Edexcel International A Level (IAL) Chemistry

Your notes

Transition Metal Reactions

Contents

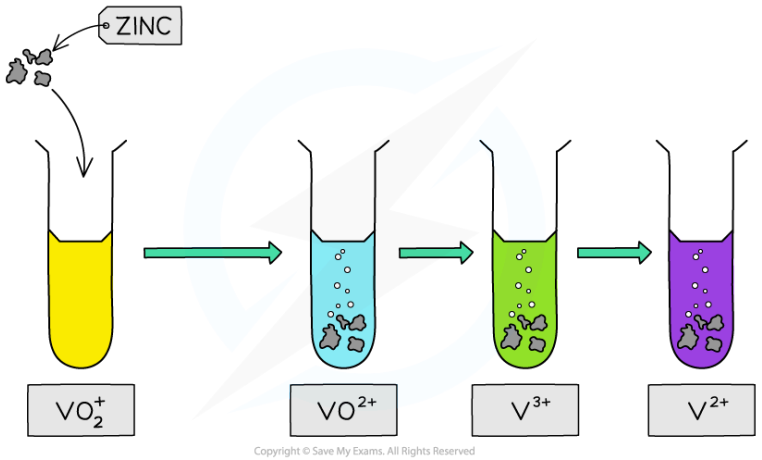
Your notes

Vanadium – Colours & Oxidation States

- Vanadium is a transition metal which has variable oxidation states
- The table below shows the important ones you need to be aware of

Oxidation number	Formula	Name	Colour of aqueous solutions
+2	V^{2+}	Vanadium (II)	Purple
+3	V^{3+}	Vanadium (III)	Green
+4	VO^{2+}	Oxovanadium (IV)	Blue
+5	VO_2^+	Dioxovanadium (V)	Yellow

- The variation in oxidation states of transition metal ions is illustrated by the reaction of zinc with ammonium vanadate(V) (also known as ammonium metavanadate) under acidic conditions
- Vanadium had four common oxidation states, from +2 to +5
- Zinc is a reducing agent that is capable to reducing vanadium(V) to vanadium(II) in a sequence of steps accompanied by vibrant colour changes



The reduction of vanadate(V) ions by zinc in acidic conditions is one of the most colourful reactions in chemistry

Vanadium – Interconversions of Ions

- For vanadium, we need to consider the following standard electrode potential values

Your notes

	Redox equation	$E^{\ominus}$ value
1.	$V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$	−1.18 V
2.	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76 V
3.	$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	−0.26 V
4.	$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34 V
5.	$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00 V

- The half equations are arranged from the most negative E^{θ} at the top to the most positive E^{θ} at the bottom
  - The strongest oxidising agent is the reactant from the electrode reaction with the most positive standard electrode potential
    - In this case, the most positive value is + 1.00 V, which means that VO_2^+ is the strongest oxidising agent
  - The strongest reducing agent is the product from the electrode reaction with the most negative standard electrode potential
    - In this case, the most negative value is – 1.18 V, which means that V is the strongest reducing agent
- For all of the following reactions, we will use zinc as the reducing agent

Reduction of V from +5 to +4 by Zn

- Vanadium is being reduced from an oxidation number of +5 to +4 in half equation 5
- So, the two half equations we need to consider are:
  - 2. $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^{\theta} = -0.76$ V
  - 5. $VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$ $E^{\theta} = +1.00$ V
- Half equation 5 has the most positive standard electrode potential, E^{θ}, value
  - Therefore, this is the reduction reaction
  - $VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$
- Half equation 2 has the least positive standard electrode potential, E^{θ}, value
  - Therefore, this is the oxidation reaction and needs to be reversed
  - $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$


Your notes

- We can obtain the overall equation by combining the reduction equation (half equation 5) and the oxidation equation (the reversed half equation 2)
  - **Remember:** When combining half equations, they must have the same number of electrons in both equations

$2VO_2^+ (aq) + 4H^+ (aq) + 2e^-$	⇌	$2VO^{2+} (aq) + 2H_2O (l)$
$Zn (s)$	⇌	$Zn^{2+} (aq) + 2e^-$

  - The equal number of electrons on both sides of the equation cancel out to give the overall equation:

$$2VO_2^+ (aq) + 4H^+ (aq) + Zn (s) \rightleftharpoons 2VO^{2+} (aq) + Zn^{2+} (aq) + 2H_2O (l)$$

Reduction of V from +4 to +3 by Zn

- Vanadium is being reduced from an oxidation number of +4 to +3 in half equation 4
- So, the two half equations we need to consider are:
  - 2. $Zn^{2+} (aq) + 2e^- \rightleftharpoons Zn (s)$ $E^\theta = -0.76\,V$
  - 4. $VO^{2+} (aq) + 2H^+ (aq) + e^- \rightleftharpoons V^{3+} (aq) + H_2O (l)$ $E^\theta = +0.34\,V$
- Half equation 4 has the most positive standard electrode potential, E^θ, value
  - Therefore, this is the reduction reaction
  - $VO^{2+} (aq) + 2H^+ (aq) + e^- \rightleftharpoons V^{3+} (aq) + H_2O (l)$
- Half equation 2 has the least positive standard electrode potential, E^θ, value
  - Therefore, this is the oxidation reaction and needs to be reversed
  - $Zn (s) \rightleftharpoons Zn^{2+} (aq) + 2e^-$
- We can obtain the overall equation by combining the reduction equation (half equation 5) and the oxidation equation (the reversed half equation 2)
  - **Remember:** When combining half equations, they must have the same number of electrons in both equations

$2VO^{2+} (aq) + 4H^+ (aq) + 2e^-$	⇌	$2V^{3+} (aq) + 2H_2O (l)$
$Zn (s)$	⇌	$Zn^{2+} (aq) + 2e^-$

  - The equal number of electrons on both sides of the equation cancel out to give the overall equation:

$$2VO^{2+} (aq) + 4H^+ (aq) + Zn (s) \rightleftharpoons 2V^{3+} (aq) + Zn^{2+} (aq) + 2H_2O (l)$$

Reduction of V from +3 to +2 by Zn

- Vanadium is being reduced from an oxidation number of +3 to +2 in half equation 3
- So, the two half equations we need to consider are:
  - 2. $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^\theta = -0.76\,V$
  - 3. $V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$ $E^\theta = -0.26\,V$
- Half equation 3 has the most positive / least negative standard electrode potential, E^θ, value
  - Therefore, this is the reduction reaction
  - $V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$
- Half equation 2 has the least positive standard electrode potential, E^θ, value
  - Therefore, this is the oxidation reaction and needs to be reversed
  - $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$
- We can obtain the overall equation by combining the reduction equation (half equation 5) and the oxidation equation (the reversed half equation 2)
  - **Remember:** When combining half equations, they must have the same number of electrons in both equations

$\mathbf{2V^{3+}(aq) + 2e^-}$	$\rightleftharpoons$	$\mathbf{2V^{2+}(aq)}$
$\mathbf{Zn(s)}$	$\rightleftharpoons$	$\mathbf{Zn^{2+}(aq) + 2e^-}$

  - The equal number of electrons on both sides of the equation cancel out to give the overall equation:

$$\mathbf{2V^{3+}(aq) + Zn(s) \rightleftharpoons 2V^{2+}(aq) + Zn^{2+}(aq)}$$

Reduction of V from +2 to 0 by Zn

- Vanadium is being reduced from an oxidation number of +3 to +2 in half equation 1
- So, the two half equations we need to consider are:
  - 2. $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^\theta = -0.76\,V$
  - 1. $V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$ $E^\theta = -1.18\,V$
- Half equation 1 has the most negative standard electrode potential, E^θ, value
  - Therefore, this is the oxidation reaction and needs to be reversed
  - $V(s) \rightleftharpoons V^{2+}(aq) + 2e^-$
- Half equation 2 has the most positive / least negative standard electrode potential, E^θ, value
  - Therefore, this is the reduction reaction
  - $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$

Your notes

- We can obtain the overall equation by combining the reduction equation (half equation 5) and the oxidation equation (the reversed half equation 2)
  - When combining these half equations, there is no need to change them as they have the same number of electrons in both equations

$V(s)$	$\rightleftharpoons$	$V^{2+}(aq) + 2e^-$
$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$

  - The equal number of electrons on both sides of the equation cancel out to give the overall equation:

$$V(s) + Zn^{2+}(aq) \rightleftharpoons V^{2+}(aq) + Zn(s)$$

- Zn is not electron releasing with respect to V^{2+}
  - This means this reaction is not thermodynamically feasible

Predicting oxidation reactions

- The same method can be used to predict whether a given oxidising agent will oxidise a vanadium species to one with a higher oxidation number

Examiner Tips and Tricks

It is important to not get confused between the two oxo ions of vanadium VO_2^+ and VO^{2+}

Your notes

Your notes

Chromium – Reduction & Oxidation

- For chromium we need to consider the following standard electrode potential values

	Redox equation	$E^{\ominus}$ value
1.	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76 V
2.	$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$	−0.41 V
3.	$CrO_4^{2-}(aq) + 4H_2O(l) + 3e^- \rightleftharpoons Cr(OH)_3(aq) + 5OH^-(aq)$	−0.13 V
4.	$H_2O_2(aq) + 2e^- \rightleftharpoons 2OH^-(aq)$	+1.24 V
5.	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33 V

- The half equations are arranged from the most negative E^{θ} at the top to the most positive E^{θ} at the bottom
  - The strongest oxidising agent is the reactant from the electrode reaction with the most positive standard electrode potential
    - In this case, the most positive value is + 1.33 V, which means that $Cr_2O_7^{2-}(aq)$ is the strongest oxidising agent
  - The strongest reducing agent is the product from the electrode reaction with the most negative standard electrode potential
    - In this case, the most negative value is – 0.76 V, which means that Zn (s) is the strongest reducing agent

Oxidation of Cr from +3 to +6 by H_2O_2

- The two half equations we need to consider are 3 and 4
- Chromium is being oxidised from an oxidation number of +6 to +3 in half equation 3
- So, the two half equations we need to consider are:
  - 3. $CrO_4^{2-}(aq) + 4H_2O(l) + 3e^- \rightleftharpoons Cr(OH)_3(aq) + 5OH^-(aq)$ $E^{\theta} = -0.13\,V$
  - 4. $H_2O_2(aq) + 2e^- \rightleftharpoons 2OH^-(aq)$ $E^{\theta} = +1.24\,V$
- Half equation 4 has the most positive standard electrode potential, E^{θ}, value
  - Therefore, this is the reduction reaction
  - $H_2O_2(aq) + 2e^- \rightleftharpoons 2OH^-(aq)$

- Half equation 3 has the least positive standard electrode potential, E^{θ}, value
  - Therefore, this is the oxidation reaction and needs to be reversed
  - $Cr(OH)_3\,(aq) + 5OH^-\,(aq) \rightleftharpoons CrO_4^{2-}\,(aq) + 4H_2O\,(l) + 3e$
- We can obtain the overall equation by combining the reduction equation (half equation 4) and the oxidation equation (the reversed half equation 3)
  - **Remember:** When combining half equations, they must have the same number of electrons in both equations

$3H_2O_2\,(aq) + 6e^-$	$\rightleftharpoons$	$6OH^-\,(aq)$
$2Cr(OH)_3\,(aq) + 10OH^-\,(aq)$	$\rightleftharpoons$	$2CrO_4^{2-}\,(aq) + 8H_2O\,(l) + 6e^-$

  - The equal number of electrons on both sides of the equation cancel out and $6OH^-\,(aq)$ cancel out on both sides to give the overall equation:

$$2Cr(OH)_3\,(aq) + 4OH^-\,(aq) + H_2O_2\,(aq) \rightleftharpoons CrO_4^{2-}\,(aq) + 8H_2O\,(l)$$

- This reaction is carried out in alkaline conditions due to the presence of OH^- ions in the equation

Reduction of Cr from +6 to +3 by Zn

- Chromium is being reduced from an oxidation number of +6 to +3 in half equation 5
- So, the two half equations we need to consider are:
  - 1. $Zn^{2+}\,(aq) + 2e^- \rightleftharpoons Zn\,(s) \quad E^{\theta} = -0.76\,V$
  - 5. $Cr_2O_7^{2-}\,(aq) + 14H^+\,(aq) + 6e^- \rightleftharpoons 2Cr^{3+}\,(aq) + 7H_2O\,(l) \quad E^{\theta} = +1.33\,V$
- Half equation 5 has the most positive standard electrode potential, E^{θ}, value
  - Therefore, this is the reduction reaction
  - $Cr_2O_7^{2-}\,(aq) + 14H^+\,(aq) + 6e^- \rightleftharpoons 2Cr^{3+}\,(aq) + 7H_2O\,(l)$
- Half equation 1 has the least positive / most negative standard electrode potential, E^{θ}, value
  - Therefore, this is the oxidation reaction and needs to be reversed
  - $Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2e^-$
- We can obtain the overall equation by combining the reduction equation (half equation 3) and the oxidation equation (the reversed half equation 1)
  - **Remember:** When combining half equations, they must have the same number of electrons in both equations

$Cr_2O_7^{2-}\,(aq) + 14H^+\,(aq) + 6e^-$	$\rightleftharpoons$	$2Cr^{3+}\,(aq) + 7H_2O\,(l)$

Your notes

$3Zn\ (s)$	$\rightleftharpoons$	$3Zn^{2+}\ (aq) + 6e^-$

Your notes

- The equal number of electrons on both sides of the equation cancel out to give the overall equation:

$$Cr_2O_7^{2-}\ (aq) + 14H^+\ (aq) + 3Zn\ (s) \rightleftharpoons 2Cr^{3+}\ (aq) + 7H_2O\ (l) + 3Zn^{2+}\ (aq)$$

- This reaction is carried out under acidic conditions due to the presence of H^+ in the equation

Reduction of Cr from +3 to +2 by Zn

- Chromium is being reduced from an oxidation number of +3 to +2 in half equation 2
- So, the two half equations we need to consider are:
  - 1. $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn\ (s)$ $\quad E^\theta = -0.76\ V$
  - 2. $Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$ $\quad E^\theta = -0.41\ V$
- Half equation 2 has the most positive / least negative standard electrode potential, E^θ, value
  - Therefore, this is the reduction reaction
  - $Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$
- Half equation 2 has the least positive standard electrode potential, E^θ, value
  - Therefore, this is the oxidation reaction and needs to be reversed
  - $Zn\ (s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$
- We can obtain the overall equation by combining the reduction equation (half equation 2) and the oxidation equation (the reversed half equation 1)
  - **Remember:** When combining half equations, they must have the same number of electrons in both equations

$2Cr^{3+}\ (aq) + 2e^-$	$\rightleftharpoons$	$2Cr^{2+}\ (aq)$
$Zn\ (s)$	$\rightleftharpoons$	$Zn^{2+}\ (aq) + 2e^-$

  - The equal number of electrons on both sides of the equation cancel out to give the overall equation:

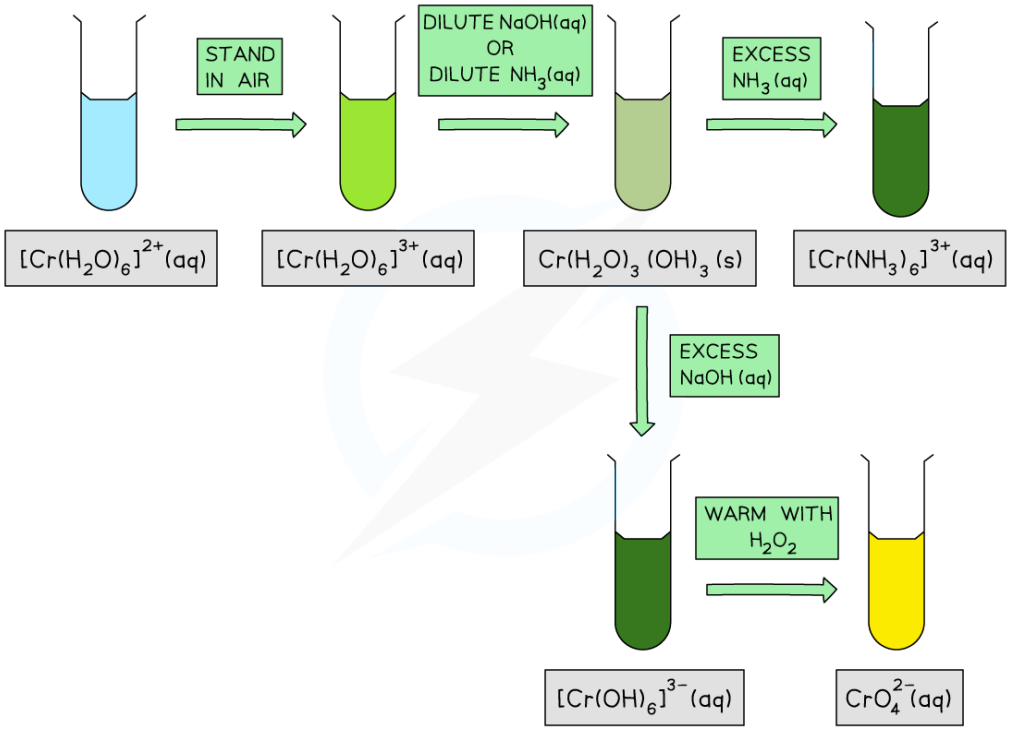
$$2Cr^{3+}\ (aq) + Zn\ (s) \rightleftharpoons 2Cr^{2+}\ (aq) + Zn^{2+}\ (aq)$$

- As this reaction is a further step from the previous reduction this reaction is also carried out under acidic conditions

Colour changes of chromium

- Another approach to transition metal chemistry is to look at the reactions of transition metal ions and complexes with various reagents

- This information is sometimes presented in the form of a reaction scheme:



Reaction scheme outlining the colour changes associated with the reactions of different chromium species

- You would be expected to know:
  - The formula and corresponding state, (aq) or (s), of the transition metal species
  - The colour of the transition metal species
  - The reagents and conditions required to convert one transition metal species into another
  - How to write the equation for the conversion of one transition metal species into another
- For example:
  - A green solution of hexaaquachromium(III) ions, $[Cr(H_2O)_6]^{3+}$ (aq), will react with dilute NaOH (aq) to form a grey-green precipitate of $Cr(H_2O)_3(OH)_3$ (s)
  - $[Cr(H_2O)_6]^{3+}$ (aq) + $3OH^-$ (aq) → $[Cr(H_2O)_3(OH)_3]$ (s) + $3H_2O$ (l)

Dichromate(VI) & Chromate(VI) Equilibrium

- The chromate CrO_4^{2-} and dichromate $Cr_2O_7^{2-}$ ions can be converted from one to the other by the following equilibrium reaction

Your notes

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

- Chromate(IV) ions are stable in alkaline solution, but in acidic conditions the dichromate(VI) ion is more stable
- Addition of acid will push the equilibrium to the dichromate
  - This results in a colour change from yellow to orange
- Addition of alkali will remove the H^+ ions and push the equilibrium to the chromate
- This is not a redox reaction as both the chromate and dichromate ions have an oxidation number of +6
  - This is an acid base reaction

Your notes

Your notes

Substitutions with Hydroxide & Ammonia

- When transition metal ions in an aqueous solution react with aqueous sodium hydroxide and aqueous ammonia they form precipitates
- However, some of these precipitates will dissolve in an excess of sodium hydroxide or ammonia to form complex ions in solution

The Reactions of Aqueous Transition Metal Ions with Aqueous Sodium Hydroxide

Transition Metal Ion	Metal-aqua ion	With NaOH (aq)	With excess NaOH (aq)
Cr^{3+}	Green solution $[Cr(H_2O)_6]^{3+}$ (aq)	Green precipitate $Cr(OH)_3(H_2O)_3$ (s)	Green solution $[Cr(OH)_6]^{3-}$ (aq)
Fe^{2+}	Green solution $[Fe(H_2O)_6]^{2+}$ (aq)	Green precipitate $Fe(OH)_2(H_2O)_4$ (s)	No further change
Fe^{3+}	Yellow-brown solution $[Fe(H_2O)_6]^{3+}$ (aq)	Brown precipitate $Fe(OH)_3(H_2O)_3$ (s)	No further change
Co^{2+}	Pink solution $[Co(H_2O)_6]^{2+}$ (aq)	Blue precipitate $Co(OH)_2(H_2O)_4$ (s)	No further change
Mn^{2+}	Pale pink solution $[Mn(H_2O)_6]^{2+}$ (aq)	Pale brown precipitate $Mn(OH)_2(H_2O)_4$ (s)	No further change
Ni^{2+}	Green solution $[Ni(H_2O)_6]^{2+}$ (aq)	Green precipitate $Ni(OH)_2(H_2O)_4$ (s)	No further change
Cu^{2+}	Blue solution $[Cu(H_2O)_6]^{2+}$ (aq)	Blue precipitate $Cu(OH)_2(H_2O)_4$ (s)	No further change
Zn^{2+}	Colourless solution $[Zn(H_2O)_6]^{2+}$ (aq)	White precipitate $Zn(OH)_2(H_2O)_4$ (s)	Colourless solution $[Zn(OH)_4(H_2O)_2]^{2-}$ (aq)

- Examples of ionic equations for the reactions in the table above
  - $[Fe(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow [Fe(H_2O)_4(OH)_2](s) + 2H_2O(l)$

- $[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow [Cu(H_2O)_4(OH)_2](s) + 2H_2O(l)$
- $[Fe(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightarrow [Fe(H_2O)_3(OH)_3](s) + 3H_2O(l)$

Your notes

The Reactions of Aqueous Transition Metal Ions with Ammonia

Transition Metal Ion	Metal-aqua ion	With NH_3 (aq)	With excess NH_3 (aq)
Cr^{3+}	Green solution $[Cr(H_2O)_6]^{3+}(aq)$	Green precipitate $Cr(OH)_3(H_2O)_3(s)$	Purple solution $[Cr(NH_3)_6]^{3+}(aq)$
Fe^{2+}	Green solution $[Fe(H_2O)_6]^{2+}(aq)$	Green precipitate $Fe(OH)_2(H_2O)_4(s)$	No further change
Fe^{3+}	Yellow-brown solution $[Fe(H_2O)_6]^{3+}(aq)$	Brown precipitate $Fe(OH)_3(H_2O)_3(s)$	No further change
Co^{2+}	Pink solution $[Co(H_2O)_6]^{2+}(aq)$	Blue precipitate $Co(OH)_2(H_2O)_4(s)$	Yellow solution $[Co(NH_3)_6]^{2+}(aq)$
Mn^{2+}	Pale pink solution $[Mn(H_2O)_6]^{2+}(aq)$	Pale brown precipitate $Mn(OH)_2(H_2O)_4(s)$	No further change
Ni^{2+}	Green solution $[Ni(H_2O)_6]^{2+}(aq)$	Green precipitate $Ni(OH)_2(H_2O)_4(s)$	Dark blue solution $[Ni(NH_3)_6]^{2+}(aq)$
Cu^{2+}	Blue solution $[Cu(H_2O)_6]^{2+}(aq)$	Blue precipitate $Cu(OH)_2(H_2O)_4(s)$	Dark blue solution $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$
Zn^{2+}	Colourless solution $[Zn(H_2O)_6]^{2+}(aq)$	White precipitate $Zn(OH)_2(H_2O)_4(s)$	Colourless solution $[Zn(NH_3)_4]^{2+}(aq)$

- Solutions of metal aqua ions react as acids with aqueous ammonia
- This means that the ammonia solution will initially act as a base to remove one H^+ ion per ammonia molecule used
  - Examples of ionic equations for this type of reaction from the table above:
    - $[Fe(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightarrow Fe(H_2O)_4(OH)_2(s) + 2NH_4^+(aq)$
    - $[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightarrow Cu(H_2O)_4(OH)_2(s) + 2NH_4^+(aq)$
    - $[Fe(H_2O)_6]^{3+}(aq) + 3NH_3(aq) \rightarrow Fe(H_2O)_3(OH)_3(s) + 3NH_4^+(aq)$

- Some metal aqua ions will react further and undergo ligand substitution with **excess** ammonia
  - Two specific examples to be aware of are Co^{2+} and Cu^{2+} with excess ammonia:
  - Starting with the hexa aqua ions:
    - $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(H_2O)_2(NH_3)_4]^{2+}(aq) + 4H_2O(l)$
    - $[Co(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightarrow [Co(NH_3)_6]^{2+}(aq) + 6H_2O(l)$
  - Starting with the precipitates:
    - $[Cu(H_2O)_4(OH)_2](s) + 4NH_3(aq) \rightarrow [Cu(H_2O)_2(NH_3)_4]^{2+}(aq) + 2H_2O(l) + 2OH^-(aq)$
    - $[Co(H_2O)_4(OH)_2](s) + 6NH_3(aq) \rightarrow [Co(NH_3)_6]^{2+}(aq) + 4H_2O(l) + 2OH^-(aq)$

Your notes

Examiner Tips and Tricks

It is easiest to remember the formulas of the precipitates by remembering that the number of OH^- ions substituted is the same as the value of the charge on the initial ion

Ionic Equations

Reaction with limited OH^- and limited NH_3

- The bases OH^- and ammonia when in limited amounts form the same hydroxide precipitates.
- They form in deprotonation acid base reactions
- For example, consider the reaction that occurs when aqeuous sodium hydroxide is added to copper(II) sulfate solution

$$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow [Cu(H_2O)_4(OH)_2](s) + 2H_2O(l)$$

- This seems like a ligand substitution reaction - two hydroxide ions replacing two water molecules
- However this is actually a deprotonation reaction - two hydroxide ions removing hydrogen ions from two of the water ligands converting them into water molecules
  - The two ligands that have lost hydrogen ions are now hydroxide ligand

Reaction with excess OH^-

- From above, we have seen how hydrated transition metal ions can be deprotonated by adding a base such as aqueous sodium hydroxide to form a metal hydroxide precipitate
- For example

$$[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightarrow [Cr(H_2O)_3(OH)_3](s) + 3H_2O(l)$$

- When an excess of sodium hydroxide is added further deprotonation takes place

$$[Cr(H_2O)_3(OH)_3]\ (s) + 3OH^-\ (aq) \rightarrow [Cr(OH)_6]^{3-}\ (aq) + 3H_2O\ (l)$$

- In this reaction, chromium(III) hydroxide acts as an acid, as it is reacting with a base
- Chromium(III) hydroxide can also act as a base because it can react with acids as follows

$$[Cr(H_2O)_3(OH)_3]\ (s) + 3H^+\ (aq) \rightarrow [Cr(H_2O)_6]^{3+}\ (aq)$$

- A metal hydroxide that can act as both an acid and a base is called an amphoteric hydroxide
  - This is an example of amphoteric behaviour

Reaction with excess NH_3

- With excess NH_3 ligand substitution reactions occur with Cu, Co and Cr and their precipitates dissolve
- The ligands NH_3 and H_2O are similar in size and are uncharged
- Ligand exchange occurs without a change of co-ordination number for Co and Cr
- For example when excess aqueous ammonia is added to a copper(II) hydroxide precipitate it dissolves forming a deep blue solution

$$[Cu(H_2O)_4(OH)_2]\ (s) + 4NH_3\ (aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}\ (aq) + 2H_2O\ (l) + 2OH^-\ (aq)$$

- This is a ligand substitution - four ammonia molecules replace two water molecules and two hydroxide ions
- In these reactions NH_3 is acting as a Lewis base donating an electron pair

Your notes

Your notes

Heterogeneous Catalysis

- A **heterogeneous** catalyst is in a different physical state (phase) from the reactants
- Heterogeneous catalysts are usually solids whereas the reactants are gaseous or in solution
- The reaction occurs at active sites on the surface of the catalyst

Surface adsorption theory

- This theory can be used to explain how a heterogeneous catalyst works

1. **Adsorption**, in which one or more reactants becomes attached to the surface of the catalyst
2. Reaction, following the weakening of the bonds in the adsorbed reactants
3. **Desorption**, in which the reaction product becomes detached from the surface of the catalyst

- Adsorption of reactants at active sites on the surface may lead to catalytic action
- The active site is the place where the reactants adsorb onto the surface of the catalyst
- This can result in the bonds within the reactant molecules becoming weaker, or the molecules being held in a more reactive configuration
- There will also be a higher concentration of reactants at the solid surface so leading to a higher collision frequency

Strength of adsorption

- The strength of adsorption helps to determine the effectiveness of the catalytic activity
- Some metals e.g. W have too strong adsorption and so the products cannot be released
- Some metals e.g. Ag have too weak adsorption, and the reactants do not adsorb in high enough concentration
- Ni and Pt have about the right strength and are most useful as catalysts

Surface area

- Increasing the surface area of a solid catalyst will improve its effectiveness.
- A support medium is often used to maximise the surface area and minimise the cost (e.g. Rh on a ceramic support in catalytic converters)

Advantages of heterogeneous catalysts

- Heterogeneous catalysts can be filtered off and are easy to separate from any liquid or gaseous products

- They are also suited to continuous processes rather than batch processes


Your notes

Impurities

- The effectiveness of a heterogenous catalyst can be decreased by the presence of impurities in the gas involved in the reaction.
- The impurities can:
  - Adsorb onto catalyst surface and occupy active sites
  - Prevent bond weakening in the reactants
  - 'Take up' the surface area of catalyst by forming strong bonds to surface of catalyst so are less likely to desorb from surface of catalyst

Catalysis of the Contact Process

- The manufacture of sulfuric acid is a very important piece of industrial chemistry that makes use of heterogeneous catalysis
- The first step of the process is roasting sulfur in air to produce sulfur dioxide

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

- The second step is an equilibrium reaction which is catalysed by vanadium(V) oxide, V_2O_5,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

- The vanadium(V) oxide catalyst converts sulfur dioxide into sulfur trioxide and is reduced to vanadium(IV) oxide
  - The oxidation number of the vanadium decreases from +5 to +4

$$SO_2(g) + V_2O_5(s) \rightarrow V_2O_4(s) + SO_3(g)$$

- The vanadium(V) oxide is then re-generated by reaction with oxygen, fulfilling its role as a catalyst
  - The original catalyst is regenerated as the oxidation number of vanadium increases from +4 to its original value of +5

$$O_2(g) + 2V_2O_4(s) \rightarrow 2V_2O_5(s)$$

- This reaction shows that a variable oxidation state can also be utilised in heterogenous catalysis

Catalytic Converters & Emissions

- Catalytic converters are used in car exhaust boxes to reduce air pollution. They usually consist of a mixture of finely divided platinum and rhodium supported on a ceramic base

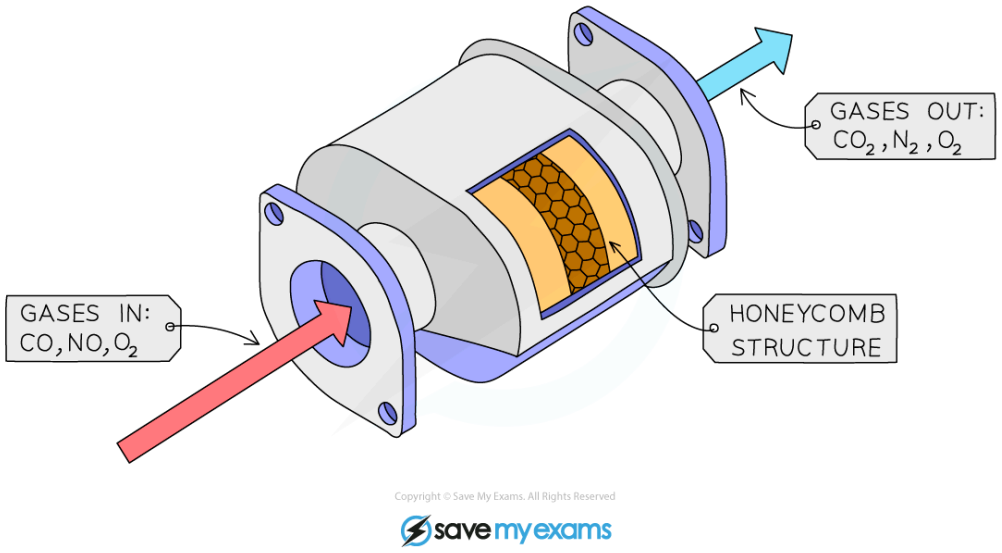


Diagram of a catalyst on an inert support medium in a vehicle catalytic converter

- Carbon monoxide, nitrogen dioxide and unburnt hydrocarbons are sources of pollution in car exhaust
  - Carbon monoxide is toxic and interferes with oxygen transport in the body
  - Nitrogen monoxide is easily oxidised in the atmosphere to form nitrogen dioxide which is a respiratory irritant and contributes to the formation of acid rain
- The transition metal catalysts facilitate the conversion of these pollutants into less harmful products

$$2NO\,(g) + 2CO\,(g) \rightarrow N_2\,(g) + 2CO_2\,(g)$$

$$CH_3CH_2CH_3\,(g) + 5O_2\,(g) \rightarrow 3CO_2\,(g) + 4H_2O\,(g)$$

- The method of action can be described using surface adsorption theory

1. Molecules of carbon monoxide and nitrogen monoxide are adsorbed onto the surface
2. The bonds in both molecules are weakened causing them to react together to form carbon dioxide and nitrogen
3. The products are then desorbed from the surface of the catalyst

- Some of the transition metals are precious metals so they can be very expensive
- In order to minimise the cost and maximise the efficiency of the catalyst the following measures can be taken:
  - Increasing the surface area of the catalyst
  - Coating an inert surface medium with the catalyst to avoid using large amounts of the catalyst

Your notes

- This is achieved by spreading the catalyst over a hollow matrix such as a honeycomb-like structure

Your notes

Examiner Tips and Tricks

Make sure not to confuse absorb/absorption with adsorb/adsorption.

Absorption involves one substance becoming distributed throughout another (like water in a sponge)

Adsorption only happens at the surface of a substance

Your notes

Homogeneous Catalysis

- **Homogeneous** catalyst is in the same physical state (phase) as the reactants
- This means they are either all gases, or more often, all in aqueous solution
- Homogenous catalysts tend to be much less common in industry
- The key feature of homogeneous catalysis is the formation of an intermediate species for which a specific formula can be written

Iron(II) Ion Catalysts

- Transition element ions can adopt more than one **stable oxidation state**
- This means that they can accept and lose electrons easily to go from one oxidation state to another
- They can therefore catalyse **redox** reactions, by acting as both **oxidising agents** and **reducing agents**
- For example, iron (Fe) is often used as a catalyst due to its ability to form Fe(II) and Fe(III) ions, acting as an oxidising agent and a reducing agent
  - When Fe(II) acts as a reducing agent, it will reduce another species and become oxidised itself

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

- The Fe^{3+} formed in the catalytic cycle, can then also act as an oxidising agent by oxidising another species and getting reduced itself to reform the Fe^{2+} ion

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

- Iron(II) ions catalyse the reaction between iodide ions, I^-, and peroxodisulfate ions, $S_2O_8^{2-}$
- The overall reaction is quite slow because the repulsion of two negative ions coming together hinders the reaction

$$S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2SO_4^{2-}$$

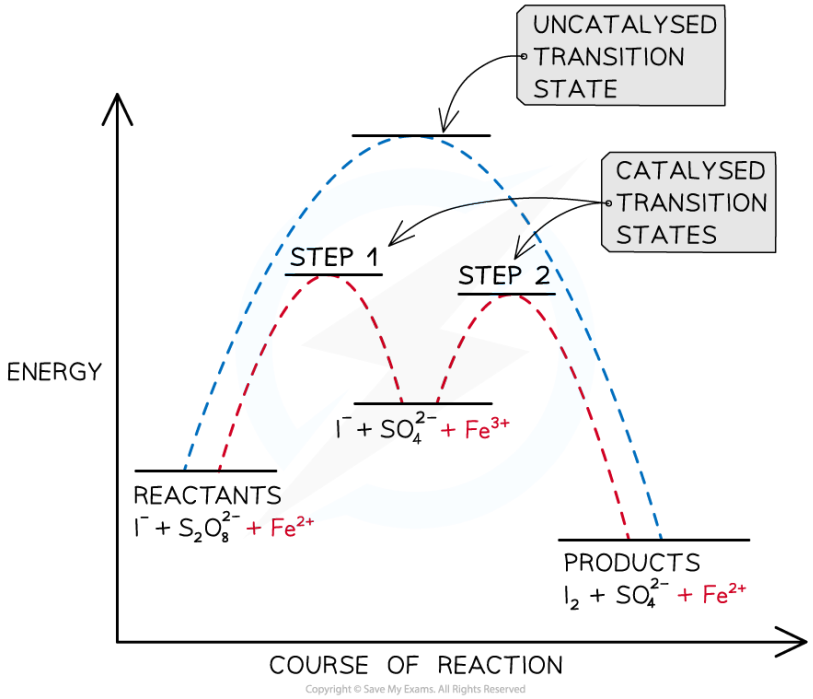
- The reaction is quite slow even though it is energetically favourable. Both ions are negatively charged, so they are unlikely to make successful collisions with one another. However, if iron(II) ions are added to the reaction, the rate is much quicker. Starch is often added to this reaction, which will form a blue-black colour showing the formation of iodine
- The addition of iron(II) ions reduces the peroxodisulfate to sulfate ions and produces iron(III) in the process

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

- The iron(III) ions will oxidise iodide ions to iodine and then are reduced once again to iron(II)

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

- The iron(II) produced can then go on to reduce more peroxodisulfate so fulfils its role as a catalyst
- As all of the reactants and products and the catalyst are in the aqueous phase this reaction is an example of homogeneous catalysis
- A catalyst provides a reaction pathway of lower energy which can be illustrated graphically:



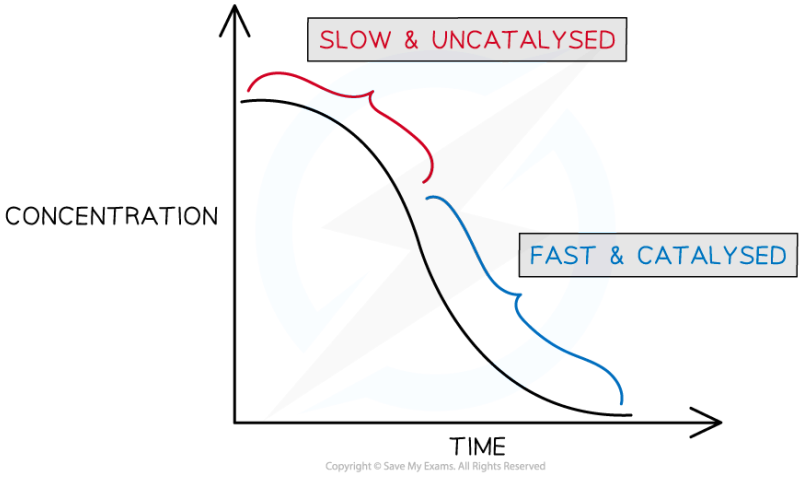
An energy profile showing the alternative reaction pathway provided by iron(II) catalyst in the reaction between iodide ions and peroxodisulfate ions

Your notes

Your notes

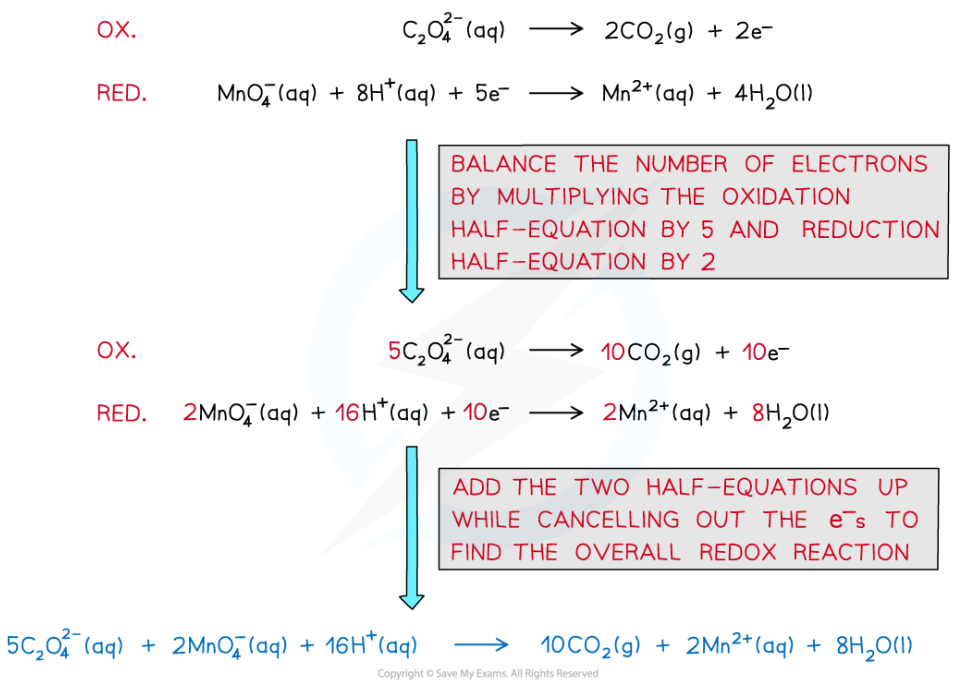
Manganese(II) ions as an Autocatalyst

- Autocatalysis the term used to describe a reaction which is sped up by a product which acts as a catalyst for the reaction
- If you plot a rate graph of concentration versus time it has an usual shape



Concentration versus time for an autocatalytic reaction

- The gradient becomes steeper during the course of the reaction which tells you the rate is speeding up, not slowing down over time as the reactants become used up
- An example of an autocatalysed reaction takes place between **manganate(VII)** ions and **oxalate** (ethandioate) ions
- The overall equation can be deduced from the half equations



Your notes

- You can see that one of the products is manganese(II) ions - this is the catalyst
- As more manganese(II) is formed the reaction speeds up
- Like to the role of iron(II) in the previous section, manganese(II) ions take part in a redox cycle between two different oxidation states (+2 → +3 → +2)

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

$$2Mn^{3+}(aq) + C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2Mn^{2+}(aq)$$

- The manganese(II) is not present in the beginning of the reaction, but as it is formed is speeds up the reaction and is re-generated during the redox cycle
- This reaction is easily followed on a colorimeter as the rate at which the purple manganate(VII) ion is consumed accelerates with time