5.3 Redox and the chemistry of the transition metals

1 Application of redox equilibria

5.3.1a. Redox

5.3.1a. demonstrate an understanding of the terms ‘oxidation number’, ‘redox’, ‘half-reactions’ and use these to interpret reactions involving electron transfer

The oxidation number of an element in a chemical species is a measure of the extent of the oxidation of that element. The more positive the oxidation number the greater the extent of oxidation. Oxidation number is also a measure of the extent of reduction of an element. Using oxidation numbers it is possible to decide whether oxidation or reduction (redox) has occurred. An atom is said to be oxidised when its oxidation number increases and reduced when its oxidation number decreases.

The oxidation state can be defined as the number of electrons that need to be added or removed from either a positive/negative ion in order to get a neutral atom. E.g. $\text{Fe}^{2+}$ needs to gain two electrons for it to become neutral iron atom therefore its oxidation state is $+2$.

**Task 1.5a** Explain what is happening in terms of electron transfer if the oxidation number of sulfur changes from +4 in $\text{SO}_2$ to +6 in $\text{SO}_4^{2-}$.
Chlorine changes from -1 in chloride to 0 in chlorine,
iron changes from +3 in $\text{Fe}^{3+}$ to +2 in $\text{Fe}^{2+}$,
aluminium changes from +3 in $\text{Al}_2\text{O}_3$ to zero in aluminium,
carbon changes from +2 in carbon monoxide to +4 in carbon dioxide.

The reaction of acidified potassium manganate (VII) with iron (II) sulphate solution:

Reduction half equation: $\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$

Oxidation half equation: $\text{Fe}^{2+}(aq) \rightarrow \text{Fe}^{3+}(aq) + e^-$

When combining these equations, the number of electrons used must equal the number formed, therefore the oxidation equation above must be multiplied by 5

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

$5\text{Fe}^{2+}(aq) \rightarrow 5\text{Fe}^{3+}(aq) + 5e^-$

and then the equations must be added together.

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

In this equation the manganate (VII) is the oxidising agent and the iron (II) is the
reducing agent. The element manganese is reduced and the element iron is oxidised. Half equations can be balanced as follows:

e.g. balance the equation: \( \text{NO}_3^- \rightarrow \text{NH}_4^+ \)

a) balance oxygen atoms with water
b) balance hydrogen atoms with hydrogen ions
c) balance the charges

a) gives \( \text{NO}_3^- \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O} \)
b) gives \( \text{NO}_3^- + 10\text{H}^+ \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O} \)
c) gives \( 8\text{e}^- + \text{NO}_3^- + 10\text{H}^+ \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O} \)

Task 1.5d.1 constructing half equations
Task 1.5d.2 combining half equations

5.3.1b. relate changes in oxidation number to reaction stoichiometry

The total increase in oxidation number in a reaction = the total decrease.

For the reaction

\( 3\text{ClO}^-\text{(aq)} \rightarrow 2\text{Cl}^-\text{(aq)} + \text{ClO}_3^-\text{(aq)} \) the oxidation numbers are

+1 \( \rightarrow \) -1 \( \rightarrow \) +5

Total decrease 2 Cl atoms at +1 to 2 Cl ions at -1 = 4
Total increase = 1 Cl atom ox. no. +1 to ClO\(_3^-\) ion ox. no. +5 = 4

Task 5.1a

5.3.1c. recall the definition of standard electrode potential and standard hydrogen electrode and understand the need for a reference electrode

The standard electrode potential is sometimes called the standard reduction potential. The symbol used is \( \text{E}^\circ \).

e.g \( \text{Pb}^{2+}\text{(aq)}|\text{Pb(s)} \) \( \text{E}^\circ = -0.13\text{V} \) or

\( \text{Pb}^{2+}\text{(aq)} + 2\text{e}^- \rightarrow \text{Pb(s)} \) \( \text{E}^\circ = -0.13\text{V} \)

This is the potential of a half - cell measured relative to the Standard Hydrogen Electrode under standard conditions of 298K, 1atm and in a solution of concentration 1 mol dm\(^{-3}\).

For the reaction

\( \text{Cu}^{2+}\text{(aq)} + \text{Zn(s)} = \text{Cu(s)} + \text{Zn}^{2+}\text{(aq)} \)

The convention for representation of cells is

\( \text{Zn(s)} | \text{Zn}^{2+}\text{(aq)} \parallel \text{Cu}^{2+}\text{(aq)} | \text{Cu(s)} \)

oxidation reduction

Reduced substances on the outside, oxidised substances on the inside.

The standard electrode potential of a metal and its solution cannot be measured directly. Only potential differences between a metal and a standard electrode can be measured. A hydrogen electrode, defined as having a potential of 0.00V, is used as the standard.

\( 2\text{H}^+\text{(aq)} + 2\text{e}^- \rightarrow \text{H}_2\text{(g)} \) \( \text{E}^\circ = 0.00\text{V} \)

Task 5.1c Write some simple ionic equations or cell diagrams for the following:
The anti-clockwise rule:
Write the more positive electrode potential on the bottom then follow anticlockwise arrows for direction of spontaneous change:

\[ \text{Cu}^{2+}(aq) + e^- \rightarrow \text{Cu}(s); E^o = +0.34 \text{V} \]
\[ \text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s); E^o = +0.80 \text{V} \quad \text{(most +ve at bottom)} \]

spontaneous reaction is \( \text{Ag}^+(aq) + \text{Cu}(s) \rightarrow \text{Ag}(s) + \text{Cu}^{2+}(aq) \)
Copper is a stronger reducing agent than silver as the \( E^o \) value of copper is more negative than that of \( \text{Ag} \).

where the cell diagram for the above reaction is

\[ \text{Cu(s)} | \text{Cu}^{2+}(aq) || \text{Ag}^+(aq) | \text{Ag(s)} \]

\[ E_{\text{cell}} = E^o_{\text{right}} - E^o_{\text{left}} = +0.80 \text{V} - (+0.34 \text{V}) = +0.46 \text{V} \]

The reaction proceeds as emf is positive.
or for half equations written as above
\[ E_{\text{cell}} = E^o_{\text{bottom}} - E^o_{\text{top}} \]

Or

Write half equations but reverse sign on half equation written back to front. Then add values to give emf.
Cu(s) ---> Cu^{2+}(aq) + e^- ; E^o = -0.34V
Ag^+ (aq) + e^- ---> Ag(s) ; E^o = +0.80V

If E_{cell} is positive then the reaction is spontaneous

**Task 5.1d**

5.3.1e. demonstrate an understanding that $E_{cell}^o$ is directly proportional to the total entropy change and to lnK for a reaction

<table>
<thead>
<tr>
<th></th>
<th>No reaction</th>
<th>Position to left</th>
<th>Reactants = products</th>
<th>Position to right</th>
<th>Complete reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kc</td>
<td>&lt;10^{-10}</td>
<td>0.01</td>
<td>1</td>
<td>100</td>
<td>&gt;10^{+10}</td>
</tr>
<tr>
<td>Log Kc</td>
<td>-10</td>
<td>-2</td>
<td>0</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>$E^o$</td>
<td>&lt;-0.6</td>
<td>-0.1</td>
<td>0</td>
<td>0.1</td>
<td>&gt;0.6</td>
</tr>
<tr>
<td>$\Delta S_{total}$</td>
<td>&lt;-200</td>
<td>-40</td>
<td>0</td>
<td>+40</td>
<td>&gt;+200</td>
</tr>
</tbody>
</table>

5.3.1f. demonstrate an understanding of why the predictions in 5.3.1d may not be borne out in practice due to kinetic effects and non-standard conditions

Standard conditions of 1 molar solutions, 1 atmosphere pressure and 298K must exist for the rules that predict feasibility from $E^o$ to apply. In practise the conditions in many reactions are not standard. If the $E^o$ values are close (or E_{cell} is small) then non-standard conditions can change $E^o$ values. In these cases a reaction does not always happen as expected. Even if a reaction is feasible its rate may be so slow that it is not observed.

5.3.1g. carry out and evaluate the results of an experiment involving the use of standard electrode potentials to predict the feasibility of a reaction, eg interchange of the oxidation states of vanadium or manganese

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>+5</th>
<th>+4</th>
<th>+3</th>
<th>+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour in aqueous solution</td>
<td>yellow</td>
<td>blue</td>
<td>green</td>
<td>violet</td>
</tr>
<tr>
<td>Ion</td>
<td>VO_3^- or VO_2^+</td>
<td>VO^{2+}</td>
<td>V^{3+}</td>
<td>V^{2+}</td>
</tr>
<tr>
<td>Name</td>
<td>vanadate(V) or dioxovanadium(V)ion</td>
<td>oxovanadium (IV) ion</td>
<td>vanadium (III)</td>
<td>vanadium (II)</td>
</tr>
</tbody>
</table>

Vanadium can be reduced from the +5 states right through to the +2 state by zinc. Each step can be predicted using $E^o$ values. For example for the first step (reduction from +5 to +4):

Zn^{2+}(aq) + 2e^- ---> Zn(s) \quad E^o = -0.76 V
\[
\text{VO}_2^+(aq) + 2H^+(aq) + e^- \rightarrow \text{VO}^{2+}(aq) + H_2O(l) \quad E^\circ = +1.00 \text{ V}
\]

Zinc is the stronger reducing agent here because its \(E^\circ\) value is more negative than for vanadium. So Zinc will reduce vanadium +5 to +4.

OR

Write the half equations with the most negative on top (as above). Apply the anticlockwise rule. So \(\text{VO}_2^+(aq)\) is reduced to \(\text{VO}^{2+}(aq)\) while \(\text{Zn(s)}\) is oxidised to \(\text{Zn}^{2+}(aq)\).

OR

The equation for the reduction of vanadium is
\[
2\text{VO}_2^+(aq) + 4H^+(aq) + \text{Zn(s)} \rightarrow 2\text{VO}^{2+}(aq) + 2H_2O(l) + \text{Zn}^{2+}(aq)
\]

The cell diagram is:
\[
\text{Zn(s)}|\text{Zn}^{2+}(aq)||[2\text{VO}_2^+(aq) + 4H^+(aq)],[\text{VO}^{2+}(aq) + H_2O(l)]|\text{Pt}
\]

\[
E_{\text{cell}} = E^\circ_R - E^\circ_L = +1.00 \text{ V} - (-0.76 \text{ V}) = +1.76 \text{ V}
\]

**Task 5.3.1g** The large positive value of \(E_{\text{cell}}\) shows that the reaction to reduce vanadium is spontaneous.

Use the data below to show that zinc reduces vanadium to \(V^{2+}\), that managanate(III) oxidises \(V^{2+}\) back up to vanadium \(V\) and that iodide oxidises vanadium from the \(+2\) to \(+3\), from \(+3\) to \(+4\) but not from \(+4\) to \(+5\).

\[
\text{V}^{3+}(aq) + e^- \rightarrow \text{V}^{2+}(aq) \quad E^\circ = -0.26 \text{ V}
\]

\[
\text{VO}^{2+}(aq) + 2H^+(aq) + e^- \rightarrow \text{V}^{3+}(aq) + H_2O(l) \quad E^\circ = +0.34 \text{ V}
\]

\[
\text{I}_2(aq) + 2e^- \rightarrow 2\text{I}^-(aq) \quad E^\circ = +0.54 \text{ V}
\]

\[
\text{MnO}_4^-(aq) + 8H^+(aq) + 5e^- = \text{Mn}^{2+}(aq) + 4H_2O(l) \quad E^\circ = +1.51 \text{ V}
\]

5.3.1h. demonstrate an understanding of the procedures of the redox titrations below (i and ii) and carry out a redox titration with one:

i. potassium manganate(III), eg the estimation of iron in iron tablets

ii. sodium thiosulfate and iodine, eg estimation of percentage of copper in an alloy

Titrations involving potassium manganate(III) ions, \(\text{MnO}_4^-\), are used to estimate concentrations of reducing agents like ethanedioate ions, \(\text{C}_2\text{O}_4^{2-}\) and iron II ions, \(\text{Fe}^{2+}\). Iron tablets can be weighed then dissolved in water. The solution formed contains iron(II) ions and is titrated against manganate(III) ions.

The ionic equations are:
\[
2\text{MnO}_4^- + 16H^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2
\]

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

The purple aqueous manganate(III) is added from the burette and the end point is signalled by a permanent pink colour in the flask. The reaction with ethanedioate needs a temperature of about 60°C. Both reactions requires excess dilute sulphuric acid.
Titrations involving iodine, I$_2$ and thiosulphate ions, $S_2O_3^{2-}$ are used to estimate concentrations of oxidising agents like manganate VII ions, iodate V ions, IO$_3^-$ or copper(II).

$$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$$

In each case a known amount of the oxidising agent reacts with iodide ions to liberate iodine in a conical flask. e.g.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

The iodine in the flask is titrated with standardised aqueous sodium thiosulphate in the burette. The reaction is:

$$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$$

The iodine solution in the flask begins with a yellow/brown colour. Near the end point of the titration, when it becomes very pale, starch should be added turning the solution a dark blue/black colour. The end-point is the appearance of a colourless solution produced by the titration of the blue/black solution.

**Task 5.3.1h**

5.3.1i. discuss the uncertainty of measurements and their implications for the validity of the final results

http://www.dartmouth.edu/~chemlab/info/resources/uncertain.html

5.3.1j. discuss the use of hydrogen and alcohol fuel cells as energy sources, including the source of the hydrogen and alcohol, eg used in space exploration, in electric cars

![Fuel Cell Diagram](https://www.ballard.com/eresources/10061/dp-000199.jpg)

The core of this fuel cell comprises two electrodes (anode and cathode) separated by a polymer exchange membrane. Each electrode is coated on one side with a platinum catalyst, which causes the hydrogen fuel to separate into free electrons and protons (positive hydrogen ions) at the anode. The free electrons are conducted in the form of usable electrical current through an external circuit.

The protons migrate through the membrane electrolyte to the cathode, where the catalyst causes the protons to combine with oxygen from the air and electrons from the external circuit to form water and heat. (Image courtesy of Ballard Power Systems.)
Video of the Ballard electric car and the operation of the cell.  
http://www.youtube.com/watch?v=oy8dzOB-Ykg

5.3.1k. Breathalysers

demonstrate an understanding of the principles of modern breathalysers based on an ethanol fuel cell and compare this to methods based on the use of IR and to the reduction of chromium compounds.

**Chromium compound breath analyser**
1. A system to sample the suspects breath
2. Containers for the reaction mixture
3. Photo cells and a meter to record the colour change linked with the reaction of ethanol.

\[ 3C_2H_5OH(g) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l) \]

**Fuel cell breath analyser**

![Diagram of fuel cell breath analyser]

Ethanol is oxidised at platinum electrodes to release electrons. The higher the ethanol concentration the higher the current is through the meter.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH}(g) + \frac{1}{2}\text{O}_2(g) & \rightarrow \text{CH}_3\text{COOH}(l) + 2\text{H}^+(aq) + 2e^- \\
\frac{1}{2}\text{O}_2(g) + 2\text{H}^+(aq) + 2e^- & \rightarrow \text{H}_2\text{O}(l)
\end{align*}
\]

\[
\text{CH}_3\text{CH}_2\text{OH}(g) + \text{O}_2(g) \rightarrow \text{CH}_3\text{COOH}(l) + \text{H}_2\text{O}(l)
\]
Transition metals and their chemistry

5.3.2a. Transition metal definition

describe transition metals as those elements which form one or more stable ions which have incompletely filled d orbitals

The elements Sc - Zn are d-block elements. They have atoms with electrons in d-orbitals.

The elements Ti - Cu are transition elements. They have ions with incomplete d orbitals.

**Task 5.2b** Why is iron a transition element? Why is CuCl white but CuCl$_2$ blue? What colour are Sc and Zn salts and why? Why is TiO$_2$ white but TiCl$_3$ violet?

5.3.2b. Electronic configurations

derive the electronic configuration of the atoms of the d- block elements (Sc to Zn) and their simple ions from their atomic number

<table>
<thead>
<tr>
<th>Element</th>
<th>atomic number</th>
<th>Symbol</th>
<th>Electronic structure of atom</th>
<th>Common ion(s)</th>
<th>Electronic structure of ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scandium</td>
<td>21</td>
<td>Sc</td>
<td>(Ar)$3d^14s^2$</td>
<td>Sc$^{3+}$</td>
<td>(Ar)</td>
</tr>
<tr>
<td>Titanium</td>
<td>22</td>
<td>Ti</td>
<td>(Ar)$3d^24s^2$</td>
<td>Ti$^{4+}$</td>
<td>(Ar)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ti$^{3+}$</td>
<td>(Ar)$3d^1$</td>
</tr>
<tr>
<td>Vanadium</td>
<td>23</td>
<td>V</td>
<td>(Ar)$3d^34s^2$</td>
<td>V$^{3+}$</td>
<td>(Ar)$3d^2$</td>
</tr>
<tr>
<td>Chromium</td>
<td>24</td>
<td>Cr</td>
<td>(Ar)$3d^54s^1$</td>
<td>Cr$^{3+}$</td>
<td>(Ar)$3d^3$</td>
</tr>
<tr>
<td>Manganese</td>
<td>25</td>
<td>Mn</td>
<td>(Ar)$3d^64s^2$</td>
<td>Mn$^{2+}$</td>
<td>(Ar)$3d^5$</td>
</tr>
<tr>
<td>Iron</td>
<td>26</td>
<td>Fe</td>
<td>(Ar)$3d^64s^2$</td>
<td>Fe$^{2+}$</td>
<td>(Ar)$3d^6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe$^{3+}$</td>
<td>(Ar)$3d^5$</td>
</tr>
<tr>
<td>Cobalt</td>
<td>27</td>
<td>Co</td>
<td>(Ar)$3d^74s^2$</td>
<td>Co$^{2+}$</td>
<td>(Ar)$3d^7$</td>
</tr>
<tr>
<td>Nickel</td>
<td>28</td>
<td>Ni</td>
<td>(Ar)$3d^84s^2$</td>
<td>Ni$^{2+}$</td>
<td>(Ar)$3d^8$</td>
</tr>
<tr>
<td>Copper</td>
<td>29</td>
<td>Cu</td>
<td>(Ar)$3d^{10}4s^1$</td>
<td>Cu$^+$</td>
<td>(Ar)$3d^{10}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cu$^{2+}$</td>
<td>(Ar)$3d^9$</td>
</tr>
<tr>
<td>Zinc</td>
<td>30</td>
<td>Zn</td>
<td>(Ar)$3d^{10}4s^2$</td>
<td>Zn$^{2+}$</td>
<td>(Ar)$3d^{10}$</td>
</tr>
</tbody>
</table>

5.3.2c. Evidence for configurations

discuss the evidence for the electronic configurations of the elements Sc to Zn based on successive ionization energies
5.3.2d. Properties of transition elements

recall that transition elements in general:

i. show variable oxidation number in their compounds, eg redox reactions of vanadium

ii. form coloured ions in solution

iii. form complex ions involving monodentate and bidentate ligands

iv. can act as catalysts both as the elements and as their compounds

Transition metals have higher melting points, higher boiling points and higher densities than other metals.

(i) the formation of coloured aqueous ions and other complex ions

[Cr(H₂O)₆]³⁺(aq) blue (but often seems green), dichromate Cr₂O₇²⁻(aq) orange in acid, chromate [CrO₄]⁻(aq) yellow in alkali, Fe²⁺(aq) green, Fe³⁺(aq) yellow/brown, Cu(H₂O)₆]²⁺(aq) blue. Managnate(VII) MnO₄⁻(aq) purple, Tetraamminecopper(II) Cu(NH₃)₄²⁺(aq) deep blue/purple, Tetrachlorocuprate(II) CuCl₄²⁻(aq) yellow, hydrated thiocyanate complex of iron (III) [Fe(SCN)(H₂O)₅]²⁺ blood red, [Co(H₂O)₆]³⁺(aq) pink, [CoCl₄]²⁻(aq) blue,

Coloured compounds:- When electrons move from a d-orbital (with lower energy) to another d-orbital (with higher energy), energy is taken in. This energy in the form of light is missing from the reflected light thus producing coloured compounds.
**Task 5.3.2d.1** Match formulae above to following names: hexaaquachromium(III), tetrachlorocobaltate(II), hexaaquacopper(II), hexaaquacobalt(II).

(ii) the formation of a range of compounds in which they are present in different stable oxidation states

Transition metals show the following characteristic properties:

1. Variable oxidation states: - Transition metals have electrons of similar energy in both the 3d and 4s levels. This means that one particular element can form ions of roughly the same stability by losing different numbers of electrons. Thus, all transition metals from titanium to copper can exhibit two or more oxidation states in their compounds.

Oxidation states of some Transition Metals:

<table>
<thead>
<tr>
<th>Transition Metal</th>
<th>Oxidation States</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>+2, +3, +4</td>
</tr>
<tr>
<td>Vanadium</td>
<td>+2, +3, +4, +5</td>
</tr>
<tr>
<td>Chromium</td>
<td>+2, +3, +6</td>
</tr>
<tr>
<td>Manganese</td>
<td>+2, +3, +4, +5, +6, +7</td>
</tr>
<tr>
<td>Iron</td>
<td>+2, +3</td>
</tr>
<tr>
<td>Cobalt</td>
<td>+2, +3</td>
</tr>
<tr>
<td>Nickel</td>
<td>+2, +3, +4</td>
</tr>
<tr>
<td>Copper</td>
<td>+1, +2</td>
</tr>
</tbody>
</table>

When Transition Metals form positive ions they loose their electrons from the 4s sub-shell first, then the 3d sub-shell.

**Task 5.3.2d.2** Give electronic structures for the ions in the following:
- copper(II)oxide, Copper(I)oxide, iron(II)sulphate, Iron(III)chloride, chromium(III)chloride.

2. Formation of complex ions: - As a lot of the transition metals have some empty spaces in their 3d-orbitals, they can receive lone pairs of electrons and form dative covalent bonds thus producing complex compounds. **Monodentate** ligands are Lewis bases that donate a single pair ("mono") of electrons to a metal atom. Monodentate ligands can be either ions (usually anions) or neutral molecules.

<table>
<thead>
<tr>
<th>Some Monodentate Ligands</th>
<th>ligand</th>
<th>Lewis structure</th>
<th>name</th>
<th>ligand</th>
<th>Lewis structure</th>
<th>name</th>
</tr>
</thead>
<tbody>
<tr>
<td>F⁻</td>
<td><img src="image" alt="F⁻" /></td>
<td>fluoride ion</td>
<td>F⁻</td>
<td>Cl⁻</td>
<td><img src="image" alt="Cl⁻" /></td>
<td>chloride ion</td>
</tr>
<tr>
<td>Br⁻</td>
<td><img src="image" alt="Br⁻" /></td>
<td>bromide ion</td>
<td>Br⁻</td>
<td>I⁻</td>
<td><img src="image" alt="I⁻" /></td>
<td>iodide ion</td>
</tr>
</tbody>
</table>
Chemists often represent ligands as spheres for simplicity, even though the "sphere" sometimes has three-dimensional structure of its own. For example, when chemists draw the structure for $\text{[Ni(NH}_3\text{)}_6\text{]}^{2+}$, each ammonia ligand is represented as a sphere. The sphere represents the donor atom of the ligand. In $\text{[Ni(NH}_3\text{)}_6\text{]}^{2+}$, the donor atoms are the nitrogen atoms of the NH$_3$ ligands (NOT the hydrogen atoms).

**Monodentate and Bidentate Cobalt Ligands**

![Monodentate and Bidentate Cobalt Ligands](image)

Story about complex compounds at University College London

4. Catalytic properties:- As Transition Metals have variable oxidation states, they tend to have catalytic properties. The small differences in ionisation energies make variable oxidation numbers possible. The reversible redox reactions involving transition metal ions make lower energy routes for other reactions. Transition metals as elements are also often catalysts. Here the reaction is catalysed on the surface of the metal.  

**Task 5.3.2d.3** Explain how V$_2$O$_5$ might catalyse sulfur dioxide reacting with oxygen
in the contact process. Use $2V^{5+} + O^{2-} + SO_2 \rightarrow 2V^{4+} + SO_3$ and $2V^{4+} + 1/2O_2 \rightarrow 2V^{5+} + O^2-$

5.3.2e. Shapes of complex ions

recall the shapes of complex ions limited to linear $[\text{CuCl}_2]^{-}$, planar $[\text{Pt(NH}_3)_2\text{Cl}_2]$, tetrahedral $[\text{CrCl}_4]^{-}$ and octahedral $[\text{Cr(NH}_3)_6]^{3+}$, $[\text{Cu(H}_2\text{O})_6]^{2+}$ and other aqua complexes.

Complex ions (cationic or anionic) are composed of a central metal ion surrounded by a cluster of anions or molecules, called ligands (species donating electron(s)). In transition metal complexes, non-bonded pairs of electrons on the ligand form coordinate bonds or dative covalent bond to the central ion by donating these unshared electron pairs into vacant orbitals of the transition metal ion. The number of coordinate bonds from ligands to the central ion is known as the co-ordination number of the central ion.

Co-ordination number: 6, 4, 2 Shape: Octahedral $[\text{Fe(H}_2\text{O})_6]^{3+}$, tetrahedral $[\text{Ni(CO)}_4]^{2+}$, and linear $[\text{CuCl}_2]^{-}$, respectively.

Task 2.5d.2 Show the location of the unpaired electrons which form the dative covalent bond.

Draw similar diagrams for $[\text{Ag(NH}_3)_2]^{+}$, $[\text{CuCl}_2]^{-}$, planar $[\text{Pt(NH}_3)_2\text{Cl}_2]$, tetrahedral $[\text{CrCl}_4]^{-}$, octahedral $[\text{Cr(NH}_3)_6]^{3+}$, $[\text{Cu(H}_2\text{O})_6]^{2+}$ and $[\text{Ni(CO)}_4]^{2+}$.

5.4.2f. Explaining properties

use the chemistries of chromium and copper to illustrate and explain some properties of transition metals as follows:

i. the formation of a range of compounds in which they are present in different oxidation states

<table>
<thead>
<tr>
<th>Chromium</th>
<th>24</th>
<th>Cr</th>
<th>(Ar)3d$^5$4s$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium(II), (Ar)3d$^4$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chromium(III), (Ar)3d^3
Chromium(VI), (Ar)3d^0

<table>
<thead>
<tr>
<th>Copper</th>
<th>29</th>
<th>Cu</th>
<th>(Ar)3d^{10}4s^1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper(I), (Ar)3d^{10}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper(II), (Ar)3d^9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ii. the presence of dative covalent bonding in complex ions, including the aqua-ions

![Diagram of aqua-ion structure]

iii. the colour or lack of colour of aqueous ions and other complex ions, resulting from the splitting of the energy levels of the d orbitals by ligands

The colour of a substance is due to the light that it reflects.
A black substance absorbs all light, none is reflected.
A white substance absorbs no light, it is all reflected.
A coloured substance absorbs some wavelengths (of visible light), the remainder are reflected.
Atoms can absorb energy when electrons are promoted from lower to higher energy levels. Transitions between many orbitals require more energy than is available in visible light. Transitions between d orbitals can happen with the energy from visible light so transition metal compounds are coloured.
d orbitals are normally of similar energy but when surrounded by ligands the orbitals are split into higher and lower energy sets. This theory is called crystal field theory. [Ti(H_2O)_6]^{3+} is violet. Green light is absorbed by this ion leaving red and blue light to combine and give the ion its violet colour. The electronic transition involved is shown below.
Task 5.2d.4 Draw the ground state and an excited state of the Fe$^{2+}$ ion. Using the diagram explain why iron(II) sulfate is green.

iv. simple ligand exchange reactions

Ligand exchange - This involves the replacement of one ligand by another.

E.g. \[ [\text{Cu(H}_2\text{O)}_4]^{2+} \text{(aq)} + 4\text{Cl}^- \rightleftharpoons [\text{CuCl}_4]^{2-} \text{(aq)} + 4\text{H}_2\text{O(l)} \]

Draw a diagram to show the difference in splitting between d orbitals in the metal atoms in the above complexes.

The Cl$^-$ ligands have replaced the H$_2$O ligands. The colour change is because the different ligands create a different amount of splitting between d orbitals in the copper ion. In the above case the position of the equilibrium lies to the right.

Deprotonation seems similar but is not just an exchange. It involves a water ligand losing a hydrogen ion (proton) to a proton acceptor such as an hydroxide ion.

\[ [\text{Cu(H}_2\text{O})_6]^{2+} + \text{OH}^- \rightleftharpoons [\text{Cu(OH)(H}_2\text{O)}_5]^{2+} + \text{H}_2\text{O} \]

Task \([\text{CoCl}_4]^{2-}\) is a tetrahedral ion, \([\text{Co(H}_2\text{O)}_6]^{2+}\), Co(OH)$_2$ (H$_2$O)$_4$] are octahedral ions. Write equations to show ligand exchange and deprotonation using Cl$^-$, H$_2$O and OH$^-$. Draw the shapes of the complex ions involved.

v. relate relative stability of complex ions to the entropy changes of ligand exchange reactions involving polydentate ligands (qualitatively only), eg EDTA
Large ligands include ethanedioic ions, diaminoethane and edta
\[ \text{Cu(H}_2\text{O)}\text{)}_4^{2+} + 2\text{ethanedioic ions} = \text{Cu(ethanedioic)}_2 + 4\text{H}_2\text{O} \]
3 species changes to 5 species so entropy increases, reaction likely
\[ \text{Cu(diaminoethane)}_2 + \text{EDTA} = \text{Cu(EDTA)} + 2\text{diaminoethane} \]
2 species form 3 so entropy increases, reaction likely

vi. relate disproportionation reactions to standard electrode potentials and hence to \( E_{cell} \)

Disproportionation is the oxidation and reduction of the same element in the same reaction. For example in solution \( \text{Cu}^+(\text{aq}) \) disproportionates.

\[ 2\text{Cu}^+(\text{aq}) \rightarrow \text{Cu(s)} + \text{Cu}^{2+}(\text{aq}) \]
\(+1 \) -reduction-> 0
\(+1 \) -oxidation --------> +2
Cu^{2+}(aq) + e^- \rightarrow Cu^{+}(aq) \quad E^\circ = +0.15V
Cu^{+}(aq) + e^- \rightarrow Cu(s) \quad E^\circ = +0.52V

Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + e^- \quad E^\circ = -0.15V
Cu^{+}(aq) + e^- \rightarrow Cu(s) \quad E^\circ = +0.52V
E_{cell} = \text{Sum of } E^\circ = +0.37V

Positive emf makes this reaction likely.

Task 5.1e

g. carry out experiments to:
   i. investigate ligand exchange in copper complexes
   \[ \text{Cu(H}_2\text{O)}\text{}_4^{2+} + 4\text{NH}_3 = \text{Cu(NH}_3\text{)}\text{}_4^{2+} + 4\text{H}_2\text{O} \]
   Blue \quad \text{deep blue/purple}
   ii. study the redox chemistry of chromium in oxidation states Cr(VI), Cr(III) and Cr(II)
   \[ \text{http://www.chemguide.co.uk/inorganic/transition/chromium.html} \]
   iii. prepare a sample of a complex, eg chromium(II) ethanoate

An aqueous solution of a Cr(III) compound is first reduced to the chromous state using zinc. The resulting blue solution is treated with sodium acetate, which results in the rapid precipitation of chromous acetate as a bright red powder.

\[ 2 \text{Cr}^{3+} + \text{Zn} \rightarrow 2 \text{Cr}^{2+} + \text{Zn}^{2+} \]
\[ 2 \text{Cr}^{2+} + 4 \text{OAc}^- + 2 \text{H}_2\text{O} \rightarrow \text{Cr}_2(\text{OAc})_4(\text{H}_2\text{O})_2 \]

The synthesis of Cr_2(OAc)_4(H_2O)_2 has been traditionally used to test the synthetic skills and patience of inorganic laboratory students in universities because the accidental introduction of a small amount of air into the apparatus is readily indicated by the discoloration of the otherwise bright red product.

source: \[ \text{http://en.wikipedia.org/wiki/Chromium(II)_acetate#Preparation} \]

h. recall that transition metals and their compounds are important as catalysts and that their activity may be associated with variable oxidation states of the elements or surface activity, eg catalytic converters in car exhausts

As Transition Metals have variable oxidation states, they tend to have catalytic properties. The small differences in ionisation energies make variable oxidation numbers possible. The reversible redox reactions involving transition metal ions make lower energy routes for other reactions.
**Task 5.2c(ii).2** Explain how V$_2$O$_5$ might catalyse sulfur dioxide reacting with oxygen in the contact process. Use 2V$^{5+}$ + O$^{2-}$ + SO$_2$ --> 2V$^{4+}$ + SO$_3$ and 2V$^{4+}$ + 1/2O$_2$ --> 2V$^{5+}$ + O$^{2-}$

i. explain why the development of new catalysts is a priority area for chemical research today and, in this context, explain how the scientific community reports and validates new discoveries and explanations, eg the development of new catalysts for making ethanoic acid from methanol and carbon monoxide with a high atom economy (green chemistry)

j. carry out and interpret the reactions of transition metal ions with aqueous sodium hydroxide and aqueous ammonia, both in excess, limited to reactions with aqueous solutions of Cr(III), Mn(II), Fe(II), Fe(III), Ni(II), Cu(II), Zn(II)

<table>
<thead>
<tr>
<th>ion</th>
<th>aqueous sodium hydroxide</th>
<th>aqueous ammonia solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$^{3+}$</td>
<td>Cr$^{3+}$(aq) + 3OH$^{-}$(aq) -----&gt; Cr(OH)$_3$(s) grey green</td>
<td>Cr$^{3+}$(aq) + 3OH$^{-}$(aq) -----&gt; Cr(OH)$_3$(s) grey green</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>Mn$^{2+}$(aq) + 2OH$^{-}$(aq) -----&gt; Mn(OH)$_2$(s) white/brown</td>
<td>Mn$^{2+}$(aq) + 2OH$^{-}$(aq) -----&gt; Mn(OH)$_2$(s) white/brown</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>Fe$^{2+}$(aq) + 2OH$^{-}$(aq) -----&gt; Fe(OH)$_2$(s) muddy/green</td>
<td>Fe$^{2+}$(aq) + 2OH$^{-}$(aq) -----&gt; Fe(OH)$_2$(s) muddy/green</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>Fe$^{3+}$(aq) + 3OH$^{-}$(aq) -----&gt; Fe(OH)$_3$(s) rust brown</td>
<td>Fe$^{3+}$(aq) + 3OH$^{-}$(aq) -----&gt; Fe(OH)$_3$(s) rust brown</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>Cu$^{2+}$(aq) + 2OH$^{-}$(aq) -----&gt; Cu(OH)$_2$(s) pale blue</td>
<td>Cu(H$_2$O)$_6^{2+}$(aq) + 2OH$^{-}$(aq) ---&gt; Cu(OH)$_2$(H$_2$O)$_4$(s) pale blue ligand exchange - dissolves in excess to give deep blue [Cu(NH$_3$)$_4$(H$_2$O)$_2$]$^{2+}$(aq)</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>Zn$^{2+}$(aq) + 2OH$^{-}$(aq) -----&gt; Zn(OH)$_2$(s) white</td>
<td>Zn$^{2+}$(aq) + 2OH$^{-}$(aq) -----&gt; Zn(OH)$_2$(H$_2$O)$_2$(aq) ligand exchange - dissolves in excess to give [Zn(NH$_3$)$_4$]$^{2+}$(aq)</td>
</tr>
</tbody>
</table>
k. write ionic equations to show the difference between amphoteric behaviour and ligand exchange in the reactions in 5.3.2g

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\([\text{Cu(H}_2\text{O)}_6]^2+ + \text{OH}^- <----- [\text{Cu(OH)(H}_2\text{O)}_5]^+ + \text{H}_2\text{O}\]

1. discuss the uses of transition metals and/or their compounds, eg in polychromic sun glasses, chemotherapy drugs.