate**.

Ligand	Formula	Charge
Water	**:OH_2**	**0**
Ammonia	**:NH_3**	**0**
Cyanide	**:CN^-**	**-1**
Chloride	**:Cl^-**	**-1**
Hydroxide	**:OH^-**	**-1**

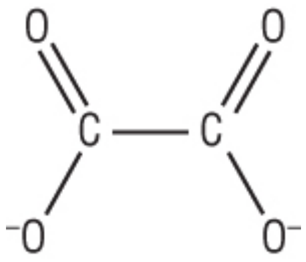
- The **number of dative bonds a ligand** is able to form is reflected in the prefix – **mono, bi, hexa or multi**.

Bidentate ligands

- Some ligands contain **2 lone pairs** of electrons forming **2 coordinate bonds each**.
- Ethane - 1,2 - diamine, $H_2NCH_2CH_2NH_2$ abbreviated to **'en'** $[Ni(en)_3]^{2+}$

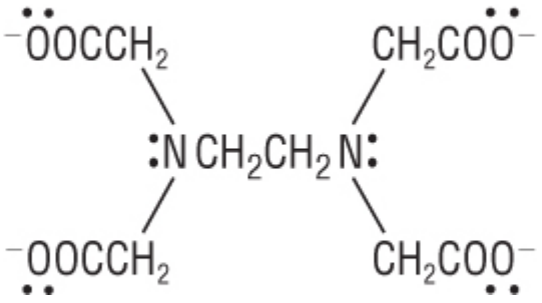


Another bidentate ligand:
Ethanedioate ligand, $C_2O_4^{2-}$



- **Coordination number = 6**

Hexadentate ligand:



$EDTA^{4-}$

- **Hexa = 6**

- **Hexadentate ligands** is a molecule with **6 lone pairs** of electrons forming **6 dative covalent (co-ordinate) bonds**:

Working out oxidation states in complex ions:

- The charge on the complex ion is the sum of the charges of the transition metal and ligands

1) $[Ti(H_2O)_6]^{3+}$

- Water as a ligand has no charge.
- The complex ion has a charge of 3+
- This means that the charge on the transition metal must be the same as the charge on the complex ion, 3+

The central metal ion must be: **Ti^{3+}** with an oxidation state of **3+**

2) $[CoCl_4]^{2-}$

- Chloride as a ligand has a 1- charge and there are 4 of them = 4-
- The complex ion has a charge of 2-
- The charge on the transition metal must be 2+ to give an overall charge of 2-

The central metal ion must be: **Co^{2+}** with an oxidation state of **2+**

Questions:

1) What is the **coordination number** and **oxidation state** of the transition metal in the following complex ions:

a) $[Fe(H_2O)_6]^{3+}$

b) $[CuCl_4]^{2-}$

c) $[Fe(H_2O)_3(OH)_3]$

d) $[Cr(H_2O)_2(OH)_2]^{1+}$

f) $[Co(NH_3)_4Cl_2]^{1+}$

f) $[Pt(NH_3)_2Cl_2]$

g) $[Cr(C_2O_4)_2(H_2O)_2]^{1-}$

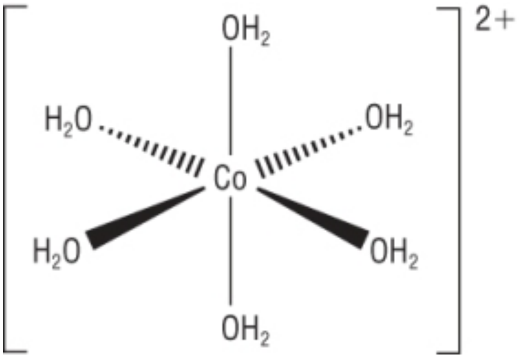
h) $[Fe(EDTA)]^{1-}$

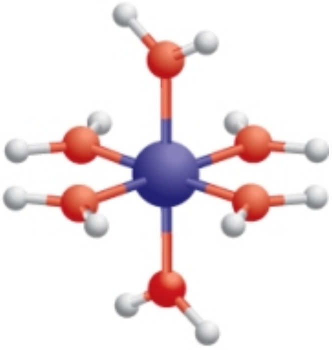
Shapes of complex ions:

- Complex ions have different shapes and this depends upon its coordination number.
- If the ligands are small you usually get a coordination number of 6
- If the ligands are large you usually get a coordination number of 4

Coordination number = 6

- The shape is **octahedral** formed by **6 ligands**
- The most common is the hexaaqua ion, six water ligands:

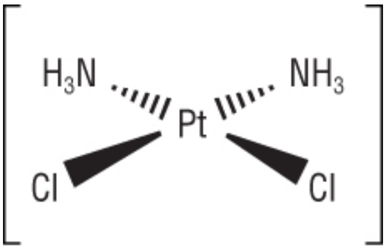


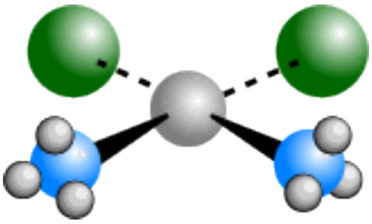


Coordination number = 4

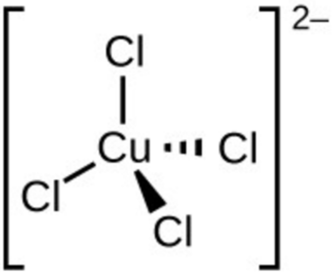
- The shape can be **square planar** or **tetrahedral** and is formed by **4 ligands**

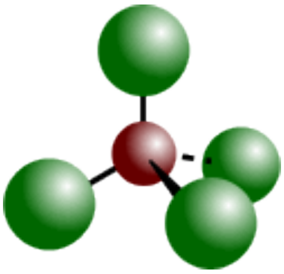
Square planar





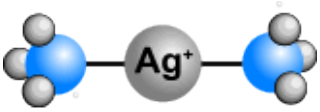
Tetrahedral





Coordination number = 2

- The shape is **linear** and is formed by **2 ligands**
- **$[Ag(NH_3)_2]^+$**



Stereoisomerism in complex ions

Stereoisomerism:
A Molecule with the same structural formula but its atoms are arranged differently in space

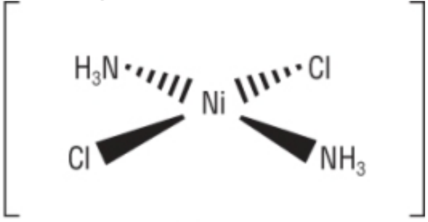
Optical isomer:
These are non superimposable mirror images

A) Stereoisomerism: Cis / Trans isomerism

1) Square planar with 2 of one ligand and 2 of another ligand:

Cis

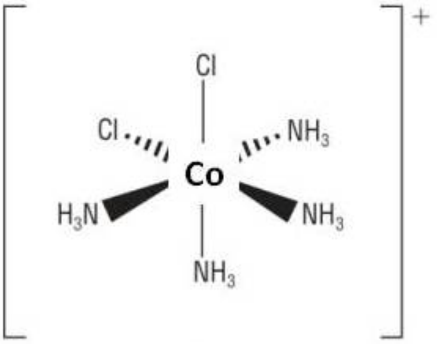
CIS = 2 ligands are at 90° to each other



Trans

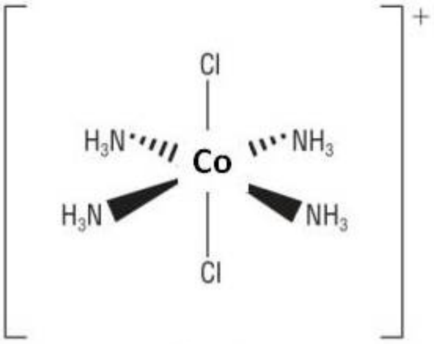
TRANS = 2 ligands are at 180° to each other

2) Octahedral with 4 of one ligand and 2 of another ligand, $[Co(NH_3)_4Cl_2]^+$:



Cis

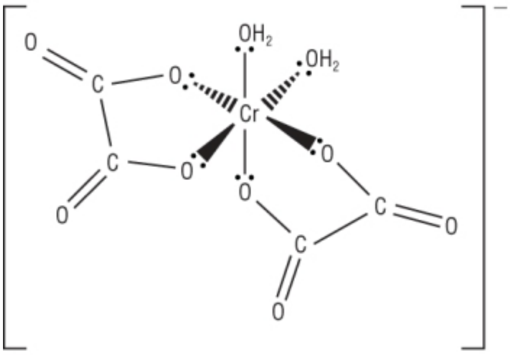
CIS = 2 ligands are at 90° to each other



Trans

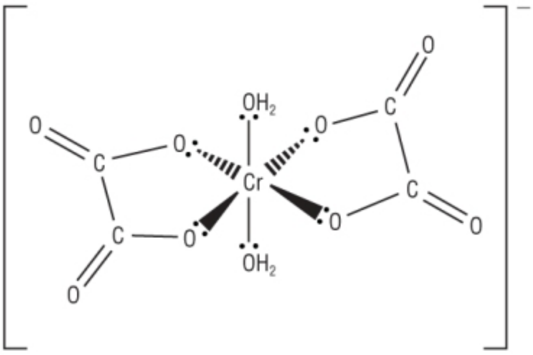
TRANS = 2 ligands are at 180° to each other

3) Octahedral with 2 bidentate and 2 monodentate ligands:



Cis

CIS = 2 monodentate ligands are at 90° to each other

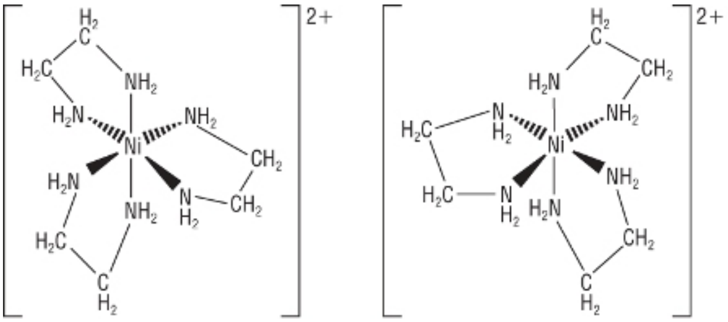


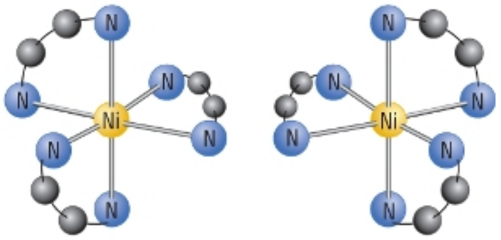
Trans

TRANS = 2 monodentate ligands are at 180° to each other

B) Optical isomerism

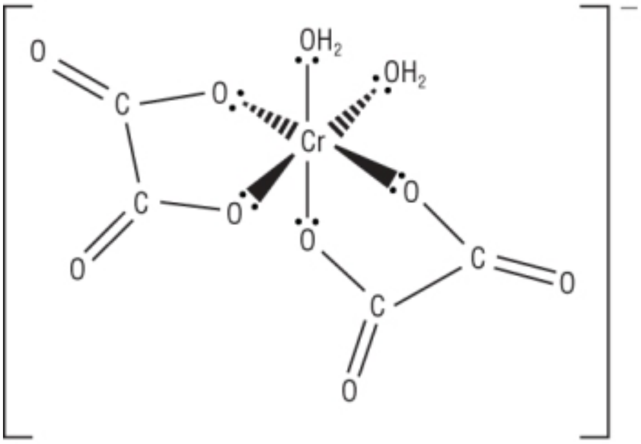
1) With 3 bidentate ligands





2) 2 bidentate ligands / 2 monodentate ligands in the cis isomer only:

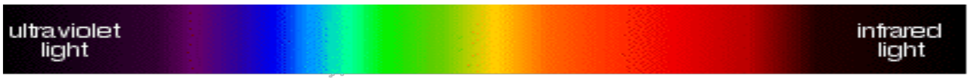
- Draw the other optical isomer next to the one below:



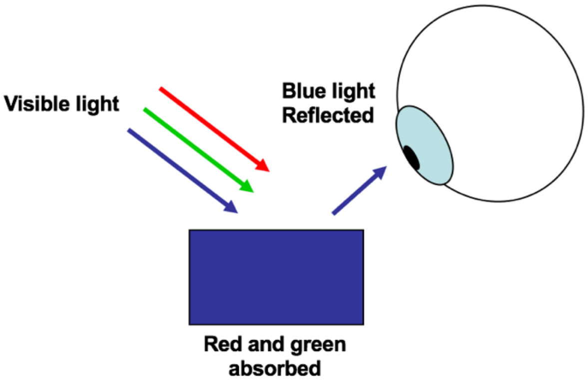
Cis

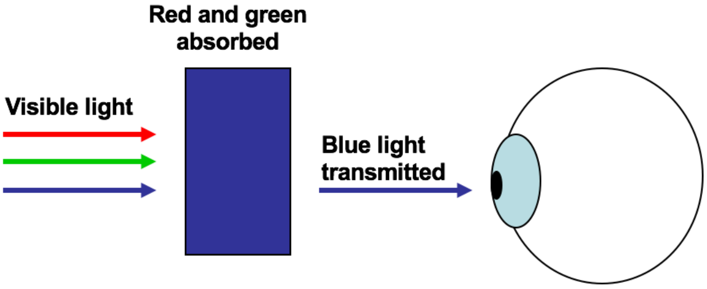
Coloured ions:

- Transition metal solutions are coloured because they absorb frequencies of light from the visible spectrum:

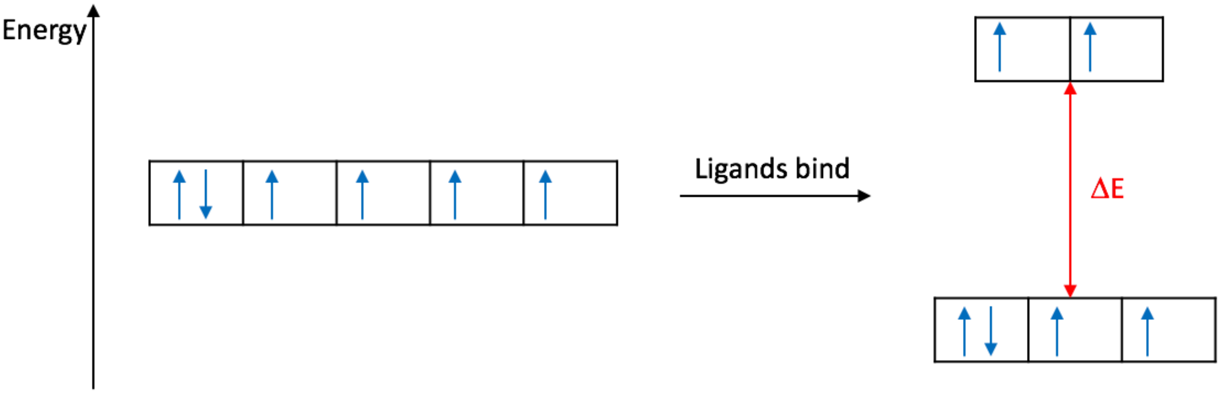


- All other frequencies are reflected or pass through the solution

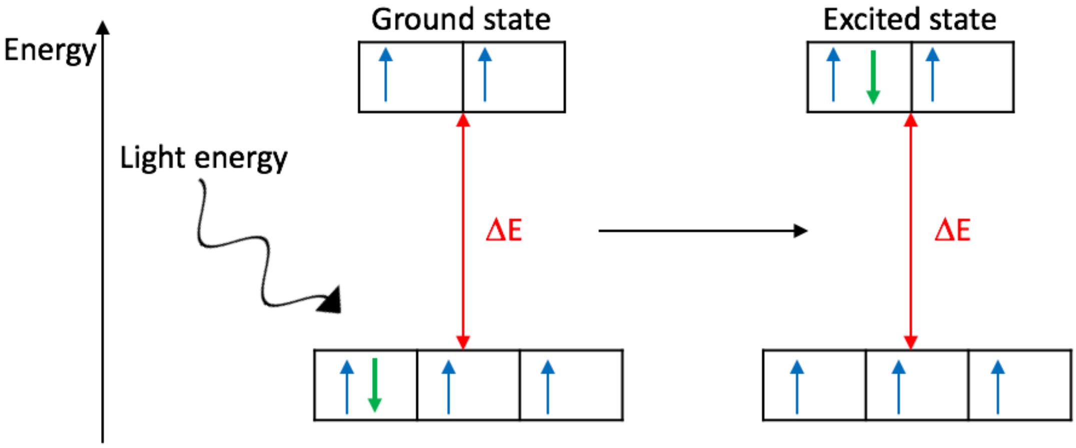




- The complimentary frequencies combine producing the complimentary colour.
- The colours are linked to the incomplete d shell:



Orbitals split to 2 different energy levels



A specific frequency of light will have the same E as the ΔE between the d orbitals

What affects the colours:

- The frequency of light and ΔE are linked by the following equations:

$$\Delta E = \hbar\nu$$

$$\nu = c/\lambda$$

$$\Delta E = \hbar c/\lambda$$

ΔE = Energy absorbed (j)

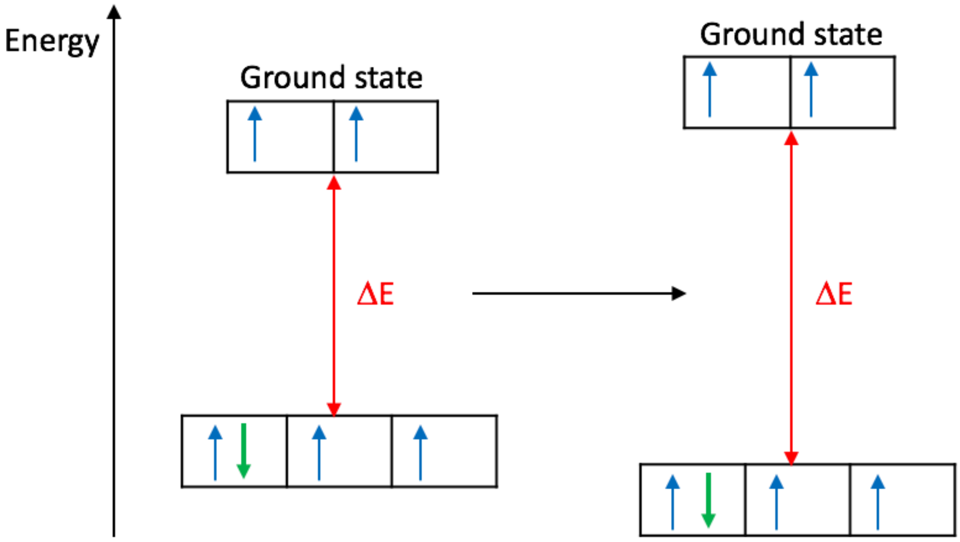
$\hbar$ = Plank's constant (6.63×10^{-34} js)

ν = Frequency of light (Hz)

c = Speed of light (3×10^{8} ms^{-1})

λ = Wavelength of light (m)

- Any changes in the following will alter the size of ΔE between the d orbitals:
  - Oxidation states
  - Co-ordination number
  - Ligands
- This will affect the E (and therefore the frequency) of the light required to promote the electron.
- As a different frequency is absorbed, the complimentary colours will be different.
- This give rise to a colour change:



A different frequency of light will have the same E as the new ΔE
Note: The ΔE may get smaller

Examples:

Change in oxidation state:

	$[Fe(H_2O)_6]^{2+}$	→	$[Fe(H_2O)_6]^{3+}$
Colour	Green		Yellow
Ox State	**+2**		**+3**
Co-ordination number	6		6

Change in co-ordination number:

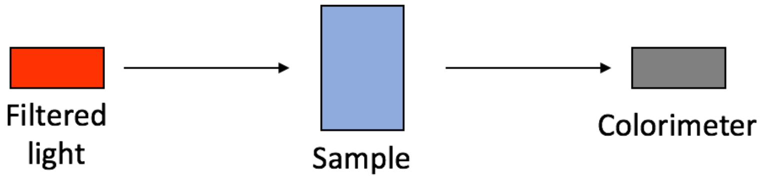
	$[Cu(H_2O)_6]^{2+}$	→	$[CuCl_4]^{2-}$
Colour	Blue		Yellow
Ox State	+2		+2
Co-ordination number	**6**		**4**

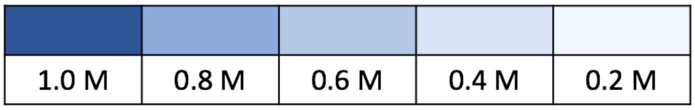
Change in ligand:

	$\mathbf{[Co(H_2O)_6]^{2+}}$	→	$\mathbf{[Co(NH_3)_6]^{2+}}$
Colour	Pink		Straw colour
Ox State	+2		+2
Co-ordination number	6		6

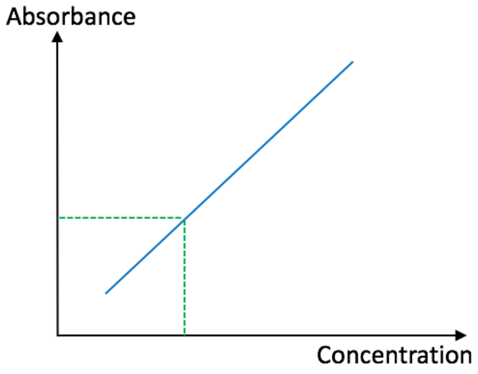
Spectroscopy – Colorimetry:

- $[Cu(H_2O)_6]^{2+}$ ions are blue. The more concentrated the more intense the blue colour.
- During a reaction the concentration of $[Cu(H_2O)_6]^{2+}$ may decrease.
- This means that the colour intensity will decrease.
- Which means less light will be absorbed.





- A colorimeter will monitor the intensity of the colour which is proportional to the concentration of copper sulphate.
- A calibration graph would be made first using known concentrations and measuring the absorbance's:



Ligand substitution reactions

- Where on ligand substitutes another.
- If ligands have a similar size, the co-ordination number remains the same: NH_3 and H_2O.
- With larger ligands, the co-ordination number decreases: Cl^- is larger than NH_3 and H_2O.

Same sized ligands: Cobalt (II) ions and ammonia, NH_3

$$[Co(H_2O)_6]^{2+}{}_{(aq)} + 6NH_{3(aq)} \rightleftharpoons [Co(NH_3)_6]^{2+}{}_{(aq)} + 6H_2O_{(l)}$$

Colour:	Pink	Straw colour
Ox State:	+2	+2
C-O No:	6	6
Shape:	Octahedral	Octahedral

Different sized ligands: Copper (II) ions and hydrochloric acids, Cl^-

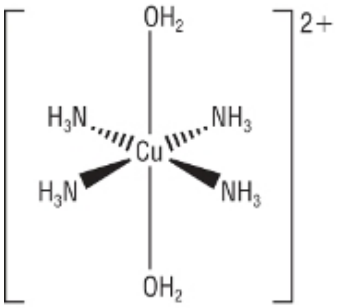
$$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)} \rightleftharpoons [CuCl_4]^{2-}{}_{(aq)} + 6H_2O_{(l)}$$

Colour:	Pale blue	Yellow / green
Ox State:	+2	+2
C-O No:	6	4
Shape:	Octahedral	Tetrahedral

Partial substitution: Copper (II) ions and hydrochloric acids, Cl^-

$$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 4NH_{3\,(aq)} \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}{}_{(aq)} + 6H_2O_{(l)}$$

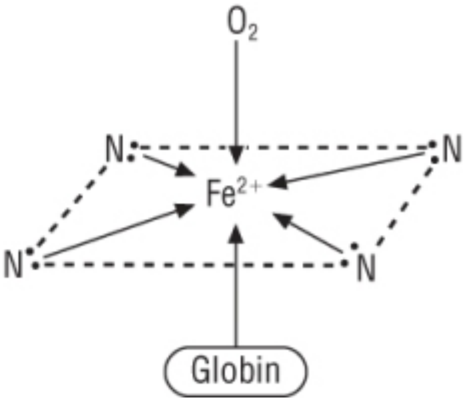
Colour:	Pale blue	Deep blue
Ox State:	+2	+2
C-O No:	6	6
Shape:	Octahedral	Octahedral (elongated):



Note: When NH_3 is initially added a precipitate is seen before the ligand substitution reaction. This is covered later.

Haemoglobin and ligand substitution

- It contains an Fe^{2+} ion with a co-ordination number of 6 in an octahedral arrangement.
- 4 positions are taken up from a dative covalent bond from the Haem (ring type structure - Porphyrin) – a multidentate ligand.
- A protein called Globin occupies a 5th position.
- The 6th position is for H_2O or O_2 to bind.



Lungs:

- In the lungs the O_2 concentration is high therefore water is substituted for oxygen – oxyhaemoglobin and transported.
- The O_2 is then exchanged for water and transported back to the lungs.
- It also forms a complex with CO_2, transporting CO_2 back to the lungs.

Carbon monoxide - the silent killer

- CO can bind to haemoglobin sites in the same way as oxygen.
- CO however forms a stronger dative covalent bond.
- The CO cannot be removed.
- That haemoglobin is now useless.
- This reaction is a simple **ligand substitution reaction** where the CO complex is more stable:

Complex ion stability:

- Ligand substitution reactions are mostly easily reversible – Le Chatelier's Principle
- Those that are not easily reversed have ligands that form stronger bonds than the original ligand.
- This has already been seen with CO in the haemoglobin complex but there are other reasons:

1) Dative covalent bond strength:

$$[Fe(H_2O)_6]^{3+}_{(aq)} \quad + \quad 6CN^-_{(aq)} \quad \rightarrow \quad [Fe(CN)_6]^{3-}_{(aq)} \quad + \quad 6H_2O_{(l)}$$

- The CN^- ligand forms a stronger dative covalent bond with Fe^{3+} making it so stable it is hard to reverse.

2) Multidentate ligand substitution:

$$[Cu(H_2O)_6]^{2+}_{(aq)} \quad + \quad 3NH_2CH_2CH_2NH_{2(aq)} \quad \rightarrow \quad [Cu(NH_2CH_2CH_2NH_2)_3]^{2+}_{aq)} \quad + \quad 6H_2O_{(l)}$$

- Multidentate ligands are more stable than monodentate ligands and are hard to reverse.
- The bond enthalpies of the ligands with the metal ion are about the same.
- If it is not due to bond enthalpy it must be down to something else:

The chelate effect:

- Consider this reaction again and consider the 2 factors that could determine the feasibility of the reaction:

$$[Cu(H_2O)_6]^{2+}_{(aq)} \quad + \quad 3NH_2CH_2CH_2NH_{2(aq)} \quad \rightarrow \quad [Cu(NH_2CH_2CH_2NH_2)_3]^{2+}_{aq)} \quad + \quad 6H_2O_{(l)}$$

a) Enthalpy

- Bonds are broken and new bonds are formed (between the metal ion and the ligand).
- As ligands have similar bond strengths with the metal ion, the enthalpy changes involved are usually very small.
- This means it is not down to enthalpy (in this case).

b) Entropy

$$[Cu(H_2O)_6]^{2+}_{(aq)} \quad + \quad 3NH_2CH_2CH_2NH_{2(aq)} \quad \rightarrow \quad [Cu(NH_2CH_2CH_2NH_2)_3]^{2+}_{aq)} \quad + \quad 6H_2O_{(l)}$$

4 particles **7 particles**

- When monodentate ligands are replaced with bidentate / multidentate ligands there is an increase in entropy (disorder): 4→ 7 particles.
- As the enthalpy change is minimal, the feasibility of the reaction is overwhelming down to entropy.

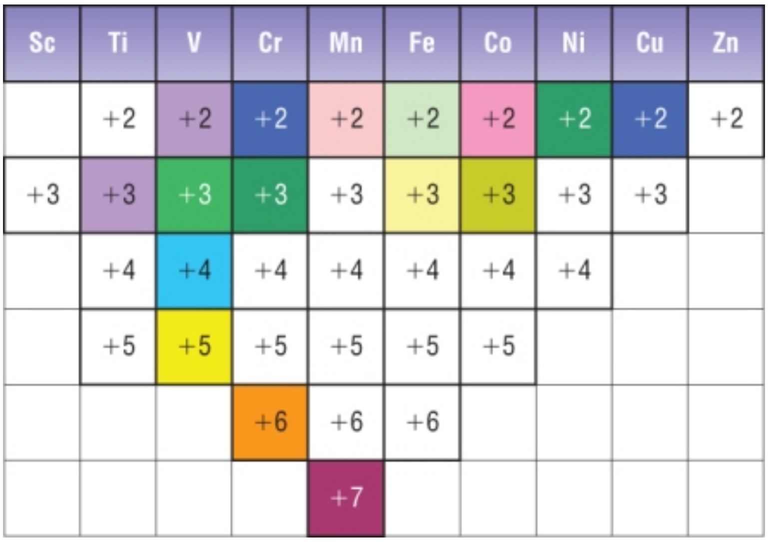
$$\boxed{\Delta G \quad = \quad \Delta H \quad - \quad T\Delta S}$$

Surroundings System

- The stability of the bidentate / multidentate complex ion therefore is high.

Variable oxidation states

- One of the Transition metal properties that separates them from other metals is their ability to exist in variable oxidation states:



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
	+5	+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

- Movement between these oxidation states will be oxidation or reduction.
- An example of this is Vanadium which can exist in 4 oxidation states and these can be identified by their colours in solution (see table above):

Oxidation state	Formula	Colour
+5	$VO_2^+{}_{(aq)}$	Yellow
+4	$VO^{2+}{}_{(aq)}$	Blue
+3	$V^{3+}{}_{(aq)}$	Green
+2	$V^{2+}{}_{(aq)}$	Violet

- Vanadium (V) can be reduced all the way to vanadium (II) using acidified zinc:

Construct the balanced chemical equations for each change, add the colour changes to your final equation. Tip: Write the half equations first:

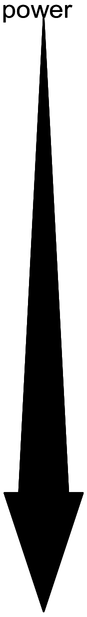
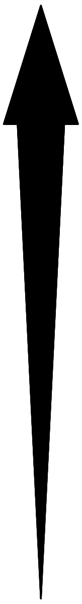
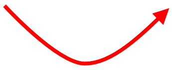
Vanadium (V) → Vanadium (IV):

Vanadium (IV) → Vanadium (III):

Vanadium (III) → Vanadium (II):

REDOX potentials (electrode potentials):

- In 1.11 Electrochemistry, the E^θ value gave an indication of an element's ability to be reduced / oxidised.
- In REDOX reactions, we call them REDOX potentials.
- It is the same thing:

	Element	**Oxidised form**	**Reduced form**	**E^θ_{cell}**	
					
Oxidising power 	Potassium	K^+	K	-2.92	Reducing power 
	Sodium	Na^+	Na	-2.71	
	Lithium	Li^+	Li	-2.59	
	Calcium	Ca^{2+}	Ca	-2.44	
	Magnesium	Mg^{2+}	Mg	-2.37	
	Aluminium	Al^{3+}	Al	-1.66	
	Zinc	Zn^{2+}	Zn	-0.76	
	Iron	Fe^{2+}	Fe	-0.44	
	Tin	Sn^{2+}	Sn	-0.14	
	Lead	Pb^{2+}	Pb	-0.13	
	(Hydrogen)	H^+	H	0.00	
	Copper	Cu^{2+}	Cu	+0.34	
	Mercury	Hg^{2+}	Hg	+0.79	
	Silver	Ag^+	Ag	+0.80	
	Gold	Au^+	Au	+1.89	
					

Summary:

The most negative E^θ value	**The most positive E^θ value**
• Releases electrons the best	• Gains electrons the best
• Oxidised more easily	• **Reduced more easily**
• Reducing agent	• Oxidising agent

This means:

- The more (+)ve REDOX potential is most likely to be reduce to a lower oxidation state.
- Making it the least stable ion:

Example:

$$Cr^{3+}_{(aq)} \quad + \quad e^- \quad \rightleftharpoons \quad Cr^{2+}_{(aq)} \qquad E^{\theta} = -0.74V$$

$$Cu^{2+}_{(aq)} \quad + \quad e^- \quad \rightleftharpoons \quad Cu^{+}_{(aq)} \qquad E^{\theta} = +0.15V$$

- The copper half equation has the more positive value.
- This means it will gain e^- the best.
- This means the Cu^{2+} is the least stable and more likely to be reduced than Cr^{3+}

Factors affecting REDOX potentials (electrode potentials):

1) Ligands:

- Standard electrode potentials are measured as aqueous ion in solution.
- The metal ion would be surrounded by different ligands.
- These ligands will have stronger / weaker bonds with the metal ion.
- This will affect its ability to gain / lose electrons and hence its REDOX potential.

2) pH:

- Some standard REDOX half equations require H^+ ions and others require OH^- ions:

$$2VO_2^{+}{}_{(aq)} \quad + \quad 4H^{+}_{(aq)} \quad + \quad 2e^- \quad \rightleftharpoons \quad 2VO^{2+}_{(aq)} \quad + \quad 2H_2O_{(l)}$$

$$CrO_4^{2-}{}_{(aq)} \quad + \quad 4H_2O_{(l)} \quad + \quad 3e^- \quad \rightleftharpoons \quad Cr(OH)_{3(s)} \quad + \quad 5OH^-_{(aq)}$$

- Generally, REDOX potentials become more positive in more acidic conditions:
  - Adding more H^+ ions move the equilibrium to the right.
  - This increases the ions ability to accept electrons
  - Increasing its ability to be reduced.

Tollens' Reagent:

- Silver nitrate dissolved in ammonia solvent makes the complex ion:

$$[Ag(NH_3)]^+$$

- When added to aldehydes a silver solid is produced – the silver ions are reduced
- The aldehyde is oxidised:

$$RCHO_{(aq)} \quad + \quad 2[Ag(NH_3)]^{+}_{(aq)} \quad + \quad 3OH^-_{(aq)} \rightarrow RCOO^-_{(aq)} \quad + \quad 2Ag_{(s)} \quad + \quad 4NH_{3(aq)} \quad + \quad 2H_2O_{(l)}$$

Redox titrations

- Remember transition metals have variable oxidation states associated with colours.
- This means that they can undergo oxidation and reduction with a built-in indicator:

$$\underset{\text{Purple}}{MnO_4^-{}_{(aq)}} + 8H^+{}_{(aq)} + 5e^- \rightarrow \underset{\text{Colourless}}{Mn^{2+}{}_{(aq)}} + 4H_2O_{(l)}$$

Titration reactions:

- You need to be able to perform calculations involving MnO_4^- and Fe^{2+} or $C_2O_4^{2-}$:

1) MnO_4^- and Fe^{2+}

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$$

$$Fe^{2+}{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + e^-$$

- Combined:

$$\underset{\text{Purple}}{MnO_4^-{}_{(aq)}} + 8H^+{}_{(aq)} + 5Fe^{2+}{}_{(aq)} \rightarrow \underset{\text{Colourless}}{Mn^{2+}{}_{(aq)}} + 4H_2O_{(l)} + 5Fe^{3+}{}_{(aq)}$$

2) MnO_4^- and $C_2O_4^{2-}$

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$$

$$C_2O_4^{2-}{}_{(aq)} + 2e^- \rightarrow 2CO_{2(g)}$$

- Combined:

$$\underset{\text{Purple}}{2MnO_4^-{}_{(aq)}} + 16H^+{}_{(aq)} + 5C_2O_4^{2-}{}_{aq)} \rightarrow \underset{\text{Colourless}}{2Mn^{2+}{}_{(aq)}} + 8H_2O_{(l)} + 10CO_{2(g)}$$

Carrying out redox titrations

- These are carried out in the same way as an acid - base titration.
- The only difference is that instead of neutralisation, an oxidising agent is titrated against a reducing agent.
- Instead of an indicator, there is an associated colour change.
- The 'end point' would be the first permanent pink colour.
- This is then followed by a moles calculation:

Worked example:

25.0cm^3 of a solution of iron (II) salt required 23.00cm^3 of 0.0200 mol dm^{-3} potassium manganate (VII) for complete oxidation in acidic solution.

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5Fe^{2+}{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)} + 5Fe^{3+}{}_{(aq)}$$

MnO_4^-: 23cm^3, 0.02 mol dm^{-3}

n = C x V

= 0.02 x 0.023

= 4.60 x 10^{-4}

1 : 5

x 5

= 2.30 x 10^{-3}

Fe^{2+}: 25cm^3

C = n / V

= 2.3 x 10^{-3} / 0.025

= 0.092 mol dm^{-3}

Examples of redox titrations

- The common uses of these redox titrations are:

1) Calculate the Mr and formula of an iron (II) salt

2) Calculating the % mass of iron in iron tablets

3) Calculating the purity of iron samples

4) Applying your knowledge to unfamiliar redox reactions / titrations

- Some examples:

1) Calculate the Mr and formula of an iron (II) salt

2.950g of hydrated iron (II) sulphate, $FeSO_4.xH_2O$, was dissolved in 50cm^3 of sulphuric acid. This was made up to 250cm^3 with distilled water.
25cm^3 of this was titrated with 0.01 mol dm^{-3} $KMnO_4$ and 21.20$cm^3$of this was used

$$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5Fe^{2+}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)} + 5Fe^{3+}_{(aq)}$$

21.20cm^3 25.00cm^3

0.01 mol dm^{-3}

↓

n = C x V 1 : 5

= 0.01 x 0.0212 →

= 2.12 x 10^{-4} x 5 = 1.06 x 10^{-3}

n MnO_4^- = C x V

n MnO_4^- = 0.01 x 0.0212

n MnO_4^- = 2.12 x 10^{-4}

Ratio 1 : 5, therefore x 5

n Fe^{2+} = 1.06 x 10^{-3} in 25cm^3 of solution (x 10 in 250cm^3)

n Fe^{2+} = 1.06 x 10^{-3} in 25cm^3 of solution (x 10 in 250cm^3)

n Fe^{2+} = 0.0106 x 10^{-3} in 250cm^3 of solution

Mr = m / n

Mr - 2.950 / 0.0106 = 278.3 $gmol^{-1}$

For Mr of all waters, deduct the Mr of $FeSO_4$ = 278.3 - 151.9 = 126.4

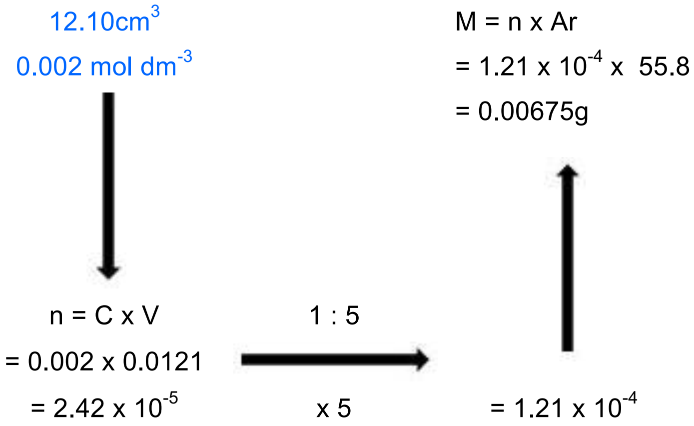
No waters = 126.4 / 18 = 7

Formula: $FeSO_4.7H_2O$

2) Calculating the % mass of iron in iron tablets

A multivitamin tablet has a mass of **0.325g** and contains iron. The powdered tablet was dissolved in some water and sulphuric acid.
12.10cm^3 of 0.002 mol dm^{-3} $KMnO_4$ was titrated until the first permanent pink colour.

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5Fe^{2+}{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)} + 5Fe^{3+}{}_{(aq)}$$



12.10cm^3
0.002 mol dm^{-3}

n = C x V
= 0.002 x 0.0121
= 2.42 x 10^{-5}

1 : 5
x 5

= 1.21 x 10^{-4}

M = n x Ar
= 1.21 x 10^{-4} x 55.8
= 0.00675g

n MnO_4^- = C x V

n MnO_4^- = 0.002 x 0.0121

n MnO_4^- = 2.42 x 10^{-5}

Ratio 1 : 5, therefore x 5

n Fe^{2+} = 1.21 x 10^{-4}

Mass of Fe = 1.21 x 10^{-4} x 55.8

Mass of Fe = 0.00675g

% Fe by mass = (Mass of element / Mass of tablet) x 100

% Fe by mass = (0.00675 / 0.325) x 100

% Fe = 2.08%

4) Applying your knowledge to unfamiliar redox reactions / titrations

25cm^3 portion of H_2O_2 was made up to 250cm^3 with distilled water.
25cm^3 portions of this was acidified and titrated with 0.0200 mol dm^{-3} $KMnO_4$, 38.00cm^3 of this was required to completely oxidise the hydrogen peroxide to oxygen.
Calculate the original concentration of the hydrogen peroxide. The following equation represents the oxidation of hydrogen peroxide

The balanced equation:

$$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$$

$$H_2O_{2(aq)} \rightarrow O_{2(g)} \quad 2H^+_{(aq)} + 2e^-$$

- Combined:

$$2MnO_4^-{}_{(aq)} + 6H^+_{(aq)} + 5H_2O_{2(aq)} \rightarrow 2Mn^{2+}_{(aq)} + 8H_2O_{(l)} + 5O_{2(g)}$$

38.00cm^3

0.02 mol dm^{-3}

25cm^3

C = n / V

= 1.9 x 10^{-3} / 0.025

= 0.0760 mol dm^{-3}

n = C x V

= 0.02 x 0.038

= 7.6 x 10^{-4}

2 : 5

x 2.5

= 1.9 x 10^{-3}

- Remember this was diluted by a factor of 10 at the beginning
- Concentration of original = 0.760 mol dm^{-3}

Transition metals as catalysts

- A catalyst speeds up a reaction and comes out unchanged.
- Providing an alternative route with a lower activation energy.
- Transition metals have variable oxidation states.
- They can provide / accept electrons using their d orbitals.
- Acting a bit like a middle man they can provide electrons at the start, then accept them at the end (or vice versa).
- In this way, they can bind to reactants forming part of the intermediate.
- Providing an alternative route with a lower activation energy:

Types of catalyst:

1) Heterogeneous catalyst

Heterogeneous catalyst:
A catalyst that is in a different phase as the reactants.

Example: The Contact process:

- A reaction used to make sulphuric acid:

$$SO_{2(g)} \quad + \quad \tfrac{1}{2}O_{2(g)} \xrightarrow{V_2O_{5(s)}} SO_{3(g)}$$

- Vanadium (V) oxide catalyses the reaction is 2 steps:

1) The vanadium (V) oxide oxidises the SO_2 while it is itself reduced to vanadium (IV) oxide:

$$SO_2 \quad + \quad \underset{+5}{V_2O_5} \longrightarrow SO_3 \quad + \quad \underset{+4}{V_2O_4}$$

2) The vanadium (IV) oxide is then oxidised back to vanadium (IV) oxide by the oxygen:

$$\tfrac{1}{2}O_2 \quad + \quad \underset{+4}{V_2O_4} \longrightarrow SO_3 \quad + \quad \underset{+5}{V_2O_5}$$

- This can only happen because vanadium has variable oxidation states.

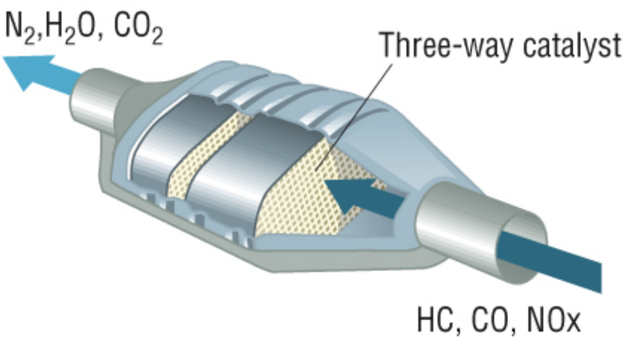
Another example: The Haber process:

- A reaction used to make ammonia:

$$N_{2(g)} \quad + \quad 3H_{2(g)} \xrightarrow{Fe_{(s)}} 2NH_{3(g)}$$

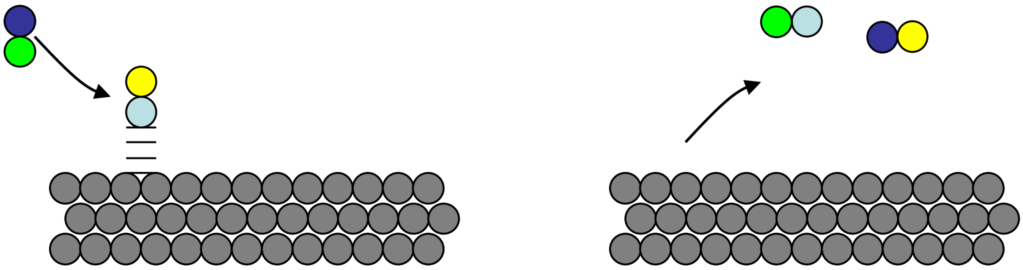
Solid support → Surface area:

- With heterogeneous catalysts, the reaction occurs on the surface of the catalyst.
- Surface area needs to be as big as possible in order for as many reaction to occur at the same time ie increasing the rate.
- A lattice structure coated with the catalyst increases the surface area, eg catalytic converters:



Catalytic poisoning:

- Heterogeneous catalysts interact with reactants by **adsorption**:



- Impurities will also be adsorbed to the catalyst surface.
- This blocks that particular site which eventually reduces the surface area and amount of product made.
- The catalyst is said to be poisoned and may need replacing.
- This can be expensive as many Transition metals are often precious metals:

Lead poisoning catalytic converters:

- Lead compounds in petrol coat the surface of the catalyst.
- Therefore, catalytic converters only run on unleaded petrol.

Sulphur poisoning in the Haber process:

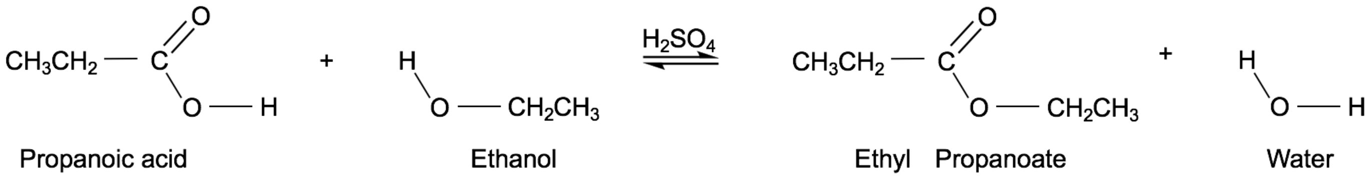
- The hydrogen is made from methane.
- This is obtained from natural gas.
- Natural gas contains sulphur compounds as impurities.
- Sulphur forms iron sulphide and coats the iron catalyst.

❖ Purifying the reactants will increase the life of a catalyst.

2) Homogeneous catalyst

Homogeneous catalyst:
A catalyst that is in the same phase as the reactants

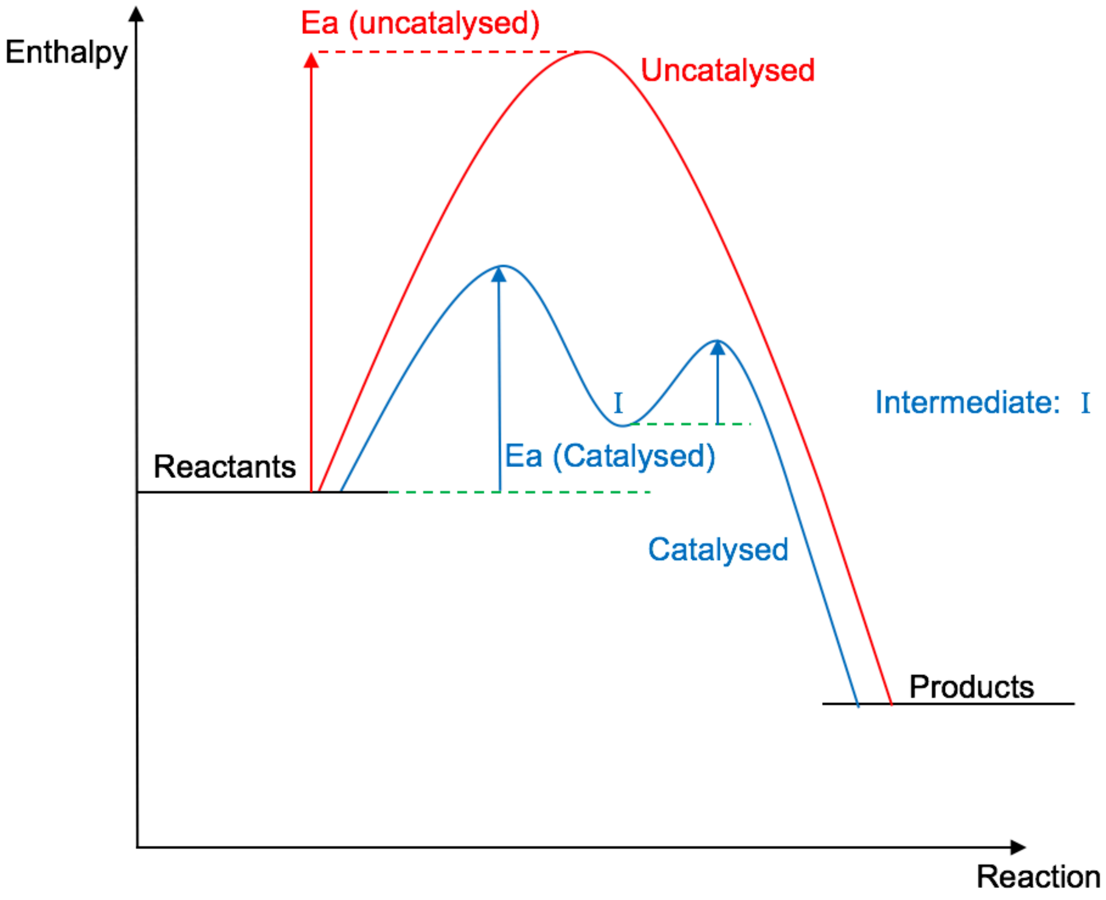
Example: Sulphuric acid in esterification



- Transition metals as catalysts in the same phase are usually in the aqueous phase.

How it works:

- A homogeneous catalyst works by combining with one of the reactants making an intermediate species.
- The intermediate species then reacts with the other reactant forming the product whilst regenerating the original catalyst.
- The activation energies of the 2 stages are lower than the activation energy of the uncatalysed reaction:



Examples:

Fe^{2+} catalysed reaction between $S_2O_8^{2-}$ and I^-

- This reaction occurs very slowly due to 2 negative ions required to collide – repulsion.

$$S_2O_8{}^{2-}{}_{(aq)} + 2I^-{}_{(aq)} \longrightarrow I_{2(aq)} + 2SO_4{}^{2-}{}_{(aq)}$$

- Fe^{2+} catalyses the reaction is 2 steps:

1) The Fe^{2+} is oxidised while reducing the $S_2O_8^{2-}$ to SO_4^{2-}:

$$S_2O_8{}^{2-}{}_{(aq)} + 2Fe^{2+}{}_{(aq)} \longrightarrow 2Fe^{3+}{}_{(aq)} + 2SO_4{}^{2-}{}_{(aq)}$$

2) The Fe^{3+} is then reduced back to Fe^{3+} while oxidising I^- to I_2:

$$2I^-{}_{(aq)} + 2Fe^{3+}{}_{(aq)} \longrightarrow 2Fe^{2+}{}_{(aq)} + I_{2(aq)}$$

- Each stage now involves a positive and negative ion.
- The Iodine can be tested by the addition of starch → blue black
- This can only happen because iron has variable oxidation states.

Mn^{2+} autocatalysis reaction between MnO_4^- and $C_2O_4^{2-}$

- This reaction occurs very slowly however as again there are 2 negative ions involved in the reaction – The activation energy is high.
- Mn^{2+} catalyses the reaction.
- As Mn^{2+} is a product in the reaction, it automatically catalyses:

$$2MnO_4{}^-{}_{(aq)} + 16H^+{}_{(aq)} + 5C_2O_4{}^{2-}{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)} + 10CO_{2(g)}$$

- Mn^{2+} catalyses the reaction is 2 steps:

1) The Mn^{2+} is oxidised and the MnO_4^- is reduced forming Mn^{3+}:

$$4Mn^{2+}{}_{(aq)} + MnO_4{}^-{}_{(aq)} + 8H^+{}_{(aq)} \longrightarrow 5Mn^{3+}{}_{(aq)} + 4H_2O_{(l)}$$

2) The Mn^{3+} is then reduced back to Mn^{2+} while oxidising $C_2O_4^{2-}$ to CO_2:

$$2Mn^{3+}{}_{(aq)} + C_2O_4{}^{2-}{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 2CO_{2(g)}$$

- Each stage now involves a positive and negative ion.
- This can only happen because manganese has variable oxidation states.

How the rate changes: