Redox

The term REDOX stands for **RED**UCTION-**OXID**ATION.
Oxidation can be defined as gain of oxygen or loss of hydrogen.
Reduction can be defined as loss of oxygen or gain of hydrogen.

The most important definition is given in terms of electrons.

OXIDATION is LOSS of ELECTRONS
REDUCTION is GAIN of ELECTRONS

One way of accounting for electrons is to use **OXIDATION NUMBERS**.

Oxidation number

The oxidation number of an atom shows the number of electrons which it has lost or gained as a result of forming a compound

e.g. Fe^{2+} needs to gain two electrons for it to become neutral iron atom therefore its oxidation number is +2.

Using oxidation numbers it is possible to decide whether redox has occurred.
Increase in oxidation number is oxidation.
Decrease in oxidation number is reduction.

We can apply a series of rules to assign an oxidation state to each atom in a substance.

Oxidation Number Rules

1. The oxidation number of an uncombined element is 0.

2. Certain elements have fixed oxidation numbers.
   All group 1 elements are +1.
   All group 2 elements are +2.
   Hydrogen is always +1 except in hydrides.
   Fluorine is always –1.
   Oxygen is always –2 except in peroxides, superoxides and when combined with fluorine.
   Chlorine is always –1 except when combined with fluorine and oxygen.

3. The sum of oxidation numbers in a compound is always 0.

4. The sum of oxidation numbers in an ion always adds up to the charge on the ion.

Examples

1. The oxidation number of S in H_2SO_4

H_2	S	O_4	
2 x +1	?	4 x -2	= 0
+2	?	-8	= 0
+2	+6	-8	= 0
	s = +6		

2. The oxidation number of S in $S_2O_8^{2-}$

S_2	O_4	
?	8 x -2	= -2
?	-16	= -2
+14	-16	= -2
S = +7		

3. The oxidation number of Cl in $NaClO_3$.

Na	Cl	O_3	
+1	?	3 x -2	= 0
+1	?	-6	= 0
+1	+5	-6	= 0
	Cl = +5		

4. The oxidation number of Mn in MnO_4^-

Mn	O_4	
?	4 x -2	= -1
?	-8	= -1
+7	-8	= -1
Mn = +7		

Redox Reactions

When magnesium is placed into a solution of copper sulphate, a reaction occurs which in simple terms is called a "**displacement reaction**".

Chemical equation: $Mg + CuSO_4 \rightarrow MgSO_4 + Cu$

Ionic equation: $Mg_{(s)} + Cu^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$

The copper in this reaction is taking electrons from the magnesium.

The copper gains electrons - it is **REDUCED**

The magnesium loses electrons - it is **OXIDISED**

So this is a **REDOX** reaction.

Whenever one substance gains an electron another substance must lose an electron, so reduction and oxidation always go together.

Oxidising and reducing reagents

An oxidising agent causes another material to become oxidised. In the above example of adding magnesium to copper sulphate, the magnesium is oxidised.
Since the copper ions in the copper sulphate cause this oxidation, they are the **oxidising agent**.
In the same way the Mg causes the reduction of copper ions so it is the **reducing agent**.

$$\underbrace{Mg_{(s)}}_{\text{reducing agent}} + \underbrace{Cu^{2+}_{(aq)}}_{\text{oxidising agent}} \longrightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$$

In this example the oxidising agent (copper ions) is reduced and the reducing agent (magnesium) is oxidised.

This always happens with redox reactions:- in a redox reaction the oxidising agent is reduced and the reducing agent is oxidised.

REDUCING AGENT + MATERIAL

The reducing agent loses electrons and so is oxidised.

Oxidation number and redox reactions

When a redox reaction occurs an electron transfer takes place and so the oxidation numbers of the substances involved changes.

Consider the following reaction: $\mathbf{2HOBr + 2H^+ + 2I^- \rightarrow Br_2 + I_2 + 2H_2O}$

Reactants			Products	
Species	Oxid'n No		Species	Oxid'n No
H in HOBr	+1		Br in Br_2	0
O in HOBr	-2		I in I_2	0
Br in HOBr	+1		H in H_2O	+1
H^+	+1		O in H_2O	-2
I^-	-1			

The table shows us that the oxidation number of Br goes from +1 to 0, so it is reduced. The iodine goes from -1 to 0, so this is oxidised.

Another example $\mathbf{3NaOCl \rightarrow 2NaCl + NaClO_3}$

Reactants			Products	
Species	Oxid'n No		Species	Oxid'n No
Na in NaOCl	+1		Na in NaCl	+1
O in NaOCl	-2		Na in $NaClO_3$	+1
Cl in NaOCl	+1		Cl in NaCl	-1
			Cl in $NaClO_3$	+5
			O in $NaClO_3$	-2

In this reaction the Cl in NaOCl is oxidised in one reaction to +5 and in another reaction is reduced to -1. Such an occurrence is called **disproportionation**.

Disproportionation takes place a particular species undergoes simultaneous oxidation and reduction.

Half Equations

When a redox reaction occurs, one substance gains electrons and one substance losed electrons. These two processes can be considered separately.

Using the example of magnesium and copper sulphate:

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

Electron loss $Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^-$

These are called **half equations**.

Constructing Half Equations

Half equations can be constructed as follows:

a) Add H_2O molecules to balance any oxygen atoms
b) Add H^+ ions to balance any hydrogen atoms
c) Add electrons to balance any charge in the equation.

NB – To write a balanced half equation you may only add;

H_2O molecules
H^+ ions
OH^- ions (not usually done)
Electrons

e.g. Construct a half equation for: $NO_3^- \rightarrow NH_4^+$

a) balance oxygen atoms with water $N\mathbf{O_3}^- \rightarrow NH_4^+ + \mathbf{3}H_2\mathbf{O}$

b) balance hydrogen atoms with hydrogen ions $NO_3^- + \mathbf{10H^+} \rightarrow N\mathbf{H_4}^+ + \mathbf{3H_2}O$

c) balance the charges using electrons $\mathbf{8e^-} + NO_3^- + \mathbf{10}H^{\mathbf{+}} \rightarrow NH_4^{\mathbf{+}} + 3H_2O$

Further example.

Construct a half equation for: $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$

a) balance oxygen atoms with water $Cr_2\mathbf{O_7}^{2-} \rightarrow 2Cr^{3+} + \mathbf{7H_2O}$

b) balance hydrogen atoms with hydrogen ions $\mathbf{14H^+} + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + \mathbf{7H_2}O$

c) balance the charges using electrons $\mathbf{6e^- + 14}H^{\mathbf{+}} + Cr_2O_7^{\mathbf{2-}} \rightarrow \mathbf{2}Cr^{3+} + 7H_2O$

Constructing full equations from half equations

A **full equation** is written by adding two half equations together. The process is as follows:

- Write first half equation
- Write second half equation
- Balance in terms of electrons
- Add equations together

Example - Potassium reacts with fluorine to form potassium fluoride.

Write the half equation for the oxidation of potassium

$K \rightarrow K^+ + e^-$

Write the half equation for the reduction of fluorine

$F_2 + 2e^- \rightarrow 2F^-$

To balance for electrons, the first equation must be multiplied by 2

$2K \rightarrow 2K^+ + 2e^-$

$F_2 + 2e^- \rightarrow 2F^-$

Adding the equations together;

$2K + F \rightarrow 2K^+ + 2F^-$

Other examples

1. Chlorine reacts with potassium iodide to form potassium chloride and iodine.
   (a) Write the half equation for the oxidation of iodide $2I^- \rightarrow I_2 + 2e^-$

   (b) Write the half equation for the reduction of chlorine $Cl_2 + 2e^- \rightarrow 2Cl^-$

   (c) Combine the two half equations. $2I^- + Cl_2 \rightarrow I_2 + 2Cl^-$

2. Bromine reacts with iron(II) to form iron(III) and bromide.
   (a) Write the half equation for the oxidation of iiron(II) $Fe^{2+} \rightarrow Fe^{3+} + e^-$

   (b) Write the half equation for the reduction of bromine $Br_2 + 2e^- \rightarrow 2Br^-$

   (c) Combine the two half equations $2Fe^{2+} \rightarrow 2Fe^{3+} + e^-$

   $Br_2 + 2e^- \rightarrow 2Br^-$

   $Br_2 + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2Br^-$

3. Chlorine reacts with a solution of sulphur dioxide to form sulphate and chloride ions.
   (a) The half equation for the oxidation of sulphur dioxide is:

   $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$

   (b) Write the half equation for the reduction of bromine. $Br_2 + 2e^- \rightarrow 2Br^-$

   (c) Combine the two half equations. $SO_2 + 2H_2O + Br_2 \rightarrow SO_4^{2-} + 4H^+ + 2Br^-$