Edexcel Chemistry A-Level

Topic 14: Redox II

Detailed Notes
Redox

Oxidation is loss of electrons and reduction is gain of electrons. Oxidation results in oxidation number becoming more positive and with reduction, it becomes more negative.

Electrochemical Cells

Electrochemical cells use redox reactions as the electron transfer between products creates a flow of electrons. This flow of charged particles is an electrical current which flows between electrodes in the cell. A potential difference is produced between the two electrodes which can be measured.

Most electrochemical cells consist of two solutions with metal electrodes and a salt bridge. A salt bridge is a tube of unreactive ions that can move between the solutions to carry the flow of charge but will not interfere with the reaction.

Electrochemical diagram:

Each solution is a half-cell which make up the full chemical cell. These half-cells have a cell potential which indicates how it will react, either as an oxidation or reduction reaction.

Cell Potentials ($E^\circ$)

If measured under standard conditions, cell potentials are measured compared to the Standard Hydrogen Electrode (SHE) to give a numerical value for the half-cell potential.

Positive potentials mean the substances are more easily reduced and will gain electrons. Negative potentials mean the substances are more easily oxidised and will lose electrons to become more stable.
Standard Hydrogen Electrode (SHE)
The standard hydrogen electrode is the measuring standard for half-cell potentials. It has a cell potential of 0.00V, measured under standard conditions. These conditions are:

- Solutions of 1.0 moldm$^{-3}$ concentration
- A temperature of 298K
- 100 kPa pressure

The cell consists of hydrochloric acid, hydrogen gas and uses platinum electrodes. These are very useful as they are metallic, so will conduct electricity, but are inert, so will not interfere with the reaction.

Example:

Conventional Cell Representation
Cells are represented in a simplified way so that they don't have to be drawn out each time. This representation has specific rules to help show the reactions that occur:

- The half-cell with the most negative potential goes on the left.
- The most oxidised species from each half-cell goes next to the salt bridge.
- A salt bridge is shown using a double line.
- Always include state symbols.
Calculating Cell Emf
Standard cell potential values are used to calculate the overall cell emf. This is always done as potential of the right of the cell minus the potential of the left of the cell when looking at the cell representation.

\[
\text{Emf}_{\text{(cell)}} = E^0_{\text{(right)}} - E^0_{\text{(left)}}
\]

It can also be remembered as the most positive potential minus the most negative potential.

If the overall cell potential is a positive value, the reaction taking place is spontaneous and favourable. The more positive the potential, the more favourable the reaction.

Cell Reactions (Anticlockwise rule)
In a similar way to redox reactions, half-cell reactions can be combined to give the overall cell reaction. The ‘anti-clockwise rule’ is a good method for ensuring the reaction is formed correctly.

1. Write the most negative emf out of the pair on top.
2. Draw anticlockwise arrows around the reactions.
3. Balance the electrons on both sides of the reaction.
4. Write out the cell reaction.
Example:

\[
\begin{align*}
\text{Ni}^{2+} \, \text{(aq)} + 2e^- & \rightarrow \text{Ni} \, \text{(s)} & E^0 = -0.25\text{V} \\
\text{Cu}^{2+} \, \text{(aq)} + 2e^- & \rightarrow \text{Cu} \, \text{(s)} & E^0 = +0.34\text{V}
\end{align*}
\]

\[
\text{Ni} \, \text{(s)} + \text{Cu}^{2+} \, \text{(aq)} \rightarrow \text{Cu} \, \text{(s)} + \text{Ni}^{2+} \, \text{(aq)}
\]

Oxidising and Reducing Agents
Standard electrode potentials can be ordered into a series.

Electrode potentials that are very positive are better oxidising agents and will oxidise those species more negative than it.
Species that are very negative are better reducing agents and will reduce those less negative than it.

Example:

<table>
<thead>
<tr>
<th>Species</th>
<th>Half Reaction</th>
<th>Standard Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F\textsubscript{2}</td>
<td>+ 2e\textsuperscript{-} \rightarrow 2F\textsuperscript{-}</td>
<td>+2.87</td>
</tr>
<tr>
<td>Pb\textsuperscript{4+}</td>
<td>+ 2e\textsuperscript{-} = Pb\textsuperscript{2+}</td>
<td>+1.67</td>
</tr>
<tr>
<td>Cl\textsubscript{2}</td>
<td>+ 2e\textsuperscript{-} = 2Cl\textsuperscript{-}</td>
<td>+1.36</td>
</tr>
<tr>
<td>O\textsubscript{2} + 4H\textsuperscript{+} + 4e\textsuperscript{-} = 2H\textsubscript{2}O</td>
<td>+1.23</td>
<td></td>
</tr>
<tr>
<td>Ag\textsuperscript{+}</td>
<td>+ 1e\textsuperscript{-} = Ag</td>
<td>+0.80</td>
</tr>
<tr>
<td>Fe\textsuperscript{3+}</td>
<td>+ 1e\textsuperscript{-} = Fe\textsuperscript{2+}</td>
<td>+0.77</td>
</tr>
<tr>
<td>Cu\textsuperscript{2+}</td>
<td>+ 2e\textsuperscript{-} = Cu</td>
<td>+0.34</td>
</tr>
<tr>
<td>2H\textsuperscript{+}</td>
<td>+ 2e\textsuperscript{-} = H\textsubscript{2}</td>
<td>0.00</td>
</tr>
<tr>
<td>Pb\textsuperscript{2+}</td>
<td>+ 2e\textsuperscript{-} = Pb</td>
<td>-0.13</td>
</tr>
<tr>
<td>Fe\textsuperscript{2+}</td>
<td>+ 2e\textsuperscript{-} = Fe</td>
<td>-0.44</td>
</tr>
<tr>
<td>Zn\textsuperscript{2+}</td>
<td>+ 2e\textsuperscript{-} = Zn</td>
<td>-0.76</td>
</tr>
<tr>
<td>Al\textsuperscript{3+}</td>
<td>+ 3e\textsuperscript{-} = Al</td>
<td>-1.66</td>
</tr>
<tr>
<td>Mg\textsuperscript{2+}</td>
<td>+ 2e\textsuperscript{-} = Mg</td>
<td>-2.36</td>
</tr>
<tr>
<td>Li\textsuperscript{+}</td>
<td>+ 1e\textsuperscript{-} = Li</td>
<td>-3.05</td>
</tr>
</tbody>
</table>

Image courtesy of Quora
Effects of Concentration and Pressure

Increasing the concentration of the solutions used in the electrochemical cell makes the cell emf more positive as fewer electrons are produced in the reaction. Increasing the pressure of the cell will make the cell emf more negative as more electrons are produced.

Commercial Cells

Electrochemical cells can be a useful source of energy for commercial use. They can be produced to be non-rechargeable, rechargeable or fuel cells.

Rechargeable Cells

The reaction that takes place within a rechargeable cell is a reversible reaction meaning the reactants can reform. Therefore the cell can be ‘reformed’ meaning it is a rechargeable cell.

Lithium ion cells are a commonly used as rechargeable batteries in phones, laptops and cars. They consist of a lithium cobalt oxide electrode and a graphite (carbon) electrode. An electrolyte of a lithium salt in an organic solvent is used to carry the flow of charge.

The half-cell equations for the reactions can be combined to give the full cell equation:

Example: discharging of a lithium-ion cell

\[
\text{Anode: } \text{Li} \quad \text{Li}^+ + \text{e}^- \\
\text{Cathode: } \text{e}^- + \text{Li}^+ + \text{Co}_2 \quad \text{Li}[\text{Co}_2] \\
\]

\[
\text{Li}[\text{Co}_2] \\
\text{Li} + \text{Co}_2 \\
\]

Outer Casing

Graphite Electrode - Anode

Lithium salt (in organic solvent)

Lithium-Cobalt Electrode - Cathode
In order to be recharged, a current has to be applied over the cell which forces electrons to move in the opposite direction. This causes the reaction to reverse, recharging the cell.

Non-rechargeable cells are not able to do this as the reactions used are impossible to reverse.

**Fuel Cells**
This type of electrochemical cell is used to generate an electrical current without needing to be recharged. The most common type of fuel cell is the hydrogen fuel cell, which uses a continuous supply of hydrogen and oxygen from the air to generate a continuous current.

The reaction that takes place produces water as the only waste product, meaning the hydrogen fuel cell is seen as being much more environmentally friendly.

<table>
<thead>
<tr>
<th>Anode</th>
<th>H₂</th>
<th>2H⁺ + 2e⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>( \frac{1}{2} )O₂ + 2H⁺ + 2e⁻</td>
<td>H₂O</td>
</tr>
<tr>
<td>Overall</td>
<td>H₂ + ( \frac{1}{2} )O₂</td>
<td>H₂O</td>
</tr>
</tbody>
</table>
The downsides to hydrogen fuel cells include the high flammability of hydrogen and that they are expensive to produce meaning they are not yet used too commonly.