# Redox Equilibria

Electrochemical cells

This type of cell can be called a Voltaic cell or Galvanic cell. Voltaic cells convert energy from spontaneous, exothermic chemical processes to electrical energy.

•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).
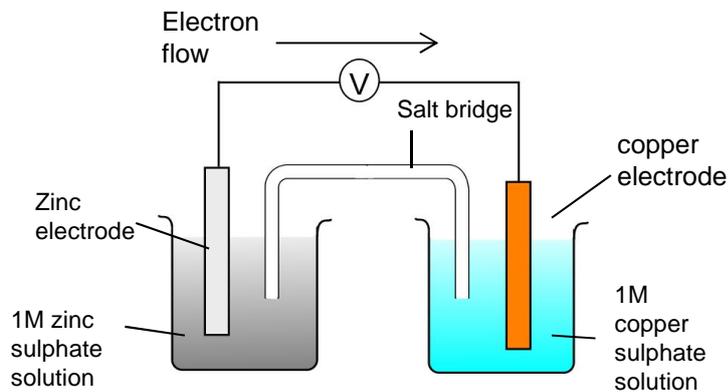
Why does a voltage form?
In the cell pictured above
When connected together the zinc half-cell has more of a tendency to oxidise to the Zn^{2+} ion and release electrons than the copper half-cell. ($Zn \rightarrow Zn^{2+} + 2e^-$)
More electrons will therefore build up on the zinc electrode than the 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.

$$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$$
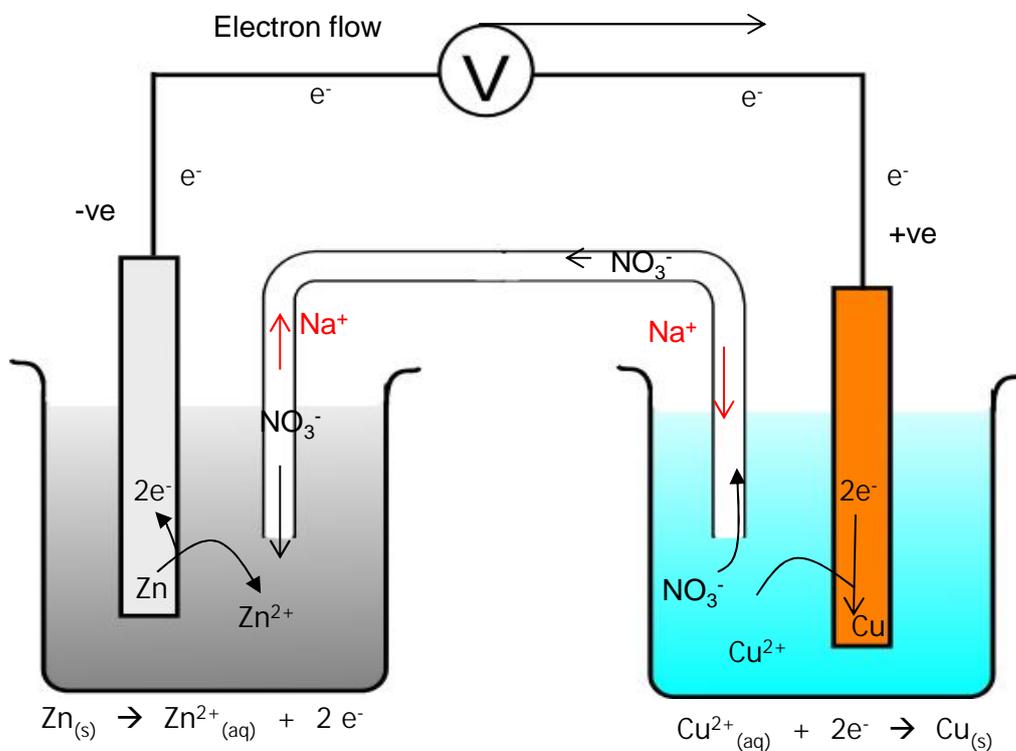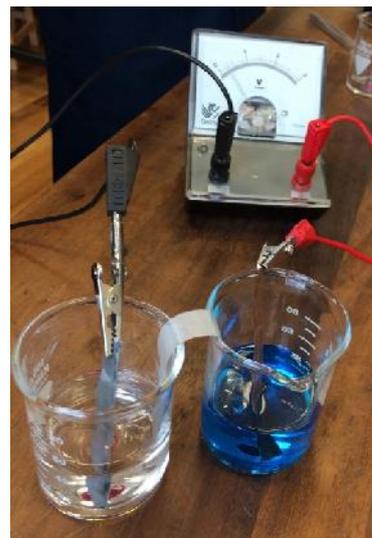
Oxidation occurs at the anode (negative electrode)

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

reduction occurs at the cathode (positive electrode)

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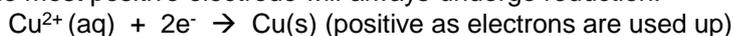
The most negative electrode will always undergo oxidation.
 $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (negative as electrons are given off)

Terminology: Cathode and Anode

In electrochemical (galvanic cells) the cathode and anode have the opposite signs to what they have in electrolysis cells. The key point to remember is that in both galvanic and electrolytic cells **red**uction always occurs at **cat**hode and **oxi**dation always occurs at **an**ode

|	Process that occurs at electrode	Sign of electrode in electrolysis cells	Sign of electrode in voltaic cells
cathode	reduction	Negative	Positive
anode	oxidation	Positive	Negative

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.
 A platinum electrode is used because it is **unreactive** and **can conduct electricity.**

1M $FeSO_4$ and 0.5 M $Fe_2(SO_4)_3$

copper electrode

Pt electrode

1M copper sulfate solution
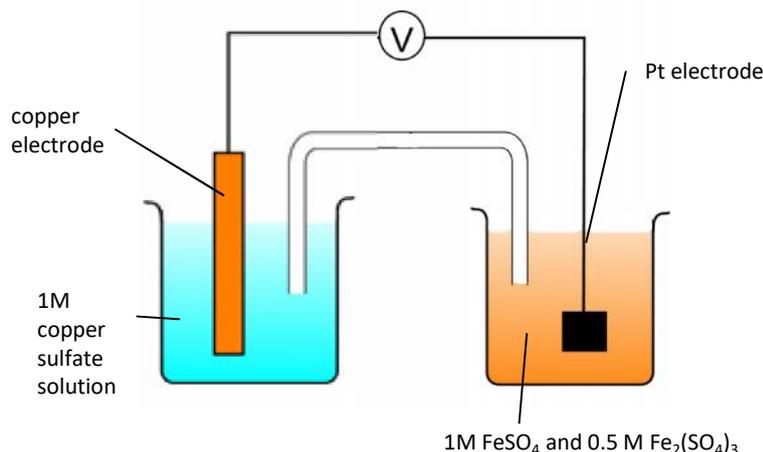
Cell Diagrams

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

$$Zn(s) \mid Zn^{2+} (aq) \mid\mid Cu^{2+} (aq) \mid Cu (s) \qquad E= +1.1V$$
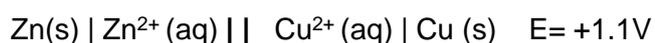
Most oxidised form is put next to the double line

• 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.

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

The cell diagram is drawn as:
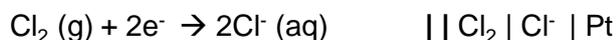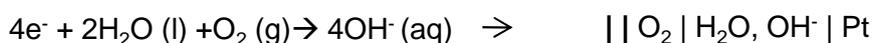$$\mid\mid Fe^{3+} (aq), Fe^{2+} (aq) \mid Pt$$
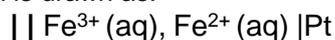
Still with more oxidised form near double line
A comma separates the oxidised from the reduced species.

If the system contains several species
 e.g. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
then in the cell diagram the balancing numbers, H^+ ions and H_2O can be left out.

$$\mid \mid MnO_4\text{-} , Mn^{2+} \mid Pt$$
or if on left hand side
$$Pt \mid Mn^{2+} , MnO_4^- \mid\mid$$
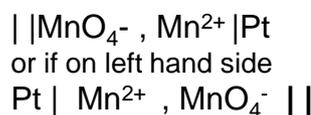
If a half equation has several physical states then the solid vertical line should be used between each different state boundary.

$$4e^- + 2H_2O (l) + O_2 (g) \rightarrow 4OH^- (aq) \qquad \rightarrow \qquad \mid\mid O_2 \mid H_2O, OH^- \mid Pt$$

$$Cl_2 (g) + 2e^- \rightarrow 2Cl^- (aq) \qquad \mid\mid Cl_2 \mid Cl^- \mid Pt$$

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

Standard Cell potential is the potential of a cell composed of two electrodes under standard conditions

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

In a cell diagram the hydrogen electrode is represented by: $Pt \,|H_2 (g) \,| H^+ (aq)$

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 M** (solution is usually 1M HCl)
3. Temperature at **298K**

Standard conditions are needed because the position of the redox equilibrium will change with conditions.
For example, in the equilibrium:
$$M^{n+}(aq) + n e^- \rightleftharpoons M(s)$$
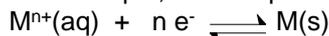
An increase in the concentration of M^{n+} would move the equilibrium to the right, so making the potential more positive.
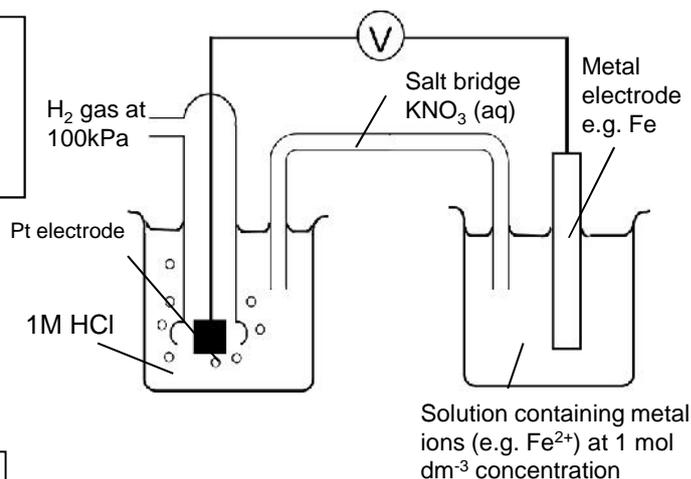
Because the equilibrium does not include a conducting metal surface a platinum wire is used which is coated in finely divided platinum. (The platinum black acts as a catalyst, because it is porous and can absorb the hydrogen gas.)

 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

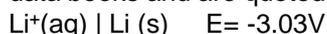## Standard Electrode Potentials $E^{\ominus}$

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 1M
•temperature 298K
•gases at 100kPa pressure
•No current flowing

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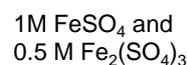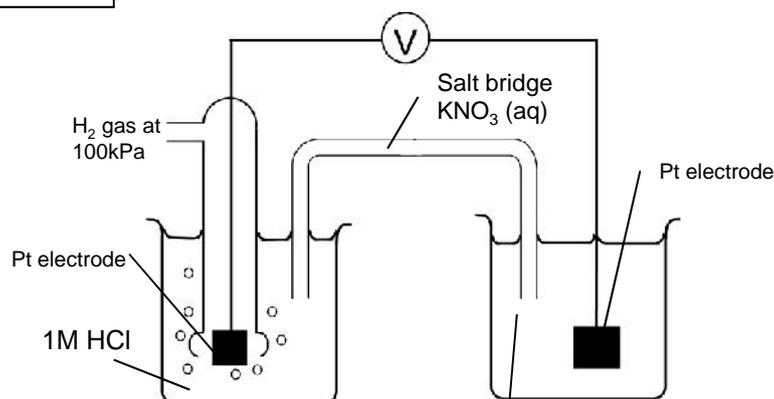$Li^+(aq) \,| Li (s)$ E= -3.03V
more oxidised form on left

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

$Pt|H_2|H^+||Fe^{3+},Fe^{2+}|Pt$

1M $FeSO_4$ and
0.5 M $Fe_2(SO_4)_3$

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

Calculating the EMF of a cell

Mg(s) | Mg^{2+} (aq) || Cu^{2+} (aq) | Cu (s)   E= +1.1V
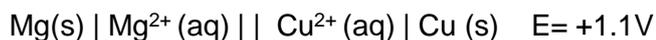
In order to calculate the Ecell, we must use '**standard electrode potentials**' for the half cells.

use the equation

$$Ecell= Erhs - Elhs$$

For the cell diagram above
Ecell = 0.34 - -2.37
= + 2.71 V

Each half cell has a **standard electrode potential** value
Mg^{2+} (aq)| Mg(s) E= -2.37V
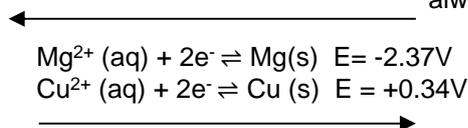Cu^{2+} (aq) | Cu (s) E = +0.34V
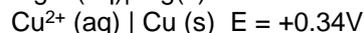
Using electrode potentials

The most useful application of electrode potentials is to show the direction of spontaneous change for redox reactions
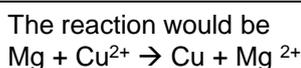
The easiest way to use electrode potentials is as follows:

For any two half equations

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

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

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

The reaction would be
Mg + Cu^{2+} → 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) → Zn^{2+} (aq) +2e$^-$
Electrons are given off (lost) and travel to positive electrode
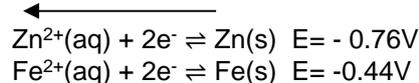
The more **positive** electrode will **reduce** and go from **left to right** Fe^{2+} (aq) +2e- → Fe(s)
Electrons arrive at this electrode and are absorbed (gained)
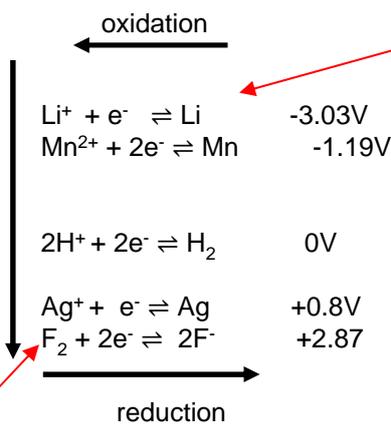
Zn^{2+}(aq) + 2e$^-$ ⇌ Zn(s) E= - 0.76V
Fe^{2+}(aq) + 2e$^-$ ⇌ Fe(s) E= -0.44V

To get the full equation of the reaction add the two half reactions together, cancelling out the electrons.
Zn + Fe^{2+} → Fe + Zn^{2+}
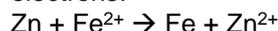
Using series of standard electrode potentials

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$^-$ ⇌ Li	-3.03V
Mn^{2+} + 2e$^-$ ⇌ Mn	-1.19V
2H$^+$ + 2e$^-$ ⇌ H$_2$	0V
Ag$^+$ + e$^-$ ⇌ Ag	+0.8V
F$_2$ + 2e$^-$ ⇌ 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
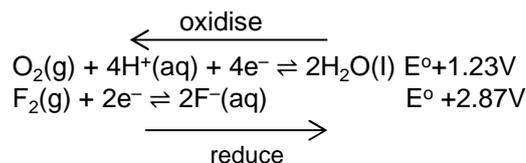**Ecell = Ered – Eox**

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)
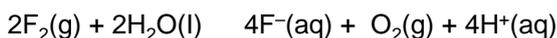
oxidise →

$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^o +1.23V$
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$ $E^o +2.87V$

reduce →

Explanation to write

As E^o F_2/F^- > E^o O_2/H_2O, and Ecell is a positive value of +1.64V, F_2 will oxidise H_2O to O_2

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

Equation

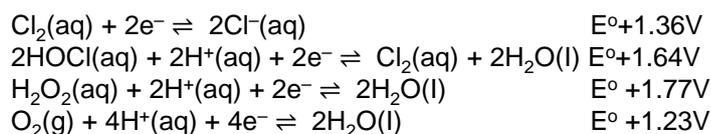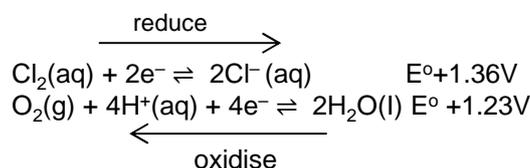$2F_2(g) + 2H_2O(l) \quad 4F^-(aq) + O_2(g) + 4H^+(aq)$

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.

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

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)

reduce →

$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^o +1.36V$
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^o +1.23V$

← oxidise

Explanation to write

As E^o Cl_2/Cl^- > E^o O_2/H_2O, and Ecell is a positive value of +0.13V, Cl_2 will oxidise H_2O to O_2

Equation

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

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.

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

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)
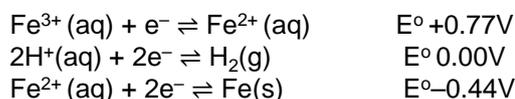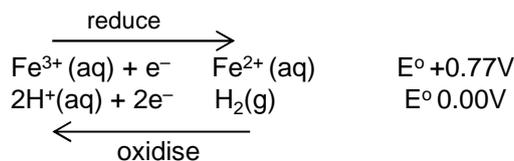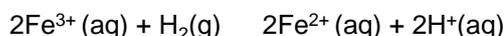
reduce →

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

← 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 and Ecell is a positive value of +0.77V

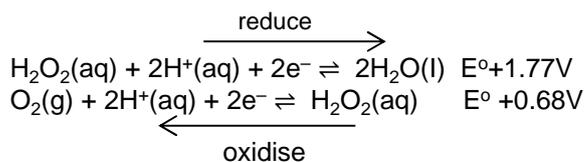**Equation**

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

Example 4
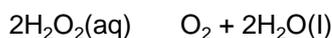
Use the half-equations to explain in terms of oxidation states what happens to hydrogen peroxide when it is reduced.

reduce →

$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$ $E^o +1.77V$
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$ $E^o +0.68V$

← oxidise

Explanation to write

As E^o H_2O_2/H_2O > E^o O_2/H_2O_2 and Ecell 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

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

Ecell and equilibrium constants can all be used to predict if a reaction might occur.

Reaction 'does not go'	Reactants predominate in an equilibrium	equal amounts of products and reactants	Products predominate in an equilibrium	Reaction goes to completion
$K_c < 10^{-10}$	$K_c \approx 0.1$	$K_c = 1$	$K_c \approx 10$	$K_c > 10^{10}$
E < -0.6	E≈ -0.1 V	E =0	E≈ +0.1 V	E>0.6 V

*E*cell is directly proportional to the total entropy change and to ln*K* (where K is equilibrium constant)for a reaction

A positive Ecell will lead to a positive total entropy change
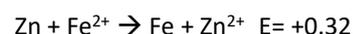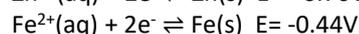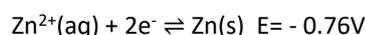
Effect of Conditions on Cell e.m.f

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

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.

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.

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

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

Nernst equation

The Nernst equation enables the electrode potential for a system with non- standard concentrations to be calculated.

$$E = E^\ominus + (0.059/z) \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

Z = the number of electrons transferred in the reaction equation

Example
Consider the half cell with the equilibrium $Ag^+ + e^- \rightleftharpoons Ag$
Calculate the Ecell for the half cell when $[Ag^+]$ = 0.33 mol dm^{-3} was used instead of the standard Ag^+ solution.

$E = E^\ominus + (0.059/z) \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$

z=1 as one e$^-$ in half equation
The reduced species is given a value of 1 as it is a solid (silver)

$E = 0.80 + (0.059) \log [0.33]$

    =0.77 V

Example
Consider the half cell with the equilibrium $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$
Calculate the Ecell for the half cell when $[Fe^{2+}]$ = 0.43 mol dm^{-3} and $[Fe^{3+}]$ = 1.20 mol dm^{-3} were used instead of the standard solutions.

$E = E^\ominus + (0.059/z) \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$

$E = 0.77 + (0.059) \log \frac{[1.20]}{[0.43]}$

    =0.86 V

Uses of Cells

Electrochemical cells are used as a commercial source of electrical energy in every piece of portable electrical equipment from torches to mobile phones. The chemical reactions that take place in the cells produce electricity. The cells can be non-rechargeable (irreversible), rechargeable and fuel cells.

Primary: non rechargeable cells

Primary cells are non-rechargeable ones. These are the ones which have to be thrown away when they become flat. Cells are non-rechargeable when the reactions that occur with in them are non-reversible.
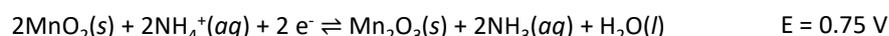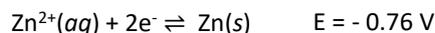
Dry Cell

The dry cell is the standard 1.5V cell used in toys, remote controls etc.
There are several variations on the chemical reactions inside them but the negative electrode tends to be zinc metal and the positive electrode contains manganese (IV) oxide

The outer container of the dry cell is a zinc can (This is the negative electrode). This contains a layer of NH_4Cl with $ZnCl_2$ aqueous paste. This is separated by a porous separator from a mixture of powdered carbon & manganese (IV) oxide (MnO_2), which is packed around a carbon rod (this is the positive pole).
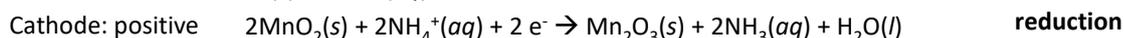
The porous separator allows the passage of ions through so charge is conducted within the cell. The carbon rod is the electrode conducting surface.
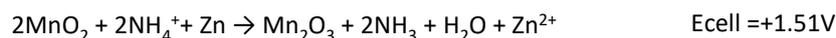
+ carbon rod
layer of powdered carbon & MnO$_2$
porous separator
Zinc casing
Moist paste of NH$_4$Cl with ZnCl$_2$
−
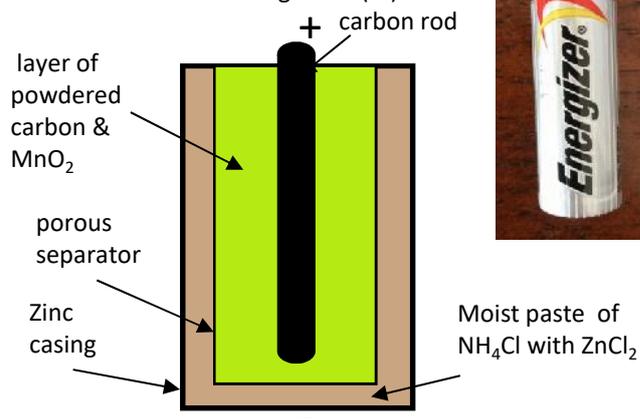
Example standard electrode potentials for reactions in cell

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

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

The more negative half equation will oxidise so the two reactions are

Anode: negative $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ **oxidation**

Cathode: positive $2MnO_2(s) + 2NH_4^+(aq) + 2 e^- \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$ **reduction**

Overall reaction

$2MnO_2 + 2NH_4^+ + Zn \rightarrow Mn_2O_3 + 2NH_3 + H_2O + Zn^{2+}$ Ecell =+1.51V
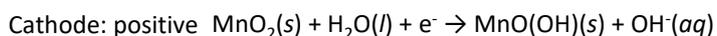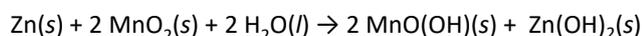
The zinc electrode acts as a container for the cell and is protected from external damage. During the reaction the outer zinc casing will be used up. A cell often leaks after being used for a long time because the zinc case has become weakened due to being used up
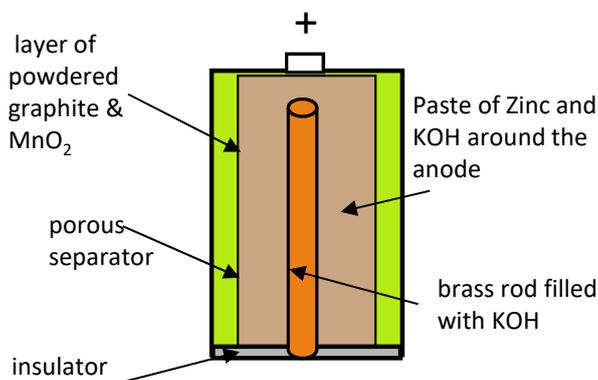
Alkaline Dry Cell

This is a variation of the dry cell. The alkaline conditions in these long life cells prevent the acid attack on the zinc casing. Notice the position of the manganese oxide and zinc are reversed in this cell. The outer casing of this cell is usually steel

Anode: negative $Zn(s) + 2 OH^- (aq) \rightarrow Zn(OH)_2(s) + 2e^-$

Cathode: positive $MnO_2(s) + H_2O(l) + e^- \rightarrow MnO(OH)(s) + OH^-(aq)$

overall reaction

$Zn(s) + 2 MnO_2(s) + 2 H_2O(l) \rightarrow 2 MnO(OH)(s) + Zn(OH)_2(s)$

The cell produces a voltage of around 1.5V

+
layer of powdered graphite & MnO$_2$
Paste of Zinc and KOH around the anode
porous separator
brass rod filled with KOH
insulator
−

Example primary

Lithium –manganese dioxide cell is a type of non rechargeable cell.
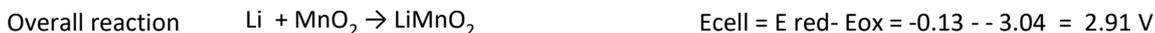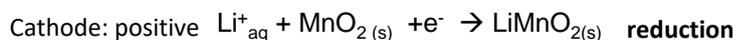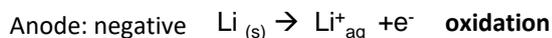These are small cells used in many portable consumer electronic devices

The cell uses metallic lithium as anode and manganese dioxide as the cathode. A salt of lithium dissolved in an organic solvent is the electrolyte
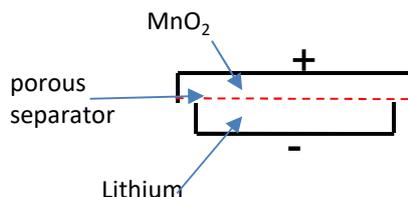
porous separator — MnO$_2$ — Lithium — + / -

standard electrode potentials for reactions in cell

$Li^+_{aq} + e^- \rightleftharpoons Li_{(s)}$ E = - 3.04 V   More negative half equation will oxidise

$Li^+_{aq} + MnO_{2 (s)} + e^- \rightleftharpoons LiMnO_{2(s)}$ E = - 0.13 V   *(Mn will reduce changing oxidation state from +4 to +3)*

Anode: negative $Li_{(s)} \rightarrow Li^+_{aq} + e^-$ **oxidation**

Cathode: positive $Li^+_{aq} + MnO_{2 (s)} + e^- \rightarrow LiMnO_{2(s)}$ **reduction**

Overall reaction $Li + MnO_2 \rightarrow LiMnO_2$ Ecell = E red- Eox = -0.13 - - 3.04 = 2.91 V

Conventional cell diagram $Li_{(s)} | Li^+_{aq} || Li^+_{aq} | MnO_{2 (s)}, LiMnO_{2(s)} | Pt (s)$ Ecell =+2.91V
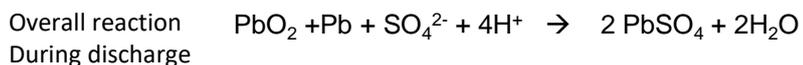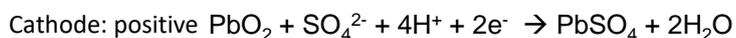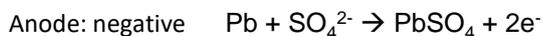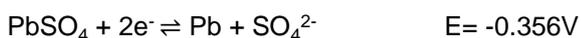
Example secondary rechargeable cells

Lead acid Cell

The lead acid rechargeable battery made from several of these cells in series is used commonly as batteries in cars.
The anode has a spongy lead covering on a lead-antinomy grid. The cathode is lead(IV) oxide on a similar lead-antinomy grid. The electrolyte is sulfuric acid

standard electrode potentials for reactions in cell

$PbSO_4 + 2e^- \rightleftharpoons Pb + SO_4^{2-}$ E= -0.356V

$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons PbSO_4 + 2H_2O$ E= +1.685 V

spongy lead covering on a lead grid

PbO$_2$ on a lead grid

Anode: negative $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Cathode: positive $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

Overall reaction
During discharge $PbO_2 + Pb + SO_4^{2-} + 4H^+ \rightarrow 2 PbSO_4 + 2H_2O$ Ecell= +2.04V

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

Overall reaction
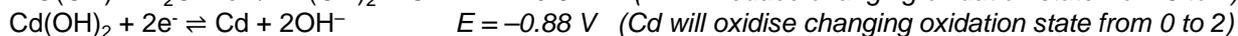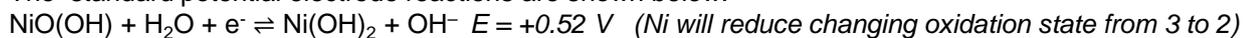During recharging $2 PbSO_4 + 2H_2O \rightarrow PbO_2 + Pb + SO_4^{2-} + 4H^+$
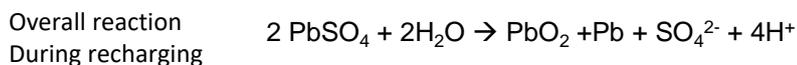
Reversible cells only work if the product stays attached to the electrode and does not disperse
PbSO$_4$ is insoluble and does not disperse
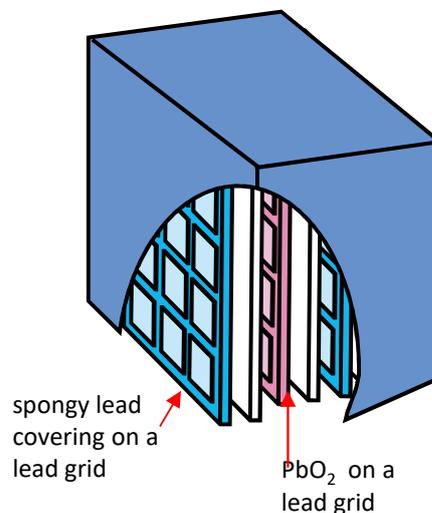
Example secondary Nickel–cadmium cells are used to power electrical equipment such as drills and shavers.
They are rechargeable cells.
This cell has an anode made from cadmium and a cathode made from NiO(OH)
The electrolyte is potassium hydroxide

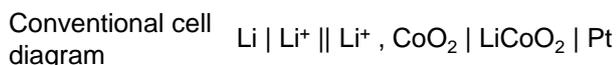The standard potential electrode reactions are shown below.
$NiO(OH) + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^-$ *E = +0.52 V   (Ni will reduce changing oxidation state from 3 to 2)*
$Cd(OH)_2 + 2e^- \rightleftharpoons Cd + 2OH^-$ *E = –0.88 V   (Cd will oxidise changing oxidation state from 0 to 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
$2Ni(OH)_2 + Cd(OH)_2 \rightarrow 2NiO(OH) + Cd + 2H_2O$
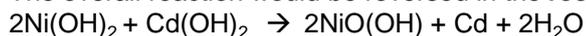
Example secondary   Lithium ion cells are used to power cameras and mobile phones.

        $Li^+ + CoO_2 + e^- \rightleftharpoons Li^+[CoO_2]^-$ E=+0.6V   *(Co will reduce changing oxidation state from 4 to 3*

        $Li^+ + e^- \rightleftharpoons Li$ E=-3.0V

Overall **discharge** $Li + CoO_2 \rightarrow LiCoO_2$ E=3.6V
reaction

Conventional cell
diagram $Li \mid Li^+ \parallel Li^+ , CoO_2 \mid LiCoO_2 \mid Pt$

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 electrolyte is a lithium compound dissolved in an organic solvent

   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)

Fuel cells oxidise a fuel to produce an electric current. They 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. Fuels cells operate continuously as long as the reactants are supplied

H$_2$ from fuel

K$^+$

KOH Electrolyte

OH$^-$

O$_2$ from air

H$_2$O +heat

standard electrode potentials for reactions in hydrogen fuel cell in alkaline conditions

$4e^- + 4H_2O \rightleftharpoons 2H_2 + 4OH^-$ E=-0.83V
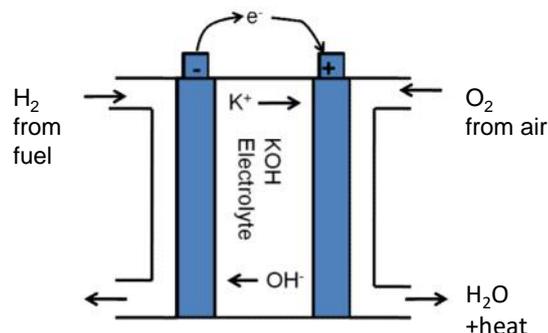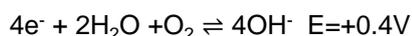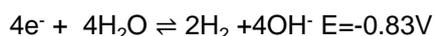
$4e^- + 2H_2O + O_2 \rightleftharpoons 4OH^-$ E=+0.4V

Anode: negative $2H_2 + 4OH^- \rightarrow 4e^- + 4H_2O$

Cathode: positive $4e^- + 2H_2O + O_2 \rightleftharpoons 4OH^-$

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

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

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

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

Overall $2H_2 + O_2 \rightarrow 2H_2O$ E=1.23V
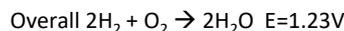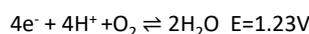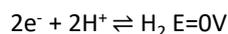
In acidic conditions these are the electrode potentials. The Ecell is the same as alkaline conditions as the overall equation is the same

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.

Equation that occurs at oxygen electrode
$4e^- + 4H^+ + O_2 \rightarrow 2H_2O$ E=1.23V

Equation that occurs at ethanol electrode
$C_2H_5OH + 3H_2O \quad 2CO_2 + 12H^+ + 12e^-$

Overall equation
$C_2H_5OH + 3O_2 \quad 2CO_2 + 3H_2O$

Breathalysers

The earliest breathalysers used the colour change that occurs when dichromate(VI) ions react with ethanol to measure the amount of alcohol. They could measure the extent to which dichromate turns green

Fuel cells measure the current from an ethanol fuel cell. More alcohol means larger current measured. Fuel cell breathalysers are portable

Infrared breath analysers can determine the amounts of alcohol from an infrared spectrum. More alcohol means greater absorbance. The infrared breathalysers do not use the OH absorption to detect the amount of alcohol on the breath because Water in the breath also has an OH bond.

Many countries will use evidence from both fuel cells and infrared breath analysers for evidence for prosecution, because additional evidence is more reliable.