# 10   OXIDATION AND REDUCTION

The importance of oxidation-reduction reactions was recognized from the beginning of chemistry. In oxidation-reduction, some entity is given or taken between two reacting chemicals. The situation is similar to that in acid-base reactions. In brief, oxidation-reduction and acid-base reactions form a pair of systems in chemistry. Oxidation-reduction and acid-base reactions share a common feature in that both had been put into practice before the nature of the reactions was clarified.

Important concepts have gradually been developed: for example, the oxidation number, an oxidant (an oxidizing agent), a reductant (a reducing agent), electromotive force, Nernst's equation, Faraday's law of electromagnetic induction, and electrolysis. The development of electric cells was significant.

Assembling the components of an oxidation-reduction reaction is good practice and a satisfying intellectual challenge. Cells and electrolysis are two particularly important examples because both are strongly related to everyday life and the chemical industry.

## 10.1 The concept of oxidation-reduction

**(a)   Discovery of oxygen**

Since air contains substantial amounts of oxygen, the combination between substances and oxygen, *i.e.*, **oxidation**, is the most frequently occurring reaction in nature. Combustion and rusting of metals must have attracted the attention of ancient people.

However, it was not until the end of the 18th century that chemists could understand the true nature of combustion, namely, The nature of combustion could be understood only when the nature of oxygen was understood. Until the Aristotelian doctrine that air is an element and the only gas was denied, the mechanism of oxidation was not understood.

Possible existence of gases other than air was recognized by Helmont as early as the beginning of the 17th century. The method to separate gases uncontaminated by vapor using the pneumatic trough was reported by Hales around that time. Regardless of these advances, however, one misconception hampered understanding the role of oxygen in combustion. This is a false theory of combustion known as the phlogiston theory which was already mentioned in Ch. 1.

This theory was advocated by two German chemists, Georg Ernst Stahl (1660-1734) and Johann Joachim Becher. According to this theory, combustion was a process of discharge of phlogiston from combustible substances. Smoke and fume coming from burning wood was accepted as a good evidence for this theory. The mass of ash after wood burned was lighter than the wood itself and that was consistent with the theory.   However, there was a major discrepancy in this theory, namely the residue (metal oxide) after the combustion of a metal was heavier than the metal.

Both Priestley and Scheele, who discovered oxygen at the end of the 18th century, were adherents of the phlogiston theory. Hence they failed to comprehend the role of oxygen in combustion. In contrast, Lavoiseur, not being preoccupied with the theory, correctly understood the role of oxygen and proposed a new theory of combustion to the effect that oxidation is the combination of oxygen and combustible substances.

He supported his theory with accurate and quantitative experiments that were far superior to the standards of the day. He realized that it was necessary to account for the quantity of gases involved in the reaction in order to understand chemical reactions in a quantitative manner. Hence he carried out the reactions in closed vessels. The role of oxygen in combustion was identified by Lavoiseur; the oxidation-reduction was defined as below.

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**Oxidation-reduction and oxygen**

Oxidation: to accept oxygen

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| Reduction: to donate oxygen |
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## (b) The role of hydrogen

It turned out that not all oxidation-reduction reactions with organic compounds could be explained in terms of donation-acceptance of oxygen. For example, although the reaction to prepare aniline by reacting nitrobenzene and iron in the presence of hydrochloric acid is an oxidation-reduction reaction explicable in terms of donation-acceptance of oxygen, the formation of ethane $CH_3CH_3$ by the addition of hydrogen to ethylene $CH_2=CH_2$, involves no donation-acceptance of oxygen involved. Yet, the addition of hydrogen has the same effect as the removal of oxygen. Hence, ethylene is reduced in this reaction. In other words, it is also necessary to define oxidation-reduction in terms of donation-acceptance of hydrogen.

| **Oxidation-reduction and hydrogen** |
| --- |
| Oxidation: to donate hydrogen(s) |
| Reduction: to accept hydrogen(s) |

## (c) The role of electrons

The combustion of magnesium is clearly an oxidation-reduction reaction in which donation-acceptance of oxygen is involved.

$$2Mg + O_2 \rightarrow 2MgO$$
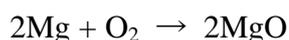
The reaction between magnesium and chlorine is not accompanied with donation-acceptance of oxygen.

$$Mg + Cl_2 \rightarrow MgCl_2$$
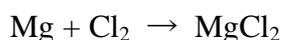
However, considering the valence state of magnesium, it is natural to treat the two reactions in the same category. Indeed, the change of magnesium, $Mg \rightarrow Mg^{2+} + 2e^-$, is common to the two reactions, and in both reactions magnesium was oxidized. In this regard, greater generality will be achieved if oxidation-reduction is defined in terms of donation-acceptance of electrons.

| **Oxidation-reduction and electron** |
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| Oxidation: to donate electron(s) |
| Reduction: to accept electron(s) |

If we use this definition, oxidation-reduction reactions can be divided into two; one the oxidation reaction, and the other reduction. Thus,

$$Mg \rightarrow Mg^{2+} + 2e^- \text{ (to donate electrons } \rightarrow \text{ oxidized)}$$
$$Cl_2 + 2e^- \rightarrow 2Cl^- \text{ (to accept electrons } \rightarrow \text{ reduced)}$$

Each of the two reactions is called a **half-reaction**. It will be shown that the oxidation-reduction reactions are generally most conveniently represented by a set of half-reaction (one for the oxidant and one for the reductant).

**Sample question 10.1**   Construction of an equation of oxidation-reduction reaction

Draw the oxidation reaction of oxalic acid $(COOH)_2$ to give carbon dioxide $CO_2$ and water in three different ways; donation-acceptance of oxygen, hydrogen and electron, respectively. Fill the blanks with appropriate chemical formulas and coefficients.

(1) oxygen:    $(COOH)_2 + (O) \rightarrow$ [    ] $+$

(2) hydrogen: $(COOH)_2 \rightarrow 2H +$

(3) electron: $(COOH)_2 \rightarrow 2e^- + \boxed{\phantom{xxxxx}} +$

**Answer**

(1) oxygen:  $H_2O$ is formed from two H of oxalic acid and one O of oxidant.

$(COOH)_2 + (O) \rightarrow 2CO_2 + H_2O$
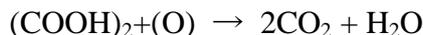
(2) hydrogen: Formally oxalic acid gave two H and $CO_2$.

$(COOH)_2 \rightarrow 2H + 2CO_2$
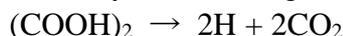
(3) electron:  The method for making this type of equation will be given later.

$(COOH)_2 \rightarrow 2e^- + 2CO_2 + 2H^+$
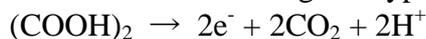

**(d)  Oxidants and reductants (oxidizing and reducing agents)**

Oxidation and reduction are something like the two sides of a piece of paper, and hence neither oxidation nor reduction take place without being accompanied by the other. If some substance accepts electrons, there should be some corresponding substance that donates them.

In oxidation-reduction, the compound that accepts electron(s) from the counterpart is called an **oxidant** (an oxidizing agent) because the counterpart is oxidized. The counterpart of the oxidant, which donates electron(s) to the oxidant, is called a reductant (the reducing agent) since the counterpart (the oxidant) is reduced.

Among the above examples, magnesium, which gave electrons to chlorine, is a reductant, and chlorine, which gained electrons from magnesium, is a reductant. Generally, such electropositive elements as alkali metals or alkaline earth metals are strong reductants; such electronegative elements as chlorine are good oxidants.

A compound can act as an oxidant and as a reductant as well. If it can easily donate electron(s) to the counterpart, it can be a reductant. If it can easily accept electron(s), it can be an oxidant. In Table 10.1, the half-reactions of common oxidants and reductants are listed.

**Table 10.1** Some examples of oxidants and reductants

Oxidants

$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$

$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq)$

Reductants

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

$H_2(g) \rightarrow 2H^+(aq) + 2e^-$

$H_2S(aq) \rightarrow 2H^+(aq) + S(s) + 2e^-$

$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
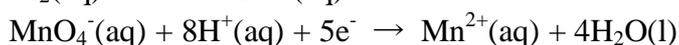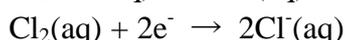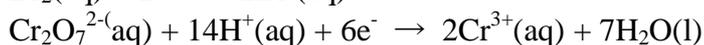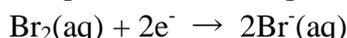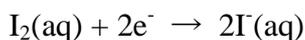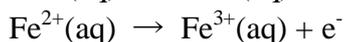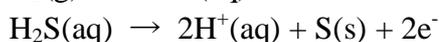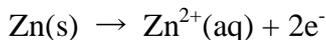

**(e)  Oxidation number**

Iron is a good reductant and it becomes $Fe^{2+}$ or $Fe^{3+}$ depending on the reaction conditions.

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

$Fe \rightarrow Fe^{3+} + 3e^-$


Thus, it is necessary to specify the number of electrons to be donated and to be accepted. For this purpose, a parameter, **oxidation number**, was defined. The oxidation number for monatomic

elements is the number of charges possessed by that atom. The oxidation numbers of Fe, $Fe^{2+}$ and $Fe^{3+}$ are 0, +2 and +3, respectively.

In order to extend the concept of oxidation number to polyatomic molecules, it is necessary to know the accurate distribution of electrons in the molecule. Since this is a difficult procedure, it was decided that a formal charge is to be assigned to each atom under some rule, and the oxidation number is defined based on the formal charge. The outline of definition is given below.

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**Definition of oxidation number**

1) Oxidation numbers of elements (including allotropes) is always 0.
2) Oxidation number of oxygen is -2 except that of peroxide, which is -1.
3) Oxidation number of hydrogen is +1 except that of metal hydride, which is -1.
4) Oxidation numbers of alkali metals are +1 and those of alkaline earth metals are +2.
5) For polyatomic molecules and ions, the oxidation number of each atom is so defined such that their sum will equal their electric charges.

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**Sample exercise 10.2**   Determination of the oxidation number

In the smelting of lead from its ore (lead sulfide) the following two-step oxidation-reduction reactions occurr. Indicate the oxidants and reductants in these reactions and find the oxidation numbers of each atom.

**Answer**

The oxidation number of each atom is indicated under its atomic symbol.

$$2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$$
  +2 -2       0         +2 -2       +4 -2

$$PbO(s) + CO(g) \rightarrow Pb(s) + CO_2(g)$$
 +2 -2     +2 -2        0        +4 -2
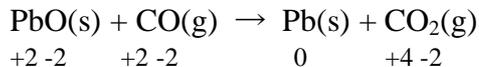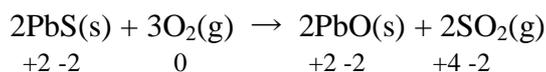
In the 1st stage of the reaction, the oxidation number of S changed from -2 to +4, and hence was oxidized. Thus PbS is a reductant. The oxidation number of O decreased from 0 to -2. Thus oxygen is an oxidant.

In the 2nd stage of the reaction, the oxidation number of C changed from +2 to +4, and hence was oxidized. Thus CO is a reductant. The oxidation number of Pb decreased from +2 to 0. Thus PbO is an oxidant.

In the smelting of metals such as iron, carbon monoxide often is a reductant.

(f)   **Construction of oxidation-reduction equations**

The equations of oxidants or reductants as shown in Table 10.1 can be easily made by the following procedure.

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**Construction of equations of oxidants or reductants (half-reaction)**

(1) Write the equation for the change of oxidants or reductants.
(2) Equalize the number of oxygen on both sides of the equations by adding an appropriate number of $H_2O$'s.
(3) Equalize the number of hydrogens on both sides of the equations by adding an appropriate number of $H^+$'s.
(4) Equalize the number of electric charge on both sides of the equations by adding an appropriate number of $e^-$'s.

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Once the reactions of oxidants and reductants (half-reactions) are constructed, it is easy to

construct the equation of the whole reaction of oxidation-reduction. In oxidation-reduction, the decrease in oxidation number of the oxidants and the increase in oxidation number of reductants should be equal. This is exactly the same as the equivalence relation in acid-base reactions.

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### Construction of oxidation-reduction equations

(1)   Choose the equations for the oxidant and the reductant involved in the reaction, and multiply each equation so that the number of electrons involved will be equal.
(2)   Sum up the two equations (note the electron terms are cancelled).
(3)   The counterions of the ions that appear in the equation should be added to both sides of the equation so that a material balance is maintained.

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As an example, the oxidation reaction of iodine by potassium permanganate $KMnO_4$ is as follows.

(1) Equation of the oxidant
   a)   $MnO_4^- \rightarrow Mn^{2+}$
   b)   $MnO4^- \rightarrow Mn^{2+} + 4H_2O$
   c)   $MnO_4^- + 8H+ \rightarrow Mn^{2+} + 4H_2O$
   d)   $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (half-reaction)

(2)   Equation of the reductant
   e)   $I^- \rightarrow 1/2\ I_2$
   f)   $I^- \rightarrow 1/2\ I_2 + e^-$
        $2I^- \rightarrow I_2 + 2e^-$ (half-reaction)
Note that the 2$^{nd}$ equation was doubled to eliminate the fraction.

(3)   To sum up the equations of the oxidant and the reductant
   g)   $2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$
        $10I^- \rightarrow 5I_2 + 10e^-$
   h)   $2MnO_4^- + 16H^+ + 10I^- \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$ (the whole-reaction)
   Note that the electron terms were cancelled.
   i)   $2KMnO_4 + 8H_2SO_4 + 10KI \rightarrow 2MnSO_4 + 5I_2 + 8H_2O + 6K_2SO_4$
   The above equation was obtained by adding appropriate counterions to both sides so that all ionic terms were cancelled to complete an equation of oxidation-reduction in which ten electrons were transferred from the reductant to the oxidant.

**Sample exercise 10.3** Oxidation of toluene
   Toluene $C_6H_5CH_3$ is oxidized to benzoic acid $C_6H_5COOH$ by $KMnO_4$ in $H_2SO_4$. Write the equations for this oxidation-reduction.
**Answer**
   The equation of the oxidant is already given. The equation for the reductant (toluene) is obtained as follows.

   b)   $C_6H_5CH_3 + 2H_2O \rightarrow C_6H_5COOH$
   c)   $C_6H_5CH_3 + 2H_2O \rightarrow C_6H_5COOH + 6H^+$
   d)   $C_6H_5CH_3 + 2H_2O \rightarrow C_6H_5COOH + 6H^+ + 6e^-$
   e)   The equation for the oxidant is multiplied by 6, and that for the reductant by 5 so that the number of electron involved in both reactions is identical ($= 30$).
   f)   To sum up the two equations (the electron terms will be cancelled)

$$6MnO_4^- + 48H^+ + 30e^- \rightarrow 6Mn^{2+} + 24H_2O$$
$$5C_6H_5CH_3 + 10H_2O \rightarrow 5C_6H_5COOH + 30H^+ + 30e^-$$

g) $5C_6H_5CH_3 + 6MnO_4^- + 18H^+ \rightarrow 5C_6H_5COOH + 6Mn^{2+} + 14H_2O$

i) $6K+ + 9SO4-$ is added to both sides to complete the reaction.
$$5C_6H_5CH_3 + 6KMnO_4 + 9H_2SO_4. \rightarrow 5C_6H_5COOH + 6Mn\,SO_4 + 3K_2SO_4 + 14H_2O$$
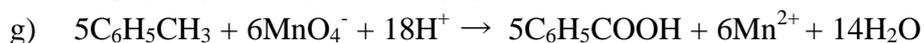
## (g) Stoichiometry of oxidation-reduction

The quantitative amounts of oxidants and reductants such that their oxidation-reduction reactions is complete is similar with that of acid-base reactions.

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**Stoichimometry of oxidation-reduction**

$$n_o M_o V_o \qquad = \qquad n_R M_R V_R$$

number of moles of electron accepted by reductant    number of moles of electron donated by reductant

where subscripts O and R are oxidants and reductants, respectively, $n$ is the change of oxidation number (absolute value), $M$ the molar concentration and $V$ is the volume of oxidants and reductants.

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The principle involved in the oxidation-reduction titration is essentially identical with that of acid-base titration. In the case of the former, the choice of indicator to show the end point is limited. Sometimes the conductivity of the solution is used as the indicator.

**Sample exercise 10.4**   Concentration of aqueous hydrogen peroxide

Commercial aqueous hydrogen peroxide $H_2O_2$ was diluted 150 times. 25.0 cm$^3$ of the sample solution was titrated with 0.02 mol dm$^{-3}$ $KMnO_4$ solution, and 26.3 cm$^3$ was required to reach the end point. Calculate the molar concentration (mol dm$^{-3}$) of $H_2O_2$.

**Answer**

Hydrogen peroxide acts as a reductant in the reaction, and it half-reaction is

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$

This means that 5 moles of $H_2O_2$ and 2 moles of $KMnO_4$ are equivalent. The molar concentration $M_R$ of commercial hydrogen peroxide is calculated as shown below.

5 x 0.02 (mol dm$^{-3}$) x 26.3 x 10$^{-3}$ (dm$^3$)
= [2 x $M_R$ (mol dm$^{-3}$) x 25.0 x 10$^{-3}$ (dm$^3$)]/150
$M_R$ = 7.89 (mol dm$^{-3}$)

## 10.2 (Electric) cells

A device to obtain electric currents with the aid of a chemical reaction is called a (**electric**) **cell**. In chemical cells, oxidation takes place at one of the electrodes, and reduction takes place at the other electrode. Electrons migrate from one electrode to the other.

## (a) Structure of cells

If you insert pieces of two metals with different ionization tendencies as electrodes in a solution of electrolytes (an electrolytic solution), and connect the two electrodes with a wire, a cell is constructed. (Fig. 10.1). First, the metal with higher ionization tendency will oxidize, generate cations, and dissolve into the electrolytic solution. The generated electrons will migrate to the metal with lower ionization tendency through the wire. At the metal with lower ionization tendency, the cations in solution will be reduced by accepting electrons which are flowing into the electrode.
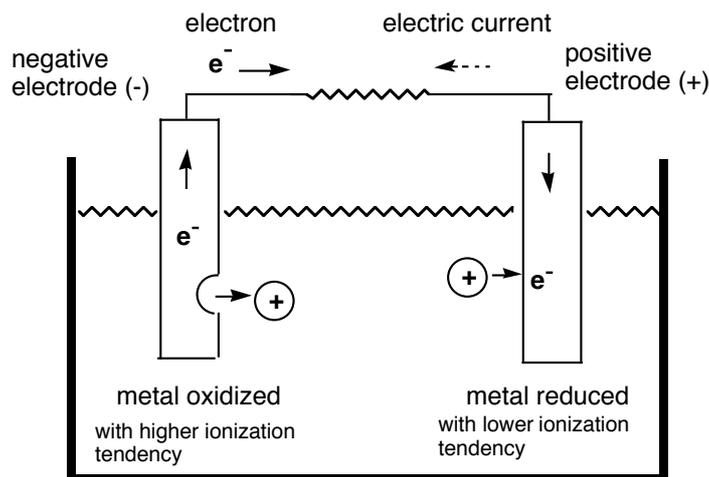
**Fig. 10.1** Schematic diagram of a cell
The metal with the higher ionization tendency is called the negative electrode and
the metal with the lower ionization tendency is called the positive electrode

In the 18$^{th}$ century, the direction of electric current was arbitrarily chosen so that it flows from the metal with lower ionization tendency to the one with higher ionization tendency. It must be admitted that, at that time, the true nature of electric current, that is, a flow of electron, was not understood. In fact this is the reverse of the direction of flow of electrons. The electrode into which the electric current flows is called the **negative electrode**, and the one from which electric current flows is called the **positive electrode**.

**(b)  Daniell cell**
Fig. 10.2 shows the mechanism of the most popular chemical cell, **Daniell cell** which was invented by the English chemist John Frederic Daniell (1790-1845).
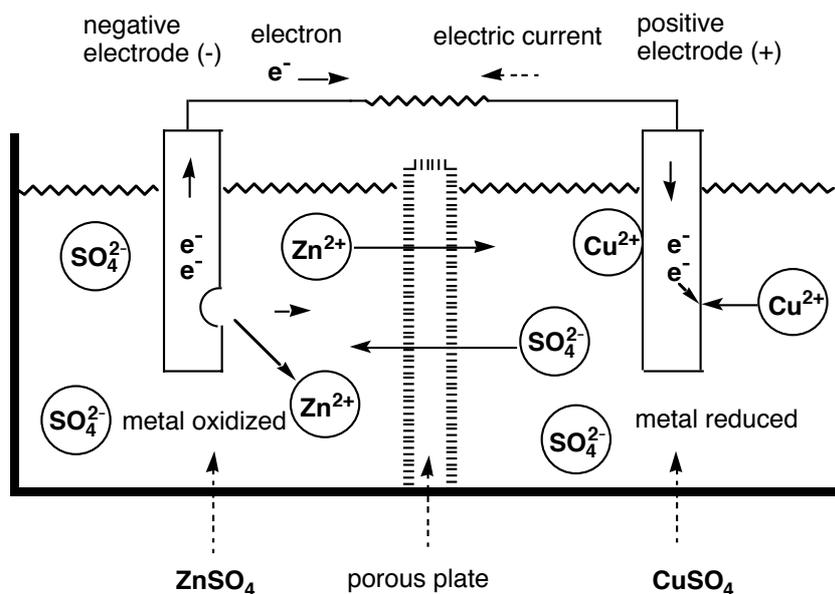


**Fig. 10.2** Daniell cell
The negative electrode consists of zinc/ zinc sulfate and
the positive electrode of copper/copper sulfate.

In Daniell cell, two metal electrodes are inserted into the solution of the two metal sulfates. The

negative electrode consists of zinc and aqueous zinc sulfate, and the positive electrode consists of copper and aqueous copper sulfate. These are usually designated as $Zn/ZnSO_4(aq)$ and $Cu/CuSO_4(aq)$, respectively. Sometimes, a simpler designation, *i.e.*, $Zn/Zn^{2+}$, is used.

A porous plate or similar material is used to separate the two kinds of solutions and at the same time to allow cations to migrate from the negative electrode to the positive one.

At the zinc electrode, the following reaction takes place.

$$Zn \rightarrow Zn^{2+}(aq) + 2e^-$$
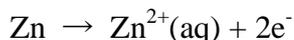
Here zinc is oxidized, and hence the zinc electrode is the negative electrode. At the copper electrode, the following reaction takes place.

$$2e^- + Cu^{2+}(aq) \rightarrow Cu$$
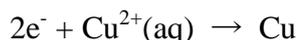
Here copper is reduced and hence the copper electrode is the positive electrode. The overall reaction is as follows.

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

or

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$
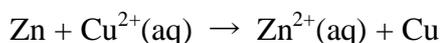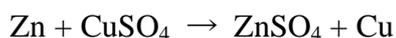
## 1.3 Electromotive force of cells

Suppose we measure the potential difference $\Delta V$ between two electrodes with the aid of a potentiometer when electric current generated by a chemical reaction is flowing. The limiting value of the potential difference when the electric current is zero is called the **electromotive force** of the cell.

The observed potential difference varies with the type of electrode material and the concentration or the temperature of the electrolytic solution. For the Daniell cell, the electromotive force at 25 C° is 1.10 *V* when the concentration of $Zn^{2+}$ and $Cu^{2+}$ ions are the same.

**(a) Standardization of electromotive force**

If the $Cu/CuSO_4$ electrode of the Daniell cell is replaced by a $Ag/AgNO_3$ electrode, the electromotive force of this cell is 1.56 V, which is substantially higher than that of the Daniell cell. Thus, the electromotive force of a cell varies to a considerable extent depending on the type of electrode material. Hence, the following method is used to compare the electromotive force of different types of cells.

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**Standardization of the electromotive force**

(1) The concentration and temperature of the electrolytic solution are to be maintained under a constant condition, *i.e.*, 25 C°and 1 mol dm$^{-3}$ (S.T.P). In fact the experimental values are extrapolated to those standard values.
(2) A cell is constructed with a common electrode that acts as a standard electrode.
(3) The electromotive force of this cell is determined including the sign (*i.e.*, which electrode will act as the positive electrode is determined.).
(4) By definition, the contribution of the standard electrode to the electromotive force of the cell is zero. Then the measured potential difference is a value characteristic of the electrode in question. This is called the **normal electrode potential** of this electrode.
(5) The electromotive force of any two cells is equal to the sum of the standard electrode potentials of the electrodes.

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The normal hydrogen electrode, which is composed of hydrogen and hydrochloric acid, $H_2$ (g, 1 atm)/$H^+$ (HCl, 1 mol $dm^{-3}$), is used as the standard electrode. In the normal hydrogen electrode, gaseous hydrogen contacts a solution containing proton (usually hydrochloric acid). Since hydrogen is not a conductor, an activated platinum plate is used as the plate of electrode. The electrode reaction is as follows.

$$1/2 \; H_2 \; \rightleftarrows \; H^+ + e^-$$

It is assumed that platinum will catalyze cleavage of the hydrogen molecule into atomic hydrogen. It is likely then that atomic hydrogen is involved in the electrode reaction.

**(b) Normal electrode potential**
The electromotive force of a cell composed of a pair of normal hydrogen electrodes (H/$H^+$) and a normalized Zn/$ZnSO_4$ electrode (Fig. 10.3) is -0.763 V. Note that the electrode reaction involved is

$$1/2 \; H_2 + 1/2 \; Zn^{2+} \rightarrow \; H^+ + 1/2 \; Zn$$
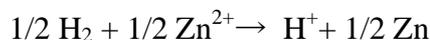
and not the one below.

$$H^+ + 1/2 \; Zn \; \rightarrow \; 1/2 \; H_2 + 1/2 \; Zn^{2+}$$

However, in view of the ionization tendency, the latter reaction is more likely to occur. The negative sign of the electromotive force indicates the difficulty for the former reaction to occur.
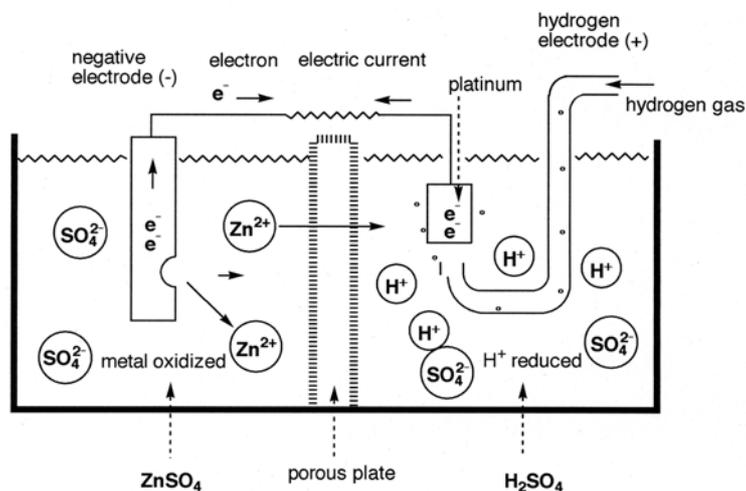


**Fig. 10.3** Standard electrode potential
From this experiment, the standard electrode potential of the reaction $1/2 \; H_2 + 1/2 \; Zn^{2+} \rightarrow \; H^+ + 1/2 \; Zn$ can be obtained. The standard electrode potential of the hydrogen electrode is defined as zero.

A cell made of a pair of Cu/$CuSO_4$ electrode and the normal hydrogen electrode is +0.337 *V*. The total reaction of the cell is as follows.

$$1/2 \; H_2 + 1/2 \; Cu^{2+} \rightarrow \; H^+ + 1/2 \; Cu$$
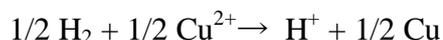
In view of the ionization tendency, this reaction is more likely to occur than the reverse

reaction. The positive sign of the electromotive force corresponds to this fact. The observed value of the electromotive force of Daniell cell, 1.1 $V$, corresponds to the difference of the normal electrode potential of the two electrodes. Thus,

$$+0.337 - (-0.763) = +1.100 \ (V)$$

The normal electrode potentials of important electrodes are given in Table 10.2.

**Table 10.2** The normal electrode potential $V$ (as aqueous solution, 25°C)

| | |
|---|---|
| $F_2 + 2e^- \rightarrow 2F^-$ | 2.87 |
| $Co^{3+} + e^- \rightarrow Co^{2+}$ | 1.92 |
| $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ | 1.776 |
| $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ | 1.695 |
| $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$ | 1.685 |
| $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ | 1.51 |
| $Au^{3+} + 3e^- \rightarrow Au$ | 1.50 |
| $PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$ | 1.455 |
| $Cl_2 \ (aq) + 2e^- \rightarrow 2Cl^-$ | 1.396 |
| $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ | 1.29 |
| $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ | 1.229 |
| $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ | 1.23 |
| $Br_2 \ (aq) + 2e^- \rightarrow 2Br^-$ | 1.087 |
| $NO^{3-} + 4H^+ + 3e^- \rightarrow NO + 2H_2O$ | 0.957 |
| $2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$ | 0.920 |
| $Ag^+ + e^- \rightarrow Ag$ | 0.799 |
| $Hg_2^{2+} + 2e^- \rightarrow 2Hg$ | 0.789 |
| $Fe^{3+} + e^- \rightarrow Fe^{2+}$ | 0.771 |
| $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ | 0.682 |
| $MnO_4^- + e^- \rightarrow MnO_4^{2-}$ | 0.558 |
| $I_2 + 2e^- \rightarrow 2I^-$ | 0.535 |
| $Cu^+ + e^- \rightarrow Cu$ | 0.521 |
| $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ | 0.401 |
| $Cu^{2+} + 2e^- \rightarrow Cu$ | 0.337 |
| $AgCl + e^- \rightarrow Ag + Cl^-$ | 0.222 |
| $SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$ | 0.171 |
| $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ | 0.154 |
| $Cu^{2+} + e^- \rightarrow Cu^+$ | 0.153 |
| $2H^+ + 2e^- \rightarrow H_2$ | 0.00 |
| $Pb^{2+} + 2e^- \rightarrow Pb$ | -0.129 |
| $Sn^{2+} + 2e^- \rightarrow Sn$ | -0.138 |
| $Ni^{2+} + 2e^- \rightarrow Ni$ | -0.228 |
| $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ | -0.355 |
| $Cd^{2+} + 2e^- \rightarrow Cd$ | -0.402 |
| $Cr^{3+} + e^- \rightarrow Cr^{2+}$ | -0.424 |
| $Fe^{2+} + 2e^- \rightarrow Fe$ | -0.440 |

| | |
|---|---|
| $Cr^{3+} + 3e^- \rightarrow Cr$ | -0.67 |
| $Zn^{2+} + 2e^- \rightarrow Zn$ | -0.763 |
| $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$ | -0.828 |
| $Mn^{2+} + 2e^- \rightarrow Mn$ | -1.18 |
| $Al^{3+} + 3e^- \rightarrow Al$ | -1.662 |
| $H_2 + 2e^- \rightarrow 2H^-$ | -2.25 |
| $Mg^{2+} + 2e^- \rightarrow Mg$ | -2.37 |
| $Na^+ + e^- \rightarrow Na$ | -2.714 |
| $Ca^{2+} + 2e^- \rightarrow Ca$ | -2.84 |
| $Ba^{2+} + 2e^- \rightarrow Ba$ | -2.92 |
| $K^+ + e^- \rightarrow K$ | -2.925 |
| $Li^+ + e^- \rightarrow Li$ | -3.045 |

Judging from the examples above, it is expected that electrodes made of metals with a large ionization tendency will have a large, negative normal electrode potential and electrodes made of halogens with large electronegativity will have a large, positive normal electrode potential. Such is indeed the case, and the normal electrode potentials of these electrode reactions,

$$Li^+ + e^- \rightleftarrows Li$$
$$F_2(g) + 2e^- \rightleftarrows 2F^-$$
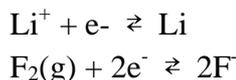
are -3.045 V and +2.87 V, respectively. You can understand the strategy to make a cell with high electromotive force. A combination of Li electrode and fluorine electrode is one possibility. Evidently care should be taken to ascertain safety of such cells if these are put to practical use. An alkali metal/alkali metal electrode is in fact used for the alkaline cell, which is one of the cells widely used.

**Sample exercise 10.5** Electromotive forces of cells
Calculate the standard electromotive force of cells (25 °C) given below with the aid of Table 10.2.
(1)  $Sn + Pb^{2+} \rightarrow Sn^{2+} + Pb$
(2)  $2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$
(3)  $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$
**Answer**
(1)   0.009 V     (2)   0.617 V   (3)    0.739 V

**(c)  Nernst's equation**
The concentration dependence of electrode potentials has already been described. For a generalized equation of cells,

$$aA + bB \rightleftarrows xX + yY$$

the electromotive force of cells is given by Nernst's equation.

$$E = E^\theta - (RT/nF) \ln([X]^x[Y]^y/[A]^a[B]^b)$$

where $E^\theta$ is the normal electromotive force (the electromotive force when all substances involved in the cell reaction are in the standard state), $n$ the number of electrons involved in the reaction, $F$ the

Faraday's constant, [A]. *etc*, are the molar concentrations of each ion involved.[a]

**Sample exercise 10.6** Nernst's equation

$K_2Cr_2O_7$/ $H_2SO_4$ is a well known oxidant, and its electrode reaction is as follows.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad (E^\theta = 1.29 \text{ V})$$

Calculate the electromotive force of this electrode under the following conditions. You can use the following values. $\ln x = 2.303 \log x$, $2.303RT/F = 0.0592$ V at 25°C.

(1)  $[Cr_2O_7^{2-}] = [Cr^{3+}] = [H^+] = 1.0$ mol dm$^{-3}$
(2)  $[Cr_2O_7^{2-}] = [Cr^{3+}] = 1.0$ mol dm$^{-3}$, $[H^+] = 10^{-7}$ mol dm$^{-3}$

Explain what can be known from these results.

**Answer**

(1) By substituting appropriate values into Nernst's equation, you will obtain the following result.
   $E = E^\theta + (0.0592/6) \log([Cr_2O_7^{2-}] [H^+]^{14}/[ Cr^{3+}]^2) = E^\theta = 1.26$ V.

In this case the electromotive force is equal to the normal electrode potential.

(2)  $E = 1.29 + (0.0592/6) \log[1.0 \times (10^{-7})^{14}]/1.0^2 = 0.33$ V.

It means that the electromotive force of the cell, and hence its power as an oxidant, is substantially decreased under neutral conditions.

When the cell reaction is in a chemical equilibrium state, then $E = 0$. Accordingly,

$$E = E^\theta - (RT/nF) \ln K$$

where $K$ is the equilibrium constant for the following equation.

$$K = ([X]^x[Y]^y/[A]^a[B]^b)_{eq}$$

where the subscript eq indicates that all molar concentrations are the values at the equilibrium state.

It is clear that the equilibrium constants can be determined by the measurements of electromotive force with the aid of Nernst's equation. Furthermore, if the concentrations of electrolyte solutions are different, electromotive force will be generated even if the same electrodes are employed. Such cells are called the **concentration cells**. The reaction proceeds in concentration cells in the direction that will equalize the difference in the concentrations at the two electrodes. This direction is in an agreement with Le Chatelier's principle.

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**Coffee Break: Cells and automobiles**

There will be a limit to the supply of fossil fuels in the near future. Cells certainly are of the candidates for the replacement of internal combustion engines. Nowadays various types of cars driven by cells are used to some extent.

One such cells that is proposed is the sodium-sulfur cell, in which sodium acts as the negative electrode (reductant) and sulfur as the positive electrode (oxidant), and both are used in the molten state. The electrolyte is called β–alumina. That is a ceramic composed of sodium, aluminum, lithium and magnesium oxide in which ions can migrate. The ceramic must be kept at a high temperature of 350 °C to maintain the electrolyte in molten state, but its efficiency per unit mass is four times as high as that of a lead storage battery. If this cell were ever put to practical use, a car loaded with molten sodium would be horrible from the viewpoint of chemists.

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## 10.4 Cells in practical use

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[a] It is necessary to use activity rather than molar concentration if a high accuracy is required.

### (a)    Lead storage battery

The value of cells consists in their utility. Among them, the **lead storage battery** has been used since *ca.* 1915. Thanks to this battery, automobiles could attain mobility, and consequently become the most important means of transportation today. The lead storage battery can stand severe conditions (variable temperature, mechanical shocks due to bad roads, *etc.*) and can be used continuously for several years.

In the lead storage battery, the negative electrode is metallic lead and the positive electrode is lead covered with lead oxide, and both electrodes are dipped in sulfuric acid, the electrolytic solution. The electrode reactions are as follows:

Negative electrode:        $Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$

Positive electrode:        $PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

Total reaction:        $Pb(s) + PbO_2 (s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
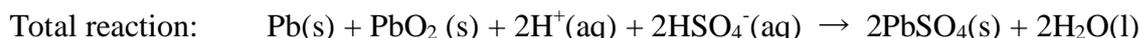
The electromotive force of one cell is *ca.* 2 V, and in practice, six cells are connected in series to obtain 12 V. During **discharge**, sulfuric acid is consumed and its concentration decreases from an initial value of 1.28 g cm$^{-3}$. Hence, by measuring the specific gravity of the electrolytic solution, the condition of the cell can be monitored.

In practice, before the decrease of the specific gravity of the electrolytic solution becomes large, electric current is supplied which reverses the above reactions. This process is called **charging**. Cells that can be charged are called **reversible cells** and those that cannot (like dry cells) are called **irreversible cells**.

During charging, lead sulfate decomposes into lead and lead oxide, and the sulfuric acid that had been consumed is regenerated. Water once formed is also reused. However, water tends to evaporate to some extent, and a side reaction, the electrolysis of water, necessarily accompanies, and hence it is necessary to supply a small amount of distilled water to conventional lead batteries. Recently a new type of electrode made of an alloy of lead and calcium, which can prevent electrolysis of water, was developed. Modern batteries with this type of electrode are a closed system and are called the **closed storage battery** for which a supply of water is unnecessary.

### (b)   Other useful cells

**The Leclanché cell** was invented by the French engineer Georges Leclanché (1839-1882) more than one hundred years ago. Various improvements have been made since then, but, surprisingly, the original design has been maintained as the **manganese dry cell**.

The manganese dry cell is composed of a zinc inner case as the negative electrode, carbon (graphite) rod as the positive electrode and the paste of solid $MnO_2$ and solid $NH_4Cl$ that acts as the electrolytic solution (Fig. 10.4).
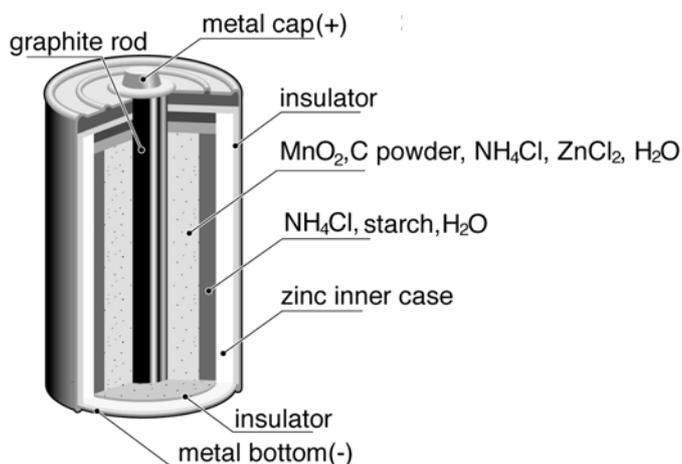
**Fig. 10.4** The structure of the manganese dry cell
Though most widely used, the details of the electrode reaction are not yet clear.

Though in fact complicated, the electrode reactions of the manganese dry cell can be approximately summarized as follows.

Negative electrode:  $Zn \rightarrow Zn^{2+} + 2e^-$

Positive electrode:  $2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$
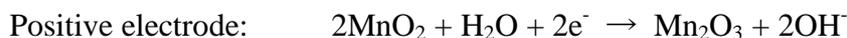
The electromotive force of the manganese dry cell is *ca*. 1.5 V.
In **alkaline dry cells**, solid KOH or NaOH is used instead of solid $NH_4Cl$. The electrode reaction is as follows.

Negative electrode:  $Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$

Positive electrode:  $2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$
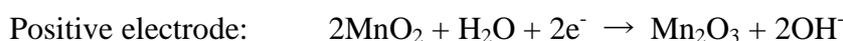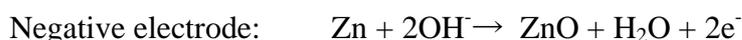
The life of manganese dry cells is shortened because of corrosion of the zinc electrode caused by acidic $NH_4Cl$. Alkaline dry cells are free from this problem since they are basic within. Hence their life is longer.
Like the lead storage battery, **nickel-cadmium cells** are reversible. Furthermore, it is possible to make nickel-cadmium cells much smaller and much lighter than the lead storage cell. Hence these are widely used as a portable power source. The electrode reaction is as follows.

Negative electrode:  $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$

Positive electrode:  $NiO_2 + 2H_2O + 2e^- \rightarrow Ni(OH)_2 + 2OH^-$
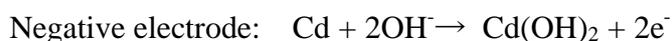
## (c) Fuel cell

The design of fuel cells is such that the reactants are continuously supplied to the cell. The fuel cell used in the Apollo project utilized the heat of formation of water from hydrogen and oxygen. Usually the heat of formation is discharged as heat. In full cells the thermal energy is converted to the electric energy. The electrode reactions are as follows.

Negative electrode:  $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

Positive electrode:  $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Total reaction:  $2H_2 + O_2 \rightarrow 2H_2O$

The structure of fuel cells is shown in Fig. 10.5.
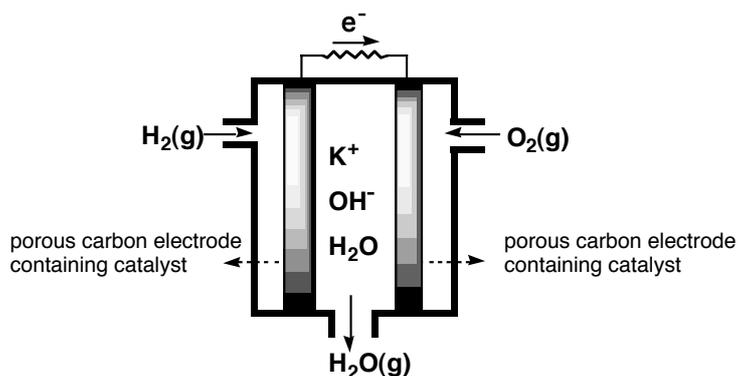
**Fig. 10.5** Structure of fuel cells
The heat of combustion generated from the reaction between oxygen
and hydrogen is converted to electric energy.

Though substantial amounts of manpower and funds have been pumped into the project, thus far, economically viable fuel cells have not yet been made. In the future, however, fuel cells will most likely be put into practice if and only if a cheap and stable supply of hydrogen and oxygen is realized. Study along this line is being promoted.

## 10.5 Electrolysis

**(a) Cells and electrolysis**

In cells, oxidation-reduction reactions proceed spontaneously, and the chemical energy accompanying the chemical reactions is converted to electric energy. If voltage is applied to the cell from the direction reverse to the electromotive force, a chemical reaction that corresponds to the negative electromotive force is induced. In other words, reactions that do not occur spontaneously are now induced by the electric energy. This process is called **electrolysis**. The charging of a lead storage battery is an example of electrolysis.

The total reaction of the Daniell cell is as follows.

$$Zn + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu$$
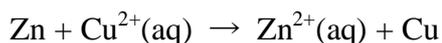
Suppose a voltage higher than 1.1 V is applied in the direction reverse to the electromotive force, the reverse reaction takes place. Thus, zinc will deposit and copper will begin to dissolve.

$$Zn^{2+}(aq) + Cu \rightarrow Zn + Cu^{2+}(aq)$$
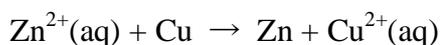
Fig. 10.6 shows a schematic representation of the chemical reaction which occurs when a reverse voltage is applied to the Daniel cell. Compare this with Fig. 10.2.
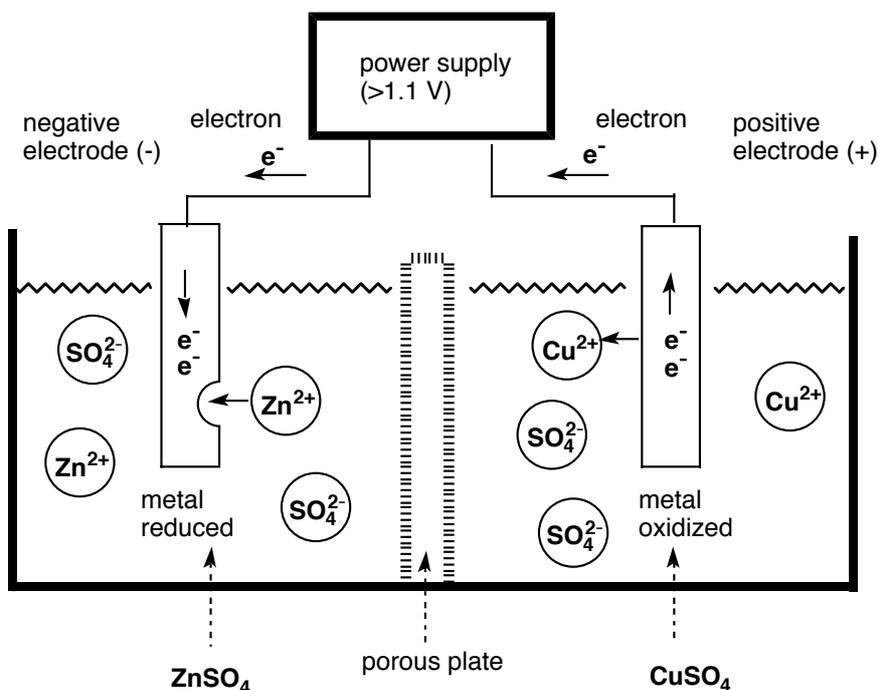
**Fig. 10.6** Electrolysis
A reaction reverse to that in the Daniell cell takes place. Zinc deposits and copper dissolves.

## (b) Faraday's law of electrolysis

In the first half of the 19th century, Faraday investigated the relation between the quantity of electricity which flows in a cell and the quantity of substances chemically changed at the electrodes during the electrolysis. He summarized the results in two laws in 1833.

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**Faraday's law of electrolysis**

(1) The quantity of substances produced at the electrodes is proportional to the quantity of electricity that flows in the cell.

(2) When a certain quantity of electricity flows in the cell, the number of moles of substances changed at the electrodes is constant regardless of the type of substance. For instance, the quantity of electricity necessary to deposit 1 mole of a monovalent metal is 96,485 C (Coulomb) regardless of the type of metal.

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C (Coulomb) is a unit of electricity, and 1 C is the quantity of electricity when 1 A (Ampere) of electric current flows for 1 s. The fundamental constant of electricity, the Faraday constant $F$, 9.65 x $10^4$ C, is defined as the quantity of electricity carried by 1 mole of electrons. It is possible to calculate the quantity of moles of chemical change caused when a constant stream of electric current flows for a certain time.

**Sample exercise 10.7** Faraday's law of electrolysis
Electric current of 0.200 A flowed through two potentiometers connected in series for 20 min. One potentiometer had a $Cu/CuSO_4$ electrode and the other a $Pt/dil. H_2SO_4$ electrode. Calculate the following values assuming Cu = 63.5.
(1) Quantity of Cu deposited on the 1st potentiometer.
(2) Volume of hydrogen at S. T. P. generated at the 2nd potentiometer.
**Answer**
The quantity of electricity that flowed is 0.200 x 20 x 60 = 240.0 C.
(1) The reaction involved is $Cu^{2+} + 2e^- \rightarrow$ C, then the mass $w$ (g) of Cu deposited is as follows.

$w$ (g) = [63.5 (g mol$^{-1}$)/2] x [240.0 (C)/96500(C mol$^{-1}$)] = 0.079 g

(2)   Since the reaction involved is $2H^+ + 2e^- \rightarrow H_2$, the volume of hydrogen generated $v$ (cm$^3$) is given below.

$v$ (cm$^3$) = [22400 (cm$^3$mol$^{-1}$)/2] x [240.0(C)/96500(C mol$^{-1}$)] = 27.85 cm$^3$

## (c) Industrially important electrolyses

The 1$^{st}$ electrolysis attempted was the hydrolysis of water (1800). Davy immediately followed and successfully isolated alkali and alkaline earth metals. Even now electrolysis is used to produce various metals. Electrolysis is particularly useful for the production of metals with high ionization tendencies (*e.g.*, aluminum).

The industrial production of aluminum by electrolysis was achieved in 1886 independently by the American inventor Charles Martin Hall (1863-1914) and the French inventor Paul Louis Toussaint Héroult (1863-1914) at the same time. The success of this electrolysis was due to the use of molten $Na_3AlF_6$ as the solvent of the ore (aluminum oxide; alumina $Al_2O_3$).

As a requirement for successful electrolysis, ions can migrate to the electrodes. An obvious way to give mobility to ions is to use its aqueous solution. However, in the case of electrolysis of alumina, an aqueous solution is inadequate because water is more readily reduced than the aluminum ion as shown below.

$Al_3^+ + 3e^- \rightarrow Al$        normal electrode potential = -1.662 V

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$        normal electrode potential = -0.828 V
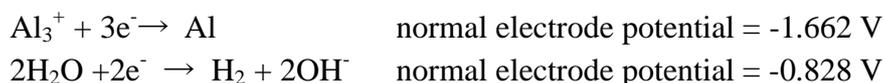
Another method would be the use of molten salt. The trouble is that the melting point of $Al_2O_3$ is as high as 2050 °C, and electrolysis at such a high temperature is not realistic. However, the melting point of a mixture of $Al_2O_3$ and $Na_3AlF_6$ is *ca.* 1000 °C, and this temperature is easy to attain.

The details of the procedure are as follows: the ore, bauxite, contains various metal oxides as impurities. The ore is treated with alkali, and only amphoteric aluminum oxide dissolves. Insoluble materials are filtered off, and carbon dioxide is blown through the filtrate to cause hydrolysis (of salts). Alumina is deposited.

$Al_2O_3(s) + 2OH^-(aq) \rightarrow 2AlO_2^-(aq) + H_2O(l)$

$2CO_2 + 2AlO_2^-(aq) + (n+1)H_2O(l) \rightarrow 2HCO_3^-(aq) + Al_2O_3 \cdot nH_2O(s)$
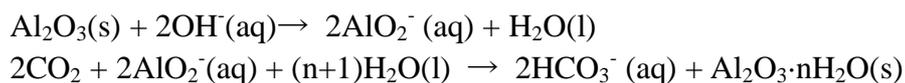
The alumina thus obtained is mixed with $Na_3AlF_6$ and then **molten salt electrolysis** of the mixture is carried out. The reactions in the electrolytic cell are complicated. It is likely that initially alumina reacts with $Na_3AlF_6$ and then electrolytic reactions take place.

$Al_2O_3 + 4AlF_6^{3-} \rightarrow 3Al_2OF_6^{2-} + 6F^-$

The electrode reactions are as follows.

Negative electrode:      $2Al_2OF_6^2 + 12F^- + C \rightarrow 4AlF_6^{3-} + CO_2 + 4e^-$

Positive electrode:      $AlF_6^{3-} + 3e^- \rightarrow Al + 6F^-$

Total reaction:      $2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2^-$
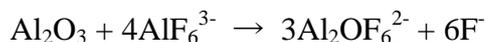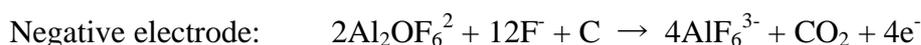
The purity of aluminum obtained by this procedure is *ca.* 99.55 %. Aluminum is used as such and as alloys with other metals. The properties are excellent and, in addition, the price is modest. However, it must be remembered that the production of aluminum requires a tremendous amount of

electricity.

## Exercise

### 10.1   Oxidation number
Indicate the oxidation number of each of underlined atom in the compounds below.
(a)  H̲Br     (b) LiH̲     (c) C̲Cl$_4$   (d) C̲O     (e) ClO$^-$
(f)  C̲l$_2$O$_7$   (g) H$_2$O̲$_2$   (h) C̲rO$_3$   (i) C̲rO$_4^{2-}$ (j) Cr$_2$O$_7^{2-}$
**Answer**
(a)   +1   (b)  -1   (c)  +4   (d)  +2   (e)   +1
(f)   +7   (g)  -1   (h)   +6   (i)   +6   (j)   +6

### 10.2 Oxidation-reduction reactions
For each of the following questions, find the oxidation number of underlined atoms. Identify oxidants and reductants and point out the atoms whose oxidation number changed.
(a)   P̲bO$_2$ + 4H$^+$ + S̲n$^{2+}$  →   P̲b$^{2+}$ + S̲n$^{4+}$ + 2H$_2$O
(b)   5A̲s$_2$O$_3$ + 4MnO$_4^-$ + 12H$^+$  → 5As$_2$O$_5$ + 4Mn$^{2+}$ + 6H$_2$O
**Answer**
(a) Pb: +4  →  +2   reduced.    Sn: +2  →  +4   oxidized
(b) As: +3  →  +5   oxidized.    Mn: +7  →  +2   reduced

### 10.3 Oxidation-reduction titration
0.2756 g of iron wire was dissolved in an acid to reduce Fe$^{3+}$ to Fe$^{2+}$. The solution was titrated with 0.0200 mol dm$^{-3}$ K$_2$Cr$_2$O$_7$ and 40.8 cm$^3$ of the oxidant solution was required to reach the end point. Calculate the purity (%) of Fe$_2$
**Answer**
99.5 %

### 10.4 Electromotive force of cells
Calculate the normal electromotive force of cells (at 25°C) whose reactions are given by the following equations. Which of these would act as an effective cell?
(a) Mg + 2H$^+$  →  Mg$^{2+}$ + H$_2$
(b) Cu$^{2+}$ + 2Ag  →  Cu + 2Ag$^+$
(c) 2Zn$^{2+}$ + 4OH$^-$  →  2Zn + O$_2$ + 2H$_2$O
**Answer**
(a) Mg  →  Mg$^{2+}$ +2e$^-$,     +2.37 ,V.    2H$^+$ + 2e$^-$→ H2,     0.00 V
electromotive force:   +2.37 V,   effective.
(b) Cu$^{2+}$ + 2e$^-$→  Cu,   0.337 V.    Ag→ Ag$^+$ + e$^-$,   -0.799 V
electromotive force:   -0.46 V,   not effective.
(c) Zn$^{2+}$ + 2e$^-$→  Zn,   -0.763 V.    4OH$^-$  → 4e$^-$ + O$_2$ + 2H$_2$O,   -0.401 V
electromotive force:   -1.16 V,   not effective.

### 10.5 Nernst's equation
Calculate the electromotive force of the cell (at 25°C) whose reactions are given by the following equations.
        Cd + Pb$^{2+}$  →  Cd$^{2+}$ + Pb
        [Cd$^{2+}$] = 0.010 mol dm$^{-3}$; [Pb$^{2+}$] = 0.100 mol dm$^{-3}$
**Answer**
    0.30 V
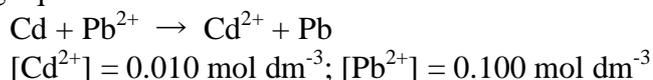
### 10.6 Faraday's law

Bismuth is produced by the electrolysis of ore according to the following equation. 5.60 A of electric current was passed for 28.3 min. through a solution containing $BiO^+$. Calculate the mass of bismuth obtained.

$$BiO^+ + 2H^+ + 3e^- \rightarrow Bi + H_2O$$

**Answer**

6.86 g