6. Electrochemistry

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*
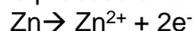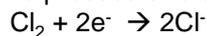
Rules for assigning oxidation numbers

1. All uncombined elements have an oxidation number of zero

eg . Zn, Cl_2, O_2, Ar all have oxidation numbers of zero

2. The oxidation numbers of the elements in a compound add up to zero

In NaCl   Na= +1 Cl= -1
Sum = +1 -1 = 0

3. The oxidation number of a monoatomic ion is equal to the ionic charge

e.g. $Zn^{2+} = +2$ $Cl^- = -1$

4. In a polyatomic ion (CO_3^{2-}) the sum of the individual oxidation numbers of the elements adds up to the charge on the ion

e.g. in CO_3^{2-} C = +4 and O = -2
   sum = +4 + (3 x -2) = -2

5. Several elements have invariable oxidation numbers in their common compounds.

Group 1 metals = +1 Group 2 metals = +2 Al = +3 H = +1 (except in metal hydrides where it is –1 eg NaH) F = -1 Cl, Br, I = –1 except in compounds with oxygen and fluorine O = -2 except in peroxides (H_2O_2) where it is –1 and in compounds with fluorine.

We use these rules to identify the oxidation numbers of elements that have variable oxidation numbers.

What is the oxidation number of Fe in $FeCl_3$

Using rule 5, Cl has an O.N. of –1
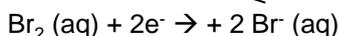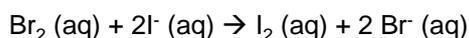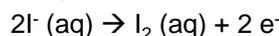Using rule 2, the O.N. of the elements must add up to 0

Fe must have an O.N. of +3
in order to cancel out 3 x –1 = -3 of the Cl's

Note the oxidation number of Cl in $CaCl_2$ = -1 and not -2 because there are two Cl's
Always work out the oxidation for one atom of the element

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
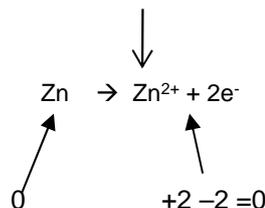
Balancing Redox equations

Writing half equations

1. Work out oxidation numbers for element being oxidised/ reduced $\quad$ *Zn $\rightarrow$ Zn^{2+}* $\quad$ *Zn changes from 0 to +2*
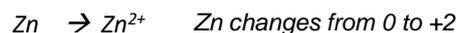
2. Add electrons equal to the change in oxidation number
   For reduction add e's to reactants
   For oxidation add e's to products

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

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

$0 \qquad +2 -2 =0$

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$_2$O.
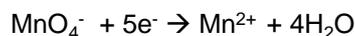
> In acidic conditions use H$^+$ and H$_2$O

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

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

2. Add H$_2$O in products to balance O's in MnO$_4^-$ $\qquad MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$

3. Add H$^+$ in reactants to balance H's in H$_2$O $\qquad \boxed{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}$

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

$-1 + 8 -5 = +2 \qquad\qquad +2$

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

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

2. Add H$_2$O in products to balance O's in SO$_4^{2-}$ $\qquad SO_4^{2-} + 2e^- \rightarrow SO_2 + 2H_2O$

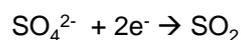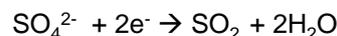3. Add H$^+$ in reactants to balance H's in H$_2$O $\qquad \boxed{SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O}$

4. check to see that the sum of the charges on the reactant side equals the sum of the charges on the product side
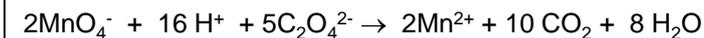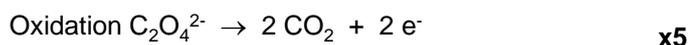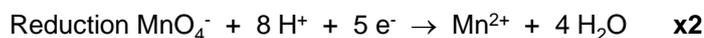
$-4 + 4 = 0 \qquad\qquad 0$

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
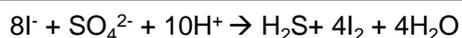
Example 1

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

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

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

Multiply the half equations to get equal electrons

Add half equations together and cancel electrons

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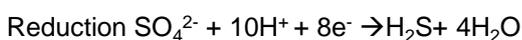
Reduction $SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$

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

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

Multiply the half equations to get equal electrons

Add half equations together and cancel electrons

Electrolysis

$F = Le$ connects the Faraday constant, the Avogadro constant and the charge on the electron

F= Faraday constant (a measure of the charge of 1 mole of electrons = 96320 coulombs

L = Avogadro constant = 6.022×10^{23} e = charge of on electron = 1.60×10^{-19} coulombs.

Electrolysis of molten salts

When a simple ionic compound is electrolysed in the molten state using inert electrodes, the salt splits and the metal ion moves to the negative electrode and the negative ion moves to the positive electrode
e.g. if molten lead bromide is electrolysed, the lead will form at the negative electrode and bro**mine** will form at the positive electrode

At the negative electrode (cathode)
At the negative electrode, positively charged ions **gain electrons** to become metal atoms.
This is classed as reduction. **Reduction** is gaining electrons
Na^+ (l)+ e^- → Na (s) (sodium ions become sodium atoms)
Cu^{2+} (l)+ $2e^-$ → Cu (s)
Al^{3+} (l)+ $3e^-$ → Al (s)

At the positive electrode (anode)
At the positive electrode, negatively charged ions **lose electrons.**
This is classed as **oxidation**. Oxidation is losing electrons
$2Cl^-$ (l) → Cl_2 (g)+ $2e^-$ (chlor**ide** ions becomes chlor**ine**)
$2Br^-$ (l) → Br_2 (l)+ $2e^-$ (brom**ide** ions becomes brom**ine**)
$2I^-$ → I_2 + $2e^-$ (Iod**ide** ions becomes Iod**ine**)
$2O^{2-}$ (l) → O_2 (g)+ $4e^-$ (ox**ide** ions becomes ox**ygen**)

OIL RIG can help remember that **O**xidation **is** **L**oss of electrons: **R**eduction **is** **G**ain of electrons

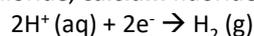### Electrolysing aqueous solutions

If an aqueous solution is electrolysed, using inert electrodes, the ions discharged depend on the electrode potentials of the ions involved.

In aqueous solutions there is a mixture of ions: H^+ and OH^- ions are present in addition to the ions from the salt
e.g. in copper chloride solution there are H^+ ,OH^- (from water) Cu^{2+} ,Cl^- (from the salt)

The negative electrode

At the negative electrode (cathode) in aqueous mixtures the cation with the **more positive electrode potential discharges**.

In **aqueous** solutions where the metal is more negative in the electrochemical series than hydrogen, the metal will not be evolved at the cathode. (e.g. **sodium** chloride, **calcium** fluoride) **Hydrogen gas** will be evolved at the cathode instead.
 $2H^+$ (aq) + $2e^-$ → H_2 (g)

In **aqueous** solutions where the metal has a more positive E° value than hydrogen in the electrochemical series (e.g. **copper** chloride or **silver** fluoride,) the **metal** will be evolved at the cathode.
Cu^{2+} (aq)+ $2e^-$ → Cu (s)
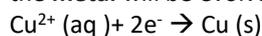
This happens because in the aqueous solution water molecules break down producing hydrogen ions and hydroxide ions that are discharged.

The positive electrode

At the positive electrode (anode), **oxygen** is produced unless the solution contains **halide ions** when the **halogen** is produced.
$4OH^-$ (aq) → O_2 (g)+ $2H_2O$ (l) + $4e^-$ or
$4OH^-$ − 4e- → O_2 + $2H_2O$
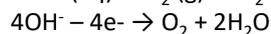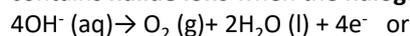
If a halide ion is present then the halogen is produced
e.g. $2Cl^-$ (aq) → Cl_2 (g)+ $2e^-$
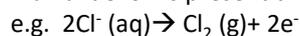
The concentration of the negative ion can change the product evolved. A concentrated solution of sodium chloride, would give mostly chlorine gas. With increasingly dilute solutions, less chlorine and more oxygen will be evolved

Calculations with Electrolysis

Various questions can be asked using the following equations and constants (found in data book)

charge passed (in Coulombs) = current x time (in secs)
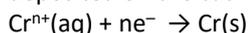
Moles of electrons = charge (in C) / F

Number of electrons passed = charge (in C) / electronic charge e

$F = 9.65 \times 10^4$ C mol^{-1}

electronic charge $e = -1.60 \times 10^{-19}$ C

Example

A chromium salt was electrolysed. The chromium metal is deposited on the cathode, according to the following equation.
$Cr^{n+}(aq) + ne^- \rightarrow Cr(s)$
A current of 1.2 A was passed for 50 minutes through a solution of the chromium salt. 0.647 g of chromium was deposited. Calculate the value of n in the above equation.

charge passed (in Coulombs) = current x time (in secs)

charge passed = 1.2 × 50 x 60 = 3600 C

Moles of electrons = charge (in C) / F

Mole of e^- = 3600/ 96500 = 3.731 × 10^{-2} mol

Moles of Cr = mass/M_r = 0.647/ 52
= 1.244 × 10^{-2} mol

n = moles of electrons/moles of Cr

n = 3.731 × 10^{-2}/ 1.244 × 10^{-2}

= 3.00

Example: Calculating Avogadro's constant

A current of 1.8 A was passed through dilute sulfuric acid for 30 minutes. 195 cm^3 of oxygen was collected at the anode. Conditions were 25 °C and 1 atm.
This is the reaction:
$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$
Calculate a value for the Avogadro constant, L
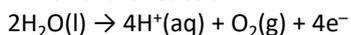
moles of O_2 made = gas volume of O_2 /molar volume

moles of O_2 = 0.195 (dm^3) /24
= 8.125 x 10^{-3} mol

Using balanced equation
moles of electrons made = 4 x 8.125 x 10^{-3}
= 3.25x 10^{-2} mol

charge passed (in Coulombs) = current x time (in secs)

charge passed = 1.8 × 30 x 60 = 3240 C

Number of electrons passed = charge (in C) / electronic charge e
= 3240/ 1.6 x 10^{-19}
= 2.025 x 10^{22}

Avogadro constant, L = number of electrons passed/ moles of electrons
= 2.025 x 10^{22} / 3.25x 10^{-2} = 6.2 x 10^{23} mol^{-1}

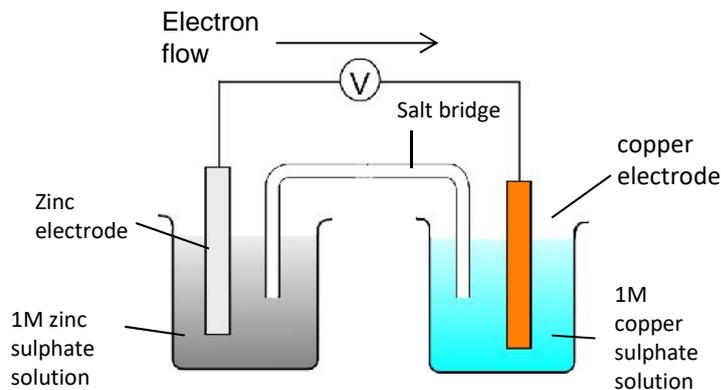## Redox Equilibria

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).

Electron flow →

V

Salt bridge

copper electrode

Zinc electrode

1M copper sulphate solution

1M zinc sulphate solution

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 because 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

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

H$_2$ gas at 100kPa

Pt electrode

1M HCl

Salt bridge KNO$_3$ (aq)

Metal electrode e.g. Fe

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 100kPa**
2. Solution containing the **hydrogen ion at 1 M** (solution is usually 1M HCl)
3. Temperature at **298K**
4. Platinum Electrode
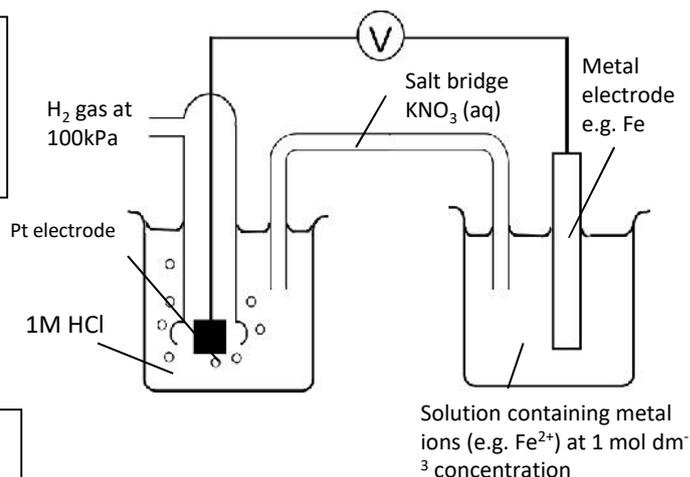
Because the equilibrium does not include a conducting metal surface a platinum wire is used which is coated in finely divided platinum. (The platinum black is used because it is porous and can absorb the hydrogen gas.)

Standard conditions are needed because the position of the redox equilibrium will change with conditions.
For example, in the equilibrium:
$$M^{n+}(aq) + n\ e^- \rightleftharpoons M(s)$$
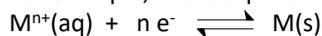
An increase in the concentration of M^{n+} would move the equilibrium to the right, so making the potential more positive.

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 <u>standard electrode potential,</u>
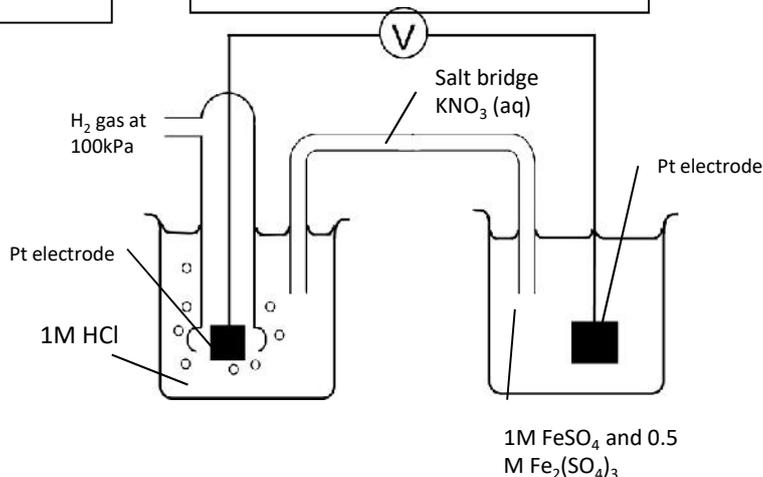
The standard conditions are :
• All ion solutions at 1M
• temperature 298K
• gases at 100kPa pressure
• No current flowing

Standard electrode potentials are found in data books

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

H$_2$ gas at 100kPa

Pt electrode

1M HCl

Salt bridge KNO$_3$ (aq)

Pt electrode
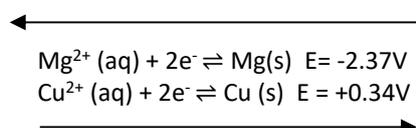
1M FeSO$_4$ and 0.5 M Fe$_2$(SO$_4$)$_3$

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 .

Using Electrode Potentials

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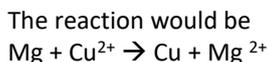
The easiest way to use electrode potentials is as follows:

For any two half equations

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

←

Mg^{2+} (aq) + 2e⁻ $\rightleftharpoons$ Mg(s) E= -2.37V
Cu^{2+} (aq) + 2e⁻ $\rightleftharpoons$ 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⁻ $\rightleftharpoons$ Zn(s) E= - 0.76V
Fe^{2+}(aq) + 2e⁻ $\rightleftharpoons$ Fe(s) E= -0.44V

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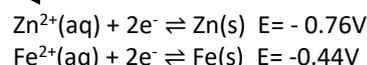
To get the full equation of the reaction add the two half reactions together, cancelling out the electrons.
Zn + Fe^{2+} → Fe + Zn^{2+}

Using series of standard electrode potentials

oxidation

←

Most strong reducing agents found here

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

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

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

$Ag^+ + e^-$ $\rightleftharpoons$ Ag   +0.8V
$F_2 + 2e^-$ $\rightleftharpoons$ $2F^-$ +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.

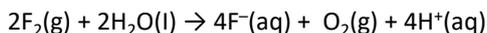First apply idea that more positive E^o will reduce (go forward) and more negative E^o will oxidise (go backwards)

$$\xleftarrow{\text{oxidise}}$$
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) \quad E^o +1.23V$
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq) \qquad\qquad E^o +2.87V$
$$\xrightarrow{\text{reduce}}$$
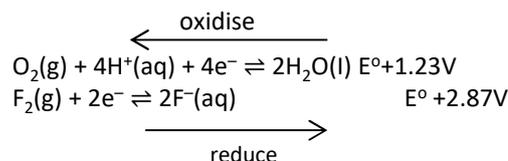
Explanation to write

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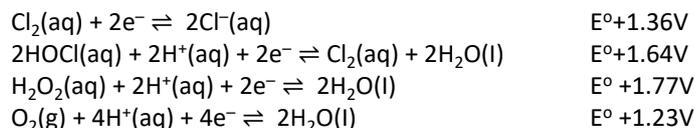
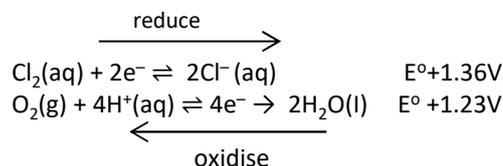$2F_2(g) + 2H_2O(l) \rightarrow 4F^-(aq) + O_2(g) + 4H^+(aq)$

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.

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

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).

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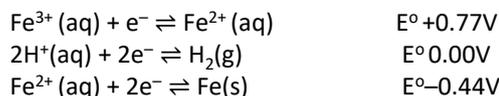$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $\qquad$ $E^o +1.36V$
$O_2(g) + 4H^+(aq) \rightleftharpoons 4e^- \rightarrow 2H_2O(l)$ $\quad$ $E^o +1.23V$
$$\xleftarrow{\text{oxidise}}$$

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

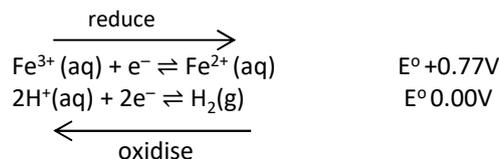$2Cl_2(g) + 2H_2O(l) \rightarrow 4Cl^-(aq) + O_2(g) + 4H^+(aq)$

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.

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

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)

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

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

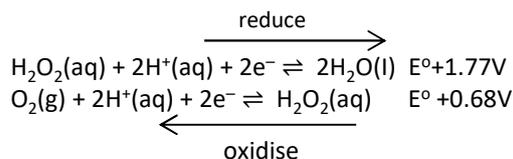**Equation**

$2Fe^{3+}(aq) + H_2(g) \rightarrow 2Fe^{2+}(aq) + 2H^+(aq)$
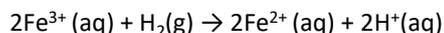
Example 4

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

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

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

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$
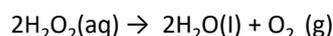
Effect of conditions on Cell voltage Ecell

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 Ecell will fall to zero as the reaction proceeds and the reactant concentrations drop.

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

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ 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.
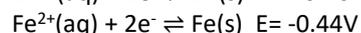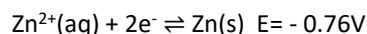
Effect of concentration on Ecell

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

Effect of temperature on Ecell

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

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 does not 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.

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

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.

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

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.

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

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

   =0.86 V

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

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

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

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

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

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.

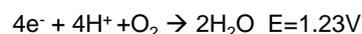Water would not be good as a solvent as it would react with the lithium metal.
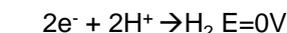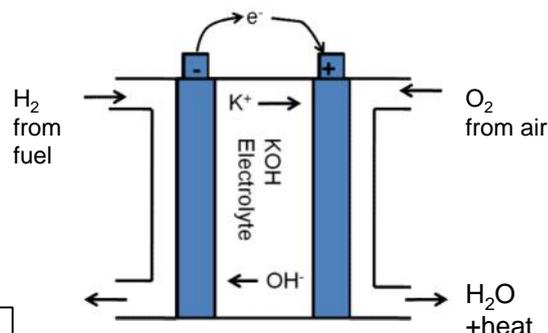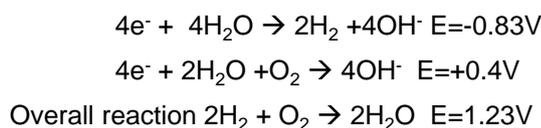
Fuel cell

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

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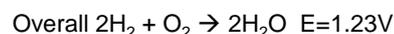
In acidic conditions these are the electrode potentials. The Ecell is the same as alkaline conditions as the overall equation is the same

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) 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