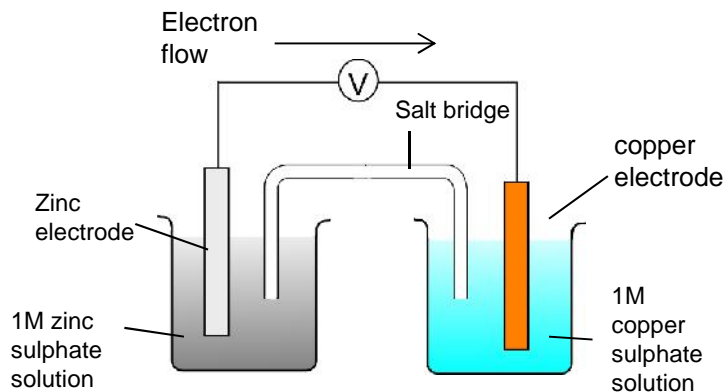


14. Redox Equilibria

Electrochemical cells

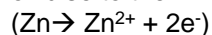
- A cell has two half-cells.
- The two half cells have to be connected with a salt bridge.
- Simple half cells will consist of a metal (acts an electrode) and a solution of a compound containing that metal (eg Cu and CuSO_4).
- These two half cells will produce a small voltage if connected into a circuit. (i.e. become a Battery or cell).



Why does a voltage form?

In the cell pictured above

When connected together the zinc half-cell has more of a tendency to oxidise to the Zn^{2+} ion and release electrons than the copper half-cell.



More electrons will therefore build up on the zinc electrode than the copper electrode.

A potential difference is created between the two electrodes.

The zinc strip is the negative terminal and the copper strip is the positive terminal.

This potential difference is measured with a high resistance voltmeter, and is given the symbol **E**. The E for the above cell is $E = +1.1\text{V}$.

Why use a High resistance voltmeter?

The voltmeter needs to be of very high resistance to stop the current from flowing in the circuit. In this state it is possible to measure the maximum possible potential difference (E).

The reactions will not be occurring because the very high resistance voltmeter stops the current from flowing.

Salt Bridge

The salt bridge is used to connect up the circuit. The **free moving ions** conduct the charge.

A salt bridge is usually made from a piece of filter paper (or material) soaked in a salt solution, usually **Potassium Nitrate**.

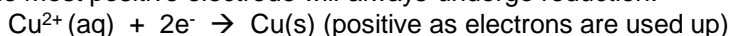
The salt should be **unreactive with the electrodes and electrode solutions**. E.g. potassium chloride would not be suitable for copper systems as Chloride ions can form complexes with copper ions.

A wire is not used because the metal wire would set up its own electrode system with the solutions.

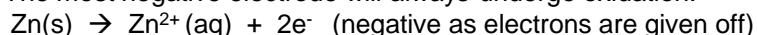
What happens if current is allowed to flow?

If the voltmeter is removed and replaced with a bulb or if the circuit is short circuited, a current flows. The reactions will then occur separately at each electrode. The voltage will fall to zero as the reactants are used up.

The most positive electrode will always undergo reduction.

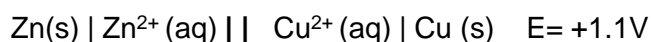


The most negative electrode will always undergo oxidation.



Cell Diagrams

Electrochemical cells can be represented by a **cell diagram**:



Most oxidised form is put next to the double line

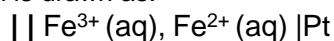
- The solid vertical line represents the boundary between **phases** e.g. solid (electrode) and solution (electrolyte)
- The double line represents the **salt bridge** between the two half cells
- the voltage produced is indicated
- the more positive half cell is written on the right if possible (but this is not essential)

Systems that do not include metals.

If a system does not include a metal that can act as an electrode, then a **platinum electrode** must be used and included in the cell diagram. It provides a **conducting surface for electron transfer**. A platinum electrode is used because it is **unreactive** and **can conduct electricity**.

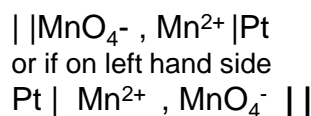
e.g. for $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$ there is no solid conducting surface, a Pt electrode must be used.

The cell diagram is drawn as:

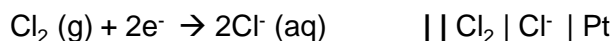
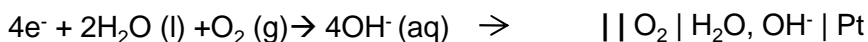


Still with more oxidised form near double line
A comma separates the oxidised from the reduced species.

If the system contains several species
e.g. $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
then in the cell diagram the balancing numbers, H^+ ions and H_2O can be left out.



If a half equation has several physical states then the solid vertical line should be used between each different state boundary.



As the phase line also separates the oxidised and reduced terms a comma is not necessary here.

Measuring the electrode potential of a cell

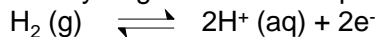
- It is not possible to measure **the** absolute potential of a half electrode on its own. It is only possible to measure the potential difference between two electrodes.
- To measure it, it has to be connected to another half-cell of known potential, and the potential difference between the two half-cells measured.
- by convention we can assign a relative potential to each electrode by linking it to a reference electrode (hydrogen electrode), which is given a potential of zero Volts

The standard hydrogen electrode

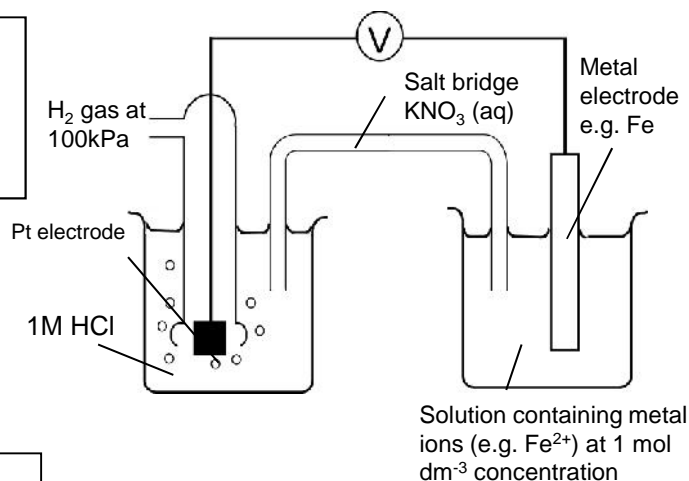
The potential of all electrodes are measured by comparing their potential to that of the standard hydrogen electrode.

The **standard hydrogen electrode (SHE)** is assigned the potential of 0 volts.

The hydrogen electrode equilibrium is:



In a cell diagram the hydrogen electrode is represented by: $\text{Pt} | \text{H}_2(\text{g}) | \text{H}^+(\text{aq})$



Solution containing metal ions (e.g. Fe^{2+}) at 1 mol dm^{-3} concentration

Components of a standard hydrogen electrode.

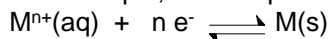
To make the electrode a standard reference electrode some conditions apply:

1. **Hydrogen gas at pressure of 100 kPa**
2. Solution containing the **hydrogen ion at 1.00 mol dm^{-3}** (solution is usually 1M HCl)
3. Temperature at **298K**

Because the equilibrium does not include a conducting metal surface a platinum wire is used which is coated in finely divided platinum. (The platinum black acts as a catalyst, because it is porous and can absorb the hydrogen gas.)

Standard conditions are needed because the position of the redox equilibrium will change with conditions.

For example, in the equilibrium:



an increase in the concentration of M^{n+} would move the equilibrium to the right, so making the potential more positive.

Secondary standards

The Standard Hydrogen Electrode is difficult to use, so often a different standard is used which is easier to use.

These other standards are themselves calibrated against the SHE.

This is known as using a **secondary standard** - i.e. a standard electrode that has been calibrated against the primary standard.

The common ones are:

silver / silver chloride

$$E = +0.22 \text{ V}$$

calomel electrode

$$E = +0.27 \text{ V}$$

Standard Electrode Potentials

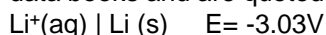


When an electrode system is connected to the hydrogen electrode system, and standard conditions apply the potential difference measured is called the standard electrode potential.

The standard conditions are :

- All ion solutions at **1 1.00 mol dm^{-3}**
- temperature 298K
- gases at 100kPa pressure
- No current flowing

Standard electrode potentials are found in data books and are quoted as

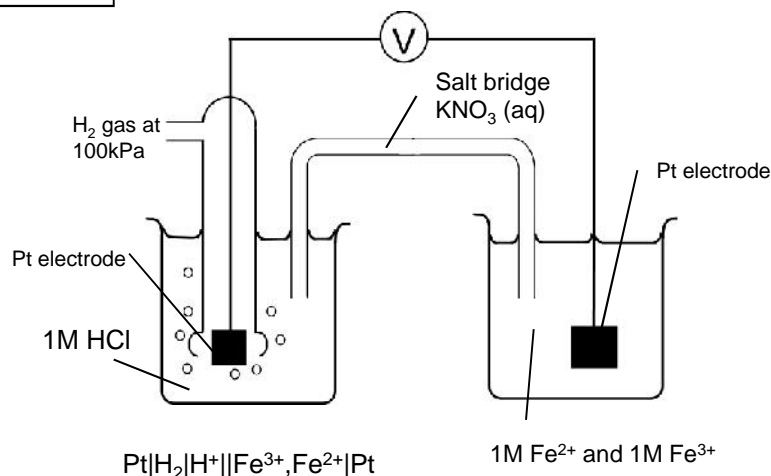


more oxidised form on left

They may also be quoted as half equations



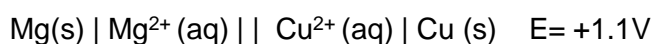
but again the more oxidised form is on the left



1M Fe^{2+} and 1M Fe^{3+}

Note: in the electrode system containing two solutions it is necessary to use a platinum electrode and **both** solutions must be of a 1M concentration.

Calculating the EMF of a cell



In order to calculate the E_{cell} , we must use '**standard electrode potentials**' for the half cells.

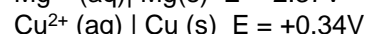
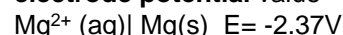
use the equation

$$E_{\text{cell}} = E_{\text{r}} - E_{\text{l}}$$

For the cell diagram above

$$E_{\text{cell}} = 0.34 - (-2.37) \\ = +2.71\text{V}$$

Each half cell has a **standard electrode potential** value



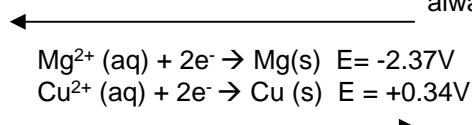
Using electrode potentials

The most useful application of electrode potentials is to show the direction of spontaneous change for redox reactions

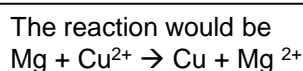
The easiest way to use electrode potentials is as follows:

For any two half equations

The more **negative** half cell will always **oxidise** (go backwards)



The more **positive** half cell will always **reduce** (go forwards)



If we want to work out the E_{cell} that corresponds to this spontaneous change then use

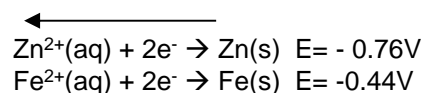
$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$

A spontaneous change will always have a positive E_{cell}

The most **negative** electrode will **oxidise** and go from **right to left**

The half equation is therefore $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$

Electrons are given off (lost) and travel to positive electrode

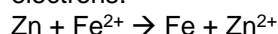


The more **positive** electrode will **reduce** and go from **left to right**

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

Electrons arrive at this electrode and are absorbed (gained)

To get the full equation of the reaction add the two half reactions together, cancelling out the electrons.



Using series of standard electrode potentials

	<p style="margin: 0;">oxidation ←</p>											
<p>As more +ve increasing tendency for species on left to reduce, and act as oxidising agents</p>	<table style="margin: auto;"> <tr> <td style="padding: 5px;">$\text{Li}^{+} + \text{e}^{-} \rightarrow \text{Li}$</td> <td style="padding: 5px;">-3.03V</td> </tr> <tr> <td style="padding: 5px;">$\text{Mn}^{2+} + 2\text{e}^{-} \rightarrow \text{Mn}$</td> <td style="padding: 5px;">-1.19V</td> </tr> <tr> <td style="padding: 5px;">$2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2$</td> <td style="padding: 5px;">0V</td> </tr> <tr> <td style="padding: 5px;">$\text{Ag}^{+} + \text{e}^{-} \rightarrow \text{Ag}$</td> <td style="padding: 5px;">+0.8V</td> </tr> <tr> <td style="padding: 5px;">$\text{F}_2 + 2\text{e}^{-} \rightarrow 2\text{F}^{-}$</td> <td style="padding: 5px;">+2.87</td> </tr> </table>	$\text{Li}^{+} + \text{e}^{-} \rightarrow \text{Li}$	-3.03V	$\text{Mn}^{2+} + 2\text{e}^{-} \rightarrow \text{Mn}$	-1.19V	$2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2$	0V	$\text{Ag}^{+} + \text{e}^{-} \rightarrow \text{Ag}$	+0.8V	$\text{F}_2 + 2\text{e}^{-} \rightarrow 2\text{F}^{-}$	+2.87	<p>As more -ve increasing tendency for species on right to oxidise, and act as reducing agents</p>
$\text{Li}^{+} + \text{e}^{-} \rightarrow \text{Li}$	-3.03V											
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$2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2$	0V											
$\text{Ag}^{+} + \text{e}^{-} \rightarrow \text{Ag}$	+0.8V											
$\text{F}_2 + 2\text{e}^{-} \rightarrow 2\text{F}^{-}$	+2.87											
<p>Most strong oxidising agents found here</p>	<p style="margin: 0;">reduction →</p>	<p>Most strong reducing agents found here</p>										

If we want to work out the E_{cell} from two standard electrode potentials then use

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$

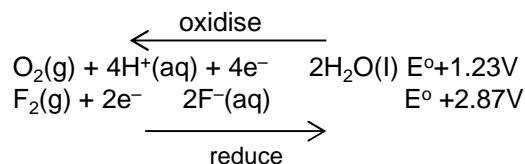
The most **powerful reducing agents** will be found at the most **negative** end of the series on the right (ie the one with the lower oxidation number)

The most **powerful oxidising agents** will be found at the most **positive** end of the series on the left (ie the one with the higher oxidation number)

Example 1

Use electrode data to explain why fluorine reacts with water.
Write an equation for the reaction that occurs.

First apply idea that more positive E° will reduce (go forward) and more negative E° will oxidise (go backwards)

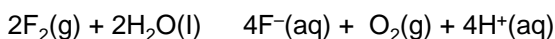


Explanation to write

As $E^\circ \text{F}_2/\text{F}^- > E^\circ \text{O}_2/\text{H}_2\text{O}$, and E_{cell} is a positive value of +1.64V, F_2 will oxidise H_2O to O_2

work out E_{cell} and quote it as part of your answer
 $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = 2.87 - 1.23 = 1.64\text{V}$

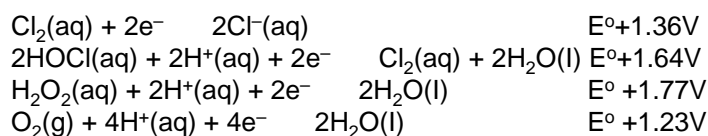
Equation



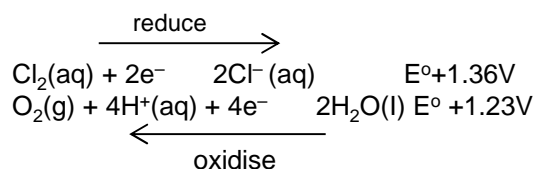
Remember to cancel out electrons in full equation

Example 2

Use data from the table to explain why chlorine should undergo a redox reaction with water. Write an equation for this reaction.



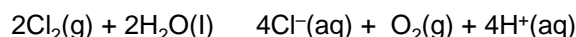
First select relevant half equations by considering the E° values and applying the idea that more positive E° will reduce (go forward) and more negative E° will oxidise (go backwards)



Explanation to write

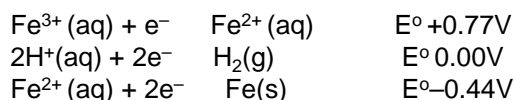
As $E^\circ \text{Cl}_2/\text{Cl}^- > E^\circ \text{O}_2/\text{H}_2\text{O}$, and E_{cell} is a positive value of +0.13V, Cl_2 will oxidise H_2O to O_2

Equation

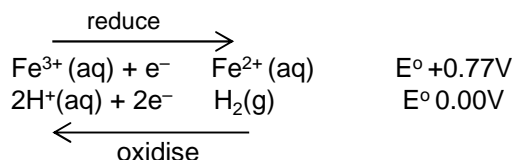


Example 3

Suggest what reactions occur, if any, when hydrogen gas is bubbled into a solution containing a mixture of iron(II) and iron(III) ions. Explain your answer.



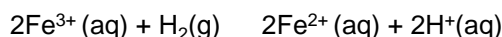
First select relevant half equations by considering the E° values and applying the idea that more positive E° will reduce (go forward) and more negative E° will oxidise (go backwards)



Explanation to write

Fe^{3+} will be reduced to Fe^{2+} by H_2 oxidising to H^+ because $E^\circ \text{Fe}^{3+}/\text{Fe}^{2+} > E^\circ \text{H}^+/\text{H}_2$ and E_{cell} is a positive value of +0.77V

Equation

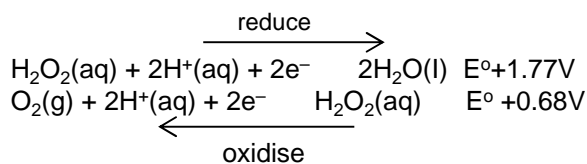


Example 4 Disproportionation

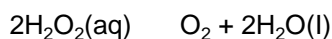
Use the half-equations to explain in terms of oxidation states what happens to hydrogen peroxide when it is reduced.

Explanation to write

As $E^\circ \text{H}_2\text{O}_2/\text{H}_2\text{O} > E^\circ \text{O}_2/\text{H}_2\text{O}_2$ and E_{cell} is a positive value of +1.09V, H_2O_2 disproportionates from -1 oxidation state to 0 in O_2 and -2 in H_2O

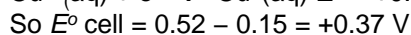
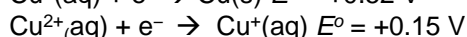
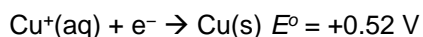


Equation



Disproportionation of copper(I) iodide

Copper(I) iodide when reacting with sulphuric acid will disproportionate to Cu^{2+} and Cu metal



As $E^\circ_{\text{Cu}^+/\text{Cu}} > E^\circ_{\text{Cu}^{2+}/\text{Cu}^+}$ and E_{cell} has a positive value of +0.37V, Cu^+ disproportionates from +1 oxidation state to 0 in Cu and +2 in Cu^{2+}

E_{cell} is directly proportional to the total entropy change and to $\ln K$ (where K is equilibrium constant) for a reaction

A positive E_{cell} will lead to a positive total entropy change

Effect of conditions on Cell voltage E_{cell}

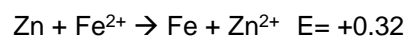
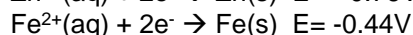
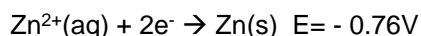
The effects of changing conditions on E_{cell} can be made by applying Le Chatelier's principle.

If current is allowed to flow, the cell reaction will occur and the E_{cell} will fall to zero as the reaction proceeds and the reactant concentrations drop.

E_{cell} is a measure of how far from equilibrium the cell reaction lies. The more positive the E_{cell} the more likely the reaction is to occur.

Effect of concentration on E_{cell}

Looking at cell reactions is a straight forward application of Le Chatelier. So increasing concentration of 'reactants' would increase E_{cell} and decreasing them would cause E_{cell} to decrease.



Increasing the concentration of Fe^{2+} and decreasing the concentration of Zn^{2+} would cause E_{cell} to increase.

Effect of temperature on E_{cell}

Most cells are exothermic in the spontaneous direction so applying Le Chatelier to a temperature rise to these would result in a decrease in E_{cell} because the equilibrium reactions would shift backwards.

If the E_{cell} positive it indicates a reaction might occur. There is still a possibility, however, that the reaction will not occur or will occur so slowly that effectively it does not happen.

If the reaction has a high activation energy the reaction will not occur.

Also if the reaction is carried out at non-standard conditions the E_{cell} using standard conditions may deviate

Cells

Electrochemical cells can be used as a commercial source of electrical energy
Cells can be non-rechargeable (irreversible), rechargeable and fuel cells.

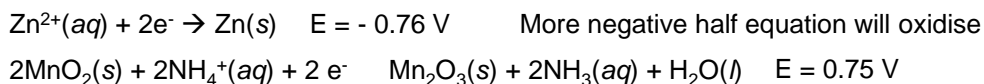
You should be able to work out E_{cell} for given half reactions.

You do not need to learn the details of most of these cells. Relevant cell information will be given. You should be able to convert between standard electrode potential half cells, full cell reactions and cell diagrams and be able to calculate potentials from given data.

Example primary non rechargeable cells

Cells are non-rechargeable when the reactions that occur with in them are non-reversible.

Dry Cell



Example primary Lithium –manganese dioxide cell- non rechargeable



$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = -0.13 - (-3.04) = 2.91 \text{ V}$$

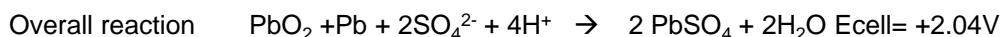
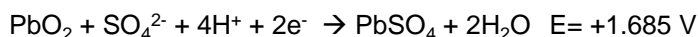
Conventional cell diagram



Example secondary rechargeable cells

The forward reaction occurs on discharge giving out charge. Charging causes the reaction to reverse

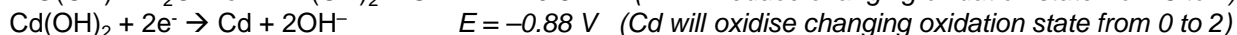
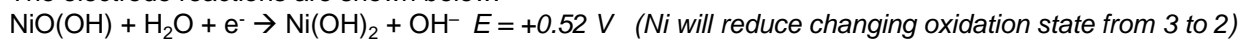
Lead acid Cell



Reversible cells only work if the product stays attached to the electrode and does not disperse

Example secondary Nickel–cadmium cells are used to power electrical equipment such as drills and shavers. They are rechargeable cells.

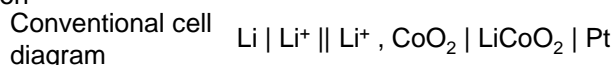
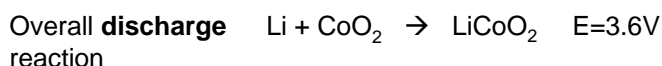
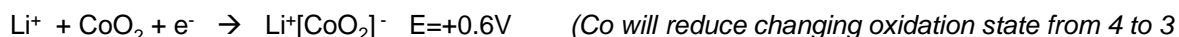
The electrode reactions are shown below.



$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = +0.52 - (-0.88) = +1.40 \text{ V}$$

Example secondary

Lithium ion cells are used to power cameras and mobile phones.



The reagents in the cell are absorbed onto powdered graphite that acts as a support medium. The support medium allows the ions to react in the absence of a solvent such as water.

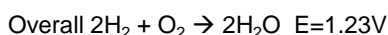
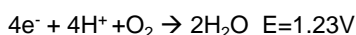
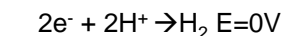
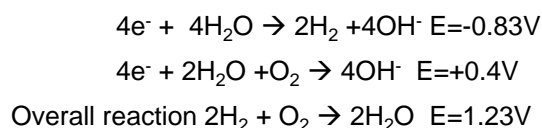
The overall reaction would be reversed in the **recharging** state

Water would not be good as a solvent as it would react with the lithium metal.

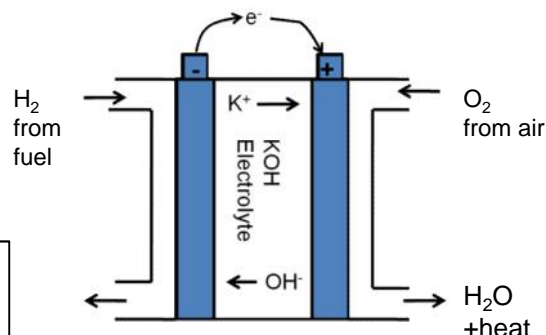
Fuel cell

A fuel cell uses the energy from the reaction of a fuel with oxygen to create a voltage

Hydrogen Fuel cell (potassium hydroxide electrolyte)



In acidic conditions these are the electrode potentials. The Ecell is the same as alkaline conditions as the overall equation is the same



Using standard conditions: The rate is too slow to produce an appreciable current.

Higher temperatures are therefore used to increase rate but the reaction is exothermic so by applying Le Chatelier would mean the emf falls.

A higher pressure can help counteract this

Fuel cells will maintain a **constant voltage** over time as they are continuously fed with fresh O_2 and H_2 so maintaining constant concentration of reactants. This differs from ordinary cells where the voltage drops over time as the reactant concentrations drop

Advantages of Fuel cells over conventional petrol or diesel-powered vehicles

- (i) less pollution and less CO_2 . (Pure hydrogen emits only water whilst hydrogen-rich fuels produce only small amounts of air pollutants and CO_2 .)
- (ii) greater efficiency;

Limitations of hydrogen fuel cells

- (i) expensive
- (ii) storing and transporting hydrogen, in terms of safety, feasibility of a pressurised liquid and a limited life cycle of a solid 'adsorber' or 'absorber'
- (iii) limited lifetime (requiring regular replacement and disposal) and high production costs,
- (iv) use of toxic chemicals in their production

Hydrogen is readily available by the electrolysis of water, but this is expensive. To be a green fuel the electricity needed would need to be produced from renewable resources

Hydrogen can be stored in fuel cells

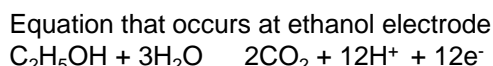
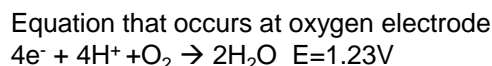
- (i) as a liquid under pressure,
- (ii) adsorbed on the surface of a solid material,
- (iii) absorbed within a solid material;

Ethanol fuel cells

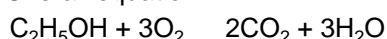
Ethanol fuel cells have also been developed. Compared to hydrogen fuel cells they have certain advantages including. Ethanol can be made from renewable sources in a carbon neutral way

Raw materials to produce ethanol by fermentation are abundant

Ethanol is less explosive and easier to store than hydrogen. New petrol stations would not be required as ethanol is a liquid fuel.



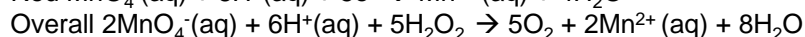
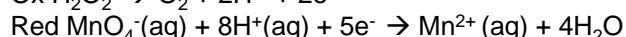
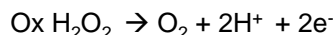
Overall equation



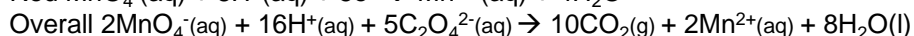
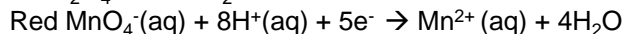
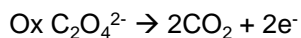
Methanol can also be used in fuel cells

Other useful manganate titrations

With hydrogen peroxide

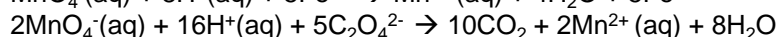
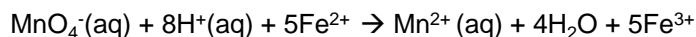


With ethanedioate

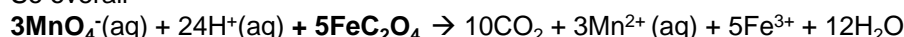


The reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ is slow to begin with (as the reaction is between two negative ions) To do as a titration the conical flask can be heated to 60°C to speed up the initial reaction.

With Iron (II) ethanedioate both the Fe^{2+} and the $\text{C}_2\text{O}_4^{2-}$ react with the MnO_4^-
 1MnO_4^- reacts with 5Fe^{2+} and 2MnO_4^- reacts with $5\text{C}_2\text{O}_4^{2-}$



So overall



So overall the ratio is **3** MnO_4^- to **5** FeC_2O_4

A 1.412 g sample of impure $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in an excess of dilute sulphuric acid and made up to 250 cm^3 of solution. 25.0 cm^3 of this solution decolourised 23.45 cm^3 of a $0.0189 \text{ mol dm}^{-3}$ solution of potassium manganate(VII).

What is the percentage by mass of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the original sample?

Step 1 : find moles of KMnO_4

moles = conc x vol

$$0.0189 \times 23.45/1000$$

$$= 4.43 \times 10^{-4} \text{ mol}$$

Step 2 : using balanced equation find moles $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 25 cm^3

$$= \text{moles of } \text{KMnO}_4 \times 5/3 \text{ (see above for ratio)}$$

$$= 7.39 \times 10^{-4} \text{ mol}$$

Step 3 : find moles $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 250 cm^3

$$= 7.39 \times 10^{-4} \text{ mol} \times 10$$

$$= 7.39 \times 10^{-3} \text{ mol}$$

Step 4 : find mass of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in $7.39 \times 10^{-3} \text{ mol}$

$$\text{mass} = \text{moles} \times \text{Mr} = 7.39 \times 10^{-3} \times 179.8 = 1.33 \text{ g}$$

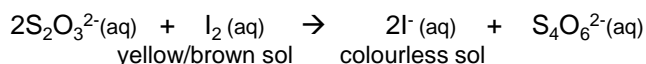
Step 5 ; find % mass

$$\% \text{mass} = 1.33/1.412 \times 100$$

$$= 94.1\%$$

Thiosulphate redox titration

The redox titration between I_2 and thiosulphate $\text{S}_2\text{O}_3^{2-}$ is a common exercise.



A starch indicator is added near the end point when the iodine fades a pale yellow to emphasise it.

With starch added the colour change is from blue/black to colourless

The starch should **not** be added until nearly all the iodine has reacted because the blue complex formed with high concentrations of iodine is insoluble and does not re-dissolve as more thiosulfate is added

Errors

Calculating apparatus errors

Each type of apparatus has a sensitivity error

- balance ± 0.001 g
- volumetric flask ± 0.1 cm³
- 25 cm³ pipette ± 0.1 cm³
- burette ± 0.05 cm³

Calculate the percentage error for each piece of equipment used by

$$\% \text{ error} = \pm \frac{\text{sensitivity error}}{\text{Measurement made on apparatus}} \times 100$$

e.g. for pipette

$$\% \text{ error} = 0.05 / 25 \times 100$$

To calculate the maximum percentage apparatus error in the final result add all the individual equipment errors together.

To decrease the apparatus errors you can either decrease the sensitivity error by using apparatus with a greater resolution (finer scale divisions) or you can increase the size of the measurement made.

If looking at a series of measurements in an investigation the experiments with the smallest readings will have the highest experimental errors.

If the burette used in the titration had an uncertainty for each reading of ± 0.05 cm³ then during a titration two readings would be taken so the error on the titre volume would be ± 0.10 cm³

Reducing errors in a titration

Replacing measuring cylinders with pipettes or burettes which have lower apparatus sensitivity error will lower the error

To reduce the error in a burette reading it is necessary to make the titre a larger volume. This could be done by: increasing the volume and concentration of the substance in the conical flask or by decreasing the concentration of the substance in the burette.

Reducing errors in measuring mass

Using a more accurate balance or a larger mass will reduce the error in weighing a solid
Weighing sample before and after addition and then calculating difference will ensure a more accurate measurement of the mass added.

Calculating the percentage difference between the actual value and the calculated value

If we calculated an Mr of 203 and the real value is 214, then the calculation is as follows:

Calculate difference $214 - 203 = 11$

$$\% = 11 / 214 \times 100 \\ = 5.41\%$$

If the %error due to the apparatus $<$ percentage difference between the actual value and the calculated value then there is a discrepancy in the result due to other errors.

If the %error due to the apparatus $>$ percentage difference between the actual value and the calculated value then there is no discrepancy and all errors in the results can be explained by the sensitivity of the equipment.