TRANSITION METALS

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1) Electron structure

1s		1s
2s		2p
3s		3p
4s	3d	
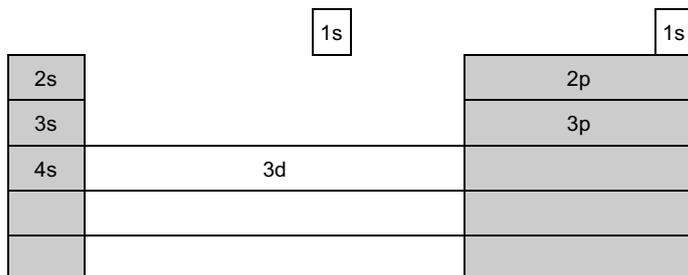
Remember that:

- 4s fills before 3d
- 4s also empties before 3d (in ions)
- Cr is [Ar] $4s^1 3d^5$
- Cu is [Ar] $4s^1 3d^{10}$

- Give the electron structure of the following atoms / ions.

Fe   [Ar] …………………………………………

Fe^{3+} [Ar] …………………………………………

Sc   [Ar] …………………………………………

Sc^{3+} [Ar] …………………………………………

V   [Ar] …………………………………………

V^{2+} [Ar] …………………………………………

Cu   [Ar] …………………………………………

Cu$^+$ [Ar] …………………………………………

Cu^{2+} [Ar] …………………………………………

Zn   [Ar] …………………………………………

Zn^{2+} [Ar] …………………………………………

Cr   [Ar] …………………………………………

2) What is a transition metal?

transition metal = **element that has an incomplete d sub-shell in either its atoms or one its common ions**

metal	atom	Common ions		Transition metal?
Sc	Sc [Ar] ………………	Sc^{3+} [Ar] ………………		
Cu	Cu [Ar] ………………	Cu$^+$ [Ar] ………………	Cu^{2+} [Ar] ………………	
Zn	Zn [Ar] ………………	Zn^{2+} [Ar] ………………		

NB – This is the latest IUPAC definition, but some exam boards incorrectly state that it is an element that has an incomplete d sub-shell in one of its common ions (and excludes the atoms part) – this only affects scandium in reality but make sure you are aware if your exam board does this.

3) Properties of transition metals

The incomplete d sub-shell is responsible for a number of general properties of transition elements:

1) variable oxidation states

2) catalytic action

3) coloured compounds

4) formation of complexes

SECTION 2 – Complex ions

1) Some definitions

Ligand   =   particle with lone pair of electrons that bonds to metals by a co-ordinate bond

Complex   =   metal ion with co-ordinately bonded ligands

Co-ordination number   =   number of co-ordinate bonds from ligands to metal ion

Lewis base   =   lone pair donor

Lewis acid   =   lone pair acceptor

2) Formation of complexes

Common, simple ligands include H_2O, NH_3 and Cl^- ions, all of which have a long pair of electrons. Complexes are formed when ligands such as these form co-ordinate bonds using their lone pairs to a metal ion.

In this example, 4 chloride ions (Cl^-) act as ligands, each forming a single co-ordinate bond to the Cu^{2+} ion using a lone pair, forming the $[CuCl_4]^{2-}$ ion.

Ligands are acting as Lewis bases when they bond to transition metals as they donate a lone pair to form a co-ordinate bond. The metal ion acts as a Lewis acid as it accepts lone pairs.
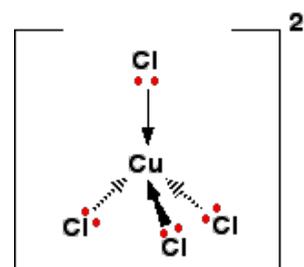
3) Shapes of complexes

The table shows the most common shapes of complexes.

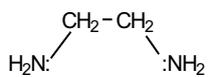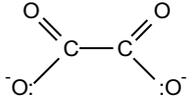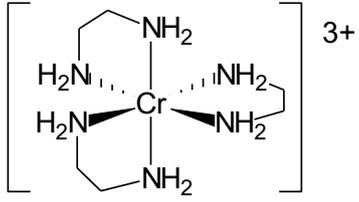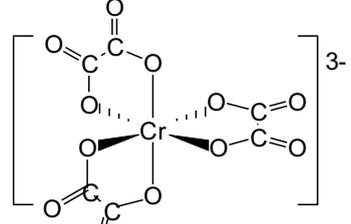|	**linear**	**square planar**	**tetrahedral**	**octahedral**
co-ordination number	2	4	4	6
shape	180° —M—	90° —M—	109.5°	90°
occurrence	Ag^+ complexes	Pt^{2+} and Ni^{2+} complexes	With larger ligands (e.g. Cl^-) (when ligands are too big for six to fit)	Most complexes with small ligands (e.g. H_2O, NH_3)
example	$[Ag(NH_3)_2]^+$ (in Tollen's reagent)	$[PtCl_4]^{2-}$	$[CuCl_4]^{2-}$	$[Cu(H_2O)_6]^{2+}$

4) Types of ligands

All ligands must have one (or more) lone pair(s) of electrons to form the co-ordinate bond(s) to the metal ion.

Unidentate ligands – ligands which form one co-ordinate bond to a metal ion

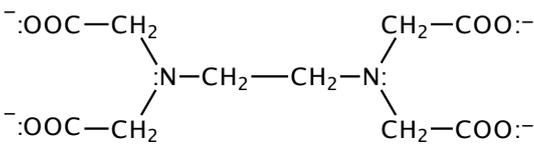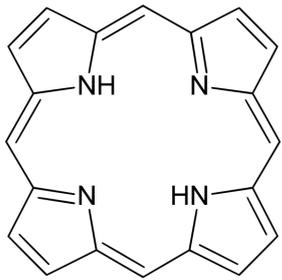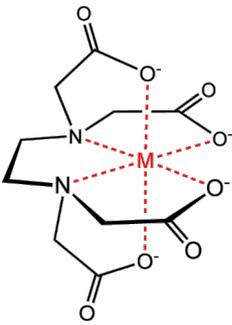| Ligand	:Cl$^-$	:OH$^-$	:CN$^-$	H$_2$O:	:NH$_3$
Example complex	[CuCl$_4$]$^{2-}$	[Cr(OH)$_6$]$^{3-}$	[Ag(CN)$_2$]$^-$	[Fe(H$_2$O)$_6$]$^{2+}$	[Cr(NH$_3$)$_6$]$^{3+}$

Bidentate ligands – ligands which form two co-ordinate bonds to a metal ion

	1,2-diaminoethane	**ethanedioate ion (C$_2$O$_4^{2-}$)**
Ligand		
Example complex

[Cr(NH$_2$CH$_2$CH$_2$NH$_2$)$_3$]$^{3+}$ |

[Cr(C$_2$O$_4$)$_3$]$^{3-}$ |
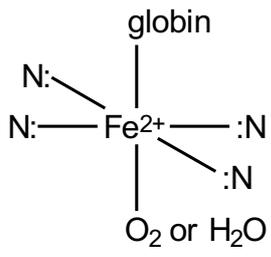
Multidentate ligands – ligands which form more than two co-ordinate bonds to a metal ion

|	**EDTA^{4-}** forms 6 bonds	**porphyrin** forms 4 bonds
Ligand		
How it bonds		
Example	[Cu(EDTA)]$^{2-}$	haemoglobin

Haemoglobin

Haemoglobin is a globular protein that contains four Fe^{2+} centres, each with a porphryin ligand taking up four of the six co-ordination sites.

One of the other two sites is bonded to the rest of the haemoglobin structure leaving one site to which oxygen can bond as a ligand.

The oxygen is carried around the body in blood bonded to iron in haemoglobin in this way. It is not a particularly good ligand and so easily comes off the iron when needed to transfer to cells for respiration.

Cyanide ions (CN^-) and carbon monoxide (CO) are better ligands than oxygen (O_2) and so will bond to haemoglobin in preference to oxygen. This is why carbon monoxide and cyanide compounds are toxic as they prevent the transfer of oxygen around the body.
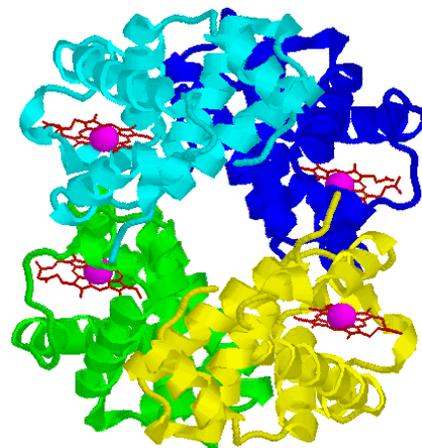
TASK 1 – Drawing complexes

Formula	$[Ag(CN)_2]^-$	$[Cr(NH_3)_6]^{3+}$	$[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$
Sketch			
Shape			
Bond angles			
Metal oxidation state			
Ligand(s)			
Co-ordination number			

Formula	$[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$	$[Pt(NH_3)Cl_3]^-$	$[Fe(C_2O_4)_3]^{3-}$
Sketch			
Shape			
Bond angles			
Metal oxidation state			
Ligand(s)			
Co-ordination number			

5) Stereoisomerism in complexes

a) Cis-trans isomerism

- This is a special case of *E-Z* isomerism.
- It can occur in octahedral and square planar complexes where there are two ligands of one type different to the other ligands.

		cis (next to each other)	trans (opposite each other)
Square planar	e.g. $Pt(NH_3)_2Cl_2$	$$Cl-Pt-NH_3$$ with Cl above and NH_3 below **cisplatin** (effective anti-cancer drug)	$$Cl-Pt-Cl$$ with NH_3 above and NH_3 below **transplatin** (no effect on cancer)
Octahedral	e.g. $[Co(NH_3)_4Cl_2]^+$		

b) Optical isomerism

- This occurs in an octahedral complex with three bidentate ligands.
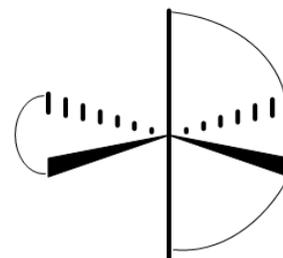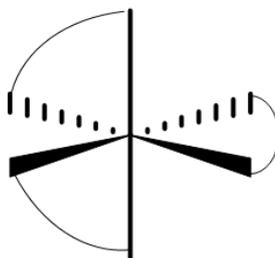
TASK 2 – Drawing pairs of complexes that are isomers

1 Draw and identify the cis and trans isomers of square planar complex $PdCl_2(CN)_2$.

2 Draw and identify the cis and trans isomers of octahedral complex $[Cr(OH)_2(H_2O)_4]^+$

3 Draw the two optical isomers of octahedral complex $[Cr(C_2O_4)_3]^{3-}$

4 Draw the two optical isomers of octahedral complex $[Cu(NH_2CH_2CH_2NH_2)_3]^{2+}$

1) What is ligand substitution

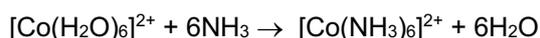- A ligand substitution reaction is one where one ligand is replaced by another ligand.

2) Substitution by similar sized ligands

- If the ligands are a similar size (actually the atom/ion in the ligand that bonds to the metal), then there will be no change in co-ordination number if a substitution reaction takes place.

- For example, H_2O and NH_3 ligands are a similar size.

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$$

- In some ligand substitution reactions, only some of the ligands are replaced, for example

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(H_2O)_2(NH_3)_4]^{2+} + 4H_2O$$
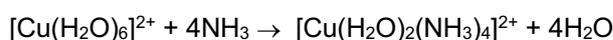
3) Substitution by bigger/smaller ligands

- If the ligands are a different size then the co-ordination number may change.

- For example, Cl^- ligands are significantly bigger than the O on H_2O or the N in NH_3 and only four Cl^- ligands can bond to most transition metal ions. In this reaction, the co-ordination number changes from 6 to 4 due to this.

$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$$
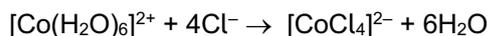
4) Substitution by ligands that form more co-ordinate bonds (the chelate effect)

- Ligands can be replaced by ligands that form more co-ordinate bonds. For example, six monodentate ligands can be replaced by three bidentate ligands.

$$[Cr(NH_3)_6]^{3+} + 3\ NH_2CH_2CH_2NH_2 \rightarrow [Cr(NH_2CH_2CH_2NH_2)_3]^{3+} + 6NH_3$$
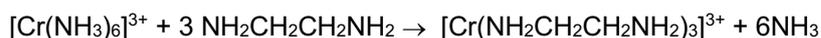
- In many ligand substitution reactions, ΔH is negligible as the same number of the same type of similar bonds are being broken and formed. In this example above, six Cr-N bonds are being broken and six Cr-N bonds being formed and so ΔH is negligible.

- However, where ligands are replaced by those that form more co-ordinate bonds, there is a significant increase in entropy (ΔS). In the example above we go from 4 aqueous particles to 7 aqueous particles.

- As the feasibility of a reaction depends on $\Delta G = \Delta H - T\Delta S$, if ΔH is negligible and ΔS very positive (a big increase in entropy), then ΔG is very negative and the reaction is feasible.

- It follows that the opposite reaction in which ligands would be replaced by those that form fewer co-ordination bonds would not be feasible due to an entropy decrease (ΔS negative).

- Therefore in general, in a ligand substitution reaction where ligands are replaced with by those that form more co-ordinate bonds, the reaction is feasible and this is driven by the entropy increase. Reactions which would have ligands replaced by those that make fewer co-ordinate bonds are not feasible due to an entropy decrease.

- This is known as the chelate effect (stemming from the Latin for crab – the idea being of a crab's claw grabbing the metal from two sides).

- Ligands that form more than one co-ordinate bond, and in particular those that form many, are sometimes called **chelating agents** as they are very good at bonding to a metal ion and are very difficult to then remove. This renders the metal ion harmless as it cannot bond to anything else.

- $EDTA^{4-}$ is a particularly good ligand for this as it forms 6 co-ordinate bonds.

TASK 3 – Substitution reactions

1 Use the following equations to answer the questions after them.

1 $[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$

2 $[Co(H_2O)_6]^{2+} + 6F^- \rightarrow [CoF_6]^{4-} + 6H_2O$

3 $[Co(H_2O)_6]^{2+} + 2H_2O_2 \rightarrow [Co(H_2O)_6]^{3+} + 4OH^-$

4 $[Co(H_2O)_6]^{2+} + 3C_2O_4^{2-} \rightarrow [Co(C_2O_4)_3]^{4-} + 6H_2O$

5 $[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$

6 $[Co(C_2O_4)_3]^{4-} + EDTA^{4-} \rightarrow [Co(EDTA)]^{2-} + 3C_2O_4^{2-}$

7 $[Co(NH_2CH_2CH_2NH_2)_3]^{2+} + 3C_2O_4^{2-} \rightarrow [Co(C_2O_4)_3]^{4-} + 3NH_2CH_2CH_2NH_2$
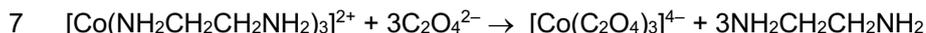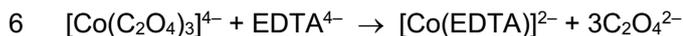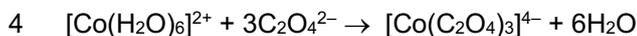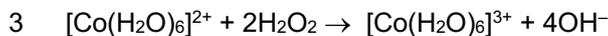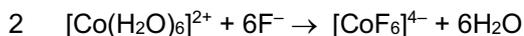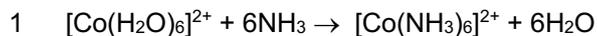
a) What happens in a ligand substitution reaction?

b) Identify which, if any, of the reactions involve ligand substitution.

c) Identify which, if any, of the reactions involve a change in co-ordination number.

d) In any reaction(s) where the co-ordination number changes, explain why this change occurs.

e) Identify which, if any, of the reactions involve an increase in entropy.

2 If someone is poisoned with $[Pb(H_2O)_6]^{2+}$ ions, the chelating agent $CaNa_2EDTA$ can be used to render the lead(II) ions harmless,

a) What is the charge on the negative ion in $CaNa_2EDTA$?

b) Write an equation for the reaction of the ions from $CaNa_2EDTA$ with $[Pb(H_2O)_6{}^{2+}]$ ions.

c) Explain why this reaction is feasible by discussing and explaining the sign of ΔH and ΔS for this reaction.

d) The lead(II) ions are rendered harmless in this reaction. Explain why this reaction cannot be reversed to release reactive lead(II) ions again.

SECTION 4 – Coloured ions

1) Why complexes are coloured

- In transition metal compounds, the five d orbitals do not all have the same energy.

- The gap in energy between the d orbitals corresponds to the energy of UV/visible light.

- The electrons absorb UV/visible light to provide the energy to promote (excite) electrons to the higher energy level.

- If the gap in energy between the higher and lower d orbitals is written as ΔE.

$$\Delta E = hf = \frac{hc}{\lambda}$$

where

ΔE = gap in energy (J)
h = Planck's constant (6.63×10^{-34} Js)
f = frequency of light (s^{-1})
c = velocity of light (3.00×10^8 ms^{-1})
λ = wavelength of light (m)
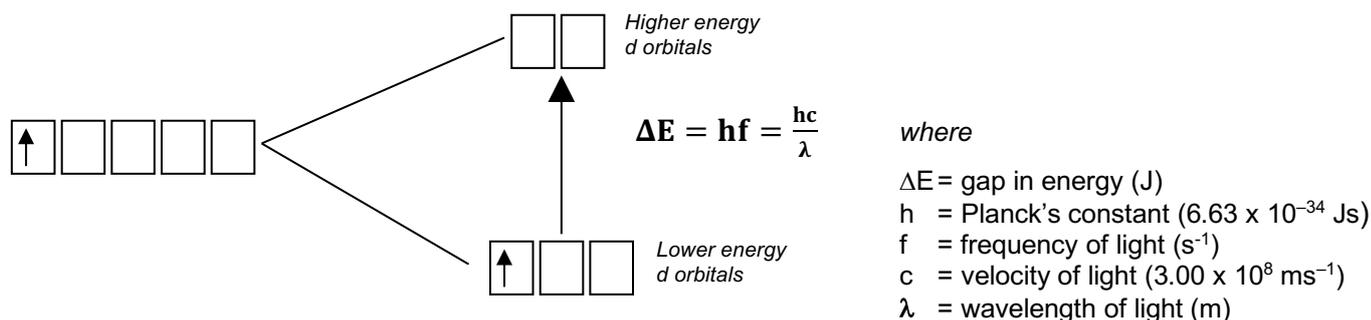
- The colour that you see is a mixture of the colours of visible light that are **NOT** absorbed. For example, hydrated copper sulfate is blue because other colours of white light (e.g. red) are absorbed to promote d electrons from lower to higher d orbitals.

- The colour you see of solids is due to light being reflected. For example, a blue compound is blue because the blue is reflected while other colours are absorbed. With a solution, a blue compound is blue because the blue is transmitted (passes through) while other colours are absorbed

- Zn^{2+} ([Ar] $3d^{10}$), Cu^+ ([Ar] $3d^{10}$), Sc^{3+} ([Ar]) are not coloured (i.e. white as solids, colourless in solution). This is because their d sub-shells are either empty or full meaning that electrons cannot be promoted from the lower to higher d orbitals.

2) Factors that affect the colour

Factor	Complex 1	Complex 2
Identify of metal	$[Cu(H_2O)_6]^{2+}$ blue	$[Fe(H_2O)_6]^{2+}$ green
Oxidation state of metal	$[Fe(H_2O)_6]^{3+}$ pale violet	$[Fe(H_2O)_6]^{2+}$ green
Identify of ligands	$[Cu(H_2O)_6]^{2+}$ blue	$[Cu(H_2O)_4(NH_3)_2]^{2+}$ deep blue
Co-ordination number	$[Cu(H_2O)_6]^{2+}$ blue	$[CuCl_4]^{2-}$ yellow

- If any of these factors are changed, then the size of the energy gap between the higher and lower d orbitals changes, and so the frequency of light absorbed changes and so the colour seen changes.

3) Ultraviolet/visible spectroscopy

- The frequencies at which a complex absorbs uv/visible light can be measured with a uv/visible spectrometer.

- Uv/visible light is passed through the complex, and the frequencies of uv/vis light passing through detected – those that do not pass through are absorbed.

- The more concentrated the solution the more light that is absorbed, so uv/vis can be used to measure the concentration of the solution.
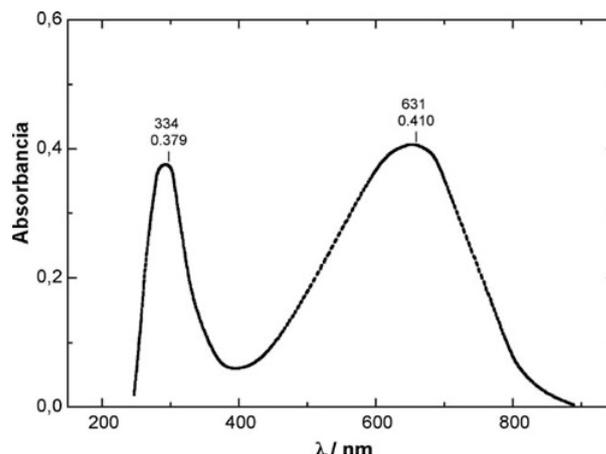
4) Colorimetry

- The more concentrated the solution, the more it absorbs.

- This can be used to find the concentration of solutions – this is done in colorimeters.

- For some ions, a ligand is added to intensify the colour (e.g. SCN⁻) as the colour would be too weak otherwise (particularly for solutions with very low concentrations of ions).

- A colour of light is chosen that the compound absorbs (e.g. blue compounds absorb orange-red light).

- The strength of absorption of a range of solutions of known concentration is measured and a graph (calibration curve) produced.
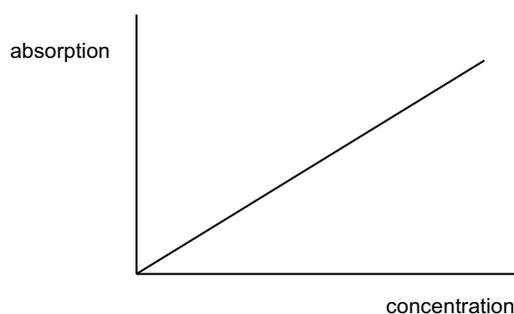
- The concentration of a solution of unknown concentration can be found by measuring the absorption and using the graph.

TASK 4 – Coloured complexes

1 a) Explain why transition metal complexes are coloured.

   b) Identify four factors that affect the colour of transition metal complexes and explain why these changes affect the colour.

2 The complex $[Co(H_2O)_6]^{3+}$ absorbs is blue due to the absorption of orange light with wavelength 901 nm. The complex $[Co(NH_3)_6]^{3+}$ is brown due to the absorption of blue light at 475 nm. Planck's constant is 6.63×10^{-34} Js and the velocity of light is 3.00×10^8 ms^{-1}.

   a) State the equation that links the wavelength of light absorbed by a transition metal complex to the gap in energy between d orbitals.

   b) Explain why the complex $[Co(H_2O)_6]^{3+}$ is blue.

   c) Calculate the energy gap between the d orbitals in $[Co(H_2O)_6]^{3+}$ in J. Give your answer to the appropriate number of significant figures.

   d) Calculate the energy gap between the d orbitals in $[Co(NH_3)_6]^{3+}$ in kJ mol^{-1} (the Avogadro constant (L) is 6.022×10^{23} mol^{-1}). Give your answer to the appropriate number of significant figures.

   e) Explain why the complex $[Co(NH_6)_6]^{3+}$ is a different colour to $[Co(H_2O)_6]^{3+}$.

3 Colorimetry can be used to find the concentration $[Fe(H_2O)_6]^{2+}$ in solution. The colour of this complex is weak and so a ligand such as bipyradine ('bipy') (structure shown below) is added. This is a bidentate ligand that forms $[Fe(bipy)_3]^{2+}$.
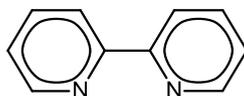
Data was recorded to produce a calibration curve and is shown below.

Concentration of $[Fe(H_2O)_6]^{2+}$ (mol dm^{-3})	0.00	0.10	0.20	0.30	0.40	0.50
absorbance	0.00	0.14	0.29	0.40	0.55	0.69

   a) Explain the terms *ligand* and *bidentate*.

   b) Why is bipy added to the $[Fe(H_2O)_6]^{2+}$ solution?

   c) Write an equation for the formation of $[Fe(bipy)_3]^{2+}$ from $[Fe(H_2O)_6]^{2+}$.

   d) What shape is $[Fe(bipy)_3]^{2+}$.

   e) What is the co-ordination number in the complex $[Fe(bipy)_3]^{2+}$.

   f) Draw the structure of $[Fe(bipy)_3]^{2+}$.

   g) Plot a calibration curve using the data in the table.

   h) A sample of $[Fe(H_2O)_6]^{2+}$ was analysed by addition of bipy an then colorimetry. It was found to have an absorbance of 0.21. What is the concentration of the $[Fe(H_2O)_6]^{2+}$?

SECTION 5 – Variable oxidation states

1) Variable oxidation states

- Transition metals can have a range of oxidation states. For example, common oxidation states of
  - iron (Fe): +2, +3, +6,
  - manganese (Mn): +2, +4, +6, +7
  - copper (Cu): +1, +2
- In many reactions transition metals change oxidation states.

2) Examples of uses

General use	Reagent	Notes
Testing for aldehydes	Tollen's reagent (contains $[Ag(NH_3)_2]^+$)	• Silver mirror formed in presence of aldehydes. • Ag(+1) in $[Ag(NH_3)_2]^+$ reduced to Ag(0) in silver mirror. • Aldehyde oxidised to carboxylic acid
	Fehling's solution (contains Cu^{2+})	• Brick-red precipitate (Cu_2O) formed in presence of aldehydes. • Cu(+2) reduced to Cu(+1) in Cu_2O. • Aldehyde oxidised to carboxylic acid
Testing for alcohols (primary & secondary) aldehydes	Acidified $K_2Cr_2O_7$	• Colour change from orange ($Cr_2O_7^{2-}$) to green (Cr^{3+}). • Cr(+6) in $Cr_2O_7^{2-}$ reduced to Cr(+3). • Alcohols / aldehyde oxidised
Redox titrations		• e.g. acidified $KMnO_4$ can be used to analyse Fe^{2+}, $C_2O_4^{2-}$ and H_2O_2
Catalysis		• many reactions are catalysed by transition metals and this often involves the transition metal changing oxidation state

3) The effect of pH and ligand

- How easily it is to change the oxidation state of a transition metal depends on the pH and the ligands present.
- In general, it is easier to
  - oxidise a transition metal in alkaline conditions
  - reduce a transition metal in acidic conditions
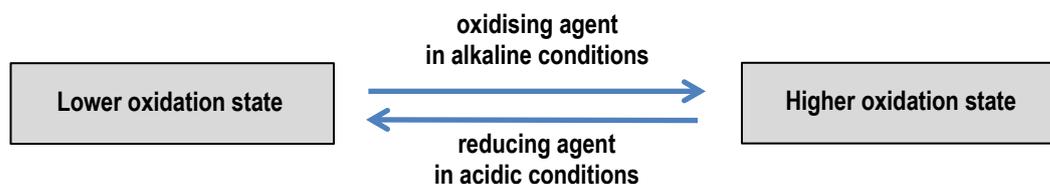
- This can be shown using electrode potentials.

effect of ligand

e.g. Co(+2) to/from Co(0)

$[Co(NH_3)_6]^{2+} + 2e^- \rightleftharpoons Co + 6NH_3$ $E° = -0.43$ V

$[Co(H_2O)_6]^{2+} + 2e^- \rightleftharpoons Co + 6H_2O$ $E° = -0.28$ V
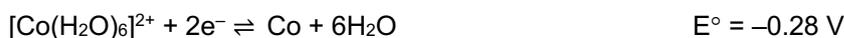
easier to reduce $[Co(H_2O)_6]^{2+}$ than $[Co(NH_3)_6]^{2+}$

effect of pH

e.g. Cr(+6) to/from Cr(3)

$CrO_4^{2-} + 7H_2O + 3e^- \rightleftharpoons [Cr(H_2O)_3(OH)_3] + 5OH^-$ $E° = -0.13$ V   (in alkali)

$\frac{1}{2}Cr_2O_7^{2-} + 7H^+ + 3e^- \rightleftharpoons [Cr(H_2O)_6]^{3+} + 3\frac{1}{2}H_2O$ $E° = +1.33$ V   (in acid)
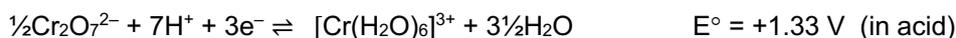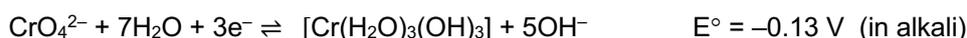
<u>much</u> easier to reduce $Cr_2O_7^{2-}$ (present in acid) than CrO_4^{2-} (present in alkali)

<u>much</u> easier to oxidise $[Cr(H_2O)_3(OH)_3]$ (present in alkali) than $[Cr(H_2O)_6]^{3+}$ (present in acid)

effect of ligand and pH

e.g. Fe(+3) to/from Fe(+2)

$[Fe(H_2O)_3(OH)_3] + H_2O + e^- \rightleftharpoons [Fe(H_2O)_4(OH)_2] + OH^-$ $E° = -0.56$ V   (in alkali)

$[Fe(H_2O)_6]^{3+} + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+}$ $E° = +0.77$ V   (in acid)
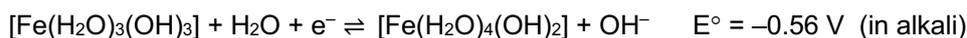
<u>much</u> easier to reduce $[Fe(H_2O)_6]^{3+}$ (present in acid) than $[Fe(H_2O)_3(OH)_3]$ (present in alkali)

<u>much</u> easier to oxidise $[Fe(H_2O)_4(OH)_2]$ (present in alkali) than $[Fe(H_2O)_6]^{2+}$ (present in acid)

<u>e.g. reduction from V(+5) to V(+2)</u>

- The vanadium in ammonium vanadate(V) can be reduced from V(+5) to V(+4) to V(+3) to V(+2) in acidic conditions (hydrochloric acid or sulfuric acid) using zinc as the reducing agent.
- A cotton wool plug is inserted into the neck of the flask or tube to keep air out which would prevent V(+2) being formed.
- As the reaction takes place, the colour changes in succession from yellow to blue to green to violet. (remember: **Y**ou **B**etter **G**et **V**anadium)

oxidation state	species present	colour
V(+5)	VO_2^+	yellow
V(+4)	VO^{2+}	blue
V(+3)	V^{3+}	green
V(+2)	V^{2+}	violet

- You cannot reduce the V(+5) down to V(+2) in alkaline condition.

TASK 5 – Variable oxidation states

1   The redox potentials for the conversion of Zn(+2) to Zn(0) for two Zn(+2) species are shown.

$[Zn(NH_3)_4(H_2O)_2]^{2+} + 2e^- \rightleftharpoons Zn + 4NH_3 + 2H_2O$ E° = –1.03 V

$[Zn(OH)_4(H_2O)_2]^{2-} + 2e^- \rightleftharpoons Zn + 4OH^- + 2H_2O$ E° = –1.22 V

a) Which of these two Zn(+2) species is easiest to reduce?

b) What is different about the two Zn(+2) species that causes a difference in their ease of reduction?

2   A sample of ammonium vanadate(V) was mixed with hydrochloric acid in a conical flask. Zinc was added and cotton wool inserted into the mouth of the flask.

a) Describe the colour changes that you would see and identify the species responsible for each colour with its oxidation state.

b) What is the role of the zinc in this experiment?

c) Write a half equation to show what happens to the zinc.

d) Why is the experiment done in acidic conditions?

e) Why is there some fizzing during this experiment? Write an equation for the reaction that causes the fizzing (hint – the fizzing is not caused by a reaction of any vanadium containing species).

f) Why is the cotton wool inserted in the flask?

g) Derive half equations for the formation of each successive vanadium species from the last.

h) Use your answers from (c) and (g) to write equations formation of each successive vanadium species from the last.

3   Methanal is oxidised to methanoic acid by Tollen's reagent. A silver mirror is formed.

a) Identify the reactive species in Tollen's reagent.

b) Write a half equation for the formation of the silver mirror.

c) Write a half equation for the oxidation of methanal to methanoic acid.

d) Combine your half equations to give a balanced equation for the reaction.

4   Iron(II) hydroxide is oxidised to iron(III) hydroxide by oxygen. Redox potentials for these reactions are shown. Write a balanced equation for this reaction.

$[Fe(H_2O)_3(OH)_3] + H_2O + e^- \rightleftharpoons [Fe(H_2O)_4(OH)_2] + OH^-$ E° = –0.56 V

$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ E° = +0.40 V
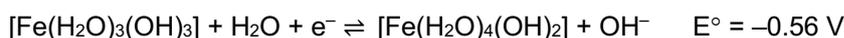
SECTION 6 – Redox titrations

1) Use of acidified KMnO$_4$ in redox titrations

- Redox reactions can be used in titrations (just as you have met acid-base reactions previously).

- Potassium manganate(VII), which contains the MnO$_4^-$ ion is a very common oxidising agent used in redox titrations.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

- It needs to be used in acidic conditions, and **dilute sulfuric acid** is the acid used. Unsuitable acids are:

  - hydrochloric acid **cannot** be used as the MnO$_4^-$ would also oxidise Cl$^-$ to Cl$_2$ so affect the volume of KMnO$_4$ required in the titration

  - conc sulfuric acid or conc nitric acid **cannot** be used as they are oxidising agents themselves so affect the volume of KMnO$_4$ required in the titration

  - ethanoic acid **cannot** be used as it is a weak acid and would not provide enough H$^+$ ions

- In a normal redox titration like this, the purple potassium manganate(VII) is in the burette. The sample being analysed is in the flask with an excess of dilute sulfuric acid.

- As the purple potassium manganate(VII) is added it reacts and forms colourless Mn^{2+}. At the end point, the purple MnO$_4^-$ ions no longer react and their colour remains. This means that the end point is the first hint of pink. It also means that the titration does not need an indicator as it is **self-indicating**.

2) Analysis of Fe^{2+}

- Fe^{2+} is analysed in redox titrations with acidified potassium manganate(VII).

- Half equation: Fe$^{2+} \rightarrow$ Fe^{3+} + e$^-$

- Overall equation: 5Fe^{2+} + MnO$_4^-$ + 8H$^+ \rightarrow$ 5Fe^{3+}+ Mn^{2+} + 4H$_2$O

- The reacting ratio is: Fe^{2+}: MnO$_4^-$ = 5 : 1

- If the iron is not in the +2 oxidation state then

  - if it is the element Fe (0) then it reacted with sulfuric acid to oxidise it to Fe^{2+} ready for analysis

  - if it is Fe (+3) then it is reacted with Zn to reduce it to Fe^{2+} ready for analysis (the remaining zinc must be removed first to stop it reducing Fe^{3+} formed in the titration back to Fe^{2+})

3) Analysis of C$_2$O$_4^{2-}$

- The ethanedioate ion (C$_2$O$_4^{2-}$) is analysed in redox titrations with acidified potassium manganate(VII).

- Half equation: C$_2$O$_4^{2-} \rightarrow$ 2CO$_2$ + 2 e$^-$

- Overall equation: 5C$_2$O$_4^{2-}$ + 2MnO$_4^-$ + 16H$^+ \rightarrow$ 10CO$_2$ + 2Mn^{2+} + 8H$_2$O

- The reacting ratio is: C$_2$O$_4^{2-}$: MnO$_4^-$ = 2½ : 1

- As the C$_2$O$_4^{2-}$ and MnO$_4^-$ ions are both negative, they repel each other and the reaction is slow and does needed warming at the start of the titration to proceed. It therefore takes a while at the start for the purple manganate(VII) to react and be decolourised.

- However, the Mn^{2+} produced in the reaction acts as a catalyst and so the reaction speeds up.

   4Mn^{2+} + MnO$_4^-$ + 8H$^+ \rightarrow$ 5Mn^{3+} + 4H$_2$O

   2Mn^{3+} + C$_2$O$_4^{2-} \rightarrow$ 2CO$_2$ + 2Mn^{2+}

- This is an example of **autocatalysis** – a reaction where one of the products as a catalyst.

Example 1   Calculate the percentage of iron in a sample of steel wire if 1.51 g of the wire was dissolved in excess of dilute sulfuric acid and the solution made up to 250 cm^3 in a volumetric flask. 25.0 cm^3 of this solution was pipetted into a conical flask and needed 25.45 cm^3 of 0.0200 mol dm^{-3} KMnO$_4$ for complete oxidation.

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Example 2   A cleaning agent called Bar Keeper's Friend contains ethanedioic acid (H$_2$C$_2$O$_4$) as the active ingredient. 2.34 g of the powder was dissolved in water and made up to 250 cm^3 in a volumetric flask. 25.0 cm^3 portions of this solution was acidified with sulfuric acid and reacted with 27.75 cm^3 of 0.00300 mol dm^{-3} KMnO$_4$ on average in a titration. Calculate the percentage by mass of the ethanedioic acid in the cleaner

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TASK 6 – Redox titrations

1   24.3 cm^3 of 0.0200 mol dm^{-3} KMnO$_4$ reacted with 20.0 cm^3 of an iron(II) solution in the presence of sulfuric acid. Calculate the concentration of the iron(II) ion.

2   3.00 g of a lawn sand containing an iron(II) salt was shaken with dilute H$_2$SO$_4$. The resulting solution required 25.00 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) to oxidise the Fe^{2+} ions in the solution to Fe^{3+} ions. Use this to calculate the percentage by mass of Fe^{2+} ions in this sample of lawn sand.

3   Calculate x in the formula $FeSO_4.xH_2O$ from the following data: 12.18 g of iron(II) sulfate crystals were made up to 500 cm^3 acidified with sulfuric acid in a volumetric flask. 25.0 cm^3 of this solution required 43.85 cm^3 of 0.0100 mol dm^{-3} $KMnO_4$ for complete oxidation.

4   An experiment was carried out to find the value of n in hydrated calcium ethanedioate, $CaC_2O_4nH_2O$. 2.01 g of the compound was dissolved in deionised water and made up to 250 cm^3 solution in a volumetric flask. When 25.0 cm^3 of this solution was acidified using an excess of dilute sulfuric acid, it was found to react with 27.50 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII).

  a) Explain why the conical flask had to be heated during this titration.

  b) Explain why after a while the managnate(VII) ions did decolourise straight away.

  c) Find the relative formula mass of hydrated calcium ethanedioate and the value of n.

5   A tablet with mass 0.940 g was dissolved in dilute sulfuric acid made up to 250 cm^3 with water. 25.0 cm^3 of this solution was titrated with 0.00133 mol dm^{-3} $KMnO_4$ requiring 32.5 cm^3 of the $KMnO_4$. Calculate the percentage by mass of Fe^{2+} in the tablet.

6   An experiment was carried out to find the value of n in hydrated iron(II) ethanedioate, $FeC_2O_4nH_2O$. 1.71 g of the compound was dissolved in deionised water and made up to 250 cm^3 solution in a volumetric flask. When 25.0 cm^3 of this solution was acidified using an excess of dilute sulfuric acid, it was found to react with 28.50 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII).

  a) Deduce the number of moles of MnO_4^- that react with one mole of $FeC_2O_4nH_2O$. Remember that both the Fe^{2+} and $C_2O_4^{2-}$ ions react.

  b) Find the relative formula mass of hydrated iron(II) ethanedioate and the value of n.

7   Ammonium iron(II) sulfate crystals have the following formula: $(NH_4)_2SO_4.FeSO_4.nH_2O$. In an experiment to find n, 8.492 g of the salt were dissolved and made up to 250 cm^3 solution with distilled water and dilute sulfuric acid in a volumetric flask. A 25.0 cm^3 portion of the solution was titrated against 0.0150 mol dm^{-3} $KMnO_4$, 22.65 cm^3 being required. Calculate n.

8   A 25.0 cm^3 aliquot of a solution containing Fe^{2+} and Fe^{3+} ions was acidified and titrated against 0.0200 mol dm^{-3} potassium manganate(VII) solution, requiring 15.0 cm^3. Zn reduces Fe^{3+} to Fe^{2+} and a second aliquot was reduced by zinc and after filtering off the excess zinc, was titrated with the same potassium manganate(VII) solution, requiring 19.0 cm^3. Calculate the concentrations of the Fe^{2+} and Fe^{3+} in the solution.

9   13.2 g of iron(III) alum were dissolved in water and reduced to an iron(II) ion solution by zinc and dilute sulfuric acid. The mixture was filtered and the filtrate and washings made up to 500 cm^3 in a standard volumetric flask. 20.0 cm^3 of this solution required 26.5 cm^3 of 0.0100 mol dm^{-3} $KMnO_4$ for oxidation. Calculate the percentage by mass of iron in iron alum.

10   A sample of solid ethanedioic acid ($H_2C_2O_4.2H_2O$) has been contaminated with potassium ethanedioate ($K_2C_2O_4.xH_2O$). A 1.780 g sample of this mixture was made up to a 250 cm^3 solution with distilled water in a volumetric flask. A 25.0 cm^3 sample was titrated against 0.100 mol dm^{-3} sodium hydroxide, requiring 17.35 cm^3. Another 25.0 cm^3 sample was acidified with sulfuric acid and titrated against 0.0200 mol dm^{-3} $KMnO_4$ solution, requiring 24.85 cm^3. Calculate x.

11   A piece of rusted iron was analysed to find out how much of the iron had been oxidised to rust [hydrated iron(III) oxide]. A small sample of the iron was dissolved in excess dilute sulfuric acid to give 250 cm^3 of solution in a volumetric flask. The solution contains Fe^{2+} ions from the unrusted iron dissolving in the acid, and, Fe^{3+} ions from the rusted iron.

  a) 25.0 cm^3 of this solution required 16.9 cm^3 of 0.0200 mol dm^{-3} $KMnO_4$ for complete oxidation of the Fe^{2+} ions. Calculate the moles of Fe^{2+} ions in the sample titrated.

  b) To a second 25.0 cm^3 of the rusted iron solution an oxidising agent was added to convert all the Fe^{2+} ions present to Fe^{3+} ions. The Fe^{3+} ions were titrated with a solution of $EDTA^{4-}(aq)$ ions and 17.6 cm^3 of 0.10 mol dm^{-3} EDTA were required. Assuming 1 mole of EDTA reacts with 1 mole of Fe^{3+} ions, calculate the moles of Fe^{3+} ions in the sample.

  c) From your calculations in (a) and (b) calculate the ratio of rusted iron to unrusted iron and hence the percentage of iron that had rusted.

SECTION 7 – Catalysis

1) What is a catalyst?

- A catalyst is a substance that increases the rate of a chemical reaction, but is not used up in the reaction.

- Catalysts work by providing an alternative route with a lower activation energy (catalysts do not alter ΔG, ΔH or ΔS for a reaction, only the activation energy).

- Catalysts speed the rate at which an equilibrium is reached by speeding up the forward and reverse reaction - they do not alter the position of the equilibrium.

2) Heterogeneous catalysis

### a) What is a heterogeneous catalyst?

- A catalyst that is in a different phase to the reactants is a heterogeneous catalyst.
- The catalyst is usually a solid and the reaction takes place on the surface.
- The bulk of industrial processes involve heterogeneous catalysis.

e.g.	Haber process	$3\,H_2\ +\ N_2\ \rightleftharpoons\ 2\,NH_3$	Fe catalyst
e.g.	Contact process	$2\,SO_2\ +\ O_2\ \rightleftharpoons\ 2\,SO_3$	V_2O_5 catalyst

b) How does a heterogeneous catalyst work?

- At least one of the reactants is **adsorbed** onto the surface (i.e. forms bonds to the atoms in the solid surface). (note that a<u>d</u>sorption is to go <u>onto</u> something, but a<u>b</u>sorption is to go <u>into</u> something).

- The places on the surface where molecules are adsorbed are called **active sites**.

- In an effective catalyst, the molecules can move about the surface, bonding to different active sites.

- The adsorption of reactants onto the surface can result in increased reaction in a number of ways:

  a) adsorption onto the surface effectively concentrates the reactants, i.e. brings them closer together than in the gas phase, so increasing the likelihood of collision;

  b) it may weaken some of the bonds in the molecule, making reaction easier;

  c) it may position the molecule in a favourable orientation for reaction.

- For the catalyst to work, molecules must be adsorbed onto the surface. However if:

  adsorption is too weak: not many molecules will be adsorbed so the catalyst will have very little effect

  adsorption is too strong: molecules will not be able to move around the active sites, and so be less likely to meet another reactant and so be less likely to react (also any product will tend to remain adsorbed on the surface)
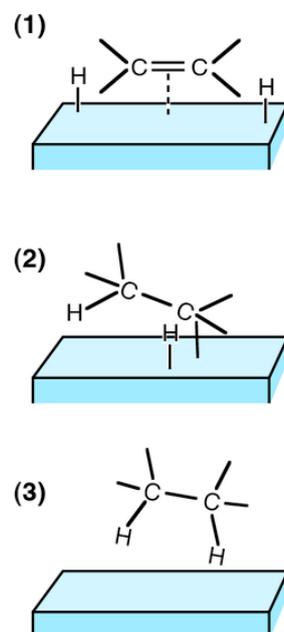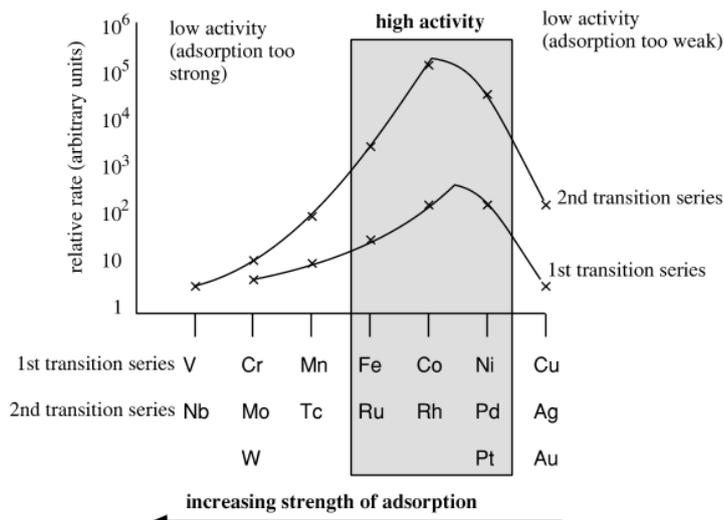
- There is a fine balance between adsorption being too weak and too strong. For a catalyst to be effective it must have adsorption of the right strength. Examples are:

  Ag   adsorption usually too weak - poor catalyst

  W   adsorption usually too strong - poor catalyst

  Ni & Pt   ideal adsorption strength - so make excellent catalysts

c) The nature of the catalyst

- It is obvious that the larger the surface area of these catalysts, the less quantity of catalyst that is needed to produce the same effect.

- Many surface catalysts are very expensive, and so maximising surface area has important cost savings.

- The surface area is maximised by using a very thin coating of the catalyst on some type of support medium (a support is required as the layer is too thin to support itself - often a ceramic "honeycomb" structure is used as support - note that the catalyst must be able to bind to the support).
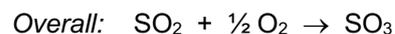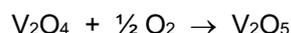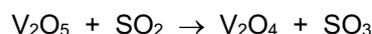
d) Catalyst poisoning

- Some surface catalysts are prone to poisoning, where other substances adsorb strongly to the surface, blocking the active sites.

- This lowers the efficiency of the catalyst, or makes it totally ineffective depending on the extent of the poisoning.

- These poisons are extremely difficult to remove and the catalyst is ruined, which can be very costly (particularly with expensive catalysts).

  e.g. lead poisoning of catalytic converters in cars - both the Rh and Pt catalysts are poisoned by lead (from leaded petrol) - and are very expensive to replace.

  e.g. sulphur poisoning in the Haber process - the hydrogen is obtained from natural gas which is contaminated by S, which if not removed will poison the Fe catalyst (S is added to natural gas to give it an odour, so leaks can be smelt).

e) Contact process

- More concentrated H_2SO_4 is manufactured than any other chemical. The key step in this process (the Contact process) is the conversion of SO_2 to SO_3 which is a slow, reversible reaction.

- It is catalysed by vanadium (V) oxide, V_2O_5.

$$V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$$

$$V_2O_4 + \tfrac{1}{2}O_2 \rightarrow V_2O_5$$

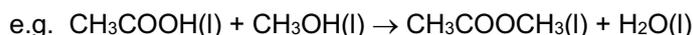$$\textit{Overall:} \quad SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3$$

3) Homogeneous catalysis
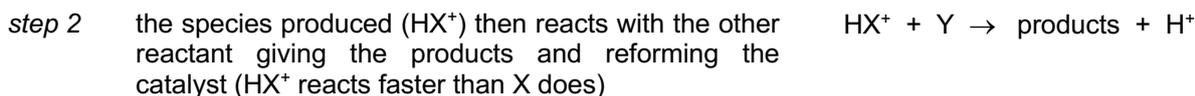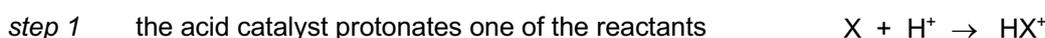
a) What is a homogeneous catalyst?

- A homogeneous catalyst is one that is in the same phase as the reactants.

- Most reactions involving homogeneous catalysts take place in solution (where all species are either liquids or are dissolved, so they are all in the same phase).

- Reactions involving homogeneous catalysis proceed via an intermediate species formed from a reactant and the catalyst, which then reacts further and regenerates the catalyst.

b) How does an acid homogeneous catalyst work?

- An example of an acid catalysed reaction is esterification:

$$\text{e.g.} \quad CH_3COOH(l) + CH_3OH(l) \rightarrow CH_3COOCH_3(l) + H_2O(l)$$

- Imagine a reaction catalysed by an acid: $\quad X + Y \xrightarrow{\text{cat } H^+} \text{products}$

   step 1   the acid catalyst protonates one of the reactants $X + H^+ \rightarrow HX^+$

   step 2   the species produced (HX^+) then reacts with the other reactant giving the products and reforming the catalyst (HX^+ reacts faster than X does) $HX^+ + Y \rightarrow \text{products} + H^+$

c) How does a transition metal homogeneous catalyst work?

- Transition metal compounds have the ability to vary their oxidation states which allows them to act as catalysts.

   Example 1 – *reaction between iodide ions and peroxodisulfate ions – catalyst Fe^{2+} or Fe^{3+}*
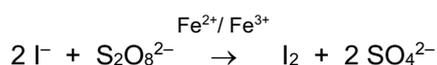
   $$2\,I^- + S_2O_8^{2-} \xrightarrow{Fe^{2+}/\,Fe^{3+}} I_2 + 2\,SO_4^{2-}$$

   - This reaction is very slow in the absence of a catalyst because it involves the reaction of two negative ions (they repel each other so collision is difficult).
   - However it is catalysed by $Fe^{2+}(aq)$ or $Fe^{3+}(aq)$, which can act as a catalyst because it easily changes between the oxidation states Fe(+2) and Fe(+3).

   The catalysed reaction proceeds by the Fe^{2+} reducing $S_2O_8^{2-}$ to SO_4^{2-} (the Fe^{2+} is oxidised to Fe^{3+}). $2\,Fe^{2+} + S_2O_8^{2-} \rightarrow 2\,Fe^{3+} + 2\,SO_4^{2-}$

   The Fe^{3+} then oxidises the I^- to I_2, reforming Fe^{2+}. $2\,Fe^{3+} + 2\,I^- \rightarrow 2\,Fe^{2+} + I_2$

   The reactions can occur either way round – hence both Fe^{2+} and Fe^{3+} can act as catalyst

   NB $S_2O_8^{2-} + 2\,e^- \rightleftharpoons 2\,SO_4^{2-}$ $E° = +2.01$ V
   $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E° = +0.77$ V
   $I_2 + 2\,e^- \rightleftharpoons 2\,I^-$ $E° = +0.54$ V

Example 2 – *autocatalysis in the reaction between manganate(VII) ions and ethanedioate ions*
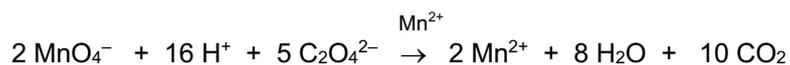
$$2\,MnO_4^- \ + \ 16\,H^+ \ + \ 5\,C_2O_4^{2-} \ \xrightarrow{Mn^{2+}} \ 2\,Mn^{2+} \ + \ 8\,H_2O \ + \ 10\,CO_2$$
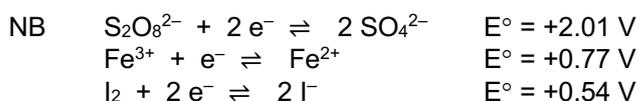
- This reaction is very slow in the absence of a catalyst because it involves the reaction of two negative ions (they repel each other so collision is difficult).

- However it is catalysed by Mn^{2+}(aq), which can act as a catalyst because it easily changes between the oxidation states Mn(+2) and Mn(+3).

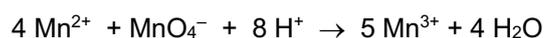- The catalyst is a product of the reaction – this reaction is slow until some Mn^{2+} is formed, but then it speeds up as catalyst is formed.

- Reactions which produce their own catalyst are known as autocatalysis reactions

  The catalysed reaction proceeds by the Mn^{2+} reducing MnO_4^- to Mn^{3+}.

  $$4\,Mn^{2+} \ + \ MnO_4^- \ + \ 8\,H^+ \ \rightarrow \ 5\,Mn^{3+} + 4\,H_2O$$

  The Mn^{3+} then oxidises the $C_2O_4^{2-}$ to CO_2, reforming Mn^{2+}.

  $$2\,Mn^{3+} \ + \ C_2O_4^{2-} \ \rightarrow \ 2\,CO_2 \ + \ 2\,Mn^{2+}$$
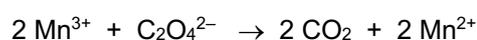
SECTION 8 – Reactions of ions in aqueous solution

1) Metal aqua ions

- When in aqueous solution, without the presence of other ions, metal ions exist as "metal aqua ions" – these have a central metal ion with six water ligands. (**NB** – this section includes Al^{3+} which is __not__ a transition metal ion).

- When salts are crystallised from solution, these metal aqua ions are often present in the crystals. For example, the pink colour in crystals of hydrated cobalt (II) chloride is due to the same ion $[Co(H_2O)_6]^{2+}$ as is in solutions of cobalt (II) chloride.

Complex	$[Cu(H_2O)_6]^{2+}$	$[Fe(H_2O)_6]^{2+}$	$[Fe(H_2O)_6]^{3+}$	$[Al(H_2O)_6]^{3+}$
Colour	blue	green	pale violet*	colourless

* Note that solutions containing $[Fe(H_2O)_6]^{3+}$ appear yellow/orange rather than pale violet due to the presence of small amounts of $[Fe(H_2O)_5(OH)]^{2+}$ formed by hydrolysis.

2) Reactions of metal aqua ions

1	**Hydrolysis**	loss of H^+ from H_2O ligands (O-H bond in H_2O ligand breaks)
2	**Substitution**	replacement of H_2O by other ligands (metal-ligand bond breaks)
3	**Redox**	metal changes oxidation state (gain or loss of electrons)

3) Hydrolysis reaction

- In solution, metal aqua ions lose H^+ from one or more H_2O ligands in a **hydrolysis** reaction.

Hydrolysis of M^{2+} aqua ions	Hydrolysis of M^{3+} aqua ions
$[M(H_2O)_6]^{2+} \rightleftharpoons [M(H_2O)_5(OH)]^+ + H^+$	$[M(H_2O)_6]^{3+} \rightleftharpoons [M(H_2O)_5(OH)]^{2+} + H^+$
$[M(H_2O)_5(OH)]^+ \rightleftharpoons \mathbf{[M(H_2O)_4(OH)_2]} + H^+$	$[M(H_2O)_5(OH)]^{2+} \rightleftharpoons [M(H_2O)_4(OH)_2]^+ + H^+$
$\mathbf{[M(H_2O)_4(OH)_2]} \rightleftharpoons [M(H_2O)_3(OH)_3]^- + H^+$	$[M(H_2O)_4(OH)_2]^+ \rightleftharpoons \mathbf{[M(H_2O)_3(OH)_3]} + H^+$
$[M(H_2O)_3(OH)_3]^- \rightleftharpoons [M(H_2O)_2(OH)_4]^{2-} + H^+$	$\mathbf{[M(H_2O)_3(OH)_3]} \rightleftharpoons [M(H_2O)_2(OH)_4]^- + H^+$
$[M(H_2O)_2(OH)_4]^{2-} \rightleftharpoons [M(H_2O)(OH)_5]^{3-} + H^+$	$[M(H_2O)_2(OH)_4]^- \rightleftharpoons [M(H_2O)(OH)_5]^{2-} + H^+$
$[M(H_2O)(OH)_5]^- \rightleftharpoons [M(OH)_6]^{4-} + H^+$	$[M(H_2O)(OH)_5]^{2-} \rightleftharpoons [M(OH)_6]^{3-} + H^+$

- The neutral complex ions, e,g. $M(H_2O)_4(OH)_2$ or $M(H_2O)_3(OH)_3$ are insoluble in water and form as precipitates. They are known as metal(II) hydroxides or metal(III) hydroxides. Sometimes they are simply written as $M(OH)_2$ or $M(OH)_3$.

4) Acidity of solutions of aqueous metal ions

- In solution, metal aqua ions lose H^+ from one or more H_2O ligands.

- In water, the main species present is still $[M(H_2O)_6]^{n+}$, but some hydrolysis happens making the solution acidic.

Aqua ion	$[M(H_2O)_6]^+$	$[M(H_2O)_6]^{2+}$	$[M(H_2O)_6]^{3+}$	$[M(H_2O)_6]^{4+}$
pH of typical solution	7	6	3	0

- The higher the charge on the metal in the metal aqua ion, the more acidic the solution.

- WHY? - to lose H^+, the O-H bond in a water ligand must break. To break, the electrons in the bond are pulled towards the O. The higher the charge on the metal ion and/or the smaller the metal ion, the stronger the pull on the electrons away from the H and towards the O, breaking the O-H bond.

- For example, therefore a solution containing $[Fe(H_2O)_6]^{3+}$ is more acidic than a solution of similar concentration containing $[Fe(H_2O)_6]^{2+}$.
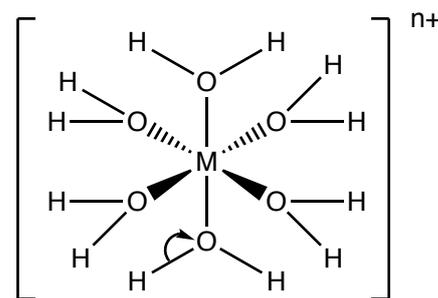
5) Reaction with bases

- If a base is added to a metal aqua ion, hydrolysis may take place (the base removes the H^+ pushing the equilibria right). Common bases are hydroxide ions (OH^-), ammonia (NH_3) and carbonate ions (CO_3^{2-}).

- Note that other reactions could also take place (e.g. ligand substitution with NH_3 or precipitation with CO_3^{2-}).

- If hydrolysis happens, the insoluble, neutral complex will form as a precipitate.

- With addition of an excess of the base, the insoluble complex may react further (or may not!).

6) Reaction of metal aqua ions with NaOH(aq)

aqua ion	reaction	observation	equation
$Fe(H_2O)_6^{2+}$	add some OH^-	green solution → green precipitate	$[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow [Fe(H_2O)_4(OH)_2] + 2H_2O$
	add XS OH^-	no visible reaction	–
$Cu(H_2O)_6^{2+}$	add some OH^-		
	add XS OH^-		
$Fe(H_2O)_6^{3+}$	add some OH^-		
	add XS OH^-		
$Al(H_2O)_6^{3+}$	add some OH^-		
	add XS OH^-		

Summary	- Metal(II) aqua ions react with NaOH to form precipitates of metal(II) hydroxides by hydrolysis - Metal(III) aqua ions react with NaOH to form precipitates of metal(III) hydroxides by hydrolysis - Al(OH)_3 reacts further with excess NaOH to form $[Al(H_2O)_2(OH)_4]^-$

7) Reaction of metal aqua ions with NH$_3$(aq)

aqua ion	reaction	observation	equation
Fe(H$_2$O)$_6$$^{2+}$	add some NH$_3$	green solution → green precipitate	[Fe(H$_2$O)$_6$]$^{2+}$+ 2NH$_3$ → [Fe(H$_2$O)$_4$(OH)$_2$] + 2NH$_4$$^+$
	add XS NH$_3$	no visible reaction	_
Cu(H$_2$O)$_6$$^{2+}$	add some NH$_3$		
	add XS NH$_3$		
Fe(H$_2$O)$_6$$^{3+}$	add some NH$_3$		
	add XS NH$_3$		
Al(H$_2$O)$_6$$^{3+}$	add some NH$_3$		
	add XS NH$_3$		

Summary	• Metal(II) aqua ions react with NH$_3$ to form precipitates of metal(II) hydroxides by hydrolysis
	• Metal(III) aqua ions react with NH$_3$ to form precipitates of metal(III) hydroxides by hydrolysis
	• Cu(+2) reacts further with excess NH$_3$ to form [Cu(H$_2$O)$_2$(NH$_3$)$_4$]$^{2+}$ by ligand substitution

8) Reaction of metal aqua ions with Na$_2$CO$_3$(aq)

aqua ion	reaction	observation	equation
Fe(H$_2$O)$_6$$^{2+}$	add some CO$_3$$^{2-}$	green solution → green precipitate	[Fe(H$_2$O)$_6$]$^{2+}$+ CO$_3$$^{2-}$ → FeCO$_3$ + 6H$_2$O
Cu(H$_2$O)$_6$$^{2+}$	add some CO$_3$$^{2-}$		
Fe(H$_2$O)$_6$$^{3+}$	add some CO$_3$$^{2-}$		
Al(H$_2$O)$_6$$^{3+}$	add some CO$_3$$^{2-}$		

Summary	• Metal(II) aqua ions react with CO$_3$$^{2-}$ to form precipitates of metal(II) carbonates by precipitation
	• Metal(III) aqua ions react with CO$_3$$^{2-}$ to form bubbles of CO$_2$ gas and precipitates of metal(III) hydroxides by hydrolysis
	• The difference is because [M(H$_2$O)$_6$]$^{3+}$ is acidic enough to react in an acid-base reaction with CO$_3$$^{2-}$ ions by hydrolysis, but [M(H$_2$O)$_6$]$^{2+}$ is not acidic enough

8) Acid-base character of metal hydroxide precipitates

add excess acid		metal hydroxide	add excess alkali	
observation	equation		observation	Equation
green ppt → green solution	$[Fe(H_2O)_4(OH)_2] + 2H^+ \rightarrow$ $[Fe(H_2O)_6]^{2+}$	$[Fe(H_2O)_4(OH)_2]$	no visible reaction	–
		$[Cu(H_2O)_4(OH)_2]$		
		$[Fe(H_2O)_3(OH)_3]$		
		$[Al(H_2O)_3(OH)_3]$		

Type of hydroxide	**Acidic hydroxide**	**Amphoteric hydroxide**	**Basic hydroxide**
What it means	hydroxide that only reacts with bases	hydroxide that reacts with both acids and bases	hydroxide that only reacts with acids
Which hydroxides		$[Al(H_2O)_3(OH)_3]$	$[Cu(H_2O)_4(OH)_2]$ $[Fe(H_2O)_4(OH)_2]$ $[Fe(H_2O)_3(OH)_3]$

9) Substitution reactions with similar sized ligands (e.g. NH_3)

aqua ion	reaction	observation	equation
$Fe(H_2O)_6^{2+}$	add excess NH_3	green solution → green precipitate	$[Fe(H_2O)_6]^{2+}+ 2NH_3 \rightarrow [Fe(H_2O)_4(OH)_2] + 2NH_4^+$
$Cu(H_2O)_6^{2+}$	add excess NH_3		
$Fe(H_2O)_6^{3+}$	add excess NH_3		
$Al(H_2O)_6^{3+}$	add excess NH_3		

Summary	• Metal(II) aqua ions react with NH_3 to form precipitates of metal(II) hydroxides by hydrolysis
	• Metal(III) aqua ions react with NH_3 to form precipitates of metal(III) hydroxides by hydrolysis
	• Cu(+2) reacts further with excess NH_3 to form $[Cu(H_2O)_2(NH_3)_4]^{2+}$ by ligand substitution

10) Substitution reactions with bigger ligands (add conc HCl to provide Cl⁻ ligands)

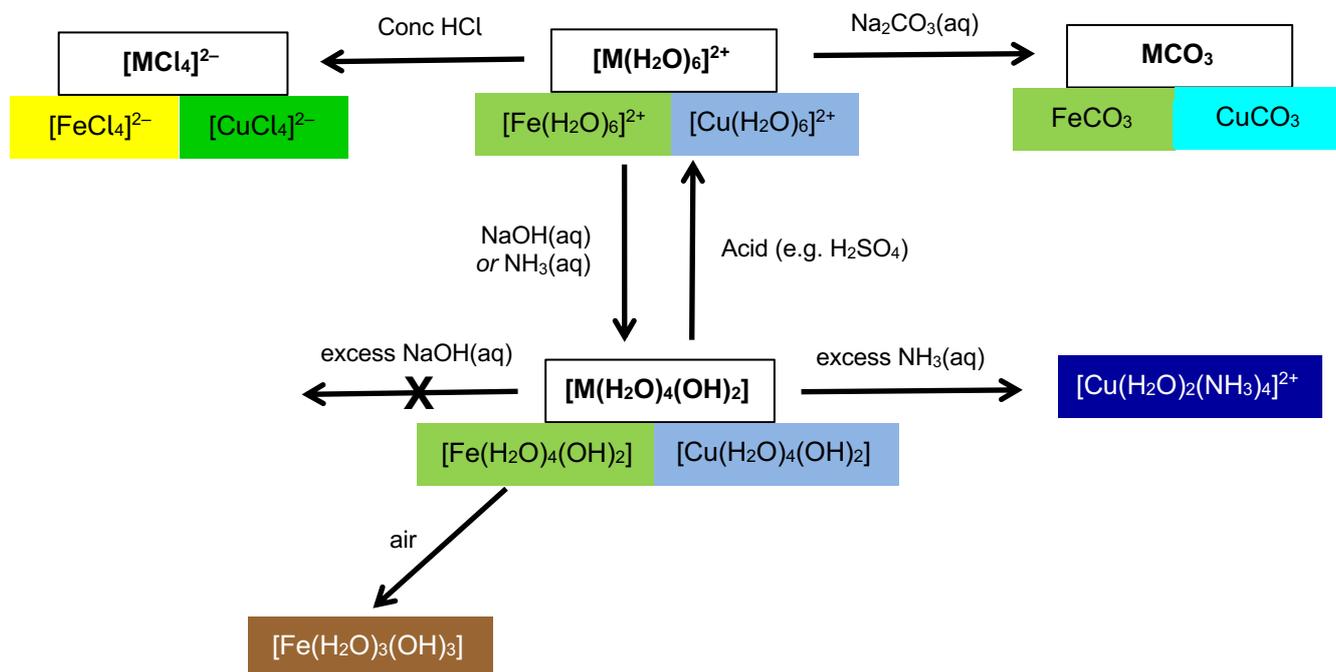| aqua ion	reaction	observation	equation
$Fe(H_2O)_6{}^{2+}$	add excess Cl⁻	green solution → yellow solution	$[Fe(H_2O)_6]^{2+} + 4Cl^- \rightarrow [FeCl_4]^{2-} + 6H_2O$
$Cu(H_2O)_6{}^{2+}$	add excess Cl⁻		
$Fe(H_2O)_6{}^{3+}$	add excess Cl⁻		
$Al(H_2O)_6{}^{3+}$	add excess Cl⁻		

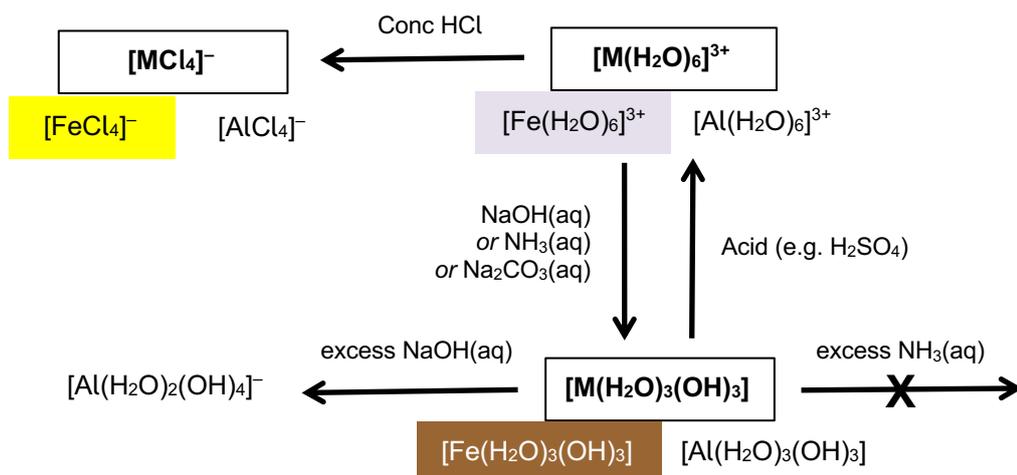| ***Summary***	• Metal aqua ions react with conc HCl to undergo substitution reactions in which the six H_2O ligands are replaced by four Cl⁻ ligands.

SUMMARY OF REACTIONS OF AQUA IONS

	$[Fe(H_2O)_6]^{2+}$ green solution	$[Cu(H_2O)_6]^{2+}$ blue solution	$[Fe(H_2O)_6]^{3+}$ pale violet but solution appears orange due to hydrolysis to some $[Fe(H_2O)_5(OH)]^{2+}$	$[Al(H_2O)_6]^{3+}$ colourless solution
In aqueous solution				
add NaOH(aq) or dropwise	$[Fe(H_2O)_4(OH)_2]$ green precipitate (darkens on standing due to oxidation to $[Fe(H_2O)_3(OH)_3]$)	$[Cu(H_2O)_4(OH)_2]$ blue precipitate	$[Fe(H_2O)_3(OH)_3]$ brown precipitate	$[Al(H_2O)_3(OH)_3]$ white precipitate
then excess NaOH(aq)	no further reaction	no further reaction	no further reaction	$[Al(H_2O)_2(OH)_4]^-$ re-dissolves to give colourless solution
add NH₃(aq) or dropwise	$[Fe(H_2O)_4(OH)_2]$ green precipitate (darkens on standing due to oxidation to $[Fe(H_2O)_3(OH)_3]$)	$[Cu(H_2O)_4(OH)_2]$ blue precipitate	$[Fe(H_2O)_3(OH)_3]$ brown precipitate	$[Al(H_2O)_3(OH)_3]$ white precipitate
then excess NH₃(aq)	no further reaction	$[Cu(H_2O)_2(NH_3)_4]^{2+}$ deep blue solution	no further reaction	no further reaction
add Na₂CO₃(aq)	$FeCO_3$ green precipitate	$CuCO_3$ blue-green precipitate	$[Fe(H_2O)_3(OH)_3]$ brown precipitate & bubbles of gas (CO_2)	$[Al(H_2O)_3(OH)_3]$ white precipitate & bubbles of gas (CO_2)
add conc HCl	$[FeCl_4]^{2-}$ yellow solution	$[CuCl_4]^{2-}$ green solution	$[FeCl_4]^-$ yellow solution	$[AlCl_4]^-$ colourless solution

[M(H₂O)₆]²⁺(aq) SUMMARY

$[M(H_2O)_6]^{2+}$ **SUMMARY**

$[MCl_4]^{2-}$ ← Conc HCl — **$[M(H_2O)_6]^{2+}$** — Na₂CO₃(aq) → **MCO₃**

$[FeCl_4]^{2-}$ $[CuCl_4]^{2-}$ | $[Fe(H_2O)_6]^{2+}$ $[Cu(H_2O)_6]^{2+}$ | $FeCO_3$ $CuCO_3$

NaOH(aq) *or* NH₃(aq) ↓   ↑ Acid (e.g. H₂SO₄)

excess NaOH(aq) ✗ ← **$[M(H_2O)_4(OH)_2]$** → excess NH₃(aq) → **$[Cu(H_2O)_2(NH_3)_4]^{2+}$**

$[Fe(H_2O)_4(OH)_2]$ $[Cu(H_2O)_4(OH)_2]$

air ↘

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

[M(H₂O)₆]³⁺(aq) SUMMARY

$[M(H_2O)_6]^{3+}$ **SUMMARY**

$[MCl_4]^{-}$ ← Conc HCl — **$[M(H_2O)_6]^{3+}$**

$[FeCl_4]^{-}$ $[AlCl_4]^{-}$ | $[Fe(H_2O)_6]^{3+}$ $[Al(H_2O)_6]^{3+}$

NaOH(aq) *or* NH₃(aq) *or* Na₂CO₃(aq) ↓   ↑ Acid (e.g. H₂SO₄)

excess NaOH(aq) → $[Al(H_2O)_2(OH)_4]^{-}$ ← **$[M(H_2O)_3(OH)_3]$** → excess NH₃(aq) ✗

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

∴

TASK 9 – REACTIONS OF INORGANIC COMPLEXES

For each of the following reactions, write observations and equations for what happens.

1 Addition of sodium hydroxide solution dropwise and then in excess to a solution of copper(II) sulfate.

2 Addition of ammonia solution dropwise and then in excess to a solution of aluminium nitrate.

3 Addition of sodium carbonate solution dropwise and then in excess to a solution of iron(II) nitrate.

4 Addition of sodium carbonate solution dropwise and then in excess to a solution of iron(III) nitrate.

5 Addition of concentrated hydrochloric acid solution dropwise and then in excess to a solution of iron(III) nitrate.

6   Addition of sodium hydroxide solution dropwise and then in excess to a solution of aluminium sulfate.

7   Addition of ammonia solution dropwise and then in excess to a solution of copper(II) nitrate.

8   Addition of concentrated hydrochloric acid solution dropwise and then in excess to a solution of cobalt(II) nitrate.

9   Addition of sodium hydroxide solution dropwise and then in excess to a solution of iron(II) sulfate.

10   Addition of concentrated hydrochloric acid solution dropwise and then in excess to a solution of zinc(II) nitrate.

11   Addition of sodium carbonate solution dropwise and then in excess to a solution of zinc(II) nitrate.

ANSWERS to ALL tasks plus FULL WORKED solutions are available to subscribers of **www.chemsheets.co.uk**.

TASK 6 – Redox titrations

1 0.122 mol dm^{-3} (3sf)

2 4.65% (3sf)

3 $x = 7$ (nearest integer), $M_r = 126$ (3sf)

4c $n = 1$ (nearest integer), $M_r = 146$ (3sf)

5 12.8% (3sf)

6 $1:0.6$; $x = 2$ (nearest integer), $M_r = 180$ (3sf)

7 $x = 12$ (nearest integer), $M_r = 500$ (3sf)

8 $[Fe^{2+}] = 0.0600$ mol dm^{-3} (3sf); $[Fe^{3+}] = 0.0160$ mol dm^{-3} (3sf)

9   % Fe $= 14.0\%$ (3sf)

10 $x = 1$ (nearest integer), $M_r = 183$ (3sf)

11 4.0% (sf is arguable!)