2.5 Transition metals

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>Zn</td>
<td>Sc</td>
<td>Zn</td>
<td>Sc</td>
<td>Zn</td>
<td>Sc</td>
<td>Zn</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sc 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\)3d\(^1\)4s\(^2\)  Sc\(^{3+}\) 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\)

Zn 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\)3d\(^10\)4s\(^2\)  Zn\(^{2+}\) 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\)3d\(^{10}\)

Electron configurations review:

- This means that Scandium and Zinc are not Transition elements.
- Transition element: A metal that can form one or more stable ions with an incomplete d sub-level

**d – Block element:**

Is found between Group 2 and Group 3 on the Periodic table.

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

<table>
<thead>
<tr>
<th>Element</th>
<th>Z</th>
<th>Electron configuration</th>
<th>Noble gas configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scandium</td>
<td>21</td>
<td>1s(^2)2s(^2)2p(^6)3s(^2)3p(^6)3d(^1)4s(^2)</td>
<td>[Ar] 4s(^2)3d(^1)</td>
</tr>
<tr>
<td>Titanium</td>
<td>22</td>
<td>1s(^2)2s(^2)2p(^6)3s(^2)3p(^6)3d(^2)4s(^1)</td>
<td>[Ar] 4s(^2)3d(^2)</td>
</tr>
<tr>
<td>Vanadium</td>
<td>23</td>
<td>1s(^2)2s(^2)2p(^6)3s(^2)3p(^6)3d(^2)4s(^2)</td>
<td>[Ar] 4s(^2)3d(^2)</td>
</tr>
<tr>
<td>Chromium</td>
<td>24</td>
<td>1s(^2)2s(^2)2p(^6)3s(^2)3p(^6)3d(^3)4s(^1)</td>
<td>[Ar] 4s(^2)3d(^3)</td>
</tr>
<tr>
<td>Manganese</td>
<td>25</td>
<td>1s(^2)2s(^2)2p(^6)3s(^2)3p(^6)3d(^3)4s(^2)</td>
<td>[Ar] 4s(^2)3d(^3)</td>
</tr>
<tr>
<td>Iron</td>
<td>26</td>
<td>1s(^2)2s(^2)2p(^6)3s(^2)3p(^6)3d(^5)4s(^1)</td>
<td>[Ar] 4s(^2)3d(^5)</td>
</tr>
<tr>
<td>Cobalt</td>
<td>27</td>
<td>1s(^2)2s(^2)2p(^6)3s(^2)3p(^6)3d(^6)4s(^1)</td>
<td>[Ar] 4s(^2)3d(^6)</td>
</tr>
<tr>
<td>Nickel</td>
<td>28</td>
<td>1s(^2)2s(^2)2p(^6)3s(^2)3p(^6)3d(^7)4s(^1)</td>
<td>[Ar] 4s(^2)3d(^7)</td>
</tr>
<tr>
<td>Copper</td>
<td>29</td>
<td>1s(^2)2s(^2)2p(^6)3s(^2)3p(^6)3d(^{10})4s(^1)</td>
<td>[Ar] 4s(^2)3d(^{10})</td>
</tr>
<tr>
<td>Zinc</td>
<td>30</td>
<td>1s(^2)2s(^2)2p(^6)3s(^2)3p(^6)3d(^{10})4s(^2)</td>
<td>[Ar] 4s(^2)3d(^{10})</td>
</tr>
</tbody>
</table>
Chromium and copper:

- Chromium and Copper fills differently:

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

The electron configurations of transition metal ions:

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

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

Examples:

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>[Ar]3d^{6}4s^{2}</td>
</tr>
<tr>
<td>Fe^{2+}</td>
<td>[Ar]3d^{6}</td>
</tr>
<tr>
<td>Fe^{3+}</td>
<td>[Ar]3d^{5}</td>
</tr>
<tr>
<td>Cu</td>
<td>[Ar]3d^{10}4s^{1}</td>
</tr>
<tr>
<td>Cu^{+}</td>
<td>[Ar]3d^{10}</td>
</tr>
<tr>
<td>Cu^{2+}</td>
<td>[Ar]3d^{9}</td>
</tr>
<tr>
<td>Cu^{3+}</td>
<td>[Ar]3d^{8}</td>
</tr>
</tbody>
</table>

Questions:

1) Write electron configurations for the following atoms:

   a) Sc       b) Mn       c) Co       d) Cu
   e) V        f) Fe       g) Ni       h) Cr

2) Write electron configurations for the following ions:

   a) Sc^{3+}   b) Mn^{2+}   c) Co^{2+}   d) Cu^{+}
   e) V^{3+}    f) Cu^{2+}   g) Cr^{3+}   h) Ti^{3+}
Properties of transition metals

Physical properties - general metals

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

Chemical properties - transition metals

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

Variable oxidation states and colours

<table>
<thead>
<tr>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>+2</td>
<td>+2</td>
<td>+2</td>
<td>+2</td>
<td>+2</td>
<td>+2</td>
<td>+2</td>
<td>+2</td>
<td>+2</td>
<td>+2</td>
</tr>
<tr>
<td>+3</td>
<td>+3</td>
<td>+3</td>
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<td>+3</td>
<td>+3</td>
<td>+3</td>
<td>+3</td>
<td>+3</td>
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<tr>
<td>+4</td>
<td>+4</td>
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<tr>
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<tr>
<td>+6</td>
<td>+6</td>
<td>+6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+7</td>
</tr>
</tbody>
</table>

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

MAKE SURE YOU CAN WORK OUT OXIDATION STATES

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

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

**Complex ion:**
*A central metal ion surrounded by ligands*

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

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

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

- Fe$^{2+}$ is the Transition metal ion.
- Ligands are the water molecules.
- Coordination number is the number of coordinate bonds to the central metal ion = 6.
- Square brackets group the species and the overall charge is written outside the brackets.
- Overall charge is the sum of the charges of the metal ion and the ligands (if the ligands have a charge)
Monodentate ligands:
- Ligands have a pair of electrons that donors which is used to make a dative covalent bond to the central metal ion.
- All the ligands in the table have 1 lone pair and can form 1 dative covalent bond with the central metal ion.
- These types of ligands are called monodentate.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Formula</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>:OH₂</td>
<td>0</td>
</tr>
<tr>
<td>Ammonia</td>
<td>:NH₃</td>
<td>0</td>
</tr>
<tr>
<td>Cyanide</td>
<td>:CN⁻</td>
<td>-1</td>
</tr>
<tr>
<td>Chloride</td>
<td>:Cl⁻</td>
<td>-1</td>
</tr>
<tr>
<td>Hydroxide</td>
<td>:OH⁻</td>
<td>-1</td>
</tr>
</tbody>
</table>

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

Bidentate ligands
- Some ligands contain 2 lone pairs of electrons forming 2 coordinate bonds each.
- Ethane - 1,2 - diamine, H₂NCH₂CH₂NH₂ abbreviated to 'en' [Ni(en)₃]²⁺

Another bidentate ligand:
Ethanedioate ligand, C₂O₄²⁻

- Coordination number = 6
Hexadentate ligand:

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

EDTA$^{4-}$

Working out oxidation states in complex ions:

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

1) $[\text{Ti(H}_2\text{O)}_6]^3+$

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

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

2) $[\text{CoCl}_4]^{2-}$

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

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

Questions:

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

a) $[\text{Fe(H}_2\text{O)}_6]^3+$  
b) $[\text{CuCl}_4]^{2-}$  
c) $[\text{Fe(H}_2\text{O)}_3\text{(OH)}_3]$  
d) $[\text{Cr(H}_2\text{O)}_2\text{(OH)}_2]^{1+}$

e) $[\text{Co(NH}_3)_4\text{Cl}_2]^{1+}$  
f) $[\text{Pt(NH}_3)_2\text{Cl}_2]$  
g) $[\text{Cr(C}_2\text{O}_4)_2\text{(H}_2\text{O)}_2]^{1-}$  
h) $[\text{Fe(EDTA)}]^{1-}$
Shapes of complex ions:

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

**Coordination number = 6**

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

![Hexaaqua ion diagram]

**Coordination number = 4**

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

**Square planar**

![Square planar diagram]

**Tetrahedral**

![Tetrahedral diagram]

**Coordination number = 2**

- The shape is **linear** and is formed by 2 ligands
- \([\text{Ag(NH}_3\text{)}_2]^+\)
Stereoisomerism in complex ions

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

Optical isomer:
*These are non superimposable mirror images*

A) Stereoisomerism: Cis / Trans isomerism

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

   ![Square planar Cis](image1) ![Square planar Trans](image2)

   *Cis* = 2 ligands are at 90° to each other  
   *Trans* = 2 ligands are at 180° to each other

2) Octahedral with 4 of one ligand and 2 of another ligand, \([\text{Co(NH}_3\text{)}_4\text{Cl}_2]^+\):

   ![Octahedral Cis](image3) ![Octahedral Trans](image4)

   *Cis* = 2 ligands are at 90° to each other  
   *Trans* = 2 ligands are at 180° to each other

3) Octahedral with 2 bidentate and 2 monodentate ligands:

   ![Octahedral Cis](image5) ![Octahedral Trans](image6)

   *Cis* = 2 monodentate ligands are at 90° to each other  
   *Trans* = 2 monodentate ligands are at 180° to each other
B) Optical isomerism

1) With 3 bidentate ligands

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

- Draw the other optical isomer next to the one below:
Coloured ions:
- Transition metal solutions are coloured because they absorb frequencies of light from the visible spectrum:
  - All other frequencies are reflected or pass through the solution.
  - The complimentary frequencies combine producing the complimentary colour.
  - The colours are linked to the incomplete d shell:

![Diagram of light absorption and transition](image)

A specific frequency of light will have the same E as the $\Delta E$ between the d orbitals.
What affects the colours:

- The frequency of light and $\Delta E$ are linked by the following equations:

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

$$\nu = c/\lambda$$

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

$\Delta E$ = Energy absorbed (j)

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

$\nu$ = Frequency of light (Hz)

$c$ = Speed of light ($3 \times 10^8$ ms$^{-1}$)

$\lambda$ = Wavelength of light (m)

- Any changes in the following will alter the size of $\Delta E$ between the d orbitals:
  - Oxidation states
  - Co-ordination number
  - Ligands

- This will affect the $E$ (and therefore the frequency) of the light required to promote the electron.
- As a different frequency is absorbed, the complimentary colours will be different.
- This give rise to a colour change:

![Energy diagram](image)

A different frequency of light will have the same $E$ as the new $\Delta E$

Note: The $\Delta E$ may get smaller
Examples:

Change in oxidation state:

\[\text{[Fe(H}_2\text{O)}_6]\text{]}^{2+} \rightarrow \text{[Fe(H}_2\text{O)}_6]\text{]}^{3+}\]

<table>
<thead>
<tr>
<th>Colour</th>
<th>Ox State</th>
<th>Co-ordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green</td>
<td>+2</td>
<td>6</td>
</tr>
<tr>
<td>Yellow</td>
<td>+3</td>
<td>6</td>
</tr>
</tbody>
</table>

Change in co-ordination number:

\[\text{[Cu(H}_2\text{O)}_6]\text{]}^{2+} \rightarrow \text{[CuCl}_4\text{]}^{2-}\]

<table>
<thead>
<tr>
<th>Colour</th>
<th>Ox State</th>
<th>Co-ordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td>+2</td>
<td>6</td>
</tr>
<tr>
<td>Yellow</td>
<td>+2</td>
<td>4</td>
</tr>
</tbody>
</table>

Change in ligand:

\[\text{[Co(H}_2\text{O)}_6]\text{]}^{2+} \rightarrow \text{[Co(NH}_3\text{)}_6]\text{]}^{2+}\]

<table>
<thead>
<tr>
<th>Colour</th>
<th>Ox State</th>
<th>Co-ordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pink</td>
<td>+2</td>
<td>6</td>
</tr>
<tr>
<td>Straw colour</td>
<td>+2</td>
<td>6</td>
</tr>
</tbody>
</table>

Spectroscopy – Colorimetry:

- \([\text{Cu(H}_2\text{O)}_6]\text{]}^{2+}\) ions are blue. The more concentrated the more intense the blue colour.
- During a reaction the concentration of \([\text{Cu(H}_2\text{O)}_6]\text{]}^{2+}\) may decrease.
- This means that the colour intensity will decrease.
- Which means less light will be absorbed.

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

- Where on ligand substitutes another.
- If ligands have a similar size, the co-ordination number remains the same: NH$_3$ and H$_2$O.
- With larger ligands, the co-ordination number decreases: Cl$^-$ is larger than NH$_3$ and H$_2$O.

Same sized ligands: Cobalt (II) ions and ammonia, NH$_3$

$$[\text{Co(H}_2\text{O)}_6]^{2+}_{(aq)} + 6\text{NH}_3_{(aq)} \rightleftharpoons [\text{Co(NH}_3)_6]^{2+}_{(aq)} + 6\text{H}_2\text{O}_{(l)}$$

Colour: Pink

Ox State: +2

C-O No: 6

Shape: Octahedral

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

$$[\text{Cu(H}_2\text{O)}_6]^{2+}_{(aq)} + 4\text{Cl}^-_{(aq)} \rightleftharpoons [\text{CuCl}_4]^{2-}_{(aq)} + 6\text{H}_2\text{O}_{(l)}$$

Colour: Pale blue

Ox State: +2

C-O No: 6

Shape: Octahedral

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

$$[\text{Cu(H}_2\text{O)}_6]^{2+}_{(aq)} + 4\text{NH}_3_{(aq)} \rightleftharpoons [\text{Cu(NH}_3)_4(H}_2\text{O)}_2]^{2+}_{(aq)} + 6\text{H}_2\text{O}_{(l)}$$

Colour: Pale blue

Ox State: +2

C-O No: 6

Shape: Octahedral

Note: When NH$_3$ is initially added a precipitate is seen before the ligand substitution reaction. This is covered later.
Haemoglobin and ligand substitution

- It contains an Fe$^{2+}$ ion with a co-ordination number of 6 in an octahedral arrangement.
- 4 positions are taken up from a dative covalent bond from the Haem (ring type structure - Porphyrin) – a multidentate ligand.
- A protein called Globin occupies a 5th position.
- The 6th position is for H$_2$O or O$_2$ to bind.

![Diagram of Haemoglobin structure]

Lungs:

- In the lungs the O$_2$ concentration is high therefore water is substituted for oxygen – oxyhaemoglobin and transported.
- The O$_2$ is then exchanged for water and transported back to the lungs.
- It also forms a complex with CO$_2$, transporting CO$_2$ back to the lungs.

Carbon monoxide - the silent killer

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

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

1) Dative covalent bond strength:

\[
[\text{Fe(H}_2\text{O)}_6]^{3+}(\text{aq}) + 6\text{CN}^-(\text{aq}) \rightarrow [\text{Fe(CN)}_6]^{3-}(\text{aq}) + 6\text{H}_2\text{O(l)}
\]

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

2) Multidentate ligand substitution:

\[
[\text{Cu(H}_2\text{O)}_6]^{2+}(\text{aq}) + 3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2(\text{aq}) \rightarrow [\text{Cu(NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{2+}(\text{aq}) + 6\text{H}_2\text{O(l)}
\]

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

The chelate effect:

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

\[
[\text{Cu(H}_2\text{O)}_6]^{2+}(\text{aq}) + 3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2(\text{aq}) \rightarrow [\text{Cu(NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{2+}(\text{aq}) + 6\text{H}_2\text{O(l)}
\]

a) Enthalpy

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

b) Entropy

\[
[\text{Cu(H}_2\text{O)}_6]^{2+}(\text{aq}) + 3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2(\text{aq}) \rightarrow [\text{Cu(NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{2+}(\text{aq}) + 6\text{H}_2\text{O(l)}
\]

4 particles \(\rightarrow\) 7 particles

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

\[
\Delta G = \Delta H - T\Delta S
\]

Surroundings  System

- The stability of the bidentate / multidentate complex ion therefore is high.
Variable oxidation states
- One of the Transition metal properties that separates them from other metals is their ability to exist in variable oxidation states:

![Transition Metals Oxidation States Chart]

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

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>Formula</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>+5</td>
<td>VO$_2^+$,(aq)</td>
<td>Yellow</td>
</tr>
<tr>
<td>+4</td>
<td>VO$^2+$,(aq)</td>
<td>Blue</td>
</tr>
<tr>
<td>+3</td>
<td>V$^{3+}$,(aq)</td>
<td>Green</td>
</tr>
<tr>
<td>+2</td>
<td>V$^{2+}$,(aq)</td>
<td>Violet</td>
</tr>
</tbody>
</table>

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

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

Vanadium (V) → Vanadium (IV):

Vanadium (IV) → Vanadium (III):

Vanadium (III) → Vanadium (II):
REDOX potentials (electrode potentials):

- In 1.11 Electrochemistry, the \( E^0 \) value gave an indication of an element’s ability to be reduced / oxidised.
- In REDOX reactions, we call them REDOX potentials.
- It is the same thing:

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidised form</th>
<th>Reduced form</th>
<th>( E^0 )_{cell}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium</td>
<td>K(^+)</td>
<td>K</td>
<td>-2.92</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na(^+)</td>
<td>Na</td>
<td>-2.71</td>
</tr>
<tr>
<td>Lithium</td>
<td>Li(^+)</td>
<td>Li</td>
<td>-2.59</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca(^{2+})</td>
<td>Ca</td>
<td>-2.44</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg(^{2+})</td>
<td>Mg</td>
<td>-2.37</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Al(^{3+})</td>
<td>Al</td>
<td>-1.66</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn(^{2+})</td>
<td>Zn</td>
<td>-0.76</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe(^{2+})</td>
<td>Fe</td>
<td>-0.44</td>
</tr>
<tr>
<td>Tin</td>
<td>Sn(^{2+})</td>
<td>Sn</td>
<td>-0.14</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb(^{2+})</td>
<td>Pb</td>
<td>-0.13</td>
</tr>
<tr>
<td>(Hydrogen)</td>
<td>H(^+)</td>
<td>H</td>
<td>0.00</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu(^{2+})</td>
<td>Cu</td>
<td>+0.34</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg(^{2+})</td>
<td>Hg</td>
<td>+0.79</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag(^+)</td>
<td>Ag</td>
<td>+0.80</td>
</tr>
<tr>
<td>Gold</td>
<td>Au(^+)</td>
<td>Au</td>
<td>+1.89</td>
</tr>
</tbody>
</table>

Summary:

<table>
<thead>
<tr>
<th>The most negative ( E^0 ) value</th>
<th>The most positive ( E^0 ) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Releases electrons the best</td>
<td>Gains electrons the best</td>
</tr>
<tr>
<td>Oxidised more easily</td>
<td>Reduced more easily</td>
</tr>
<tr>
<td>Reducing agent</td>
<td>Oxidising agent</td>
</tr>
</tbody>
</table>

This means:

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

\[
\begin{align*}
Cr^{3+}_{(aq)} + e^- & \rightleftharpoons Cr^{2+}_{(aq)} & E^0 = -0.74V \\
Cu^{2+}_{(aq)} + e^- & \rightleftharpoons Cu^+_{(aq)} & E^0 = +0.15V
\end{align*}
\]

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

Factors affecting REDOX potentials (electrode potentials):

1) Ligands:

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

2) pH:

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

\[
\begin{align*}
2VO_2^{+}_{(aq)} + 4H^+_{(aq)} + 2e^- & \rightleftharpoons 2VO^{2+}_{(aq)} + 2H_2O(l) \\
CrO_4^{2-}_{(aq)} + 4H_2O(l) + 3e^- & \rightleftharpoons Cr(OH)_3(s) + 5OH^-_{(aq)}
\end{align*}
\]

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

Tollens' Reagent:

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

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

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

\[
RCHO_{(aq)} + 2[Ag(NH_3)]^+_{(aq)} + 3OH^-_{(aq)} \rightarrow RCOO^-_{(aq)} + 2Ag(s) + 4NH_3(aq) + 2H_2O(l)
\]
Redox titrations

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

\[
\text{MnO}_4^{-}(aq) + 8H^+ + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)
\]

Purple \(\rightarrow\) Colourless

Titration reactions:

- You need to be able to perform calculations involving \(\text{MnO}_4^{-}\) and \(\text{Fe}^{2+}\) or \(\text{C}_2\text{O}_4^{2-}\):

1) \(\text{MnO}_4^{-}\) and \(\text{Fe}^{2+}\)

\[
\text{MnO}_4^{-}(aq) + 8H^+ + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)
\]

\[
\text{Fe}^{2+}(aq) \rightarrow \text{Fe}^{3+}(aq) + e^-
\]

- Combined:

\[
\text{MnO}_4^{-}(aq) + 8H^+ + 5\text{Fe}^{2+}(aq) \rightarrow 5\text{Fe}^{3+}(aq) + 2\text{CO}_2(g)
\]

Purple \(\rightarrow\) Colourless

2) \(\text{MnO}_4^{-}\) and \(\text{C}_2\text{O}_4^{2-}\)

\[
\text{MnO}_4^{-}(aq) + 8H^+ + 5\text{C}_2\text{O}_4^{2-}(aq) \rightarrow 2\text{Mn}^{2+}(aq) + 8H_2O(l) + 10\text{CO}_2(g)
\]

Purple \(\rightarrow\) Colourless

Carrying out redox titrations

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

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

\[
\begin{align*}
\text{MnO}_4^{-} (aq) &+ 8\text{H}^{+} (aq) + 5\text{Fe}^{2+} (aq) \rightarrow \text{Mn}^{2+} (aq) + 4\text{H}_2\text{O} (l) + 5\text{Fe}^{3+} (aq) \\
23\text{cm}^3 &\text{ 0.02 mol dm}^{-3} \\
25\text{cm}^3
\end{align*}
\]

\[
C = \frac{n}{V} \\
= \frac{2.3 \times 10^{-3}}{0.025} \\
= 0.092 \text{ mol dm}^{-3}
\]

\[
n = C \times V \\
= 0.02 \times 0.023 \\
= 4.60 \times 10^{-4} \times 5 \\
= 2.30 \times 10^{-3}
\]

Examples of redox titrations

- The common uses of these redox titrations are:

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

2) Calculating the % mass of iron in iron tablets

3) Calculating the purity of iron samples

4) Applying your knowledge to unfamiliar redox reactions / titrations

- Some examples:
1) Calculate the Mr and formula of an iron (II) salt

2.950g of hydrated iron (II) sulphate, FeSO₄·xH₂O, was dissolved in 50cm³ of sulphuric acid. This was made up to 250cm³ with distilled water. 25cm³ of this was titrated with 0.01 mol dm⁻³ KMnO₄ and 21.20cm³ of this was used

\[
\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{Fe}^{2+} (\text{aq}) \rightarrow \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O}(l) + 5\text{Fe}^{3+} (\text{aq})
\]

\[
\begin{align*}
21.20\text{cm}^3 & \quad 25.00\text{cm}^3 \\
0.01\text{ mol dm}^{-3} &
\end{align*}
\]

\[
\frac{n}{C \times V} = \frac{1}{5}
\]

\[
= 0.01 \times 0.0212
\]

\[
= 2.12 \times 10^{-4}
\]

\[
\times 5 = 1.06 \times 10^{-3}
\]

\[
n_{\text{MnO}_4^-} = C \times V
\]

\[
n_{\text{MnO}_4^-} = 0.01 \times 0.0212
\]

\[
n_{\text{MnO}_4^-} = 2.12 \times 10^{-4}
\]

Ratio 1 : 5, therefore x 5

\[
n_{\text{Fe}^{2+}} = 1.06 \times 10^{-3} \text{ in 25cm}^3 \text{ of solution (x 10 in 250cm}^3\text{)}
\]

\[
n_{\text{Fe}^{2+}} = 1.06 \times 10^{-3} \text{ in 25cm}^3 \text{ of solution (x 10 in 250cm}^3\text{)}
\]

\[
n_{\text{Fe}^{2+}} = 0.0106 \times 10^{-3} \text{ in 250cm}^3 \text{ of solution}
\]

\[
\text{Mr} = \frac{m}{n}
\]

\[
\text{Mr} - \frac{2.950}{0.0106} = 278.3 \text{ gmol}^{-1}
\]

For Mr of all waters, deduct the Mr of FeSO₄ = 278.3 - 151.9 = 126.4

No waters = 126.4 / 18 = 7

Formula: FeSO₄·7H₂O
2) Calculating the % mass of iron in iron tablets

A multivitamin tablet has a mass of 0.325g and contains iron. The powdered tablet was dissolved in some water and sulphuric acid. 12.10cm³ of 0.002 mol dm⁻³ KMnO₄ was titrated until the first permanent pink colour.

\[
\text{MnO}_4^- \text{(aq)} + 8\text{H}^+ \text{(aq)} + 5\text{Fe}^{2+} \text{(aq)} \rightarrow \text{Mn}^{2+} \text{(aq)} + 4\text{H}_2\text{O(l)} + 5\text{Fe}^{3+} \text{(aq)}
\]

\[
12.10 \text{cm}^3 \\
0.002 \text{ mol dm}^{-3}
\]

\[
\begin{align*}
n &= C \times V \\
&= 0.002 \times 0.0121 \\
&= 2.42 \times 10^{-5}
\end{align*}
\]

\[
\begin{align*}
n \text{ MnO}_4^- &= C \times V \\
n \text{ MnO}_4^- &= 0.002 \times 0.0121 \\
n \text{ MnO}_4^- &= 2.42 \times 10^{-5}
\end{align*}
\]

Ratio 1 : 5, therefore x 5

\[
\begin{align*}
n \text{ Fe}^{2+} &= 1.21 \times 10^{-4} \\
\text{Mass of Fe} &= 1.21 \times 10^{-4} \times 55.8 \\
\text{Mass of Fe} &= 0.00675 \text{g}
\end{align*}
\]

\[
\begin{align*}
\% \text{ Fe by mass} &= \left( \frac{\text{Mass of element}}{\text{Mass of tablet}} \right) \times 100 \\
\% \text{ Fe by mass} &= \left( \frac{0.00675}{0.325} \right) \times 100 \\
\% \text{ Fe} &= 2.08\%
\end{align*}
\]
4) Applying your knowledge to unfamiliar redox reactions / titrations

25cm³ portion of H₂O₂ was made up to 250cm³ with distilled water. 25cm³ portions of this was acidified and titrated with 0.0200 mol dm⁻³ KMnO₄. 38.00cm³ of this was required to completely oxidise the hydrogen peroxide to oxygen. Calculate the original concentration of the hydrogen peroxide. The following equation represents the oxidation of hydrogen peroxide:

The balanced equation:

\[
\text{MnO}_4^- (aq) + 8\text{H}^+(aq) + 5\text{e}^- \rightarrow \text{Mn}^{2+} (aq) + 4\text{H}_2\text{O}(l)
\]

\[
\text{H}_2\text{O}_2(aq) \rightarrow \text{O}_2(g) \quad 2\text{H}^+(aq) + 2\text{e}^-)
\]

Combined:

\[
2\text{MnO}_4^- (aq) + 6\text{H}^+(aq) + 5\text{H}_2\text{O}_2(aq) \rightarrow 2\text{Mn}^{2+} (aq) + 8\text{H}_2\text{O}(l) + 5\text{O}_2(g)
\]

\[
\text{C} = \frac{n}{V} = \frac{1.9 \times 10^{-3}}{0.025} = 0.0760 \text{ mol dm}^{-3}
\]

\[
n = \text{C} \times V = 0.02 \times 0.038 = 7.6 \times 10^{-4}
\]

\[
2 : 5 \rightarrow 1.9 \times 10^{-3}
\]

- Remember this was diluted by a factor of 10 at the beginning
- Concentration of original = 0.760 mol dm⁻³
Transition metals as catalysts

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

Types of catalyst:

1) Heterogeneous catalyst

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

Example: The Contact process:
- A reaction used to make sulphuric acid:
\[
\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \xrightarrow{\text{V}_2\text{O}_5(\text{s})} \text{SO}_3(\text{g})
\]
- Vanadium (V) oxide catalyses the reaction is 2 steps:
  1) The vanadium (V) oxide oxidises the SO₂ while it is itself reduced to vanadium (IV) oxide:
  \[
  \text{SO}_2 + \text{V}_2\text{O}_5 \xrightarrow{+5} \text{SO}_3 + \text{V}_2\text{O}_4 \xrightarrow{+4}
  \]
  2) The vanadium (IV) oxide is then oxidised back to vanadium (IV) oxide by the oxygen:
  \[
  \frac{1}{2}\text{O}_2 + \text{V}_2\text{O}_4 \xrightarrow{+4} \text{SO}_3 + \text{V}_2\text{O}_5 \xrightarrow{+5}
  \]
- This can only happen because vanadium has variable oxidation states.

Another example: The Haber process:
- A reaction used to make ammonia:
\[
\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \xrightarrow{\text{Fe}(\text{s})} 2\text{NH}_3(\text{g})
\]
Solid support → Surface area:

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

Catalytic poisoning:

- Heterogeneous catalysts interact with reactants by adsorption:

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

Lead poisoning catalytic converters:

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

Sulphur poisoning in the Haber process:

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

- Purifying the reactants will increase the life of a catalyst.
2) Homogeneous catalyst

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

Example: Sulphuric acid in esterification

![Chemical reaction diagram]

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

**How it works:**

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

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

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

\[
S_2O_8^{2-} (aq) + 2I^- (aq) \rightarrow I_2 (aq) + 2SO_4^{2-} (aq)
\]

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

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

\[
S_2O_8^{2-} (aq) + 2Fe^{2+} (aq) \rightarrow 2Fe^{3+} (aq) + 2SO_4^{2-} (aq)
\]

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

\[
2I^- (aq) + 2Fe^{3+} (aq) \rightarrow 2Fe^{2+} (aq) + I_2 (aq)
\]

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

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

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

\[
2MnO_4^- (aq) + 16H^+ (aq) + 5C_2O_4^{2-} (aq) \rightarrow 2Mn^{2+} (aq) + 8H_2O (l) + 10CO_2 (g)
\]

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

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

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

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

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

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

Concentration

Uncatalysed section

Rate increases as catalyst is produced

Rate decreases as MnO₄⁻ is used up

Time