9

Oxidation and reduction

- What is an electrochemical cell?
- What are the electrode materials in nickel–metal-hydride batteries?
- What information is contained in a Pourbaix diagram?

Oxidation and reduction involve the transfer of electrons from one compound to another. Reactions involving oxidation and reduction are called redox reactions. The first important application of a redox reaction was the construction of the first battery, reported by Alessandro Volta in 1800. Volta's battery simply consisted of a stack of alternating silver and zinc discs. A sheet of porous material, parchment, cloth or hide, saturated with a salt solution, was inserted between each silver and zinc disc. A current was found to flow when a wire connected the bottom silver disc to the top zinc disc. The voltage increased as the number of layers in the stack increased. What happens, in fact, is that one component is being oxidised, and one is being reduced. The subsequent electron transfer takes place in the external circuit, and is observed as an electric current.

One of the major problems encountered with the Volta pile was severe corrosion of the metals, and many early experiments were directed towards solving this problem. Thus it is apparent that batteries and corrosion are closely linked and, indeed, both are oxidation and reduction reactions. Oxidation and reduction is also involved in the related process of electrolysis, which underlies electroplating, a method of preventing corrosion. Finally, oxidation and reduction reactions underpin all life processes, although this aspect is not covered here.

9.1 Redox reactions

9.1.1 Oxidation and reduction

Oxidation and reduction reactions involve the transfer of electrons from one chemical compound to another. Oxidation is electron loss. It is characterised by an increase in the oxidation number of the species oxidised (see Section S3.3). For example, when solid zinc metal in contact with water is oxidised it forms zinc ions in solution and releases two electrons:

$$\mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}(aq)} + 2\mathrm{e^-} \quad [0 \rightarrow +2]$$

The change in oxidation number is shown in brackets, $[M \rightarrow N]$.

Understanding solids: the science of materials. Richard J. D. Tilley
ISBNs: 0 470 85275 5 (Hbk) 0 470 85276 3 (Pbk)

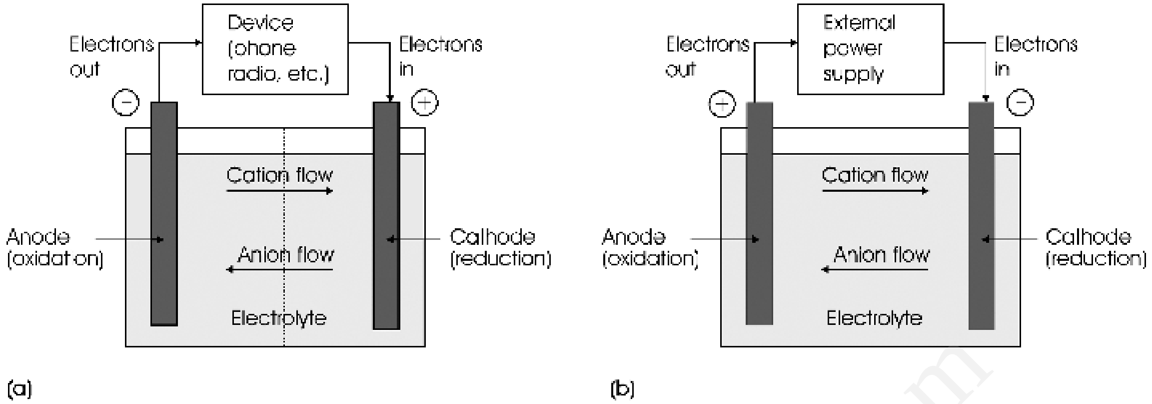

Figure 9.1 The principle of (a) a galvanic cell and (b) an electrolytic cell

An oxidising agent causes oxidation. It takes electrons from the species being oxidised and becomes reduced in the process.

Reduction is the opposite of oxidation and is equivalent to electron gain. The oxidation number of a species decreases on reduction. For example, copper ions in water solution can gain two electrons and form metallic solid copper in the process:

$$\mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)} \quad [+2 \rightarrow 0]$$

A reducing agent causes reduction. It gives up electrons to the species being reduced and becomes oxidised itself.

These reactions, which cannot occur in isolation, are called half-reactions. The reduced and oxidised pair of species found in a half-reaction is called a redox couple. The redox couple is written: oxidised species/reduced species, for example, Cu^{2+}/Cu or Zn^{2+}/Zn. A reaction involving oxidation and reduction, two half-reactions, is called a redox reaction. The redox reaction in the above examples is:

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

9.2 Galvanic cells

An electrochemical cell is a device for the conversion of electrical to chemical energy, and vice versa, by way of redox reactions. Electrochemical cells consist of two metal electrodes (an anode and a cathode) in contact with an electrolyte that is able to conduct ions but not electrons (Figure 9.1). A galvanic cell (Figure 9.1a) uses a spontaneous chemical reaction to produce an external electric current. Galvanic cells are called batteries in colloquial speech. Electrolytic cells (Figure 9.1b), employed for electrolysis and electroplating, use external electrical power to force nonspontaneous chemical reactions to take place.

9.2.1 The Daniel cell

The principle behind all galvanic cells can be explained with reference to one of the simplest, the Daniell cell, which was invented in 1836. It consists of a zinc rod in a solution of zinc sulphate, and a copper rod in a solution of copper sulphate. To complete the circuit, a porous solid layer, which allows ions to pass between the sulphate electrolytes, and an external metallic conductor between the zinc and copper, are needed. In this case, electrons then pass around the external circuit and ions travel through the electrolyte solutions (Figure 9.2).

Experiment will show that the zinc rod is negative and is called the anode, whereas the copper rod is positive and is called the cathode. When the external connection is completed, a current of electrons

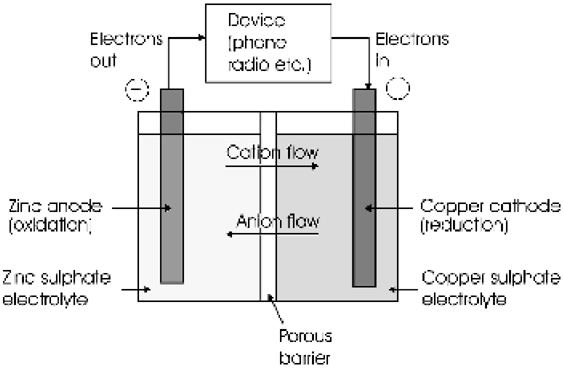

Figure 9.2 A Daniell cell

flows from the zinc anode to the copper cathode. The reaction is spontaneous and needs no external assistance. The current will persist until one of the reactants is consumed.

The electrons are generated by a spontaneous redox reaction in the cell. Oxidation occurs at the zinc anode and reduction takes place at the copper cathode. The reactions taking place are as follows.
Anode half-reaction (oxidation, electron generation):

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

Cathode half-reaction (reduction, electron consumption):

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

Zinc is oxidised to Zn^{2+} ions on one side of the porous barrier and Cu^{2+} ions are reduced to metallic copper on the other. Electrons pass via the external circuit. Ions pass through the electrolytes to maintain charge balance in the cell. The chemical reaction being used to generate electricity, called the cell reaction, is obtained by adding the anode and cathode half-reactions, ensuring, by appropriate multiplication, that the number of electrons cancels out, as follows.
Cell reaction (redox reaction):

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

There are a number of other processes occurring as well as the generation of an electric current. The zinc anode is being dissolved. If left for sufficient time the rod degrades and is noticeably corroded. At the same time the copper rod gains weight and a layer of new copper metal forms on the surface. Electroplating is occurring.

9.2.2 *Standard electrode potentials*

A combination of *any* two dissimilar metallic conductors can be used to construct a galvanic cell. The cell potential defines the measure of the energy available in a cell. A high cell potential signifies a vigorous spontaneous redox reaction. The unit of potential is the volt, V. A Daniell cell, for example, has a potential of 1.1 V.

Because of the multiplicity of possible cells it is more convenient to consider the cell potential as being made up from separate voltage contributions from anode and cathode half-reactions. We can then write:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}}(\text{reduction half-reaction}) \\ &\quad + E_{\text{anode}}(\text{oxidation half-reaction}) \end{aligned}$$

In general, only the reduction half-reaction potentials are listed in tables, as in Table 9.1. The potential of an oxidation half-reaction is the negative of the value of the reduction half-reaction. Moreover, it is convenient to standardise the concentrations of the components of the cells. If the cell components are in their standard states, standard electrode potentials, E°, are recorded:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} + E^\circ_{\text{anode}}$$

For cells involving ionic solutions the standard state is a solution of 1 molar concentration, and for cells involving gases these are at 1 atmosphere pressure.(1)

It is not possible to measure the voltage generated by half a cell, and it has been agreed that the voltage should be measured with respect to a reference electrode using hydrogen gas, called the standard hydrogen electrode. The reference electrode is a

---

(1) The recommended standard state pressure is 10^5 Pa, but all tabulated data, including that listed here, refer to a standard state of 1 atmosphere (101325 Pa).

Table 9.1 Standard reduction potentials, E°, at 25 °C

Half-reaction	E°/V
$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Au^+ + e^- \rightarrow Au$	+1.69
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23[a]
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.85
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$I_2 + 2e^- \rightarrow 2I^-$	+0.54
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40[a]
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22
$2H^+ + 2e^- \rightarrow H_2$	0[b]
$Fe^{3+} + 3e^- \rightarrow Fe$	−0.04
$O_2 + H_2O + 2e^- \rightarrow OH^- + HO_2^-$	−0.08
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.25
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$Fe(OH)_3 + e^- \rightarrow Fe(OH)_2 + OH^-$	−0.56
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$2H_2O + 2e^- \rightarrow 2OH^- + H_2$	−0.83[c]
$Ti^{2+} + 2e^- \rightarrow Ti$	−1.63
$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$Be^{2+} + 2e^- \rightarrow Be$	−1.85
$Sc^{3+} + 3e^- \rightarrow Sc$	−2.10
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.36
$La^{3+} + 3e^- \rightarrow La$	−2.52
$Na^+ + e^- \rightarrow Na$	−2.71
$K^+ + e^- \rightarrow K$	−2.93
$Li^+ + e^- \rightarrow Li$	−3.05

[a] +0.81 at pH 7.
[b] Zero, by definition.
[c] −0.42 at pH 7.
Standard conditions: concentration of each ion is 1 mol l^{-1} and all gases are at 1 atm pressure.

mixture of H^+ ions and H_2 gas in the standard state of $H^+(aq)$ at 1 mol l^{-1} and $H_2(g)$ at 1 atm. The standard electrode potential of this half-reaction is defined as zero:

$$2H^+(aq) + 2e^- \rightarrow H_2(g), \quad E^\circ = 0 \text{ V}$$

When the hydrogen electrode is incorporated in a cell, it will form either the anode or the cathode, depending on the other metal involved. For example, in a cell made with zinc, the zinc electrode is found to be the anode and the hydrogen electrode is the cathode, as follows.

Anode half-reaction (oxidation, electron generation):

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad E^\circ = +0.76 \text{ V}$$

Cathode half-reaction (reduction, electron consumption):

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \quad E^\circ = 0 \text{ V}$$

Cell reaction:

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \quad E_0 = +0.76 \text{ V}$$
$$E^\circ(\text{cell}) = +0 \text{ V} + (+0.76 \text{ V}) = 0.76 \text{ V}$$

The Zn is oxidised to Zn^{2+}, and the $H^+(aq)$ is reduced to $H_2(g)$. Note that because zinc is the anode, the value of E° for the anode half-reaction is the negative of that given in Table 9.1.

In a cell using copper, the hydrogen electrode is found to be the anode and the copper electrode the cathode, as follows.

Anode half-reaction (oxidation, electron generation):

$$H_2(g) \rightarrow 2H^+(aq) + 2e^- \quad E^\circ = 0 \text{ V}$$

Cathode half-reaction (reduction, electron consumption):

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E_0 = +0.34 \text{ V}$$

Cell reaction:

$$H_2(g) + Cu^{2+}(aq) \rightarrow 2H^+(aq) + Cu(s)$$
$$E_0 = +0.34 \text{ V}$$
$$E^\circ(\text{cell}) = +0.34 \text{ V} + 0 \text{ V} = +0.34 \text{ V}$$

When many cells are compared, it is found that the anode is always the material that has the lowest tendency to be reduced. From the two examples above, it is seen that the order of the electrodes with respect to this tendency is $Zn^{2+}/Zn < H^+/H_2(g) < Cu^{2+}/Cu$. Thus, in a Daniell cell, zinc forms the anode and copper the cathode, as follows.

Anode half-reaction (oxidation, electron generation):

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad E^\circ = +0.76\,V$$

Cathode half-reaction (reduction, electron consumption):

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E^\circ = +0.34\,V$$

Cell reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$$
$$E^\circ = +0.34\,V$$
$$E^\circ(\text{cell}) = +0.34\,V + (+0.76\,V) = 1.10\,V$$

As before, note that because zinc is the anode, the value of E° is the negative of that given in Table 9.1.

The comparison of each element to a hydrogen electrode in a standard galvanic cell allows the reduction tendency to be ranked. A table of these values arranged so that the elements with the greatest tendency to be reduced (the most strongly oxidising) are at the top is referred to as the electrochemical series. An abbreviated electrochemical series is given in Table 9.1. The oxidised species in a redox couple has the ability to oxidise the reduced species in any redox couple below it in the table. Moreover, such a reaction will be spontaneous. For example, fluorine gas, F_2, will have the highest tendency to be reduced, or gain electrons, and lithium metal, Li, has the highest tendency to be oxidised, or lose electrons. Mixing these elements will lead to a spontaneous, and very vigorous, reaction, leading to the production of Li^+ and F^- ions.

When forming a galvanic cell, the couple higher in the table forms the cathode and the couple below in the table forms the anode. This is written using a standard notation (see Section 53.4):

$$\text{lower couple (anode)} \,||\, \text{higher couple (cathode)}$$

When written out fully this means:

The lower couple, which forms the anode, undergoes the reaction

‘reduced species → oxidised species + ne^-’,

whereas the higher couple, which forms the cathode, undergoes the reaction

‘oxidised species + ne^- → reduced species’

The cell diagrams and cell voltages for the cells described earlier are written:

$$Zn(s)|Zn^{2+}(aq)||H^+(aq)|H_2(g)|Pt \quad E^\circ = 0.76\,V$$
$$Pt|H_2(g)|H^+(aq)||Cu^{2+}(aq)|Cu(s) \quad E^\circ = 0.34\,V$$
$$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s) \quad E^\circ = 1.10\,V$$

- E°(cathode) is obtained directly from the table of standard reduction potentials;
- E°(anode) is the *negative* of the standard reduction potential;
- E°(cell) is the cathode standard reduction potential plus the *negative* of the anode standard reduction potential.

The voltage of a cell when all of the reactants are in the standard conditions defined above is called the standard cell potential, E°. The standard cell potential of any cell can be derived from the appropriate standard reduction potentials.

9.2.3 Cell potential and free energy

The free energy of a reaction is a measure of the tendency for a chemical reaction to take place (see Section S3.2). The direction of spontaneous change in a process is that of decreasing free energy. If we write ΔG_r as the free energy change of a reaction, ΔG_r is *negative* for a spontaneous change. The cell potential is related to the Gibbs energy of the cell reaction by:

$$\Delta G_r = -nE_{\text{cell}}F$$

Where E_{cell} is the cell potential in volts, defined to be positive; F is the Faraday constant, 96485 C mol^{-1}; and n is the number of moles of electrons that migrate from anode to cathode in the cell reaction. Thus a galvanic cell is also a Gibbs energy meter.

When the electrodes are in their standard states, the free energy change is called the standard reaction free energy, $\Delta G^\circ{}_\text{r}$, and the cell voltage is just the standard cell potential, E°. In this case:

$$\Delta G_\text{r}^\circ = -nE^\circ F$$

For example, in the Daniell cell:

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

Two electrons are transferred in the cell reaction, hence $n = 2$. [Note that the number of electrons taking part in the reaction is usually clear from the half-reactions rather than from the cell reaction.] Hence,

$$\begin{aligned}\Delta G_\text{r} &= -2E_{\text{cell}}F \\ &= -(1.93 \times 10^5)E_{\text{cell}}\end{aligned}$$

When E_{cell} is measured in volts, the value of ΔG_r is in joules. When the concentrations of both Cu^{2+} and Zn^{2+} are 1 mol l^{-1} (the standard state),

$$\Delta G_\text{r}^\circ = -nE^\circ F$$

9.2.4 Concentration dependence

The potential generated by a cell is dependent on the concentration of the components present. The relationship is given by the equation:

$$\Delta G_\text{r} = -nE_{\text{cell}}F = RT\ln\left(\frac{Q}{K}\right)$$

where R is the gas constant, T is the temperature (in kelvin), Q is the reaction quotient, and K is the equilibrium constant (see Section 8.1).

The reaction quotient, Q_c, of a reaction

$$a\text{A} + b\text{B} \rightleftharpoons x\text{X} + y\text{Y}$$

is given by:

$$Q_\text{c} = \frac{[\text{X}]^x[\text{Y}]^y}{[\text{A}]^a[\text{B}]^b}$$

where [A] denotes the concentration of compound A at any time, and so on. For reactions involving gases, the concentration term can be replaced by the partial pressure of the gaseous reactants, to give:

$$Q_\text{p} = \frac{p_\text{X}^x p_\text{Y}^y}{p_\text{A}^a p_\text{B}^b}$$

These expressions are identical to those for the equilibrium constant given in Section 8.1.2, except that they apply to any concentrations or partial pressures, not just those when the system is at equilibrium. Pure liquids or solids, or water in solutions, appearing in the reaction equation do not appear in the equations for Q. (The quantity of importance is the activity rather than the concentration. Activity and concentration are equal in dilute solutions; see Section S3.2).

At equilibrium:

$$Q = K$$

The cell voltage is then given by rearrangement of

$$-nE_{\text{cell}}F = RT\ln\left(\frac{Q}{K}\right)$$

to yield

$$E_{\text{cell}} = -\frac{RT}{nF}\ln\left(\frac{Q}{K}\right)$$

This equation for E_{cell} shows:

- if $Q/K < 1$, $E_{\text{cell}} > 0$, $\Delta G_\text{r} < 0$, and the cell reaction is spontaneous from left to right.
- if $Q/K > 1$, $E_{\text{cell}} < 0$, $\Delta G_\text{r} > 1$, and the cell reaction is spontaneous from right to left;
- if $Q/K = 1$, $E_{\text{cell}} = 0$, $\Delta G_\text{r} = 0$, and the cell reaction is at equilibrium.

It is convenient to separate the term relating to the equilibrium constant and write the equation for the cell voltage as

$$E_{\text{cell}} = \frac{RT}{nF}\ln K - \frac{RT}{nF}\ln Q \qquad (9.1)$$

When all species are in the standard state, $Q = 1$, $\ln Q = 0$, and the cell voltage is E°, hence:

$$E_{\text{cell}} = E^\circ = \frac{RT}{nF}\ln K$$

substituting E° into Equation (9.1) gives:

$$E_{\text{cell}} = E^\circ - \frac{RT}{nF}\ln Q \qquad (9.2)$$

where E_{cell} is the cell voltage, E° is the standard cell voltage, R is the gas constant, T is the absolute temperature, n is the number of electrons transferred in the cell reaction, F is the Faraday constant, and Q is the reaction quotient of the cell reaction. Equation (9.2) is the Nernst equation. Inserting values for the constants, the Nernst equation can be written:

$$E = E^\circ - \frac{0.02569}{n}\ln Q$$

or

$$E = E^\circ - \frac{0.05916}{n}\log Q$$

9.2.5 Chemical analysis using galvanic cells

The measurement of the potential of a galvanic cell can be used to determine the concentration of the ions in a solution via the Nernst equation. For example, the cell reaction of the Daniell cell is:

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

The appropriate form of the Nernst equation is:

$$E = E^\circ - \frac{0.02569}{n}\ln\left\{\frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]}\right\}$$

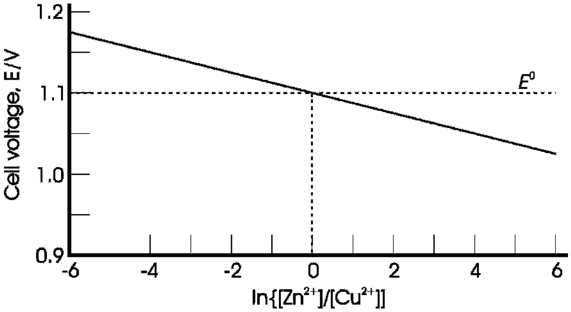

Figure 9.3 Plot of cell voltage, E, versus $\ln\{[\mathrm{Zn^{2+}}]/[\mathrm{Cu^{2+}}]\}$ for a Daniell cell

A plot of E versus $\ln\{[\mathrm{Zn^{2+}}]/[\mathrm{Cu^{2+}}]\}$ is (ideally) a straight line (Figure 9.3). Provided that the concentration of one of the ions is known, the concentration of the other can be determined from the experimental value of the cell potential.

The most widespread use of this analytical technique is the measurement of the concentration of hydrogen ions (pH). To illustrate this, consider how the combination of a standard electrode with a (nonstandard) hydrogen electrode can be used to measure the concentration of hydrogen ions present at the hydrogen electrode. The standard electrode is often a particularly stable electrode, called a calomel electrode, which uses the redox couple $\mathrm{Hg_2Cl_2/Hg, Cl^-}$. The cell is:

$$\mathrm{Pt \mid H_2(g) \mid H^+(aq) \parallel Cl^-(aq) \mid Hg_2Cl_2 \mid Hg(l)}$$

Anode reaction:

$$\mathrm{H_2(g) \rightarrow 2H^+(aq) + 2e^-} \quad E^\circ = 0\,\mathrm{V}$$

Cathode reaction:

$$\mathrm{Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)}$$
$$E^\circ = +0.27\,\mathrm{V}$$

Cell reaction:

$$\mathrm{Hg_2Cl_2(s) + H_2(g) \rightarrow 2H^+(aq) + 2Cl^-(aq) + 2Hg(l)}$$

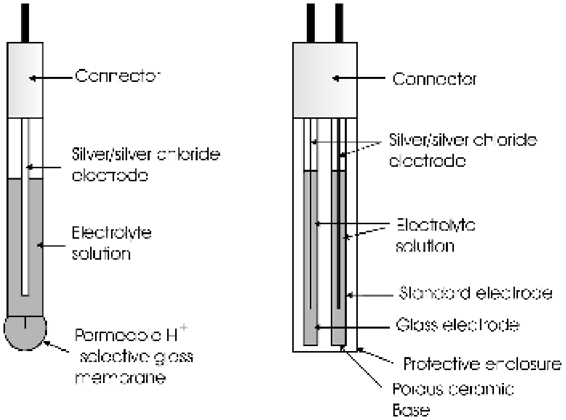

Figure 9.4 (a). A glass electrode for the measurement of pH and (b) experimental arrangement of glass electrode and standard electrode in a single cell

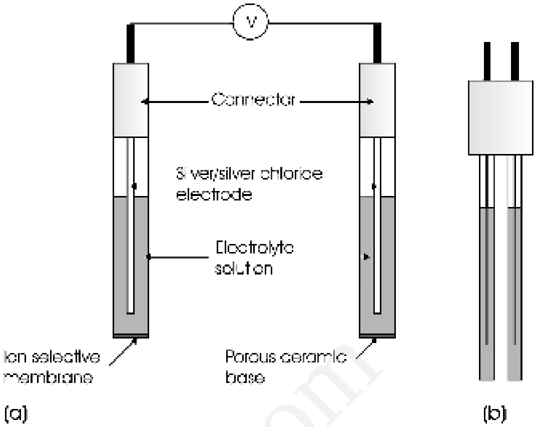

Figure 9.5 (a) Schematic arrangement of an ion selective electrode for the measurement of ion concentrations in solution and (b) experimental arrangement, where the electrodes are attached to a connecting unit

The cell voltage is found to be directly proportional to the pH:

$$E(\text{cell}) = E' + 0.0592 \times \text{pH}$$

Where E′ is the cell constant, which depends on the Cl^- concentration. The pH can be read directly on a voltage scale.

The hydrogen electrode is not practical, and commercial pH meters are constructed with a glass electrode that has a sensing element made of a thin membrane of a special glass sensitive only to H^+ ions (Figure 9.4a). The potential of the electrode is found to be proportional to the pH of the surrounding solution, and the response of this electrode is similar to that of a hydrogen electrode.

Apart from the calomel electrode, one of the most common standard electrodes used in pH meters is a silver/silver chloride electrode. This consists of a silver wire coated with silver chloride immersed in a four-molar solution of potassium chloride (KCl), saturated with silver chloride (AgCl). The half-reaction is:

$$\text{AgCl(s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^-$$
$$E^\circ = 0.2046\,\text{V at } 25\,^\circ\text{C}$$

In practice, the hydrogen ion selective electrode and the standard electrode are packaged together in a small plastic cylinder, which is easily transported (Figure 9.4b). Measurement is made by dipping the electrode into the solution to be checked, and the voltage is transformed into a pH reading electronically.

The same measurement principle can be used to determine the concentration of other ions in solution. An electrode that is (ideally) sensitive to one ion only, called an ion selective electrode, is paired with a standard electrode (Figure 9.5). The potential developed by such a combination is of the general form

$$E = E' + \frac{2.303RT}{nF}\log(c)$$

where E′ is a constant characteristic of the ion selective electrode and the reference electrode, and c is the concentration of the ion. This is a linear dependence, in which the slope is $(2.303RT/nF)$. Experimentally, the value of the slope is found to lie between 50–60 mV for monovalent ions and 25–30 mV for divalent ions.

The critical component of an ion selective electrode is a membrane that acts to pass the selected ions into the interior of the electrode assembly (Figure 9.5a). These are of two principal types. Crystal membranes consist of a polycrystalline or single-crystal plate. For example, fluoride ion (F^-)

sensors are made from single-crystal lanthanum trifluoride (LaF_3) doped with europium difluoride (EuF_2). The Eu^{2+} ions substitute for La^{3+} in the LaF_3 matrix, and each substituted ion is accompanied by a vacancy on the F substructure to maintain charge neutrality. The large number of vacancies thus generated increases the diffusion coefficient of F^- in LaF_3 enormously. The membrane has a similar permeability to F^- as the surrounding liquid and is found to be highly selective for the passage of F^- ions.

The other type of membrane in use consists of a polyvinyl chloride (PVC) disc, impregnated with a large organic molecule that can react with the ion. The binding must be weak enough for the ion to be passed from one molecule to another across the membrane under the driving force of a concentration gradient. For example, K^+ ion selective membranes are made using the antibiotic valinomycin. This has a structure that accommodates the K^+ ions and can pass them on from one molecule to another. The operation of this material mimics the way in which living cells transfer ions across the cell membrane. Unfortunately, such molecules are not usually completely specific for a single ion and usually also channel chemically similar species. The potassium membrane, for example, can also pass lesser amounts of sodium ions.

9.3 Batteries

Batteries, which are galvanic cells, fall into one of three main types. A primary cell is a battery that cannot be recharged. A secondary cell is a battery that can be recharged and reused. A fuel cell has a continuous input of chemicals (fuel) to produce a continuous output of current.

In all batteries, oxidation occurs at the anode of the cell; the electrode removes electrons from the species in the electrolyte. It is given a negative sign in diagrams (Figures 9.1 and 9.2). It consists of a relatively easily oxidised metal such as zinc, cadmium or nickel, sometimes in contact with a current collector such as a graphite rod. At the cathode of a battery, reduction occurs; the electrode gives electrons to species in the electrolyte. The cathode is marked as positive in a diagram (Figures 9.1 and 9.2). The active component in the cathode is often a metal oxide such as MnO_2 or PbO_2, which is capable of being reduced, sometimes in contact with a metallic current collector. Electrons flow from anode to cathode (negative to positive) via an external circuit. Anions (negative ions) travel towards the anode through the electrolyte. Cations (positive ions) travel towards the cathode through the electrolyte. Normally, a redox reaction in a battery will stop if the reactants are separated. However, if the electrons are allowed to travel via an external circuit from one electrode to the other the reaction can continue, even when the components are separated.

In a battery, the electrons moving around the external circuit are used to do useful work. The driving force for this is the energy of the cell reaction. Batteries are spent, or need recharging, when one or both of the components has been used up.

There are large numbers of different batteries manufactured, and in the descriptions that follow only a small selection of commonly encountered batteries is described.

9.3.1 ‘Dry’ and alkaline primary batteries

The widely used primary ‘dry-cell’ or, Leclanché cell, which was invented in 1866, gives a voltage of about 1.5 V. It is especially used for intermittent applications, such as for flashlights. In this cell the redox couple used is Zn/MnO_2. The current collector is a graphite rod buried in the positive cathode, a mixture of MnO_2 and carbon. This is kept moist by the electrolyte, aqueous ammonium chloride, NH_4Cl. The anode (negative terminal) is the container itself, made from zinc (Figure 9.6).

As with all commercial batteries, the real cell reaction is complex, and the reactions are approximated as follows.

Anode reaction (oxidation, electron generation):

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

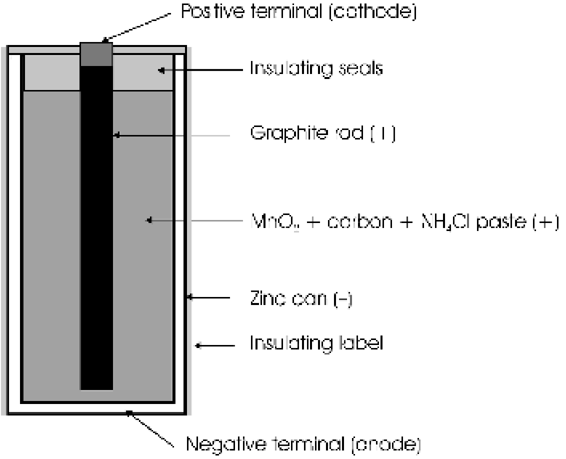

Figure 9.6 Section through a dry cell

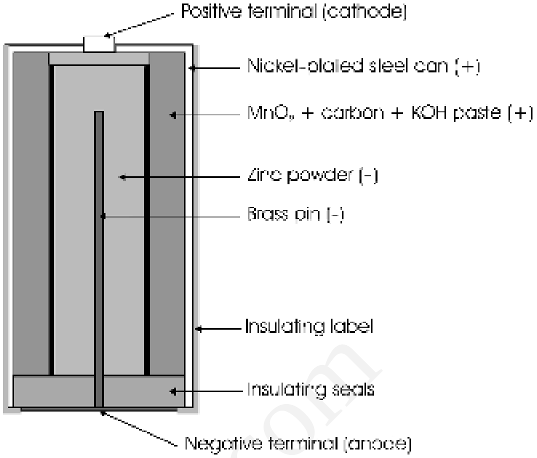

Figure 9.7 Section through an alkaline cell

Cathode reaction (reduction, electron consumption):

$$MnO_2(s) + H_2O(l) + e^- \rightarrow MnO(OH)(s) + OH^-(aq)$$

Cell reaction:

$$Zn(s) + 2MnO_2(s) + 2H_2O(l) \rightarrow 2MnO(OH)(s) + 2OH^-(aq) + Zn^{2+}(aq)$$

The main problem encountered with this cell is the buildup of Zn^{2+} and OH^- at the respective electrodes, which is why the battery is mainly used intermittently. When the battery is not being used the concentrations of these reaction products falls again. This is because the OH^- ions migrate to the Zn anode where they form ammonia with NH_4^+ ions in the electrolyte:

$$NH_4^+(aq) + OH^-(aq) \rightarrow H_2O(l) + NH_3(aq)$$

The concentration of the Zn^{2+} ions in the vicinity of the anode subsequently drops as a result of reaction with the NH_3:

$$Zn^{2+}(aq) + 4NH_3(aq) \rightarrow Zn(NH_3)_4^{2+}(aq)$$

The cell is spent when ionic conduction is no longer possible because of the buildup of $Zn(NH_3)_4Cl_2$.

Alkaline cells use the same zinc–manganese dioxide couple as Leclanché cells. However, the ammonium chloride electrolyte is replaced with a solution of about 30 wt% potassium hydroxide (KOH) to improve ionic conductivity. The cell reactions are identical to those above, but the battery construction is rather different (Figure 9.7). The negative material is zinc powder, and the anode (negative terminal) is a brass pin. The positive component is a mixture of MnO_2 and carbon powder that surrounds the anode. A porous cylindrical barrier separates these components. The positive terminal (cathode) is the container, which is a nickel-plated steel can.

9.3.2 *Lithium-ion primary batteries*

Lithium has a number of advantages over other materials for battery manufacture. It is the lightest true metal, and it also has a high electrochemical reduction potential, that is, it occurs at the bottom of Table 9.1. There is one disadvantage in using lithium in that it is very reactive, a feature that poses problems not only in manufacture but also in the selection of the other battery components. Despite this, there are a large number of lithium-based primary cells available, both in traditional cylindrical form and as button and flat coin cells.

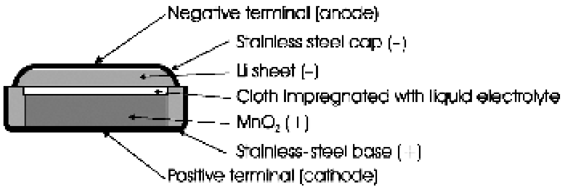

Figure 9.8 Section through a lithium coin cell

The lithium forms the anode in such cells, and a variety of compounds may form the anode. The most usual of these is manganese dioxide (MnO_2), giving a working potential of approximately 3 V. Because lithium reacts vigorously with water, the electrolyte must be nonaqueous and is frequently a solution of lithium salts in a polar organic liquid. The conductivity of such solutions is low compared with that of aqueous solutions of hydroxides, which means that the design of a cell is constrained by the need for large electrode areas separated by a thin electrolyte. The coin cell is a natural result of such considerations (Figure 9.8).

The cell reactions are poorly understood, but can be written schematically as follows.

Anode reaction (oxidation, electron generation):

$$\mathrm{Li(s)} \rightarrow \mathrm{Li^{+}(aq)} + \mathrm{e^{-}}$$

Cathode reaction (reduction, electron consumption):

$$\mathrm{MnO_2(s)} + \mathrm{e^{-}} \rightarrow \mathrm{MnO_2^{-}(s)}$$

Cell reaction:

$$\mathrm{Li(s)} + \mathrm{MnO_2(s)} \rightarrow \mathrm{LiMnO_2(s)} \quad E^{\circ} = 3.2\ \mathrm{V}$$

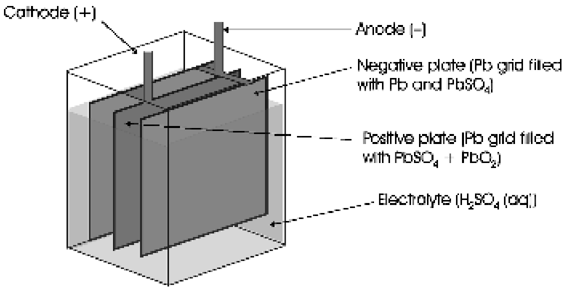

Figure 9.9 A single cell in a lead – acid battery

9.3.3 The lead–acid secondary battery

Plante discovered the basic technology of the rechargeable lead–acid battery in 1859. Since then there have been many refinements to the materials used, but the operating principles remain the same. This battery is the widely used car battery in use to this day. The anode is lead (Pb), the cathode lead dioxide (PbO_2) and the electrolyte is dilute sulphuric acid [H_2SO_4(aq)] (Figure 9.9). As with all batteries, the chemical reactions taking place are complex, but schematically the processes are as follows.

Anode reaction (oxidation, electron generation):

$$\mathrm{Pb(s)} + \mathrm{HSO_4^{-}(aq)} \rightarrow \mathrm{PbSO_4(s)} + \mathrm{H^{+}(aq)} + 2\mathrm{e^{-}}$$

Cathode reaction (reduction, electron consumption):

$$\mathrm{PbO_2(s)} + 3\mathrm{H^{+}(aq)} + \mathrm{HSO_4^{-}(aq)} + 2\mathrm{e^{-}} \rightarrow \mathrm{PbSO_4(s)} + 2\mathrm{H_2O(l)}$$

Cell discharge reaction:

$$\mathrm{PbO_2(s)} + \mathrm{Pb(s)} + 2\mathrm{H^{+}(aq)} + \mathrm{HSO_4^{-}(aq)} \rightarrow 2\,\mathrm{PbSO_4(s)} + 2\mathrm{H_2O(l)}$$

The cell potential is about 2 V. A car battery consists of (usually) six cells in series (a battery of cells), to give 12 V. Sulphuric acid is used up during operation, so the state of charge of the battery can be estimated by measuring the concentration of the acid, usually via density.

The cell-charging reaction is the reverse of the discharge reaction, and to charge a battery the cell reaction is simply driven backwards by an imposed external voltage.

9.3.4 Nickel–cadmium (Ni–Cd, nicad) rechargable batteries

These were, until recently, the most widespread rechargeable batteries available for home use.

However, concerns about the toxicity of cadmium have accelerated the replacement of these batteries by nickel–metal hydride batteries, described in Section 9.3.5. In nickel–cadmium (nicad) batteries, the anode is cadmium and the cathode is an unstable nickel oxyhydroxide, formed in the unusual conditions found in the cell, and written variously as $Ni(OH)_3$ or NiO(OH). It is generally formed together with stable nickel hydroxide, $Ni(OH)_2$. The electrolyte is NaOH or KOH. The anode and cathode are assembled in a roll separated by a cellulose separator containing the electrolyte. The cathode/separator/anode roll is contained in a nickel-plated stainless steel can (Figure 9.10). The cell voltage is 1.3 V but the working voltage is usually nearer to 1.2 V. The schematic cell reactions are as follows.

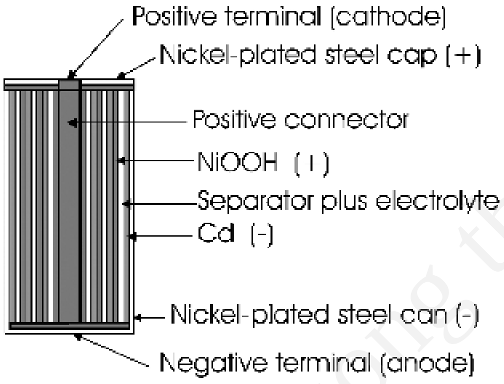

Figure 9.10 Section through a nichel–cadmium (nicad, Ni – Cd) cell

Anode reaction (oxidation, electron generation):

$$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(aq) + 2e^-$$

Cathode reaction (reduction, electron consumption):

$$2NiO(OH)(s) + 2H_2O(l) + 2e^- \rightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$$

Cell discharge reaction:

$$Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$$

The charging reaction is the reverse of the discharge reaction, driven by an external voltage.

9.3.5 Nickel-metal-hydride rechargeable batteries

These batteries, frequently called Ni–*M*H batteries, are now replacing nicad batteries (Section 9.3.4) for many uses. They rely on hydrogen storage in a metal alloy for the reversible operation.

Many metals absorb large quantities of hydrogen to form, initially, nonstoichiometric interstitial alloys and, at greater concentrations, various alloy phases with definite compositions M_aH_b (see also Section 6.1.3.2). In many of these materials the hydrogen incorporation is reversible, so that hydrogen is taken up at high hydrogen pressure and released at lower pressure. This reversible uptake of hydrogen is exploited in Ni–*M*H batteries.

The positive electrode, the cathode, is similar to that in nicad cells and consists of a mixture of $NiO(OH)/Ni(OH)_3$ and $Ni(OH)_2$. An alloy that supports hydride formation replaces the cadmium as the negative anode. The alloy most commonly used is derived from $LaNi_5$, in which a mixture of other lanthanides replaces the lanthanum, and a nickel-rich alloy replaces the nickel, to give a general formula LnM_5. The anode is composed of an agglomeration of alloy powder. A small amount of potassium hydroxide is added as an electrolyte. The cell voltage is 1.3 V, making these cells suitable for the direct replacement of nicad batteries. The cell construction is identical to that of the nicad cell (Figure 9.10), with the cadmium replaced by metal hydride. The approximate cell reactions are as follows.

Anode reaction (oxidation, electron generation):

$$MH_x(s) + OH^-(aq) \rightarrow MH_{x-1}(s) + H_2O(l) + e^-$$

Cathode reaction (reduction, electron consumption):

$$2\,NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$$

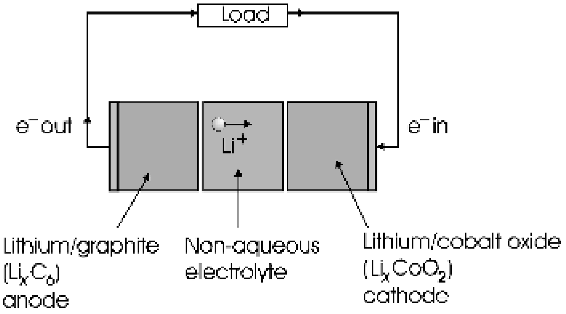

Figure 9.11 A lithium rechargable 'Sony' cell, in discharge operation

Cell discharge reaction:

$$M\mathrm{H_x(s)} + 2\,\mathrm{NiO(OH)(s)} \rightarrow M\mathrm{H_{x-1}(s)} + \mathrm{Ni(OH)_2(s)}$$

The charging reaction is the reverse of the discharge reaction, driven by an external voltage.

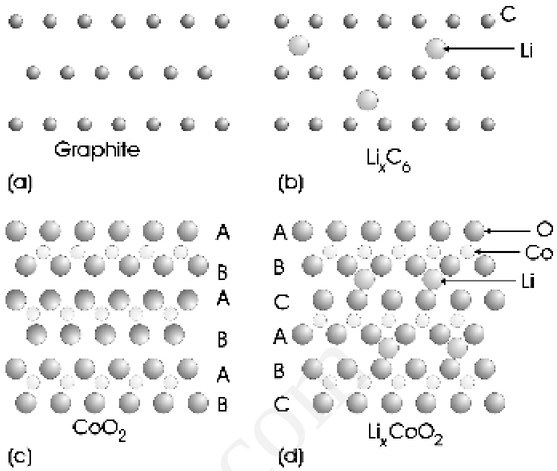

Figure 9.12 Transformations in electrode materials; graphite (part a) changes layer stacking when lithium atoms are intercalated (part b); $\mathrm{CoO_2}$ changes from hexagonal closest packing of the oxygen anions to cubic closest packing when lithium atoms are intercalated (part d)

9.3.6 Lithium-ion rechargeable batteries

The advantages of lithium primary cells extend to secondary cells. In particular, the high power available and the lightness make them ideal for portable electronic devices. The first successful lithium-ion rechargeable battery was introduced by Sony in 1991 and is often called the Sony cell. The principle of the cell is shown in Figure 9.11. The difficulties of working with lithium metal are overcome by using nonstoichiometric intercalation compounds (see Section 3.4.5). The electrolyte is, as with the lithium primary cells, a nonaqueous solution of lithium salts in a polar organic liquid.

The active component of the anode is lithium metal contained in graphite. The structure of graphite (Figure 5.21, page 132), consists of strongly linked layers of carbon atoms, arranged in a hexagonal array, linked by weak van der Waals bonds. It has long been known that graphite can take in alkali metal atoms between the weakly linked layers of carbon hexagons to form intercalation compounds. The nominal composition of the lithium–graphite intercalation material is $\mathrm{Li}_x\mathrm{C}_6$, with x varying from 0 to approaching 1.0. The stacking of the hexagonal carbon layers is staggered in the pure compound (Figure 9.12a), but in the lithium-containing phase they are directly over each other (Figure 9.12b). The stacking, therefore, alters with the degree of lithium incorporation, limiting the performance of the electrode. The cathode material is the nonstoichiometric oxide $\mathrm{Li}_x\mathrm{CoO}_2$. This material is also an intercalation compound, in which the Li^+ ions lie between layers of composition $\mathrm{CoO_2}$ (see Figures 9.12c and 9.12d). In theory, the composition range of the cathode material is from $\mathrm{LiCoO_2}$ to $\mathrm{CoO_2}$ (i.e., x varying from 1 to 0) but in battery operation the degree of nonstoichiometry is restricted, and x generally takes values in the range of 0 to about 0.45. As with graphite, intercalation of lithium changes the layer stacking. In this case, $\mathrm{CoO_2}$ is built of hexagonal close-packed (ABAB) layers of oxygen atoms (Figure 9.12c), whereas $\mathrm{LiCoO_2}$ has cubic (ABCABC) close packing (Figure 9.12d). This change degrades the oxide during use and is the major reason why the useful composition range is limited.

At present there is much research work on improving the cathode and the anode materials in these cells, and a number of alternative layer compounds are actively being tested.

The cell reactions are similar to those utilised in the lithium primary cell. During discharge, Li^+ ions are transported from the anode to the cathode via the following reactions.
Anode reaction (oxygen, electron generation):

$$Li_xC_6(s) \rightarrow 6C(s) + xLi^+(s) + xe^-$$

Cathode reaction (reduction, electron consumption):

$$Li_{0.55}CoO_2(s) + xLi^+(s) + xe^- \rightarrow Li_{0.55+x}CoO_2(s)$$

Cell discharge reaction:

$$Li_xC_6(s) + Li_{0.55}CoO_2(s) \rightarrow 6C(s) + Li_{0.55+x}CoO_2(s)$$

These reactions can also be written as:
Anode reaction (oxidation, electron generation):

$$Li(s) \rightarrow Li^+(s) + e^-$$

Cathode reaction (reduction, electron consumption):

$$Co^{4+}(s) + e^- \rightarrow Co^{3+}(s)$$

Cell discharge reaction:

$$Li(s) + Co^{4+}(s) \rightarrow Li^+(s) + Co^{3+}(s)$$

The charging reaction is the reverse of the discharge reaction, driven by an external voltage.

9.3.7 Fuel cells

Batteries have a fixed amount of reactants present, stored in the battery casing. Fuel cells are primary cells with a continuous input of chemical reactants and a continuous output of power. The reactants are stored separately from the electrodes and electrolyte and can be replenished when necessary. There is much research at present on fuel cells as a source of clean electricity. The reaction chosen is the production of water from hydrogen gas, H_2, and oxygen gas, O_2, giving a cell voltage of about 1.2 V. The concept is simple (Figure 9.13), and early fuel cells, containing an alkaline solution, typically potassium hydroxide solution, KOH(aq), as electrolyte, demonstrate the principles involved.

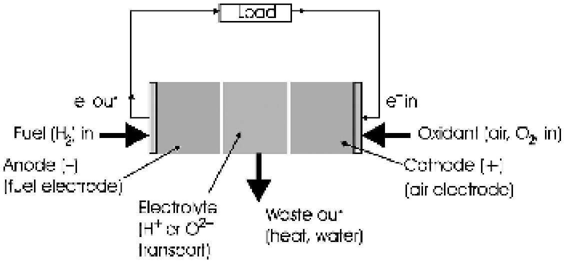

Figure 9.13 A fuel cell: fuel is added continuously to the electrodes, and electricity is produced continuously; waste products are heat and water

Anode reaction (oxidation of H_2; electron generation):

$$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$$
$$E^\circ = -0.83\ V$$

Cathode reaction (reduction of O_2; electron consumption):

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \quad E^\circ = 0.40\ V$$

Cell discharge reaction:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Current research is centred on making compact cells of high efficiency. They are described in terms of the electrolyte that is used. The principle types are alkali fuel cells, described above, with aqueous KOH as electrolyte, MCFCs (molten carbonate fuel cells), with a molten alkali metal or alkaline earth carbonate electrolyte, PAFCs (phosphoric acid fuel cells), PEMs (proton exchange membranes), using a solid polymer electrolyte that conducts H^+ ions, and SOFCs, (solid oxide fuel cells), with solid electrolytes that allow oxide ion, O^{2-}, transport. The majority of cells use a catalyst to speed up the reactions taking place. These are mostly platinum-based and are deposited on the electrodes as small, highly dispersed particles, but the MCFC has an advantage in that it uses a nickel catalyst, which is much cheaper than platinum.

As the cell reaction is between hydrogen and oxygen, the continuous supply of these gases is vital. Oxygen poses no problem, as it is freely available from the air. The best way to provide hydrogen fuel has not yet been resolved. Hydrogen reservoirs containing pressurised gas, or liquid hydrogen, have been considered. Another approach envisages the formation of hydrogen directly on demand from a hydrocarbon store such as methane, petrol or oil, using a catalyst. One promising avenue seems to be the use of hydrides for this purpose. Nonstoichiometric metal hydrides, similar to those used in Ni–*M*H batteries, which can reversibly store hydrogen as atoms, are contenders for this purpose.

Of the cells available, SOFCs appear to be nearest to commercial use for large-scale electricity generation. A variety of designs are being explored, including planar and tubular geometries (Figure 9.14). In all cases, single cells are linked to give a fuel-cell stack by an interconnect material. The electrolyte in these cells is derived from calcia-stabilised zirconia (see Section 3.4.5). This nonstoichiometric oxide has approximately 15 % of the oxygen sites unoccupied. Because of this, the oxygen ion diffusion coefficient in the solid is very high. The cell operating principle is drawn in Figure 9.14. Oxygen in the form of air is supplied to the cathode, often called the air electrode. The oxygen gas is ionised and oxygen ion transport across the electrolyte ensues. Hydrogen fuel is supplied to the anode or fuel electrode. Here it reacts with the oxide ions to form water.

Anode reaction (oxidation of H_2; electron generation):

$$H_2(g) + O^{2-}(s) \rightarrow H_2O(l) + 2e^-.$$

Cathode reaction (reduction of O_2; electron consumption):

$$\tfrac{1}{2}O_2(g) + 2e^- \rightarrow O^{2-}(s).$$

Cell discharge reaction:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l).$$

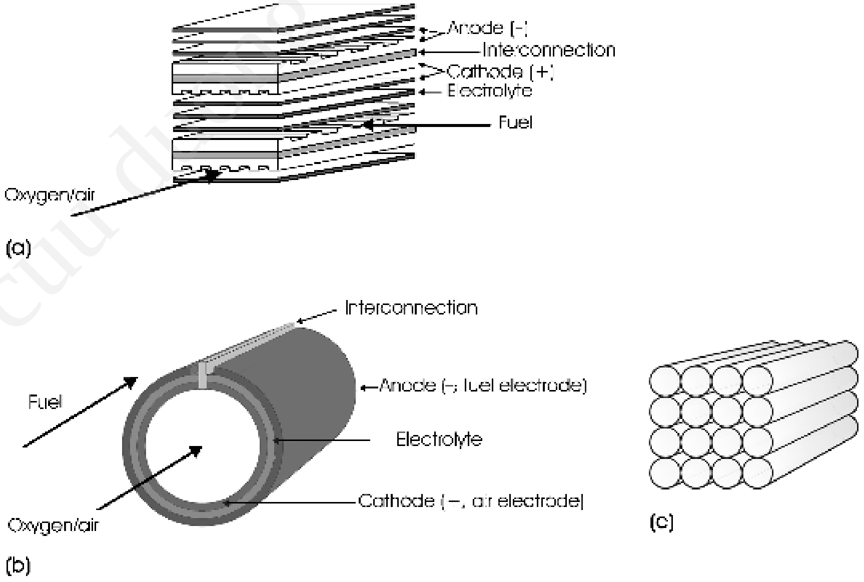

Figure 9.14 (a) An expanded view of a stack of planar design solid-oxide fuel cells (SOFCs); (b) tubular design of an SOFC; (c) a stack of tubular SOFCs

A problem with SOFCs is that diffusion of oxygen ions in the electrolyte is too slow at room temperature to make the cells viable. At present, satisfactory cell operation is accomplished only when the electrolyte is held at temperatures in excess of 650 °C, although intensive research is continually lowering this temperature.

9.4 Corrosion

Corrosion refers to the degradation of a metal by electrochemical reaction with the environment. At room temperature, the most important corrosion reactions involve water, and the process is known as aqueous corrosion. (Corrosion at high temperatures in dry air, called oxidation tarnishing, or direct corrosion, is considered in Section 8.5.) Aqueous corrosion involves a set of complex electrochemical reactions in which the metal reverts to a more stable condition, usually an oxide or mixture of oxides and hydroxides (Figure 9.15). In many cases the products are not crystalline and are frequently mixtures of compounds. Aside from the loss of metal, the corrosion products may be voluminous. In this case, they force overlying protective layers away from the metal and so allow corrosion to proceed unchecked, which exacerbates the damage.

The extent of aqueous corrosion often depends on the presence of impurities and trace contaminants in the water present. For example, carbon-steel reinforcing bars in concrete corrode more severely in acidic conditions and in the presence of chloride ions, a process called electrochemical attack. On the other hand, alkaline conditions inhibit the rate of corrosion.

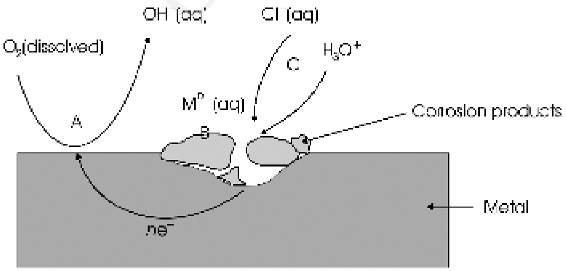

Figure 9.15 Aqueous corrosion reactions: A, electrode reactions; B, deposition reactions; C, impurity reactions

In principle, corrosion is easily prevented by one of two methods – by modifying the environment (which includes coating the metal) or by replacing the corrodible metal with a corrosion-resistant metal. However, these simple remedies are not always possible, and corrosion is a major economic factor across the world.

9.4.1 The reaction of metals with water and aqueous acids

The reaction of a metal with an aqueous acid to yield hydrogen, a severe form of corrosion, involves oxidation of the metal and reduction of hydrogen ions in solution, $H^+(aq)$, to H_2 gas, and so can be thought of in terms of an electrochemical cell. The tendency for a reaction to occur follows the order of the electrochemical series (Table 9.1). Metals below H_2 in the electrochemical series – those with a negative standard reduction potential – will react with aqueous acids to release hydrogen gas. Those above it will not react with acid. Thus, zinc will dissolve in acid to give hydrogen, whereas copper will not.

Such reactions are generally written in terms of the overall reaction:

$$\mathrm{Zn} + 2\mathrm{HCl} \rightarrow \mathrm{ZnCl_2} + \mathrm{H_2(g)}$$

However, more insight into the process is given by using the two half-reactions:

$$2\mathrm{H^+(aq)} + 2\mathrm{e^-} \rightarrow \mathrm{H_2(g)}$$
$$\mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}(aq)} + 2\mathrm{e^-}$$

that is,

$$\mathrm{Zn(s)} + 2\mathrm{H^+(aq)} \rightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{H_2(g)}$$

The same information can also be used to predict which metals may dissolve in acid rain. For example, both lead and tin can enter the water supply in acid rain areas, and, for the same reason, acidic water will react with lead water pipes.

The reaction of metals with water can be examined by using identical principles. Two reactions are important: oxidation and reduction. When water acts as an oxidising agent it is reduced to H_2. This is similar to the oxidation of a metal by an acid (H^+) to give H_2. Metals in the electrochemical series *below* the couple,

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$
$$E^\circ = -0.83\ \text{V at pH } 14$$

will react with water and produce hydrogen gas. These metals (Al, Mg, Na, K and Li) are the most reactive. For example, the reaction of magnesium with water is written:

$$Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2 + H_2(g)$$

and, in terms of half reactions,

$$\begin{gathered} 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \\ Mg(s) \rightarrow Mg^{2+}(aq) + 2e^- \\ Mg(s) + 2H_2O(l) \rightarrow H_2(g) + 2OH^-(aq) + Mg^{2+}(aq) \end{gathered}$$

In practice, the reaction products from these low-temperature processes are invariably ill-defined amorphous materials consisting of poorly soluble oxyhydroxides.

Under standard conditions ($E^\circ = -0.83$ V), the concentration of the OH^-(aq) ions is 1 molar and the pH is 14 – very alkaline conditions indeed. In order to determine whether neutral water, at pH 7, will react, it is necessary to use the Nernst equation to redefine the reaction voltage:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$
$$E = -0.42\ \text{V at pH } 7$$

The revised reduction potential is −0.42 V. It is of interest to compare this with the reduction potential for iron. The Fe^{2+}/Fe couple has $E^\circ = -0.44$ V, which is almost equal to that of neutral water. Thus, surprisingly, iron has no (or at best only a slight tendency) to be corroded by pure water. Corrosion of iron only takes place in water containing dissolved oxygen, discussed in Sections 9.4.3 and S3.6.

When water acts as a reducing agent it is oxidised to O_2. The relevant equation is:

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$$

This is the reverse of the reduction half-reaction

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$
$$E^\circ = +1.23\ \text{V at pH } 0$$

The presence of the H^+(aq) ions indicates that the water is acidic. The concentration of H^+(aq) in the standard state is 1 molar, and the pH will be 0, equivalent to very acidic conditions. In these conditions, water will be able to reduce redox couples above this reaction in the electrochemical series and liberate O_2. For example, the couple Co^{3+}/Co^{2+} has $E^\circ = +1.82$ V, so that Co^{3+} is reduced by acidified water to give O_2 thus:

$$\begin{gathered} Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq) \\ O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \end{gathered}$$

that is,

$$4Co^{3+}(aq) + 2H_2O(l) \rightarrow 4Co^{2+}(aq) + O_2(g) + 4H^+(aq)$$

The reduction potential for neutral water can be calculated via the Nernst equation:

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l),$$
$$E = +0.81\ \text{V at pH } 7$$

There are a number of half-reactions involving nonmetals that lie above this value in the electrochemical series, and these will be reduced. In all of these cases, reaction will produce oxygen gas. For example, the dissolution of chlorine, Cl_2, in water will produce oxygen, although the unstable oxyacid, HOCl, forms as an intermediate. The reaction is:

$$\begin{gathered} 2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^- \\ 2Cl_2(g) + 4e^- \rightarrow 4Cl^-(aq) \\ 2Cl_2 + 2H_2O \rightarrow 4HCl + O_2(g) \end{gathered}$$

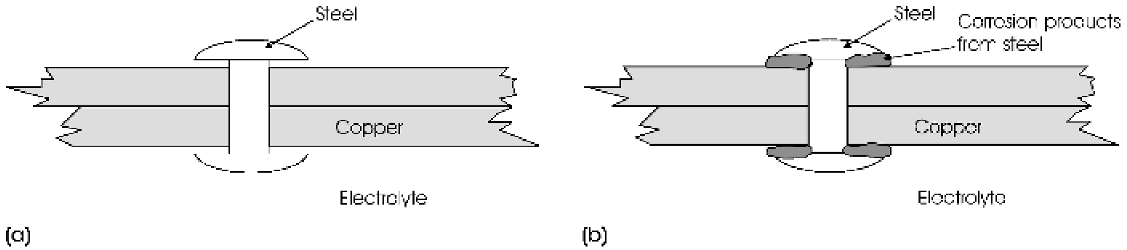

Figure 9.16 Dissimilar metal corrosion of a steel rivet in contact with copper and an electrolyte: (a) before and (b) after corrosion

9.4.2 Dissimilar-metal corrosion

Two different metals that are connected and immersed in an electrolyte form an electrochemical cell. If a current is allowed to flow, one metal will be consumed and one will remain the same or be increased in some way. These processes lead to dissimilar metal corrosion. In order for dissimilar metal corrosion to occur, it is necessary to have an anode, a cathode, an electrolyte and a connection from anode to cathode. The anode component corrodes whereas the cathode remains unattacked. The tendency for such reactions to take place spontaneously can be judged from the electrochemical series. Three examples follow.

9.4.2.1 Copper and iron/steel

Copper and iron or steel in juxtaposition can form a cell in which the copper becomes the cathode and the iron the anode. Several reactions are possible. One of these is as follows.

Anode reaction:

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

Cathode reaction:

$$\mathrm{O_2} + 2\mathrm{H_2O(l)} + 4\mathrm{e^-} \rightarrow 4(\mathrm{OH^-})$$

Cell reaction:

$$2\,\mathrm{Fe(s)} + \mathrm{O_2} + 2\mathrm{H_2O(l)} \rightarrow 4(\mathrm{OH^-}) + 2\mathrm{Fe^{2+}(aq)}$$

The Fe^{2+} is soluble and the iron will gradually dissolve (Figure 9.16). The copper is not attacked and serves only to complete the cell. If there is a small anode area, such as an exposed nail head, the attack is more pronounced.

These cells have had considerable influence historically. Wooden sailing ships were attacked below the waterline by wood-boring barnacles. Severe infestation could ultimately lead to the destruction of the bottom of the hull and catastrophic loss of the vessel. To prevent this, ships were sheathed in copper, a practice that gave rise to the expression ‘copper-bottomed’, meaning sound or reliable. Unfortunately, iron or steel nails were often used to secure the copper sheathing. In the presence of alkaline water and oxygen (i.e. surface seawater, which has a pH of about 8.5 and a high content of dissolved oxygen) the nails corroded and the copper sheathing was lost.

9.4.2.2 Galvanization

Coating steel sheet with zinc, a procedure called galvanizing, is widely used to prevent corrosion of the steel. The zinc coating does not corrode in air because initial reaction produces a dense layer of insulating zinc oxide that protects the surface from further reaction (as described for aluminium and chromium in Section 8.5.3). Should the zinc coating become penetrated, so that both zinc and steel (iron) are exposed to the air, corrosion is inhibited by the formation of a galvanic cell (Figure 9.17). The reason is that in the presence of water and oxygen the zinc will become the anode in the cell formed and will corrode in preference to the exposed iron. Several reactions are possible, including the following.

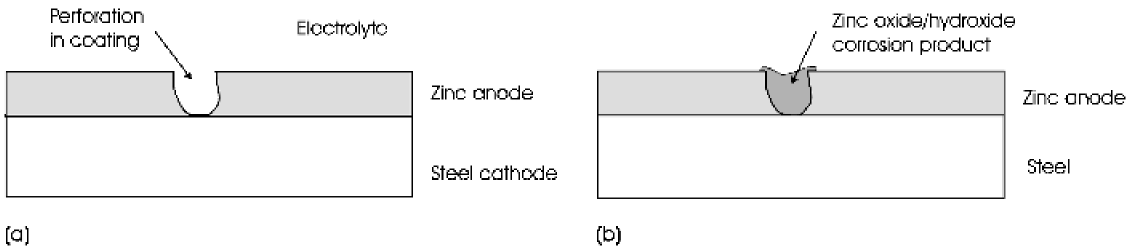

Figure 9.17 The protective coating formed by zinc on steel: galvanisation. (a) Before and (b) after formation of the protective corrosion product

Anode reaction:

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

Cathode reaction:

$$O_2 + 2H_2O(l) + 4e^{-} \rightarrow 4(OH^{-})$$

Cell reaction:

$$2\,Zn(s) + O_2 + 2\,H_2O(l) \rightarrow 4(OH^{-}) + 2\,Zn^{2+}(aq)$$

The Zn^{2+} ions react in ordinary conditions to produce ZnO or a zinc oxyhydroxide. These are inert and form insoluble deposits that help to prevent further corrosion. Overall, steel coated with zinc corrodes far more slowly than does bare steel.

9.4.2.3 Tin plate

Steel coated with tin was widely used on food cans, or ‘tins’, until replaced by aluminium or plastic coatings. Steel coated with tin corrodes faster than steel alone. Unlike the situation with zinc, a scratch in the coating allows an electrochemical cell to form in which the steel (iron) forms the anode and corrodes as follows.
Anode reaction:

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

Cathode reaction:

$$O_2 + 2H_2O(l) + 4e^{-} \rightarrow 4(OH^{-})$$

Cell reaction:

$$2Fe(s) + O_2 + 2H_2O(l) \rightarrow 4(OH^{-}) + 2Fe^{2+}(aq)$$

No protective oxide forms and the corrosion is enhanced compared with uncoated steel. This accounts for the fact that old ‘tin cans’ on rubbish tips are always badly corroded.

9.4.3 Single-metal electrochemical corrosion

Two subtle corrosion effects can occur when a single metal is in contact with an electrolyte – differential aeration and crevice corrosion. Differential aeration can cause corrosion when no obvious galvanic cells are in evidence. To illustrate this effect, suppose we have a cell with a copper anode and cathode. If the concentration of the electrolyte and the temperature of each cell compartment is the same, no potential is generated and no corrosion occurs. However, bubble O_2 into the one compartment, which becomes the cathode compartment, and corrosion will occur in the other, which forms the anode compartment. Differential aeration is, in fact, a concentration effect, and can be understood by using the Nernst equation. Electrons will flow from anode to cathode and the anode will corrode.
Anode reaction:

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

Cathode reaction:

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4(OH^{-})$$

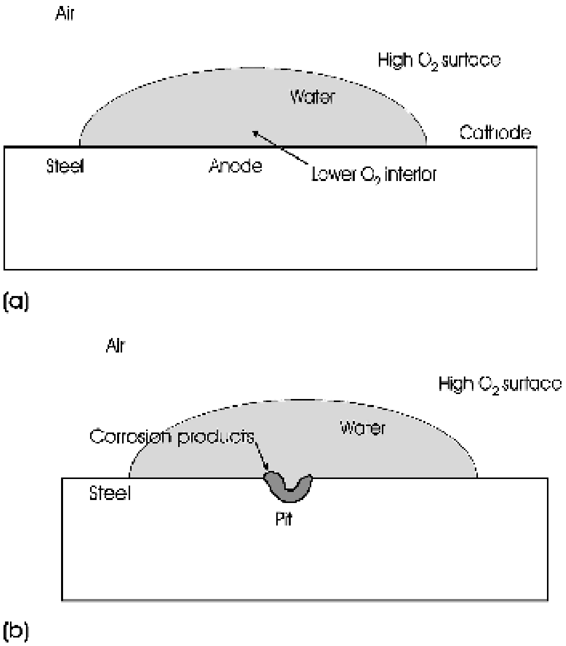

Figure 9.18 Differential aeration leading to pitting in steel: (a) before and (b) after corrosion

Cell reaction:

$$2Cu(s) + O_2 + 2H_2O(l) \rightarrow 4(OH^-) + 2Cu^{2+}(aq)$$

This type of corrosion can happen within a water drop on steel. The surface contains more dissolved oxygen than the interior of the drop and creates a circular cathode (Figure 9.18). The less-aerated centre forms an anode, and corrosion produces a pit at the centre of the drop.

Anode reaction:

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

Cathode reaction:

$$O_2(g) + H_2O(e) + 4e^- \rightarrow 4(OH^-)$$

Cell reaction:

$$2Fe(s) + O_2 + 2H_2O(l) \rightarrow 4(OH^-) + 2Fe^{2+}(aq)$$

Similar corrosion effects can be seen in narrow crevices. For example, narrow channels between a damp steel rivet and a damp plate can receive less oxygen than the surface of either. The crevice becomes anodic, and corrosion may occur (Figure 9.19). This problem is often enhanced when the corrosion product has a high volume. The resulting stress may lever the rivet head off. This effect is termed crevice corrosion.

Corrosion of a single metal can also occur even in the absence of significant differential aeration. This puzzling occurrence is due to the presence of anodic and cathodic regions on the metal. These can be generated during heat treatment and cold working of metals. For example, the regions of a metal subjected to cold working are often anodic compared with the remainder of the material. In contact with an electrolyte these areas will tend to corrode as a result of the formation of a galvanic cell, even though no concentration effects exist.

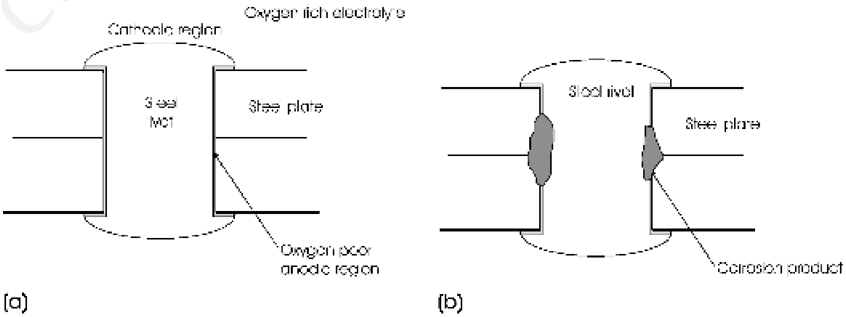

Figure 9.19 Corrosion in a crevice as a result of differential aeration: (a) before and (b) after corrosion

9.5 Electrolysis

Whereas a galvanic cell uses a spontaneous chemical reaction to produce an electric current, an electrolytic cell uses an electric current to drive a nonspontaneous chemical reaction. A rechargeable battery thus operates as a galvanic cell when being used and as an electrochemical cell when being charged. The process occurring in an electrochemical cell is called electrolysis. Electrolytic cells are widely used in the preparation of chemicals such as magnesium and aluminium and in electroplating.

9.5.1 Electrolytic cells

Electrolytic cells do not, in general, require the electrodes to be in separate compartments, and so are simpler in construction than are galvanic cells (compare Figures 9.1a,b and 9.20). However, the reactions at the anode (oxidation) and at the cathode (reduction) are identical to those in a galvanic cell. Similarly, during operation, electrons from the external supply enter the cell via the cathode, and leave it via the anode, as in a galvanic cell. Cations in the electrolyte move away from the anode and towards the cathode, whereas anions in the electrolyte move away from the cathode and towards the anode. Unfortunately, the anode of an electrolytic cell is labelled + and the cathode −, whereas in a galvanic cell the reverse is true, and the anode is labelled − and the cathode +.

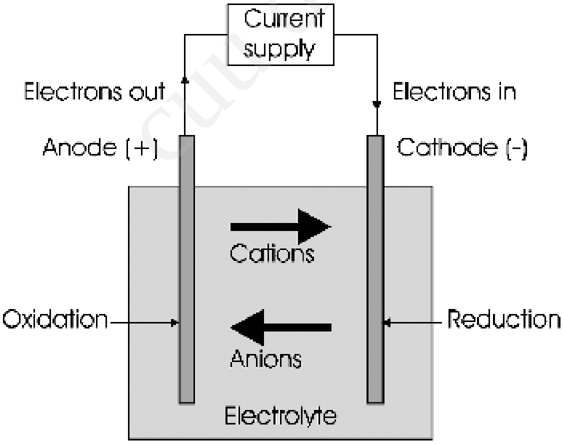

Figure 9.20 An electrolysis cell

The potential that has to be supplied to make the nonspontaneous reactions occur must be (in principle) the reverse of the potential generated by the spontaneous reaction. That is, the potential must be the potential encountered in the cell reaction, but reversed. In practice, this minimum amount of potential has to be exceeded. The actual amount of extra potential to be supplied, the overpotential, is a function of the electrode materials and surface conditions.

In a situation where the fluid contains several species that could be oxidised or reduced, those requiring the least input of energy will preferentially react. This aspect is explored in more detail below.

9.5.2 Electrolysis of fused salts

Davy electrolysed fused hydroxides of potassium and sodium in 1807, and in this way he discovered the metals potassium and sodium. A number of important metals are still produced by a similar route, the electrolysis of fused salts, including sodium (Na), magnesium (Mg), calcium (Ca) and aluminium (Al). Sodium, magnesium and calcium are all produced via electrolysis of the molten chloride. Taking molten sodium chloride (NaCl), as an example, the reactions are as follows.
Anode reaction:

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

Cathode reaction:

$$Na^+(l) + e^- \rightarrow Na(l)$$

Electrolysis reaction:

$$2NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g)$$

In order to lower the temperature of the process, a eutectic mixture of $CaCl_2$ and NaCl is used, which

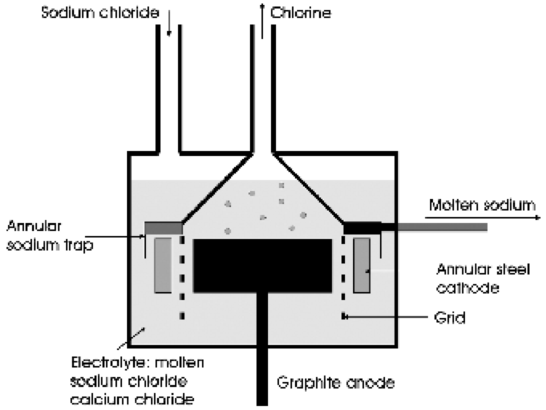

Figure 9.21 The Downs cell for the production of sodium; the cathode is steel and the anode is graphite

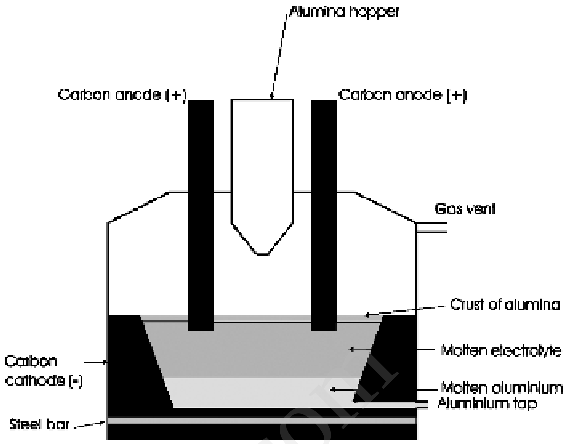

Figure 9.22 The Hall – Héroult cell for aluminium production; both electrodes are made of carbon

considerably reduces the melting point of the solid. The cells employed, Downs cells, use a steel cathode and inert carbon anodes (Figure 9.21). Because of the inclusion of $CaCl_2$, some calcium metal is also released during the operation of the cell. This is returned to the melt, whereas the sodium is recovered.

The electrolytic production of aluminium is more complex. Hall and Héroult developed the current process independently in 1886. In this process, alumina, Al_2O_3, is dissolved in molten sodium aluminium fluoride (Na_3AlF_6) and electrolysed (Figure 9.22). Originally, the aluminium oxide was derived directly from the mineral bauxite, and the sodium aluminium fluoride was used in the form of the naturally occurring mineral cryolite. These days, synthetic cryolite is used, and the aluminium oxide is produced from a wider variety of mineral sources, consisting of aluminium oxide-hydroxides.

The composition of the electrolyte is approximately 80–90 % cryolite. The amount of Al_2O_3 is continuously replenished as the electrolysis continues. The anode, which is consumed in the reaction, is carbon, and the cathode is carbon reinforced with steel bars, contained in a steel 'pot'. Although the fine details of the reactions occurring are still not completely known, the framework of the process is believed to be as follows.

Anode reaction:

$$2Al_2O_3(l) + 3C(s) + 24F^-(l) \rightarrow 4AlF_6^{3-}(l) + 3CO_2(g) + 12e^-$$

Cathode reaction:

$$4AlF_6^{3-}(l) + 12e^- \rightarrow 4Al(l) + 24F^-(l)$$

Electrolysis reaction:

$$2Al_2O_3(l) + 3C(s) \rightarrow 4\,Al(l) + 3CO_2(g)$$

A lesser reaction,

$$2Al(l) + 3CO_2(g) \rightarrow Al_2O_3(s) + 3CO(g)$$

produces alumina, which forms a protective crust on the molten cryolite.

9.5.3 The electrolytic preparation of titanium by the Fray–Farthing–Chen Cambridge process

The preparation of titanium metal uses a batch process, the Kroll process, which involves the reduction of titanium tetrachloride with magnesium metal. The starting material is usually the ore ilmenite, $FeTiO_3$. This is heated with chlorine and carbon at 900 °C to form titanium tetrachloride, $TiCl_4$:

$$2\,FeTiO_3 + 7Cl_2 + 6C \rightarrow 2TiCl_4 + 2FeCl_2 + 6CO$$

The chloride mixture must then be distilled to separate the $TiCl_4$ from the $FeCl_2$. Titanium tetrachloride is a reactive and corrosive liquid that requires very careful handling at all times. This chemical is reduced with molten magnesium metal in a sealed vessel under argon at 950–1150 °C:

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$$

The resulting titanium is purified by reaction with acids, including aqua regia (a 1:3 mixture of concentrated nitric and hydrochloric acids). This final product can then be cast into ingots under vacuum. The final titanium metal product is very expensive, not only because of the chemicals involved but also because production is a batch process and not continuous.

Because of the expense of this process, schemes using electrolysis of molten titanium salts, similar to the production of aluminium, have been widely investigated. To date, none of these has worked well. Although metal can be produced in this way, it is often dendritic in form, and very reactive, oxidising on contact with air. The various valence states of titanium found in melts (4+, 3+ and 2+) lower the efficiency of the methods and contribute to unreliable results.

A new process, called the FCC Cambridge Process, uses a slightly different electrochemical approach. The method is named after its discoverers, Fray, Farthing and Chen, working in the University of Cambridge, England. The key to the method, and what distinguishes it from earlier electrolysis attempts, lies in the use of slightly nonstoichiometric titanium dioxide, TiO_2, as the cathode in an electrochemical cell. Titanium dioxide itself is an insulator with a very high relative permittivity. For the rutile form of the oxide, the values are approximately 80 parallel to the *a* axis and about 137 parallel to the *c* axis of the tetragonal unit cell. However, removal of oxygen from rutile to give a nonstoichiometric oxide is easy. Moreover, these nonstoichiometric materials are good electronic conductors, and even a composition as close to TiO_2 as $TiO_{1.995}$ conducts electricity well. Thus, the trick is not to dissolve the oxide in a flux, and transport titanium ions, but to make the cathode of pellets of slightly reduced rutile, and transport oxygen ions. The electrolyte is molten $CaCl_2$, and graphite is used as the anode (Figure 9.23). During electrolysis, oxygen is pulled out of the titanium oxide cathode and transported to the graphite anode, where some of it reacts to form carbon oxides and some is released as oxygen. The oxide cathode is gradually converted to pellets of titanium metal in a sponge-like form. This material does not oxidise easily and can be melted and turned into ingots with minimum additional processing.

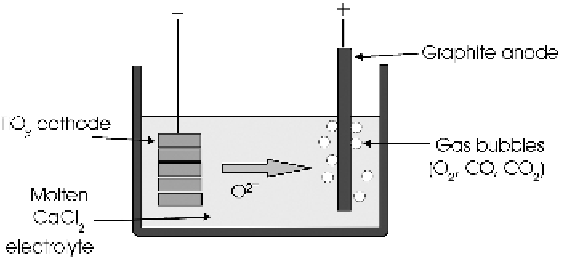

Figure 9.23 The design of the FFC Cambridge cell for the production of titanium metal by the electrolysis of slightly reduced titanium dioxide, TiO_x. Oxygen is transported through the electrolyte, molten $CaCl_2$, and liberated at the graphite anode, as oxygen gas, carbon monoxide and carbon dioxide

The cell reaction can be written in a simplified form as follows.

Anode reaction (oxidation, electron generation):

$$xC(s) + xO^{2-}(l) \rightarrow xCO(g) + 2xe^{-}$$

Cathode reaction (reduction, electron consumption):

$$TiO_x(s) + 2xe^{-} \rightarrow xO^{2-}(l) + Ti(l)$$

Electrolysis reaction:

$$TiO_x + xC(s) \rightarrow Ti(s) + xCO(g)$$

In reality, carbon monoxide, carbon dioxide and oxygen are produced at the anode. These anode reactions can be approximated by:

$$aC(s) + aO^{2-}(l) \rightarrow aCO(g) + 2ae^-$$
$$bC(s) + 2bO^{2-}(l) \rightarrow bCO_2(g) + 2be^-$$
$$cO^{2-}(l) \rightarrow \frac{c}{2}O_2(g) + 2ce^-$$

where $(a + 2b + c)$ is equal to x in TiO_x; that is, the cell reaction is:

$$TiO_{a+2b+c} + (a+b)C(s) \rightarrow Ti + aCO(g) + bCO_2(g) + \frac{c}{2}O_2(g)$$

This new process works well with a number of other oxides that are difficult to convert into metals by conventional redox methods, including Cr_2O_3, ZrO_2, Nb_2O_5 Ta_2O_5 and WO_3, which can all be produced in an electronically conducting form. Moreover, if the cathode is made of solid solutions or mixed oxides, alloys can be produced directly. Using this technique, simple alloys such as $TiAl_3$ and Ni_3Ti and more complex compounds such as Ti_6Al_4V have been synthesised.

9.5.4 Electrolysis of aqueous solutions

The central equation in the electrolysis of water is

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \quad E = -1.23\ \text{V at pH 7}$$

This nonspontaneous reaction is the reverse of that used in the fuel cell. There are two aspects of the reaction to note. First, pure water is a poor conductor of electricity, and dilute solutions, often of acids such as sulphuric acid, H_2SO_4, are used. Second, because of overpotentials, it is necessary for a voltage greater than 2 V to be applied to the electrodes for the reactions to take place. These are as follows.

Anode reaction (oxidation of H_2O; electron generation):

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$
$$E = +0.81\ \text{V at pH 7}$$

Cathode reaction (reduction of H_2O, electron consumption):

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$
$$E = -0.42\ \text{V at pH 7}$$

Electrolysis reaction:

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

When other anions and cations are present they can be discharged in preference if the energy requisite is less than that of the reactions above. For example, in the presence of sulphate ions, $SO_4^{-2}(aq)$, these may also give up electrons at the anode and be oxidised. However, this needs a potential of 2.05 V, which is more than the competing water reaction and so does not occur to any extent.

The same principles apply to all other aqueous electrolysis reactions. The two reactions involving the oxidation and reduction of water will always be competitors, and the oxidation or reduction reaction taking place will be that requiring the lowest potential. For example, consider the reduction of brine (concentrated salt solution) (Figure 9.24). The solution contains $Na^+(aq)$ and $Cl^-(aq)$. The two competing cathode reactions are:

$$Na^+(aq) + e^- \rightarrow Na(s) \quad E^\circ = -2.17\ \text{V}$$
$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$
$$E^\circ = -0.83\ \text{V}$$

This indicates that hydrogen gas will be evolved at the cathode rather than sodium metal. The two anode reactions are:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \quad E^\circ = +1.36\ \text{V}$$
$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$
$$E^\circ = +1.23\ \text{V}$$

It would be expected, therefore, that oxygen gas would be evolved at the anode. However, the overpotential for oxygen production is substantial and in

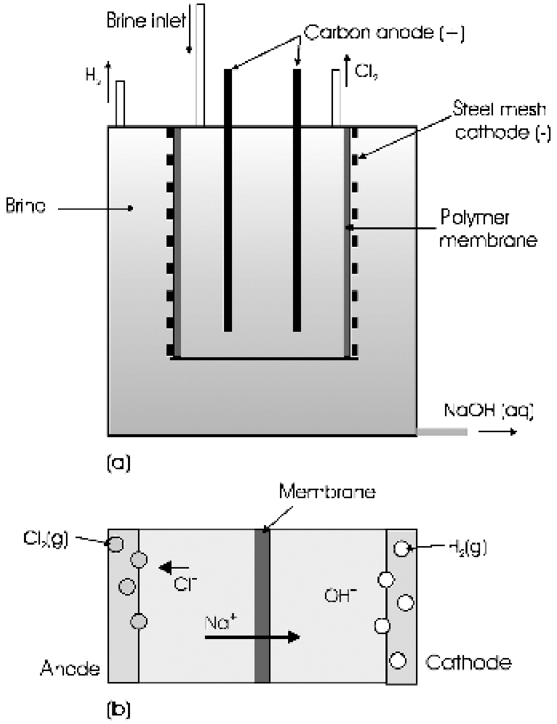

Figure 9.24 The chloralkali process: (a) membrane cell: (b) the membrane is permeable only to Na^+ ions, leading to segregation of Cl^- and OH^- in the anode and cathode compartments

fact chlorine production occurs experimentally. The overall electrolysis reaction is:

$$2\,NaCl(aq) + 2\,H_2O(l) \rightarrow 2\,NaOH(aq) + Cl_2(g) + H_2(g)$$

The chloralkali process, which involves the electrolysis of brine, is widely used for the production of sodium hydroxide and chlorine gas. During electrolysis it is necessary to keep the sodium hydroxide separate from the chlorine, to prevent the formation of sodium hypochlorite, NaOCl, and this determines cell design. In older processes, the cathode used was flowing mercury. At this electrode, sodium is formed, and this dissolves in the mercury to form a sodium amalgam. The sodium amalgam is removed continually from the cell and reacted with water to produce hydrogen gas and caustic soda in a separate reactor. Pollution from the mercury has made this cell unviable, and the electrolysis of brine is now carried out by means of membrane cells.

In a membrane cell, a polymer membrane separates the anode and cathode compartments. This allows the passage of Na^+ ions but blocks the Cl^- and OH^- ions (Figure 9.24). The concentration of $Na^+(aq)$ and $OH^-(aq)$ gradually rises in the cathode region and is continuously removed.

9.5.5 The amount of product produced during electrolysis

The chemical nature of the products of electrolysis is determined by the reduction potential of the appropriate redox couple. The amount of product formed depends only on the amount of electricity that has passed through the cell. This fact was first recognised by Faraday, who formulated what are now known as Faradays laws of electrolysis:

1. The mass of substance produced at an electrode is directly proportional to the quantity of electricity that has passed through the cell;
2. The mass of a substance produced by a given quantity of electricity is directly proportional to the molar mass of the substance and inversely proportional to the numbers of electrons transferred per molecule of the substance.

The amount of electricity that is provided in an electrolysis experiment, Q, is given by:

$$Q = I\,t$$

where the amount of electricity is measured in coulombs, the current, I, is in amperes, and the time, t, in seconds. One mole of electrons has a charge

$$(1.6022 \times 10^{-19}\,C) \times (6.0222 \times 10^{23}\,mol^{-1}) = 9.6485 \times 10^{4}\,C\,mol^{-1}$$

This is called the Faraday constant, F. Thus, the quantity of electricity needed to produce one mole of a monovalent element is 9.6485×10^4 C. Double this amount is needed for a divalent element, and so on. The number of moles of electrons provided in any electrolysis experiment, Q_m, is given by

$$Q_m = \frac{I\,t}{F}$$

To obtain the mass of an element that is formed, it is necessary to multiply by the molar mass produced by 1 mole of electrons,

$$m = \left(\frac{I\,t}{F}\right)\left(\frac{M}{z}\right)$$

where m is the mass produced, I is the current (A), t is the time (s), M is the molar mass of the element (g mol^{-1}), and z is the charge on the ion involved.

9.5.6 Electroplating

Electroplating is the deposition of a metallic coating onto a metal object by means of electrolysis. It is widely carried out for decorative purposes and for corrosion prevention. The principles of electroplating do not differ from those given for electrolysis. However, in practice, the production of a high-quality film is critically dependent on a large number of factors, especially the cleanliness of the surface to be plated. In addition, commercial plating solutions also contain organic additives to enhance film adherence.

To illustrate the process, consider a (schematic) description of nickel plating (Figure 9.25). The metal object to be plated is connected to negative input from a direct current (dc) source, so as to form the cathode of the cell. The electrolyte is a solution of a soluble nickel salt in water, $NiCl_2$ for example. The anode of the cell is a rod of nickel metal. The current drives the nickel ions in solution towards the cathode, where they are deposited via the following reaction:

$$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \quad E^\circ = +0.23\,V$$

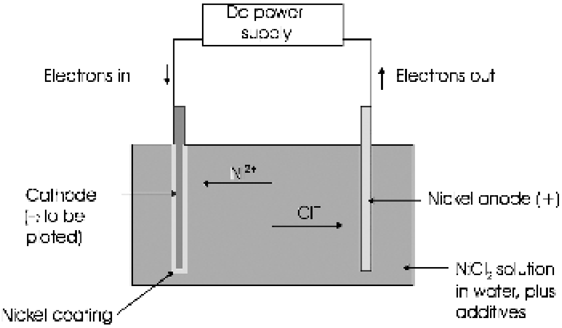

Figure 9.25 Nickel electroplating: the nickel anode is dissolved and transported to the object to be plated, which is the cathode, under the driving force of the external power supply

Two moles of electrons must be supplied to deposit 1 mole of nickel. At the anode, the chloride ions are discharged, as in the chloralkali process:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \quad E^\circ = +1.36\,V$$

Chlorine gas is evolved, and the electrons released oxidise the nickel anode, which dissolves in the process:

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

The overall result is the transfer of nickel from the anode to the cathode:

$$Ni(s)\ \text{anode} \rightarrow Ni(s)\ \text{cathode}$$

It is this same process that causes the corrosion of anodes in all batteries. As mentioned above, the real reactions that take place during electroplating are far more complex than this. As a first approximation these can be written as follows.

Anode reaction:

$$Ni(s) + 2Cl^-(aq) \rightarrow Ni^{2+}(aq) + Cl_2(g) + 4e^-$$

Cathode reaction:

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

Plating reaction:

$$Ni(s) + 2Cl^-(aq) + Ni^{2+}(aq) \rightarrow 2Ni(s) + Cl_2(g)$$

9.6 Pourbaix diagrams

9.6.1 Passivation and corrosion

Many reactions that occur in water are sensitive to acidity (pH), concentration and to the relative oxidising or reducing conditions in the neighbourhood. This is especially true of corrosion. However, corrosion does not always occur, and under certain combinations of acidity and reduction potential iron, copper, zinc and other metals can resist corrosion. This feature is called passivation.

In order to determine whether a metal will corrode, it necessary to write down all the possible half-reactions that can be envisaged and then determine how these will vary with acidity, concentration and oxidation potential. It is tedious to carry out these calculations, and the results are often not especially lucid. The overall scheme of reactivity can, however, be represented graphically. Such diagrams are called Pourbaix diagrams. Although initially formulated to assist in demarcation of corrosion-resistant conditions for metals, they have found applicability in other areas, including electrochemistry, the earth sciences, chemical engineering and metallurgy and in the disposal of hazardous or radioactive waste.

A Pourbaix diagram uses the oxidising/reducing potential and the acidity of the environment as parameters to quantify the reactivity of the system under consideration, usually for aqueous environments. The oxidising capability is plotted on the ordinate (y axis) as a voltage. The use of voltage to express oxidation and reduction is simply an adaptation of the electrochemical series, and the voltage used is that of the half-reaction measured against a standard hydrogen electrode. A table of reduction half-reactions and associated voltages is also a table of relative oxidising and reducing capabilities. The acidity is plotted on the abscissa (x axis) as pH. The area of the diagram is divided up into stability fields, which show where a certain species is stable.

Most corrosion reactions of interest take place in the presence of water, and the area of the diagram in which water is present is indicated. This region, the stability field of water, is defined as the range of pH and oxidation/reduction potential over which water is stable both to oxidation and to reduction at 25 C and 1 atm pressure (Figure 9.26). Above the upper boundary, water is oxidised to O_2 gas, and below the lower line it is reduced to H_2 gas. The calculation of the stability field of water is given in Section S3.5.

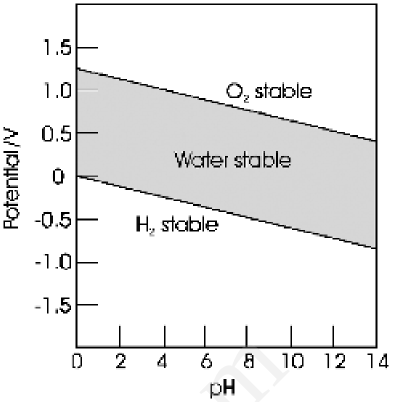

Figure 9.26 A Pourbaix diagram showing the stability field of water (shaded)

9.6.2 Variable valence states

Transition metals display several valence states. Generally, the valence state that is stable depends on the acidity and the oxidation potential of the environment. Iron (Fe), and its compounds, illustrate these possibilities. Iron is present in the Earth's core as liquid metal, Fe^0. In the mantle, or in reducing conditions in sediments, Fe is present as Fe^{2+} [Fe(II), ferrous]. In oxidising conditions, Fe exists as Fe^{3+} [Fe(III), ferric]. The commonest iron-containing minerals, Fe_2O_3 (haematite, Fe^{3+}), Fe_3O_4 (magnetite, lodestone, Fe^{2+}, Fe^{3+}) and $FeCO_3$ (siderite, Fe^{2+}), reflect the different formation conditions of the minerals in the Earth's crust.

Irrespective of origin, all iron compounds tend to the stable Fe^{3+} state in air. Iron itself corrodes in moist air and reacts with nonoxidising acids to yield H_2 and Fe(II) salts. Fe(II) salts are subsequently oxidised to Fe(III) salts in air. This is a slow reaction in acidic solution and is rapid in a basic

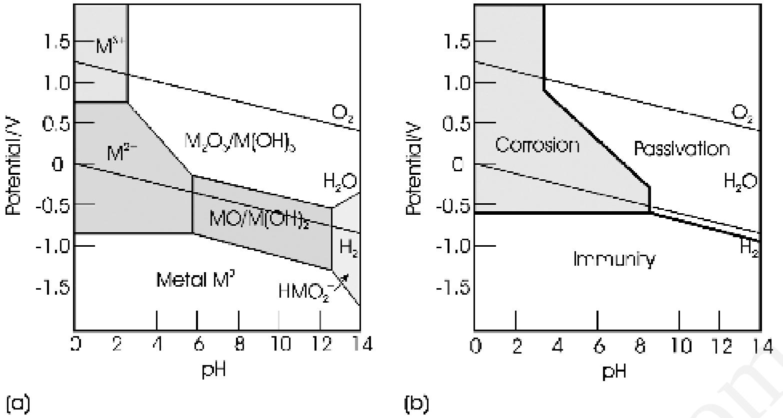

Figure 9.27 (a) Pourbaix diagram for an element, M, with two valence states, M^{2+} and M^{3+}, in water; (b) simplified version of the diagram in part (a), showing the range of conditions over which corrosion, passivation and immunity are likely to occur

solution, when insoluble oxyhydroxides, typically labelled $Fe(OH)_3$, are precipitated.

These confusing relations occur for most transition metals, as well as for the lanthanides and actinides. The various stability regions are most easily understood via the appropriate Pourbaix diagram.

9.6.3 Pourbaix diagram for a metal showing two valence states, M^{2+} and M^{3+}

A schematic Pourbaix diagram for a typical transition metal such as iron, showing two valence states, M^{2+} and M^{3+}, is drawn in Figure 9.27(a). Remember that the boundaries are concentration dependent, and the figure is representative of a typical concentration. [The method of construction of the diagram for the real iron–water–air system is given in Section S3.6.]

The upper left-hand corner of the diagram represents conditions that are oxidising and acidic. Under these conditions the higher valence state, M^{3+}, is the stable form. The region over which this remains true is called the stability field of the M^{3+} ions. [Note that, in reality, the stable species is generally a hydrated ion such as $M(H_2O)_6^{3+}(aq)$.]

As the pH increases, that is, as the acidity decreases, one moves towards the right-hand side of the diagram. Ultimately, the stable ion M^{3+} is replaced by the oxide, M_2O_3, or the hydroxide, $M(OH)_3$, as the stable species, and a new stability field is entered. The half-reaction is:

$$M^{3+}(aq) + 3H_2O(l) \rightarrow M(OH)_3(s) + 3H^+(aq)$$

The change in acidity is revealed by the formation of $H^+(aq)$, but the oxidation state of the M^{3+} valence has not changed during this transformation, and the metal is trivalent in both M_2O_3 and $M(OH)_3$. [Once again, note that in real systems the material that forms in solution is often an ill-defined oxyhydroxide and not a simple compound.] Somewhere between the high-pH and low-pH regions a boundary exists that separates the two stability fields. The boundary on Figure 9.27 (a) is a vertical line. The boundary therefore indicates the pH at which a precipitate of hydroxide would be expected to form as the acidity of the environment changes. *Vertical boundaries separate stability fields that involve a change in acidity (H^+ or OH^- concentration) and no change in oxidation state (e^- transfer).*

Return to the upper left-hand corner of Figure 9.27(a), the M^{3+} stability field. As the oxidising power of the environment decreases, that is, as the voltage on the ordinate decreases, one moves towards the bottom left-hand side of the diagram, representing more reducing conditions. Ultimately, the lower valence state, M^{2+}, becomes the stable species. The half-reaction is:

$$M^{3+} + e^- \rightarrow M^{2+}$$

The change in oxidation state is revealed by the half-reaction, which also confirms that there is no change in acidity. At some point, a boundary between the stability field of M^{3+} and M^{2+} is crossed. The boundary between the two stability fields is horizontal. *Horizontal boundaries separate stability fields that involve a change in oxidation state (e^- transfer) and no change in acidity (H^+ or OH^- concentration).*

A continued reduction in the oxidising potential, moving further towards the lower left-hand side of the diagram, causes the M^{2+} ion to be replaced by more stable metal, M^0. The boundary between the stability fields for M^{2+} and M^0 is horizontal, for the reason given above.

Return to the lower part of the M^{2+} stability field and consider the consequence of decreasing the acidity, that is, increasing the pH. Ultimately, the M^{2+} stability field gives way to one in which the oxide MO or the hydroxide $M(OH)_2$ are preferred. The boundary between the stability fields is vertical as no change in oxidation state is involved.

Repeat this in the upper part of the M^{2+} stability field. The conditions then correspond to a decrease in acidity under oxidising conditions. The M^{2+} stability field will now give way to a field in which either oxide, M_2O_3, or hydroxide, $M(OH)_3$, are preferred. In this case, the stability field boundary marks a change in both oxidation state and acidity, and the stability field boundary is sloping. For example, when M^{2+} produces a trivalent hydroxide, $M(OH)_3$, the half-reaction is:

$$2M^{2+}(aq) + 6H_2O \rightarrow 2M(OH)_3 + 6H^+(aq) + 2e^-$$

The redox nature of the reaction is revealed by the production of electrons, and the acid–base nature of the reaction by the production of H^+. *Sloping boundaries separate stability fields that involve a change in acidity (H^+ or OH^- concentration) and a change in oxidation state (e^- transfer).*

The sloping nature of the boundary shows that the formation of a precipitate will depend on the local pH and oxidising power. Small changes can make a large difference in whether an ion will stay in solution or transform into a solid. These considerations are important in whether dangerous metals can dissolve and spread out from spoil tips or radioactive waste dumps.

One other stability field is mapped out, the acid ion HMO_2^-. This is included as illustrative of the complex species that can form. Although they do not usually play a part in normal environmental concerns, they are relevant to reactions in unusual or extreme conditions.

9.6.4 Pourbaix diagram displaying tendency for corrosion

Figure 9.27(a) is redrawn in Figure 9.27(b) with the stability fields labelled differently. There are no chemical species indicated but instead the tendency for corrosion is indicated. Corrosion is likely when the metal is in an environment corresponding to the stability fields in which aqueous M^{3+} and M^{2+} ions are stable. The regions in which a solid occurs are less likely to corrode extensively as the initial formation of a precipitate will prevent further corrosion from taking place. In these stability fields the metal is passivated. Finally, the region in which metal is stable is labelled as immune to corrosion. The range of oxidation and pH conditions under which the metal would be immune to corrosion, passivated or corrode are clearly distinguished.

9.6.5 Limitations of Pourbaix diagrams

The positions of the boundaries to the phase fields are concentration-dependent, and diagrams are usually constructed with concentrations that are relevant to the problems under consideration. It is important to keep this in mind when using these diagrams. Moreover, they are derived by means of equilibrium thermodynamic data and are only as accurate as the available data. This is of high quality for well-known systems such as iron–water–air, but for some systems involving radioactive materials the data are less accurate. In addition, these diagrams do not consider any kinetic or crystallographic aspects. For example, both glass and diamonds are thermodynamically unstable but are of importance for all that. Unstable reaction products may be of considerable importance in corrosion. Moreover, kinetic factors such as the flow rate of any solutions, or changes in temperature, are not catered for. Similarly, the definition of passivation must be treated with caution. An important feature of a passive film is that it is coherent with the metal and does not crack or contain pores. The Pilling–Bedworth ratio (Section 8.5.3) is an attempt to determine if a film is likely to fulfil the requirements of passivation.

Answers to introductory questions

What is an electrochemical cell?

An electrochemical cell is a device for the conversion of electrical to chemical energy, and vice versa, by way of redox reactions. Electrochemical cells consist of two metal electrodes (an anode and a cathode) in contact with an electrolyte that is able to conduct ions but not electrons.

There are two types of electrochemical cell. A galvanic cell uses a spontaneous chemical reaction to produce an external electric current. Galvanic cells are called ‘batteries’ in colloquial speech. Electrolytic cells, employed for electrolysis and electroplating, use external electrical power to force nonspontaneous chemical reactions to take place.

What are the electrode materials in nickel-metal-hydride batteries?

These batteries, frequently called Ni–*M*H batteries, rely on hydrogen storage in a metal alloy for the reversible operation. The positive electrode, the cathode, does not consist of nickel. It consists of a complex mixture of $NiO(OH)/Ni(OH)_3$ and $Ni(OH)_2$.

The negative electrode, the anode, consists of an alloy that supports metal hydride formation. Many metals absorb large quantities of hydrogen to form nonstoichiometric interstitial alloys. In many of these materials the hydrogen incorporation is reversible, so that hydrogen is taken up at high hydrogen pressure and released at lower pressure. This reversible uptake of hydrogen is exploited in nickel–metal-hydride batteries. The alloy most commonly used is derived from $LaNi_5$, in which a mixture of other lanthanides replaces the lanthanum, and a nickel-rich alloy replaces the nickel, to give a general formula LnM_5. The anode is composed of an agglomeration of alloy powder. A small amount of potassium hydroxide is added as an electrolyte. The cell voltage is 1.3 V, and the approximate cell reactions are as follows.

Anode reaction (oxidation, electron generation):

$$MH_x(s) + OH^-(aq) \rightarrow MH_{x-1}(s) + H_2O(aq) + e^-$$

Cathode reaction (reduction, electron consumption):

$$2NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$$

Cell discharge reaction:

$$MH_x(s) + 2NiO(OH)(s) \rightarrow MH_{x-1}(s) + Ni(OH)_2(s)$$

The charging reaction is the reverse of the discharge reaction, driven by an external voltage.

What information is contained in a Pourbaix diagram?

Many reactions that occur in water are sensitive to acidity (pH), and to the relative oxidising or reducing conditions in the neighbourhood. This is especially true of corrosion.

In order to determine whether a metal will corrode, it necessary to write down all of the possible half-reactions that can be envisaged and then determine how these will vary with acidity, concentration and oxidation potential. It is tedious to carry out these calculations and the results are often not especially lucid. The overall scheme of reactivity can be represented graphically on Pourbaix diagrams. Although initially formulated to assist in demarcation of corrosion-resistant conditions for metals, they have found applicability in other areas, including electrochemistry, the earth sciences, chemical engineering and metallurgy and in the disposal of hazardous or radioactive wastes.

The raw information on a Pourbaix diagram is essentially the oxidising/reducing potential, plotted along the *y* axis, and the acidity of the environment, plotted along the *x* axis. The area of the diagram is divided up into stability fields, which show the oxidation and acidity limits between which a particular chemical species is stable. Because most of the reactions of interest take place in the presence of water, the area of the diagram in which water remains stable is indicated. This region, the stability field of water, is defined as the range of pH and oxidation/reduction potential over which water is stable to both oxidation and reduction. Above the upper boundary water is oxidised to O_2 gas, and below the lower line it is reduced to H_2 gas.

The stability fields are labelled in a fashion determined by the application of the diagram. For geochemical applications, these are usually ionic species or minerals. For the purposes of corrosion science, the fields are labelled corrosion, passivation or inert, depending on which of these possibilities is judged as the most likely to occur.

Further reading

D.A. Brookins, 1998, *Eh – pH Diagrams for Geochemistry*, Springer-Berlin.

R.M. Dell, D.A.J. Rand, 2001, *Understanding Batteries*, Royal Society of Chemistry, Cambridge.

D.A. McQuarrie, D.A. Rock, 1991, *General Chemistry*, 3rd edn, Freeman, New York, Ch. 21.

D.R. Sadoway, A.M. Mayes, 2002, ‘Portable Power: Advanced Rechargable Lithium Batteries’, *Materials Research Society Bulletin* **27** 590.

D.F Shriver, P.W. Atkins, C.H. Langford, 1994, *Inorganic Chemistry*, 2nd edn, Oxford University Press, Oxford, Ch. 7.

K.R. Trethewey, J. Chamberlain, 1995, *Corrosion*, 2nd edn, Longman, Harlow, Essex.

S.C. Singhal, 2002, ‘Science and Technology of Solid-oxide Fuel Cells’, *Materials Research Society Bulletin* **25** (March), 16.

Problems and exercises

Quick quiz

1 Oxidation is equivalent to:
   (a) Electron gain
   (b) Electron loss
   (c) Electron transfer

2 During reduction, the oxidation number of the species being reduced
   (a) Increases
   (b) Decreases
   (c) Does not change

3 A redox reaction is one in which:
   (a) Oxidation *and* reduction occurs
   (b) Oxidation *or* reduction occurs
   (c) Oxygen takes part

4 A galvanic cell uses:
   (a) An external power supply to cause a chemical change
   (b) A battery to cause chemical change
   (c) A spontaneous chemical reaction to produce an external electric current

5 An electrolytic cell uses:
   (a) A spontaneous chemical reaction to produce an external electric current
   (b) An external power supply to cause a chemical change
   (c) A battery to cause chemical change

6 In a galvanic cell the anode:
   (a) Is the negative terminal
   (b) Is the positive terminal
   (c) Links the cell compartments

7 Batteries are examples of:
   (a) Electrolytic cells

(b) Corrosion cells
(c) Galvanic cells

8 In a battery, oxidation takes place at the:
(a) Cathode
(b) Anode
(c) Neither

9 A hydrogen electrode can be:
(a) The anode of a cell
(b) The cathode of a cell
(c) Either the cathode or the anode

10 The tendency for reduction of an element is given by:
(a) The electrochemical series
(b) The standard cell potential
(c) The hydrogen electrode

11 The couple *higher* in the electrochemical series:
(a) Forms the cathode
(b) Forms the anode
(c) Sometimes forms the cathode and sometimes the anode

12 The cell potential is a measure of:
(a) The free energy change of the cell reaction compared with the hydrogen electrode
(b) The free energy of the anode reaction
(c) The free energy of the cell reaction

13 The Nernst equation describes:
(a) The free energy of a galvanic cell
(b) The variation of the potential of a galvanic cell with concentration
(c) The reaction equation of a galvanic cell

14 pH meters are based on the operating principles of:
(a) Batteries
(b) Galvanic cells
(c) Electrolytic cells

15 A rechargable battery is called:
(a) A primary cell
(b) A secondary cell
(c) A fuel cell

16 In an alkaline dry cell the zinc is:
(a) Oxidised and forms the anode
(b) Reduced and forms the cathode
(c) Is neutral and forms the container

17 In a lithium primary cell the lithium is:
(a) Oxidised and forms the anode
(b) Reduced and forms the cathode
(c) Is neutral and forms the container

18 In a Ni–*M*H battery the anode is formed by:
(a) Nickel
(b) Nickel hydroxides
(c) A metal alloy hydride

19 When a metal reacts with an acid it is:
(a) Reduced
(b) Oxidised
(c) Neither oxidised nor reduced, simply dissolved

20 When a metal reacts with water it is:
(a) Oxidised
(b) Reduced
(c) Neither oxidised nor reduced, simply corroded

21 During dissimilar metal corrosion, the metal that corrodes is:
(a) The anode
(b) The cathode
(c) Neither

22 During electrolysis for the production of a metal, the metal is produced:
(a) At the anode
(b) At the cathode
(c) Between the anode and cathode

23 The amount of chemical produced during electrolysis is governed by:
(a) The voltage applied
(b) The concentration of the reactants
(c) The amount of electricity passed

24 A Pourbaix diagram plots:
(a) Oxidation potential against free energy

(b) Oxidation potential against temperature
(c) Oxidation potential against pH

25 A Pourbaix diagram does *not* give information about:
(a) The corrosion resistance of a metal
(b) The rate of corrosion of a metal
(c) The solubility of a metal

Calculations and Questions

9.1 Classify the following reactions as oxidation (ox), reduction (red.) or redox reactions. The equations are representative and not balanced.
(a) $Fe_3O_4 \rightarrow Fe_2O_3$.
(b) $O_2(g) \rightarrow 2O^{-2}$.
(c) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$.
(d) $Br_2(l) \rightarrow Br^{-}(aq)$.
(e) $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$.
(f) $Fe_2O_3(s) \rightarrow 2Fe(l)$.

9.2 Classify the following reactions as oxidation (ox.), reduction (red.) or redox reactions. The equations are representative and not balanced.
(a) $Co_3O_4 \rightarrow Co_2O_3$.
(b) $CuO \rightarrow Cu$.
(c) $Zn(s) + H^{2+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$.
(d) $N_2(l) \rightarrow 2N^{3-}(aq)$.
(e) $2Ca(s) + O_2(g) \rightarrow 2CaO(s)$.
(f) $Al_2O_3(s) \rightarrow 2Al(l)$.

9.3 A Volta pile is made with six silver and six zinc discs.
(a) Which metal forms the anode and which the cathode?
(b) Write the anode reaction, the cathode reaction and the cell reaction.
(c) Determine the voltage of the pile.

9.4 What is the standard reaction free energy for the cell reaction of a Daniel cell?

9.5 Estimate the value of RT/nF for monovalent, divalent and trivalent ions at 27 °C.

9.6 (a) Write the cathode and anode reactions and the overall cell reaction for a cell with nickel and zinc electrodes.
(b) Determine the standard cell voltage.
(c) Calculate the cell voltage if the concentrations of the ions in solution are: Zn^{2+}, $0.016\ \text{mol dm}^{-3}$, Ni^{2+}, $0.087\ \text{mol dm}^{-3}$.

9.7 Determine the voltage of the cell in Question 9.6 if the cell is operated at 50 °C.

9.8 A cell constructed with a hydrogen electrode is represented by:

$$Pt|H_2(g)|H^+(aq)||Cu^{2+}(aq)|Cu \quad E^\circ = 0.34\ \text{V}$$

(a) Write the anode reaction, the cathode reaction and the overall cell reaction.
(b) Derive an expression for the variation of the cell voltage with the pH of the acid solution and the Cu^{2+} concentration.
(c) A cell constructed with a Cu^{2+} concentration of $1\ \text{mol dm}^{-3}$ and a hydrogen pressure of 1 atm has a voltage of 0.855 V. Estimate the pH of the acid solution.

9.9 For the cell with an overall cell reaction:

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

(a) Write the anode and cathode reactions.
(b) Determine the standard cell potential of the cell reaction.
(c) Determine the reaction free energy of the cell reaction.

9.10 What will the voltage of the cell in the Question 9.9 be (a) if the Fe^{2+} ion concentration is changed to $0.35\ \text{mol dm}^{-3}$ and (b), if the temperature of the cell is subsequently raised to 35 °C?

9.11 Derive the equation for the pH meter using a calomel electrode. This is a particularly stable electrode, which uses the redox couple Hg_2Cl_2/Hg, Cl^-. The cell is:

$$Pt|H_2(g)|H^+(aq)||Cl^-(aq)|Hg_2Cl_2|Hg(l)$$
$$E^\circ = +0.27\ \text{V}$$

The cell reaction is:

$$Hg_2Cl_2(s) + H_2(g) \rightarrow 2H^+(aq) + 2Cl^-(aq) + 2Hg(l)$$

The calomel half-reaction is:

$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$$
$$E^\circ = 0.27\ V$$

9.12 A voltammeter connected to the cell in Question 9.11 was calibrated with a buffer solution of pH 7.0 and showed a voltage of 0.12 V. What is the pH of a solution that gives a voltage of (a) 0.195 V, (b) 0.48 V?

9.13 A cell of the type in Question 9.11 is made up with a $Cl^-(aq)$ concentration of 0.5 mol dm^{-3}. The cell voltage is 0.48 V. Determine the pH of the $H^+(aq)$ component.

9.14 E° for for the couple NiO(OH)/$Ni(OH)_2$ is +0.49 V. Determine the standard reduction potential for the anode reaction

$$MH_x(s) + OH^-(aq) \rightarrow MH_{x-1}$$

in a Ni–MH cell, knowing that the cell voltage is 1.3 V.

9.15 Three clean steel nails are treated in the following ways: (a) completely immersed in tap water; (b) completely immersed in boiled distilled water; (c) partly immersed in tap water. The results found after several days are: for treatment (a), rust present, especially on the head and point; for treatment (b), little rust present; for treatment (c), dense ring of rust at the waterline and pitting just below the surface of the water. Explain these findings [see P.J. Guichelaar and M.W. Williams, 1990. 'A Simple Demonstration of Corrosion Cells', *Journal of Material Education* **12** 331].

9.16 A titanium container is to be used to store nuclear waste in mine conditions that are damp and broadly reducing so that corrosion will tend to produce $Ti^{2+}(aq)$. If the container lid is fixed with steel bolts, should these be plated and, if so, what metals might be considered?

9.17 Buried metal pipes can be protected from corrosion by connecting them to blocks of metal such as magnesium, called sacrificial anodes, which corrode in preference to the pipe. A cell made from the redox couples Fe/Fe^{2+} and Mg/Mg^{2+} is a laboratory representation of a sacrificial anode. (a) Draw the cell diagram [not shown in the answers at the end of this book], (b) write the cell half-reactions and the cell reaction and (c) calculate the standard cell voltage.

9.18 Explain how pitting can occur under a water droplet on a steel plate. [Note: answer is not provided at the end of this book.]

9.19 Water coming from a waste tip contains (a) Cu^{2+}; (b) Zn^{2+}; (c) Pb^{2+} and (d) Sn^{2+} ions in solution. What will happen when these come into contact with a steel pipe? Write the half-reactions and the overall reactions expected.

9.20 (a) Write an equation for the electrolysis of molten $MgCl_2$ to produce Mg metal and Cl_2 gas. (b) What mass of each of these elements is produced if a current of 30 A is passed for 3 hours through the cell?

9.21 The simplified equation for the production of aluminium by the Hall–Héroult process is:

$$2Al_2O_3(l) + 3C(s) \rightarrow 4Al(l) + 3CO_2(g)$$

What quantity of electricity must be passed to produce (a) 2 moles and (b) 2 kg of aluminium? (c) If a current of 25 A is used, how long will it take to produce these amounts?

9.22 A solution of a metal sulphate, MSO_4, is used to electroplate an object. The plating bath is operated for 2 hours at a current of 0.5 A. If 1.095 g of metal plates out, determine the molar mass of the metal and identify it.

9.23 On a Pourbaix diagram,

(a) What general types of equilibria apply to horizontal lines?

(b) What general types of equilibria apply to vertical lines?

(c) What general types of equilibria apply to sloping lines?

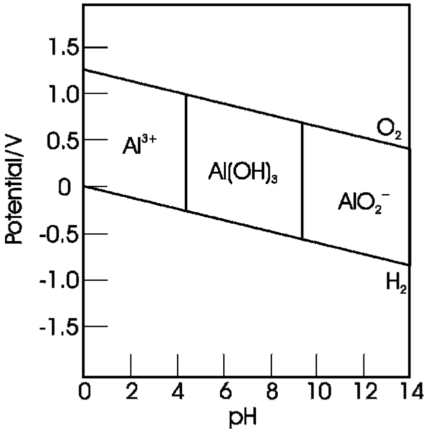

Figure 9.28 Pourbaix diagram for the Al–H_2O system within the water stability field, for Question 9.24

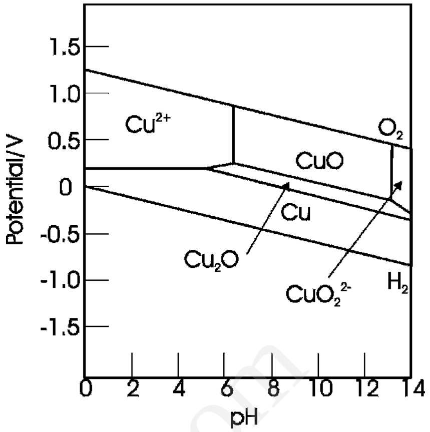

Figure 9.29 Pourbaix diagram for the Cu–H_2O system within the water stability field, for Question 9.25

[Note: answer is not provided at the end of this book.]

9.24 Figure 9.28 shows the Pourbaix diagram for the Al – H_2O system within the water stability field, for an Al^{3+} concentration of 1×10^{-6} mol dm^{-3}.

(a) What oxidation states of Al exist?

(b) Why are there no sloping boundaries on this diagram?

(c) Will Al be soluble in water with an acidity of pH 3?

(d) What species will exist in the surface waters of lakes and streams (pH $\sim$ 7, $E \sim 0.6$ V)?

(e) Over what pH range is Al passivated?

9.25 Figure 9.29 shows the Pourbaix diagram for the Cu – H_2O system within the water stability field, for a Cu^{2+} concentration of 1×10^{-6} mol dm^{-3}.

(a) What oxidation states of Cu exist?

(b) Under what conditions will copper be soluble in water of pH 3?

(c) Label the diagram to show the regions where copper corrodes, is passivated and is immune to corrosion.

(d) What equilibria do the two vertical lines on the diagram represent?

(e) What equilibrium does the horizontal line represent?

(f) What equilibrium does the sloping line between the copper and Cu_2O stability fields represent?

(g) What equilibrium does the sloping line between the Cu_2O and CuO stability fields represent?

9.26 The water types met with in nature are:

(a) fresh surface waters, pH $\sim$ 7, $E \sim 0.6$ V;

(b) organic-rich fresh water, pH $\sim$ 5, $E \sim 0$ V;

(c) organic-rich waterlogged soil, pH $\sim$ 4.5, $E \sim -0.1$ V;

(d) acid bog water, pH $\sim$ 3, $E \sim 0.1$ V;

(e) fresh water polluted by mine drainage, pH $\sim$ 3, $E \sim 0.8$ V;

(f) surface ocean water, pH $\sim$ 8, $E \sim 0.55$ V;

(g) organic-rich ocean water, pH $\sim$ 9, $E \sim -0.4$ V

Sketch these onto the stability field of water on the Pourbaix diagram of Figure 9.29 [sketch not shown at the end of this book.]. What copper species will be present in each of these?