

# Redox Equilibria

## Review

Unit 5 redox chemistry builds on the redox chemistry first encountered in Unit 2.

Important terms introduced then were redox, oxidation number and half equations.

A redox reaction is an electron transfer reaction.

**Oxidation Is Loss of electrons**

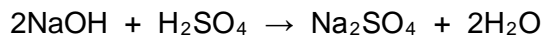
**Reduction Is Gain of electrons**

The oxidation number of an atom shows the number of electrons which it has lost or gained as a result of forming a compound.

Half equations involve looking at the electron gain and electron loss processes separately.

## Stoichiometry

Stoichiometry is the ratio between substances in a chemical reaction. So in the reaction between sodium hydroxide and sulphuric acid;



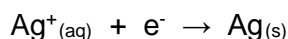
The stoichiometry for this reaction is that 2 moles of NaOH react with 1 mole of H<sub>2</sub>SO<sub>4</sub>

In a redox reaction, electrons are transferred from one material to another.

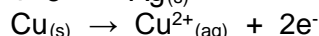
The redox equation must balance in terms of numbers of electrons and oxidation number.

For example in the reaction between silver(I) and copper, metallic silver and copper(II) are formed.

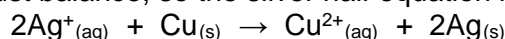
The silver half equation is



The copper half equation is



The electron loss and gain must balance, so the silver half equation has to be doubled.



This stoichiometry can also be deduced by examining oxidation number change.

- The oxidation number of copper increases by 2.
- The oxidation number of silver decreases by 1
- This means that they react in the ratio 2 silver to 1 copper.

## Redox Titrations

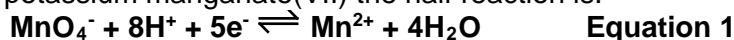
It is possible to use redox reactions in titrations.

Common reagents used for these are manganate(VII) and thiosulphate with iodine.

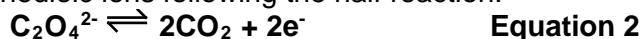
### **Potassium manganate(VII) titrations**

A known concentration of potassium manganate(VII) can be used to determine the quantity of a **reducing agent** present in a sample.

In titrations involving potassium manganate(VII) the half reaction is:



This may react with ethanedioic ions following the half reaction:



To combine these half equations we must x Equation 1 by 2 and x Equation 2 by 5 and add;

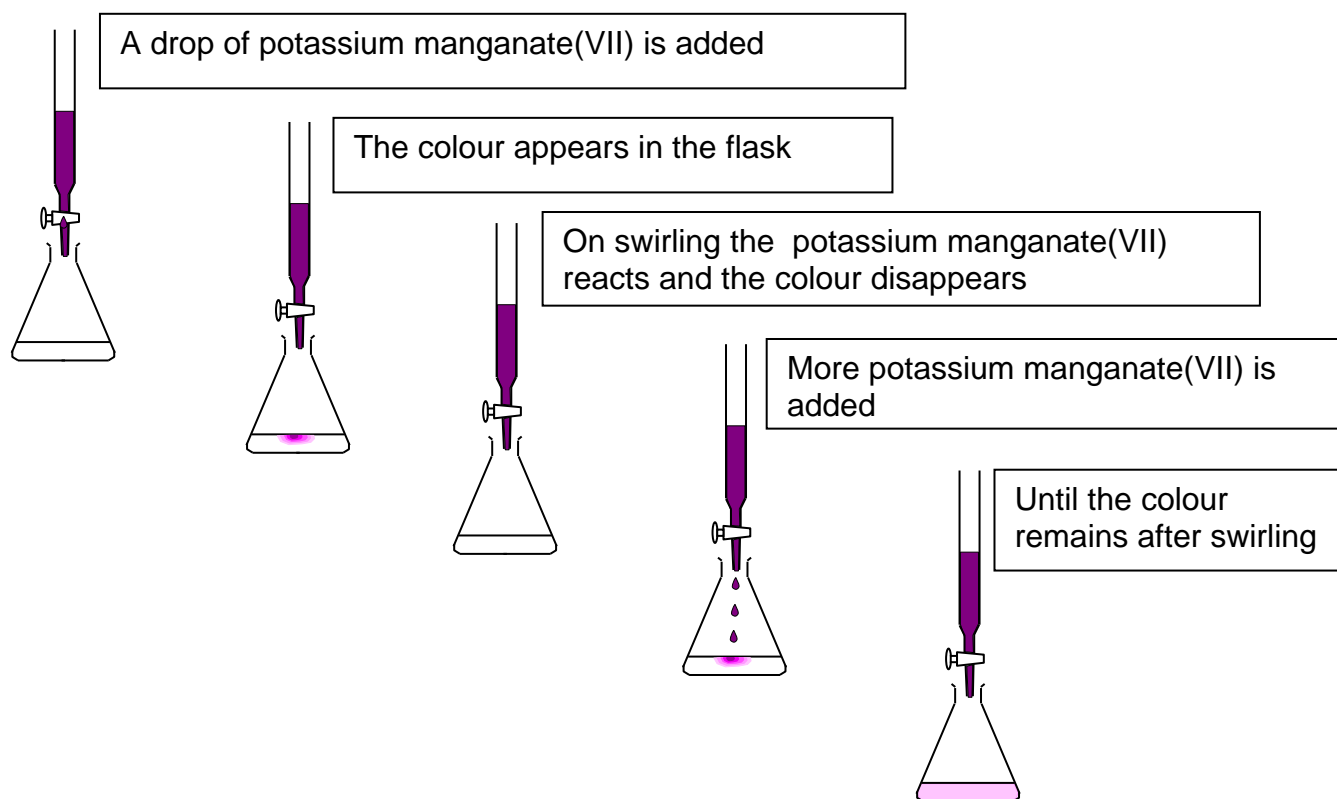
The full reaction is:  $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$

The reaction requires excess dilute sulphuric acid and a temperature of about 60°C.

Manganate(VII) is a deep purple colour in solution, but the manganese(II) ion, to which it is reduced, is almost colourless.

As the manganate(VII) is added, from a burette, it reacts turning colourless.

When all the reducing agent has reacted, the manganate(VII) no longer reacts and its colour remains in the flask.



From the concentration of the manganate(VII) and the volume used, the number of moles can be determined. Using the chemical equation, the number of moles of reducing agent can be found, and so its concentration.

### Example

An iron tablet, containing an iron(II) compound was crushed. 2.500 g of the tablet were dissolved and made up to 250 cm<sup>3</sup> of solution. 25.0 cm<sup>3</sup> of this solution was transferred to a flask by pipette, 25 cm<sup>3</sup> dilute sulphuric acid was added to acidify the solution and the flask contents titrated against 0.005 mol dm<sup>-3</sup> potassium manganate(VII) solution. The average titre value was 26.45 cm<sup>3</sup>.

Calculate the percentage iron in the tablet.

$$\text{Moles of potassium manganate(VII)} = 26.45 / 1000 \times 0.005 = 1.3225 \times 10^{-4} \text{ mol}$$



$$\text{Moles of iron(II) (in 25.0 cm}^3 \text{ sample)} = 1.3225 \times 10^{-4} \times 5 = 6.6125 \times 10^{-4} \text{ mol}$$

$$\text{Moles of iron(II) (in 250.0 cm}^3 \text{ sample)} = 6.6125 \times 10^{-4} \times 250 / 25 = 6.6125 \times 10^{-3} \text{ mol}$$

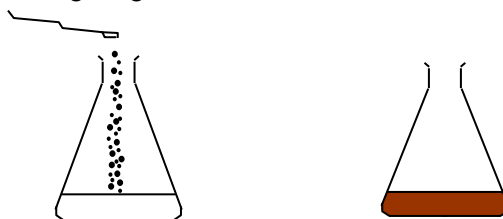
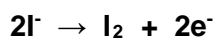
$$\text{Mass of iron(II)} = 6.6125 \times 10^{-3} \times 56 = 0.370 \text{ g}$$

$$\% \text{ iron} = 0.370 / 2.500 \times 100 = 14.8$$

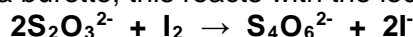
## Thiosulphate titrations

Thiosulphate and iodine titrations are used to determine the concentration of **oxidising agents**.

First of all the oxidising agent is added to a solution containing excess iodide ions. This oxidises the iodide ions to iodine giving a brown colour.



Thiosulphate is then added from a burette; this reacts with the iodine to form colourless products.



During the titration, the colour intensity decreases, eventually reaching a pale yellow colour. At this point, a few drops of starch solution are added to give the deep blue complex showing the last traces of iodine. Thiosulphate is then added dropwise, until the mixture becomes colourless.

As thiosulphate is added the colour of the iodine fades

Starch is added to give a deep blue colour

The titration is then continued until the mixture becomes colourless

From a known concentration of thiosulphate, it is possible to determine the number of moles of chemical involved in the reaction.

### Example

2.049g of a copper alloy was dissolved in concentrated nitric acid and made up to 250 cm<sup>3</sup> of solution. 25.0 cm<sup>3</sup> of this solution was transferred to a flask by pipette and an excess of potassium iodide added to it. The resulting mixture was titrated against 0.100 mol dm<sup>-3</sup> sodium thiosulphate solution. The average titre value was 24.65 cm<sup>3</sup>. Calculate the percentage copper in the alloy.

- Moles of sodium thiosulphate =  $24.65 / 1000 \times 0.100 = 2.465 \times 10^{-3}$  mol
- Equation:  $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$
- Moles of I<sub>2</sub> in flask =  $2.465 \times 10^{-3} \times 0.5 = 1.2325 \times 10^{-3}$  mol
- Equation:  $2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} + \text{I}_2$
- Moles of Cu<sup>2+</sup> {in 25.0 cm<sup>3</sup> sample} =  $1.2325 \times 10^{-3} \times 2 = 2.465 \times 10^{-3}$  mol
- Moles of Cu<sup>2+</sup> {in 250.0 cm<sup>3</sup> sample} =  $2.465 \times 10^{-3} \times 250 / 25 = 2.465 \times 10^{-2}$  mol
- Mass of Cu<sup>2+</sup> =  $2.465 \times 10^{-2} \times 63.5 = 1.565$ g
- % copper =  $1.565 / 2.049 \times 100 = 76.4\%$

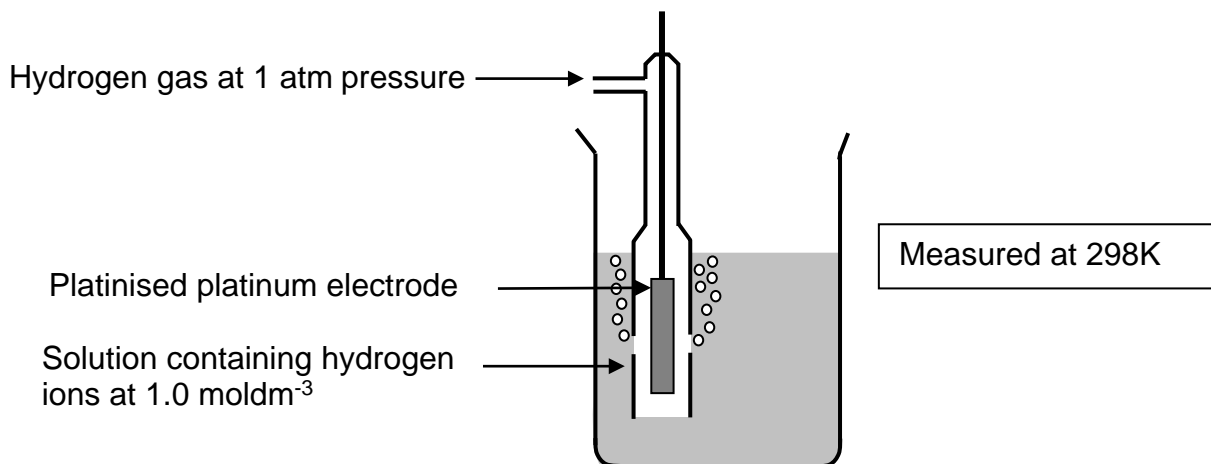
**Standard Electrode Potential  $E^\ominus$** 

If a metal is placed in a solution of its ions at a concentration of  $1.0 \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ , the potential obtained (the tendency to release electrons) is the standard electrode potential,  $E^\ominus$ .

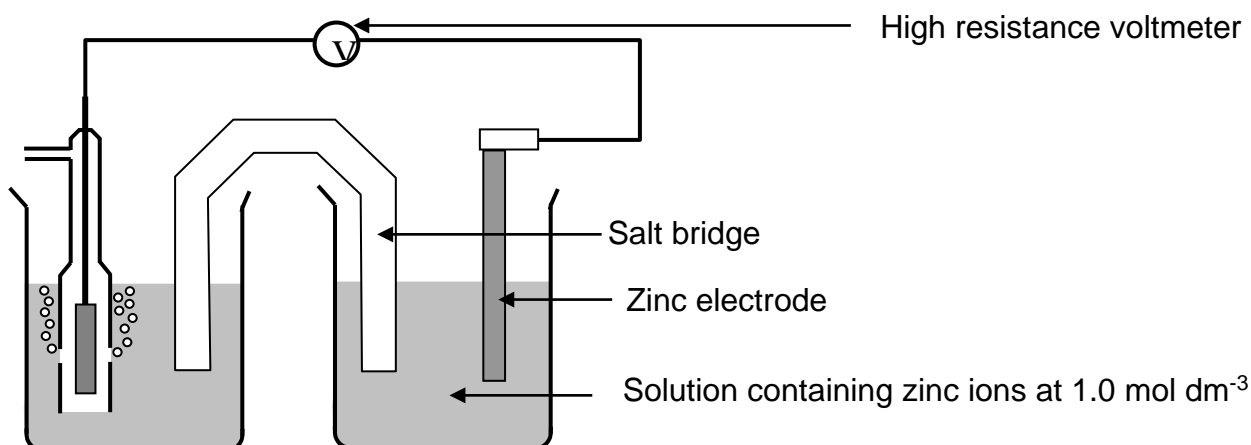
**Standard Electrode**

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 standard cell, to measure them all against is required.

This standard cell, taken as having a  $E^\ominus$  of 0.00, is the hydrogen half cell;



To measure the  $E^\ominus$  of the zinc half cell, the following set up is used



When the hydrogen half cell is connected to the negative side of a high resistance voltmeter, the e.m.f. of the cell gives the  $E^\ominus$  for that half cell.

The value obtained from this is  $E^\ominus = -0.76 \text{ V}$

The negative value indicates that the zinc loses electrons more readily than the hydrogen, and that it is a more powerful reducing agent. The more negative a value is, the more powerful the reducing agent.

For a cell of hydrogen and copper the value obtained from this is  $E^\ominus = +0.34 \text{ V}$

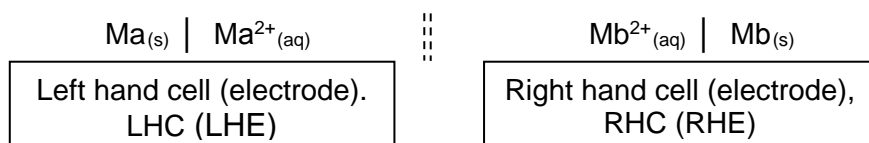
The positive value indicates that copper is a weaker reducing agent than hydrogen, and the  $\text{Cu}^{2+}$  is a more powerful oxidising agent.

**In general, the more positive the  $E^\ominus$ , the more powerful the oxidising agent.**

**Use of  $E^\theta$  values**

Since the  $E^\theta$  values can be used to determine in which way the electrons will flow, it is possible to use them to decide whether a reaction occurs.

Cells can be represented using formulae. Using Ma and Mb to represent the metals in two half cells, the formulaic representation would be:



By convention change in this representation takes place from left to right, so the reactions taking place in this cell would be;



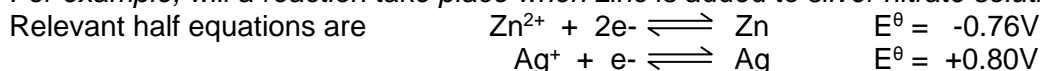
The feasibility of a reaction can be found directly from the  $E^\theta$  values using the following equation:

$$E^\theta_{\text{CELL}} = E^\theta_{\text{RHC}} - E^\theta_{\text{LHC}}$$

A **positive value** indicates that a reaction is **feasible**.

Notice that in the left hand cell the reaction is the reverse of the half equation as it is normally written.

*For example, will a reaction take place when zinc is added to silver nitrate solution?*



If a reaction takes place the zinc will become zinc ions.

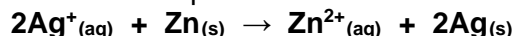
This involves losing electrons so it corresponds to the left hand cell.

(This is the reverse of the usually written half equation, so this will be the left hand cell.)

So the Ag is the RHC and Zn is the LHC

$$E^\theta_{\text{CELL}} = E^\theta_{\text{RHC}} - E^\theta_{\text{LHC}}$$

$$E^\theta_{\text{CELL}} = +0.8 - -0.76 = \mathbf{+1.56} \quad \text{The positive value indicates that the reaction is feasible:}$$



*Another example; will a reaction take place when acidified hydrogen peroxide is added to bromide ions?*

Relevant half equations are

Half equation 1	$\text{Br}_2 + 2e^- \rightleftharpoons 2\text{Br}^-$	$E^\theta = +1.07$
Half equation 2	$\text{O}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{O}_2$	$E^\theta = +0.68\text{V}$
Half equation 3	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons 2\text{H}_2\text{O}$	$E^\theta = +1.77\text{V}$

The oxidation of bromide ions is  $2\text{Br}^- \rightarrow \text{Br}_2 + 2e^-$

Since this process involves losing electrons, it is the left hand cell

There are two half equation for hydrogen peroxide. Looking at half equation 2 first;

$$E^\theta_{\text{CELL}} = E^\theta_{\text{RHC}} - E^\theta_{\text{LHC}}$$

$$E^\theta_{\text{CELL}} = +0.68 - +1.07 = \mathbf{-0.39} \quad \text{The negative value tells us that this reaction is not feasible.}$$

Inspection of the half equation would also tell us this of course since in a redox equation one half equation always has to be the reverse of the usual form.

Looking now at the other hydrogen peroxide half equation;

$$E^\theta_{\text{CELL}} = E^\theta_{\text{RHC}} - E^\theta_{\text{LHC}}$$

$$E^\theta_{\text{CELL}} = +1.77 - +1.07 = \mathbf{+0.70} \quad \text{The positive value indicates that the reaction is feasible:}$$



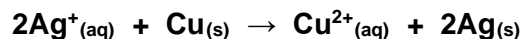
## Limitations of $E^\theta$ values

The electrode potential values have limitations because;

- they refer to standard conditions
- they indicate the energetic feasibility of a reaction, not the kinetics.

If the conditions are different from the standard, the emf can change. For example, the measurement of  $E^\theta$  is made at a concentration of  $1\text{ mol dm}^{-3}$ . If the concentration of one of the solutions is changed, this will change the emf of the reaction.

For example



For the Cu and Ag cell, the standard value for the reaction is:

$$E^\theta_{\text{CELL}} = E^\theta_{\text{RHC}} - E^\theta_{\text{LHC}}$$

$$E^\theta_{\text{CELL}} = +0.8 - +0.34 = +0.46\text{V}$$

Values of emf for different silver ion concentrations are shown in the table below.

Concentration of $\text{Cu}^{2+}$ $\text{mol dm}^{-3}$	Concentration of $\text{Ag}^+$ / $\text{mol dm}^{-3}$	emf
1.0	$1.0 \times 10^{-2}$	+0.34
1.0	$1.0 \times 10^{-3}$	+0.28
1.0	$1.0 \times 10^{-4}$	+0.22
1.0	$1.0 \times 10^{-5}$	+0.16
1.0	$1.0 \times 10^{-6}$	+0.10
1.0	$1.0 \times 10^{-7}$	+0.04
1.0	$1.0 \times 10^{-8}$	-0.02
1.0	$1.0 \times 10^{-9}$	-0.08

At low silver ion concentration, the reaction will tend to go in the opposite direction.

Changes in temperature and pressure can also affect the emf for a particular reaction.

For example the reaction:  $\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{aq})$

$$E^\theta_{\text{CELL}} = E^\theta_{\text{RHC}} - E^\theta_{\text{LHC}}$$

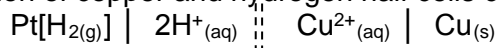
$$E^\theta_{\text{CELL}} = +1.23 - +1.36 = -0.13 \quad \text{The negative value tells us that this reaction is not feasible.}$$

If concentrated HCl and solid  $\text{MnO}_2$  are mixed and then heated, a reaction readily takes place.

**The emf values only indicate the energetic feasibility of a reaction, it gives us no information about the kinetics.**

The  $E^\theta$  of a cell gives no information about the kinetics of a reaction.

The combination of copper and hydrogen half cells can be written:



$$\text{Calculating } E^\theta \text{ for this cell; } E^\theta_{\text{CELL}} = E^\theta_{\text{RHC}} - E^\theta_{\text{LHC}}$$

$$E^\theta_{\text{CELL}} = +0.34 - 0 = +0.34\text{V}$$

The positive value indicates that the reaction is feasible:  $\text{H}_2(\text{g}) + \text{Cu}^{2+}(\text{aq}) \rightarrow 2\text{H}^+(\text{aq}) + \text{Cu}(\text{s})$

When hydrogen is bubbled through copper sulphate solution no reaction can be observed. The reaction has a high activation energy, so although the reaction is energetically favourable, the high activation energy means that the reaction is so slow as to be negligible.

## Redox Chemistry of Vanadium

Vanadium can form four oxidation states.

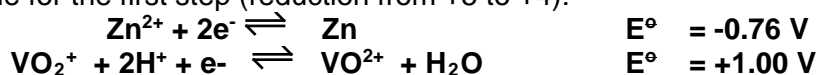
Oxidation number	2	3	4	5
Species present	V <sup>2+</sup>	V <sup>3+</sup>	VO <sup>2+</sup>	VO <sub>2</sub> <sup>+</sup>
Colour	Violet	Green	Blue	Yellow

Standard redox potentials for these conversions are shown below

Conversion	Standard redox potential /V
$V^{3+} + e^{-} \rightleftharpoons V^{2+}$	-0.26
$2H^{+} + VO^{2+} + e^{-} \rightleftharpoons V^{3+} + H_2O$	+0.34
$2H^{+} + VO_2^{+} + e^{-} \rightleftharpoons VO^{2+} + H_2O$	+1.00

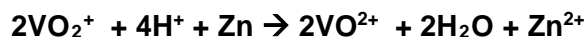
Vanadium can be reduced from the +5 states right through to the +2 state by zinc. Each step can be predicted using E° values.

For example for the first step (reduction from +5 to +4):

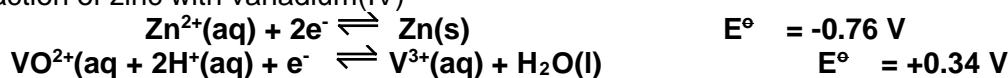


$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{R}} - E^{\circ}_{\text{L}} = +1.00 \text{ V} - (-0.76 \text{ V}) = +1.76 \text{ V}$$

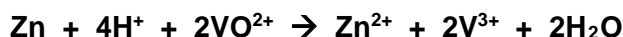
The large positive value of E<sub>cell</sub> shows that the reaction to reduce vanadium is spontaneous.



Reaction of zinc with vanadium(IV)



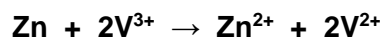
$$E^{\circ}_{\text{CELL}} = 0.34 - (-0.76) = +1.10\text{V} \text{ reaction is feasible}$$



Reaction of zinc with vanadium(III)



$$E^{\circ}_{\text{CELL}} = -0.26 - (-0.76) = +0.50\text{V} \text{ reaction is feasible}$$



Heating with zinc and sulphuric acid will therefore reduce vanadate(V) from yellow to blue to green, and finally to lavender (violet).

## Standard Electrode Potentials and Equilibrium



It has been established that the feasibility of a reaction can be found directly from the  $E^\theta$  values using the equation:  $E^\theta_{\text{CELL}} = E^\theta_{\text{RHC}} - E^\theta_{\text{LHC}}$

It has also been noted that if the concentrations are changed the value of  $E^\theta$  values will change.

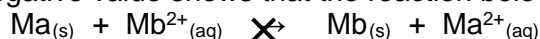
Let us apply some hypothetical values to the right and left hand cells of our hypothetical reaction.

LHC half equation	$\text{Ma}^{2+}_{(aq)} + 2e^- \rightleftharpoons \text{Ma}_{(s)}$	+0.66V
RHC half equation	$\text{Mb}^{2+}_{(aq)} + 2e^- \rightleftharpoons \text{Mb}_{(s)}$	+0.64V

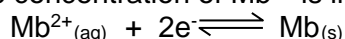
$$E^\theta_{\text{CELL}} = E^\theta_{\text{RHC}} - E^\theta_{\text{LHC}}$$

$$E^\theta_{\text{CELL}} = 0.64 - 0.66 = -0.02\text{V}$$

The negative value shows that the reaction below is not feasible.

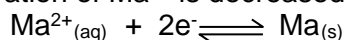


However if the concentration of  $\text{Mb}^{2+}$  is increased, the equilibrium



will shift to the right and more Mb is formed, so the  $E^\theta$  of this half cell increases

If the concentration of  $\text{Ma}^{2+}$  is decreased, the equilibrium



will shift to the left and more  $\text{Ma}^{2+}$  is formed, so the  $E^\theta$  of this half cell decreases

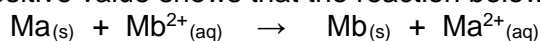
Applying new hypothetical values

LHC half equation	$\text{Ma}^{2+}_{(aq)} + 2e^- \rightleftharpoons \text{Ma}_{(s)}$	+0.66V	+0.63V
RHC half equation	$\text{Mb}^{2+}_{(aq)} + 2e^- \rightleftharpoons \text{Mb}_{(s)}$	+0.64V	+0.67V

$$E^\theta_{\text{CELL}} = E^\theta_{\text{RHC}} - E^\theta_{\text{LHC}}$$

$$E^\theta_{\text{CELL}} = 0.67 - 0.63 = +0.06\text{V}$$

The positive value shows that the reaction below is now feasible.



This demonstrates that these are equilibrium processes.

The relationship between  $E^\theta_{\text{CELL}}$  and the equilibrium constant, K, is

$$E^\theta_{\text{CELL}} \propto \ln K$$

We know from the equilibrium section in Unit 4 (Topic 4.5)

$$\Delta S_{\text{tot}} = R \ln K$$

Therefore it follows that;

$$E^\theta_{\text{CELL}} \propto \Delta S_{\text{tot}}$$

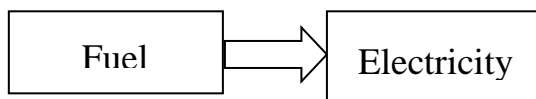


## Fuel Cells

Electricity is generally produced by burning fuel and using the heat to generate electricity.



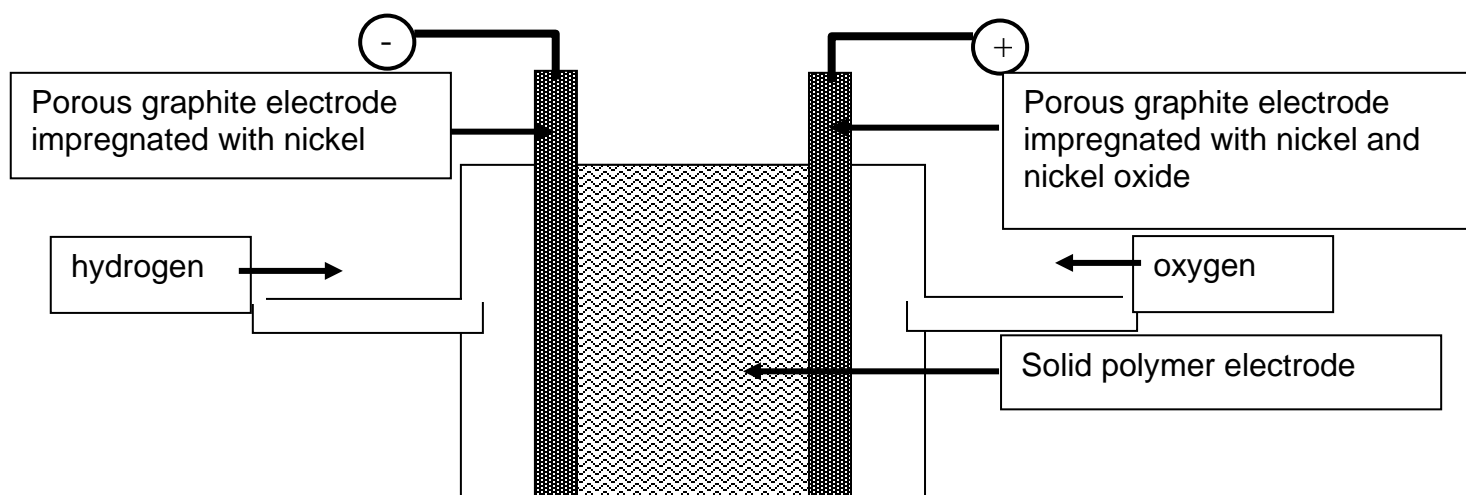
Fuel cells are electrochemical cells which convert chemical energy in fuels directly to electrical energy



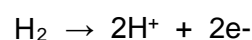
Fuel cells can be 70% or more efficient at converting the chemical energy in fuels to electrical energy, whereas a typical modern power plant is only capable of about 40%

Fuel cells differ from other cells, such as the dry cell, in having a continuous supply of reactant to generate the electrical current. Fuels include hydrogen, hydrocarbons and alcohols.

The diagram below shows the basic design of a fuel cell.



At the negative electrode the following reaction takes place



At the positive electrode the catalyst causes dissociation of the oxygen;  $\frac{1}{2}\text{O}_2 \rightarrow \text{O}$

And then the following reaction takes place  $\text{O} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$

The overall reaction is  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

An ethanol fuel cell has a similar design, the reactions being:

At the negative electrode:  $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO}_2\text{H} + 4\text{H}^+ + 4\text{e}^-$

At the positive electrode:  $4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$

The overall reaction is:  $\text{C}_2\text{H}_5\text{OH} + \text{O}_2 \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O}$

## Breathalysers

Breathalysers measure the quantity of alcohol in the blood by determining the amount in a sample of expired air.

The original breathalysers used potassium dichromate and sulphuric acid. The dichromate oxidized the ethanol to ethanal and ethanoic acid. This caused a consequential reduction in the dichromate in which the orange crystals turned green. It was possible to deduce the rough level of alcohol in 1dm<sup>3</sup> of breath. Accurate measurements were difficult to obtain. This combined with the toxicity of the dichromate led to dichromate breathalysers being replaced by an ethanol fuel cell which gave more accurate results.

The ethanol fuel cell consists of two electrodes made of a material such as platinum with a permeable membrane between containing sodium hydroxide.

Alcohol passing through the cell causes the reactions below.

At the negative electrode:  $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO}_2\text{H} + 4\text{H}^+ + 4\text{e}^-$

At the positive electrode:  $4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$

The cell voltage is directly proportional to the ethanol concentration.

The breathalyzer is initially calibrated with air containing a known ethanol concentration.

Once calibrated the cell can be used to determine the ethanol concentration in a breath sample, with the values being read directly from a scale.

This type of breathalyzer does not give a printed read out so it is not usually given as evidence in court.

If the breathalyzer gives a reading above the legal limit, the driver has to give a second sample of breath at the police station. At the police station, the ethanol concentration is determined by using infra-red absorption. This measures the absorption of the C-H stretching at 2950cm<sup>-1</sup>. The instrument is again calibrated to give an ethanol concentration measurement which can be printed out and used as evidence in court.