OXIDATION & REDUCTION

9

CORE

TOK   Are oxidation numbers real?

I remember contemplating on the nature of reality back in Chapters 2 and 4, with regard to electrons and hybridization respectively. The implication always seems to be that reality is in some way desirable. Maybe my bank account might be a useful analogy to oxidation numbers? At the end of every month there is a number assigned to it, but as the month progresses this number gets smaller and the numbers assigned to the local supermarket, the petrol station, the government etc. all go up. Hardly any of it gets turned into bank notes for me to carry around and even then is a bank note any more real than the number printed on my bank statement. Isn't the fact that this piece of paper is worth $20 just another, very convenient, shared fiction? Along as we are all happy to share the belief that the figures on my bank statement and the number on my bank notes mean something then real or not these numbers, like oxidation numbers, are very useful and certainly a lot easier than pushing around wheelbarrows full of gold, or wearing a necklace of sea-shells with holes drilled in them. The whole thing is perhaps closely related to the philosophy of Charles Sanders Peirce, who developed the concept of "pragmatic truth" - that in which it was convenient for society to believe; in other words truth is more an attribute of a society than an attribute of the physical world. Are oxidation numbers useful? Certainly they are capable of giving us a definitive answer as to whether in a chemical change, a particular atom is oxidised, reduced, or neither, but is the change any more than "electron accounting" that helps us balance equations? F going to F^- is just a change of -1 whereas N going to N^{3-} is a change of -3, but the former is far more energetically favourable.

9.1 INTRODUCTION TO OXIDATION & REDUCTION

Oxidation and reduction are most commonly defined in terms of the loss and gain of electrons. **Oxidation** is the loss of electrons, so if an iron(II) ion (Fe^{2+}) is converted to an iron(III) ion (Fe^{3+}), then the iron(II) ion has lost an electron and so has been oxidised.

$$Fe^{2+} \text{ (aq)} \longrightarrow Fe^{3+} \text{ (aq)} + e^-$$
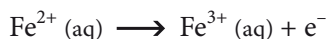
Conversely **reduction** is the gain of electrons, so if hydrogen ions (H^+) are converted to hydrogen gas (H_2) the hydrogen ion has gained electrons and is therefore reduced.

$$2\,H^+ \text{ (aq)} + 2\,e^- \longrightarrow H_2 \text{ (g)}$$
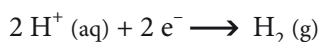
Note that in these equations the charge as well as the numbers of atoms must balance.

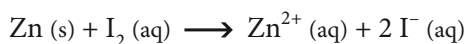A useful mnemonic (memory aid) for this is:

LEO *(the lion)* **goes GER**

Loss of **E**lectrons is **O**xidation;
**G**ain of **E**lectrons is **R**eduction.

Alternatively:

OILRIG
(**O**xidation **I**s **L**oss of electrons, **R**eduction **I**s **G**ain of electrons).

Consider the reaction between zinc and iodine:

$$Zn \text{ (s)} + I_2 \text{ (aq)} \longrightarrow Zn^{2+} \text{ (aq)} + 2\,I^- \text{ (aq)}$$

In this the zinc atom loses two electrons to form the zinc ion and so is oxidised. The iodine molecule gains two electrons to form iodide ions and so is reduced. This is most clearly shown by splitting the overall equation into two 'half equations', i.e.

$$Zn \text{ (s)} \longrightarrow Zn^{2+} \text{ (aq)} + 2\,e^- \quad \&$$
$$I_2 \text{ (aq)} + 2\,e^- \longrightarrow 2\,I^- \text{ (aq)}$$
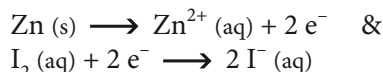
The full equation can be produced by combining the appropriate half equations in such a way that the electrons cancel.

There are occasions when the atoms in the species change and so the definition above is difficult to apply. For example nitrogen is reduced in the conversion of nitrogen gas (N_2) to ammonia (NH_3), even though there is no obvious gain of electrons. Even worse, when nitrogen dioxide (NO_2) is converted to the nitrate ion (NO_3^-) it is oxidised even though it gains a negative charge (remember, the addition of electrons = reduction)! These problems are removed by the use of oxidation numbers.

The **oxidation number**, or oxidation state, of an atom is the charge which that atom would have if all covalent bonds were broken so that the more electronegative element kept all the electrons in the bond, hence the sign (+ or –) is always given. So for example in water the ions produced would be two H^+ and an O^{2-} hence in water the oxidation state of hydrogen is +1 and that of oxygen is –2.

In practice, rather than having to consider the breaking of every covalent bond in a molecule to find the oxidation number, it is easier to calculate this using a number of rules:

1. The total oxidation state of the atoms in a species is equal to the electrical charge it carries. Hence all elements in the elemental state have an oxidation state of zero, the total oxidation number of a neutral molecule is zero and that of ions is equal to the charge

2. Some elements almost always have the same oxidation state in their compounds, with a few exceptions. In order of decreasing numbers of exceptions:

   a) fluorine is –1 (no exceptions)

   b) hydrogen is +1 (except in the hydride ion, H^- where it is –1)

   c) oxygen is –2 (except +1 in hydrogen peroxide, H_2O_2, and related compounds)

d) the halogens (group 7 elements Cl, Br, & I) are –1 (except when bonded to oxygen or a halogen that is higher in the group)
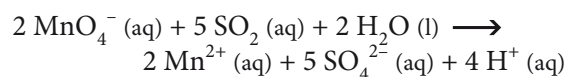
Elements which commonly change their oxidation states are carbon, nitrogen, phosphorus, sulfur and the transition metals. The rules above are best illustrated by examples:

Hydrogen in H_2 is 0	In their elemental state the oxidation state of elements is always zero.
Iron in Fe^{2+} is +2	The total oxidation number is equal to the charge, and in this case there is only one element present.
Carbon in CH_4 is –4	There is no charge on CH_4, so the total must be zero. Hydrogen is +1, so that four hydrogens are +4. The carbon is therefore –4.
Sulfur in H_2SO_4 is +6	H_2SO_4 is a neutral molecule so he total is again zero. The four oxygens are –8 (–2 each) and the two hydrogens are +2 (+1 each) so that sulfur must be +6.
Phosphorus in PCl_4^+ is +5	The total is +1 (equal to the electrical charge). The four chlorines are –4 (–1 each) so phosphorus must be +5.
Iodine in IO_4^- is +7	The total is –1 (charge) and the four oxygens are –8 (–2 each) so that iodine must be +7. (Note that this is one of the exceptions mentioned in rule 2d.)

In terms of oxidation number, oxidation is an increase in oxidation number and reduction is a decrease in oxidation number. If the oxidation number does not change, then that element has not been oxidised or reduced. This covers the definition in terms of electrons, as well as many other cases.

Returning to the dilemmas at the start of the section it can be seen that in going from N_2 to NH_3, the oxidation number of nitrogen has decreased from 0 to –3, so it has been reduced. Similarly in going from NO_2 to NO_3^- the oxidation number has increased from +4 to +5 so it is an oxidation.

Consider the **redox** reaction (one in which **red**uction and **ox**idation occurs) below:

$$2\ MnO_4^-\ (aq) + 5\ SO_2\ (aq) + 2\ H_2O\ (l) \longrightarrow$$
$$2\ Mn^{2+}\ (aq) + 5\ SO_4^{2-}\ (aq) + 4\ H^+\ (aq)$$

In order to determine which elements have been oxidised and which reduced, the appropriate oxidation numbers must be calculated. If none of the elements change their oxidation number then the reaction is not a redox reaction. It is unusual for the oxidation state of hydrogen and oxygen to change (unless the reaction involves the elements or hydrogen peroxide). Application of the rules above to manganese and sulfur shows that:

Manganese is reduced as its oxidation number decreases: $MnO_4^- = +7$, $Mn^{2+} = +2$

Sulfur is oxidised as its oxidation number increases: $SO_2 = +4$, $SO_4^{2-} = +6$

For elements that have a variable oxidation number the oxidation state of the element in a particular compound is often signfied by the use of Roman numerals in the name, for example the permanganate(VII) ion and the manganese(II) ion in the above reaction. Another example would be iron(II) chloride for $FeCl_2$ and iron(III) chloride for $FeCl_3$.

In some cases a reaction can occur in which the same species is both oxidised and reduced. Reactions of this type are described as **disproportionation** (or self oxidation-reduction) reactions. An example would be the disproportionation of copper(I) ions in aqueous solution, when it is both oxidised to the copper(II) ion and simultaneously reduced to copper metal:

$$2\ Cu^+\ (aq) \longrightarrow Cu^{2+}\ (aq) + Cu\ (s)$$
$$+1 \qquad\qquad +2 \qquad\quad 0$$
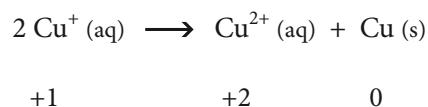
Commonly if there are a number of atoms of the same element in a species then they will all have the same oxidation number (for example chromium in $Cr_2O_7^{2-}$), but sometimes when they are in rather different environments, different atoms will have different oxidation numbers. Consider the two carbons in CH_3COOH. The normal calculation will give,the oxidation number of carbon as 0 [$2x + 4 + (2 \times -2) = 0$; thus $x = 0$]. This is the average oxidation number of the two carbon atoms in the molecule. In fact the oxidation number of the —CH_3 carbon is –3 and that of the —COOH carbon is +3 (imagine pulling apart the bonds). Another example is Fe_3O_4, a mixed oxide in which contains iron(II) and iron(III) ions in a 1:2 ratio and could be written as $FeO \cdot Fe_2O_3$.

TOK   The changing language of chemistry

The language of chemistry, like all living languages undergoes continual change. I'm not quite old enough to have meaningfully used names like "spirit of hartshorn" and "muriatic acid" (old names for aqueous ammonia and hydrochloric acid respectively), but I was certainly aware of them. These old names were often related to where things came from; "spirit of hartshorn" is obvious and "muriatic acid" comes from *muria* – the Latin word for brine (saltwater). Sometimes they would also indicate relationships between things, as with the various vitriols; blue vitriol (copper(II) sulfate), green vitriol (iron(II) sulfate), oil of vitriol (concentrated sulfuric acid) etc. When I learnt my chemistry, in the 1960s we mainly used different endings and prefixes to indicate the "valency" (oxidation state) of metals or the amount of oxygen in an acid, or its salts. We therefore had ferrous chloride ($FeCl_2$) and ferric chloride ($FeCl_3$) and though it seemed to operate fairly effectively for simple cases, it couldn't cope with the multiple oxidation states of transition metals, hence the introduction of the Roman numeral oxidation number convention. This also helped with the nomenclature of acids and their salts, for example those involving hydrogen and chlorine:

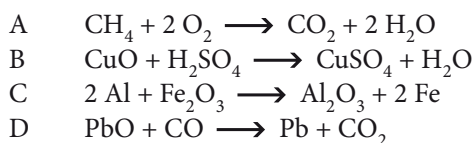| Ending	Meaning	Example	Modern name	Formula
...ide	No oxygen	Sodium chloride	Sodium chloride	NaCl
Hypo......ite	Least oxygen	Sodium hypochlorite	Sodium chlorate(I)	NaClO
...ite	More oxygen	Sodium chlorite	Sodium chlorate(III)	$NaClO_2$
...ate	More oxygen	Sodium chlorate	Sodium chlorate(V)	$NaClO_3$
Per......ate	Most oxygen	Sodium perchlorate	Sodium chlorate(VII)	$NaClO_4$

In simpler cases the prefixes were left out, so with nitrogen for example there was just nitride (N^{3-}), nitrite (NO_2^-) and nitrate (NO_3^-). In organic chemistry the changes have been more noticeable with **IUPAC** names now being preferred to "trivial" names, but as always there is resistance to new ways, especially as the old names tended to be shorter! Biologists still talk of alanine rather than 2-aminopropanoic acid and industrial chemists would always refer to ethoxyethane as ether. Even the IBO retreated, for example from using the technically more correct alkanals to the more widely used aldehydes, on their syllabus and examination papers.

What is in a name? What is lost when a name is lost? I suppose that we are conditioned to think of older names as seeming more "quaint" and "poetic" than the new "sterile" systematic names. Both give us information, but it could probably be argued that knowing that formic acid is produced by ants (French - *formis*) is less important than knowing that methanoic acid is a carboxylic; Oops, alkanoic acid containing one carbon atom.
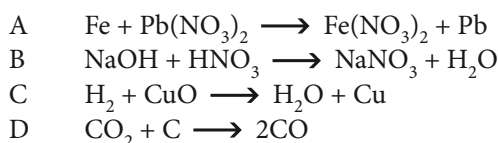
Exercise   9.1

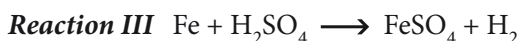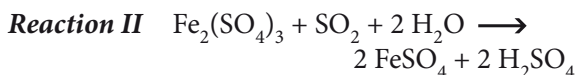1. Which one of the following reactions is not a redox reaction?

   A $CH_4 + 2 O_2 \longrightarrow CO_2 + 2 H_2O$
   B $CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$
   C $2 Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2 Fe$
   D $PbO + CO \longrightarrow Pb + CO_2$

2. In which one of the following reactions is the first reagent reduced?

   A $Fe + Pb(NO_3)_2 \longrightarrow Fe(NO_3)_2 + Pb$
   B $NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$
   C $H_2 + CuO \longrightarrow H_2O + Cu$
   D $CO_2 + C \longrightarrow 2CO$

3. In which of the following changes has the oxidation number of sulfur increased?

   A $H_2SO_4 \longrightarrow SO_2$
   B $H_2S \longrightarrow S_8$
   C $SO_2 \longrightarrow H_2S$
   D $SO_2 \longrightarrow S_8$
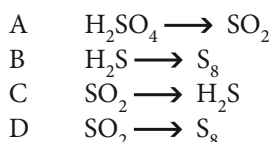
4. The three reactions below could all be used to prepare iron(II) sulfate:

   Reaction I $FeCl_2 + Ag_2SO_4 \longrightarrow$
   $$FeSO_4 + 2 AgCl$$

   Reaction II $Fe_2(SO_4)_3 + SO_2 + 2 H_2O \longrightarrow$
   $$2 FeSO_4 + 2 H_2SO_4$$

   Reaction III $Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$

   Which of the following best summarises what is happening to the iron in each of these reactions?

	Reaction I	*Reaction II*	*Reaction III*
A	reduction	neither	neither
B	neither	oxidation	reduction
C	neither	reduction	oxidation
D	reduction	reduction	oxidation

5. In which one of the following reactions is the species in **bold** type acting as an oxidising agent?

   A $\mathbf{FeCl_3} + 3 AgNO_3 \longrightarrow Fe(NO_3)_3 + 3 AgCl$
   B $\mathbf{Fe} + 2 Ag^+ \longrightarrow Fe^{2+} + 2 Ag$
   C $2 \mathbf{H^+} + Mg \longrightarrow Mg^{2+} + H_2$
   D $2 \mathbf{Fe^{2+}} + Cl_2 \longrightarrow 2 Fe^{3+} + 2 Cl^-$
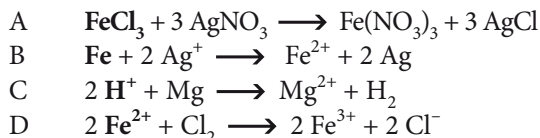
6. Give the oxidation number of the stated element in each of the following species:

   a)   Iron in Fe^{2+}
   b)   Phosphorus in P_4
   c)   Silicon in SiO_2
   d)   Sulfur in SCl_4
   e)   Nitrogen in N_2O
   f)   Carbon in CH_3OH
   g)   Vanadium in VO^{2+}
   h)   Bromine in BrO^-
   i)   Iodine in IF_6^-
   j)   Chromium in $Cr_2O_7^{2-}$

7. Give one example of the following:

   a)   An iron compound with an oxidation state of +2.
   b)   A nitrogen compound with an oxidation state of –3.
   c)   A manganese compound with an oxidation state of +7.
   d)   A carbon compound with an oxidation state of 0.
   e)   A phosphorus compound with an oxidation state of +5.

8. For each of the following transformations, give the initial and final oxidation number of the element in **bold** type and hence state whether it has been oxidised, been reduced, or neither.

   a) $\mathbf{Cu^{2+}} \longrightarrow \mathbf{Cu}I$
   b) $\mathbf{NO_2} \longrightarrow \mathbf{N_2O_4}$
   c) $\mathbf{PH_3} \longrightarrow \mathbf{HPO_2^{2-}}$
   d) $\mathbf{CH_3OH} \longrightarrow \mathbf{HCOOH}$
   e) $\mathbf{S_2O_3^{2-}} \longrightarrow \mathbf{S_4O_6^{2-}}$

9. Hydrazine (N_2H_4) and dinitrogen tetroxide (N_2O_4) react violently to form nitrogen as a product from both reactants.

   a)   Explain why this is considered to be a redox reaction stating, with reasons, what is being oxidised and what is being reduced.
   b)   Write a balanced equation for this reaction.
   c)   It has been suggested that this reaction is a very 'environmentally friendly' source of energy. Explain this.

10. In any redox reaction, the total increase in oxidation number must equal the total decrease in oxidation number. When ammonium dichromate(VI) is heated, it decomposes in a spectacular redox reaction.

a)   Write the formula for ammonium dichromate(VI).

b)   What is the significance of the (VI) in the name ammonium dichromate(VI)?

c)   The chromium is reduced to chromium(III) oxide, a green powder. What is the **total** decrease in oxidation number of chromium in each ammonium dichromate(VI)?

d)   What is the initial oxidation state of the nitrogen in the ammonium ion?

e)   Taking into account the total number of nitrogens in ammonium dichromate(VI), by how much must the oxidation number of each nitrogen increase?

f)   What must the final oxidation state of the nitrogen in the product be?

g)   Suggest a substance containing nitrogen in this oxidation state.

h)   What colour change would you see during this reaction?

i)   The reaction gives out heat and a shower of sparks. What does this show about the reaction?

9.2 REDOX EQUATIONS

9.2.1   Deduce simple oxidation and reduction half-equations given the species involved in a redox reaction.

9.2.2   Deduce redox equations using half-equations.

9.2.3   Define the terms oxidizing agent and reducing agent.

9.2.4   Identify the oxidizing and reducing agents in redox equations.

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With many substances, the oxidation or reduction that occurs during redox reactions in aqueous solution is independent of the particular **oxidant** or **reductant** that is causing the change. It is therefore convenient to write an equation for this change in terms of the loss or gain of electrons. For example, whenever the purple permanganate(VII) ion is reduced in acidic solution the almost colourless manganese(II) ion is formed, so the change occurring is:

$$MnO_4^-\,(aq) + 8\,H^+\,(aq) + 5\,e^- \longrightarrow Mn^{2+}\,(aq) + 4\,H_2O\,(l)$$
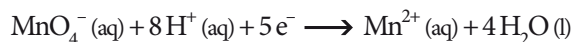
These equations are known as **half equations** and for a redox reaction the half equations for the substance being oxidized and the substance being reduced can be combined in such a way that the electrons cancel out, so as to give a balanced equation for the redox reaction.

Half equations must balance in the same way as normal equations (with respect to number of atoms of each element and charge), the only difference being that they contain electrons. When constructing a half equation it is easiest to follow a sequence of steps. This will be illustrated using the half equation for the reduction of the orange dichromate(VI) ion to the green chromium(III) ion in acidic aqueous solutions, as an example:
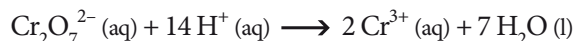
$$Cr_2O_7^{2-}\,(aq) \longrightarrow Cr^{3+}\,(aq)$$
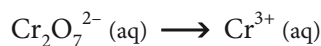
1) balance the number of atoms of the element being oxidized or reduced (in this case Cr is being reduced from +6 to +3) on the two sides:
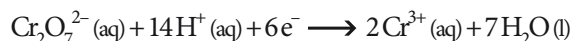
$$Cr_2O_7^{2-}\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq)$$
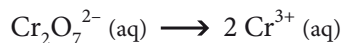
2) add water molecules to balance the number of oxygen atoms on the two sides:

$$Cr_2O_7^{2-}\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l)$$

3) add hydrogen ions to balance the number of hydrogen atoms on the two sides:

$$Cr_2O_7^{2-}\,(aq) + 14\,H^+\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l)$$

4) add electrons so that the electrical charges on both sides balance:

$$Cr_2O_7^{2-}\,(aq) + 14\,H^+\,(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l)$$
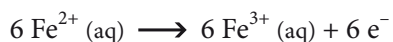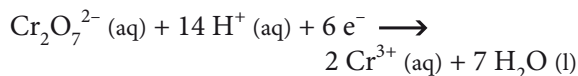
Because this is a reduction, the electrons appear on the left hand side of the equation (GER) and their number is equal to the total change in oxidation number (two chromiums changing in oxidation state from +6 to +3 is a change in oxidation number of –6 (2 × –3) and hence requires a total of 6 electrons). In an oxidation, the electrons would appear on the right hand side of the equation (LEO). For example the half equation for the oxidation of iron(II) to iron(III) is:

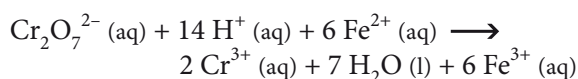$$Fe^{2+}\,(aq) \longrightarrow Fe^{3+}\,(aq) + e^-$$
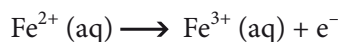
To write a balanced equation for a redox reaction, the two half equations involved must be multiplied by suitable factors so that when added together the number of

electrons lost by one equals the number gained by the other so that the electrons cancel. In the case of the oxidation of iron(II) to iron(III) by the reduction of dichromate(VI) to chromium(III), the equation for the oxidation of the iron(II) must be multiplied by six because six electrons are involved in the reduction of the dichromate(VI), so that the half equations involved become:

$$Cr_2O_7^{2-} \text{ (aq)} + 14 \text{ H}^+ \text{ (aq)} + 6 \text{ e}^- \longrightarrow$$
$$2 \text{ Cr}^{3+} \text{ (aq)} + 7 \text{ H}_2O \text{ (l)}$$

$$6 \text{ Fe}^{2+} \text{ (aq)} \longrightarrow 6 \text{ Fe}^{3+} \text{ (aq)} + 6 \text{ e}^-$$

When added together, the electrons cancel and the final balanced equation is:

$$Cr_2O_7^{2-} \text{ (aq)} + 14 \text{ H}^+ \text{ (aq)} + 6 \text{ Fe}^{2+} \text{ (aq)} \longrightarrow$$
$$2 \text{ Cr}^{3+} \text{ (aq)} + 7 \text{ H}_2O \text{ (l)} + 6 \text{ Fe}^{3+} \text{ (aq)}$$
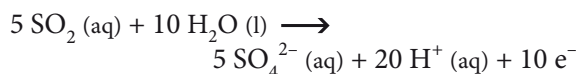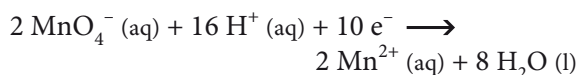
In the example above, the dichromate(VI) ion is described as an oxidizing agent (or oxidant) as it oxidizes iron(II) to iron(III). Similarly the iron(II) ion is a reducing agent because it reduces the dichromate(VI) ion to the chromium(III) ion. Note that an oxidizing agent oxidizes another substance, but is itself reduced; conversely a reducing agent reduces another substance, but is itself oxidized in the process.
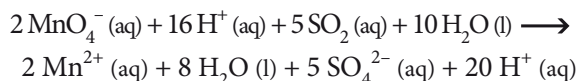
When balancing redox equations, sometimes it will then be necessary to cancel hydrogen ions and water molecules that appear on both sides of the equation. This is best illustrated by a second example – the half equation for the oxidation of sulfur dioxide to the sulfate ion is:

$$SO_2 \text{ (aq)} + 2 \text{ H}_2O \text{ (l)} \longrightarrow SO_4^{2-} \text{ (aq)} + 4 \text{ H}^+ \text{ (aq)} + 2 \text{ e}^-$$
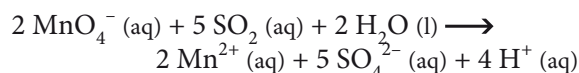
If this is to be combined with the half equation for the reduction of the permanganate(VII) ion, given at the start of this section, then it is necessary to multiply the permanganate(VII) half equation by two and the sulfur dioxide half equation by five, so that both involve ten electrons:

$$2 \text{ MnO}_4^- \text{ (aq)} + 16 \text{ H}^+ \text{ (aq)} + 10 \text{ e}^- \longrightarrow$$
$$2 \text{ Mn}^{2+} \text{ (aq)} + 8 \text{ H}_2O \text{ (l)}$$

$$5 \text{ SO}_2 \text{ (aq)} + 10 \text{ H}_2O \text{ (l)} \longrightarrow$$
$$5 \text{ SO}_4^{2-} \text{ (aq)} + 20 \text{ H}^+ \text{ (aq)} + 10 \text{ e}^-$$

When these are initially combined, the equation is:

$$2 \text{ MnO}_4^- \text{ (aq)} + 16 \text{ H}^+ \text{ (aq)} + 5 \text{ SO}_2 \text{ (aq)} + 10 \text{ H}_2O \text{ (l)} \longrightarrow$$
$$2 \text{ Mn}^{2+} \text{ (aq)} + 8 \text{ H}_2O \text{ (l)} + 5 \text{ SO}_4^{2-} \text{ (aq)} + 20 \text{ H}^+ \text{ (aq)}$$

By cancelling the water molecules and hydrogen ions that appear on both sides, this simplifies to give the final balanced equation, which is:

$$2 \text{ MnO}_4^- \text{ (aq)} + 5 \text{ SO}_2 \text{ (aq)} + 2 \text{ H}_2O \text{ (l)} \longrightarrow$$
$$2 \text{ Mn}^{2+} \text{ (aq)} + 5 \text{ SO}_4^{2-} \text{ (aq)} + 4 \text{ H}^+ \text{ (aq)}$$

In this example, the permanganate(VII) ion is the oxidizing agent as it oxidizes sulfur in sulfur dioxide to sulfate (+4 to +6) and is itself reduced to the manganese(II) ion. On the other hand, sulfur dioxide is the reducing agent as it reduces manganese from the permanganate(VII) ion to the manganese(II) ion (+7 to +2) and is itself oxidized to sulfate.

CORE

Exercise 9.2

1. Which one of the following is the correct half equation for the iodate(V) ion in acidic solution changing to iodine?

   A $IO_3^- + 6 \text{ H}^+ \longrightarrow I + 3 \text{ H}_2O + 5 \text{ e}^-$
   B $IO_3^- + 6 \text{ H}^+ + 5 \text{ e}^- \longrightarrow I + 3 \text{ H}_2O$
   C $IO_3^- + 6 \text{ H}^+ + 5 \text{ e}^- \longrightarrow I_2 + 3 \text{ H}_2O$
   D $2 \text{ IO}_3^- + 12 \text{ H}^+ + 10 \text{ e}^- \longrightarrow I_2 + 6 \text{ H}_2O$

2. In the half equation for a substance acting as a reductant (reducing agent)

   A   the oxidation number increases and the electrons are on the right hand side.
   B   the oxidation number increases and the electrons are on the left hand side.
   C   the oxidation number decreases and the electrons are on the right hand side.
   D   the oxidation number decreases and the electrons are on the left hand side.

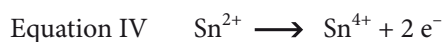3. The overall equation for nitric acid oxidising iron(II) ions to iron(III) ions is

   $$HNO_3 + 3 \text{ Fe}^{2+} + 3 \text{ H}^+ \longrightarrow NO + 3 \text{ Fe}^{3+} + 2 \text{ H}_2O$$

   The half equation for the reduction of the nitric acid must therefore be

   A $HNO_3 + 4 \text{ H}^+ + 4 \text{ e}^- \longrightarrow NO + 2 \text{ H}_2O$
   B $HNO_3 + 3 \text{ H}^+ + 3 \text{ e}^- \longrightarrow NO + 2 \text{ H}_2O$
   C $HNO_3 + 3 \text{ H}^+ \longrightarrow NO + 2 \text{ H}_2O + 3 \text{ e}^-$
   D $HNO_3 + \text{ H}^+ \longrightarrow NO + \text{ H}_2O + \text{ e}^-$

4. Write balanced half equations for the following changes:

   a) Zinc metal being oxidised to the zinc ion.
   b) Bromine being reduced to the bromide ion.
   c) Hydrogen sulfide being oxidised to sulfur.
   d) Nitric acid being reduced to nitrogen dioxide [nitrogen(IV) oxide].
   e) The vanadate(V) ion (VO_3^-) being reduced to the vanadium(III) ion.

5. Below are given some half equations for redox reactions. Combine these, as indicated, to produce balanced equations for the redox reactions involved.

   Equation I $\quad Co^{3+} + e^- \longrightarrow Co^{2+}$

   Equation II $\quad PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O$

   Equation III $\quad ClO_3^- + 6H^+ + 6e^- \longrightarrow Cl^- + 3H_2O$

   Equation IV $\quad Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$

   Equation V $\quad NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-$

   a) Equations II and IV.
   b) Equations I and IV.
   c) Equations II and V.
   d) Equations III and IV.
   e) Equations III and V.

6. Use the half equation method to write balanced equations for the following reactions:

   a) Magnesium reducing lead ions to lead metal.
   b) Sulfur dioxide being oxidised to sulfate through reducing iodine to iodide ions.
   c) Hydrogen peroxide oxidising iron(II) to iron(III) in acidic solution.
   d) Zinc reducing acidified dichromate(VI) ions to chromium(III).
   e) Acidified permanganate(VII) ions oxidising methanol to carbon dioxide and water.

7. A disproportionation reaction is one in which a single species is both oxidised and reduced in the same reaction. An example of this occurs when potassium chlorate(V) ($KClO_3$) is heated to just above its melting point. The chlorate ion is oxidised to the perchlorate [chlorate(VII)] ion (ClO_4^-) and reduced to the chloride ion (Cl^-).

   a) What is the oxidation state of the chlorine in these various species?
   b) Write a half equation for the oxidation of the chlorate(V) ion to the perchlorate(VII) ion in aqueous solution.
   c) Write a half equation for the reduction of the chlorate(V) ion to the chloride ion in acidic solution.
   d) Write a balanced chemical equation for the disproportionation of potassium chlorate(V).
   e) Why is there no need for the substances to be in aqueous solution for this reaction to occur?

8. If wine is left in an open bottle it often tastes 'vinegary' a few days later. This is because of the oxidation of the ethanol to ethanoic acid by atmospheric oxygen.

   a) Write the half equation for the oxidation of ethanol to ethanoic acid.
   b) What is the initial and final average oxidation number of the carbons in this change?
   c) Write the half equation for the reduction of oxygen in acidic solution.
   d) Combine these to produce an overall equation for the reaction.
   e) Normally, oxygen is a poor oxidant in aqueous solution. This change only occurs in the presence of bacteria which produce enzymes. Why is oxygen a poor oxidant and how do the enzymes affect this?

SOME COMMON OXIDISING AGENTS AND REDUCING AGENTS

Some of the more common oxidising agents and reducing agents are given below along with their half equations and other characteristics.

OXIDISING AGENTS

Oxygen

Oxygen is not a very effective oxidant for substances in aqueous solution as a result of the high activation energy associated with breaking the $O=O$ double bond. It will however oxidise many substances when they are heated in a stream of air or oxygen, the reaction being described as burning, or combustion, e.g.

$$2\,Mg\,(s) + O_2\,(g) \longrightarrow 2\,MgO\,(s)$$
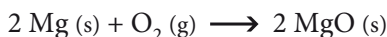
Chlorine and the other halogens

Strong oxidants both in aqueous solution and when the substance is heated with the element. Going down Group 7 the halogens become less powerful oxidants. The usual colour change with bromine and iodine is from brown to colourless, though if iodide ions are completely oxidised to iodine it appears as a black solid. Using X as the symbol for the halogen, the half equation is:

$$X_2\,(aq) + 2e^- \longrightarrow 2\,X^-\,(aq)$$

Iron(III) ion

The yellow–brown iron(III) ion acts as a mild oxidant and is reduced to the pale green iron(II) ion. The oxidation state of the iron can best be demonstrated by adding aqueous sodium hydroxide and observing the colour of the precipitate.

$$Fe^{3+}\,(aq) + e^- \longrightarrow Fe^{2+}\,(aq)$$
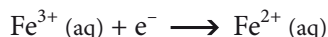
Hydrogen peroxide

A moderate strength oxidant which in aqueous solution is reduced to water. The reactants and products are all colourless.

$$H_2O_2\,(aq) + 2\,H^+\,(aq) + 2\,e^- \longrightarrow 2\,H_2O\,(l)$$
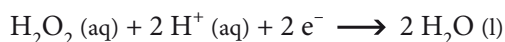
[Note that very powerful oxidants, such as the permanganate(VII) ion can oxidise hydrogen peroxide to oxygen: $H_2O_2\,(aq) \longrightarrow O_2\,(g) + 2\,H^+\,(aq) + 2\,e^-$].

Manganate(VII) ion (Permanganate ion)

This very powerful oxidant is usually used in acidic solution when the purple permanganate(VII) ion is reduced to the almost colourless manganese(II) ion.

$$MnO_4^-\,(aq) + 8\,H^+\,(aq) + 5\,e^- \longrightarrow Mn^{2+}\,(aq) + 4\,H_2O\,(l)$$
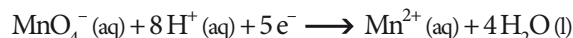
At other pHs the product can be manganese(IV) oxide (a brown solid) or the manganate(VI) ion (a dark green solution).

Dichromate(VI) ion

This too is a powerful oxidant that is usually used in acidic solution. The orange dichromate(VI) ion is reduced to the green chromium(III) ion.

$$Cr_2O_7^{2-}\,(aq) + 14\,H^+\,(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l)$$
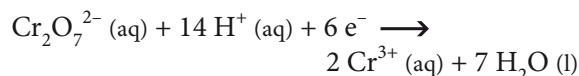
REDUCING AGENTS

Hydrogen

This is not an effective reductant for aqueous solutions owing to a high activation energy. When passed over the heated oxides of metals below zinc in the reactivity series however, it reduces the oxide to the metal:

$$MO\,(s) + H_2\,(g) \longrightarrow M\,(s) + H_2O\,(g)$$
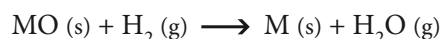
Carbon and carbon monoxide

Like hydrogen, activation energy considerations prevent being it effective in aqueous solution, but when heated with the oxide of zinc or metals lower in the reactivity series, they reduce the oxide to the metal:

$$2\,MO\,(s) + C\,(s) \longrightarrow M\,(s) + CO_2\,(g)$$

$$MO\,(s) + CO\,(s) \longrightarrow M\,(s) + CO_2\,(g)$$

These are very important reactions for obtaining metals from their ores.

Metals

The more reactive the metal the stronger it is as a reductant, so that metals such as magnesium, zinc and iron are very effective reductants. The metal is oxidised to the aqueous

Oxidised form			Reduced form		
Permanganate(VII)	MnO_4^-	Purple	Manganese(II)	Mn^{2+}	Colourless
Dichromate(VI)	$Cr_2O_7^{2-}$	Orange	Chromium(III)	Cr^{3+}	Green
Iron(III)	Fe^{3+}	Red-brown	Iron(II)	Fe^{2+}	Pale green
Iodine	I_2	Brown, if excess I^-; blue-black if starch is present	Iodide	I^-	Colourless
Bromine	Br_2	Brown	Bromide	Br^-	Colourless

Figure 901   Colour changes in some common redox systems

cation, so that if this is **divalent**, using M as the symbol for the metal, the half equation is:
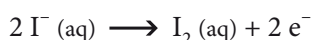
$$M \text{ (s)} \longrightarrow M^{2+} \text{ (aq)} + 2\,e^-$$

Iron(II) ion

The pale green iron(II) ion acts as a mild reductant in aqueous solution, being oxidised to the red–brown iron (III) ion:

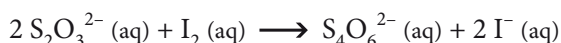$$Fe^{2+} \text{ (aq)} \longrightarrow Fe^{3+} \text{ (aq)} + e^-$$
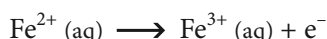
Iodide ion

The colourless iodide ion acts as a mild reductant in aqueous solution, being oxidised to iodine, which appears as a brown solution if excess iodide is present:

$$2\,I^- \text{ (aq)} \longrightarrow I_2 \text{ (aq)} + 2\,e^-$$

Thiosulfate ion

The thiosulfate ion is a mild reductant that reacts readily with iodine in aqueous solution according to the equation:

$$2\,S_2O_3^{2-} \text{ (aq)} + I_2 \text{ (aq)} \longrightarrow S_4O_6^{2-} \text{ (aq)} + 2\,I^- \text{ (aq)}$$

Starch forms a very intense blue-black coloured complex with iodine and the sudden colour change from blue-black to colorless is used to determine the end point in redox titrations involving iodine.

Sulfur dioxide

Sulfur dioxide is a moderately powerful reductant in aqueous solution, being oxidised to the sulfate ion:

$$SO_2 \text{ (aq)} + 2\,H_2O \text{ (l)} \longrightarrow SO_4^{2-} \text{ (aq)} + 4\,H^+ \text{ (aq)} + 2\,e^-$$

The reactants and products are all colourless.

The colour changes that accompany some of these redox changes are summarised in Figure 901.

EXTENSION

Exercise

1. Which one of the following is least likely to oxidise iron(II) ions to iron(III) ions in aqueous solution?

   A   Magnesium
   B   Chlorine
   C   Hydrogen peroxide
   D   Dichromate(VI) ions

2. Which one of the following redox changes would not give rise to a change in colour of the solution?

   A   Iron(II) being oxidised by acidified permanganate(VII).
   B   Sulfur dioxide being oxidised by hydrogen peroxide.
   C   Dichromate(VI) ions being reduced by zinc.
   D   Iodide ions being oxidised by chlorine.

3. Which one of the reactions below, to reduce metal oxides, is least likely to occur?

   A $PbO + H_2 \longrightarrow Pb + H_2O$
   B $Fe_2O_3 + 2\,Al \longrightarrow Al_2O_3 + 2\,Fe$
   C $MgO + CO \longrightarrow Mg + CO_2$
   D $2\,CuO + C \longrightarrow 2\,Cu + CO_2$

4. The concentration of copper(II) ions in aqueous solution can be determined by adding an excess of potassium iodide, when the following reaction occurs:

$$2\,Cu^{2+} \text{ (aq)} + 4\,I^- \text{ (aq)} \longrightarrow 2\,CuI \text{ (s)} + I_2 \text{ (aq)}$$
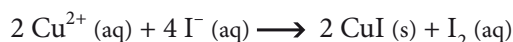
The iodine liberated is then titrated with standardised aqueous sodium thiosulfate.

a) In the above equation, what is the initial and final oxidation state of the copper.

b) Given that copper(I) iodide is a white solid, what colour change would be seen when the above reaction occurs?

c) Write a balanced equation for the reaction of iodine with sodium thiosulfate.

d) Calculate the initial and final average oxidation states of the sulfur in this reaction.

e) What indicator is usually used and what is the colour change at the end point?

f) In such a titration it is found that 20 cm^3 of an aqueous solution containing copper(II) sulfate required exactly 15 cm^3 of aqueous sodium thiosulfate of concentration 0.2 mol dm^3 to react with the iodine formed. What was the concentration of the copper(II) sulfate solution?

5. A 2.00 g iron nail is dissolved in excess sulfuric acid. The resulting solution is then titrated with 0.200 mol m^3 aqueous potassium permanganate(VII).

a) What colour change would occur at the end point of the titration?

b) What volume of aqueous potassium permanganate(VII) would be required if the nail were pure iron?
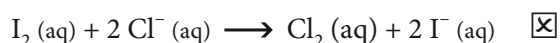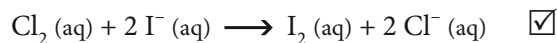
9.3 REACTIVITY

CORE

Usually a certain species will give a particular product as a result of gaining/losing electrons – this pair of species (for example Zn^{2+}/Zn) is referred to as a **redox couple**. (There are however a few exceptions, such as the permanganate(VII) ion where the product depends on other conditions such as the pH.) If one species in the couple is a powerful oxidising agent (has a great attraction for electrons) then it follows that the other half of the couple, that it forms when it has gained this electrons, will not readily give them up again, that is it will be a very weak reducing agent. This is similar to the relationship that exists between the strengths of a conjugate acid–base pair though in that case a hydrogen ion rather than an electron is being exchanged. This allows us to arrange redox pairs as a reactivity series in order of increasing oxidising/reducing power. A very simple **reactivity series**, showing some common metals and the halogens, is shown in Figure 902.
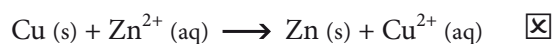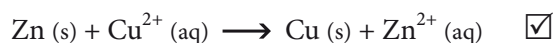
Redox Couple

Oxidised form		Reduced form
$Na^+ + e^-$	$\rightleftharpoons$	Na
$Mg^{2+} + 2\,e^-$	$\rightleftharpoons$	Mg
$Zn^{2+} + 2\,e^-$	$\rightleftharpoons$	Zn
$Fe^{2+} + 2\,e^-$	$\rightleftharpoons$	Fe
$2\,H^+ + 2\,e^-$	$\rightleftharpoons$	H_2
$Cu^{2+} + 2\,e^-$	$\rightleftharpoons$	Cu
$I_2 + 2\,e^-$	$\rightleftharpoons$	$2\,I^-$
$Br_2 + 2\,e^-$	$\rightleftharpoons$	$2\,Br^-$
$Cl_2 + 2\,e^-$	$\rightleftharpoons$	$2\,Cl^-$
$F_2 + 2\,e^-$	$\rightleftharpoons$	$2\,F^-$

Increasingly powerful oxidising agent (downward)

Increasingly powerful reducing agent (upward)

Figure 902   A simple redox reactivity series

The gain of electrons to complete valence shells is behaviour that is typical of non–metals, hence non–metals tend to be oxidising agents and occur in the left hand column of the table. Going down the left hand column the elements become more reactive (note the relationship to the order of the elements in Group 7) so that an element lower in the table can oxidise the ion formed from an element higher in the table, but the reverse cannot occur. For example chlorine (Cl_2) attracts electrons more strongly than iodine (I_2), so that chlorine can oxidise iodide ions to iodine, but iodine cannot oxidise chloride ions to chlorine:

$$Cl_2 \text{ (aq)} + 2\ I^- \text{ (aq)} \longrightarrow I_2 \text{ (aq)} + 2\ Cl^- \text{ (aq)} \quad ☑$$

$$I_2 \text{ (aq)} + 2\ Cl^- \text{ (aq)} \longrightarrow Cl_2 \text{ (aq)} + 2\ I^- \text{ (aq)} \quad ☒$$

Conversely the loss of electrons to form empty valence shells is behaviour that is typical of metals, so metals behave as reductants and occur in the right hand column of the table. The most reactive metals are at the top and the reactivity decreases going down the table. A metal higher in the series will displace a metal lower in the series from its salts, but the reverse reaction cannot occur. For example zinc will displace copper from copper(II) salts (i.e. zinc is a powerful enough reductant to reduce copper ions to copper), but copper will not displace zinc from zinc salts (i.e. copper is not a powerful enough reductant to reduce zinc ions to zinc):

$$Zn \text{ (s)} + Cu^{2+} \text{ (aq)} \longrightarrow Cu \text{ (s)} + Zn^{2+} \text{ (aq)} \quad ☑$$

$$Cu \text{ (s)} + Zn^{2+} \text{ (aq)} \longrightarrow Zn \text{ (s)} + Cu^{2+} \text{ (aq)} \quad ☒$$

The above reactions of both the halogens and the metals are known as **displacement reactions**, because they involve are more reactive metal/non-metal displacing the less reactive one from its salt.

The position of a metal in the series relative to hydrogen can also be used to predict whether a metal will liberate hydrogen from dilute acids. Metals above hydrogen are powerful enough reducing agents to reduce hydrogen ions to hydrogen, for example magnesium:

$$Mg \text{ (s)} + 2\ H^+ \text{ (aq)} \longrightarrow H_2 \text{ (g)} + Mg^{2+} \text{ (aq)}$$
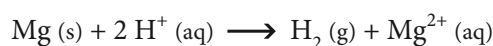
Metals below hydrogen, such as copper, are not strong enough reducing agents to reduce hydrogen ions and hence will not react with dilute acids.

Hence if zinc foil is dipped into aqueous copper sulfate, the zinc will acquire a reddish-brown coating of metallic copper and the blue colour of the solution will fade. See Figure 903
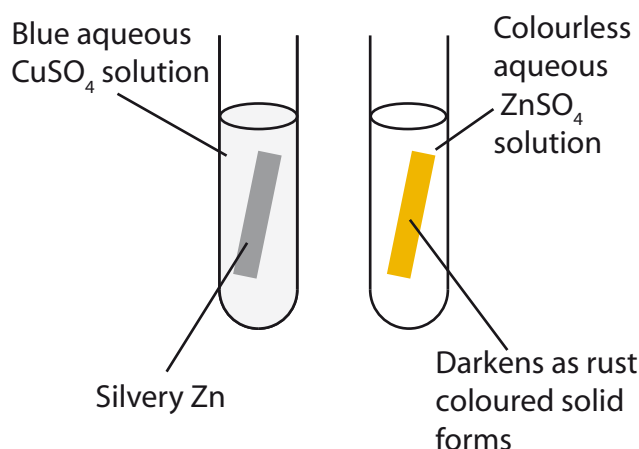

Figure 903   Reaction of metals and salts

1.   Which one of the following metals is the most powerful reductant (reducing agent)?

    A   Copper
    B   Magnesium
    C   Iron
    D   Zinc

2.   In which one of the following would you expect a reaction to occur?

    A   Copper placed in aqueous zinc chloride
    B   Zinc placed in aqueous silver nitrate
    C   Iron placed in aqueous magnesium sulfate
    D   Magnesium placed in aqueous sodium chloride

3.   Zinc reacts with dilute acids to liberate hydrogen. This is because

    A   the zinc ion is a more powerful oxidising agent than the hydrogen ion.
    B   the hydrogen ion is a more powerful oxidising agent than the zinc ion.
    C   the zinc ion is a more powerful reducing agent than the hydrogen ion.
    D   the hydrogen ion is a more powerful reducing agent than the zinc ion.

4.   a)   What would you observe when chlorine is bubbled through aqueous sodium bromide?

    b)   What would you see when bromine is added to aqueous sodium chloride?

c)   Interpret these results {in a) and b)} in terms of the reactions that occur and explain what this shows about the relative oxidising power of chlorine and bromine.

5.   You have a sample of a metal M and an aqueous solution of its sulfate, MSO_4. Describe some simple experiments that you could do to try and determine the reactivity of M relative to other common metals such as copper, zinc and magnesium. Explain how you would interpret the results of these experiments.

9.4 VOLTAIC CELLS

9.4.1   Explain how a redox reaction is used to produce electricity in a Voltaic cell.

9.4.2   State that oxidation occurs at the negative electrode (anode) and reduction occurs at the positive electrode (cathode).

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A **Voltaic** (Galvanic or electrochemical) **cell** is a device for converting chemical energy into electrical energy using a spontaneous redox reaction as a source of electrical energy and this is the basis of commercial **electrochemical cell**s (batteries). The opposite, which uses electrical energy to carry out a non-spontaneous redox reaction is known as electrolysis.

Consider a metal in contact with an aqueous solution of its ions. A redox equilibrium will be established and the metal will acquire an electrical charge:

$$M_{(s)} \rightleftharpoons M^{n+}_{(aq)} + n\,e^-$$

In the case of a reactive metal, the equilibrium will tend to the right, a little of the metal will dissolve and the remaining metal will become negatively charged because of the excess of electrons. The opposite may be true for an unreactive metal. It is not possible to measure these electrode potentials directly, but an electrical circuit can be constructed to compare the potentials of two such electrodes, using apparatus such as that illustrated in Figure 904.

The more reactive metal will always be the negative electrode and the greater the difference in reactivity of the metals, the greater the cell potential. A high resistance voltmeter connected between the metals will measure the potential difference between them. If however they are connected by a wire then this allows electrons to flow from the negative electrode (in this case the zinc) to the positive electrode (in this case the copper). At the negative electrode, the metal will slowly dissolve as these electrons are removed. In this case the reaction is:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2\,e^-$$

Because electrons are lost from the negative electrode an oxidation reaction must occur to produce these electrons (LEO) and hence this is the anode, as oxidation always occurs at the anode. At the positive electrode, the electrons react with the metal ions to form a layer of the metal. In this case the reaction is:

$$Cu^{2+}_{(aq)} + 2\,e^- \longrightarrow Cu_{(s)}$$
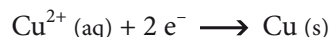
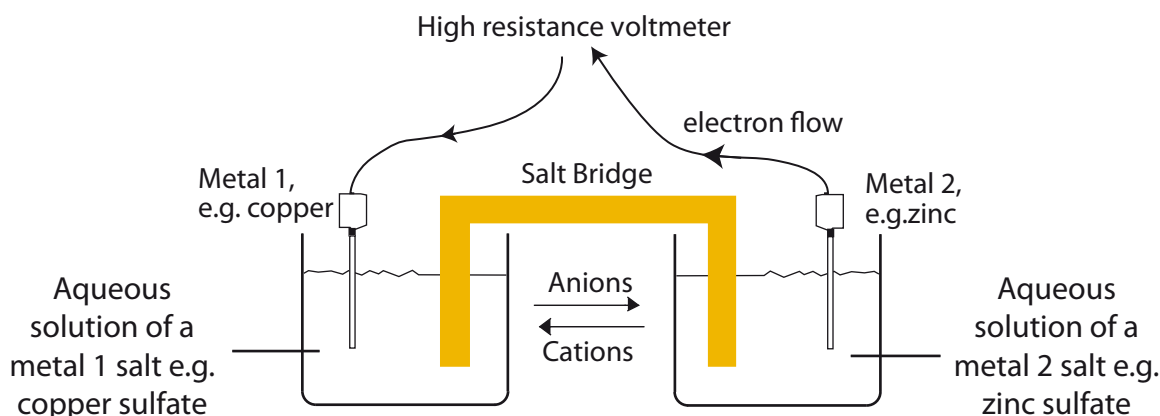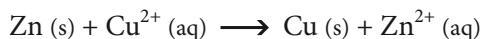As electrons flow to the positive electrode, a reduction reaction must occur to consume these electrons (GER)

Figure 904   A typical Voltaic cell

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and hence this is the cathode, as reduction always occurs at the cathode. Overall the cell reaction is:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

Note that this is the same as the displacement reaction mentioned in the previous section, but in this case the energy produced in this spontaneous reaction is converted to electrical energy rather than heat. The cell will therefore continue to generate electricity until the zinc or the copper sulfate is all consumed.

The salt bridge in the electrochemical cell allows the movement of ions between the solutions, thus completing the circuit and maintaining electrical neutrality. This is frequently a piece of filter paper dipped in a solution of a strong electrolyte, such as potassium nitrate. At the right hand electrode in Figure 904 positive ions are being produced and at the left hand one they are being consumed. For this reason positive ions move from right to left in the salt bridge and negative ions from left to right.

Exercise 9.4

1. Two different metals are connected together in an electrochemical cell. Which of the following is true of the electrode made of the more reactive metal?

    A   It will be the negative electrode and it will undergo oxidation.
    B   It will be the negative electrode and it will undergo reduction.
    C   It will be the positive electrode and it will undergo oxidation.
    D   It will be the positive electrode and it will undergo reduction.

2. An electrochemical cell is capable of doing work. What is the source of the energy for this?

    A   It comes from the thermal energy.
    B   It comes from stored electrons.
    C   It comes from an endothermic chemical reaction.
    D   It comes from an exothermic chemical reaction.

3. An electrochemical cell is constructed using magnesium in aqueous magnesium sulphate and iron in aqueous iron(II) sulphate. What reactions would occur at the electrodes?

	Magnesium electrode	Iron electrode
A	$Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2\,e^-$	$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2\,e^-$
B	$Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2\,e^-$	$Fe^{2+}_{(aq)} + 2\,e^- \longrightarrow Fe_{(s)}$
C	$Mg^{2+}_{(aq)} + 2\,e^- \longrightarrow Mg_{(s)}$	$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2\,e^-$
D	$Mg^{2+}_{(aq)} + 2\,e^- \longrightarrow Mg_{(s)}$	$Fe^{2+}_{(aq)} + 2\,e^- \longrightarrow Fe_{(s)}$

4. (a) Draw a fully labelled diagram of an electrochemical cell using iron and copper as the two metals.

    (b)   Show a wire connecting the two electrodes and mark on it the direction of electron flow.
    (c)   Write half equations for the reactions that take place at the two electrodes.
    (d)   State clearly which electrode is the anode and which the cathode.
    (e)   Explain the function of the salt bridge.

5. You are intending to construct an electrochemical cell using two metals, chosen from copper, iron, magnesium and zinc, in aqueous solutions of their salts. Explain how you can use a reactivity series to choose the pair of metal that will produce the greatest potential difference for the cell and to predict which metal will be the anode and which the cathode.

HIGHER LEVEL

19.1 STANDARD ELECTRODE POTENTIALS (AHL)

19.1.1 Describe the standard hydrogen electrode.

19.1.2 Define the term standard electrode potential (E^θ).

19.1.3 Calculate cell potentials using standard electrode potentials.

19.1.4 Predict whether a reaction will be spontaneous using standard electrode potential values.

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The potential of any two electrodes can be compared using the apparatus shown in Figure 904, and connecting the electrodes with a very high resistance voltmeter. (The high internal resistance of the cell means that the potential difference falls very rapidly if any current is allowed to flow, hence the need for a very high resistance voltmeter.) Conventionally electrode potentials are measured relative to the **standard hydrogen electrode** (SHE), which is defined as having a potential of zero. The potential differences of electrodes relative to this are known as standard electrode potentials (E^θ). Standard electrode potentials also refer to a temperature of 298K, normal atmospheric pressure (101.3 kPa) and the concentration of all solutions being 1 mol dm^{-3}. The construction of the standard hydrogen electrode is shown in Figure 906:

'Platinum black' is very finely divided platinum, which catalyses the electrode equilibrium:

$$2\,H^+ \text{(aq)} + 2\,e^- \rightleftharpoons H_2 \text{(g)}$$
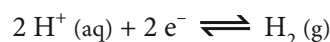
Thus, the standard electrode potential of a half-cell, (also called standard reduction potential) is the **e.m.f.** of the half-cell when it is connected to the standard hydrogen electrode. If the half-cell is the positive terminal of the cell, then the sign of the standard electrode potential is positive (for example Ag$^+$/Ag is + 0.80 V); if however the half-cell is the negative terminal of the cell, then the sign of the standard electrode potential is negative (for example Zn^{2+}/Zn is – 0.76 V).

The electrode potential concept can be extended to redox couples that do not involve metals, for example iodine and the iodide ion. In this case the electrode consists of an inert metal, such as platinum, dipped into a solution containing both the oxidised and reduced form of the couple, so that the redox reaction can occur on the surface of the metal.

Reactive metals, that lose electrons easily have large negative electrode potentials (for example –2.71 V for Na$^+$/Na) and reactive non-metals, that gain electrons easily, have large positive electrode potentials (for example +2.87 V for F$_2$/2 F$^-$). The greater the E^θ, the stronger the oxidising agent (on the left hand side of the equation as written below) and the weaker the reducing agent (on the right hand side). For example fluorine is a very powerful
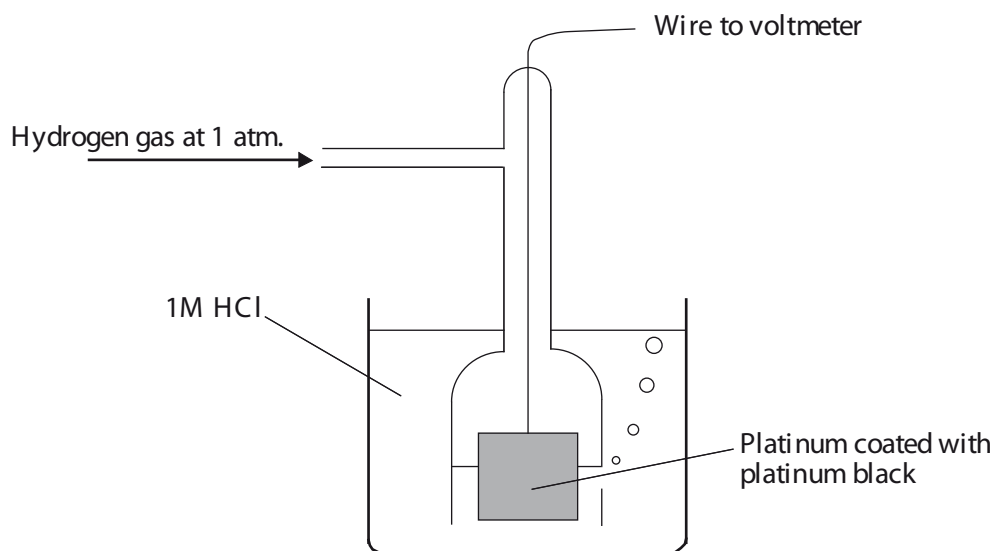
AHL

Figure 906   The standard hydrogen electrode

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oxidising agent, but the fluoride ion is a very weak reducing agent. Conversely species with a very negative E^θ comprise weak oxidising agents and strong reducing agents. Electrode potentials are usually quoted for the oxidised form gaining electrons and being converted to the reduced form. Some species commonly involved in redox reactions and their E^θ values are given in Figure 907.
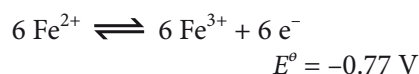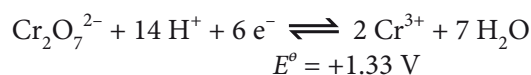
Half equation In standard form: Oxidised + electrons $\rightleftharpoons$ Reduced	E^θ in Volts
$Li^+ + e^- \rightleftharpoons Li$	−3.03
$K^+ + e^- \rightleftharpoons K$	−2.92
$Ca^{2+} + 2\,e^- \rightleftharpoons Ca$	−2.87
$Na^+ + e^- \rightleftharpoons Na$	−2.71
$Mg^{2+} + 2\,e^- \rightleftharpoons Mg$	−2.36
$Al^{3+} + 3\,e^- \rightleftharpoons Al$	−1.66
$Mn^{2+} + 2\,e^- \rightleftharpoons Mn$	−1.18
$H_2O + e^- \rightleftharpoons \tfrac{1}{2}\,H_2 + OH^-$	−0.83
$Zn^{2+} + 2\,e^- \rightleftharpoons Zn$	−0.76
$Fe^{2+} + 2\,e^- \rightleftharpoons Fe$	−0.44
$Ni^{2+} + 2\,e^- \rightleftharpoons Ni$	−0.23
$Sn^{2+} + 2\,e^- \rightleftharpoons Sn$	−0.14
$Pb^{2+} + 2\,e^- \rightleftharpoons Pb$	−0.13
$H^+ + e^- \rightleftharpoons \tfrac{1}{2}\,H_2$	0.00
$SO_4^{2-} + 4\,H^+ + 2\,e^- \rightleftharpoons SO_2 + 2\,H_2O$	+0.17
$Cu^{2+} + 2\,e^- \rightleftharpoons Cu$	+0.34
$\tfrac{1}{2}\,O_2 + H_2O + 2\,e^- \rightleftharpoons 2\,OH^-$	+0.40
$Cu^+ + e^- \rightleftharpoons Cu$	+0.52
$I_2\,(s) + 2\,e^- \rightleftharpoons 2\,I^-$	+0.54
$I_2\,(aq) + 2\,e^- \rightleftharpoons 2\,I^-$	+0.62
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Br_2 + 2\,e^- \rightleftharpoons 2\,Br^-$	+1.09
$\tfrac{1}{2}\,O_2 + 2\,H^+ + 2\,e^- \rightleftharpoons H_2O$	+1.23
$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightleftharpoons 2\,Cr^{3+} + 7\,H_2O$	+1.33
$Cl_2 + 2\,e^- \rightleftharpoons 2\,Cl^-$	+1.36
$MnO_4^- + 8\,H^+ + 5\,e^- \rightleftharpoons Mn^{2+} + 4\,H_2O$	+1.51
$F_2 + 2\,e^- \rightleftharpoons 2\,F^-$	+2.87

More powerful oxidizing agent

More powerful reducing agent

Figure 907   The standard electrode potentials of common species in aqueous solution
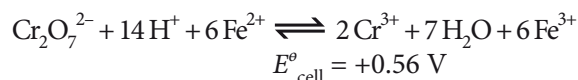
Standard electrode potentials allow predictions to be made about which reactions can theoretically occur. For example chlorine is a more powerful oxidant than bromine, as it has a more positive E^θ, so chlorine could oxidise bromide to bromine (because it 'wants the electrons more'), but bromine could not oxidise chloride to chlorine. Similarly, considering zinc and copper, zinc is the more powerful reducing agent, so it can reduce copper(II) ions to copper, but copper could not reduce zinc(II) ions to zinc.

A more formal way of considering this is to calculate the **cell potential** that would be generated by a particular redox reaction, if the half reactions were combined in an electrolytic cell. Consider the question of whether acidified potassium dichromate(VI) will oxidise iron(II) to iron(III). The equation for the reaction can be produced by combining the two half equations. That for the iron(II)/iron(III), as well as being multiplied by six, needs to be reversed to give the required equation, so the sign of its electrode potential is changed – note that the fact that the iron(III)/iron(II) equation needed multiplying by a factor, does not affect the magnitude of the electrode potential. Thus, you must not multiply the E^θ values by coefficients in front of balanced equations.
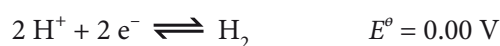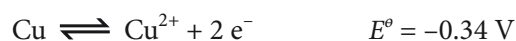
Half equations:

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightleftharpoons 2\,Cr^{3+} + 7\,H_2O$$
$$E^\theta = +1.33\ V$$

$$6\,Fe^{2+} \rightleftharpoons 6\,Fe^{3+} + 6\,e^-$$
$$E^\theta = -0.77\ V$$

Cell equation:

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,Fe^{2+} \rightleftharpoons 2\,Cr^{3+} + 7\,H_2O + 6\,Fe^{3+}$$
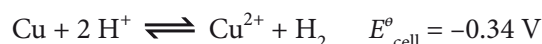$$E^\theta_{cell} = +0.56\ V$$

The cell potential is calculated by adding the electrode potentials. If the cell potential is positive, as in the above case, then the reaction could occur spontaneously (meaning it is capable of doing work in the form of electrical energy), if negative then it could not. As a further example, consider whether copper metal can reduce hydrogen ions to hydrogen gas:

Half equations:

$$Cu \rightleftharpoons Cu^{2+} + 2\,e^- \qquad E^\theta = -0.34\ V$$

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2 \qquad E^\theta = 0.00\ V$$

Cell equation:

$$Cu + 2\,H^+ \rightleftharpoons Cu^{2+} + H_2 \qquad E^\theta_{cell} = -0.34\ V$$

In this case the cell potential is negative so a spontaneous reaction cannot occur, which fits in with the experimental observation that copper does not dissolve in dilute acids. The reverse reaction (hydrogen reducing copper(II) ions to copper) is however spontaneous. In aqueous solution however the activation energy is too high, but it does occur if hydrogen is passed over heated copper(II) oxide.
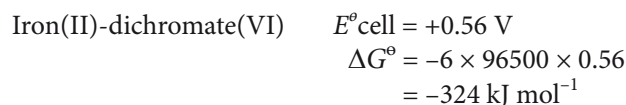
It must be remembered that predictions made using electrode potentials give no indication of the activation energy and so even the most favourable reaction may not occur in practice if it has a very high activation energy. These predictions, made either by considering which species is the more powerful oxidant/reductant, or by calculating E_{cell}, only give predictions about the reaction under standard conditions (T = 298 K, P = 101.3 kPa, all concentrations 1 mol dm^{-3}). If the electrode potentials are quite close (< 0.2 V different) then an equilibrium rather than complete reaction will result. It may then be possible to produce some product from an unfavourable reaction by altering the conditions in accordance with Le Chatelier's principle.

EXTENSION

Predictions about whether a reaction can occur or not can also result from calculating free energy change for a reaction. There is actually a relationship between E^θ_{cell} and $\Delta G^\ominus$:

$$\Delta G^\ominus = -nFE^\theta_{cell}$$

Where n is the number of electrons transferred and F the Faraday constant (the charge on 1 mole of electrons = 96,500 C mol^{-1}). From this it can be seen that if E^θ_{cell} is positive then $\Delta G^\ominus$ will be negative so a spontaneous reaction is possible and *vice versa*. Using the above examples:

Iron(II)-dichromate(VI) E^θcell = +0.56 V
$$\Delta G^\ominus = -6 \times 96500 \times 0.56$$
$$= -324\ kJ\ mol^{-1}$$

Copper - dilute acid E^θcell = -0.34 V
$$\Delta G^\ominus = -2 \times 96500 \times (-0.34)$$
$$= +66\ kJ\ mol^{-1}$$

The greater the value of E^θcell, the more negative will be the value of $\Delta G^\ominus$ and the more spontaneous the reaction.

Consider the general equilibrium:

$$Ox + n\,e^- \rightleftharpoons Red$$

EXTENSION

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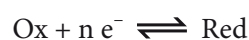
Increasing [Ox], or decreasing [Red] will shift the position of equilibrium to the right, reducing the number of electrons and hence making E^θ more positive. Similarly E^θ will become more negative if [Ox] is decreased or [Red] increased. In the case of metal/metal ion electrodes, the reduced form is the solid metal and so its concentration is fixed, the equilibrium being:

$$M^{n+} + n\,e^- \rightleftharpoons M$$
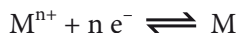
This means that increasing the concentration of the metal ions will make E^θ more positive and decreasing the concentration will make it more negative, and hence a better reducing agent. Consider a zinc-copper cell which is initially at standard conditions. The spontaneous reaction will be:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$
$$E^\theta_{cell} = +1.10\ V.$$
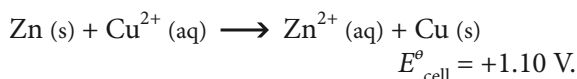
With time, $[Zn^{2+}]$ increases and so the zinc electrode becomes more positive. At the same time $[Cu^{2+}]$ decreases and so the copper electrode becomes more negative. As a result the cell potential decreases with time. Eventually the ratio $[Zn^{2+}]/[Cu^{2+}]$ becomes equal to K_c for the cell (= 10^{37}) and equilibrium is reached. As $\Delta G = 0$ at equilibrium, the voltage = 0 and the cell is 'dead'.

The effect of concentration on the potential of a half-cell is quantified in the **Nernst equation**:

$$E = E^0 - \frac{RT}{nF}\ln\left(\frac{a_{Ox}}{a_{Red}}\right)$$

Where again n is the number of electrons transferred and F the Faraday constant (96,500 C mol^{-1}), R the gas constant (8.314 J mol^{-1} K^{-1}) and T the absolute temperature (in K).

To save drawing the apparatus used, the cell can be represented by a shorthand notation, called a cell diagram. By convention this is written so that the oxidation half-reaction is placed on the left and the reduction half reaction placed on the right. A single vertical line (|) is placed between the metal and its ions and the salt bridge represented by two complete (||) or dashed (¦¦) lines. Taking the zinc-copper cell as an example:

Cell Diagram:
$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \;\vdots\vdots\; Cu^{2+}_{(aq)} \mid Cu_{(s)} \quad E^\theta_{cell} = +1.10V$$
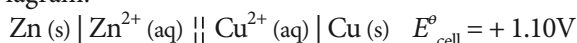
E^θ_{cell} is the difference between the two standard electrode potentials. The convention is to write E^θ_{cell} as (E^θ(right hand side) – E^θ(left hand side)); in this case (+0.34 – (–0.76)) = +1.10V. The positive sign of E^θ_{cell} indicates that the right hand (copper) electrode is the positive electrode.

Exercise

1. Which one of the following is not a condition for the standard hydrogen electrode?

    A   The temperature must be 298K.
    B   The pressure of hydrogen must be 101.3 kPa.
    C   The concentration of hydrogen ions in solution must be 1 mol dm^{-3}.
    D   The concentration of hydrogen gas in solution must be 1 mol dm^{-3}.

2. The standard electrode potentials of nickel and lead are:

    $$Ni^{2+} + 2e^- \rightleftharpoons Ni \qquad E^\theta = -0.23\ V$$
    $$Pb^{2+} + 2e^- \rightleftharpoons Pb \qquad E^\theta = -0.13\ V$$

    What is the cell potential for the reaction $Ni^{2+} + Pb \rightleftharpoons Ni + Pb^{2+}$?
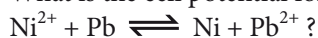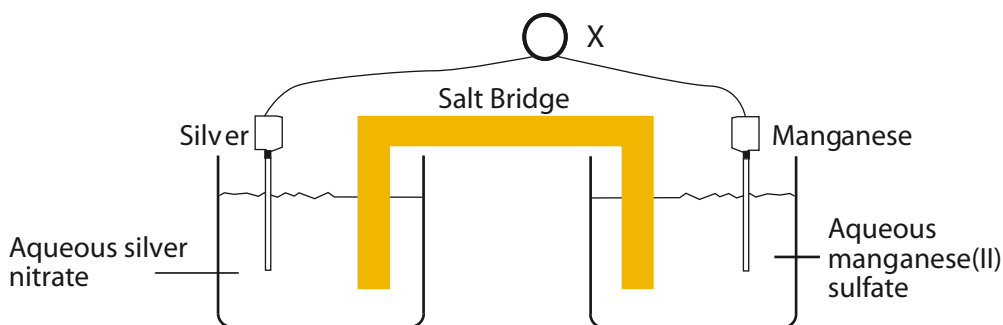
    A   +0.36 V
    B   +0.1 V
    C   –0.1 V
    D   –0.36 V

3. A number of possible oxidising agents are suggested to oxidise bromide ions to bromine. Given the information below, which is the most likely to suceed?

    $$\tfrac{1}{2}\,Br_2 + e^- \rightleftharpoons Br^- \qquad E^\theta = +1.09\ V$$

    A   Iodate(V) ions
         ($2\,IO_3^- + 12\,H^+ + 10\,e^- \rightleftharpoons I_2 + 6\,H_2O$
         $E^\theta = +1.19\ V$)
    B   Copper ions
         ($Cu^{2+} + 2\,e^- \rightleftharpoons Cu$
         $E^\theta = +0.34\ V$)
    C   Phosphoric acid
         ($H_3PO_4 + 2\,H^+ + 2\,e^- \rightleftharpoons H_3PO_3 + H_2O$
         $E^\theta = -0.28\ V$)
    D   Hydrogen gas
         ($H_2 + 2\,e^- \rightleftharpoons 2\,H^-$
         $E^\theta = -2.25\ V$)

4.

The apparatus above can be used to compare the electrode potentials of silver and manganese. According to reference sources, the standard electrode potentials of these metals are:

$$Mn^{2+} + 2e^- \rightleftharpoons Mn \qquad E^\theta = -1.18 \text{ V}$$
$$Ag^+ + e^- \rightleftharpoons Ag \qquad E^\theta = +0.80 \text{ V}$$

a) In order for the comparison to be of standard electrode potentials, what conditions must be imposed?

b) If the experiment was to determine the standard electrode potential of manganese, what must replace the silver/silver nitrate electrode?

c) What instrument is the instrument labelled '**X**' in the diagram?

d) What could be used as a 'salt bridge'?

e) Supposing the silver and manganese electrodes are joined directly with a wire:

   i. In which direction will the electrons flow?

   ii. Describe the changes that will take place at the silver electrode.

   iii. Describe the changes that will take place at the manganese electrode.

   iv. In what direction will the anions and cations in the salt bridge move?

f) Give the shorthand notation for the cell.

g) What would you expect the cell potential to be? (Ensure that the sign corresponds to your notation in f). What is the corresponding cell reaction?

h) Calculate ΔG^θ for this reaction and state what this indicates about the spontaneity of the reaction.

i) If the silver nitrate solution were diluted, would you expect the cell potential to increase or decrease? Explain your answer.

9.5 ELECTROLYTIC CELLS

9.5.1 Describe, using a diagram, the essential components of an electrolytic cell.

9.5.2 State that oxidation occurs at the positive electrode (anode) and reduction occurs at the negative electrode (cathode).

9.5.3 Describe how current is conducted in an electrolytic cell.

9.5.4 Deduce the products of the electrolysis of a molten salt.

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In **electrolysis** electrical energy is used to bring about a non-spontaneous redox reaction. This is done by passing an electric current through a liquid containing ions, known as an **electrolyte**. In contrast to metals, the current in electrolytes is carried by the movement of ions rather than the movement of electrons. The solid conductors inserted into the liquid are called electrodes, the one with a positive charge is called the **anode** (because it attracts anions) and the one with the negative charge is called the **cathode.** When the anions reach the anode they lose electrons and are therefore oxidized (LEO). Similarly when the cations reach the cathode they gain electrons and are therefore reduced (GER). This process is illustrated in Figure 909.

Consider the electrolysis of molten sodium chloride. The negative chloride ions are attracted to the positive anode, where they lose electrons and are therefore oxidized to chlorine gas:

$$2\,Cl^- \text{ (l)} \longrightarrow Cl_2 \text{ (g)} + 2\,e^-$$
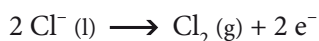
The positive sodium ions are attracted to the negative cathode, where they gain electrons and are therefore reduced to sodium metal:

$$Na^+ \text{ (l)} + e^- \longrightarrow Na \text{ (l)}$$
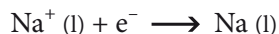
Electrolysis of a molten electrolyte is often used to obtain reactive metals from their ores.

Exercise	9.5

1. Which one of the following statements about electrolysis is correct?

    A Oxidation always occurs at the anode because oxygen is often evolved here.
    B Oxidation always occurs at the anode because it removes electrons from the electrolyte.
    C Oxidation always occurs at the cathode because hydrogen is often evolved here.
    D Oxidation always occurs at the cathode because it donates electrons to the electrolyte.

2. By what means is an electrical current carried in a molten salt?

    A By the movement of anions only.
    B By the movement of cations only.
    C By the movement of both anions and cations.
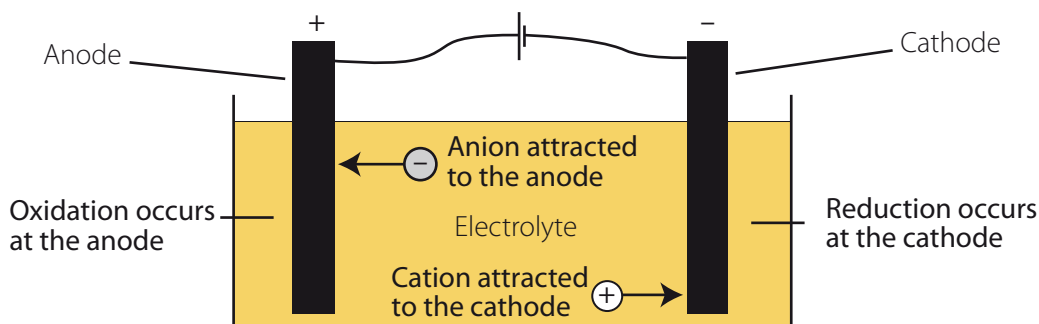   D By the movement of electrons.

Figure 909   A diagrammatic representation of electrolysis

3. When molten lead(II) bromide is electrolysed,

    A   the lead ions gain electrons at the anode to form lead.
    B   the lead ions gain electrons at the cathode to form lead.
    C   the lead ions lose electrons at the anode to form lead.
    D   the lead ions lose electrons at the cathode to form lead.

4. This question concerns the passage of electricity through sodium chloride.

    a)   Is the bonding in sodium chloride metallic, ionic or covalent?
    b)   State whether the following would conduct electricity.
         i)   Solid sodium chloride
         ii)   Molten sodium chloride
         iii) Aqueous sodium chloride

    c)   What names are given to the following?
         i)   Passing an electric current through a liquid containing ions.
         ii)   The liquid containing ions.
         iii) The solid conductors put into the liquid.

    d)   A D.C. current is used and particular names are given to the solid conductors attached to the positive and negative terminals of the power supply. What are these names?
    e)   Oxidation occurs on the surface of one of the solid conductors. Which one?

5. This question concerns the electrolysis of copper chloride.

    a)   Solid copper chloride does not conduct electricity? Explain why.
    b)   Give two ways in which it can be made to conduct.
    c)   Write a balanced half equation for the reaction that occurs at the anode.
    d)   What would be observed on the surface of this electrode?
    e)   Write a balanced half equation for the reaction that occurs at the cathode.
    f)   What would be observed on the surface of this electrode?
    g)   Does e) represent an oxidation or a reduction reaction? Explain why.

19.2 ELECTROLYSIS (AHL)

19.2.1 Predict and explain the products of electrolysis of aqueous solutions.

19.2.2 Determine the relative amounts of the products formed during electrolysis.

19.2.3 Describe the use of electrolysis in electroplating.

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AHL

When a molten salt is electrolysed the cations are attracted to the cathode where they undergo reduction and the anions are attracted to the anode where they undergo oxidation. If the electrolyte is an aqueous solution, then the water present can also be oxidised or reduced. At the cathode, the water can be reduced to hydrogen gas and this will occur unless the electrolyte contains the ions of a metal low in the electrochemical series (with $E^{\ominus} > 0$), such as silver and copper, or other easily reduced cations.

$$2\,H_2O\,(l) + 2\,e^- \longrightarrow H_2\,(g) + 2\,OH^-\,(aq)$$

Alternatively this can be regarded as the reduction of hydrogen ions produced from the dissociation of water:

$$2\,H^+\,(aq) + 2\,e^- \longrightarrow H_2\,(g)$$
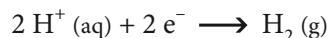
Similarly at the anode the water can be oxidised to oxygen gas and this will occur unless the electrolyte contains easily oxidised anions, such as bromide and iodide ions, with $E^{\ominus} < 1.23$ V, the $E^{\ominus}$ for the oxygen/water half-cell.

$$2\,H_2O\,(l) \longrightarrow O_2\,(g) + 4\,H^+\,(aq) + 4\,e^-$$
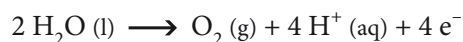
Again this may regarded as the oxidation of hydroxide ions produced from the dissociation of water:

$$4\,OH^-\,(aq) \longrightarrow O_2\,(g) + 2\,H_2O\,(l) + 4\,e^-$$
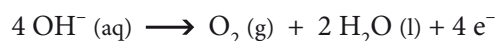
Usually in electrolysis the electrodes are made from an inert conductor, such as graphite or platinum. If however the anode is made from a metal that is not inert, such as copper, then the anode itself may be oxidised and dissolve

into the solution as the E^θ for this half cell (E^θ Cu^{2+}/Cu = +0.34 V) is less than that for the oxygen/water half-cell.

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

Hence, if aqueous copper sulfate is electrolysed between copper electrodes, copper is in effect transferred from the anode (which decreases in mass) to the cathode (which increases in mass). This process is used to purify copper for use as an electrical conductor. The cathode becomes coated in a layer of the metal, a process called electroplating. Similarly electrolysis of a solution containing silver ions (or the ions of some other easily reduced metal) will result in the metal being deposited on the cathode and this process is often used to electroplate less reactive metals on to cathodes made of more reactive metals, either for decoration or protection against corrosion.

When considering the products from the electrolysis of an aqueous solution the possible reactions:

Cathode - formation of the metal or formation of hydrogen,
Anode - formation of the non-metal, formation of oxygen or oxidation of the electrode,

must be considered and the most energetically favourable will take place. For the cathode this will be the one with the most positive; for the anode the one with the most negative electrode potential. For most common electrolytes:

**Cathode** - hydrogen is formed unless Cu^{2+} or Ag^+ are present,
Anode - oxygen is formed unless Br^- or I^- are present.

This is illustrated by the examples of the products from the electrolysis of aqueous solutions given in Figure 910.

Aqueous electrolyte	Product at the **cathode**	Product at the **anode**
Copper(II) bromide	Copper	Bromine
Sodium iodide	Hydrogen	Iodine
Silver nitrate	Silver	Oxygen
Potassium sulfate	Hydrogen	Oxygen
Copper sulfate	Copper	Copper(II) ions (if Cu anode)

Figure 910   The products from the electrolysis of some aqueous solutions

Pure water cannot of course be electrolysed because the concentration of ions is too low to allow it to conduct the current. If, however, an electrolyte producing ions that are the same as those of water, or less easily oxidised/reduced (such as aqueous sulfuric acid, aqueous sodium hydroxide or potassium sulfate - see Figure 909) is added, then hydrogen is produced at the cathode and oxygen at the anode. The volume of hydrogen produced at the cathode is twice that of oxygen produced at the anode because the production of one mole of oxygen gas requires twice the number of electrons that are needed for the production of one mole of hydrogen gas.
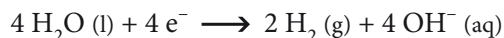
$$4\,H_2O_{(l)} + 4\,e^- \longrightarrow 2\,H_2{}_{(g)} + 4\,OH^-{}_{(aq)}$$
4 moles of electrons produces two moles of H_2 gas
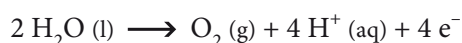
$$2\,H_2O_{(l)} \longrightarrow O_2{}_{(g)} + 4\,H^+{}_{(aq)} + 4\,e^-$$
4 moles of electrons are given off when one mole of O_2 gas is produced

In effect the energy from the electric current is being used to split water into its component elements.

In some cases, when there is little difference in the ease of discharge of the ion and water, the concentration of the electrolyte may be the determining factor. The E^θ for the oxidation of chloride ions (+1.36 V) is not much greater than that for the oxidation of water (+1.23 V). In dilute aqueous sodium chloride for example, the major product of electrolysis at the anode is oxygen. If however a saturated solution of sodium chloride is used, then E^θ for the oxidation of chloride ions falls and the major product is chlorine. The electrolysis of sodium chloride, both molten and aqueous, is very important industrially and is covered in considerable detail in Section C.12.

The amount of product that results from electrolysis will depend upon:

- The number of electrons required to produce one mole of product.
- The magnitude of the **current** (the rate of flow of electrons).
- The time for which the current is passed.

For example if the same current is passed for the same time through an aqueous solution containing silver ions and an aqueous solution containing copper ions, then the amount of metal produced at the cathode of the silver cell would be twice as large as that produced in the copper cell, because the reduction of a silver ion requires one electron whereas the reduction of a copper ion requires two electrons:

$$Ag^+ + e^- \longrightarrow Ag \qquad Cu^{2+} + 2\,e^- \longrightarrow Cu$$

To produce the same amount of copper would require doubling the number of electrons passed, either by doubling the current or doubling the time it was passed for. The mass of product would of course also depend on the molar masses of the metals concerned.

EXTENSION

The amount of product can be calculated knowing the current and the time for which it is passed. The unit of electrical charge is the Coulomb (C). The number of Coulombs passed during electrolysis may be calculated by multiplying the current passing (in Amps) by the length of time for which it is passed (in seconds)

Charge (in Coulombs) = Current (in Amps) × Time (in secs)

The charge carried by one mole of electrons can be found by multiplying the charge on the electron (1.60×10^{-19} C) by the Avogadro constant (6.02×10^{23} mol^{-1}). The result (96500 C mol^{-1}) is known as the **Faraday constant**. Knowing the charge passed and this constant, the number of moles of electrons may be calculated:

$$\text{Amount of electrons} = \frac{\text{Charge passed (in C)}}{96\ 500}$$

The amount of product formed can then be calculated from the balanced equation for the reaction at the electrode, which gives the ratio of the amount of electrons to the amount of product.
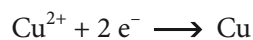
Example

Find the mass of copper produced at the cathode by passing a current of 3.00A through aqueous copper(II) sulfate for exactly 2 hours.

Solution

Charge (in C) = Current (in Amps)× Time (in sec)
$$= 3.00 \times (2 \times 60 \times 60)$$
$$= 21600\ \text{C}$$

$$\text{Amount of electrons} = \frac{\text{Charge passed (in C)}}{96\ 500}$$
$$= \frac{21\ 600}{96\ 500}$$
$$= 0.2238\ \text{moles}$$

$$Cu^{2+} + 2\ e^{-} \longrightarrow Cu$$

Amount of Cu = ½ Moles of electrons
$$= \tfrac{1}{2} \times 0.2238$$
$$= 0.1119\ \text{moles}$$

Mass of Cu $\quad = n \times M$
$$= 0.1119 \times 63.55$$
$$= 7.11\ \text{g}$$

Exercise 19.2

1. Which one of the following salts would give the same products irrespective of whether the molten salt or the aqueous solution is electrolysed?

   A   Magnesium bromide
   B   Copper(II) sulfate
   C   Magnesium sulfate
   D   Copper(II) bromide

2. An electric current is passed through two electrolysis cells in series. In the first, copper is deposited on the cathode from aqueous copper(II) sulfate. In the second, silver is deposited on the cathode from aqueous silver nitrate. After a certain length of time the mass of the copper cathode has increased by 1 g. Given that the relative atomic masses of silver and copper are 107.87 and 63.55 respectively, what will the increase in mass of the silver electrode be?

   A $\dfrac{2 \times 107.87}{63.55}$

   B $\dfrac{2 \times 63.55}{107.87}$

   C $\dfrac{107.87}{2 \times 63.55}$

   D $\dfrac{63.55}{2 \times 107.87}$

3. When an aqueous solution of a metal salt is electrolysed so that the metal is deposited on the cathode, which one of the following will not affect the increase in mass of the cathode, if the other variables are fixed?

   A   The charge on the ion.
   B   The molar mass of the metal.
   C   The charge passed.
   D   The potential difference applied.

4. With aqueous solutions containing ions, the water may be oxidised or reduced in preference to the ions present. Consider the electrolysis of a concentrated aqueous solution of calcium chloride.

a) Which ion(s) will be attracted to the anode?

b) Does oxidation or reduction occur at the anode?

c) Which will be changed most easily, the ion from the calcium chloride or the water?

d) Write a balanced equation for the reaction at the anode.

e) What would be seen at the anode?

f) Describe how diluting the electrolyte may affect the product at the anode

g) Which ion(s) will travel to the cathode?

h) Which ion will be changed most easily, the ion from the calcium chloride or the water?

i) Write a balanced equation for the reaction at the cathode.

j) What would be seen at the cathode?

k) What would the aqueous solution eventually change into?

l) As electrical energy is required for this change, what is the probable sign of $\Delta G^\ominus$ for the reaction?

EXTENSION

5. When aqueous copper(II) sulfate is electrolysed using copper electrodes, copper is transferred from the anode to the cathode. A current of 0.200 A is passed through such a cell for exactly 5 hours.

a) The value of the Faraday constant is 96500 C mol^{-1}. What does the Faraday constant represent?

b) What is the total charge passed through the cell?

c) Given that the molar mass of copper is 63.55 g mol^{-1}, calculate the increase in mass of the cathode.