# 4.   REDOX REACTIONS

4.1   Introduction

Earlier concepts of redox reactions simply referred to oxidation as reactions in which oxygen is added to a substance. An oxidizing agent is then a supplier of oxygen for addition to another substance. By this concept, only reactions such as those in Table 4.1 are regarded as oxidation reactions, while the opposite of the addition of oxygen (i.e. removal of oxygen), is termed a reduction. An example of such a reduction is
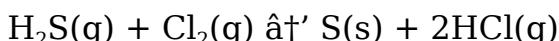
TABLE 4.1 REACTIONS INVOLVING ADDITION OF OXYGEN

| Oxidation reaction	Oxidizing agent
$2Cu(s) + O_2(g) \rightarrow 2CuO(g)$	O_2
$4FeO(s) + 2H_2O_2(l) \rightarrow 2Fe_2O_3(s) + 2H_2O(l)$	H_2O_2
$3Fe(s) + 4H_2O(l) \rightarrow Fe_3O_4(s) + 4H_2(g)$	H_2O

$CuO(s) + H^2(g) →' Cu(s) + H_2O(l)$
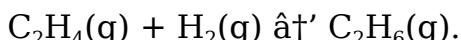
Hydrogen is the reducing agent (remover of oxygen).

In terms of oxidation and reduction, hydrogen has an opposite effect to that of oxygen. Hence in the earlier concept, the removal of hydrogen is regarded as an oxidation, while the addition of hydrogen is equivalent to a reduction. For example, in the reaction:

$H_2S(g) + Cl_2(g) →' S(s) + 2HCl(g)$

hydrogen sulphide is regarded as being oxidised to sulphur by the removal of hydrogen from it. The remover of the hydrogen,chlorine, is the oxidizing agent. The same reaction involves the addition of hydrogen to chlorine. So it is the reduction of chlorine by addition of hydrogen from a reducing agent, H_2S. Hydrogenation of alkenes and alkynes is likewise regarded as reduction by addition of hydrogen.

$C_2H_4(g) + H_2(g) →' C_2H_6(g)$.
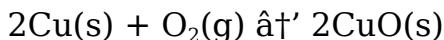
Rusting of iron when exposed to air and water is also a redox reaction.
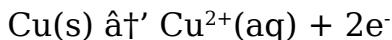
4.2 Modern Definition of Oxidation and Reduction

The scope of reactions which can be regarded as oxidation-reduction reactions is expanded by redefining the reactions under a concept of electron transfer. **Oxidation is the loss of electrons. Reduction is the gain of electrons. An oxidizing agent is an electron acceptor. A reducing agent is an electron donor**.
In the reaction

$$2Cu(s) + O_2(g) \rightarrow 2CuO(s)$$

each copper atom loses two electrons to form the Cu^{2+} ion present in the product.

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

This is the oxidation reaction. Each oxygen atom has gained two electrons to form the oxide ion

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

This is the reduction reaction. The electron donor, copper, is the reducing agent, and the electron acceptor, oxygen, is the oxidizing agent. Both reduction and oxidation have taken place simultaneously. The reaction is thus called a redox reaction.
The reaction:

$$H_2S(g) + Cl_2(g) \rightarrow S(s) + 2HCl(g)$$
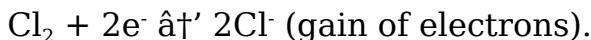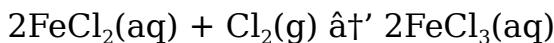
which does not involve oxygen, is also a redox reaction by this new concept. The oxidation reaction is

$$S^{2-} \rightarrow S + 2e^- \text{ (loss of electrons).}$$

The reduction reaction is

$$Cl_2 + 2e^- \rightarrow 2Cl^- \text{ (gain of electrons).}$$

Similarly,

$$2FeCl_2(aq) + Cl_2(g) \rightarrow 2FeCl_3(aq)$$

is a redox reaction.

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \text{ is the oxidation reaction, while}$$

$$Cl_2 + 2e^- \rightarrow 2Cl^- \text{ is the reduction reaction:}$$

The reaction.

$$4Fe(OH)_2(s) + 2H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s)$$
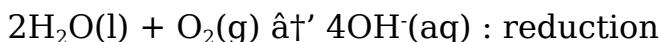
is a redox reaction with the two half reactions as follows:

$$Fe^{2+} \rightarrow Fe^{3+} + e^- : \text{oxidation}$$

$$2H_2O(l) + O_2(g) → 4OH^-(aq) : \text{reduction}$$
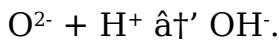
Actually, reduction is

$$O + 2e^- → O^{2-},$$

before

$$O^{2-} + H^+ → OH^-.$$
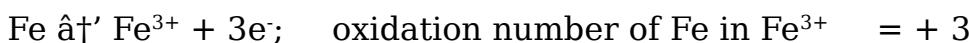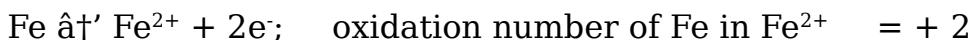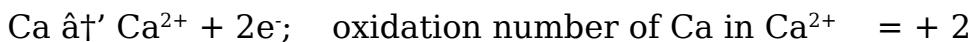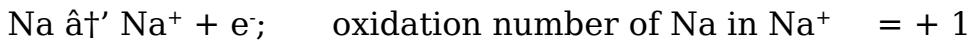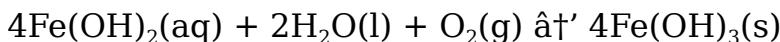
4.3 The Use of Oxidation Numbers (Oxidation States)

The group I metals form ions by loss of an electron, and group II metals by loss of two electrons. The transition metals may lose different numbers of electrons. They are said to show variable combining powers. Similarly the group VII elements gain one electron to form anions, and the group VI elements gain two. **The number of electrons an atom gains or loses to form an ion is referred to as its oxidation number** (or oxidation state). A positive sign is assigned to the cations and a negative sign to the anions, to distinguish them.

$Na → Na^+ + e^-$;   oxidation number of Na in Na^+ $= + 1$

$Ca → Ca^{2+} + 2e^-$;   oxidation number of Ca in Ca^{2+} $= + 2$

$Fe → Fe^{2+} + 2e^-$;   oxidation number of Fe in Fe^{2+} $= + 2$

$Fe → Fe^{3+} + 3e^-$;   oxidation number of Fe in Fe^{3+} $= + 3$

In the reaction

$$4Fe(OH)_2(aq) + 2H_2O(l) + O_2(g) → 4Fe(OH)_3(s)$$
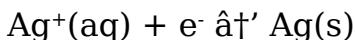
the oxidation number of iron in Fe(OH)2 is +2;
the oxidation number of iron in Fe(OH)3 is +3.

Therefore the oxidation number has increased from +2 to +3 during the reaction. Another modern concept of oxidation and reduction is in terms of increase/decrease in oxidation number. **Oxidation is an increase in oxidation number. Reduction is a decrease in oxidation number.**

Consider the reaction

$$Ag^+(aq) + e^- → Ag(s)$$

The oxidation number of silver has changed from +1 to 0. (The oxidation number of elements in their free state is zero). Therefore the oxidation number of silver has decreased. Thus, silver has been reduced.

The implication of this is that if we can determine the oxidation number of an atom before and after a reaction, we can determine whether the element has been oxidized, reduced, or undergone no

redox change. The determination of the oxidation number of an element in a compound or a radical is governed by the following rules:

1. The oxidation number of an element in its free state is zero.
2. The oxidation number of oxygen in compounds is usually -2, except in peroxides where it is -1.
3. The algebraic sum of the oxidation numbers of all the atoms in a neutral compound is zero.
4. The algebraic sum of the oxidation numbers of the atoms in a radical or other charged species is equal to the charge on the radical or species.

Oxidation number of copper in CuO

Since the oxidation number of oxygen is -2, that of copper must be +2 for the compound, CuO, to be neutral.

Oxidation number of sulphur in $FeSO_4$

The oxidation number of oxygen is -2

∴ Total oxidation number for the four oxygen atoms = -8.

Oxidation number of Fe = +2.

∴ For the compound to be neutral, oxidation number of sulphur must be + 6.
   The compound is named iron(II) tetraoxosulphate(VI), to indicate that the oxidation number of iron in this compound is +2 (Roman figure (II)), and that of sulphur is +6 (Roman Figure (VI)).

Oxidation number of manganese in MnO_4^-

Total oxidation number of the four oxygen atoms = 4 × -2 = -8. For the radical to have only a charge of -1, oxidation number of Mn must be + 7; so that (+ 7) -8 = -1.
The ion, MnO_4^-, is named tetraoxomanganate(VH), the Roman figure (VII) depicting the oxidation state of manganese.

Oxidation number of chromium in $Gr_2O_7^{2-}$

The seven oxygen atoms have a total oxidation number of-14. For the radical to have a charge of -2 the two chromium atoms must have total oxidation number of +12.

∴ Each chromium atom has an oxidation number of +6.
The ion is thus named heptaoxodichromate(VI).

WORKED EXAMPLES

1. What is the oxidation number of chlorine in (i) NaClO, (ii) $NaClO_3$? What do the oxidation numbers become when these compounds react with hydrogen chloride acid (hydrochloric acid)?

SOLUTION

The oxidation number of oxygen = -2
The oxidation number of sodium = +1
For the total oxidation number of NaClO to be 0, the oxidation number of Cl must be +1, i.e, +1 + 1-2 = 0.
NaClO is thus named sodium oxochlorate(I).
The total oxidation number of the three oxygen atoms in $NaClO_3$ = -6
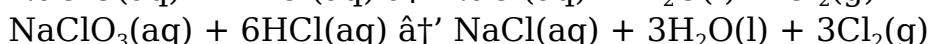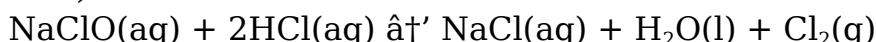
Oxidation number of Na = +1

∴ Oxidation number of Cl + 1-6 = 0

∴ Oxidation number of Cl = 6-1 = + 5
Hence the name sodium trioxochlorate(V).
Equations of the reactions with hydrogen chloride acid (hydrochloric acid):
$NaClO(aq) + 2HCl(aq) → NaCl(aq) + H_2O(l) + Cl_2(g)$
$NaClO_3(aq) + 6HCl(aq) → NaCl(aq) + 3H_2O(l) + 3Cl_2(g)$
In both NaClO and $NaClO_3$, chlorine is changed to chlorine gas. The oxidation number of chlorine in chlorine gas (the free state of the element), is zero.

2. Is the reaction

$3Cu(s) + 8HNO_3(aq) → 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$
a redox reaction? If so, name

(i)   the oxidizing agent

(ii) the reducing agent.
What is the oxidizing agent reduced to, and what is the reducing agent oxidized to?

SOLUTION

Oxidation number of Cu in Cu(s) = 0
Oxidation number of Cu in $Cu(NO_3)_2$ = +2
∴ Copper has been oxidized from Cu to Cu^{2+}
Oxidation number of N in HNO_3 = + 5
Oxidation number of N in NO = + 2

∴ Nitrogen has been reduced from +5 to +2

∴ The reaction is a redox reaction.

(i)   The oxidizing agent is trioxonitrate(V) acid.

(ii) The reducing agent is copper.

The oxidizing agent is reduced to nitrogen(II) oxide.

The reducing agent is oxidised to copper(II) trioxonitrate(V), or simply to Cu^{2+}.
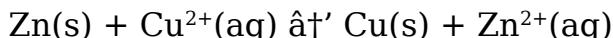
Exercise 4A

(1)   Calculate the oxidation number of chlorine in the following compounds: NaCl, Cl_2, $HClO_3$; and of nitrogen in N_2, N_2O, NO, NO_2, N_2O_4, N_2O_5.

(2)   Name the oxidizing agent, the reducing agent, the product of oxidation and the product of reduction in the following redox reactions:

(i) $H_2S(g) + Cl_2(g) \rightarrow S(s) + 2HCl(g)$

(ii) $2FeCl_2(s) + Cl_2(g) \rightarrow 2FeCl_3(s)$

(iii) $2NH_3(g) + 3Cl_2(g) \rightarrow N_2(g) + 6HCl(g)$

(iv) $10FeSO_4(aq) + 2KMnO_4(aq) + 8H_2SO_4(aq) \rightarrow 5Fe_2(SO_4)_3(aq)$
$+ K_2SO_4(aq) + 2MnSO_4(aq) + 8H_2O(l)$
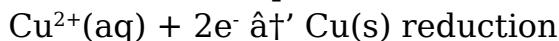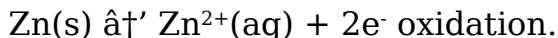
4.4   Redox Cells

Since redox reactions involve transfer of electrons, it should be possible to arrange the oxidation and reduction halves of the reaction in such a way that the electrons move through an external conducting wire. Such an arrangement produces electricity and is known as a redox cell.

The Daniel cell which uses the reaction

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

is a redox cell. The two half-reactions are

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ oxidation.
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ reduction
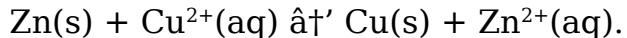
In the cell, a porous pot containing zinc tetraoxosulphate(VI) solution into which zinc metal is dipped, is put into a solution of copper(II) tetraoxosulphate(VI) into which copper metal is dipped. The two metals are joined by a conducting wire to complete the cell.

A more general arrangement for all redox cells is described in Experiment 4.1.
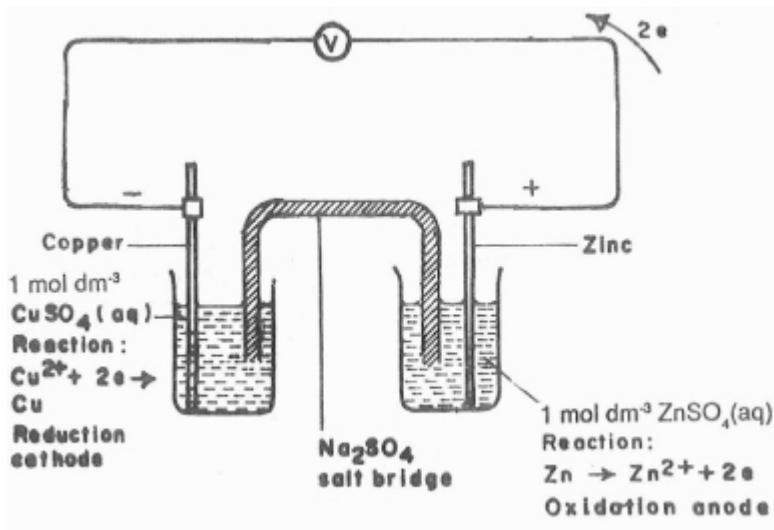
Experiment 4.1: Making a Daniel Cell.

Pour 50 cm³ of 1 mol dm⁻³ solutions of zinc tetraoxosulphate(VI) and copper(II) tetraoxosulphate(VI) into separate beakers. Add 4g of sodium tetraoxosulphate(VI) crystals to 50 cm³ of water and heat, while stirring to dissolve. Add the hot solution to 1g of agar soaked in 5 cm³ of water in a U-tube overnight. Allow the mixture to cool. It forms a gel in the U-tube as it cools. Place the U-tube across both solutions as shown in Figure 4.1. Connect a copper rod through a sensitive voltameter to a zinc rod. Dip the copper into the copper(II)

tetraoxosulphate(VI) solution and the zinc into the zinc tetraoxosulphate(VI) solution. The voltameter records a reading of 1.1 volts. This is a measure of the driving force for the reaction:

$Zn(s) + Cu^{2+}(aq) → Cu(s) + Zn^{2+}(aq)$.
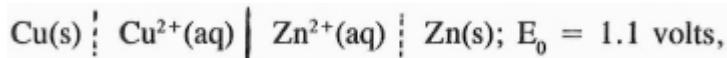
The substance in the U-tube is known as a **salt-bridge**. Its function is to separate the ions and ensure that the electrons move through the external wire.


Figure 4.1 Daniel cell

The cell can be represented by the symbol

$$Cu(s) \vdots Cu^{2+}(aq) \mid Zn^{2+}(aq) \vdots Zn(s); \ E_0 \ = \ 1.1 \ volts,$$
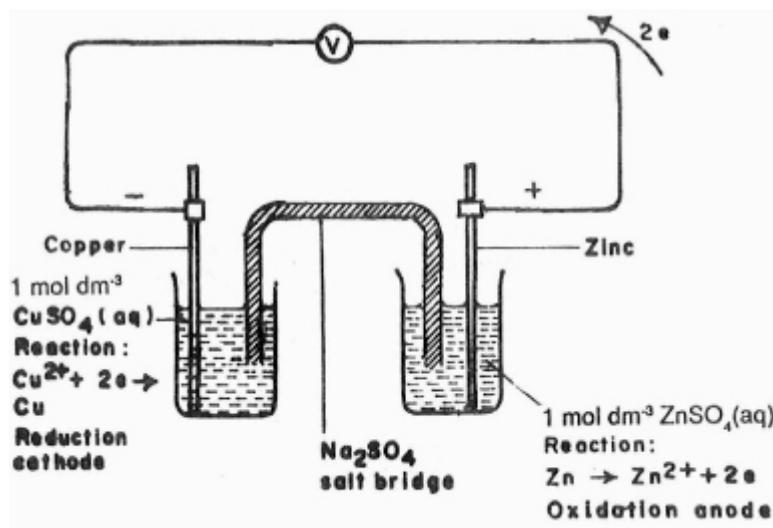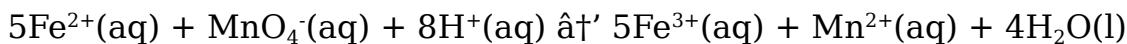
which means that copper metal dipped into 1 mol dm³ solution of Cu^{2+} ions when connected to zinc metal dipping into 1 mol dm⁻³ solution of Zn^{2+} ions gives a voltage of 1.1 volts.

Other oxidation-reduction half-reactions can be separated in like manner to generate electricity.

Experiment 4.2: Making a redox cell for the oxidation of Fe²⁺ to Fe³⁺ by MnO₄⁻.

Put some 1 mol dm⁻³ solution of potassium tetraoxomanganate(VII), acidified with dilute tetraoxosulphate(VI) acid into a beaker. Put equal volumes of 1 mol dm⁻³ solutions of iron(II) tetraoxosulphate(VI) and iron(III) tetraoxosulphate(VI) into another beaker. Dip platinum wires mounted in glass tubes into both beakers (Figure 4.2). Connect the solutions in the two beakers with a salt bridge prepared as in Experiment 4.1, and connect both platinum wires to a sensitive galvanometer. The galvanometer records 0.75 volt, the driving force for the reaction:

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) → 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$


Figure 4.2 A redox cell
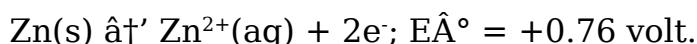
4.5   Redox Series

Some oxidizing agents are more powerful than others. Similarly some reducing agents are more powerful than others. Oxidizing or reducing strengths depend on the readiness of substances to accept or give up electrons. Thus, a substance may act as an oxidizing agent in one reaction but as a reducing agent in the presence of a more powerful oxidizing agent. The redox potential is a measure of the oxidizing or reducing action of a substance.

   The redox potential of metals (electrode potential) is measured by finding the voltage of a cell made by joining the metal, dipping in a molar solution of its own ions, to a standard hydrogen electrode. **The standard hydrogen electrode consists of an inert electrode such as platinum (over which hydrogen gas is bubbled at 1 atmosphere), dipping into a 1 M solution of H^+ ions.** It is assigned a potential of zero. Thus the voltage of the cell is due to that of the metal half-cell.
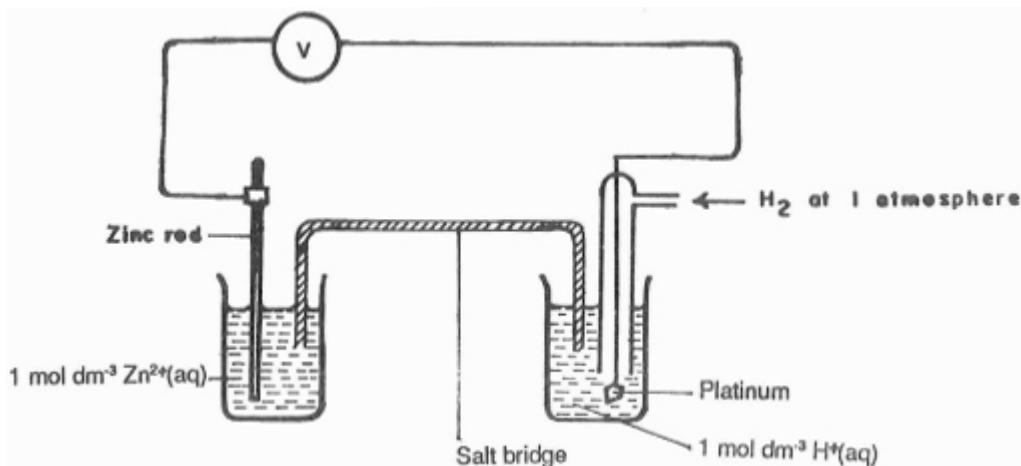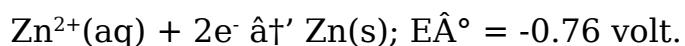
Experiment 4.3: Measuring the electrode potential of zinc.

Set up the apparatus shown in Figure 4.3. The voltage recorded by the voltameter is 0.76 volt. It is a measure of the driving force for the reaction:

   $Zn(s) → Zn^{2+}(aq) + 2e^-$; $E°$ = +0.76 volt.

It is referred to as the electrode potential of zinc. Metals more active than hydrogen are by convention assigned positive potentials for their reducing actions (loss of electrons). The reverse reaction (involving the reduction of the metal) therefore has a negative but equal

potential, i.e.

$Zn^{2+}(aq) + 2e^- → Zn(s)$; $E° = -0.76$ volt.
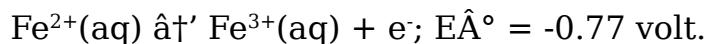
Figure 4.3 Measuring the electrode potential of zinc

Experiment 4.4: Measuring the redox potential of the reaction: $Fe^{2+} →$ $Fe^{3+} + e^-$

Carry out this experiment as in Experiment 4.2, using the set-up in Figure 4.2. The right hand beaker should however contain only the standard hydrogen electrode (i.e. platinum wire in 1M H^+ ion solution). The voltage recorded is 0.77 volt. This is the driving force of the reaction:

$Fe^{2+}(aq) → Fe^{3+}(aq) + e^-$; $E° = -0.77$ volt.

From similar measurements of the electrode potentials of half-cells, the Redox Series, a table showing the order of reducing or oxidizing strengths of reducing and oxidizing agents, is constructed. Table 4.2 is such a table. By convention, the electrode reaction is written as a reduction step, and assigned a redox potential which is a measure of the ease with which this reduction step occurs. Negative values show that the reduction step does not occur readily, while the more positive the redox potential, the more readily the reduction step occurs.

TABLE 4.2 THE REDOX SERIES

Half-cell reaction				Redox potential (volts)
K^+	+	e^-	$\rightarrow$ K	-2.92
Ca^{2+}	+	$2e^-$	$\rightarrow$ Ca	-2.87
Na^+	+	e^-	$\rightarrow$ Na	-2.71
Mg^{2+}	+	$2e^-$	$\rightarrow$ Mg	-2.37
Zn^{2+}	+	$2e^-$	$\rightarrow$ Zn	-0.76
Fe^{2+}	+	$2e^-$	$\rightarrow$ Fe	-0.44
Sn^{2+}	+	$2e^-$	$\rightarrow$ Sn	-0.14
Pb^{2+}	+	$2e^-$	$\rightarrow$ Pb	-0.13
H^+	+	e^-	$\rightarrow$ $\frac{1}{2}H_2$	0.00 (standard)
Cu^{2+}	+	$2e^-$	$\rightarrow$ Cu	+0.34
I_2	+	$2e^-$	$\rightarrow$ $2I^-$	+0.54
Fe^{3+}	+	e^-	$\rightarrow$ Fe^{2+}	+0.77
Ag^+	+	e^-	$\rightarrow$ Ag	+0.80
Br_2	+	$2e^-$	$\rightarrow$ $2Br^-$	+1.07
Cl_2	+	$2e^-$	$\rightarrow$ $2Cl^-$	+1.34
MnO_4^-	+ $8H^+$ + $5e^-$		$\rightarrow$ Mn^{2+} + $4H_2O$	+1.51
F_2	+	$2e^-$	$\rightarrow$ $2F^-$	+2.85

Increasing strength as reducing agents

Increasing strength as oxidising agents

EXERCISE 4B
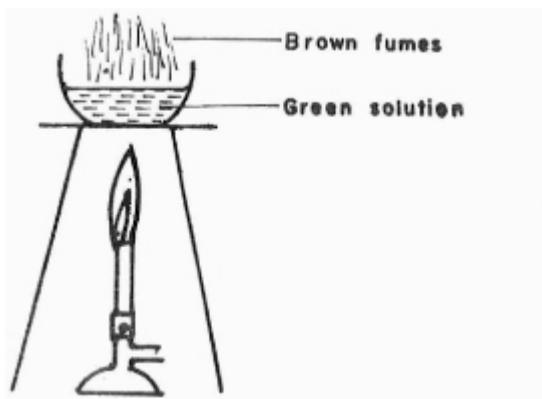
Describe what is observed and explain what happens if

(a)   copper rod dips into 1 mol dm^{-3} solution of iron(II) tetraoxosulphate(VT) overnight;

(b)   an iron rod dips into 1 mol dm^{-3} solution of copper(II) tetraoxosulphate(VI) overnight.

(c)   How can you generate electricity using the two solutions and rods?

4.6   Balancing Redox Equations
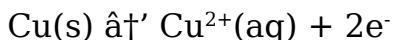
Experiment 4.5: Investigating an oxidation-reduction reaction.

Heat copper with moderately concentrated trioxonitrate(V) acid in an evaporating dish. Brown fumes of nitrogen(IV) oxide are given off. The solid copper "dissolves", and a green solution results.

Figure 4.4 Oxidation of copper
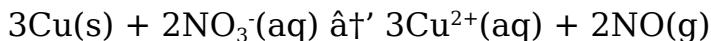
Since Cu^{2+} salts are usually green, (or blue for $CuSO_4.5H_2O$), the green solution must be due to Cu^{2+} ions. That is, each copper atom loses two electrons to become Cu^{2+}.

$Cu(s) → Cu^{2+}(aq) + 2e^-$
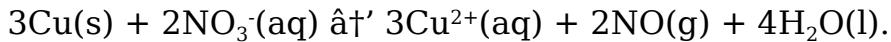
The brown fumes of nitrogen(IV) oxide are known to come from a reaction between nitrogen(II) oxide produced in the course of the reaction, and atmospheric oxygen. The nitrogen(II) oxide itself is formed from trioxonitrate(V) ion.

$NO_3^-(aq) → NO(g) + O_2(g)$
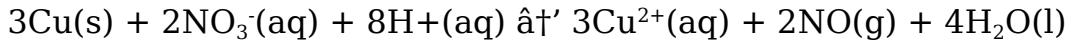
The oxidation number of nitrogen in trioxonitrate(V) is +5. In nitrogen(II) oxide, it is +2. So each nitrogen atom in NO_3^- gains three electrons to go from +5 to +2 oxidation state. The number of electrons lost by copper atoms must equal the number gained by the nitrogen atoms. Therefore, for every 3 atoms of copper there must be two atoms of nitrogen. We write:

$3Cu(s) + 2NO_3^-(aq) → 3Cu^{2+}(aq) + 2NO(g)$

The excess oxygen atoms on the left hand side are used to form water on the right hand side of the equation.

$3Cu(s) + 2NO_3^-(aq) → 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$.
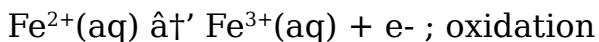
To get an equal number of hydrogen atoms, we add 8H+ to the left hand side. The ionic equation becomes:

$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) → 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$
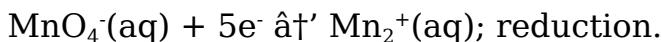
The balanced stoichiometric equation is then got by adding the spectator $6NO_3^-$ ions to both sides.

$3Cu(s) + 8HNO_3(aq) → 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$

In the oxidation of iron(II) to iron(III) by potassium tetraoxomanganate(VII) in acidic medium, the oxidation number of iron goes up from +2 to +3 by loss of an electron.

$Fe^{2+}(aq) → Fe^{3+}(aq) + e^-$; oxidation

The oxidation number of manganese goes down from +7 in MnO_4^- to +2 in $MnSO_4$ by gain of five electrons.

$MnO_4^-(aq) + 5e^- â†' Mn_2^+(aq)$; reduction.

To get the five electrons needed for the reduction we need five Fe^{2+} ions.

$5Fe^{2+}(aq) â†' 5Fe^{3+}(aq) + 5e-$

Thus, we write

$5Fe^{2+}(aq) + MnO_4^-(aq) â†' 5Fe^{3+}(aq) + Mn_2^+(aq)$
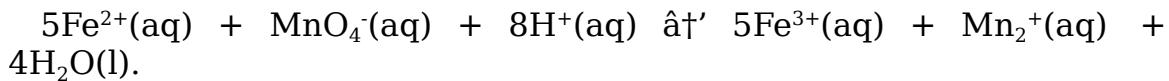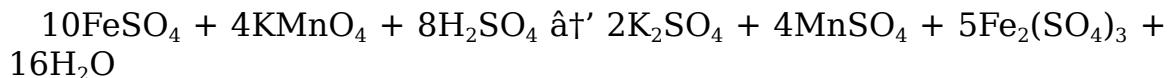
The excess oxygen atom appears on the right hand side as water.

$5Fe^{2+}(aq) + MnO_4^-(aq) â†' 5Fe^{3+}(aq) + Mn_2^+(aq) + 4H_2O(l)$

This gives eight hydrogen atoms to the right of the equation. Equalise this by adding 8H+ to the left. The ionic equation thus becomes:

$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) â†' 5Fe^{3+}(aq) + Mn_2^+(aq) + 4H_2O(l)$.
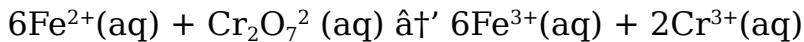
We finally add the SO_4^{2-} which is the spectator ion. The stoichiometric equation then becomes

$10FeSO_4 + 4KMnO_4 + 8H_2SO_4 â†' 2K_2SO_4 + 4MnSO_4 + 5Fe_2(SO_4)_3 + 16H_2O$

The oxidation of Fe^{2+} to Fe^{3+} may also be achieved with potassium heptaoxodichromate(VI). Again Fe^{2+} goes from +2 to +3 oxidation state by loss Of an electron. The oxidation number of chromium goes down from +6 in $Cr_2O_7^{2-}$ to +3 in Cr^{3+} by gain of three electrons per chromium atom.

$Cr_2O_7^{2-}(aq) + 6e^- â†' 2Cr^{3+}(aq)$
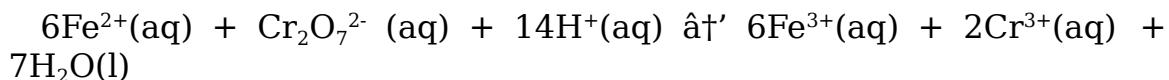
The six electrons needed by the two chromium atoms come from six Fe^{2+} ions. So we write,

$6Fe^{2+}(aq) + Cr_2O_7^2(aq) â†' 6Fe^{3+}(aq) + 2Cr^{3+}(aq)$
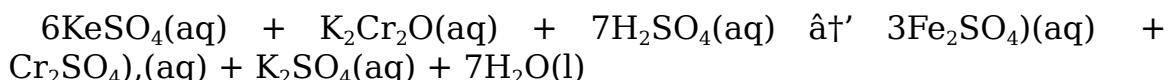
The oxygen on the left appears as water on the right.

$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) â†' 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

This introduces fourteen hydrogen atoms to the right. So, add 14H+ to the left.

$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) â†' 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

Finally, add spectator ions. The stoichiometric equation then becomes:

$6KeSO_4(aq) + K_2Cr_2O(aq) + 7H_2SO_4(aq) â†' 3Fe_2SO_4)(aq) + Cr_2SO_4),(aq) + K_2SO_4(aq) + 7H_2O(l)$

1) Balance the following ionic equations:
   (i) $Mn^{4+}(aq) + H^+(aq) + Cl^-(aq) → Mn_2^+(aq) + Cl_2(g) + H_2O(l)$
   (ii) $ClO_3^-(aq) → Cl^-(aq) + O_2(g)$
   (iii) $I_2(aq) + S_2O_3^{2-}(aq) → I^-(aq) + S_4O_6^{2-}(aq)$
   (iv) $MnO_4^-(aq) + H+(aq) + S^{2-}(aq) → Mn_2^+(aq) + S(s)\ 4\ H_2O(l)$
   (v) $S^{2-}(aq) + NO_3^-(aq) + H^+(aq) → S(s) + NO_2(g) + H_2O(l)$

2) If the oxidation number of chlorine is +7, which of the following is a correct formula?
   (A) $Al_2(ClO_4)_3$
   (B) K_2ClO_4;
   (C) $Ca(ClO_4)_2$;
   (D) Na_3ClO_4;
   (E) Mg_2ClO_4

3) Which of the following is NOT a redox reaction?
   A. $N_2(g) + 3H_2(g) → 2NH_3(g)$.
   B. $Zn(s) + 2HCl(aq) → ZnCl_2 + H_2(g)$
   C. $3Cl_2(g) + 6NaOH(aq) → NaClO_3(aq) + 5NaCl(aq) + 3H_2O(l)$
   D. $8NH_3(g) + 3Cl_2(g) → 6NH_4Cl(g) + N_2(g)$
   E. $CaCO_3(s) + 2HCl(aq) → CaCl_2(aq) + H_2O(l) + CO_2(g)$

4.7   Oxidizing Agents

The common oxidizing agents include oxygen, ozone, hydrogen peroxide, concentrated trioxonitrate(V) acid, hot concentrated tetraoxosulphate(VI) acid, chlorine, bromine, fluorine, potassium tetraoxomanganate(VII) and potassium heptaoxodichromate(VI).

Test for oxidizing agent

1. Pass hydrogen sulphide gas into a solution suspected to contain an oxidizing agent. A yellow deposit of sulphur shows that the gas has been oxidised to sulphur. This indicates the presence of an oxidizing agent.

2. Heat the suspected oxidizing agent with concentrated hydrochloric acid or a chloride. The evolution of chlorine, a greenish-yellow pungent gas which turns wet blue litmus red, then bleaches it, indicates the presence of an oxidizing agent.

3. Mix the suspected oxidizing agent with potassium iodide solution. Acidify with dilute tetraoxosulphate(VI) acid. Warm. The evolution of iodine which turns starch iodide paper blue, indicates the presence of an oxidizing agent.

4.8 Reducing Agents

Common reducing agents include hydrogen sulphide, carbon(II) oxide, carbon, sulphur(IV) oxide, hydrogen (from action of metals on acids), metals in their free atomic forms, etc.

Test for reducing agents

1.   Add dilute potassium tetraoxomanganate(VII) solution to the test solution. Acidify with dilute tetraoxosulphate(VI) acid. The decolourisation of the purple colour of the manganate(VII) ion indicates the presence of reducing agent.

2.   Repeat using acidified potassium heptaoxodichromate(VI) solution. Its orange colour changes to green if a reducing agent is present.

3.   With bromine water: reducing agents decolourise bromine water.

Chapter Summary

1. (a)   Oxidation is the loss of electrons.

    (b)   Reduction is the gain of electrons.

    Both processes occur simultaneously, and this is known as a redox reaction.

2. (a)   An oxidizing agent is an electron acceptor.

    (b)   A reducing agent is an electron donor.

3.   The number of electrons lost/gained by an atom is its oxidation number (+ve for positive ions; -ve for negative ions).

4.   An element (or ion) is oxidised if its oxidation number is increased.

5.   An element (or ion) is reduced if its oxidation number is decreased.

6.   The IUPAC nomenclature for inorganic compounds is based on the concept of oxidation number. The fact that the algebraic sum of the oxidation number of all the atoms in a compound is zero is used to calculate the oxidation numbers of the atoms. To do this, hydrogen is assigned an oxidation number of +1 (or -1 in metallic hydrides); oxygen is assigned an oxidation number of -2 (or -1 in peroxides).

7.   A redox cell is an arrangement that can be used to derive electricity from redox reactions. The electrons lost by a reducing agent are made to pass through an external wire before they are gained by an oxidising agent. This is achieved by separating the oxidising agent from the reducing agent, using a porous pot or a salt bridge.

8.   Balancing redox equations:

(a) Write the oxidation half of the reaction.

(b) Write the reduction half of the reaction.

(c) Multiply by appropriate coefficients to make the number of electrons involved in each half, the same.

(d) Add up the two half reactions such that the number of electrons lost by the reducing agent are gained by the oxidizing agent.

(e) Add the spectator ions.

9. Tests for oxidizing agents:
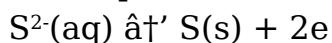
(a) With hydrogen sulphide, they form a yellow deposit of sulphur.

(b) On heating with chlorides they liberate chlorine, a greenish-yellow pungent gas that first turns wet blue litmus paper red, then bleaches it.

(c) On heating with iodides they liberate dark-brown fumes of iodine which turn starch iodide paper blue.

10. Tests for reducing agents:

(a) They decolourise acidified potassium tetraoxomanganate(VII) solution.

(b) They change the colour of acidified potassium heptaoxodichromate(VI) solution from orange to green.

(c) They decolourise bromine water.

Assessment
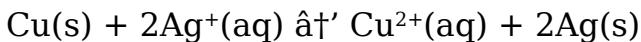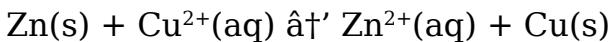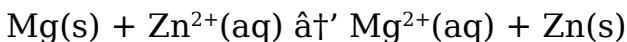
1. $2FeCl_3(aq) + H_2S(g) → 2FeCl_2(aq) + 2HCl(aq) + S(s)$ The above equation can be represented thus:

$Fe^{3+}(aq) + e- → Fe^{2+}(aq)$

$S^{2-}(aq) → S(s) + 2e$

(a) (i) Which is the oxidizing agent?

(ii) Why?

(b) (i) Which is the reducing agent?

(ii) Why?

(WAEC)

2. Below you are given the equations for reactions between some metals and metal ions:

$Mg(s) + Zn^{2+}(aq) → Mg^{2+}(aq) + Zn(s)$

$Zn(s) + Cu^{2+}(aq) → Zn^{2+}(aq) + Cu(s)$

$Cu(s) + 2Ag^+(aq) → Cu^{2+}(aq) + 2Ag(s)$

(a) Name, giving reasons,

(i) the strongest reducing species,

(ii) the strongest oxidizing species.

3. Describe the tests you would perform to show that $FeSO_4$, H_2S, SO_2, are reducing agents, and the tests you would perform to show

that H_2O_2, HNO_3, and $KMnO_4$ are oxidizing agents. For each test, state clearly the reagents used and the visual changes that would be noticed.
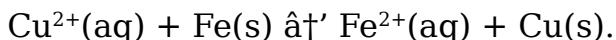
4. Write ionic equations for the following redox reactions:
    (i)   the displacement of bromine from aqueous bromide by chlorine,
    (ii)   the precipitation of silver from aqueous solution of its salt by iron,
    (iii)   the electrolysis of fused sodium chloride,
    (iv)   the direct combination of hydrogen and sulphur,
    (v)   the action of trioxonitrate(V) acid on copper.

5. In Figure 4.5, what Will happen to:
    (i)   the iron rod,
    (ii)   the copper salt solution?
    Write an equation which explains your answers. (WAEC)
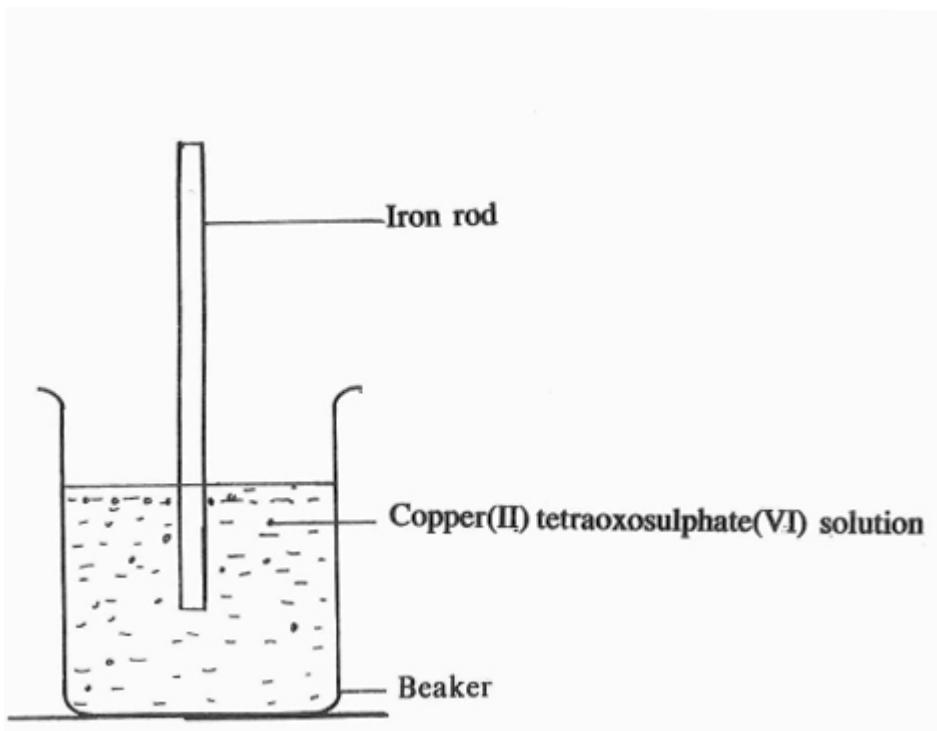
6. Draw a simple voltaic cell which makes use of the reaction

    $Cu^{2+}(aq) + Fe(s) → Fe^{2+}(aq) + Cu(s)$.

    Indicate the direction of flow of
    (i)   electrons
    (ii)   electric current in the cell.

What would be observed when the cell has been on for about two hours?

Figure 4.5

4P   LITERATURE PROJECT

4P.1   Evolution of Nomenclature

Over the years, chemical compounds have been named differently. Initially they were arbitrarily named by their discoverers. Many substances have retained their historical names. Examples of historical names and formulae of some compounds are given in Table 4P.1.

TABLE 4P.1 HISTORICAL NAMES OF SUBSTANCE S

Name	Formula
Aqua fortis	HNO_3
Muriatic acid	HCl
Quicklime	CaO
Slaked lime	$Ca(OH)_2$
Soda ash	Na_2CO_3
Glauber's salt	Na_2SO_4
Saltpetre	KNO_3
Milk of magnesia	$Mg(OH)_2$
Oil of vitriol	H_2SO_4

Because these names were unsystematic, four French chemists, Antoniue Lavoisier,Claude Berthollet, Antoniue deFourervy, and Louis de Morveay introduced names which were designed to indicate the composition of chemical compounds. The names they gave to compounds were translated literarily, into English. Below are examples of such names.
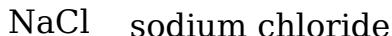
> ZnO   oxide of zinc
> SnO   oxide of tin
> $ZnCl_2$ chloride of zinc
> FeS   sulphide of iron.

The literary translations of French names were used for about 20 years before their correct English forms were introduced. ZnO became zinc oxide; $ZnCl_2$, zinc chloride; FeS, iron sulphide; etc.

4P.2 Old Nomenclature of Inorganic Compounds

The rules for this systematic nomenclature can be summarised as follows:

1.   The suffix -ide is used for naming compounds containing only two elements in its molecule. The metallic element is named first, and the suffix -ide is added to the name of the non-metal.

NaCl   sodium chloride

CaO   calcium oxide

FeS   iron sulphide.

2.   Compounds in which the metallic element may have two oxidation states require a way of distinguishing between the states. The suffix -ic of the name of the metallic element was used for the higher oxidation state, and the suffix -ous for the lower oxidation state. Examples include:

$CuCl_2$,   cupric chloride;   CuCl,   cuprous chloride

$FeCl_3$ ferric chloride; $FeCl_2$,   ferrous chloride

SnO_2,   stannic oxide;   SnO,   stannous oxide.

3.   The number of atoms of each element in a formula of the compound was denoted by a prefix. The prefixes used were:

1 = mono

2 = di

3 = tri

4 = tetra

5 = penta

6 = hexa

7 = hepta

8 = octa⁻

9 = nona

10 = deca

Thus, CO was carbon monoxide; CO_2, carbon dioxide;

N_2O,   dinitrogen monoxide;

N_2O_3,   dinitrogen trioxide;

N_2O_5,   dinitrogen pentaoxide;

PCl_3,   phosphorus trichloride;

PCl_5,   phosphorus pentachloride;

Cl_2O_7,   dichlorine heptaoxide.

4.   Binary acids were named as binary compounds, except that the acids had two names, one as binary compounds and the other as the acids.

Examples:

HCl   Hydrogen chloride, Hydrogen chloride acid (Hydrochloric

acid)

HI   Hydrogen iodide,   Hydroiodic acid

H_2S Hydrogen sulphide,   Hydrosulphuric acid.

5.   The oxygen acids (oxyacids) contain oxygen in addition to ionisable hydrogen and one other non-metallic element. The acids derive their names from the name of the other non-metallic element. If that other non-metallic element is in its higher oxidation state its name ends in -ic; if in its lower oxidation state it ends in -ous. The few that have more than two oxidation states have the prefixes hypo- or per- added. The -ic acids give rise to-ate salts, and the -ous acids give rise to -ite salts. Acid salts are named by adding bi- as prefix to the other non-metallic element (other than oxygen).

TABLE 4P.2 NAMES OF OXYGEN ACIDS AND THEIR SALTS

Acids		Salts	
Formula	Name	Formula	Name
HNO_3	Nitric acid	$NaNO_3$	Sodium nitrate
HNO_2	Nitrous acid	$NaNO_2$	Sodium nitrite
H_2SO_4	Sulphuric acid	K_2SO_4	Potassium sulphate
		$KHSO_4$	Potassium bisulphate
H_2SO_3	Sulphurous acid	Na_2SO_3	Sodium sulphite
		$NaHSO_3$	Sodium bisulphite
H_2CO_3	Carbonic acid	Na_2CO_3	Sodium carbonate
		$NaHCO_3$	Sodium bicarbonate
H_3PO_4	Phosphoric acid	Na_3PO_4	Sodium phosphate
		Na_2HPO_4	Disodium biphosphate
		NaH_2PO_4	Sodium biphosphate
$HClO_3$	Chloric acid	$NaClO_3$	Sodium chlorate
$HClO_2$	Chlorous acid	$NaClO_2$	Sodium chlorite
$HClO$	Hypochlorous acid	$NaClO$	Sodium hypochlorite
$HClO_4$	Perchloric acid	$NaClO_4$	Sodium perchlorate.

4P.3 New IUPAC Nomenclature for Inorganic Compounds

The latest nomenclature now in use is due to the Nomenclature Commission of the International Union of Pure and Applied Chemistry. The oxidation state of the metal is indicated by a Roman numeral in parenthesis. Examples are:

(1) **Binary compounds**

Cu_2O — copper(I) oxide

CuO — copper(II) oxide

$FeCl_2$ — iron(II) chloride

$FeCl_3$ — iron(III) chloride.

(2) **Oxygen acids and their salts**

|	
HNO_3, Trioxonitrate(V) acid	$NaNO_3$, Sodium trioxonitrate(V)
HNO_2, Dioxonitrate(III) acid	$NaNO_2$, Sodium dioxonitrate(III)
H_2SO_4 Tetraoxosulphate(VI) acid	Na_2SO_4, Sodium tetraoxosulphate(VI)
	$NaHSO_4$. Sodium hydrogen tetraoxo-sulphate(VI)
H_2SO_3, Trioxosulphate(IV) acid	Na_2SO_3, Sodium trioxosulphate(IV)
	$NaHSO_3$, Sodium hydrogen trioxosul-phate(IV)
H_2CO_3, Trioxocarbonate(IV) acid	Na_2CO_3, Sodium trioxocarbonate(IV)
	$NaHCO_3$, Sodium hydrogen trioxo-carbonate(IV).
H_3PO_4. Tetraoxophosphate (V) acid	Na_3PO_4. Trisodium tetraoxopho-sphate(V).
	Na_2HPO_4, Disodium hydrogen tetraoxo-phosphate(V)
	NaH_2PO_4, Sodium dihydrogen tetraoxo-phosphate(V).
$HClO_3$, Trioxochlorate(V) acid	$NaClO_3$, Sodium trioxochlorate(V)
$HClO_2$ Dioxochlorate(III) acid	$NaClO_2$, Sodium dioxochlorate(III)
$HCIO$, Monoxochlorate(I) acid	$NaCIO$, Sodium monoxochlorate(I)

$HClO_4$ Tetraoxochlorate(VII) acid	$NaClO_4$, Sodium tetraoxochlorate(VII).

## 4P.4 Old Nomenclature of Organic Compounds
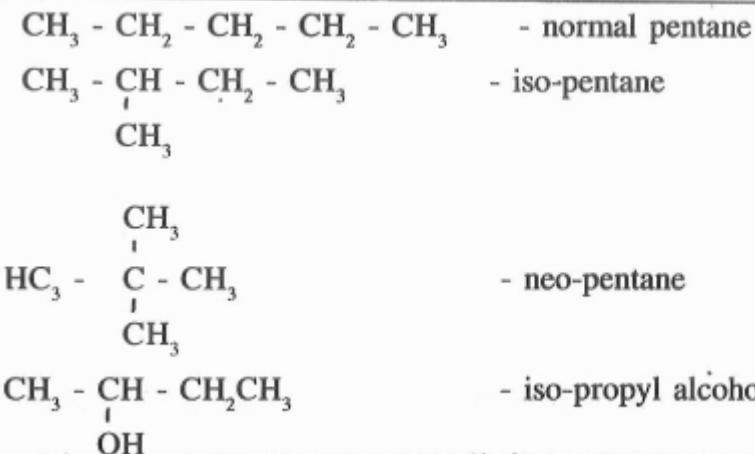
Not much was known of organic compounds before 1800. During the early 1800s a number of organic compounds were isolated from natural sources. Many of them were named according to their source.

The historical names of some of these early organic compounds are listed below.

```
HCOOH       — Formic acid, from sting of ants
CH₃COOH   — Acetic acid, from vinegar

            OH
            |
HOOC-   C - CH₂COOH - Citric acid, from lemon
            |
            CH₂COOH


            COOH
            |
    H  - C - OH          - Tartaric acid, from grapes
            |
    HO - C - H
            |
            COOH


CH₄                        - Marsh gas, from decaying leaves.

CH₂OH-CHOH-CH₂OH    - Glycerol, by-product of soap
                              manufacture.
```

The first attempt at systematic naming introduced normal-, iso-, and neoto indicate no branching, carbon branching next to an end carbon atom, and double branching from the same carbon atom, respectively. The number of carbon atoms in a compound was indicated by a Greek numeral, and a suffix to indicate the functional group present.

EXAMPLES

```
CH₃ - CH₂ - CH₂ - CH₂ - CH₃        - normal pentane

CH₃ - CH - CH₂ - CH₃               - iso-pentane
        |
        CH₃


          CH₃
           |
HC₃ -   C - CH₃                     - neo-pentane
           |
          CH₃

CH₃ - CH - CH₂CH₃                   - iso-propyl alcohol.
        |
        OH
```
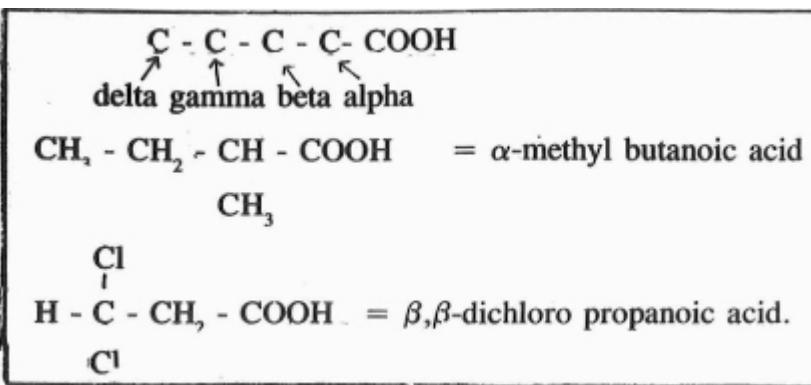
However, this system breaks down after only five carbon atoms.

4P.5 IUPAC Nomenclature for Organic Compounds

In 1892 the IUPAC met in Geneva and designed the initial rules for naming organic compounds. The rules have been revised several times, the most recent being in 1960. Originally, consecutively joined carbon atoms are numbered with Greek letters, starting from the carbon atom to which the most important functional group is attached. The positions and names of other groups attached to carbon atoms in the chain are indicated. Examples:

```
        C - C - C - C- COOH
       ↗   ↑   ↖   ↖
    delta gamma beta alpha

CH₃ - CH₂ - CH - COOH      = α-methyl butanoic acid
              |
              CH₃

      Cl
       |
H - C - CH₂ - COOH    = β,β-dichloro propanoic acid.
      |
      Cl
```

Most modern IUPAC nomenclature for organic compounds

There are three parts to the name of every organic compound by the most recent IUPAC system of nomenclature.

(i)   A root name that indicates the number of consecutively-joined carbon atoms.

(ii) A suffix that designates the most important functional group and its position in the carbon chain.

(iii) Prefix (prefixes) that indicate the position and names of groups replacing hydrogen atom(s) in the parent hydrocarbon. The

positions of these groups are indicated by numbering the carbon atoms in the chain, starting from the functional group. Examples are indicated in Table 4P.3.

TABLE 4P.3 IUPAC NOMENCLATURE OF ORGANIC COMPOUNDS

Formula	Number of atoms in longest chain	Root name	Suffix	Prefix(es)	Full name
$CH_3CHCH_2CH_3$ $\quad CH_3$	4	But	-ane	2-methyl	2-methylbutane
$CH_2=CH-CHCH_2CH_3$ $\quad CH_3$	5	Pent-	-1-ene	3-methyl	3-methylpent-1-ene
$CH_3CH_2C=CHCH_3$ $\quad C_2H_3$	4	But-	-2-ene	2-ethyl	2-ethylbut-2-ene
$\qquad OH$ CH_3-C-CH_3 $\quad CH_3$	3	Propan-	-2-ol	2-methyl	2-methylpropan-2-ol
$\qquad H$ $CH_3-C-CHO$ $\quad Cl$	3	Propan-	-al	2-chloro	2-chloropropanal
$\qquad CH_3$ $CH_3-C-C-CH_3$ $\quad O H$	4	Butan-	-one	3-methyl	3-methylbutan-2-one
$\qquad Cl$ $CH_3-C-COOH$ $\quad Cl$	3	Propan-	-oic acid	2,2-dichloro	2,2-dichloropropanoic acid