5.2.3 Electrode Potentials and Fuel Cells

Redox

oxidation is the process **of electron loss**:
$Zn \rightarrow Zn^{2+} + 2e^-$
It involves an increase in oxidation number

reduction is the process **of electron gain**:
$Cl_2 + 2e^- \rightarrow 2Cl^-$
It involves a decrease in oxidation number

Redox equations and half equations

$$Br_2\,(aq) + 2I^-\,(aq) \rightarrow I_2\,(aq) + 2\,Br^-\,(aq)$$

$Br_2\,(aq) + 2e^- \rightarrow + 2\,Br^-\,(aq)$

Br has reduced as it has gained electrons

$2I^-\,(aq) \rightarrow I_2\,(aq) + 2\,e^-$

I has oxidised as it has lost electrons

A reduction half equation only shows the parts of a chemical equation involved in reduction
The electrons are on the left

An oxidation half equation only shows the parts of a chemical equation involved in oxidation
The electrons are on the right

reducing agents are electron donors

oxidising agents are electron acceptors

The oxidising agent is Bromine water . It is an **electron acceptor**

The reducing agent is the Iodide ion. It is an **electron donor**

An oxidising agent (or oxidant) is the species that causes another element to oxidise. It is itself reduced in the reaction

A reducing agent (or reductant) is the species that causes another element reduce. It is itself oxidised in the reaction.

When naming oxidising and reducing agents always refer to full name of substance and not just name of element

Balancing redox equations

Writing half equations

1. Work out oxidation numbers for element being oxidised/ reduced
2. Add electrons equal to the change in oxidation number
   For reduction add e's to reactants
   For oxidation add e's to products
3. check to see that the sum of the charges on the reactant side equals the sum of the charges on the product side

$Zn \rightarrow Zn^{2+}$ *Zn changes from 0 to +2*

$Zn \rightarrow Zn^{2+} + 2e^-$

0

+2 –2 =0

More complex half equations

If the substance that is being oxidised or reduced contains a varying amount of O (eg $MnO_4^- \rightarrow Mn^{2+}$) then the half equations are balanced by adding H^+, OH^- ions and H_2O.

In acidic conditions use H^+ and H_2O

Example: Write the half equation for the change $MnO_4^- \rightarrow Mn^{2+}$

1. Balance the change in O.N. with electrons — *Mn changes from +7 to +2* *Add 5 electrons to reactants* — $MnO_4^- + 5e^- \rightarrow Mn^{2+}$

2. Add H_2O in products to balance O's in MnO_4^- — $MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$

3. Add H^+ in reactants to balance H's in H_2O — $\boxed{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}$

4. check to see that the sum of the charges on the reactant side equals the sum of the charges on the product side

-1 + 8 -5 = +2

+2

Example: Write the half equation for the change $SO_4^{2-} \rightarrow SO_2$

1. Balance the change in O.N. with electrons — *S changes from +6 to +4*
Add 2 electrons to reactants — $SO_4^{2-} + 2e^- \rightarrow SO_2$

2. Add H_2O in products to balance O's in SO_4^{2-} — $SO_4^{2-} + 2e^- \rightarrow SO_2 + 2H_2O$

3. Add H^+ in reactants to balance H's in H_2O — $\boxed{SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O}$

4. check to see that the sum of the charges on the reactant side equals the sum of the charges on the product side

-4 + 4 = 0

0

Combining half equations

To make a full redox equation combine a reduction half equation with a oxidation half equation

To combine two half equations there must be equal numbers of electrons in the two half equations so that the electrons cancel out

Example 1

Reduction $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ **x2**

Oxidation $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$ **x5**

Multiply the half equations to get equal electrons

$\boxed{2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}$

Add half equations together and cancel electrons

Example 2

Reduction $SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$

Oxidation $2I^- \rightarrow I_2 + 2e^-$ **x4**

Multiply the half equations to get equal electrons

$\boxed{8I^- + SO_4^{2-} + 10H^+ \rightarrow H_2S + 4I_2 + 4H_2O}$

Add half equations together and cancel electrons

Redox titrations

Thiosulfate redox titration

The redox titration between I_2 and thiosulfate $S_2O_3^{2-}$ is a common exercise.

$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

yellow/brown sol → colourless sol

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

Manganate redox titration

The redox titration between Fe^{2+} with MnO_4^- (purple) is a very common exercise. This titration is self indicating because of the significant colour change from reactant to product

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

Purple colourless

The purple colour of manganate can make it difficult to see the bottom of the meniscus in the burette.

If the manganate is in the burette then the end point of the titration will be the first permanent pink colour.
Colourless → purple

Choosing correct acid for manganate titrations.

The acid is needed to supply the $8H^+$ ions. Some acids are not suitable as they set up alternative redox reactions and hence make the titration readings inaccurate.

Only **use dilute sulfuric acid** for manganate titration

Insufficient volumes of sulfuric acid will mean the solution is not acidic enough and MnO_2 will be produced instead of Mn^{2+}
$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O$
The brown MnO_2 will mask the colour change and lead to a greater (inaccurate) volume of manganate being used in the titration
Using a weak acid like ethanoic acid would have the same effect as it cannot supply the large amount of hydrogen ions needed ($8H^+$)

It cannot be **conc HCl** as the Cl^- ions would be oxidised to Cl_2 by MnO_4^- as the E^o MnO_4^-/Mn^{2+} > E^o Cl_2/Cl^-
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ $E^o = +1.51V$
$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$ $E^o = +1.36V$
This would lead to a greater volume of manganate being used and poisonous Cl_2 being produced.

It cannot be nitric acid as it is an oxidising agent. It oxidises Fe^{2+} to Fe^{3+} as E^o NO_3^-/HNO_2 > E^o Fe^{3+}/Fe^{2+}
$NO_3^-(aq) + 3H^+(aq) + 2e^- \rightarrow HNO_2(aq) + H_2O(l)$ E^o +0.94V
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ E^o +0.77 V
This would lead to a smaller volume of manganate being used

be able to perform calculations for these titrations and for others when the reductant and its oxidation product are given.

Manganate titration example

A 2.41g nail made from an alloy containing iron is dissolved in 100cm^3 acid. The solution formed contains Fe(II) ions.
10cm^3 portions of this solution are titrated with potassium manganate (VII) solution of 0.02 mol dm^{-3}.
9.80cm^3 of $KMnO_4$ were needed to react with the solution containing the iron.
Calculate the percentage of iron by mass in the nail

$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5Fe^{2+} \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O + 5Fe^{3+}$

Step1 : find moles of $KMnO_4$
moles = conc x vol
0.02 x 9.8/1000
= 1.96×10^{-4} mol
Step 2 : using balanced equation find moles Fe^{2+} in 10cm^3
= moles of $KMnO_4$ x 5
= 9.8×10^{-4} mol
Step 3 : find moles Fe^{2+} in 100cm^3
= 9.8×10^{-4} mol x 10
= 9.8×10^{-3} mol
Step 4 : find mass of Fe in 9.8×10^{-3} mol
mass= moles x RAM = 9.8×10^{-3} x 55.8 = 0.547g

Step 5 ; find % mass

%mass = 0.547/2.41 x100

= 22.6%

Other useful manganate titrations
With hydrogen peroxide

Ox $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$
Red $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$
Overall $2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2 \rightarrow 5O_2 + 2Mn^{2+}(aq) + 8H_2O$

With ethanedioate

Ox $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$
Red $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$
Overall $2MnO_4^-{}_{(aq)} + 16H^+{}_{(aq)} + 5C_2O_4^{2-}{}_{(aq)} \rightarrow 10CO_{2(g)} + 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)}$

The reaction between MnO_4^- and $C_2O_4^{2-}$ 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 $C_2O_4^{2-}$ react with the MnO_4^-
$1MnO_4^-$ reacts with $5Fe^{2+}$ and 2 MnO_4^- reacts with $5C_2O_4^{2-}$

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+} \rightarrow Mn^{2+}(aq) + 4H_2O + 5Fe^{3+}$
$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-} \rightarrow 10CO_2 + 2Mn^{2+}(aq) + 8H_2O$
So overall
$\mathbf{3MnO_4^-}(aq) + 24H^+(aq) \mathbf{+ 5FeC_2O_4} \rightarrow 10CO_2 + 3Mn^{2+}(aq) + 5Fe^{3+} + 12H_2O$

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

A 1.412 g sample of impure $FeC_2O_4.2H_2O$ was dissolved in an excess of dilute sulfuric 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 mol dm^{-3} solution of potassium manganate(VII).
Calculate the percentage by mass of $FeC_2O_4.2H_2O$ in the original sample.

Step1 : find moles of $KMnO_4$
moles = conc x vol
0.0189 x 23.45/1000
= 4.43×10^{-4} mol
Step 2 : using balanced equation find moles $FeC_2O_4.2H_2O$ in 25cm^3
= moles of $KMnO_4$ x 5/3 (see above for ratio)
= 7.39×10^{-4} mol
Step 3 : find moles $FeC_2O_4.2H_2O$ in 250 cm^3
= 7.39×10^{-4} mol x 10
= 7.39×10^{-3} mol
Step 4 : find mass of $FeC_2O_4.2H_2O$ in 7.39×10^{-3} mol
mass= moles x *M*r = 7.39×10^{-3} x 179.8 = 1.33g

Step 5 ; find % mass

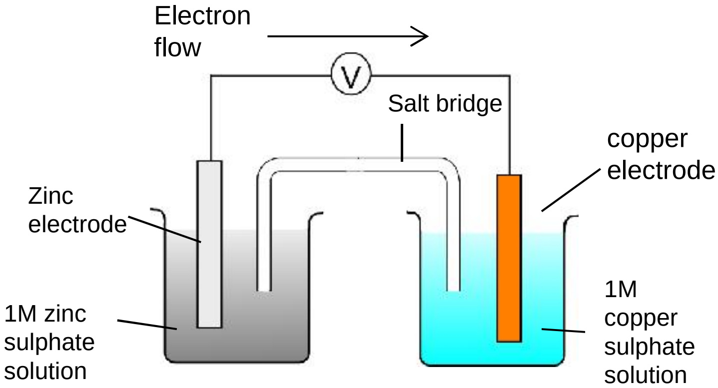
%mass = 1.33/1.412 x100

= 94.1%

Electrode Potentials

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. ($Zn \rightarrow Zn^{2+} + 2e^-$)
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= +1.1V.

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.
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ (positive as electrons are used up)

The most negative electrode will always undergo oxidation.
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (negative as electrons are given off)

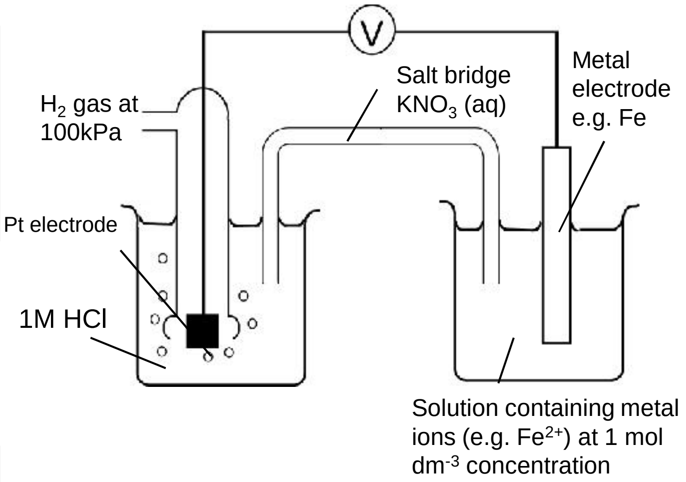
Measuring the electrode potential of a cell

- 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:
$H_2 (g) \rightleftharpoons 2H^+ (aq) + 2e^-$

Components of a standard hydrogen electrode.
To make the electrode a standard reference electrode some conditions apply:
1. **Hydrogen gas** at **pressure of 100kPa**
2. Solution containing the **hydrogen ion at 1 mol dm^{-3}** (solution is usually 1 mol dm^{-3} 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:
$M^{n+}(aq) + n e^- \rightleftharpoons M(s)$

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 V
calomel electrode	E = +0.27 V

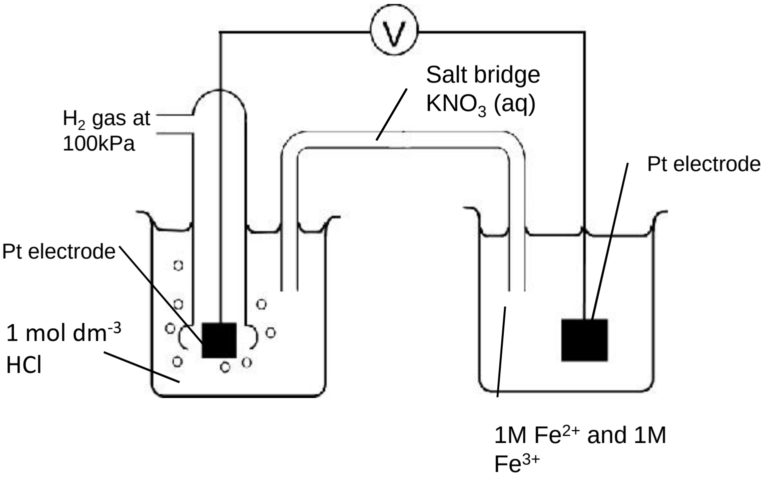
Standard Electrode Potentials $E^{\ominus}$

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 mol dm^{-3}
- •temperature 298K
- •gases at 100kPa pressure
- •no current flowing

Standard electrode potentials are found in data books and are quoted as
$Li^+(aq) | Li (s)$ E= -3.03V
more oxidised form on left

They may also be quoted as half equations
$Li^+ (aq) + e^- \rightleftharpoons Li (s)$ E= -3.03V
but again the more oxidised form is on the left



Note: in the electrode system containing two solutions it is necessary to use a platinum electrode and **both** ion solutions must be of a 1 mol dm^{-3} concentration, so $[Fe^{2+}]$ = 1 mol dm^{-3} and $[Fe^{3+}]$ = 1 mol dm^{-3} .

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)

←

$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ E= -2.37V
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ E = +0.34V

→

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

The reaction would be
$Mg + Cu^{2+} \rightarrow Cu + Mg^{2+}$

If we want to work out the Ecell that corresponds to this spontaneous change then use
Ecell = Ered – Eox
A spontaneous change will always have a positive Ecell

The most **negative** electrode will **oxidise** and go from **right to left**
The half equation is therefore $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
Electrons are given off (lost) and travel to positive electrode

←

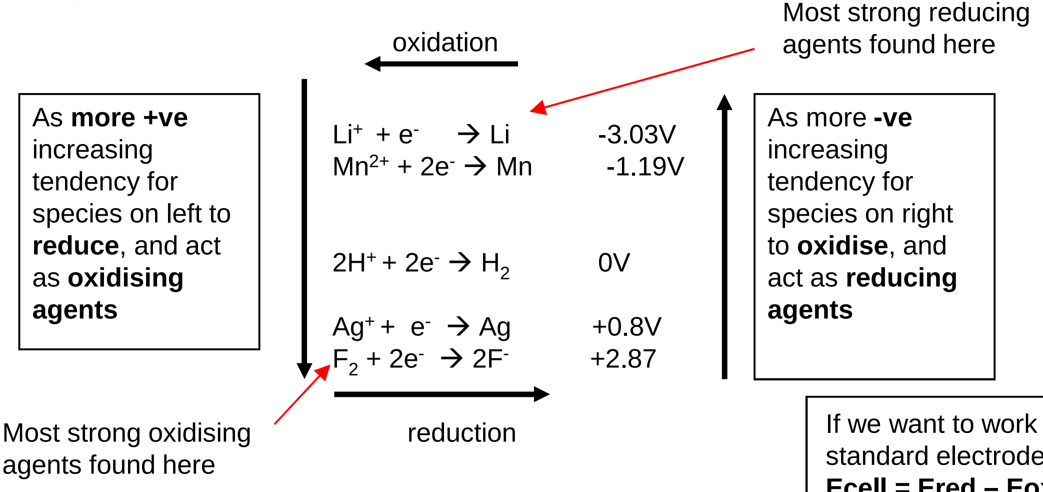
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ E= - 0.76V
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ E= -0.44V

→

The more **positive** electrode will **reduce** and go from **left to right** $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$
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.
$Zn + Fe^{2+} \rightarrow Fe + Zn^{2+}$

Using series of standard electrode potentials



Most strong reducing agents found here

oxidation

As more **+ve** increasing tendency for species on left to **reduce**, and act as **oxidising agents**

$Li^+ + e^- \rightarrow Li$ -3.03V
$Mn^{2+} + 2e^- \rightarrow Mn$ -1.19V

$2H^+ + 2e^- \rightarrow H_2$ 0V

$Ag^+ + e^- \rightarrow Ag$ +0.8V
$F_2 + 2e^- \rightarrow 2F^-$ +2.87

As more **-ve** increasing tendency for species on right to **oxidise**, and act as **reducing agents**

Most strong oxidising agents found here

reduction

If we want to work out the Ecell from two standard electrode potentials then use
Ecell = Ered – Eox

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^o will reduce (go forward) and more negative E^o will oxidise (go backwards)

$\xleftarrow{\text{oxidise}}$
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ E^o+1.23V
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$ E^o +2.87V
$\xrightarrow[\text{reduce}]{}$

Explanation to write

As E^o F_2/F^- > E^o O_2/H_2O, F_2 will oxidise H_2O to O_2

Can also work out Ecell and quote it as part of your answer
Ecell = Ered - Eox = 2.87-1.23 =1.64V

Equation

$2F_2(g) + 2H_2O(l) \rightarrow 4F^-(aq) + O_2(g) + 4H^+(aq)$

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.

$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$ E^o+1.36V
$2HOCl(aq) + 2H^+(aq) + 2e^- \rightarrow Cl_2(aq) + 2H_2O(l)$ E^o+1.64V
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$ E^o +1.77V
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ E^o +1.23V

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

$\xrightarrow{\text{reduce}}$
$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$ E^o+1.36V
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ E^o +1.23V
$\xleftarrow[\text{oxidise}]{}$

Explanation to write

As E^o Cl_2/Cl^- > E^o O_2/H_2O, Cl_2 will oxidise H_2O to O_2

Equation

$2Cl_2(g) + 2H_2O(l) \rightarrow 4Cl^-(aq) + O_2(g) + 4H^+(aq)$

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.

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ E^o +0.77V
$2H^+(aq) + 2e^- \rightarrow H_2(g)$ E^o 0.00V
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ E^o–0.44V

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

$\xrightarrow{\text{reduce}}$
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ E^o +0.77V
$2H^+(aq) + 2e^- \rightarrow H_2(g)$ E^o 0.00V
$\xleftarrow[\text{oxidise}]{}$

Explanation to write

Fe^{3+} will be reduced to Fe^{2+} by H_2 oxidising to H^+ because E^o Fe^{3+}/Fe^{2+} > E^o H^+/H_2

Equation

$2Fe^{3+}(aq) + H_2(g) \rightarrow 2Fe^{2+}(aq) + 2H^+(aq)$

Example 4

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

$\xrightarrow{\text{reduce}}$
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$ E^o+1.77V
$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$ E^o +0.68V
$\xleftarrow[\text{oxidise}]{}$

Explanation to write

As E^o H_2O_2/H_2O > E^o O_2/H_2O_2 , H_2O_2 disproportionates from -1 oxidation state to 0 in O_2 and -2 in H_2O

Equation

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2$

Effect of conditions on cell e.m.f

The effects of changing conditions on cell e.m.f can be made by applying le chateliers principle

E.m.f. is a measure of how far from equilibrium the cell reaction lies. The more positive the e.m.f the more likely the reaction is to occur.

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

Effect of concentration on cell e.m.f

Looking at cell reaction is a straight forward application of le chatelier. So increasing concentration of 'reactants' would increase EMF and decreasing them would cause EMF to decrease

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ E= - 0.76V
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ E= -0.44V

$Zn + Fe^{2+} \rightarrow Fe + Zn^{2+}$ E= +0.32

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

Effect of temperature on cell e.m.f

Most Ecells are exothermic in the spontaneous direction so applying Le chatelier to a temperature rise to these would result in a decrease in Ecell

If the Ecell 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 doesn't happen.
If the reaction has a high activation energy the reaction will not occur.

Explaining homogeneous catalysis using E values

You do not need to learn the detail about this reaction

The reaction between I^- and $S_2O_8^{2-}$ catalysed by **Fe^{2+}**
overall $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$

The uncatalysed reaction is very slow because the reaction needs a collision between **two negative ions**. **Repulsion** between the ions is going to hinder this – meaning **high activation energy**

$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$ E^o+2.01V
$Fe^{3+} + e^- \rightarrow Fe^{2+}$ E^o+0.77V
$I_2 + 2e^- \rightarrow 2I^-$ E^o+0.54V

For a substance to act as a homogenous catalyst its electrode potential must lie in between the electrode potentials of the two reactants, so it can first reduce the reactant with the more positive electrode potential and then in the second step oxidize the reactant with the more negative electrode potential

Catalysed alternative route
stage 1 $S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$
stage2 $2I^- + 2Fe^{3+} \rightarrow 2Fe^{2+} + I_2$

Both of the individual stages in the catalysed mechanism involve collision between positive and negative ions and will have lower activation energies.

Using E values to find a catalyst only shows that catalysis is possible. It does not guarantee that the rate of reaction will be increased

Fe^{3+} ions can also act as the catalyst because the two steps in the catalysed mechanism can occur in any order

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 Ecell for given half reactions.

You do not need to learn the details 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 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 $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ E = - 0.76 V More negative half equation will oxidise

$2MnO_2(s) + 2NH_4^+(aq) + 2\,e^- \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$ E = 0.75 V

Overall reaction $2MnO_2 + 2NH_4^+ + Zn \rightarrow Mn_2O_3 + 2NH_3 + H_2O + Zn^{2+}$ Ecell =+1.51V

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.

$NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$ *E = +0.52 V (Ni will reduce changing oxidation state from 3 to 2)*

$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$ *E = –0.88 V (Cd will oxidise changing oxidation state from 0 to 2)*

Overall reaction **discharge** $2NiO(OH) + Cd + 2H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2$ E= +1.40V

Ecell = E red- Eox = +0.52 - - 0.88 = + 1.40 V

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

$2Ni(OH)_2 + Cd(OH)_2 \rightarrow 2NiO(OH) + Cd + 2H_2O$

Fuel cell

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

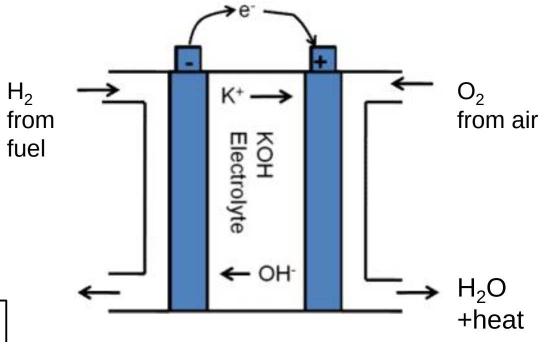
Scientists in the car industry are developing fuel cell vehicles, fuelled by:
(i) hydrogen gas,
(ii) hydrogen-rich fuels;

Hydrogen Fuel cell (potassium hydroxide electrolyte)

$4e^- + 4H_2O \rightarrow 2H_2 + 4OH^-$ E=-0.83V

$4e^- + 2H_2O + O_2 \rightarrow 4OH^-$ E=+0.4V

Overall reaction $2H_2 + O_2 \rightarrow 2H_2O$ E=1.23V



$2e^- + 2H^+ \rightarrow H_2$ E=0V

$4e^- + 4H^+ + O_2 \rightarrow 2H_2O$ E=1.23V

Overall $2H_2 + O_2 \rightarrow 2H_2O$ E=1.23V

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

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

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

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