Topic 2.4

REDOX REACTIONS

Oxidation and Reduction
Oxidising and Reducing Agents
Redox Reactions

OXIDATION AND REDUCTION

1. Simple half-equations

In inorganic chemistry, oxidation and reduction are best defined in terms of electron transfer.

Oxidation is the loss of electrons. When a species loses electrons it is said to be oxidised.

Eg $Na \rightarrow Na^+ + e$ (each sodium atom loses one electron)

$2I^- \rightarrow I_2 + 2e$ (each iodide ion loses one electron, so two in total)

Reduction is the gain of electrons. When a species gains electrons it is said to be reduced.

Eg $Cl_2 + 2e \rightarrow 2Cl^-$ (each chlorine atom gains one electron, so two in total)

$Al^{3+} + 3e \rightarrow Al$ (each aluminium ion gains three electrons)

Processes which show the gain or loss of electrons by a species are known as **half-equations**. They show simple oxidation or reduction processes.

2. Oxidation numbers

The oxidation number of an atom is the charge that would exist on an individual atom if the bonding were completely ionic.

In simple ions, the oxidation number of the atom is the charge on the ion:
Na^+, K^+, H^+ all have an oxidation number of +1.
Mg^{2+}, Ca^{2+}, Pb^{2+} all have an oxidation number of +2.
Cl^-, Br^-, I^- all have an oxidation number of -1.
O^{2-}, S^{2-} all have an oxidation number of -2.

In molecules or compounds, the sum of the oxidation numbers on the atoms is zero.
SO_3; oxidation number of S = +6, oxidation number of each O = -2.
+6 + 3(-2) = 0
H_2O_2; oxidation number of H = +1, oxidation number of O = -1.
2(+1) + 2(-1) = 0
SCl_2; oxidation number of S = +2, oxidation number of Cl = -1.
2 + 2(-1) = 0

In complex ions, the sum of the oxidation numbers on the atoms is equal to the overall charge on the ion.
SO_4^{2-}; oxidation number of S = +6, oxidation number of O = -2.
$+6 + 4(-2) = -2$
PO_4^{3-}; oxidation number of P = +5, oxidation number of O = -2.
$(+5) + 4(-2) = -3$
ClO^-; oxidation number of Cl = +1, oxidation number of O = -2.
$+1 +(-2) = -1$

In elements in their standard states, the oxidation number of each atom is zero.
In Cl_2, S, Na and O_2 all atoms have an oxidation number of zero.

Many atoms, such as S, N and Cl, can exist in a variety of oxidation states. The oxidation number of these atoms can be calculated by assuming that the oxidation number of the other atom is fixed (usually O at -2).

All group I atoms always adopt the +1 oxidation state in their compounds.
All group II atoms adopt the +2 oxidation state in their compounds.
Aluminium always adopts the +3 oxidation state in its compounds.
Fluorine always adopts the -1 oxidation state in its compounds.
Hydrogen adopts the +1 oxidation state in its compounds unless it is bonded to a metal, Silicon or boron in which case it adopts the -1 oxidation state.
Oxygen adopts the -2 oxidation state in its compounds unless it is bonded to a group I or group II metal or hydrogen (with which it sometimes adopts the -1 oxidation state), or with fluorine (with which it adopts the +2 oxidation state).

The oxidation numbers of all other atoms in their compounds can vary.

By following the above guidelines, the oxidation number of any atom in a compound or ion can be deduced.

During oxidation and reduction, the oxidation numbers of atoms change.

If an atom is oxidized, its oxidation number increases
(ie it becomes more +ve or less –ve)
If an atom is reduced, its oxidation number decreases
(ie it becomes less +ve or more –ve)

These ideas can be summarized in the following table:

Oxidation	Loss of electrons	Increase in oxidation number
Reduction	Gain of electrons	Decrease in oxidation number

3. More complex half-equations

Many oxidation and reduction processes involve complex ions or molecules and the half-equations for these processes are more complex. In such cases, oxidation numbers are a useful tool:

There are two ways to balance half-equations:

Method 1: (this shows you straight away whether oxidation or reduction is taking place)

- Identify the atom being oxidised or reduced, and make sure there are the same number of that atom on both sides (by balancing)

- insert the number of electrons being gained or lost:
  (on the left if reduction, on the right if oxidation)
  No of electrons gained/lost =
  change in oxidation number x number of atoms changing oxidation number

- balance O atoms by adding water

- balance H atoms by adding H^+

Example: Write a balanced half-equation for the process $SO_3^{2-} \rightarrow SO_4^{2-}$

- there is one sulphur on each side, so the S is already balanced
- the oxidation number of the S is increasing from +4 to +6, so two electrons are being lost (inserted on the right):
  $SO_3^{2-} \rightarrow SO_4^{2-} + 2e$
- there are three O atoms on the left and four on the right, so one water is needed on the left:
  $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2e$
- there are two H atoms on the left and none on the right, so two H ions are needed on the right:
  $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e$

The oxidation number of the S is increasing and electrons are being lost. It is an oxidation process.

Method 2: (this does not use oxidation numbers and is easier in more complex processes)

- Identify the atom being oxidised or reduced, and make sure there are the same number of that atom on both sides (by balancing)

- balance O atoms by adding water

- balance H atoms by adding H^+

- add the necessary number of electrons to ensure the charge on both sides is the same

Example: Write a balanced half-equation for the process $H_2SO_4 \rightarrow H_2S$

- there is one sulphur on each side, so the S is already balanced
- there are four O atoms on the left and none on the right, so four waters are needed on the right:
  $H_2SO_4 \rightarrow H_2S + 4H_2O$
- there are two H atoms on the left and ten on the right, so eight H ions are needed on the left:
  $H_2SO_4 + 8H^+ \rightarrow H_2S + 4H_2O$
- the total charge on the left is +8 and on the right is 0. So eight electrons must be added to the left to balance the charge:
  $H_2SO_4 + 8H^+ + 8e \rightarrow H_2S + 4H_2O$

The oxidation number of the S is decreasing and electrons are being gained. It is a reduction process.

4. Redox reactions

Half-equations consider gain and loss of electrons, but in fact electrons cannot be created or destroyed; they can only be transferred from species to species. Gain of electrons by one species necessarily involves loss of electrons by another. Oxidation and reduction thus always occur simultaneously; an oxidation is always accompanied by a reduction and vice versa. Any reaction consisting of the oxidation of one species and the reduction of another is known as a **redox** reaction.

A redox reaction can be derived by combining an oxidation half-equation with a reduction half-equation in such a way that the total number of electrons gained is equal to the total number of electrons lost.

Eg $H_2SO_4 + 8H^+ + 8e \rightarrow H_2S + 4H_2O$ - reduction
$2I^- \rightarrow I_2 + 2e$ – oxidation
(the oxidation half-equation must be multiplied by 4 to equate the electrons)
$8I^- \rightarrow 4I_2 + 8e$
overall: $H_2SO_4 + 8H^+ + 8I^- \rightarrow H_2S + 4H_2O + 4I_2$ - redox

Eg $Al^{3+} + 3e \rightarrow Al$ - reduction
$2O^{2-} \rightarrow O_2 + 4e$ - oxidation
(the reduction half-equation must be multiplied by 4 and the oxidation half-equation by 3 to equate the electrons)
$4Al^{3+} + 12e \rightarrow 4Al$
$6O^{2-} \rightarrow 3O_2 + 12e$
overall: $4Al^{3+} + 6O^{2-} \rightarrow 4Al + 3O_2$ - redox

5. Oxidising agents and reducing agents

The species which is reduced is accepting electrons from the other species and thus causing it to be oxidised. It is thus an **oxidising agent**.
H_2SO_4, Al^{3+} and Cl_2 are all oxidising agents.

The species which is oxidised is donating electrons to another species and thus causing it to be reduced. It is thus a **reducing agent**.
Na, O^{2-}, I^- and $S_2O_3^{2-}$ are all reducing agents.

A redox reaction can thus be described as a transfer of electrons from a reducing agent to an oxidising agent.

Eg $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$
Half-equations: $I_2 + 2e \rightarrow 2I^-$ (reduction)
$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e$ (oxidation)

I_2 is the oxidising agent; $S_4O_6^{2-}$ is the reducing agent.

Eg $H_2SO_4 + 8H^+ + 8I^- \rightarrow H_2S + 4H_2O + 4I_2$
Half-equations: $H_2SO_4 + 8H^+ + 8e \rightarrow H_2S + 4H_2O$ (reduction)
$2I^- \rightarrow I_2 + 2e$ (oxidation)

H_2SO_4 is the oxidising agent, I^- is the reducing agent

6. Disproportionation

There are many substances which readily undergo both oxidation and reduction, and which can therefore behave as both oxidising agents and reducing agents. H_2O_2 and ClO^- are two examples:

Eg $H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$ reduction
$H_2O_2 \rightarrow O_2 + 2H^+ + 2e$ oxidation

Eg $ClO^- + 2H^+ + 2e \rightarrow Cl^-$ reduction
$ClO^- \rightarrow ClO_3^- + 4H^+ + 4e$ oxidation

Species such as these are capable of undergoing oxidation and reduction simultaneously. **The simultaneous oxidation and reduction of the same species is known as disproportionation**.

Disproportionation reactions are special examples of redox reactions.

Eg
$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$ reduction
$H_2O_2 \rightarrow O_2 + 2H^+ + 2e$ oxidation
$2H_2O_2 \rightarrow 2H_2O + O_2$ disproportionation

oxidation numbers: +1 -2 0

Eg
$(ClO^- + 2H^+ + 2e \rightarrow Cl^-) \times 2$ reduction
$ClO^- \rightarrow ClO_3^- + 4H^+ + 4e$ oxidation
$3ClO^- \rightarrow 2Cl^- + ClO_3^-$ disproportionation

oxidation numbers +1 $\rightarrow$ -1 +5