

FACTFILE: GCE CHEMISTRY

REDOX



Redox

Students should be able to:

- 1.7.1 calculate the oxidation state for an element in a compound or ion including peroxides and metal hydrides;
- 1.7.2 define the term redox and explain oxidation and reduction in terms of electron transfer and changes in oxidation state;
- 1.7.3 demonstrate understanding that oxidising agents gain electrons and are reduced and reducing agents lose electrons and are oxidised;
- 1.7.4 define disproportionation and use oxidation numbers to classify a redox reaction as disproportionation;
- 1.7.5 write half-equations and combine half-equations to give a balanced redox equation; and
- 1.7.6 use Roman numerals to indicate the oxidation number when an element has compounds or ions with different oxidation numbers, for example chlorate(I), chlorate(V).

Redox

Oxidation is loss of electrons
Reduction is gain of electrons

Redox is when oxidation and reduction occur in the same reaction

Oxidation States

The concept of oxidation states or oxidation numbers is used to account for electrons. The oxidation state, or number, of an atom shows the total number of electrons, which have been removed from an element (a positive oxidation state) or added to an element (a negative oxidation state) to get to its present state. It can alternatively be described as the charge an atom would have if the bonding it was involved in was fully ionic. Oxidation states are determined using a series of rules.

- The oxidation state of an atom in its elemental state is zero, for example $\text{Na} = 0$.
- The oxidation state of a simple ion equals its ionic charge, for example $\text{Mg}^{2+} = +2$, $\text{Cl}^- = -1$.
- The oxidation state of fluorine in any compound is always -1
- The oxidation state of oxygen in any compound is -2 , except when in a peroxide (-1) or a fluoride ($+2$).
- The oxidation state of hydrogen in any compound is $+1$, except when in an ionic hydride (-1), for example NaH , $\text{Na} = +1$, $\text{H} = -1$.
- The sum of the oxidation states of all the atoms in any species (compound or complex ion) equals the total charge on the species.

Example 1: SO_3 Neutral compound. Let S = x
 $x + 3(-2) = 0$
 $x = 6$
 i.e. oxidation state of S is +6.

Example 2: $\text{Cr}_2\text{O}_7^{2-}$ Overall charge = -2 Let Cr = x
 $2x + 7(-2) = -2$
 $x = 6$
 i.e. oxidation state of Cr is +6.

Some elements can exhibit more than one oxidation state; Roman numerals are used to indicate the oxidation state of the element in these cases. For example, chlorine can exhibit a number of oxidation states when bonded in a molecular ion to oxygen. Bleach contains the hypochlorite ion, ClO^- in which the chlorine atom has an oxidation state of +1. The ion is named as chlorate(I) using IUPAC nomenclature.

Chlorine can also bond with oxygen to give the chlorate ion, ClO_3^- , in which the chlorine atom has an oxidation state of +5. This ion is named as chlorate(V) using IUPAC nomenclature.

For example



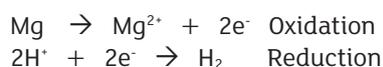
The oxidation number of chlorine increases from 0 in Cl_2 to +1 in NaClO and it is oxidised. The oxidation number of chlorine also decreases from 0 to -1 in NaCl and it is reduced. This oxidation and reduction of chlorine in the same reaction is disproportionation.

Half-equations

Magnesium reacts with hydrochloric acid to form magnesium chloride and hydrogen in a familiar reaction:



This reaction is a redox reaction which can be represented by two half-equations which illustrate the electron transfer process:



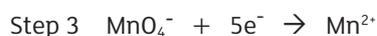
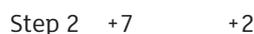
Magnesium is oxidised as it loses electrons and increases in oxidation state from 0 to +2; it acts as a reducing agent as it causes the hydrogen ions to gain electrons. The hydrogen ions are reduced

as they gain electrons and decrease in oxidation state from +1 to 0; they act as an oxidising agent as they cause the magnesium to lose electrons. An oxidising agent is an electron acceptor and a reducing agent is an electron donor.

A number of steps are taken to construct a half-equation:

- Write the formulae of the species before and after the change; balance if required.
- Determine the oxidation state of the atom undergoing change before and after the change.
- Add electrons to one side of the equation so that the total oxidation states balance.
- If the charges on the species (ions and electrons) on either side of the equation do not balance then add sufficient H^+ ions to one of the sides to balance the total charges.
- Add sufficient water molecules to one side to balance the equation.

For example, the reduction of manganate(VII) to manganese(II):



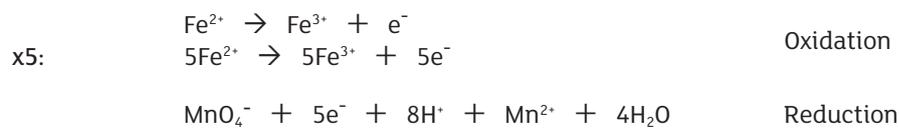
Sometimes the same species is both oxidised and reduced in the same reaction; this is known as disproportionation. For example, consider the reaction between chlorine and aqueous sodium hydroxide:



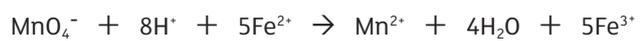
The chlorine decreases in oxidation state from 0 to -1 as it converts to sodium chloride. At the same time it also increases in oxidation state from 0 to +1 as it converts to sodium chlorate(I).

An overall equation can be constructed for a redox reaction by combining the two half-equations. The number of electrons transferred in each half-equation must be the same.

For example, the redox reaction between Fe^{2+} and MnO_4^- is given by:



Overall redox reaction:





Revision Questions

- 1** Using the half-equations below, which one of the following is the balanced ionic equation for the reaction between acidified manganate(VII) ions and ethanedioate ions?

Acidified manganate(VII) ions:



Ethanedioate ions:



- A $2\text{MnO}_4^- + 16\text{H}^+ + \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 2\text{CO}_2$
 B $\text{MnO}_4^- + 8\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 10\text{CO}_2$
 C $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$
 D $5\text{MnO}_4^- + 40\text{H}^+ + 2\text{C}_2\text{O}_4^{2-} \rightarrow 5\text{Mn}^{2+} + 20\text{H}_2\text{O} + 4\text{CO}_2$

- 2** Concentrated nitric acid (HNO_3) oxidises iodide ions to form iodine. In the reaction the nitric acid is reduced to form nitrogen monoxide (NO).

a) Reduction and oxidation can be defined in different ways.

- (i) Define oxidation in terms of electron transfer.

..... [1]

- (ii) Define reduction in terms of changes in oxidation state.

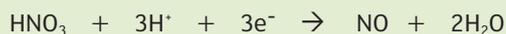
..... [1]

b) Define the oxidation number of nitrogen in.

(i) HNO_3 [1]

(ii) NO [1]

c) The half-equation for the reduction of concentrated nitric acid is shown below.



- (i) Write a half-equation for the oxidation of iodide ions to form an iodine molecule.

..... [1]

- (ii) Combine the reduction and oxidation half-equations to give the overall ionic equation.

..... [2]

3 Chlorine forms a series of oxides some of which are listed below.

Chlorine monoxide Cl_2O

Chlorine dioxide ClO_2

Chlorine hexoxide Cl_2O_6

Chlorine heptoxide Cl_2O_7

a) Deduce the systematic name for chlorine heptoxide using the oxidation state of chlorine.

..... [1]

b) Chlorine dioxide dissolves in water to form a solution which eventually forms a mixture of chloric and hydrochloric acids



The chlorine atoms in chlorine dioxide undergo disproportionation in this reaction.

(i) Explain the meaning of the term **disproportionation**.

.....

 [1]

(ii) Calculate the oxidation state of chlorine in the reactant and in the products of this reaction and use them to confirm that the reaction is a disproportionation reaction.

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 [3]

4 Which of the following is the oxidation state of nitrogen in the nitrate ion, NO_3^- ?

- A -1
- B -3
- C +5
- D +7

