9701 Chemistry Syllabus requirements:

6. Electrochemistry

Learning outcomes

Candidates should be able to:

- calculate oxidation numbers of elements in compounds and ions
- use changes in oxidation numbers to help balance chemical equations
- explain and use the terms redox, oxidation, reduction and disproportionation in terms of electron transfer and changes in oxidation number
- 4 explain and use the terms oxidising agent and reducing agent 5 use a Roman numeral to indicate the magnitude of the oxidation number of an element

A simple definition of oxidation is 'gain of oxygen by an element'. For example, when magnesium reacts with oxygen, the magnesium combines with oxygen to form magnesium oxide. Magnesium has been oxidised.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

A simple definition of reduction is 'loss of oxygen'. When copper(II) oxide reacts with hydrogen, this is the equation for the reaction:

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l)$$

Copper(II) oxide loses its oxygen. Copper(II) oxide has been reduced. But if we look carefully at the copper oxide / hydrogen equation, we can see that oxidation is also taking place. The hydrogen is gaining oxygen to form water.

The hydrogen has been oxidised.
We can see that reduction and oxidation have taken place together.

Oxidation Is Loss of electrons.

Reduction Is Gain of electrons.

The initial letters shown in bold capitals spell **OIL RIG**. This may help you to remember these two definitions!

Oxidation and reduction always take place together. We call the reactions in which this happens redox reactions.

Redox reactions are very important. For example, one redox reaction

- **photosynthesis** – provides food for the entire planet, and another one
- **respiration** – keeps you alive.

We can also define reduction as addition of hydrogen to a compound and oxidation as removal of hydrogen from a compound. This is often seen in the reaction of organic compounds.

There are two other ways of finding out whether or not a substance has been oxidised or reduced during a chemical reaction: electron transfer changes in oxidation number.

Half-equations

We can extend our definition of redox to include reactions involving ions. Sodium reacts with chlorine to form the ionic compound sodium chloride:

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

We can divide this reaction into two separate equations, one showing oxidation and the other showing reduction. We call these **half-equations**.
When sodium reacts with chlorine:

Each sodium atom loses one electron from its outer shell. Oxidation is loss of electrons (**OIL**). The sodium atoms have been oxidised.

$$Na \rightarrow Na^+ + e^-$$

This half-equation shows that sodium is oxidised. We could also write this half-equation as:

$$Na - e^- \rightarrow Na^+$$

Each chlorine atom gains one electron to complete its outer shell. Reduction is gain of electrons (RIG). The chlorine atoms have been reduced.

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

This half-equation shows chlorine being reduced. There are two chlorine atoms in a chlorine molecule, so two electrons are gained.

In another example, iron reacts with copper(II) ions, **Cu^{2+},** in solution to form iron(II) ions, **Fe^{2+}**, and copper.

$$Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$$

Each iron atom loses two electrons to form an Fe^{2+} ion. The iron atoms have been oxidised.

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

We could also write this half-equation as:

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

Each copper(II) ion gains two electrons. The copper ions have been reduced.

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

Oxidation number rules

- The oxidation number of any uncombined element is zero.
- For example, the oxidation numbers of each atom in S_8, Cl_2 and Zn is zero.
- In compounds many atoms or ions have fixed oxidation numbers:

  Group 1 elements are always **+1**
  Group 2 elements are always **+2**
  Fluorine is always **−1**
  Hydrogen is **+1** (except in metal hydrides such as **NaH**, where it is −1)
  Oxygen is **−2** (except in peroxides, where it is −1, and in **F_2O**, where it is +2).

- The oxidation number of an element in a monatomic ion is always the same as the charge.
  For example,

  Cl^- is −1, Al^{3+} is +3.

- The sum of the oxidation numbers in a compound is zero.
- The sum of the oxidation numbers in an ion is equal to the charge on the ion.
- In either a compound or an ion, the more electronegative element is given the negative oxidation number.

Redox and oxidation number

We can define oxidation and reduction in terms of the oxidation number changes of particular atoms during a reaction:

Oxidation is an increase in oxidation number.

Reduction is a decrease in oxidation number.

When tin reacts with nitric acid, the oxidation numbers of each atom of tin and nitrogen change as shown below.

reduction

$$Sn + 4HNO_3 \rightarrow SnO_2 + 4NO_2 + 2H_2O$$

oxidation numbers 0 +5 +4 +4

oxidation

Each tin atom (Sn) has increased in ox. no. by +4: tin has been oxidised.

Each nitrogen atom has decreased in ox. no. by −1: nitrogen has been reduced. The ox. no. of each oxygen atom is unchanged at −2.
The ox. no. of each hydrogen atom is unchanged at +1.

Oxygen and **hydrogen** are neither **oxidised nor reduced**.

In this reaction, **nitric acid** is acting as an **oxidising agent** because it increases the oxidation number of another atom.

In this reaction, **tin** is acting as a **reducing agent** because it decreases the oxidation number of another atom.

Oxidising agents and reducing agents

An oxidising agent (oxidant) is a substance which brings about oxidation by removing electrons from another atom or ion.

An oxidising agent increases the oxidation number of another atom or ion.

When this happens, the oxidation number of the oxidising agent decreases. Typical oxidising agents are oxygen, chlorine and potassium manganate(VII).

A reducing agent (reductant) is a substance that brings about reduction by donating (giving) electrons to another atom or ion. A reducing agent decreases the oxidation number of another atom or ion.

When this happens, the oxidation number of the reducing agent increases.

Typical reducing agents are hydrogen, potassium iodide and reactive metals such as aluminium.

Since oxidation and reduction occur together, in every redox reaction there must be an oxidising agent and a reducing agent. For example, in the reaction given by the equation:

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

- **$MnO4^-$** is the oxidising agent because the oxidation number of Mn decreases from **+7 to +2.**
- **$MnO4^-$** has increased the oxidation state of iron from **+2 to +3**.
- **Fe^{+2}** is the reducing agent because the oxidation number of **Fe** increases from **+2 to +3.**
- **Fe^{+2}** has decreased the oxidation state of **Mn** in **$MnO4^-$** from **+7 to +2**.

Disproportionation

The element chlorine (**Cl_2**, oxidation number = **0**) undergoes a type of redox reaction called disproportionation when it reacts with **alkali**.

Disproportionation can be thought of as a 'self-reduction / oxidation' reaction. When chlorine reacts with dilute alkali, some chlorine atoms are reduced and some are oxidised in the same reaction.

The actual reaction that takes place depends on the temperature. When we add chlorine to cold aqueous sodium hydroxide the following disproportionation reaction takes place:

$$\mathbf{Cl_2(aq) + 2NaOH(aq) \rightarrow NaCl(aq) + + H_2O(l)}$$

The ionic equation for this redox reaction can be split into two half-equations, showing the reduction and oxidation.

The reduction reaction is:

Cl2 + e− → Cl− ox. no.
0 − 1

The change in oxidation number of chlorine is −1. The oxidation reaction is:

Cl2 + 2OH− → ClO− + H2O + e−
ox. no. 0 + 1

The change in oxidation number of chlorine is +1. The oxidation numbers are balanced so there are equal numbers of moles of Cl− and ClO− in the equation.