Redox Reactions

Reducing and oxidizing agents
In any redox reaction there will be an oxidizing agent and a reducing agent.
- The **oxidizing agent** contains the species being reduced and therefore decreasing in oxidation number (it is the <u>whole</u> molecule/ion containing that species)
- The oxidizing agent takes electrons from the species being oxidized

- The **reducing agent** contains the species being oxidized and therefore increasing in oxidation number (it is the <u>whole</u> molecule/ion containing that species)
- The reducing agent donates electrons to the species being reduced

Constructing equations for redox reactions
<u>Method 1: combining half-equations (which show numbers of electrons transferred)</u>

Example:
Acidified manganate(VII) ions are a powerful oxidizing agent. They can oxidize Fe^{2+} ions to Fe^{3+} ions. At the same time the manganate(VII) ions are reduced to Mn^{2+} ions.

We can represent what happens to the iron ions with a half-equation. The number of electrons to include comes from the change in oxidation number of the species being oxidized or reduced:

Oxidation is loss of electrons: $Fe^{2+}_{(aq)}$ $\rightarrow$ $Fe^{3+}_{(aq)} + e^-$
oxidation number of Fe: +2   +3
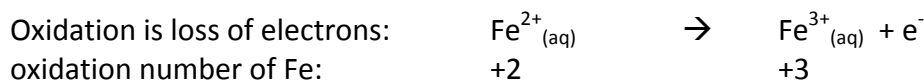
We can construct a half equation for the reduction of acidified manganate(VII) ions
Reduction is gain of electrons: $MnO_4^-{}_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)}$
oxidation number of Mn   +7   +2

This is not balanced, however. The charges are different on each side, and we need to deal with the four oxygens in the MnO_4^- ion. The clue here is the reagent is *acidified* managanate(VII). If we include H+ ions on the left hand side, we can produce water with the oxygens as a product. Four oxygens will require eight H^+ ions:
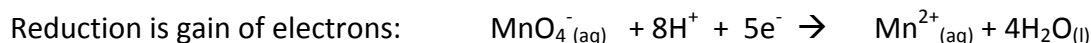
Reduction is gain of electrons: $MnO_4^-{}_{(aq)} + 8H^+ + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$
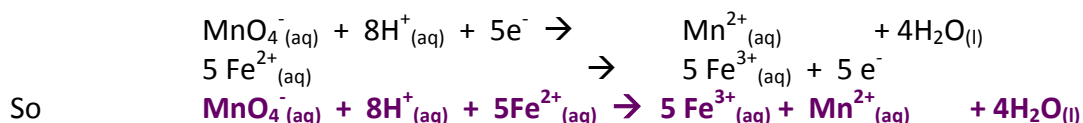This is balanced for both charges and atoms present.

To combine the two half equations into an overall equation, we now need to have the same number of electrons lost in the oxidation as are gained in the reduction, so we need to multiply the first half-equation by 5 throughout:

$5 Fe^{2+}_{(aq)}$ $\rightarrow$ $5 Fe^{3+}_{(aq)} + 5 e^-$
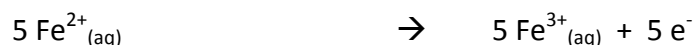
Then we can simply add the half equations together, and cancel the five electrons on each side:

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \rightarrow \quad Mn^{2+}{}_{(aq)} \quad + 4H_2O_{(l)}$$
$$5\,Fe^{2+}{}_{(aq)} \quad\quad\quad\quad \rightarrow \quad 5\,Fe^{3+}{}_{(aq)} + 5\,e^-$$

So $\quad\quad\quad \mathbf{MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5Fe^{2+}{}_{(aq)} \rightarrow 5\,Fe^{3+}{}_{(aq)} + Mn^{2+}{}_{(aq)} \quad + 4H_2O_{(l)}}$
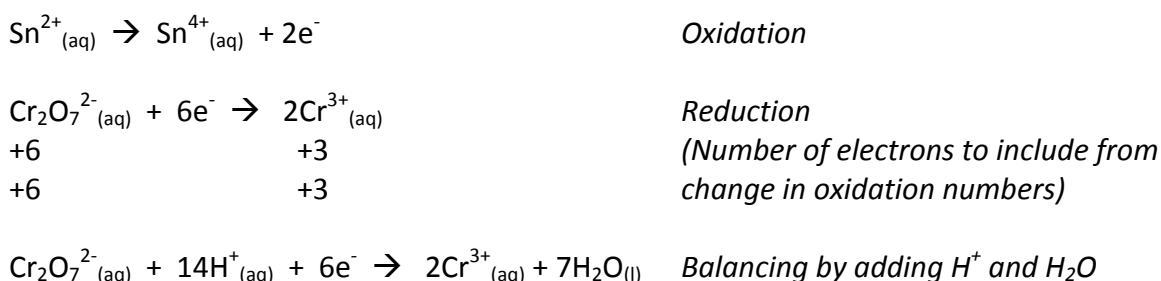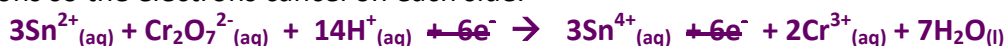
Example:
We are also familiar with acidified potassium dichromate as a powerful oxidizing agent. The dichromate ions act in a similar way to the manganate(VII) ions. For example, they can oxidize Sn^{2+} ions to Sn^{4+} ions.

You should recall that dichromate ions are an intense orange colour, and that when they act as an oxidizing agent, their colour changes to dark green. This is because they have been reduced to Cr^{3+} ions.

Again we can represent what happens with half-equations

$$Sn^{2+}{}_{(aq)} \rightarrow Sn^{4+}{}_{(aq)} + 2e^- \quad\quad\quad\quad\quad\quad\quad\quad\quad \textit{Oxidation}$$

$$Cr_2O_7^{2-}{}_{(aq)} + 6e^- \rightarrow 2Cr^{3+}{}_{(aq)} \quad\quad\quad\quad\quad \textit{Reduction}$$
$$+6 \quad\quad\quad\quad\quad\quad +3 \quad\quad\quad\quad\quad\quad\quad\quad \textit{(Number of electrons to include from}$$
$$+6 \quad\quad\quad\quad\quad\quad +3 \quad\quad\quad\quad\quad\quad\quad\quad \textit{change in oxidation numbers)}$$

$$Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6e^- \rightarrow 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)} \quad \textit{Balancing by adding }H^+\textit{ and }H_2O$$

And again we can combine these into a single redox equation by getting the same number of electrons in each half equation – i.e. multiplying the oxidation equation by 3 throughout, and adding the two half equations so the electrons cancel on each side.

$$\mathbf{3Sn^{2+}{}_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + \cancel{6e^-} \rightarrow 3Sn^{4+}{}_{(aq)} + \cancel{6e^-} + 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}}$$

N.B. we can also be asked to work out the oxidation or reduction half equation if we are given the overall equation and the other half-equation:

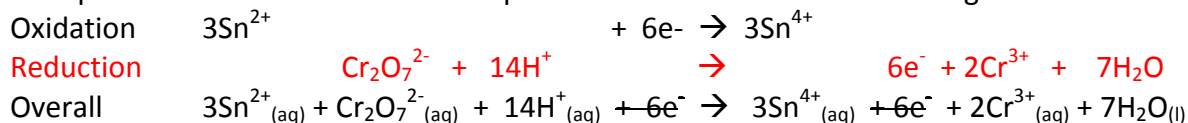Using the same example as above, we might be told that the overall equation is:
$$3Sn^{2+}{}_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} \rightarrow 3Sn^{4+}{}_{(aq)} + 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}$$
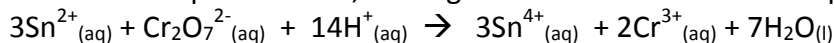
and that the oxidation going on is $Sn^{2+} \rightarrow Sn^{4+}$. We are required to work out the reduction half-equation:

Firstly multiply the given half-equation up to get the same stochiometry as in the overall equation:
$$3Sn^{2+} + 6e^- \rightarrow 3Sn^{4+}$$
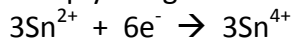
Now position this above the overall equation and work out what is missing on each side:

Oxidation $3Sn^{2+}$ $+\,6e^- \rightarrow 3Sn^{4+}$

Reduction $Cr_2O_7^{2-} + 14H^+$ $\rightarrow$ $6e^- + 2Cr^{3+} + 7H_2O$

Overall $3Sn^{2+}{}_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + \cancel{6e^-} \rightarrow 3Sn^{4+}{}_{(aq)} + \cancel{6e^-} + 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}$

Method 2: Constructing redox equations using oxidation numbers
We can balance a redox equation using oxidation numbers, <u>without</u> having to construct separate half-equations if we choose.

This works because the **total increase in oxidation numbers** in the balanced equation must be **equal to the total decrease in oxidation numbers** – a consequence of OIL RIG !

Example:
Hydrogen iodide (HI) is oxidized to iodine by concentrated sulphuric acid. The sulphuric acid is reduced to hydrogen sulphide. Construct a balanced equation for this.
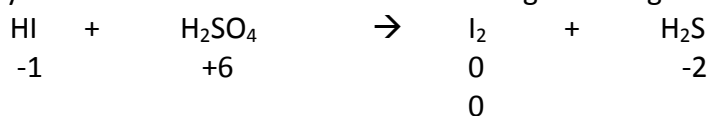
Step 1: Write an equation using the formulae for reactants and products you know about
    $HI + H_2SO_4 \rightarrow I_2 + H_2S$ - don't worry about balancing or missing atoms yet !

Step 2: Use the oxidation numbers to see what is oxidized and what is reduced

HI	+	H_2SO_4	$\rightarrow$	I_2	+	H_2S
+1 -1		+1 +6 -2-2		0		+1 -2
		+1 -2-2		0		+1
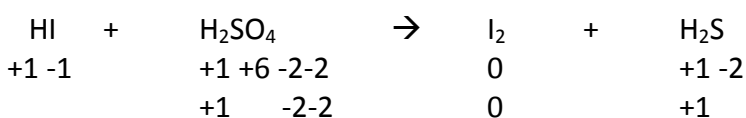
Keep only the oxidation numbers that have changed during the reaction:

HI	+	H_2SO_4	$\rightarrow$	I_2	+	H_2S
-1		+6		0		-2
				0		

Step 3: Balance the equation FOR ONLY THOSE ATOMS BEING OXIDISED OR REDUCED. Don't worry about anything else in the equation being balanced yet.

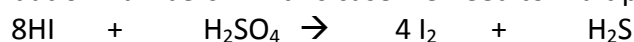| $2HI$	+	H_2SO_4 $\rightarrow$	I_2	+	H_2S
-1		+6	0		-2
-1			0		
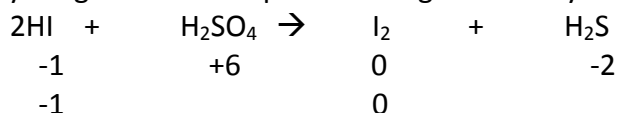
Step 4: Calculate the total increase and decrease in oxidation numbers:
    Reduction (S) is +6 to -2 = -8
    Oxidation (I) is -1,-1 to 0 = +2

Step 5: Multiply up the species in the oxidation and/or reduction to get the same increase and decrease in oxidation numbers – in this case we need to multiply the $2HI \rightarrow I_2$ by 4
        $8HI$ + H_2SO_4 $\rightarrow$ $4 I_2$ + H_2S

Step 6: Complete the balancing. If we are missing oxygen atoms, add water to that side. If we are missing hydrogen atoms, add H^+ to that side (look for 'acidic conditions' in the question as another clue as to when to include H^+ as a reactant). Under alkaline conditions we might add OH^-.

        $8HI$ + H_2SO_4 $\rightarrow$ $4 I_2$ + H_2S + $4 H_2O$

Finally: Check it is balanced for all elements
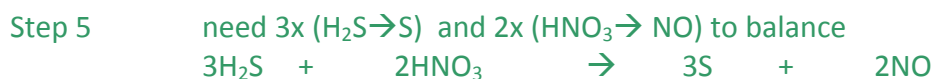   Check it is balanced for charge – total charge on each side the same.

Practice:

Hydrogen sulphide, H_2S is oxidized to sulphur, S, by nitric acid, HNO_3, which is itself reduced to nitrogen monoxide, NO.

Step 1 H_2S + HNO_3 →   S   +   NO

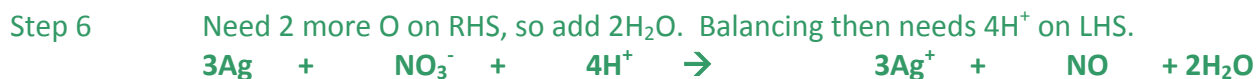Step 2   -2   +5   0   +2

Step 3,4   no further balancing needed   oxidation (S) -2 to 0 = +2
                                             reduction (N) +5 to +2 = -3

Step 5   need 3x (H_2S→S) and 2x (HNO_3→ NO) to balance
                 $3H_2S$ + $2HNO_3$ →   3S   +   2NO

Step 6   missing 4 x O on RHS so add 4x H_2O (then no need to add H^+)
                 $3H_2S$ + $2HNO_3$ →   3S   +   2NO   + $4H_2O$

In acidic conditions, silver metal, Ag, is oxidized to silver(I) ions, Ag^+ by NO_3^- ions, which are reduced to nitrogen monoxide (NO).

Step 1   Ag   + NO_3^- + H^+ → Ag^+ +   NO

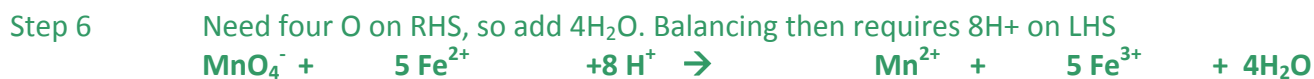Step 2   0   +5   +1   +2

Step 3,4   no further balancing needed   oxidation (Ag) 0 to +1 = +1
                                             reduction (N) +5 to +2 = -3

Step 5   Need x3 (Ag^+ → Ag)
                 3Ag   + NO_3^- + H^+ →   3 Ag^+ +   NO

Step 6   Need 2 more O on RHS, so add $2H_2O$. Balancing then needs $4H^+$ on LHS.
                 3Ag   + NO_3^- + $4H^+$ → $3Ag^+$ +   NO   + $2H_2O$

Now prove to yourself that the half-equation method used for manganate(VII) ions and iron(II) can be done this way as well, with the same result. Acidified managanate(VII) ions are capable of oxidizing iron(II) ions to iron(III) ions. The manganite(VII) is reduced to Mn^{2+} ions:

Step 1 MnO_4^- + Fe^{2+} $+H^+$ → Mn^{2+} + Fe^{3+}

Step 2   +7   +2   +2   +3

Step 3,4   no further balancing   oxidation +2 to +3 = +1   reduction +7 to +2 = -5

Step 5   Need 5x (Fe^{2+} → Fe^{3+})
                 MnO_4^- +   5 Fe^{2+} $+H^+$ → Mn^{2+} +   5 Fe^{3+}

Step 6   Need four O on RHS, so add $4H_2O$. Balancing then requires 8H+ on LHS
                 MnO_4^- +   5 Fe^{2+} $+8 H^+$ → Mn^{2+} +   5 Fe^{3+} + $4H_2O$

Redox titrations

In a redox titration we are titrating one solution in which something is going to be oxidized, against another in which something is going to be reduced. We don't use a pH indicator in a redox titration. The changes in colour of the substances when they are oxidized and reduced tell us when we have reached the endpoint. If we know the concentration of one substance, we can work out the concentration of the other from a balanced equation for the redox reaction.

There are two examples we should understand fully, although we may meet other examples of redox titrations where information about the titration is provided in the question.

Titration of iron(II) ions using manganate(VII) ions under acidic conditions

Purpose: To determine the concentration of $Fe^{2+}_{(aq)}$ in a solution.

        e.g.   determining the mass of iron in iron tablets
                   determining the %purity of iron in an alloy containing iron
                   determining the concentration of iron(II) ions in contaminated water
                   determining the molar mass and formula of an iron(II) salt

How to do it:

If the sample to be investigated isn't already a solution of iron(II) ions, the sample may need to be crushed and dissolved in water and sulphuric acid. We'll need to measure the mass of the sample before dissolving. The resulting solution will be pale green, almost colourless if the concentration of iron(II) is fairly low.

We titrate a known volume of the sample solution in a conical flask against potassium managate(VII) solution of known concentration in the burette. As the deep purple manganate(VII) ions react with the iron(II) ions they are decolourised. This continues until all the iron(II) ions have reacted. The next drop of potassium manganate(VII) stays purple, so the endpoint is when the first hint of pink/purple persists in the solution.

N.B. if the iron(II) solution is in the burette, the endpoint will be when the purple colour of the manganate(VII) in the flask disappears.

The chemistry:

The managanate(VII) ions are reduced to managese(II), while the iron(II) is oxidized to iron(III) ions. We have already constructed an equation for this:

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \rightarrow \qquad Mn^{2+}{}_{(aq)} \qquad + 4H_2O_{(l)}$$
$$5\,Fe^{2+}{}_{(aq)} \qquad\qquad\qquad \rightarrow \qquad 5\,Fe^{3+}{}_{(aq)} + 5\,e^-$$
$$\mathbf{MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5Fe^{2+}{}_{(aq)} \rightarrow 5\,Fe^{3+}{}_{(aq)} + Mn^{2+}{}_{(aq)} \qquad + 4H_2O_{(l)}}$$
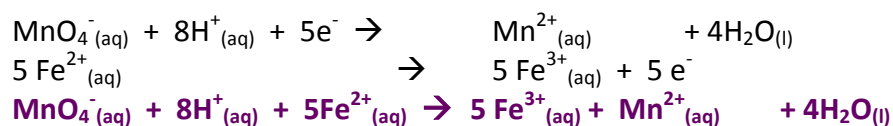
Mole ratio: 1   :   5

One mole of MnO_4^- ions reacts with five moles of Fe^{2+} so we have the mole ratio of 1:5 when we do the titration calculation.

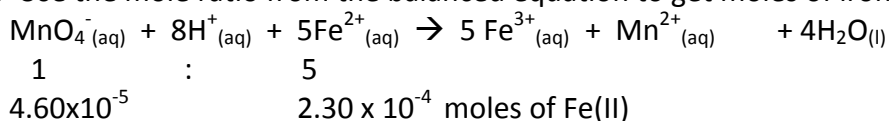The calculations:

i) 25.0cm^3 of a solution of iron(II)sulphate required 23.0cm^3 of 0.0020 mol dm^{-3} potassium manganate(VII) to completely oxidize it in acidic solution. What was the concentration of the iron(II)sulphate solution ?

Step 1: Calculate moles of the permanganate
        moles = conc. x vol   = 0.00200 x (23/1000) = 4.60 x 10^{-5} moles

Step 2: Use the mole ratio from the balanced equation to get moles of iron(II) ions
        $MnO_4^-{}_{(aq)}$ + $8H^+{}_{(aq)}$ + $5Fe^{2+}{}_{(aq)}$ → 5 $Fe^{3+}{}_{(aq)}$ + $Mn^{2+}{}_{(aq)}$ + $4H_2O_{(l)}$
         1   :   5
        4.60x10^{-5} 2.30 x 10^{-4} moles of Fe(II)

Step 3: Find concentration of iron(II) solution
        Conc of Fe^{2+} = moles / vol (in dm^3)   = 2.3x10^{-4} / 0.0025 = 0.00920 mol dm^{-3}

ii) The solution was made by dissolving a tablet containing hydrated iron(II) sulphate and sucrose (which does not react with permanganate ions) in 250cm^3 of water. Calculate the mass of $FeSO_4$ in the tablet.

Moles of $FeSO_4$ = conc x vol in dm^3 = 0.00920 x 0.25 = 0.0023 mol   *(or 10 x the moles in 25cm^3)*

Mass of $FeSO_4$= 0.0023 x M_r = 0.0023 x (55.8 + 32.1 + (16.0 x 4)) = 0.0023 x 151.9
                                        = 0.350g

iii) The formula for the hydrated iron sulphate used in the tablet is $FeSO_4.7H_2O$. If the mass of the tablet was 8.5g, calculate the % by mass of hydrated iron(II) sulphate in the tablet.

M_r of $FeSO_4.7H_2O$ = 151.9 + (7 x 18) = 277.9
Mass in tablet = moles x M_r = 0.023 x 277.9   = 0.6392g

% by mass = (0.6392 / 8.5) x 100   = 7.5 %

Practical: Nuffield expt 19.1c p.458
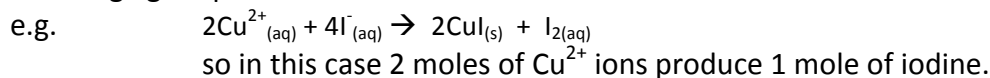
Titration of iodine in solution using thiosuphate ions
<u>Purpose:</u> To determine the concentration of an oxidizing agent in a solution e.g. $Cu^{2+}{}_{(aq)}$ ions.
        e.g.   determining the % of copper in an alloys such as brass or bronze
                determining concentration of copper ions in a solution
                determining concentration of dichromate ions in a solution
                determining the concentration of chlorate(I) ions ClO^- in bleach
                determining the concentration of hydrogen peroxide solution

<u>How to do it:</u>
The analysis is done in two stages.

In the first stage, the oxidizing agent to be determined is reacted with excess iodide ions. This results in iodine being formed in the solution, the amount of iodine being directly related to the amount of the oxidizing agent present.

e.g. $2Cu^{2+}_{(aq)} + 4I^-_{(aq)} \rightarrow 2CuI_{(s)} + I_{2(aq)}$
                        so in this case 2 moles of Cu^{2+} ions produce 1 mole of iodine.

In the second stage, the concentration of iodine in the solution is determined by titrating it against sodium thiosulphate of known concentration. The red-brown colour of the iodine in solution fades to a pale straw colour, and to colourless when all the iodine has been reduced to iodide ions. This makes the endpoint difficult to see, so close to the endpoint an amount of starch is added as an indicator. Starch is blue-black when iodine is present, but at the endpoint the starch becomes colourless.

The chemistry:
                    $I_{2(aq)} + 2e^- \rightarrow 2I^-_{(aq)}$ reduction

At the same time the thiosulphate ions are oxidized to tetrathionate ions:
                    $2 S_2O_3^{2-}_{(aq)} \rightarrow S_4O_6^{2-}_{(aq)} + 2e^-$ oxidation
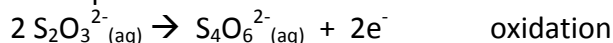
The overall equation is therefore:
                    $I_{2(aq)} + 2 S_2O_3^{2-}_{(aq)} \rightarrow 2I^-_{(aq)} + S_4O_6^{2-}_{(aq)}$
Mole Ratio: 1   :   2
This means that 2 moles of thiosulphate ions react with 1 mole of iodine.

The calculation
The calculation is also done in two stages. In the first stage, the titre for the thioulphate and its concentration are used along with the mole ratio above to work out the moles of iodine in the portion of solution that was titrated. This is then scaled up to get moles of iodine in the whole solution.

In the second stage, the moles of iodine in the whole solution are used along with the mole ratio of iodine to oxidizing agent to work out the concentration of oxidizing agent in the whole solution. This can then be used further if needed to work out the mass of the oxidizing agent given a formula etc.

e.g. 30.00cm^3 of bleach was reacted completely with iodide ions in acidic solution. The iodine formed was titrated against 0.2000 mol dm^{-3} sodium thiosulphate, requiring 29.45cm^3 of the thiosulphate solution to reach the endpoint.

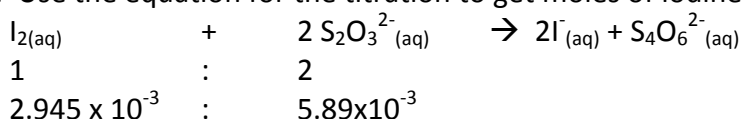The chlorate(I) ions in the bleach react with iodide ions according to the equation:
        $ClO^-_{(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \rightarrow Cl^-_{(aq)} + I_{2(aq)} + H_2O_{(l)}$
Calculate the concentration of the chlorate ions in the bleach.
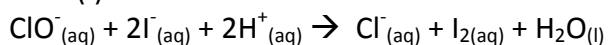
Step 1: Calculate moles of the thiosulphate ions in titration
   moles = conc x vol (in dm^3)   = 0.2000 x (29.45/1000)   = 5.890 x 10^{-3} moles

Step 2: Use the equation for the titration to get moles of iodine in the titre

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

1　　　　　　　　:　　　　2

2.945×10^{-3}　:　　　5.89×10^{-3}

The whole bleach solution was titrated, so moles of I_2 released by the ClO^- ions in the bleach = 2.945×10^{-3} mol.

Using the moles of iodine to find moles of chlorate ions:

$ClO^-{}_{(aq)} + 2I^-{}_{(aq)} + 2H^+{}_{(aq)} \rightarrow Cl^-{}_{(aq)} + I_{2(aq)} + H_2O_{(l)}$

　1　　　　　　　　　　　　:　　　　　1
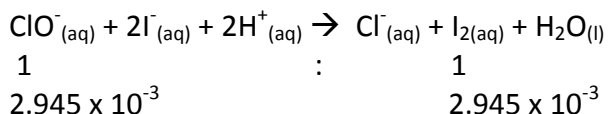
2.945×10^{-3}　　　　　　　　　2.945×10^{-3}

Therefore the 30cm^3 of bleach contained 2.945×10^{-3} moles of chlorate(I) ions.

Step 3: Calculate the concentration of the chlorate(I) ions in the bleach

conc of chlorate(I) = moles / vol in dm^3　 = 2.945×10^{-3} / 0.030 = 0.0982 mol dm^{-3}

Practical: Nuffield expt. 6.8c (potassium iodate(V) with 10% potassium iodide by mass)

Electrode Potentials

Electron transfers in redox reactions

If we dip a zinc strip into copper II sulphate, we observe a layer of copper deposited on the zinc. We might also observe that the blue colour of the copper sulphate solution fades towards colourless as zinc sulphate is formed in solution.　　　　$CuSO_{4(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + ZnSO_{4(aq)}$

　　　　　　　　　　　　　　　　　　　　　　　　+2　　　　0　　　0　　　+2
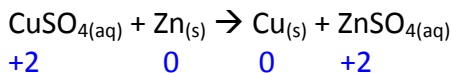
The oxidation of zinc is producing electrons, while the reduction of copper ions is consuming them. If we could separate these two reactions, we could have the electrons flow though an electrical circuit to get from where they were produced to where they are consumed. This is what happens in the cells of a battery.

Cells and half cells

An electrical cell comprises two half-cells, one in which oxidation is taking place to supply electrons, and one in which reduction is taking place to consume them.

Each half cell therefore contains an element which changes oxidation state.
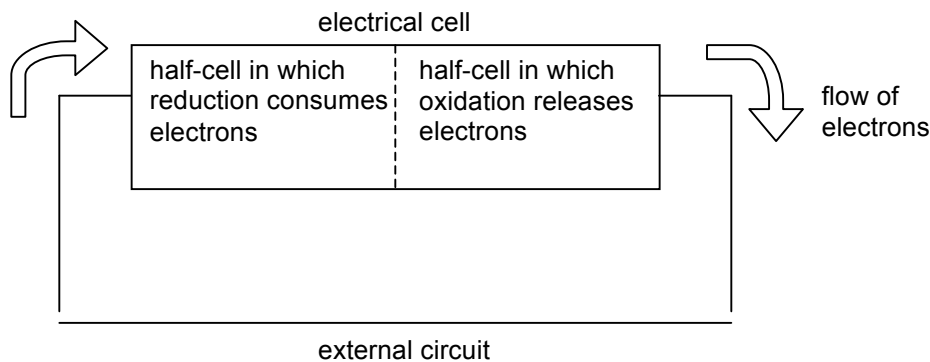
The simplest type of half-cell comprises a metal placed in an aqueous solution of its ions. **An equilibrium exists at the surface of the metal between the oxidation state of the metal and the oxidation state in its ion.**

By convention, the equilibrium is always written with the electrons on the left side:
e.g. for copper and copper II ions: $Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$

and for zinc and zinc ions: $Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$

This convention means that the forward reaction is always REDUCTION (gaining electrons) and the reverse reaction is always OXIDATION (losing electrons).

We have written these as reversible reactions because either oxidation or reduction <u>could</u> take place in any half cell, it is only when it is connected to another half cell that one goes in the oxidation direction and one goes in the reduction direction. To decide which way each reaction will go, we need to know the **electrode potential** of each half cell.

Electrode Potential
The tendency of a half cell to gain electrons is measured using a value called standard **electrode potential**. The larger (more positive) the electrode potential, the greater the tendency of that half-cell to gain electrons. It is measured in **Volts**, V.

We compare the electrode potentials of the two half cells:
In the half-cell with the **most positive** electrode potential,
   • the reaction will go in the forward direction
   • reduction will take place
   • electrons will be gained
This will be the positive terminal of the cell.

In the half-cell with the smallest (most negative or least positive) electrode potential
   • the reaction will go in the reverse direction
   • oxidation will take place
   • electrons will be released to flow around the circuit
This will be the negative terminal of the cell.

The electrode potentials for the two half cells we have considered so far are:
     $Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$ + 0.34 V
     $Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ - 0.76 V
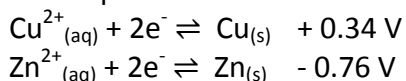
Here we can see that the Cu^{2+}/Cu half-cell has the more positive electrode potential:
     - so this will be the positive terminal of the cell
     - the reaction will be $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$
     - copper ions will be reduced
     - the electrons to do this will flow IN from the external circuit

The Zn^{2+}/Zn half-cell has the least positive electrode potential
   - so this will be the negative terminal of the cell
     - the reaction will be $Zn^{2+}_{(aq)} + 2e^- \leftarrow Zn_{(s)}$
     - zinc will be oxidized to zinc ions
     - electrons are given up to flow OUT into the external circuit

Metal/Metal ion half cells
The experimental setup for the half cells described above would require two half cells in which each metal is in contact with a solution containing ions of the same metal:

It is the <u>difference</u> between the electrode potentials for the two half-cells which drives one half-cell to produce electrons and the other to consume them – we can measure this with a voltmeter. It is referred to as the **potential difference** (same is in physics).

As the reactions proceed, both half-cell ends up with an imbalance between positive and negative ions. The Zn^{2+}/Zn half-cell ends up with extra positive ions, and the Cu^{2+}/Cu half-cell ends up with fewer positive ions. The salt bridge allows ions to move from one half-cell to the other in order to correct this imbalance, otherwise the electrons would stop flowing in the external circuit. The salt bridge could be as simple as a strip of filter paper soaked in an aqueous solution of an ionic compound, however the ionic compound chosen mustn't react with the solutions in either of the half cells. Often aqueous KNO_3 or NH_4NO_3 is used.
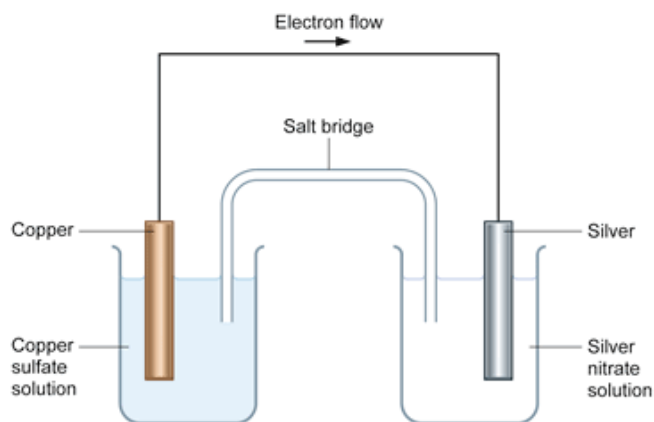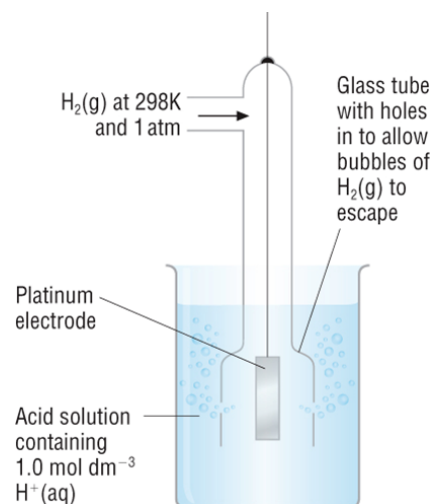
Non-metal/non-metal ion half cells
A half-cell simply has to support an equilibrium where an element is in two different oxidation states. We could therefore have a non-metal element in contact with a solution containing ions of that element.

e.g. a hydrogen half-cell comprises hydrogen gas, H_2, in contact with aqueous hydrogen ions:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$$
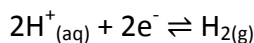
An inert platinum electrode is used to transfer the electrons into or out of the half-cell and make the connection to the rest of the electrical circuit. The platinum does not react at all. The platinum

electrode is immersed in a solution containing the H^+ ions (i.e. an acid), and hydrogen gas is bubbled over the electrode surface.

Non-metal/non-metal ion half-cells are not limited to hydrogen and positively charged ions. We could just as well have e.g. chlorine gas in contact with aqueous chloride ions:
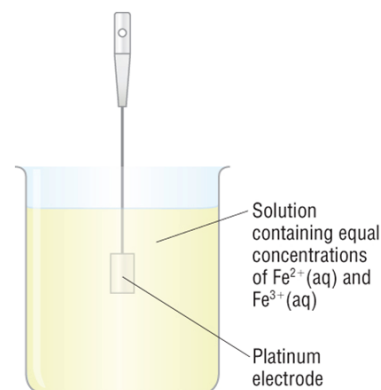
$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-_{(aq)}$
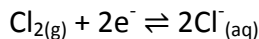
A metal ion/metal ion half cell
This type of half-cell contains an aqueous solution with ions of the same element in two different oxidation states, e.g. Iron(II) and iron(III).

$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$
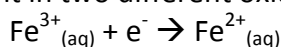
As before, an inert platinum electrode is needed to transfer the electrons into or out of the half-cell.

Standard electrode potentials
We need to measure and compare electrode potentials under controlled and reproducible conditions. We therefore choose to compare the electrode potentials of different half-cells to the electrode potential of a hydrogen half-cell (our reference standard), which we define as having an electrode potential of zero volts when under standard conditions of 298K (25°C) and with a H_2 gas pressure of 101kPa (1 atmosphere) and an H^+ solution concentration of 1 mol dm^{-3}.

Standard electrode potentials of other half-cells also need to be measured with the same standard conditions: **298K, 101kPa** gas pressure, and **1 mol dm^{-3}** solution concentrations, or with **equal concentrations** of each ion in a metal ion/metal ion half cell.

To measure the standard electrode potential of other half-cells, we combine them with a standard hydrogen electrode to form a complete cell, then measure the overall cell potential, (the potential difference across the cell) with a high resistance voltmeter. This gives a direct reading of the standard electrode potential of the half-cell being measured.
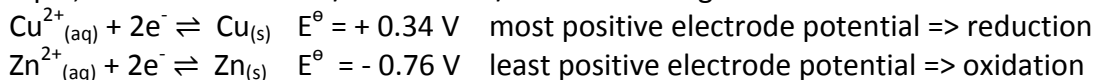
Definition: The standard electrode potential of a half-cell, $E^\ominus$, is the electrode potential of a half-cell compared with a standard hydrogen half cell, measured at 298K with solution concentrations of 1 mol dm^{-3} and a gas pressure of 101kPa.
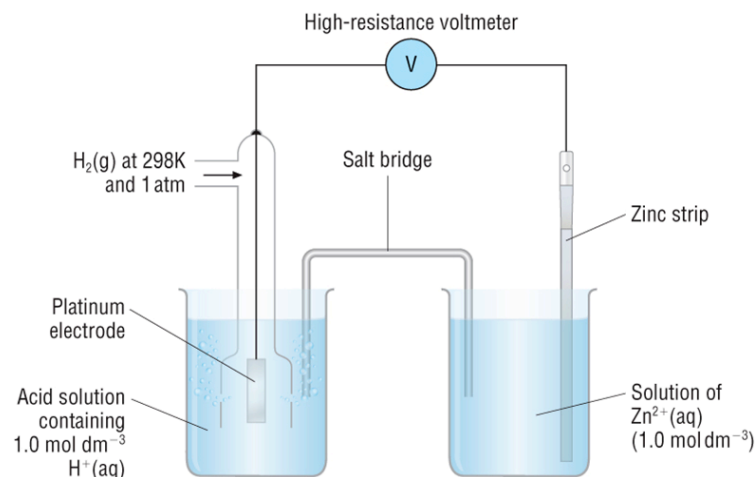
Cell potential
Electrode potentials can be used to predict the <u>cell potential</u> (potential difference) produced by any combination of half-cells.

For example, if we used our Zn^{2+}/Zn and Cu^{2+}/Cu half cells together to make a cell:
$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \quad E^\ominus = +0.34\ V \quad \text{most positive electrode potential => reduction}$$
$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \quad E^\ominus = -0.76\ V \quad \text{least positive electrode potential => oxidation}$$

We can then calculate the standard cell potential, $E^\ominus_{cell}$.
$E^\ominus_{cell}$ = $E^\ominus$ (reduction reaction) - $E^\ominus$ (oxidation reaction)

So $E^\ominus_{cell}$ = 0.34 - (-0.76) = +1.10 V   **SHOW THE + SIGN*!*

N.B. Cell potentials should be positive – if it comes out negative, you've got the wrong half-cells doing oxidation and reduction !

<u>Worked example:</u>
A silver/copper cell is made by connecting together an Ag^+/Ag half cell and a Cu^{2+}/Cu half cell.
The half-cell equilibria and standard electrode potentials are:
$$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)} \quad E^\ominus = +0.80V \qquad \text{reduction reaction}$$
$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \quad E^\ominus = +0.34V \qquad \text{oxidation reaction}$$
$$E^\ominus_{cell} = 0.80 - 0.34 \quad = +0.46V$$
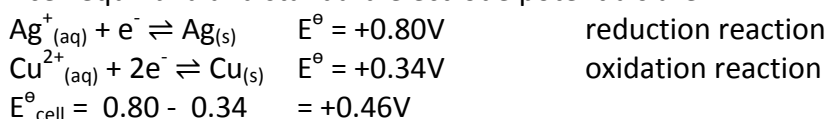
Practice:
For each of the half-cell combinations below, give the value of $E^\ominus_{cell}$

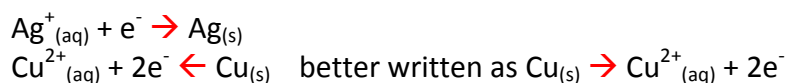|				
Ca^{2+}/Ca	|	$2H^+/H_2$	Given $E^\ominus$ values: Ca^{2+}/Ca	-2.87V
Ans: +2.87V			$2H^+/H_2$	0.00V
Mn^{2+}/Mn	|	$Cl_2/2Cl^-$	Mn^{2+}/Mn	-1.19V
Ans: +2.55V			$Cl_2/2Cl^-$	+1.36V
Cr^{3+}/Cr^{2+}	|	Mn^{2+}/Mn	Cr^{3+}/Cr^{2+}	-0.41V
Ans: +0.78V				

Cell reactions
We may also be asked to derive the <u>overall</u> equation for the redox reaction taking place in the two half-cells. This is just the same as combining a reduction and an oxidation half-equation to get the overall equation for a redox reaction, which we've done before.
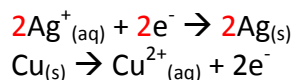
Step 1: Write the two half equations
$$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$$
$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$$
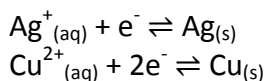
Step 2: Change the $\rightleftharpoons$ to $\rightarrow$ to show which way each is going, based on the electrode potentals

$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$

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

Step 3: Get the same number of electrons in each half-equation

$2Ag^+_{(aq)} + 2e^- \rightarrow 2Ag_{(s)}$

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

Step 4: Add the two equations and cancel the electrons on each side

$Cu_{(s)} + 2Ag^+_{(aq)} + 2e^- \rightarrow Cu^{2+}_{(aq)} + 2e^- + 2Ag_{(s)}$
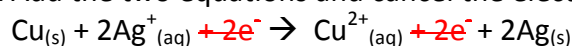
Practice:
For each of the half-cell combinations below, give the overall cell reaction:

Ca^{2+}/Ca | $2H^+/H_2$ Given $E^\ominus$ values: Ca^{2+}/Ca -2.87V
Ans: $Ca_{(s)} + 2H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + H_{2(g)}$ $2H^+/H_2$ 0.00V

Mn^{2+}/Mn | $Cl_2/2Cl^-$ Mn^{2+}/Mn -1.19V
Ans: $Cl_{2(g)} + Mn_{(s)} \rightarrow Mn^{2+}_{(aq)} + 2Cl^-_{(aq)}$ $Cl_2/2Cl^-$ +1.36V

Cr^{3+}/Cr^{2+} | Mn^{2+}/Mn Cr^{3+}/Cr^{2+} -0.41V
Ans: $2Cr^{3+}_{(aq)} + Mn_{(s)} \rightarrow 2Cr^{2+}_{(aq)} + Mn^{2+}_{(aq)}$
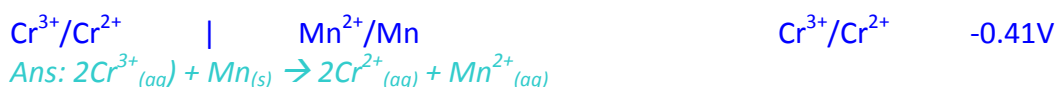
We might also be given the overall equation and one of the half equations, and asked to work out what is going on in the other half-cell:
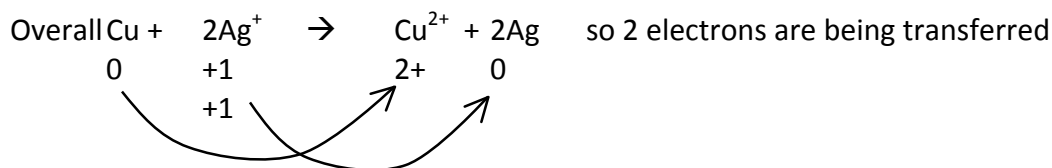
e.g.   In a cell, the following overall reaction occurs:

$Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$
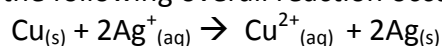
The half-equation for the Ag/Ag+ electrode is $Ag^+ + e^- \rightarrow Ag$
Work out the half-equation for what is taking place in the other half-cell:

Step 1: Calculate the changes in oxidation number taking place in the overall equation, and multiply up the known half equation to the corresponding number of electrons.

Overall Cu + $2Ag^+$ $\rightarrow$ Cu^{2+} + 2Ag   so 2 electrons are being transferred
              0   +1   2+   0
                        +1

$2Ag^+ + 2e^- \rightarrow 2Ag$ multiplying up the known half-equation

Step 2: Subtract the known half-equation from the overall equation to reveal the other half-equation:

$$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$$

minus $\quad 2Ag^+ + 2e^- \rightarrow 2Ag$

= $\quad Cu \quad\quad - 2e^- \rightarrow Cu^{2+}$
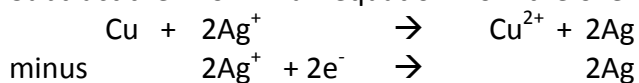
= **$Cu \rightarrow Cu^{2+} + 2e^-$** because by convention we use + not – in chemical equations.
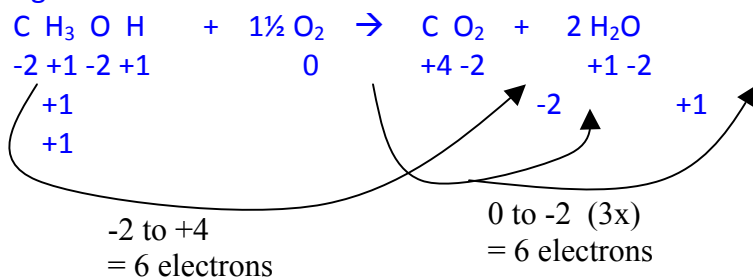
Practice:
The example above was rather trivial, and they can be quite a lot harder to figure out, but the method is as described above e.g.

In a methanol fuel cell, the overall equation is $CH_3OH + 1\frac{1}{2} O_2 \rightarrow CO_2 + 2 H_2O$
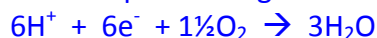At one electrode, the reaction taking place is $4H^+ + 4e^- + O_2 \rightarrow 2H_2O$
Work out what happens at the other electrode:

Oxidation number changes:

$$C\ H_3\ O\ H \quad + \quad 1\frac{1}{2} O_2 \rightarrow \quad C\ O_2 \quad + \quad 2 H_2O$$

$$\begin{array}{ccccc} -2 & +1 & -2 & +1 & \quad 0 \quad\quad +4\ -2 \quad\quad +1\ -2 \end{array}$$

+1   -2   +1

+1

-2 to +4   0 to -2 (3x)
= 6 electrons   = 6 electrons

Now multiply up known half-equation to get 6 electrons transferred:

$$6H^+ + 6e^- + 1\frac{1}{2}O_2 \rightarrow 3H_2O$$

Subtract this half equation from the overall equation (don't worry about – signs yet)

$$CH_3OH \quad\quad + 1\frac{1}{2} O_2 \quad\quad \rightarrow CO_2 \quad\quad + 2 H_2O$$
$$6H^+ + 6e^- \quad + 1\frac{1}{2}O_2 \quad\quad \rightarrow \quad\quad 3H_2O$$

$$CH_3OH - 6H^+ - 6e^- \rightarrow CO_2 - H_2O$$

Finally rearrange to get rid of subtractions (and check if the half-equation will simplify)

$$\underline{CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-}$$

Storage Cells (batteries)
Half-cells are combined to produce two types of commercial electrical storage cell, or battery.

i) non-rechargeable cells e.g. alkaline cells
These provide electrical energy until the oxidation and reduction has been carried out to such an extent that the potential difference can no longer be maintained. The cell is then "flat", and must be disposed of.

Alkaline cell construction:

Details not required

graphite
cathode (+)

zinc anode (-)

MnO_2 and
NaOH paste
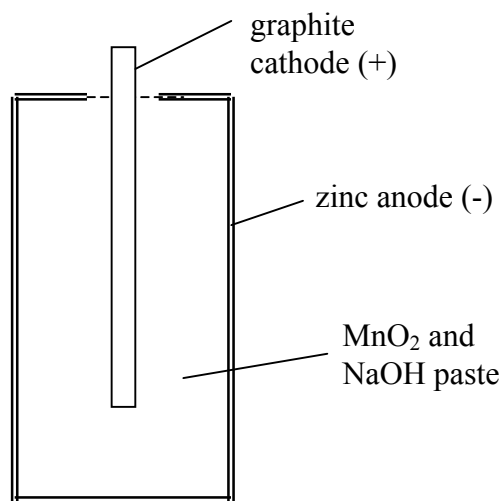
The zinc anode supplied electrons, as the zinc is oxidized by the hydroxide ions:

$$ZnO_{(s)} + H_2O_{(l)} + 2e^- \rightleftharpoons Zn_{(s)} + 2OH^-_{(aq)}$$
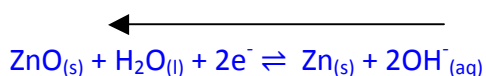
At the graphite cathode, electrons are supplied to the manganese IV oxide which is reduced. Hydroxide ions are produced, replacing those which were consumed at the anode

$$2MnO_{2(s)} + H_2O_{(l)} + 2e^- \rightleftharpoons Mn_2O_{3(s)} + 2OH^-$$
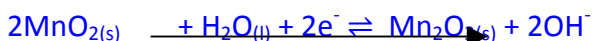
$E^\ominus_{cell}$ is + 1.5V   (typical of AA cells)

ii) Rechargeable cells e.g. NiCd, NiMH, Lithium ion batteries (in laptops), Lithium ion polymer batteries (iPod etc.)
The reduction and oxidation in the two half-cells which supplies the electrical current can be reversed during recharging. This reverses the two redox equilibria, recreating the reactants so that the cell can be used again and again.

Cadmium, along with other substances commonly used in batteries, is toxic. There are environmental problems associated with its disposal, hence its use only in rechargeable and therefore reusable cells.

Lithium is highly reactive, and reacts exothermically, so there is a risk of fire if the contents of a lithium-based battery are exposed by breaking open the battery.

In NiCd batteries the positive and negative electrodes, isolated from each other by the separator, are rolled in a spiral shape inside the case, and surrounded with potassium hydroxide as the electrolyte. This allows a NiCd cell to deliver a much higher maximum current than an equivalent size alkaline cell. The internal resistance for an equivalent sized alkaline cell is higher which limits the maximum current that can be delivered.

The oxidation half-cell reaction at the negative terminal in a NiCd battery during discharge is:
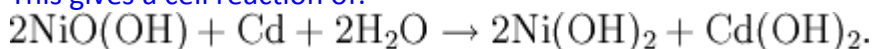$$\text{Cd} + 2\text{OH}^- \rightarrow \text{Cd(OH)}_2 + 2\text{e}^-$$
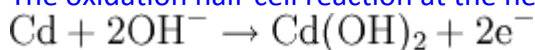
and the reduction half-cell reaction at the positive terminal in a NiCd battery is:
$$2\text{NiO(OH)} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Ni(OH)}_2 + 2\text{OH}^-$$
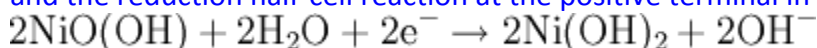
Details not required

This gives a cell reaction of:
$$2\text{NiO(OH)} + \text{Cd} + 2\text{H}_2\text{O} \rightarrow 2\text{Ni(OH)}_2 + \text{Cd(OH)}_2.$$

When the storage cell is recharged, these two reactions go in the opposite direction.

Fuel Cells
A fuel cell releases the energy from the reaction of a fuel with oxygen in electrical form, producing a voltage rather than heat. The most common fuel cells use hydrogen, although other hydrogen-rich fuels such as methanol and natural gas can be used.
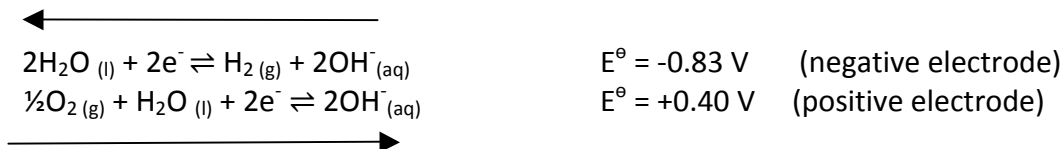
Pure hydrogen fuel emits only water as the product of the reaction, whilst hydrogen-rich fuels produce only small amounts of CO_2 and other gaseous pollutants, so vehicles fitted with fuel cells have the potential to be cause less damage to the environment than those burning petrol or diesel.

How a fuel cell works:
- The reactants (hydrogen and oxygen) flow in and the products (water) flow out, while the electrolyte remains in the cell
- Fuel cells do not have to be recharged and can operate virtually continuously as long as the fuel and oxygen continue to flow into the cell
- The electrodes are made of a catalyst material such as a titanium sponge coated in platinum
- The electrolyte is an acid or alkaline membrane that allows ions to move from one compartment of the cell to the other (like a salt bridge)
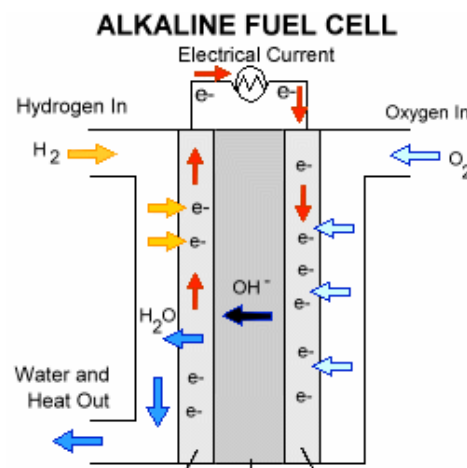
ALKALINE FUEL CELL

The equilibria involved in an alkaline fuel cell are:

$$2\text{H}_2\text{O}_{(l)} + 2\text{e}^- \rightleftharpoons \text{H}_{2\,(g)} + 2\text{OH}^-_{(aq)} \qquad E^\ominus = -0.83\text{ V} \quad \text{(negative electrode)}$$
$$\tfrac{1}{2}\text{O}_{2\,(g)} + \text{H}_2\text{O}_{(l)} + 2\text{e}^- \rightleftharpoons 2\text{OH}^-_{(aq)} \qquad E^\ominus = +0.40\text{ V} \quad \text{(positive electrode)}$$

The equilibria involved in an acidic fuel cell are:

$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2\ (g)}$ $E^\ominus = +0.00$ V   (negative electrode)
$\frac{1}{2}O_{2\ (g)} + 2H^+_{(aq)} + 2e^- \rightleftharpoons H_2O_{(l)}$ $E^\ominus = +1.23$ V   (positive electrode)
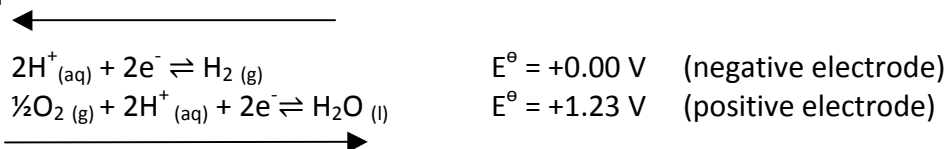
The overall reaction and cell potential in both cases is the same:

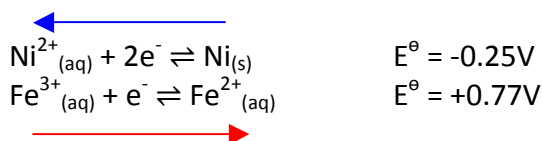$H_{2\ (g)} + \frac{1}{2}O_{2\ (g)} \rightarrow H_2O_{(l)}$ $E^\ominus_{cell} = 1.23$ V
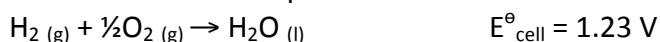
Feasibility of reactions

The benefits of using electrode potentials are not limited to calculating the cell potential of a cell. More generally, we can use electrode potentials to predict whether a redox reaction will take place.

For example, *"Will a solution containing iron(III) ions oxidise nickel to nickel(II) ions, and be reduced to iron(II)?"*

We need to look at the electrode potentials for the oxidation and reductions involved.
▪ We use the same convention of writing each half equation with the electrons on the left
▪ We change the equilibrium signs to arrows to show which way the reaction would have to go in each half cell for the reaction to go as described: in this case we want Ni $\rightarrow$ Ni^{2+} and Fe$^{3+} \rightarrow$ Fe^{2+}

$Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)}$ $E^\ominus = -0.25$V
$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$ $E^\ominus = +0.77$V

• Now check that one arrow is going in each direction. If not, you don't have a redox reaction, you have two species that both want to be oxidized, or both reduced so no reaction will occur.

• Work out the value $E^\ominus_{cell}$ would have if the reaction did happen.
     $E^\ominus_{cell} = E^\ominus_{reduction\ reaction\ (forward\ arrow)} - E^\ominus_{oxidation\ reaction\ (backward\ arrow)}$

• If the calculated $E^\ominus_{cell}$ has a positive value, the reaction is feasible. If the value is negative, the reaction is not feasible. In our example $E^\ominus_{cell} = 0.77 - (-0.25) = +1.02$V

So we can say that iron(III) ions CAN oxidize nickel to nickel(II) ions, but we need to be able to <u>explain</u> what the calculation has shown:

General explanation if the reaction is feasible:
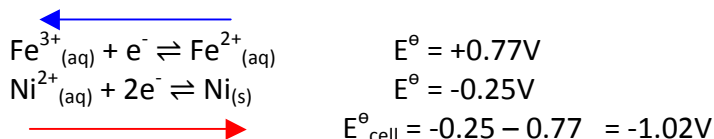*The electrode potential for the <REDUCTION HALF CELL> is **more positive** than the electrode potential for the <OXIDATION HALF CELL> so <SPECIES BEING REDUCED> is a sufficiently powerful oxidizing agent to oxidise <SPECIES BEING OXIDISED> to <SPECIES AFTER OXIDATION>, releasing the electrons needed to reduce the <SPECIES BEING REDUCED> to <SPECIES AFTER REDUCTION>.*

"Why does Fe^{3+} react with Ni ?"
*The electrode potential for the Fe^{3+}/Fe^{2+} half cell is **more positive** than the electrode potential for Ni^{2+}/Ni, so Fe^{3+} is a sufficiently powerful oxidizing agent to oxidise Ni to Ni^{2+}, releasing the electrons needed to reduce the Fe^{3+} to Fe^{2+}.*

Now let's look at the opposite effect. Another possible redox reaction might be "*Will nickel(II) ions oxidize iron(II) ions to iron(III), themselves being reduced to nickel?*"
We approach this the same way: We want $Fe^{2+} \rightarrow Fe^{3+}$ and $Ni^{2+} \rightarrow Ni$

$$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)} \qquad E^\theta = +0.77V$$
$$Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)} \qquad E^\theta = -0.25V$$
$$E^\theta_{cell} = -0.25 - 0.77 = -1.02V$$

Check: Yes we've got one arrow going each way
Since E^θ_{cell} is negative we can say that nickel(II) ions CAN'T oxidize iron(II) to iron(III). Again we need to be able to explain what the calculation has shown:
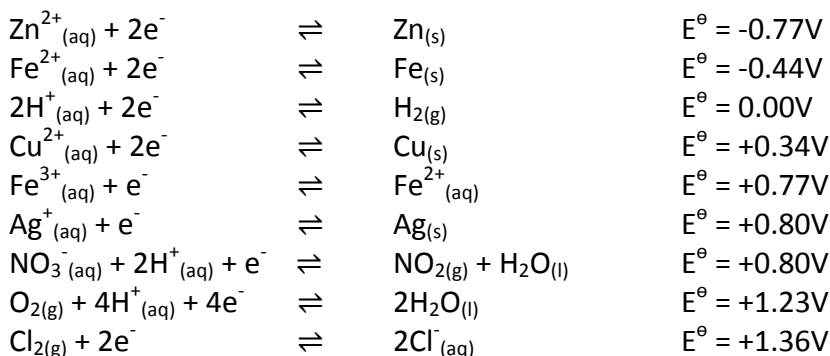
General explanation if reaction not feasible:
*The electrode potential for the <OXIDATION HALF CELL> is **more positive** than the electrode potential for <REDUCTION HALF CELL>, so the <SPECIES BEFORE REDUCTION> is not a powerful enough oxidizing agent to oxidise <SPECIES BEFORE OXI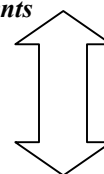DATION> to <SPECIES AFTER OXIDATION> and the necessary electrons will not be available to reduce <SPECIES BEFORE REDUCTION> to <SPECIES AFTER REDUCTION>.*

"Why do nickel(II) ions not oxidise iron(II) to iron(III)?"
The electrode potential for the Fe^{3+}/Fe^{2+}, half cell is more positive than the electrode potential for Ni^{2+}/Ni, so the Ni^{2+} is not a powerful enough oxidizing agent to oxidize Fe^{2+} to Fe^{3+} and the necessary electrons will not be available to reduce Ni^{2+} to Ni.

So long as we know the standard electrode potentials, we can deal with quite complicated redox systems.

$Zn^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Zn_{(s)}$	$E^\theta = -0.77V$	*most likely to lose electrons and be oxidised i.e. **reducing agents***
$Fe^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Fe_{(s)}$	$E^\theta = -0.44V$	
$2H^+_{(aq)} + 2e^-$	$\rightleftharpoons$	$H_{2(g)}$	$E^\theta = 0.00V$	
$Cu^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Cu_{(s)}$	$E^\theta = +0.34V$	
$Fe^{3+}_{(aq)} + e^-$	$\rightleftharpoons$	$Fe^{2+}_{(aq)}$	$E^\theta = +0.77V$	
$Ag^+_{(aq)} + e^-$	$\rightleftharpoons$	$Ag_{(s)}$	$E^\theta = +0.80V$	
$NO_3^-_{(aq)} + 2H^+_{(aq)} + e^-$	$\rightleftharpoons$	$NO_{2(g)} + H_2O_{(l)}$	$E^\theta = +0.80V$	*most likely to gain electrons and be reduced i.e. **oxidising agents***
$O_{2(g)} + 4H^+_{(aq)} + 4e^-$	$\rightleftharpoons$	$2H_2O_{(l)}$	$E^\theta = +1.23V$	
$Cl_{2(g)} + 2e^-$	$\rightleftharpoons$	$2Cl^-_{(aq)}$	$E^\theta = +1.36V$	

Example: Does copper react with acids ?

If we consider the usual reaction of a metal with an acid, i.e. metal + acid $\rightarrow$ metal salt + hydrogen then we want $H^+ \rightarrow H_2$ and $Cu \rightarrow Cu^{2+}$
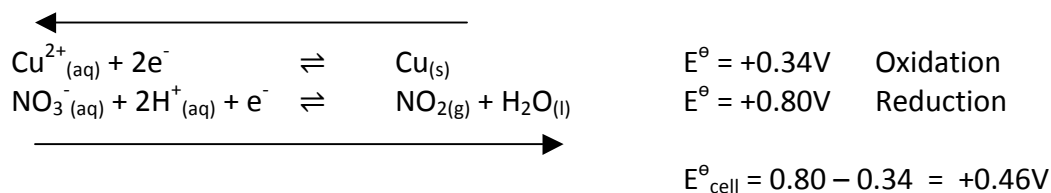
$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^\ominus = 0.00V \qquad \text{Reduction}$$
$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^\ominus = +0.34V \qquad \text{Oxidation}$$

$E^\ominus_{cell}$ for this reaction = $0.00 - 0.34 = -0.34V$ so copper won't react with the H^+ ions.

Explanation:

The electrode potential for the Cu^{2+}/Cu half cell is **more positive** than the electrode potential for $2H^+/H_2$ half cell, so the H^+ ion is not a powerful enough oxidizing agent to oxidise Cu to Cu^{2+} and the necessary electrons will not be available to reduce H^+ to H_2.

So why do we observe that copper does react with nitric acid ?

If the H+ ions aren't the oxidizing agent, it must be something to do with the other ions in the solution: the nitrate ions:

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^\ominus = +0.34V \quad \text{Oxidation}$$
$$NO_3^-{}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons NO_{2(g)} + H_2O_{(l)} \qquad E^\ominus = +0.80V \quad \text{Reduction}$$

$$E^\ominus_{cell} = 0.80 - 0.34 = +0.46V$$

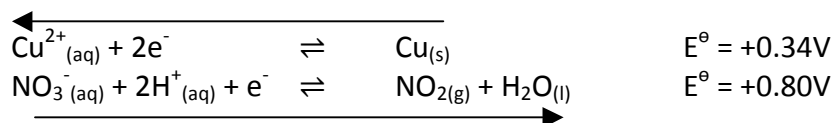So copper will react when H^+ and NO_3^- ions are both present.

Explanation:

The electrode potential for the NO_3^-/NO_2 half cell is **more positive** than the electrode potential for the Cu^{2+}/Cu half cell so NO_3^- in the presence of H^+ is a sufficiently powerful oxidizing agent to oxidise Cu to Cu^{2+}, releasing the electrons needed to reduce the NO_3^- to NO_2.

Comparing Oxidising Agents and Reducing Agents

We might be asked to compare the species in a redox reaction and say which is the better oxidizing agent, or reducing agent.

e.g. Which species is the best oxidizing agent?

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^\ominus = +0.34V$$
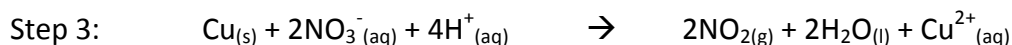$$NO_3^-{}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons NO_{2(g)} + H_2O_{(l)} \qquad E^\ominus = +0.80V$$
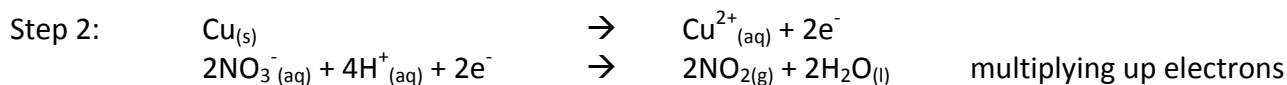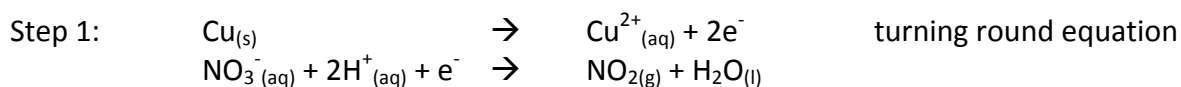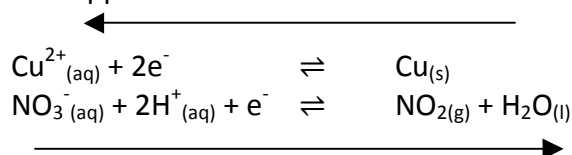
An oxidizing agent causes something else to be oxidized, so it is itself reduced. We look for the half equation that is going in the reduction direction (the one with the most positive electrode potential, so the half cell in which the reaction goes in the forward direction), and the better oxidizing agent will be the reactant(s) for that reaction: in this case, acidified nitrate ions.

If we were asked for the best reducing agent, we look for the substance that is itself oxidized, in this example the Cu, because in this half-equation the electrode potential is least positive, so the reaction is going in the reverse (oxidation) direction.

Overall equations
Once we have determined that a redox reaction will work, and we know in which direction the reaction in each half-cell is going we can multiply up to balance the electrons, and combine the half equations to get an overall equation for the redox reaction EXACTLY as we have done before with half equations.

e.g. when copper reacts with concentrated nitric acid:

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

$NO_3^-{}_{(aq)} + 2H^+{}_{(aq)} + e^- \rightleftharpoons \quad NO_{2(g)} + H_2O_{(l)}$

Step 1: $Cu_{(s)}$ $\rightarrow$ $Cu^{2+}_{(aq)} + 2e^-$ turning round equation

$NO_3^-{}_{(aq)} + 2H^+{}_{(aq)} + e^- \rightarrow \quad NO_{2(g)} + H_2O_{(l)}$

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

$2NO_3^-{}_{(aq)} + 4H^+{}_{(aq)} + 2e^- \rightarrow \quad 2NO_{2(g)} + 2H_2O_{(l)}$ multiplying up electrons

Step 3: $Cu_{(s)} + 2NO_3^-{}_{(aq)} + 4H^+{}_{(aq)}$ $\rightarrow$ $2NO_{2(g)} + 2H_2O_{(l)} + Cu^{2+}_{(aq)}$

Limitations of predictions using standard electrode potentials
1) <u>Non-standard conditions alter the values of the electrode potentials</u>, so if the redox reaction is to happen under any conditions other than 298K, 101kPa and concentrations of 1 mol dm^{-3} (or equal concentrations in a metal ion/metal ion half cell) then the electrode potentials won't be correct.

e.g. $Cu^{2+}_{(aq)} + 2e^- \quad \rightleftharpoons \quad Cu_{(s)} \quad E^\ominus = +0.34V$
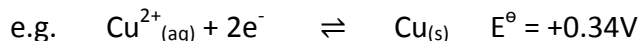
If we increase the concentration of Cu^{2+} ions, Le Chatelier tells us that the position of equilibrium moves in the forward direction to oppose the change and use up the Cu^{2+} ions. The electrode potential measures the tendency of the reaction to go in the forward direction (i.e. to gain electrons by reduction), so the electrode potential increases compared to the standard $E^\ominus$ value.
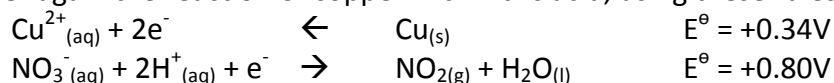
2) Standard electrode potentials apply to aqueous equilibria. Many redox reactions don't happen under these conditions, so the electrode potentials can't reflect those conditions.
e.g. $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$
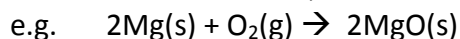
3) Even if the electrode potentials indicate that a redox reaction is feasible, it says nothing about the RATE of the reaction, which may be so unobservably slow due to a very high activation energy.

As a general rule, the larger the difference between the electrode potentials of the two redox equilibria, the more likely it is that a reaction will take place in practice.

Consider again the reaction of copper with nitric acid, using these rules.

$$Cu^{2+}_{(aq)} + 2e^- \quad \leftarrow \quad Cu_{(s)} \qquad E^\ominus = +0.34V$$
$$NO_3^-{}_{(aq)} + 2H^+{}_{(aq)} + e^- \quad \rightarrow \quad NO_{2(g)} + H_2O_{(l)} \qquad E^\ominus = +0.80V$$

Standard conditions means the concentration of nitrate ions must be 1 mol dm^{-3}. So for copper reacting with 1M nitric acid, the difference in electrode potentials is 0.80 – 0.34 = +0.46 V. This is a fairly small difference, so the reaction <u>might</u> take place.

<u>What if we use concentrated acid?</u>
If we increase [H$^+$] then the position of equilibrium for the NO_3^-/NO_2 redox equilibrium shifts to the right to use up the H$^+$. This means the electrode potential of the reduction half-cell gets more positive.

Remembering that $E^\ominus_{cell} = E^\ominus_{reduction} - E^\ominus_{oxidation}$, if $E^\ominus_{reduction}$ increases, then $E^\ominus_{cell}$ increases and the reaction is more likely to be feasible, and we can anticipate it <u>is more likely</u> take place under these conditions (i.e. go faster).

<u>Would the reaction go faster if we added Cu^{2+} ions to the solution?</u>
If we increase [Cu^{2+}] then the position of equilibrium for the Cu^{2+}/Cu redox equilibrium shifts to the right (forward direction) to use up the Cu^{2+}, in accordance with LeChatelier's principle. This means the electrode potential of the oxidation half-cell will have become more positive. Since $E^\ominus_{cell} = E^\ominus_{reduction} - E^\ominus_{oxidation}$, and increase in $E^\ominus_{oxidation}$ will reduce $E^\ominus_{cell}$ and the reaction <u>is less likely</u> to happen.