Redox Equilibria (17.11.2014, 18.11.2014, 24.11.2014)

1. Defining standard electrode potential and simple galvanic cells
2. Difference between galvanic cell and electrolytic cell and predicting feasibility of redox reactions
3. Advanced redox cells, rechargeable cells and fuel cells
4. Practical: Redox circus, Galvanic cells, Redox titration
17 Nov 2014
The more negative the $E^\circ$ value, the stronger reducing agent (Li) the more the equilibrium lies to the left.

$$\text{Li}^+ + e^- \rightleftharpoons \text{Li} \quad E^\circ = -3.03\text{V}$$

The more positive the $E^\circ$ value, the stronger oxidising agent ($\text{Au}^{3+}$) the more the equilibrium lies to the right.

$$\text{Au}^{3+} + 3e^- \rightleftharpoons \text{Au} \quad E^\circ = +3.03\text{V}$$
Standard Hydrogen Electrode (SHE)

\[
\text{Pt}_{(s)} \mid \text{H}_2(g)(1 \text{ atm}) \mid \text{H}^+_{(aq)}(1 \text{ M})
\]

\[
2\text{H}^+_{(aq)} + 2\text{e}^- \rightleftharpoons \text{H}_2(g)
\]

- The SHE is the electrode which all other half cells are compared against and is therefore arbitrarily assigned 0 V.
- In the SHE, a platinum wire acts as an electrode in an acidic electrolyte, where \([\text{H}^+] = 1 \text{ mol dm}^{-3}\). Hydrogen gas at the pressure of 1 atm (10^5 Pa) is bubbled through the solution at a temperature of 25°C (298K).
- pH of SHE solution is 0 (pH=-log[1]=0)
Standard Hydrogen Electrode (SHE)

\[ \text{Pt}^{(s)} | \text{H}_2(g) (1 \text{ atm}) | \text{H}^+_{(aq)} (1\text{M}) \]

or,

\[ \text{Pt} | \text{H}_2 | \text{H}^+ \]

\[ 2\text{H}^+_{(aq)} + 2e^- \rightleftharpoons \text{H}_2(g) \]
The standard electrode potential of a metal / metal ion combination is the emf measured when that metal / metal ion electrode is coupled to a hydrogen electrode under standard conditions.

\[
\text{Pt} | \text{H}_2 | \text{H}^+ | \text{Mg}^{2+} | \text{Mg}
\]
H$_2$ has a greater tendency to form H$^+$ than Cu to form Cu$^{2+}$.

Pt | H$_2$ | H$^+$ | | Cu$^{2+}$ | Cu

Salt bridge (filter paper contains KNO$_3$) has mobile ions allowing transfer of charge between each half-cell.

Copper Sulfate CuSO$_4$(aq) 1 mol dm$^{-3}$
Identify the: strongest oxidising agent, strongest reducing agent

Identify the: weakest oxidising agent, weakest reducing agent
<table>
<thead>
<tr>
<th>Equation number</th>
<th>Electrode half-equation</th>
<th>$E^o / V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{Cd(OH)}_2(s) + 2e^- \rightarrow \text{Cd(s)} + 2\text{OH}^-(aq)$</td>
<td>-0.88</td>
</tr>
<tr>
<td>2</td>
<td>$\text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn(s)}$</td>
<td>-0.76</td>
</tr>
<tr>
<td>3</td>
<td>$\text{NiO(OH)}(s) + \text{H}_2\text{O}(l) + e^- \rightarrow \text{Ni(OH)}_2(s) + \text{OH}^-(aq)$</td>
<td>+0.52</td>
</tr>
<tr>
<td>4</td>
<td>$\text{MnO}_2(s) + \text{H}_2\text{O}(l) + e^- \rightarrow \text{MnO(OH)}(s) + \text{OH}^-(aq)$</td>
<td>+0.74</td>
</tr>
<tr>
<td>5</td>
<td>$\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l)$</td>
<td>+1.23</td>
</tr>
</tbody>
</table>

**Oxidising agents (accept electrons)**

**Reducing agents (donate electrons)**

strongest oxidising agent is $\text{O}_2$, strongest reducing agent is $\text{Cd}$

weakest oxidising agent is $\text{Cd(OH)}_2$, weakest reducing agent $\text{H}_2\text{O}$
A series of reduction half-equations and their standard electrode potentials written with respect to the standard hydrogen electrode (SHE).

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>Standard Electrode Potential (E°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn^{2+}(aq) + 2e^- → Sn(s)</td>
<td>E° = -0.14 V</td>
</tr>
<tr>
<td>O_2(g) + 2H_2O(l) + 4e^- ⇌ 4OH^-(aq)</td>
<td>E° = +0.40 V</td>
</tr>
<tr>
<td>NO_3^-(aq) + 4H^+(aq) + 3e^- ⇌ NO(g) + 2H_2O(l)</td>
<td>E° = +0.96 V</td>
</tr>
<tr>
<td>MnO_4^-(aq) + 8H^+(aq) + 5e^- ⇌ Mn^{2+}(aq) + 4H_2O(l)</td>
<td>E° = +1.51 V</td>
</tr>
</tbody>
</table>
Redox cell (template)

\[
\begin{align*}
\text{Zn}^{2+}/\text{Zn} & \quad -0.76 \text{ V} \\
\text{2H}^+/{\text{H}}_2 & \quad 0 \text{ V} \\
\text{Cu}^{2+}/\text{Cu} & \quad +0.34 \text{ V}
\end{align*}
\]
Redox cell (template)

- Oxidation Anode
  - Zn\(^{2+}/\text{Zn} \quad -0.76 \text{ V}

- Reduction Cathode
  - Cu\(^{2+}/\text{Cu} \quad +0.34 \text{ V}

- 2H\(^+]/\text{H}_2 \quad 0 \text{ V}

Direction of electron flow
Zn\(^{2+}\)/Zn → Zn\(^{2+}\) + 2e\(^-\) at the anode, with an electrode potential of -0.76 V.

2H\(^+\)/H\(_2\) → 0 V at the cathode.

Cu\(^{2+}\)/Cu → Cu\(^{2+}\) + 2e\(^-\) at the anode, with an electrode potential of +0.34 V.

The direction of electron flow is from the anode to the cathode, indicated by the arrow between the two compartments.
Redox cell (template)

Oxidation Anode

\[ \text{Zn}^{2+}/\text{Zn} \quad -0.76 \text{ V} \]

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \]

Reduction Cathode

\[ \text{2H}^+/>H_2 \quad 0 \text{ V} \]

\[ \text{Cu}^{2+}/\text{Cu} + 0.34 \text{ V} \]

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \]

\[ \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu} \quad E^\ominus = +0.34(-0.76) = +1.10 \text{ V} \]

Direction of electron flow

Cathode

Oxidation

Anode

Zn

\[ \text{Cu} \]
\[ E^\ominus_{\text{cell}} = E_{(\text{cathode})} - E_{(\text{anode})} \]

\[ E^\ominus_{\text{cell}} = +0.34 - (-0.76) = +1.10 \text{ V} \]
### Left half-cell (Oxidation, Anode)

- **Mg$$^{2+}$$ | Mg (-2.37)
- **Mg$$^{2+}$$ | Mg (-2.37)
- **Zn$$^{2+}$$ | Zn (-0.76)

### Right half-cell (Reduction, Cathode)

- **Zn$$^{2+}$$ | Zn (-0.76)
- **Cu$$^{2+}$$ | Cu (+0.34)
- **Cu$$^{2+}$$ | Cu (+0.34)

### Conventional representation of the cell

- **Electron flow**

### EMF / V

- $E_{\text{right}} - E_{\text{left}}$
<table>
<thead>
<tr>
<th>Left half-cell (Oxidation, Anode)</th>
<th>Right half-cell (Reduction, Cathode)</th>
<th>Conventional representation of the cell</th>
<th>EMF / V $E_{\text{right}} - E_{\text{left}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>Mg (-2.37)</td>
<td>Zn$^{2+}$</td>
<td>Zn (-0.76)</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>Mg (-2.37)</td>
<td>Cu$^{2+}$</td>
<td>Cu (+0.34)</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>Zn (-0.76)</td>
<td>Cu$^{2+}$</td>
<td>Cu (+0.34)</td>
</tr>
</tbody>
</table>
Draw the diagram to show how you would measure $E^\ominus$ for Zn
And write down the overall equation for this cell  
(8 marks)
Draw the diagram to show how you would measure $E^{\text{o}}$ for Zn
And write down the overall equation for this cell

(8 marks)

Pt| $H_2$| $H^+$ || $Zn^{2+}$|Zn

- hydrogen gas 100 kPa
- $H^+$ (aq) 1 mol dm$^{-3}$
- platinum electrode
- zinc electrode
- salt bridge (filter paper soaked in KNO$_3$)
- high resistance voltmeter

Overall equation:

$\text{Pt} \mid H_2(g), 100 \text{ kPa} \mid H^+, 1 \text{ mol dm}^{-3} \mid Zn^{2+}(aq) \mid Zn$
Draw a labelled diagram of the apparatus that could be connected to a standard hydrogen electrode in order to measure the standard electrode potential of the Fe$^{3+}$/Fe$^{2+}$ electrode. State the conditions under which this cell should be operated.

Given the Fe$^{3+}$/Fe$^{2+}$ $E^\circ$ value is +0.77V, determine the overall cell equation
Draw a labelled diagram of the apparatus that could be connected to a standard hydrogen electrode in order to measure the standard electrode potential of the Fe$^{3+}$/Fe$^{2+}$ electrode.

State the conditions under which this cell should be operated.

Given the Fe$^{3+}$/Fe$^{2+}$ $E^\circ$ value is 0.77V, determine the overall cell equation.
### Conventional representation of the cell

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<tr>
<th>Left half-cell (Oxidation, Anode)</th>
<th>Right half-cell (Reduction, Cathode)</th>
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<th>EMF / V</th>
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<tbody>
<tr>
<td>Mg(^{2+})</td>
<td>Mg (-2.37)</td>
<td>Zn(^{2+})</td>
<td>Zn (-0.76)</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>Mg (-2.37)</td>
<td>Cu(^{2+})</td>
<td>Cu (+0.34)</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>Zn (-0.76)</td>
<td>Cu(^{2+})</td>
<td>Cu (+0.34)</td>
</tr>
</tbody>
</table>
Oxidation
Anode

Right half-cell
(Re-duction, Cathode)

Conventional representation of the cell

EMF / V
\[ E_{\text{right}} - E_{\text{left}} \]

<table>
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<th>Left half-cell (Oxidation, Anode)</th>
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<td>( \text{Mg}^{2+}</td>
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</tr>
<tr>
<td>( \text{Cu}^{2+}</td>
<td>\text{Cu} ) (+0.34)</td>
<td>( \text{Zn}^{2+}</td>
<td>\text{Zn} ) (-0.76)</td>
</tr>
</tbody>
</table>
The half-equations for two electrodes used to make an electrochemical cell are shown below.

\[
\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow \text{Cl}^-\text{(aq)} + 3\text{H}_2\text{O(l)} \quad E^\circ = +1.45 \text{ V}
\]

\[
\text{SO}_4^{2-}\text{(aq)} + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{SO}_3^{2-}\text{(aq)} + \text{H}_2\text{O(l)} \quad E^\circ = +0.17 \text{ V}
\]

Write the conventional representation for the cell using platinum contacts.

Write an overall equation for the cell reaction and identify the oxidising and reducing agents.
The half-equations for two electrodes used to make an electrochemical cell are shown below.

\[
\begin{align*}
\text{ClO}_3^{-}(aq) + 6\text{H}^{+}(aq) + 6\text{e}^{-} & \rightarrow \text{Cl}^{-}(aq) + 3\text{H}_2\text{O}(l) \quad & E^\ominus = +1.45 \text{ V} \\
\text{SO}_4^{2-}(aq) + 2\text{H}^{+}(aq) + 2\text{e}^{-} & \rightarrow \text{SO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \quad & E^\ominus = +0.17 \text{ V}
\end{align*}
\]

Write the conventional representation for the cell using platinum contacts.

Pt | SO\textsubscript{3}\textsuperscript{2-}(aq), SO\textsubscript{4}\textsuperscript{2-}(aq) | | ClO\textsubscript{3}^{-}(aq), Cl\textsuperscript{-}(aq) | Pt

Write an overall equation for the cell reaction and identify the oxidising and reducing agents.

\[
\text{ClO}_3^{-}(aq) + 3\text{SO}_3^{2-}(aq) \rightarrow \text{Cl}^{-}(aq) + 3\text{SO}_4^{2-}(aq)
\]

oxidising agent ClO\textsubscript{3}^{-}
reducing agent SO\textsubscript{3}\textsuperscript{2-}
Deduce the equation for the overall cell reaction of a cell that has an e.m.f. of 0.78 V.

Give the conventional cell representation for this cell. Identify the positive electrode.
Cu^{2+} + Fe → Cu + Fe^{2+}

Anode------Cathode
Fe | Fe^{2+} || Cu^{2+} | Cu

Reduction occurs at Cathode (+) (copper electrode)

$$E_{\text{cell}} = E_{(\text{cathode})} - E_{(\text{anode})}$$

$$E_{\text{cell}} = +0.34 - (-0.44) = +0.78 \text{ V}$$
Use data from the table to explain why Au\(^+\) ions are not normally found in aqueous solution.

Write an equation to show how Au\(^+\) ions would react with water.
Spontaneous reaction occurs where Au\(^+\) is reduced by H\(_2\)O to Au:

Anode------Cathode

\[
\text{H}_2\text{O} \mid \frac{1}{2} \text{O}_2 \mid \text{Au}^+ \mid \text{Au} \quad \text{with } E^{\ominus}_{\text{cell}} = +1.68-(+1.23)= +0.45 \text{V}
\]

\[
2\text{Au}^+ + \text{H}_2\text{O} \rightarrow 2\text{Au} + \frac{1}{2} \text{O}_2 + 2\text{H}^+
\]
Select the species that is the most powerful reducing agent.

State the colours of:
- Cr₂O₇²⁻
- Cr³⁺
- MnO₄⁻

[Fe²⁺(aq)] can be determined by titrating the solution, with acidified KMNO₄(aq).

(i) Explain, why HCl should not be used to acidify KMNO₄(aq).
(ii) Explain why HNO₃ should not be used to acidify KMNO₄(aq).

Calculate the e.m.f. of the cell: Pt | Mn²⁺, MnO₄⁻ | | S₂O₈²⁻, SO₄²⁻ | Pt

Deduce the equation when excess S₂O₈²⁻ is added to Mn²⁺(aq) ions.
Select the species that is the most powerful reducing agent: \( \text{Fe}^{2+} \)

State the colours of:
- \( \text{Cr}_2\text{O}_7^{2-} \) orange
- \( \text{Cr}^{3+} \) green
- \( \text{MnO}_4^- \) purple

\([\text{Fe}^{2+}(aq)]\) can be determined by titrating the solution, with acidified \( \text{KMNO}_4(aq) \).

(i) Explain why \( \text{HCl} \) should not be used to acidify \( \text{KMNO}_4(aq) \).

(ii) Explain why \( \text{HNO}_3 \) should not be used to acidify \( \text{KMNO}_4(aq) \).

\begin{align*}
\text{MnO}_4^- \text{ will oxidise } \text{Cl}^- \\
\text{Fe}^{2+} \text{ will reduce } \text{NO}_3^- 
\end{align*}

Calculate the e.m.f. of the cell: \( \text{Pt} \mid \text{Mn}^{2+}, \text{MnO}_4^- \mid \text{S}_2\text{O}_8^{2-}, \text{SO}_4^{2-} \mid \text{Pt} \)

0.5V

Deduce the equation when excess \( \text{S}_2\text{O}_8^{2-} \) is added to \( \text{Mn}^{2+}(aq) \) ions.

\[
2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{S}_2\text{O}_8^{2-} \rightarrow 10\text{SO}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ 
\]
In the external circuit of this cell, the electrons flow through the ammeter from right to left. Suggest why the electrons move in this direction.

Explain why the current in the external circuit of this cell falls to zero after the cell has operated for some time.
In the external circuit of this cell, the electrons flow through the ammeter from right to left. Suggest why the electrons move in this direction.

\[ \text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu} \]

Decreased Cu\(^{2+}\), shifts equilibrium to the left, making this electrode more electronegative and ‘anode’ relative to opposite electrode. Electrons flow from anode to cathode.

[Nernst equation]

Eventually, Cu\(^{2+}\) (aq) ions in each electrode will equalise, so no net difference in half-cell electrode potentials.
24.11.2014
Discharging vs. Re-charging redox cells
ELECTROLYTIC CELL

The power source drives the electrons from anode (+) to cathode (-)

**Anode (oxidation)**

\[
\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^- \quad E^\circ = +1.36
\]

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \quad E^\circ = -1.36
\]

**Cathode (reduction)**

\[
\text{Na}^+ + e^- \rightarrow \text{Na} \quad E^\circ = -2.71
\]

\[
2\text{Na}^+ + 2e^- \rightarrow 2\text{Na} \quad E^\circ = -2.71
\]

**Overall:** \(2\text{Na}^+ + 2\text{Cl}^- \rightarrow 2\text{Na} + \text{Cl}_2\)

\[
E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -2.71 - (+1.36) = -4.07\text{V}
\]

OR, simply directly add half-cell \(E^\circ\) as shown in overall equation: \(E^\circ = -2.71 + (-1.36) = -4.07\text{V}\)

Negative \(E^\circ\) for cell indicates voltage needs to be applied to induce the overall cell reaction.
Galvanic cell (produces EMF)

Spontaneous chemical reaction, produces electrical energy

Left electrode is anode (oxidation occurs), Anode is (-)

Right electrode is cathode (reduction occurs), Cathode is (+)

Electrolysis/Recharging cell (apply EMF)

Uses electrical energy and converts this to chemical energy in a non-spontaneous reaction

Left electrode becomes cathode (reduction occurs), Cathode is (-)

Right electrode becomes anode (oxidation occurs), Anode is (+)

Electrons always flow from Anode to Cathode, regardless of discharging or re-charging cell status
Spontaneous discharging cell

**Galvanic/Voltaic Charge Flow**

- \( \text{Cu}^{2+}/\text{Cu} +0.34 \)
- \( \text{Ag}^{+}/\text{Ag} +0.79 \)

Recharging cell

**Electrolytic Charge Flow**

- \( 2e^- \)
Galvanic cell

- Anode: Cd(s) → Cd^{2+}(aq) + 2e^-
- Cathode: Cu^{2+}(aq) + 2e^- → Cu(s)

Overall reaction: Cd(s) + Cu^{2+}(aq) → Cd^{2+}(aq) + Cu(s)

Electrolytic/Recharging cell

- Anode: Cu(s) → Cu^{2+}(aq) + 2e^-
- Cathode: Cd^{2+}(aq) + 2e^- → Cd(s)

Overall reaction: Cd^{2+}(aq) + Cu(s) → Cd(s) + Cu^{2+}(aq)
A rechargeable nickel–cadmium cell can also be constructed. Write an equation for the overall reaction that occurs when the cell is:

**discharging:**

and **being recharged:**

An ethanol–oxygen fuel cell may be also be constructed. Deduce a half-equation for the reaction at the ethanol electrode. In this half-equation, ethanol reacts with water to form carbon dioxide and hydrogen ions. The e.m.f. of an ethanol–oxygen fuel cell is 1.00 V. Calculate a value for the electrode potential of the ethanol electrode.
A rechargeable nickel–cadmium cell can also be constructed. Write an equation for the overall reaction that occurs when the cell is:

**discharging:**
\[ 2\text{NiO(OH)} + 2\text{H}_2\text{O} + \text{Cd} \rightarrow 2\text{Ni(OH)}_2 + \text{Cd(OH)}_2 \]
\[ \text{E}^{\circ} \text{cell} = +1.4 \text{ V} \]

**and being recharged:**
\[ 2\text{Ni(OH)}_2 + \text{Cd(OH)}_2 \rightarrow 2\text{NiO(OH)} + 2\text{H}_2\text{O} + \text{Cd} \]
\[ \text{E}^{\circ} \text{cell} = -1.4 \text{ V} \]

An ethanol–oxygen fuel cell may also be constructed. Deduce a half-equation for the oxidation reaction occurring at the ethanol electrode. In this half-equation, ethanol reacts with water to form carbon dioxide and hydrogen ions. The EMF of an ethanol–oxygen fuel cell is 1.00 V. Calculate a value for the electrode potential of the \( \text{CO}_2/\text{ethanol} \) electrode.

**O\text{}_2 \text{ electrode:}**
\[ \text{O}_2 \text{ (g)} + 4\text{H}^+\text{(aq)} + 4\text{e}^- \rightarrow 2\text{H}_2\text{O(l)} \]
\[ \text{E}^{\circ} \text{cell} = +1.23 \text{ V} \]

**Ethanol electrode:**
\[ \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \]
\[ 1.0 = 1.23 - \text{E}^{\circ} \text{CO}_2/\text{ethanol} \]
\[ \therefore \text{E}^{\circ} \text{CO}_2/\text{ethanol} = +0.23 \text{ V} \]
The diagram shows a non-rechargeable cell that can be used to power electronic devices.

Calculate the e.m.f. of this cell.

Write an equation for the overall reaction that occurs when the cell discharges.

Deduce one essential property of the non-reactive porous separator.

Suggest the function of the carbon rod in the cell.

The zinc electrode acts as a container for the cell and is protected from external damage. Suggest why a cell often leaks after being used for a long time.

\[
\begin{align*}
Zn^{2+}(aq) + 2e^- &\rightarrow Zn(s) & -0.76 \\
MnO_2(s) + H_2O(l) + e^- &\rightarrow MnO(OH)(s) + OH^-(aq) & +0.74
\end{align*}
\]
Calculate the e.m.f. of this cell.  

\[ +0.74 - (-0.76) = +1.5V \]

Write an equation for the overall reaction that occurs when the cell discharges

\[ 2\text{MnO}_2 + 2\text{H}_2\text{O} + \text{Zn} \rightarrow 2\text{MnO(OH)} + 2\text{OH}^- + \text{Zn}^{2+} \]

Deduce one essential property of the non-reactive porous separator

Allows ions to pass

Suggest the function of the carbon rod in the cell.  
electrode conductor

The zinc electrode acts as a container for the cell and is protected from external damage. Suggest why a cell often leaks after being used for a long time.

\[ \text{Zn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Zn}(s) \quad -0.76 \]

\[ \text{MnO}_2(s) + \text{H}_2\text{O(l)} + e^- \rightarrow \text{MnO(OH)}(s) + \text{OH}^-(\text{aq}) \quad +0.74 \]

Zn coating is ‘used up’ by redox reaction
Rechargeable cells (lead-acid accumulator)

Eye protection (chemical splash-proof)
One 150 cm³ beaker
2–4 V low voltage DC supply
1.25 V lamp in holder
Two crocodile clips
Two connecting leads
Two 8 cm lead foil electrodes
Stopclock
White tile
100 cm³ of 0.5 mol dm⁻³ sulfuric acid: irritant and corrosive
The electrode half-equations in a lead–acid cell are shown in the table below.

<table>
<thead>
<tr>
<th>Half-equation</th>
<th>$E^\ddagger$/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbO$_2$(s) + 3H$^+$&lt;sub&gt;aq&lt;/sub&gt; + HSO$_4^-$&lt;sub&gt;aq&lt;/sub&gt; + 2e$^-$ $\rightarrow$ PbSO$_4$(s) + 2H$_2$O(l)</td>
<td>+1.69</td>
</tr>
<tr>
<td>PbSO$_4$(s) + H$^+$&lt;sub&gt;aq&lt;/sub&gt; + 2e$^-$ $\rightarrow$ Pb(s) + HSO$_4^-$&lt;sub&gt;aq&lt;/sub&gt;</td>
<td>to be calculated</td>
</tr>
</tbody>
</table>

The PbO$_2$/PbSO$_4$ electrode is the positive terminal of the cell and the e.m.f. of the cell is 2.15 V.

Calculate the missing electrode potential.

Write an equation for the overall reaction that occurs when the cell is being discharged and recharged.

Give one reason why the e.m.f. of the lead–acid cell changes after several hours.

Explain why the voltage remains constant in cell X.
The electrode half-equations in a lead–acid cell are shown in the table below.

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<td>$\text{PbO}_2(s) + 3\text{H}^+(aq) + \text{HSO}_4^-(aq) + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$</td>
<td>+1.69</td>
</tr>
<tr>
<td>$\text{PbSO}_4(s) + \text{H}^+(aq) + 2e^- \rightarrow \text{Pb}(s) + \text{HSO}_4^-(aq)$</td>
<td>to be calculated</td>
</tr>
</tbody>
</table>

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

$2.15 = 1.69 - E_{\text{anode}} \therefore E_{\text{anode}} = -0.46\text{V}$

Discharged: $\text{PbO}_2 + 2\text{H}^+ + 2\text{HSO}_4^- + \text{Pb} \rightleftharpoons 2\text{PbSO}_4 + 2\text{H}_2\text{O}$

Recharged: $2\text{PbSO}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{PbO}_2 + 2\text{H}^+ + 2\text{HSO}_4^- + \text{Pb}$

Give one reason why the e.m.f. of the lead–acid cell changes after several hours. reagents used up.

Explain why the voltage remains constant in cell X. concentration of reagents remain constant (fuel cell)
Hydrogen–oxygen fuel cells can operate in acidic or in alkaline conditions. Commercial cells use porous platinum electrodes in contact with concentrated KOH(aq).

Write the conventional representation for an alkaline hydrogen–oxygen fuel cell, calculate its EMF and final equation.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>EMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O_2(g) + 4H^+ (aq) + 4e^- \rightarrow 2H_2O(l) )</td>
<td>+1.23</td>
</tr>
<tr>
<td>( O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) )</td>
<td>+0.40</td>
</tr>
<tr>
<td>( 2H^+ (aq) + 2e^- \rightarrow H_2(g) )</td>
<td>0.00</td>
</tr>
<tr>
<td>( 2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g) )</td>
<td>−0.83</td>
</tr>
</tbody>
</table>

Suggest why the EMF of \( H_2-O_2 \) fuel cell, operating in acidic conditions, is identical to an \( H_2-O_2 \) alkaline fuel cell.

What is the main advantage of a fuel cell over a rechargeable cell for propelling a vehicle?
Hydrogen–oxygen fuel cells can operate in acidic or in alkaline conditions. Commercial cells use porous platinum electrodes in contact with concentrated KOH(aq).

Write the conventional representation for an alkaline hydrogen–oxygen fuel cell, calculate its EMF and final equation.

Anode: $\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{e}^- + 2\text{H}_2\text{O}$  \hspace{1cm} +0.83
Cathode: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \hspace{1cm} +0.4$
Overall: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \hspace{1cm} +1.23$V

What is the main advantage of a fuel cell over a rechargeable cell for propelling a vehicle

Hydrogen and oxygen supplied continuously, can be operated without stopping to recharge
# Hydrogen fuel cells

<table>
<thead>
<tr>
<th>Hydrogen fuel cells are the best alternative to petrol engine cars</th>
<th>Hydrogen fuel cells are not the best alternative to petrol engine cars</th>
</tr>
</thead>
<tbody>
<tr>
<td>No pollution from the engine, the only product is water.</td>
<td>Current vehicles would need a new engine.</td>
</tr>
<tr>
<td>High efficiency.</td>
<td>Hydrogen fuel pumps would need to be rolled out across the country.</td>
</tr>
<tr>
<td>Hydrogen can be made from renewable resources such as ethanol.</td>
<td>Hydrogen is explosive and this has handling and storage safety issues.</td>
</tr>
<tr>
<td>Lightweight.</td>
<td>It is still being researched and more issues may arise.</td>
</tr>
<tr>
<td>Lower tax / no tax.</td>
<td>Drivers are sceptical.</td>
</tr>
<tr>
<td></td>
<td>As it is an emergent technology, it is unproven and the vehicles may be difficult / expensive to fix.</td>
</tr>
</tbody>
</table>
The simplified electrode reactions in a rechargeable lithium cell are:

**Electrode A**  \[ \text{Li}^+ + \text{MnO}_2 + e^- \rightarrow \text{LiMnO}_2 \quad E = -0.15 \text{ V} \]

**Electrode B**  \[ \text{Li}^+ + e^- \rightarrow \text{Li} \]

**Electrode B** is the negative electrode.

The e.m.f. of this cell is 2.90 V. Use this information to calculate a value for the electrode potential of electrode B.

Write an equation for the overall reaction that occurs when this lithium cell is being
i) discharged
ii) re-charged.
The simplified electrode reactions in a rechargeable lithium cell are:

**Electrode A**  \( \text{Li}^+ + \text{MnO}_2 + e^- \rightarrow \text{LiMnO}_2 \) \( E = -0.15 \text{ V} \)

**Electrode B**  \( \text{Li}^+ + e^- \rightarrow \text{Li} \)

**Electrode B** is the negative electrode.

The e.m.f. of this cell is 2.90 V. Use this information to calculate a value for the electrode potential of electrode B.

Write an equation for the overall reaction that occurs when this lithium cell is being
i) discharged
ii) re-charged.

**Discharged:**  \( \text{Li} + \text{MnO}_2 \rightarrow \text{LiMnO}_2 \) \( E^\theta = +2.90\text{V} \)

**Re-charged:**  \( \text{LiMnO}_2 \rightarrow \text{Li} + \text{MnO}_2 \) \( E^\theta = -2.90\text{V} \)
Use the data below, where appropriate, to answer the questions which follow.

\[
\begin{align*}
\text{Mg}^2+ (aq) + 2e^- & \rightleftharpoons \text{Mg}(s) & E^\circ / \text{V} & = -2.37 \\
\text{Fe}^2+ (aq) + 2e^- & \rightleftharpoons \text{Fe}(s) & & -0.44 \\
\text{O}_2 (g) + 2\text{H}_2\text{O}(l) + 4e^- & \rightleftharpoons 4\text{OH}^- (aq) & & +0.40
\end{align*}
\]

(a) Calculate the e.m.f. of the cell represented by \( \text{Mg}(s) || \text{Mg}^2+(aq) || \text{Fe}^2+(aq) || \text{Fe}(s) \) under standard conditions. Write a half-equation for the reaction occurring at the negative electrode of this cell when a current is drawn.

(b) Deduce how the e.m.f. of the cell \( \text{Mg}(s) || \text{Mg}^2+(aq) || \text{Fe}^2+(aq) || \text{Fe}(s) \) changes when the concentration of \( \text{Mg}^2+ \) is decreased. Explain your answer.

(c) Calculate a value for the e.m.f. of the cell represented by \( \text{Pt}(s) || \text{OH}^- (aq) || \text{O}_2 (g) || \text{Fe}^2+(aq) || \text{Fe}(s) \) and use it to explain why iron corrodes when in contact with water which contains dissolved oxygen.
Use the data below, where appropriate, to answer the questions which follow.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Standard Electrode Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg^{2+}(aq) + 2e^- ⇌ Mg(s)</td>
<td>-2.37</td>
</tr>
<tr>
<td>Fe^{2+}(aq) + 2e^- ⇌ Fe(s)</td>
<td>-0.44</td>
</tr>
<tr>
<td>O_2(g) + 2H_2O(l) + 4e^- ⇌ 4OH^-(aq)</td>
<td>+0.40</td>
</tr>
</tbody>
</table>

(a) Calculate the e.m.f. of the cell represented by Mg(s)\|Mg^{2+}(aq)\|\|Fe^{2+}(aq)\|\|Fe(s) under standard conditions. Write a half-equation for the reaction occurring at the negative electrode of this cell when a current is drawn.

E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = -0.44 - (-2.37) = +1.93V

\(\text{Mg} \rightarrow \text{Mg}^{2+} + e^-\)

(b) Deduce how the e.m.f. of the cell Mg(s)\|Mg^{2+}(aq)\|\|Fe^{2+}(aq)\|\|Fe(s) changes when the concentration of Mg^{2+} is decreased. Explain your answer.

Equilibrium shifts to left so Mg^{2+}/Mg is more electronegative, so EMF increases

(c) Calculate a value for the e.m.f. of the cell represented by Pt(s)\|OH^-(aq)\|O_2(g)\|Fe^{2+}(aq)\|Fe(s) and use it to explain why iron corrodes when in contact with water which contains dissolved oxygen.

E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = -0.44 - (+0.4) = -0.84V ;

Hence, reverse reaction is spontaneous, so Fe is oxidised by H_2O to Fe^{2+}
Excess KMNO₄ was added to V²⁺(aq). Determine the vanadium species present in the solution at the end of this reaction, its oxidation number, and write a half-equation for its formation from V²⁺(aq).

\[
\begin{align*}
V³⁺(aq) + e⁻ &\rightarrow V²⁺(aq) & -0.26 \\
SO₄²⁻(aq) + 4H⁺(aq) + 2e⁻ &\rightarrow H₂SO₃(aq) + H₂O(l) & +0.17 \\
VO²⁺(aq) + 2H⁺(aq) + e⁻ &\rightarrow V³⁺(aq) + H₂O(l) & +0.34 \\
Fe³⁺(aq) + e⁻ &\rightarrow Fe²⁺(aq) & +0.77 \\
VO₂⁺(aq) + 2H⁺(aq) + e⁻ &\rightarrow VO²⁻(aq) + H₂O(l) & +1.00 \\
MnO₄⁻(aq) + 8H⁺(aq) + 5e⁻ &\rightarrow Mn²⁺(aq) + 4H₂O(l) & +1.52
\end{align*}
\]

In cell: \( \text{Pt} | \text{H}_2\text{SO}_3, \text{SO}_4^{2-}, \text{H}^⁺ | \text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt} \)
Calculate the EMF.
Explain how EMF will change if the concentration of Fe³⁺(aq) is increased.

Deduce the overall equation for this cell reaction. State how the EMF of this cell will change if the surface area of each platinum electrode is doubled.
Excess KMNO₄ was added to V²⁺(aq). Determine the vanadium species present in the solution at the end of this reaction, its oxidation number, and write a half-equation for its formation from V²⁺(aq).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Value</th>
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<tbody>
<tr>
<td>V³⁺(aq) + e⁻ → V²⁺(aq)</td>
<td>-0.26</td>
</tr>
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</tr>
</tbody>
</table>

In cell: Pt|H₂SO₃,SO₄²⁻,H⁺| |Fe³⁺,Fe²⁺|Pt
Calculate the EMF.
Explain how EMF will change if the concentration of Fe³⁺(aq) is increased.

\[ E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{cathode}} - E^{\ominus}_{\text{anode}} = 0.77 - (0.17) = +0.60 \text{ V} \]

Fe³⁺ + e⁻ ⇌ Fe²⁺ equilibrium shifts to right, ∴ more electropositive Fe³⁺ / Fe²⁺, thus EMF increases

Deduce the overall equation for this cell reaction. State how the EMF of this cell will change if the surface area of each platinum electrode is doubled.

2H₂ → 4H⁺ + 4e⁻ \quad O₂ + 2H₂O + 4e⁻ → 4OH⁻ \quad \text{overall} \quad 2H₂ + O₂ → 2H₂O ;
Unchanged by equivalent surface area