Topic 6a – Electrode Potentials
Revision Notes

1) Redox

- Redox reactions involve the transfer of electrons e.g. in the reaction between zinc metal and copper (II) sulphate, electrons are transferred from zinc atoms to copper (II) ions

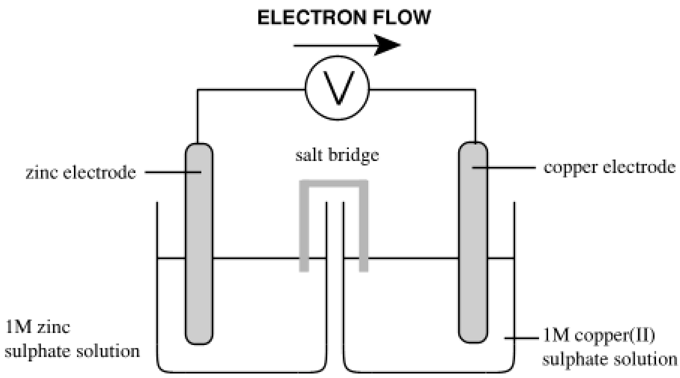
$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

- The overall equation can be split into half-equations

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	oxidation
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	reduction

2) Electrodes and cells

- The two half-reactions for zinc and copper can be carried out in separate beakers
- In this case the beakers would typically contain a piece of copper dipping into copper sulphate solution and a piece of zinc dipping into zinc sulphate solution
- The combination of a metal dipping a solution containing its ions is called an electrode
- Electrons can transfer from the zinc electrode to the copper electrode through a wire and a voltmeter.
- The circuit is completed by connecting the two electrodes with a salt bridge which is usually a piece of filter paper soaked in saturated potassium nitrate solution



- Two electrodes joined in this way make up an electrochemical cell
- Electrodes can also consist of non-metals and their ions or transition metals in two different oxidation states e.g.

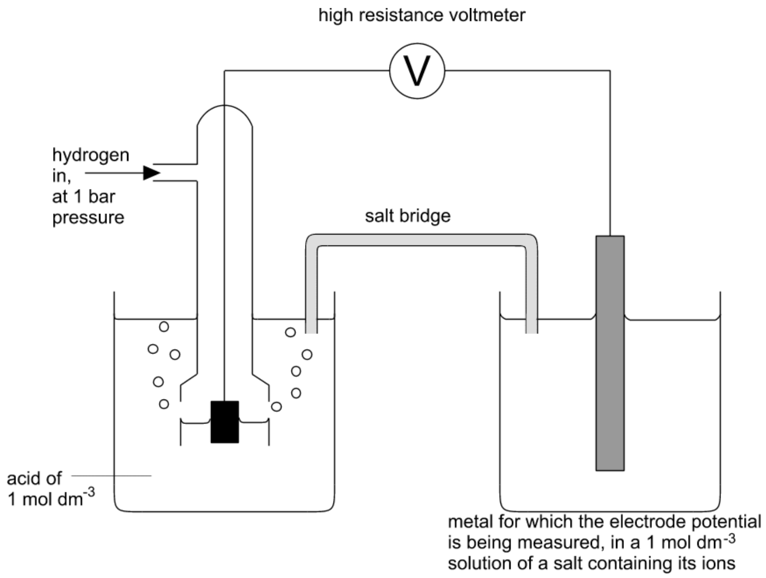
$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$$
$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$$

3) Electrode Potential

- The voltage, or potential, measured on the voltmeter will be different for different pairs of electrodes
- The voltages produced by different electrodes can be measured by pairing up each electrode with a standard electrode

- The electrode used for comparison is called the standard hydrogen electrode (SHE), which is deemed to have a potential of 0.00 V (zero volts) – see diagram below (the black rectangle is a piece of platinum which conducts electrons into or out of the acid solution). The half equation for the SHE is:

$$\mathbf{2H^+(aq) + 2e^- \rightarrow H_2(g)}$$



Source of these two diagrams: http://www.btinternet.com/~chemistry.diagrams/

- To measure standard electrode potentials the following conditions are needed: temperature of 298K, pressure of 100 kPa and solutions of concentration 1 mol dm^{-3}
- The hydrogen electrode is normally drawn on the left in diagrams showing how standard electrode potentials are measured
- Electrode potentials are always quoted as reductions (gain of electrons)
- A list of electrode potentials in descending (or ascending) order is known as the electrochemical series

4) Calculating Cell Voltage

- Electrode potentials can be used to calculate the voltage produced when electrodes are paired up
- The convention is to put the more positive electrode on the right and the less positive electrode on the left
- The electrode with the more positive potential is the positive electrode
- Electrons will then flow from left to right through the external circuit (wire and voltmeter)
- The cell voltage, E_{cell}, is calculated from

$$\mathbf{E_{cell} = E_R - E_L}$$

In the copper and zinc example

E_R = +0.34V
E_L = -0.76V
E_{cell} = 0.34 – (-0.76)
= 1.10V

5) <u>Predicting Reaction Feasibility</u>

- The electrode potential is a measure the willingness of a substance to be reduced
- The more positive the potential, the more willing the substance to be reduced
- Electrode potentials can be used to predict which substance will be oxidised and which substance will be reduced when half equations are paired up in a beaker
- The half-reaction with the more positive potential will stay as a reduction
- The half-reaction with the less positive potential will flip round and go as an oxidation

Example – copper and zinc

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ E = +0.34V
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ E = -0.76V

Cu^{2+}/Cu potential is more positive so this stays as a reduction
Zn^{2+}/Zn flips round to become an oxidation i.e. $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

- The overall equation for the feasible reaction can then be written adding the half equations together and cancelling electrons
- As with any redox reaction, one or both of the half equations may have to be multiplied to make the number of electrons equal

Overall equation

$Zn(s) + Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) + Zn^{2+}(aq) + 2e^-$

Cancelling electrons gives

$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$

The reaction is not feasible in the other direction i.e. $Cu(s) + Zn^{2+}(aq) \rightarrow$ no reaction

- Predictions on feasibility take no account of reaction rate. A reaction may be feasible based on electrode potentials but, if the rate is very low because of a high activation energy, nothing may appear to happen
- Predictions on feasible directions are based on standard electrode potentials. These predictions may become invalid if conditions are non-standard
- The effect of changing concentration can be illustrated using the Cu^{2+}/Cu electrode as an example

$Cu^{2+}(aq) + 2e^-$ $Cu(s)$ EÞ = +0.34V

- If the concentration of $Cu^{2+}(aq)$ is reduced, the equilibrium will shift to the left (by Le Chatelier's principle)
- This means that reduction (the forward reaction) is less likely, so the electrode potential will be reduced from its standard value

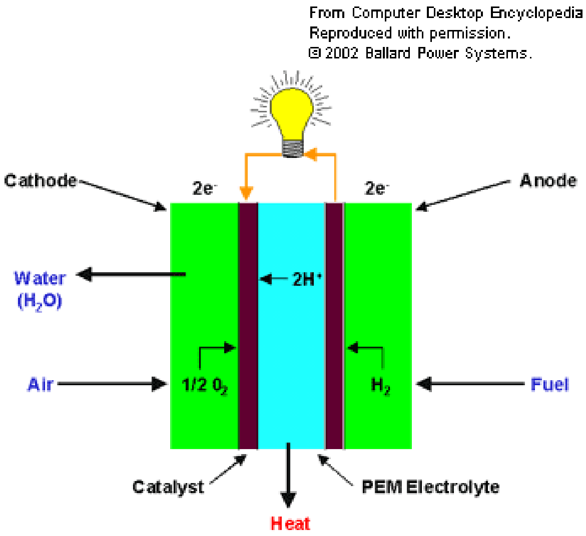
Topic 6b – Fuel Cells
Revision Notes

1) Introduction

- A fuel cell converts the energy from the reaction of a fuel with oxygen into electrical energy
- The fuel is oxidised at the positive electrode (anode)
- Electrons travel through an external circuit doing work
- Oxygen is reduced at the negative electrode (cathode)

2) Hydrogen-oxygen fuel cell

- In this cell the fuel is hydrogen. This cell can operate under either acidic or alkaline conditions



- The two half reactions for acidic conditions are:

$2H_2 \rightarrow 4H^+ + 4e^-$	**anode**
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	**cathode**

- The two half reactions for alkaline conditions are:

$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$	**anode**
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	**cathode**

- The overall equation is the same in both cases:

$$2H_2 + O_2 \rightarrow 2H_2O$$

- The reactions take place over precious metal catalysts, usually platinum or an alloy of platinum, palladium, or ruthenium

3) Fuel cell vehicles (FCVs)

- Scientists is the car industry are developing fuel cell vehicles
- These FCVs are fuelled by either hydrogen gas or hydrogen-rich fuels
- Compared with conventional petrol or diesel-powered vehicles, FCVs produce less pollution and CO_2 and are more efficient
- In FCVs hydrogen could be stored:
    - As a liquid under pressure
    - By adsorption onto the surface of a solid material
    - By absorption within a solid material
- Hydrogen fuel cells have limitations:
    - There are problems in storing and transporting hydrogen in terms of safety, feasibility of a pressurised liquid and limited life cycle of a solid adsorber or absorber
    - The cells themselves have high production costs and a limited lifetime (requiring regular replacement and disposal)
    - Toxic chemicals are used in the production of the cells
- A 'hydrogen economy' may make a large contribution to future energy requirements but has limitations including:
    - Public and political acceptance of hydrogen as a fuel
    - Handling and maintenance of hydrogen systems
    - Initial manufacture of hydrogen (including the energy required)