

chapter thirty-four

The Chemical Effect of the Current

In this chapter we shall deal both with the effects of an electric current when it is passed through a chemical solution, and with chemical generators of electric current, or cells.

ELECTROLYSIS

The chemical effect of the electric current was first studied quantitatively by Faraday, who introduced most of the technical terms which are now used in describing it. A conducting solution is called an *electrolyte* and the chemical changes which occur when a current passes through it are called *electrolysis* (*lysis* = decomposition). Solutions in water of acids, bases, and salts are electrolytes, and so are their solutions in some other solvents, such as alcohol. The plates or wires which dip into the electrolyte to connect it to the circuit are called *electrodes*; the one by which the current enters the solution is called the *anode*, and the one by which it leaves is called the *cathode* (Fig. 34.1 (i)).

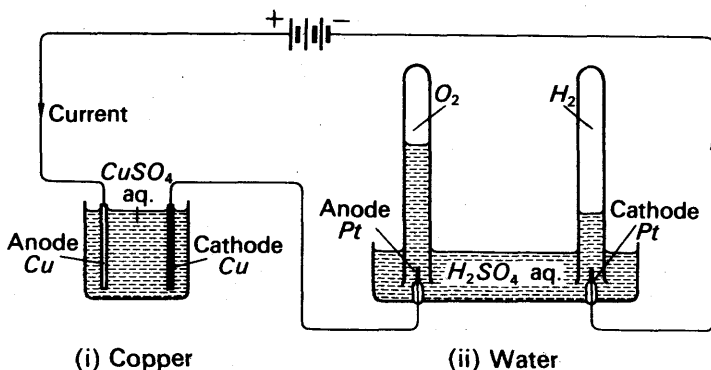


FIG. 34.1. Voltmeters.

The whole arrangement is called a *voltmeter*, presumably because it can be used to measure the current delivered by a voltaic cell; if the electrolyte is a solution of a copper or silver salt, the voltmeter is called a copper or silver voltmeter. If the electrolyte is acidulated water, then the voltmeter is called a water voltmeter, because when a current passes through it, the water, not the acid, is decomposed (Fig. 34.2 (ii)). We shall see why later.

Faraday's Laws of Electrolysis

When a current is passed through copper sulphate solution with copper electrodes, copper is deposited on the cathode and lost from the anode. Faraday showed that the mass dissolved off the anode by a given current in a given time is equal to the mass deposited on the cathode. He also showed that the mass is proportional to the product of the current, and the time for which it flows: that is to say, to the quantity of charge which passes through the voltameter. When he studied the electrolysis of water, he found that the masses of hydrogen and oxygen, though not equal, were each proportional to the quantity of charge that flowed. He therefore put forward his first law of electrolysis: *the mass of any substance liberated in electrolysis is proportional to the quantity of electric charge that liberated it.*

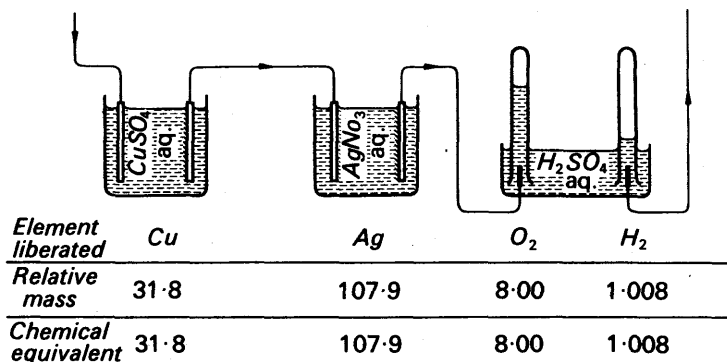


FIG. 34.2. Voltmeters in series (same quantity of charge passes through each).

Faraday's second law of electrolysis concerns the masses of different substances liberated by the same quantity of charge. An experiment to illustrate it is in Fig. 34.2. The experiment shows that *the masses of different substances, liberated in electrolysis by the same quantity of electric charge, are proportional to the ratio of the relative atomic mass to the valency* (also called the *chemical equivalent*). This is Faraday's second law; it implies that the same quantity of charge is required to liberate one mole divided by the valency (also called the 'gramme-equivalent') of any substance. Recent measurements give this quantity as 96500 coulombs; it is called Faraday's constant, symbol *F*. It is also known as the *faraday*.

Electrochemical Equivalent

The mass of a substance which is liberated by one coulomb is called its *electrochemical equivalent*. It is expressed in kilogrammes per coulomb (kg C⁻¹) in SI units. If *z* is the electrochemical equivalent of a substance, the mass of it in kilogrammes liberated by *I* amperes in *t* seconds is

$$m = zIt. \tag{1}$$

Since the chemical equivalent of hydrogen is 1.008 then 1.008 g of hydrogen is liberated by 96500 coulombs, and the electrochemical equivalent of hydrogen is

$$z_{\text{H}} = \frac{1.008}{96,500} = 10.5 \times 10^{-5} \text{ g C}^{-1} = 1.05 \times 10^{-8} \text{ kg C}^{-1}$$

And similarly, since the chemical equivalent of copper is 31.8, its electrochemical equivalent is

$$z_{\text{Cu}} = \frac{31.8}{96,500} = 3.29 \times 10^{-4} \text{ g C}^{-1} = 3.29 \times 10^{-7} \text{ kg C}^{-1}$$

Measurement of Current by Electrolysis

In the past, the chemical effect of the current was used to define the ampere, because measurements with the current balance (p. 940) could not be made as accurately as simple weighings. Nowadays they can, and the ampere is defined as on p. 939. In those days the ampere was defined as the current which, when flowing steadily, would deposit 0.001118 g of silver per second.

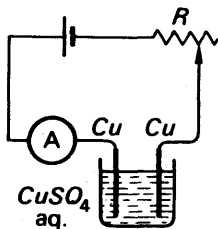


FIG. 34.3.
Current measurement
by chemical effect.

In the absence of a standard ammeter, the chemical effect can be used to find the error in a particular reading on an ammeter A (Fig. 34.3). A copper voltameter is connected in series with the ammeter, and a steady current passed for a known time t . The current is kept constant by adjusting the rheostat R to keep the deflection constant. The cathode is weighed before and after the experiment. Its increase in mass, m , gives the current I , in terms of the

electrochemical equivalent of copper, z :

$$m = zIt,$$

$$I = \frac{m}{zt}. \quad (2)$$

The error in the ammeter is then the difference in the reading on A and the current calculated from (2).

Great care must be taken in this experiment over the cleanliness of the electrodes. They must be cleaned with sandpaper at the start; and, at the finish, the cathode must be rinsed with water and dried with alcohol, or over a gentle spirit flame: strong heating will oxidize the copper deposit.

The Mechanism of Conduction; Ions

The theory of electrolytic conduction is generally attributed to Arrhenius (1859–1927), although Faraday had stated some of its essentials in 1834. Faraday suggested that the current through an electrolyte was carried by charged particles, which he called ions (Greek

ion = go). A solution of silver nitrate, he supposed, contained silver ions and 'nitrate' ions. The silver ions were silver atoms with a positive charge; they were positive because silver was deposited at the cathode, or negative electrode (Fig. 34.4). The nitrate ions were groups of

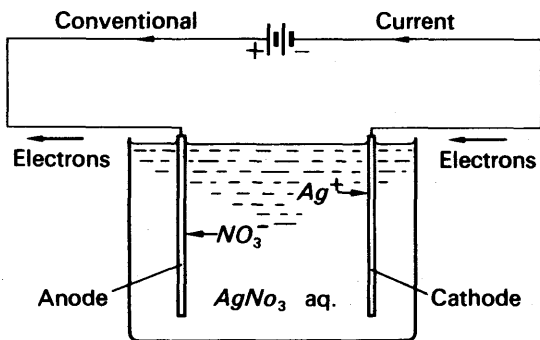


FIG. 34.4. Ions in electrolysis.

atoms—NO₃ groups—with a negative charge; they travelled towards the anode, or positive electrode, and, when silver electrodes are used, formed silver nitrate.

Nowadays, we consider that a silver ion is a silver atom which has lost an electron; this electron transfers itself to the NO₃ group when the silver nitrate molecule is formed, and gives the nitrate ion its negative charge. We denote nitrate and silver ions, respectively, by the symbols NO₃⁻ and Ag⁺. When the ions appear at the electrodes of a voltameter they are discharged. The current in the external circuit brings electrons to the cathode, and takes them away from the anode (Fig. 34.4). At the anode silver atoms lose electrons and go into solution as positive ions. *In effect*, the negative charges carried across the cell by the NO₃⁻ ions flow away through the external circuit. At the cathode, each silver ion gains an electron, and becomes a silver atom, which is deposited upon the electrode.

Ionization

The splitting up of a compound into ions in solution is called ionization, or ionic dissociation. Faraday does not seem to have paid much attention to how it took place, and the theory of it was given by Arrhenius in 1887. For a reason which we will consider later, Arrhenius suggested that an electrolyte ionized as soon as it was dissolved: that its ions were not produced by the current through it, but were present as such in the solution, before ever the current was passed.

We now consider that salts of strong bases and acids, such as silver nitrate, copper sulphate, sodium chloride, ionize completely as soon as they are dissolved in water. That is to say, a solution contains no molecules of these salts, but only their ions. Such salts are called strong electrolytes; so are the acids and bases from which they are formed, for these also ionize completely when dissolved in water.

Other salts, such as sodium carbonate, do not appear to ionize completely on solution in water. They are the salts of weak acids, and are called weak electrolytes. The weak acids themselves are also incompletely ionized in water.

Formation of Ions; Mechanism of Ionization

In the Heat section of this book we described the structure of the solid state (p. 294). In solid crystalline salts such as sodium chloride the structure is made up of sodium and chlorine ions: not of atoms, nor of NaCl molecules, but of Na^+ and Cl^- ions. In other words, we think today that ions exist in solid crystalline salts, as well as in their solutions. We do so for the reason that the idea enables us to build up a consistent theory of chemical combination, of the solid state, and of electrolytic dissociation.

A sodium atom contains eleven electrons, ten of which move in orbits close to the nucleus, and one of which ranges much more widely; for our present purposes we may represent it as in Fig. 34.5 (i). A chlorine atom has ten inner electrons and seven outer ones; for our present purposes we may lump these into two groups, as in Fig. 34.5 (ii). The outer electron of the sodium atom is weakly attracted to its nucleus, but the outer electrons of the chlorine atom are strongly attracted (because the ten inner electrons are a more effective shield round the +11 nucleus of sodium than round the +17 nucleus of chlorine). Therefore, when a sodium and a chlorine atom approach one another, the outer electron of the sodium atom is attracted more strongly by the chlorine nucleus than by the sodium nucleus. It leaves the sodium atom, and joins the outer electrons of

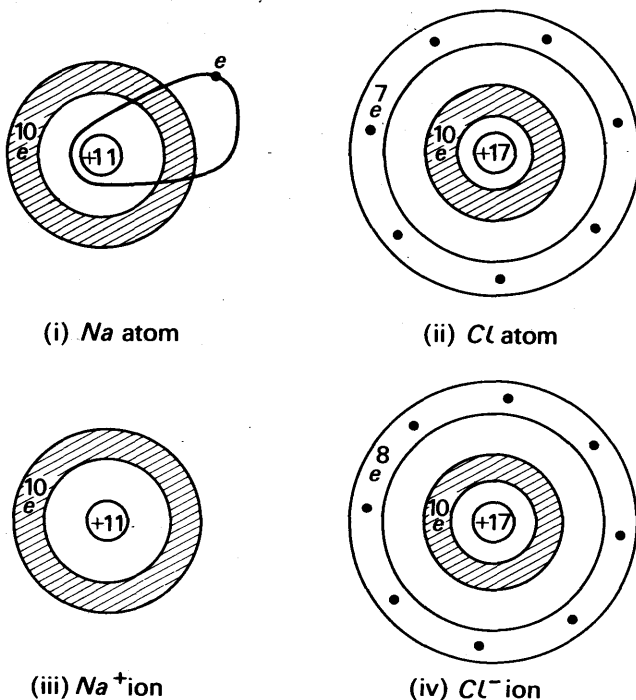


FIG. 34.5. Sodium and chlorine, atoms and ions.

the chlorine; the sodium atom becomes a positively charged sodium ion, Fig. 34.5 (iii), and the chlorine atom a negatively charged chlorine ion, Fig. 34.5 (iv). Between these two ions there now appears a strong electrostatic attraction, which holds them together as a molecule of NaCl. In the solid state, the ions are arranged alternately positive and negative; the forces between them bind the whole into a rigid crystal.

When such a crystal is dropped into water, it dissolves and ionizes. We can readily understand this when we remember that water has a very high dielectric constant: 81 (p. 774). It therefore reduces the forces between the ions 81 times, and the crystal falls apart into ions. In the same way we explain the ionization of other salts, and bases and acids. The idea that these dissociate because they are held together by electrostatic forces, which the solvent weakens, is supported by the fact that they ionize in some other solvents as well as water. These solvents also are liquids which have a high dielectric constant, such as methyl and ethyl alcohols (32 and 26 respectively). In these liquids, however, it seems that strong electrolytes behave as weak ones do in water: only a fraction of the dissolved molecules, not all of them, dissociate. In the electronic theory of atomic structure, the chemical behaviour of an element is determined by the number of its outer electrons. If it can readily lose one or two it is metallic, and forms positive ions; if it can readily gain one or two, it is acidic, and forms negative ions. Ions are not chemically active in the way that atoms are. Sodium atoms, in the form of a lump of the metal, react violently with water; but the hydroxide which they form ionizes ($\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$), and the sodium ions drift peaceably about in the solution—which is still mainly water.

Pure water is a feeble conductor of electricity, and we consider that it is but feebly ionized into H^+ and OH^- ions. These, we believe, are continually joining up to form water molecules, and then dissociating again in a dynamical equilibrium:



If, as we shall find in the electrolysis of water, H^+ and OH^- ions are removed from water, then more molecules dissociate, to restore the equilibrium.

The concentrations of H^+ and OH^- in water are so small that they do not contribute appreciably to the conduction of electricity when an electrolyte is dissolved in the water; but, as we shall see, they sometimes take part in reactions at the electrodes.

Explanation of Faraday's Laws

The theory of dissociation neatly explains Faraday's laws and some other phenomena of electrolysis. If an AgNO_3 molecule splits up into Ag^+ and NO_3^- ions, then each NO_3^- ion that reaches the anode dissolves one silver atom off it. At the same time, one silver atom is deposited on the cathode. Thus the gain in mass of the cathode is equal to the loss in mass of the anode. Also the total mass of silver nitrate in solution is unchanged; experiment shows that this is true. The mass of silver deposited is proportional to the number of ions reaching the cathode; if all the ions carry the same charge—a reasonable assumption—then the number deposited is proportional to the quantity of charge which deposits them. This is Faraday's first law.

To see how the ionic theory explains Faraday's second law, let us again consider a number of voltmeters in series (Fig. 34.6). When a

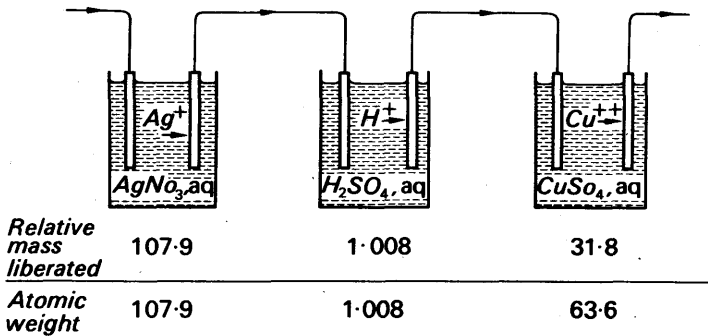


FIG. 34.6. Illustrating Faraday's second law.

current flows through them all, the same quantity of charge passes through each in a given time. Experiment shows that

$$\frac{\text{mass of silver deposited}}{\text{mass of hydrogen liberated}} = 107.0.$$

From experiments on chemical combination, we know that

$$\frac{\text{mass of silver atom}}{\text{mass of hydrogen atom}} = \frac{107.9}{1.008} = 107.0.$$

Therefore we may say that, each time a silver ion is discharged and deposited as an atom, a hydrogen ion is also discharged and becomes an atom. The hydrogen atoms thus formed join up in pairs, and escape as molecules of hydrogen gas. The theory fits the facts, on the simple assumption that the hydrogen and silver atoms carry equal charges: we now say that each is an atom which has lost one electron.

But when we consider the copper voltameter in Fig. 34.6, we find a complication. For

$$\frac{\text{mass of copper deposited}}{\text{mass of hydrogen liberated}} = \frac{31.8}{1.008}$$

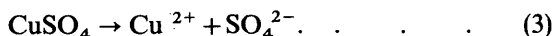
whereas

$$\frac{\text{mass of copper atom}}{\text{mass of hydrogen atom}} = \frac{63.6}{1.008}$$

To explain this result we must suppose that only one copper atom is deposited for every two hydrogen atoms liberated. In terms of the ionic theory, therefore, only one copper ion is discharged for every two hydrogen ions. It follows that a copper ion must have twice as great a charge as a hydrogen ion: it must be an atom which has lost two electrons.

This conclusion fits in with our knowledge of the chemistry of copper. One atom of copper can replace two of hydrogen, as it does, for example, in the formation of copper sulphate, CuSO_4 , from sulphuric acid, H_2SO_4 . We therefore suppose that the sulphate ion also is doubly charged: SO_4^{2-} . When sulphuric acid is formed, two hydrogen atoms

each lose an electron, and the SO_4 group gains two. When copper sulphate is formed, each copper atom gives up two electrons to an SO_4 group. And when copper sulphate ionizes, each molecule splits into two doubly charged ions:



In general, if we express the charge on an ion in units of the electronic charge, we find that it is equal to the valency of the atom from which the ion was formed. That is to say, it is equal to the number of hydrogen atoms which the atom can combine with or replace.

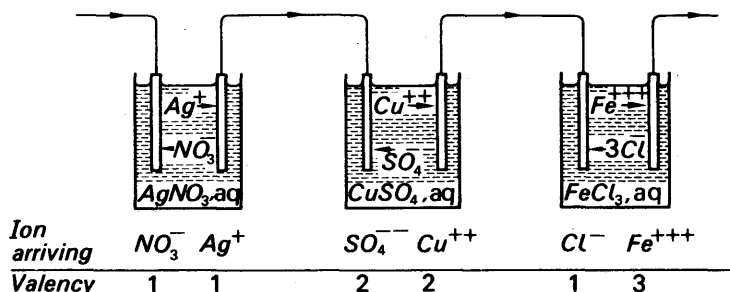


FIG. 34.7. Movement of ions in electrolysis.

This assertion, which is illustrated in Fig. 34.7, explains Faraday's second law (mass deposited \propto chemical equivalent). For if a current I passes through a voltameter for a time t , the total charge carried through it is It . And if q is the charge on an ion, the number of ions liberated is It/q . If M is the mass of an ion, the mass liberated is $M(It/q)$, and is therefore proportional to M/q . But M is virtually equal to the relative atomic mass, since the mass of an electron is negligible. And q , we have just seen, is equal, in electronic units, to the valency. Therefore the mass liberated is proportional to the ratio of relative atomic mass to valency. See also p. 845.

Electrolysis of Copper Sulphate Solution

If copper sulphate solution is electrolysed with platinum or carbon electrodes, copper is deposited on the cathode, but the anode is not dissolved away: instead, oxygen is evolved from it (Fig. 34.8). The SO_4^{2-} ions which approach the anode do not attack it; neither carbon nor platinum forms a sulphate, and each is said to be insoluble, in the electrolysis of copper sulphate. As the electrolysis proceeds, the solution becomes paler in colour; chemical tests show that it is gradually losing copper sulphate, but gaining sulphuric acid— Cu^{2+} ions are disappearing from the solution, but the SO_4^{2-} are remaining in it.

The oxygen which is evolved comes from the water of the solution. We have already seen that water is always slightly ionized, into H^+ and OH^- ions. When copper sulphate is electrolyzed with platinum or

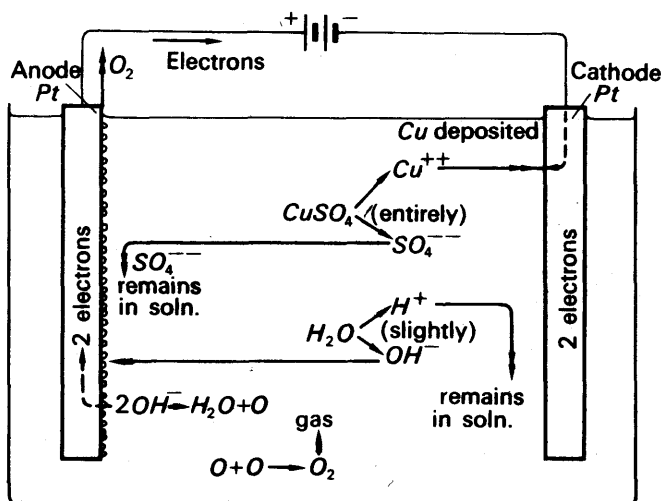
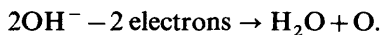
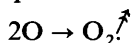


FIG. 34.8. Electrolysis of copper sulphate with insoluble electrodes.

carbon electrodes, the OH^- ions of the water are discharged at the anode. Each gives up an electron; they then combine in pairs to give a water molecule and an oxygen atom:



The oxygen atoms combine in pairs and come off as molecules:



As the OH^- ions disappear, an excess of H^+ ions appear in the solution. If the electrolysis were carried to the point where all the copper originally in the solution was deposited on the cathode, the solution would become simply one of sulphuric acid. This would be ionized into H^+ and SO_4^{2-} ions, in the proportion two H^+ to one SO_4^{2-} .

Electrolysis of Water

When a current is passed through water acidulated with dilute sulphuric acid, and platinum electrodes are used, oxygen and hydrogen are produced at the anode and cathode respectively. The amount of acid in solution remains unaltered, and the net effect is thus the electrolysis of water. The sulphuric acid ionizes into hydrogen and sulphate ions (Fig. 34.9):



The hydrogen ions from the acid greatly outnumber those from the water, but we cannot distinguish between them. All we can say is that, for every SO_4^{2-} ion that approaches the anode, two H^+ ions approach the cathode. At the cathode, the H^+ ions collect electrons, join up in pairs, and come off as molecules of hydrogen gas, H_2 . At the anode,

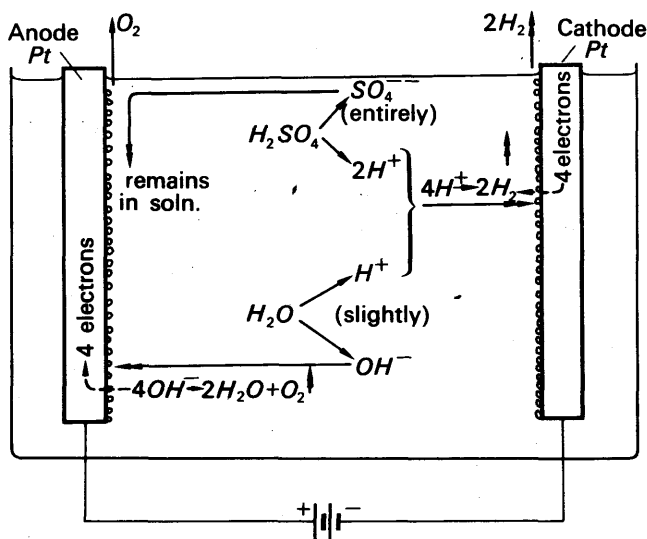


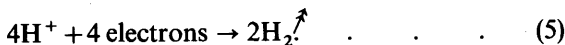
FIG. 34.9. Electrolysis of water.

however, the SO_4^{2-} ions remain in solution, and OH^- ions are discharged; as before, they form water and oxygen molecules, and the oxygen comes off as gas.

To produce one molecule of oxygen, four OH^- ions must be discharged:



And every time four OH^- ions are discharged at the anode, four H^+ ions are discharged at the cathode. (If this were not so, a net positive or negative charge would accumulate in the solution, and we could draw sparks from it.) Thus the reaction is accompanied by



Equations (4) and (5) agree with the experimental fact that hydrogen and oxygen come off in the proportions in which they are found in water: 2 to 1 by volume. This can be shown by collecting the gases in tubes filled with electrolyte and inverted over the electrodes (Fig. 34.1 (ii)). The electrolysis decomposes the water only, and leaves the acid unchanged. Equal numbers of H^+ and OH^- ions are discharged, and in the solution H^+ ions remain, in the proportion of two H^+ to one SO_4^{2-} .

The only function of the sulphuric acid is to increase the concentration of ions in the solution, and so to enable it to carry a greater current with a given potential difference than would pure water. The greater current discharges H^+ ions at a greater rate, and so causes the water to dissociate faster into H^+ and OH^- . Thus more ions are formed to carry the current.

The Electrolytic Capacitor

An electrolytic capacitor is one in which the dielectric is formed by electrolysis—by a secondary reaction at an insoluble electrode. It is made from two coaxial aluminium tubes, A and K in Fig. 34.10, with a solution or paste of ammonium borate between them. A current is passed through from A (anode) to K (cathode) and a secondary reaction at A liberates oxygen. The oxygen does not come off as a gas, however, but combines with the aluminium to form a layer of aluminium oxide over the electrode A. This layer is about $1/400$ cm thick, and is an insulator. When the layer has been formed, the whole system can be used as a capacitor, one of whose electrodes is the cylinder A, and the other the surface of the liquid or paste adjacent to A. Because the dielectric layer is so thin, the capacitance is much greater than that of a paper capacitor of the same size.

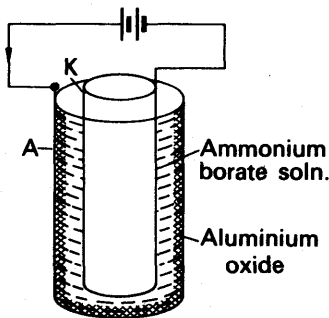


FIG. 34.10. Forming an electrolytic capacitor.

In the use of an electrolytic capacitor, some precautions must be taken. The voltage applied to it must not exceed a value determined by the thickness of the dielectric, and marked on the condenser; otherwise the layer of aluminium oxide will break down (see 'dielectric strength', p. 772). And the voltage must always be applied in the same sense as when the layer was being formed. If the plate A is made negative with respect to K, the oxide layer is rapidly dissolved away. Consequently an alternating voltage must never be applied to an electrolytic capacitor. This condition limits the usefulness of these capacitors.

Electrolytic capacitors are not very reliable, because the oxide layer is apt to break down with age. Domestic radio receivers abound in them, but in high-grade apparatus they are avoided.

Application of Ohm's Law to Electrolytes

Fig. 34.11 (i) shows how the current through an electrolyte, and the potential difference across it, may be measured. If the electrodes are soluble—copper in copper sulphate, for example—then the current is proportional to the potential difference (Fig. 34.11 (ii)). The best results in this experiment are obtained with very small currents. If the current is large, the solution becomes non-uniform: it becomes stronger near the anode, where copper is dissolved by the attack of the SO_4^{2-} ions, and weaker near the cathode, where copper is deposited, and SO_4^{2-} ions drift away. Near the cathode the solution becomes paler in colour; near the anode it becomes deeper. The total amount of copper sulphate in solution remains constant, but is gradually transferred to the neighbourhood of the anode. As the solution round the cathode becomes weaker, its resistance increases, and more than offsets the decreasing

resistance of the solution round the anode; with a given potential difference, therefore, the current gradually falls. A small current makes

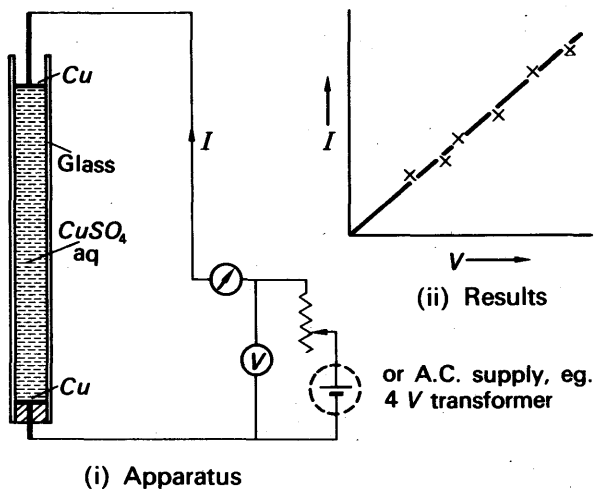


FIG. 34.11. Current/Voltage characteristic of electrolyte with soluble electrodes.

this effect unimportant, because it makes the electrolysis very slow. But the best way to do the experiment is to use an alternating current; the electrolysis reverses with the current fifty or more times per second, and no changes of concentration build up. Rectifier-type meters (p. 1011) are most suitable for measuring the current and potential difference in this case.

When the measurements are properly made they show, as we have said, that the current is proportional to the potential difference: for example, copper sulphate solution, with copper electrodes, obeys Ohm's law. The voltmeter behaves as a passive resistor; all the electrical energy delivered to it by the current appears as heat (pp. 791-2); no electrical energy is converted into mechanical or chemical work. In particular, therefore, no electrical energy is used to break up the molecules of copper sulphate into ions. This is the argument which led Arrhenius to suggest that the electrolyte dissociates into ions as soon as it is dissolved; dissociation is a result of solution, not of electrolysis.

Measurement of Resistance of Electrolyte

The resistance of an electrolyte can be measured on a Wheatstone bridge, preferably with an alternating current supply (Fig. 34.12). A telephone earpiece T is used as the detector, in place of the galvanometer—it gives minimum sound at the balance-point. 50 Hz mains

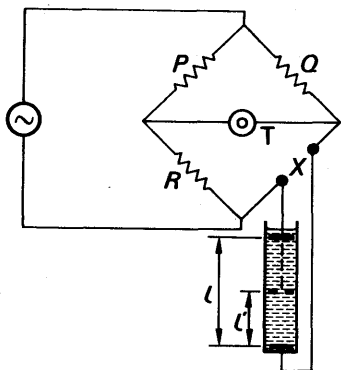


FIG. 34.12. Measurement of electrolyte resistance.

give an uncomfortably low-pitched note for listening, and a supply of frequency 400 to 1000 Hz is more satisfactory. This may be a small induction coil of a type sold for the purpose, which has fewer secondary turns than the common spark-coil, because a high voltage is not required. By sliding the upper electrode of the cell, the resistances of two lengths of electrolyte, l and l' are measured; their difference, r , is the resistance of a length $l-l'$, and is free from end-errors. If A is the cross-section of the tube, then the specific resistance of the electrolyte, ρ , is

given by

$$r = \frac{(l-l')\rho}{A}$$

It is usual, however, not to give the resistivity of an electrolyte, but to give instead its conductivity, σ . This is defined as the reciprocal of its resistivity, and is expressed in mho per centimetre:

$$\sigma = \frac{1}{\rho} = \frac{l-l'}{Ar}$$

Electrical Behaviour with Insoluble Electrodes

If we set out to find the current/voltage relationship for a water voltameter, using a d.c. supply, we find that the voltameter does not obey Ohm's law. If we apply to it a voltage E less than 1.7 volts, the current flows only for a short time and then stops, as though the voltameter were charged like a capacitor. To study the matter further, we may arrange a two-way key and a second galvanometer, G , as in Fig. 34.13. We first press the key at Y , and pass a current through the voltameter until it stops; then we press the key at X , and connect the galvanometer G straight across the voltameter. A brief current I

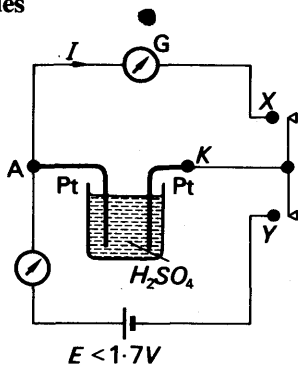
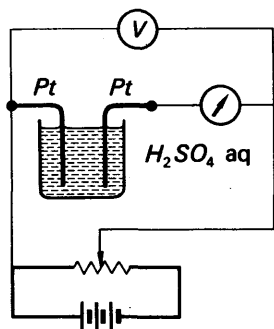


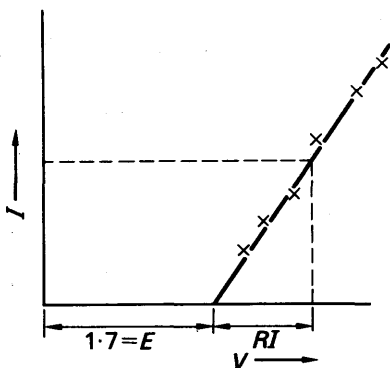
FIG. 34.13. Demonstrating back-e.m.f. of water voltameter.

flows through G , whose direction shows that the anode of the voltameter is acting as the positive pole of a current supply. It appears, therefore, that the voltameter is setting up a back-e.m.f. which prevents a steady current from flowing, unless the supply voltage is greater than 1.7 volts.

To investigate this behaviour further, let us gradually increase the potential difference across the voltmeter, as in Fig. 34.14 (i). We then



(i) Apparatus



(ii) Results

FIG. 34.14. Current/Voltage characteristic of water voltmeter.

find that, if we work with small currents, the current increases linearly with the potential difference V , when the latter is greater than 1.7 volts (Fig. 34.14 (ii)). It follows that the voltmeter does indeed exert a back-e.m.f., E , equal to 1.7 volts. If V is the potential difference applied to it, then the current through it obeys the relationship

$$I \propto (V - E).$$

We may write this as

$$I = \frac{V - E}{R},$$

where R is the resistance of the electrolyte.

Electrical Energy Consumed in Decomposition

We have not yet explained the origin of the back-e.m.f. E , but we shall try to do so later. Meanwhile let us notice that the behaviour of the voltmeter is somewhat like that of an electric motor. When the armature of a motor rotates, a back-e.m.f. is induced in it, and the current through it is given by an equation similar to that above. The back-e.m.f. in the motor, we shall see, represents the electrical power converted into mechanical work. So here the back-e.m.f. E represents this electrical power converted into chemical work—used in breaking up the water molecules. The potential difference across the voltmeter is

$$V = IR + E$$

from the equation for I ; the power equation is therefore

$$IV = I^2R + EI.$$

The left-hand term is the electrical power input; the first term on the right is the heat produced per second in the electrolyte; and the second term is the work done per second in decomposing the water.

Chemists tell us that when oxygen and hydrogen combine to form one mole of water (18 g) then 286 000 joules of heat are evolved. The energy set free is therefore 286 000 joules.

When one mole of water is decomposed, this much work must be done. In the process two moles of hydrogen are liberated (because the formula for water is H_2O). The quantity of electricity required to decompose one mole of water is therefore 2×96500 coulombs. If the back-e.m.f. is E , the corresponding amount of energy is $2 \times 96500 \times E$ joules. Therefore

$$2 \times 96500 \times E = 286\,000$$

whence

$$E = \frac{286\,000}{2 \times 96500}$$

$$= 1.48 \text{ volts.}$$

The lowest value of E which anyone has ever got by experiment is 1.67 volts—from which it appears that we have something yet to learn about what happens in a water voltameter.

CELLS

If we put plates of copper and zinc into a beaker of dilute sulphuric acid, we have a voltaic cell (p. 785). It is often called a simple cell. If we join its plates via a galvanometer, current flows through the galvanometer from the copper to the zinc (Fig. 34.15); the cell sets up an e.m.f. which acts, in the external circuit, from copper to zinc. Its value is about one volt. The copper plate is at a higher potential than the zinc plate, and is the positive terminal of the cell; the zinc is the negative terminal. Within the cell there must be some agency which

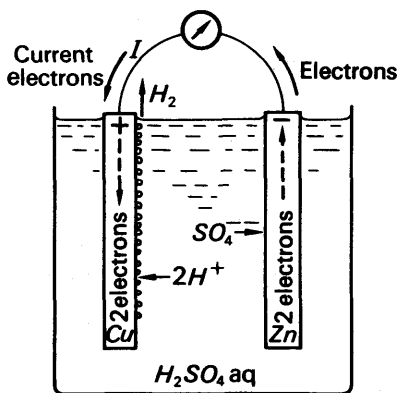


FIG. 34.15. A simple cell.

carries the current from the zinc to the copper. This is the agency which gives rise to the e.m.f. of the cell; it is analogous to the force exerted by the magnetic field on the moving electrons in the armature winding of a dynamo.

In a voltaic cell, the agency which gives rise to the e.m.f. is not so easy to track down as in a dynamo; there has been much argument about what is called the 'seat' of the e.m.f. We may start to seek it by placing a penknife blade into a strong solution of copper sulphate: a pink film of metallic copper is deposited on the blade. It appears, then, that copper ions have a tendency to go out of solution on to iron. In the same way we can show that they tend to go out on to zinc.

Do metal ions ever tend to go the other way—from solid metal into solution? They certainly do if the solution is sulphuric acid and the metal zinc or iron: the metal enters the solution in the form of ions, displaces the hydrogen ions, which are discharged and come off as gas, and turns the solution into one of iron or zinc sulphate. But this happens only if the zinc or iron is impure. Pure zinc in sulphuric acid gives no action at all—no zinc sulphate, no hydrogen.

Action in a Simple Cell

If we want to make pure zinc react with sulphuric acid, we must make it into part of a voltaic cell: we must connect it to a plate of a different metal, such as copper which also dips in the acid. Then the zinc is eaten away, and hydrogen bubbles off; but the hydrogen appears at the copper plate, and not at the zinc (Fig. 34.15). At the same time the solution becomes one of zinc sulphate—which simply means that it contains zinc ions in place of hydrogen ones. We can now form a picture of what happens when a stick of pure zinc is put alone into dilute sulphuric acid (Fig. 34.16). At first zinc ions leave the metal, and go into the liquid. But they leave negative charges on the zinc rod, which attract the zinc ions, and prevent any more from leaving. Nothing further happens. But if we introduce a plate of copper, and connect it to the zinc, electrons can flow from the zinc to the copper (Fig. 34.15). At the copper they can neutralize the charges on hydrogen ions, and to enable molecules to form and come off in bubbles. As the electrons flow away from the zinc, more zinc ions can go into solution, and so the zinc can continuously dissolve in the acid. In doing so, it maintains a continuous electric current in the wire connecting it to the copper. (When the zinc is impure each speck of impurity acts as the other plate of a minute cell, and enables the zinc around it to react with the acid. This 'local action', as it is called, makes impure zinc undesirable in voltaic cells, for it consumes the zinc without giving any useful current. It can be prevented by rubbing the zinc with mercury, which dissolves it and presents a surface of pure zinc to the acid. The process is called amalgamating the zinc.)

To explain the voltaic cell, therefore, we must suppose that zinc ions tend to dissolve

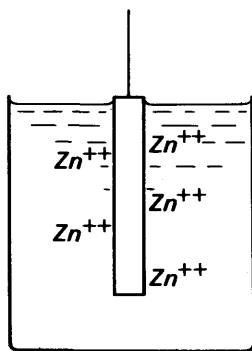


FIG. 34.16.
Pure zinc in dilute
sulphuric acid.

from zinc into sulphuric acid, but copper ions do not. This is consistent with the fact that copper does not react chemically with cold dilute sulphuric acid. The passage of ions from metals to solutions, and oppositely, was studied by Nernst about 1889; we shall give a slight account of his theory later.

Daniell's Cell

Fig 34.17 shows a cell, developed by Daniell about 1850, which has some advantages over Volta's. Daniell's cell consists of a zinc rod, Zn, in a porous pot, P, containing sulphuric acid; this in turn stands in a strong solution of copper sulphate in a copper vessel, Cu. (Sometimes the copper is just a thin sheet in a glass vessel.) When the copper and

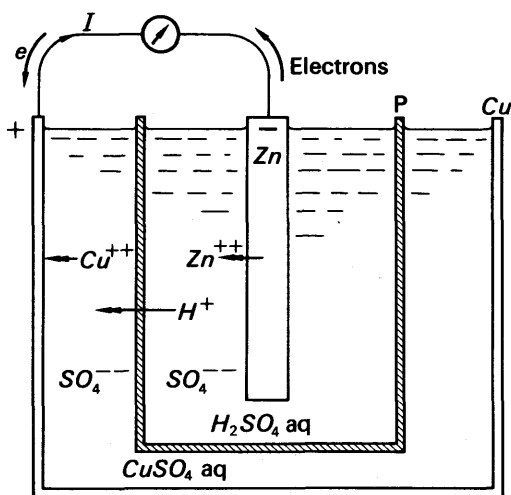


FIG. 34.17. A Daniell cell.

zinc are connected by a wire, current flows through the wire from copper to zinc. The copper is therefore the positive terminal of the cell, and the zinc the negative. As in Volta's cell, zinc ions go into solution at the zinc rod, leaving electrons on it. But at the copper plate, copper ions go out of solution—a metallic film of copper is deposited on the vessel. When the zinc and copper are joined by a wire, electrons from the zinc can go along it to the copper vessel, and discharge the copper ions as they reach it. To complete the action of the cell hydrogen ions from the sulphuric acid pass through the porous pot into the copper sulphate solution (Fig 34.17). Thus zinc is dissolved, the acid gradually changes to zinc sulphate, the copper sulphate gradually changes to sulphuric acid, and copper is deposited on the copper vessel.

The e.m.f. of a Daniell cell is about 1.08 volts. Its internal resistance depends on its size and condition—the size is usually about that of a plant-pot, and the internal resistance is of the order of several ohms.

Polarization

The great disadvantage of the simple cell is that it does not give a steady current; from the moment of making the circuit, the current starts to fall, and after a minute or two it almost ceases to flow. The current decays because a layer of hydrogen gas forms over the copper plate; scraping the plate enables the current to start once more, but it soon decays again. The hydrogen layer increases the internal resistance of the cell, but we do not believe that this is the main reason for the decay of the current. If the copper plate is replaced by one of platinum black (platinum with a finely grained surface), bubbles form on it very easily, and escape readily. The hydrogen layer may then be no more than one molecule thick; but the current decays as before.

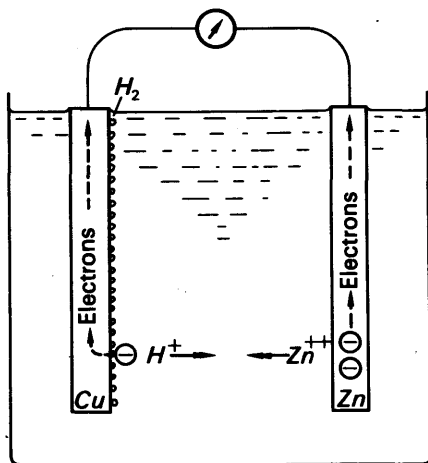


FIG. 34.18. Polarization in simple cell.

To explain this decay of the current we think that the hydrogen layer replaces the copper as an electrode of the cell. We suppose that the hydrogen tends to go back into solution as positive hydrogen ions (Fig. 34.18). In other words, it tends to behave in the same way as the zinc rod, on the other side of the cell, which also goes into solution as positive ions. Thus the hydrogen sets up an e.m.f. which opposes the original e.m.f. of the cell, and cuts down the current; the hydrogen thus sets up a 'back-e.m.f.' in the circuit. This behaviour is called polarization of the cell.

Depolarization

The advantage of Daniell's cell over Volta's is that it does not polarize. Hydrogen ions drift from the acid compartment into the copper sulphate compartment, but they are never discharged, no hydrogen molecules are formed, and no layer of hydrogen appears on the copper electrode. The copper sulphate solution is often called the depolarizer, because it prevents the formation of hydrogen gas.

Polarization in Water Voltameter

We can find support for the idea of polarization in the behaviour of the water voltameter (p. 856). When the potential difference across the voltameter is less than 1.7 volts, the current through it falls to zero in a minute or less. The voltameter itself can then deliver a current for a short time. Its positive terminal, as a source, is that which was its anode, and its negative terminal is that which was its cathode. While current was being sent through the voltameter, the cathode became covered with hydrogen, and the anode with oxygen. When the voltameter acts as a source of current it has, in effect, electrodes of oxygen and hydrogen and the current through the external circuit flows from the oxygen plate to the hydrogen (Fig. 34.19). In the simple cell, when it is polarized, there is no oxygen plate, but there is a hydrogen one, and this lies over the copper plate. We may therefore suppose

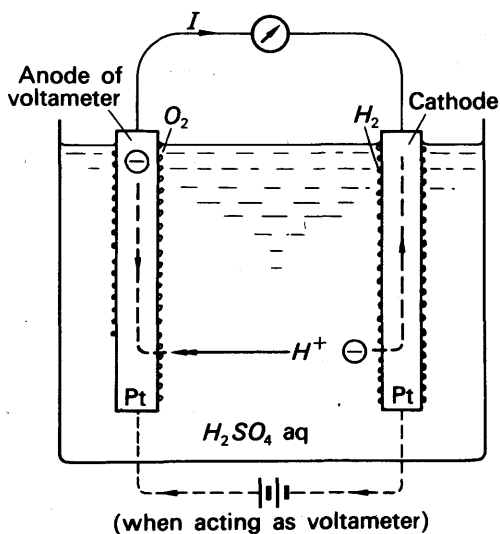


FIG. 34.19. Polarization of water voltameter.

that it tends to drive a current, through the external circuit, from zinc to copper; that is to say, it sets up an e.m.f. opposing that of the cell with the copper plate clean.

Nernst's Theory of the Voltaic cell; Electrode Potentials

If a metal is in contact with a solution of one of its own salts, it is surrounded by its own ions. Whether the ions deposit themselves on the metal, or the metal goes into solution, depends partly on the particular metal concerned, and partly on the strength of the solution: the stronger the solution the greater its tendency to deposit ions on the metal. If the solution deposits ions, the metal comes to a positive potential with respect to it; if the metal goes into solution as ions, it

becomes negative with respect to the solution (Fig. 34.20 (i)). By methods beyond the scope of this book, the potential difference between a metal and a solution can be measured. These show that copper in normal copper sulphate solution (1 g-equivalent weight per litre) becomes 0.08 volt positive with respect to the solution.

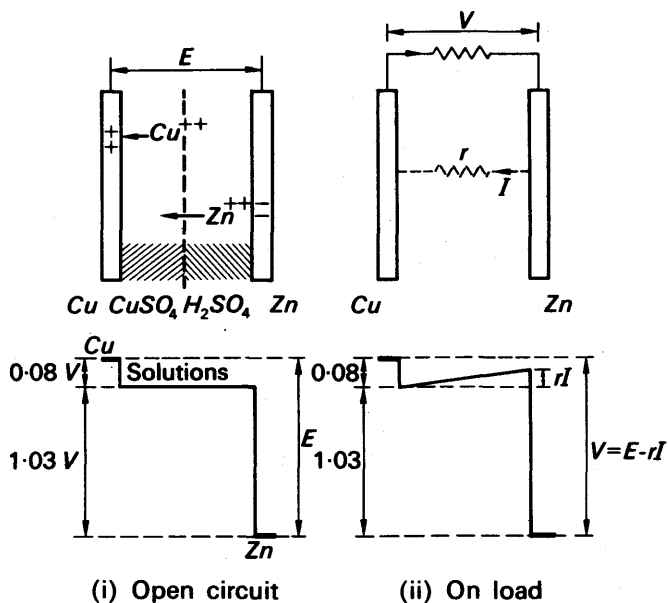


FIG. 34.20. Potential differences in voltaic cell.

Zinc in normal zinc sulphate solution becomes 1.03 volts negative. Now let us imagine a Daniell cell in which zinc sulphate replaces the sulphuric acid, and both solutions are normal. If we suppose that the solutions themselves set up no appreciable potential difference at their interface, then we get a potential distribution like that shown in Fig. 33.20 (i). The difference in potential between the copper and zinc is very nearly equal to the e.m.f. of a Daniell cell: 1.11 volts compared with 1.08. We may attribute the difference to the fact that a Daniell cell in practice has sulphuric acid, not zinc sulphate solution, in contact with the zinc; also the solutions are not normal: the acid is usually 1 to 4 of water, and the copper sulphate is saturated.

These considerations explain a striking experimental fact about all cells: the e.m.f. depends only on the nature and concentration of the constituent chemicals. The size of a cell affects only its internal resistance.

When a current I is drawn from a cell, there is a voltage drop across the internal resistance r , that is to say, across the solution or solutions. This modifies the potential diagram as shown in Fig. 34.20 (ii). The terminal voltage V , which is the observed potential difference between the copper and zinc, is now less than its open-circuit value, which is the e.m.f. of the cell.

The Leclanché Cell

Daniell's cell has the great practical disadvantage that it cannot be left set up; the solutions gradually mix by diffusion through the porous pot. It is now used only in teaching laboratories as a simple standard of e.m.f.; its e.m.f. is more nearly constant than that of any other

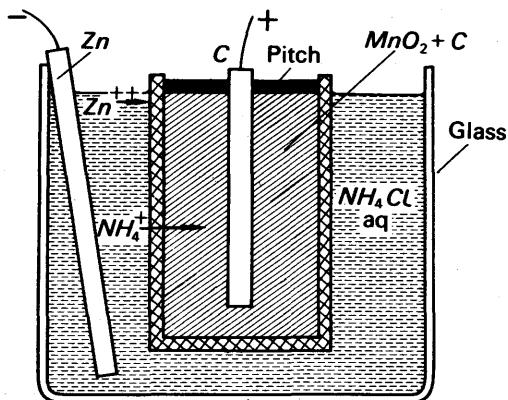


FIG. 34.21. Leclanché cell.

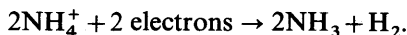
cheap and robust type of cell, and it is remarkably free from polarization.

A practically more useful cell is that devised by Leclanché. Its negative electrode is a zinc rod in a strong solution of ammonium chloride (Fig. 34.21). Its positive electrode is a carbon plate in a porous pot packed with manganese dioxide, which acts as the depolarizer. Manganese dioxide is a poor conductor of electricity, and powdered carbon is therefore packed in the pot with it.

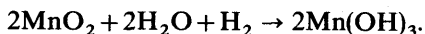
The ammonium chloride ionizes into ammonium ions and chlorine ions:



The zinc goes into solution, as zinc ions, and the ammonium ions drift through the porous pot towards the carbon plate. When a current is drawn from the cell, electrons flow from the zinc to the carbon, and discharge the NH_4^+ ions. The chemical action in this cell is complicated, but may be crudely represented as



The hydrogen tends to polarize the cell, but is gradually oxidized by the manganese dioxide; again the action is complicated, but it reduces to



The depolarizing action is slow, and a Leclanché cell is therefore not suitable for giving a large current for a long time. A short rest, however, enables the manganese dioxide to remove the hydrogen and restore

the e.m.f. of the cell. Thus Leclanché cells are suitable for giving intermittent currents: they are widely used, for example, with electric bells. They are also suitable for Wheatstone bridges, because they cannot give a current large enough to burn out the resistance coils when a wrong connexion is made. The e.m.f. of a Leclanché cell, before polarization sets in, is about 1.5 volts, and its internal resistance about 1 ohm.

Dry Cell

Fig. 34.22 shows a dry form of Leclanché cell, which has the obvious advantage that it is portable. The ammonium chloride is made into a paste with water, zinc chloride, flour, and gum; and the porous pot is replaced by a muslin bag. A cardboard spacer prevents the bag from touching the zinc and short-circuiting the cell. A dry Leclanché cell has the same e.m.f. as a wet one, but, for a given size, a lower internal resistance, because the thickness of solution between the zinc and carbon is less. It depolarizes better, because the volume of manganese dioxide is greater in relation to the overall size of the cell: the cycle-lamp size will give a useful light continuously for two hours or more.

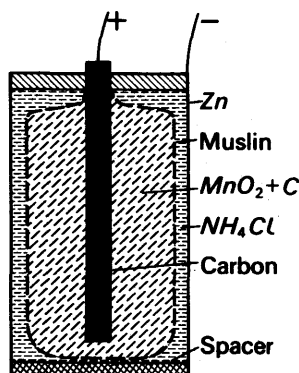


FIG. 34.22. A dry cell.

Standard Cells

A standard cell is one whose e.m.f. varies very little with time, and with temperature, so that it can be used as a standard of potential difference in potentiometer experiments. The commonest type is the Weston cadmium cell (Fig. 34.23). It is housed in an H-shaped glass

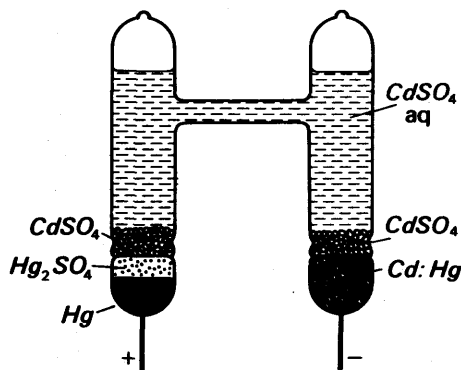


FIG. 34.23. A Weston cadmium cell.

tube because its electrodes are liquid or semi-liquid. The negative electrode is an amalgam of cadmium in mercury; the solution is of cadmium sulphate; the depolarizer is a paste of mercurous sulphate; and the positive electrode is mercury. In some cells, crystals of cadmium sulphate are placed on top of the electrodes to keep the solution saturated. The e.m.f. of one of these, in volts at a temperature $t^{\circ}\text{C}$, is

$$E = 1.01830 - 0.0000406(t - 20) + 0.00000095(t - 20)^2 + 0.00000001(t - 20)^3.$$

The e.m.f. of the type without crystals is about 1.0186 volts between 0°C and 40°C .

A standard cell without crystals of cadmium sulphate is called an unsaturated cell; one with crystals is called a saturated cell, because the crystals keep the solution saturated. Saturated cells give an accurately reproducible e.m.f., because the concentration of the solution is sharply defined at any given temperature. Unsaturated cells do not agree among one another so well, because the solution may vary a little from one to the other. But the e.m.f. of a given unsaturated cell varies less with temperature than that of a saturated cell, because the concentration of the solution is constant.

The depolarizer of a standard cell is effective only for very small currents, and the e.m.f. of the cell will change appreciably if more than about 10 microamperes are drawn from it. *A standard cell must not, in any circumstances, be used as a source of current.* In the early stages of balancing a standard cell against a potentiometer wire, a protective resistance of about 100 000 ohms should be connected in series with the cell.

Primary and Secondary Cells

The cells which we have so far described are called primary cells. When they are run-down, their active materials must be renewed; the cells cannot be recharged by passing a current through them from another source. A secondary cell is one which can be recharged in this way.

SECONDARY CELLS

The Lead Accumulator

The commonest secondary cell is the lead-acid accumulator. Its active materials are spongy lead, Pb (for the negative plate), lead dioxide, PbO_2 (the for positive plate), and sulphuric acid. The active materials of the plates are supported in grids of hard lead-antimony alloy (Fig. 34.24 (i)). These are assembled in interchanging groups, closely spaced to give a low internal resistance, and often held apart by strips of wood or celluloid (Fig. 34.24 (ii)).

When the cell is discharging—giving a current—hydrogen ions drift to the positive plate, and SO_4^{2-} ions to the negative. As they give up their charges they attack the plates, and reduce the active materials of each to lead sulphate.

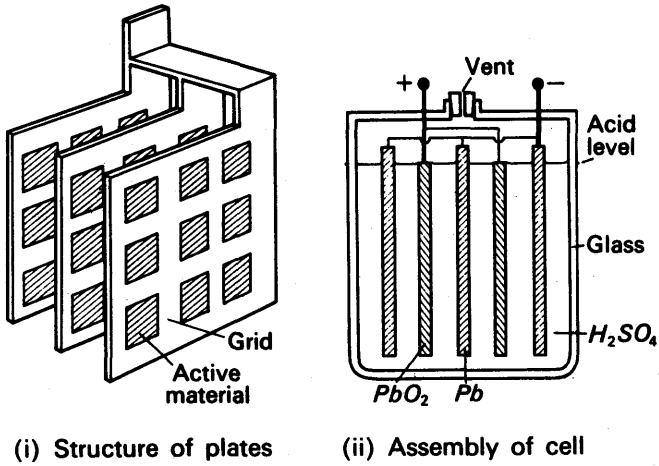
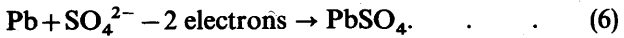
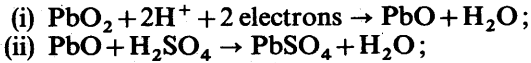


FIG. 34.24. Lead-acid accumulator.

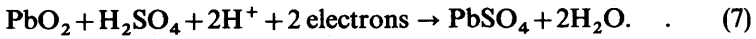
At the negative plate the reaction is



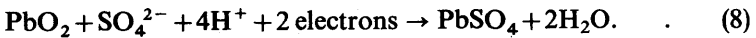
The chemical action at the positive plate is generally given as



whence, altogether



However, H₂SO₄ molecules do not exist in the solution—they are dissociated into 2H⁺ and SO₄⁻ ions. We may therefore write equation (7) as



The lead sulphate produced in these reactions is a soft form, which is chemically more active than the hard, insoluble lead sulphate familiar in the general chemistry of lead. In the discharging reactions water is formed and sulphuric acid consumed: the concentration of the acid, and therefore its specific gravity, fall.

Charging the Accumulator

When the cell is to be charged it is connected, in opposition, to a supply of greater e.m.f., via a rheostat and ammeter (Fig. 34.25). The

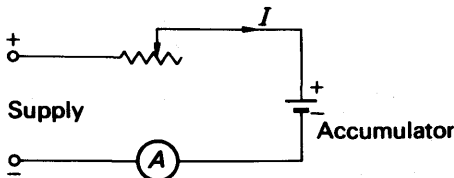
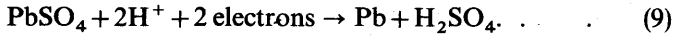


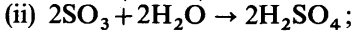
FIG. 34.25 Charging an accumulator.

supply forces a current I through the cell in the opposite direction to the discharging current, so that hydrogen ions are carried to the negative plate, and SO_4^{2-} ions to the positive. The chemical reactions are as follows.

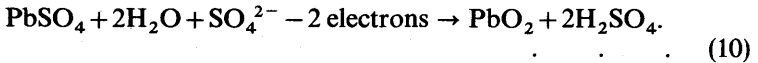
At the negative plate:



At the positive plate:



altogether:



The active materials are converted back to lead and lead dioxide, water is consumed, and sulphuric acid is formed. The acid therefore becomes more concentrated during charge, and its specific gravity rises.

Properties and Care of the Lead Accumulator

The e.m.f. of a freshly charged lead accumulator is about 2.2 volts, and the specific gravity of the acid about 1.25. When the cell is being discharged its e.m.f. falls rapidly to about 2 volts, and then becomes steady (Fig. 34.26); but towards the end of the discharge the e.m.f. begins to fall again. When the terminal voltage load has dropped below about 1.9 volts, or the specific gravity of the acid below about 1.15, the cell should be recharged. If the cell is discharged too far, or left in a discharged condition, hard lead sulphate forms on its plates, and it becomes useless.

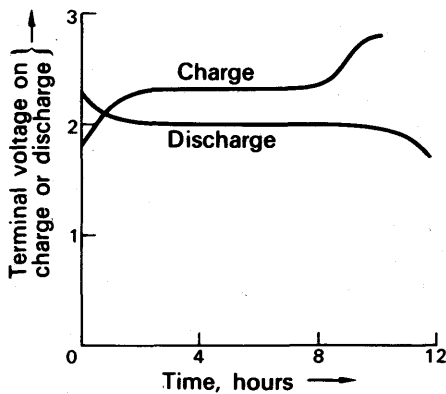


FIG. 34.26. Voltage-time curves of lead accumulator.

The internal resistance of a lead accumulator, like that of any other cell, depends on the area and spacing of its plates. It is much lower

than that of any primary cell, however, being usually of the order of 1/10 to 1/100 ohm. The amount of electricity which an accumulator can store is called its *capacity*. It is a vague quantity, but a particular accumulator may give, for example, 4 amperes for 20 hours before needing a recharge. The capacity of this accumulator would be 80 ampere-hours. (One ampere-hour = 3600 coulombs.) If the accumulator were discharged faster—at 8 amperes, say—then it would probably need recharging after rather less than 10 hours; and if it were discharged more slowly—say at 2 amperes—it might hold out for more than 40 hours. The capacity of an accumulator therefore depends on its rate of discharge; it is usually specified at the '10-hour' or '20-hour' rate. Discharging an accumulator faster than at about the 10-hour rate causes the active material to fall out of the plates.

Accumulators are usually charged at about the '8-hour' rate—say 5 amperes for the cell discussed above. The charging is continued until gas is bubbling freely off the plates. When the plates are gassing, the chemical reactions (9) and (10) have been completed, and the current through the cell is simply decomposing the water in it. Before the charge is started the vent-plugs in the cell-case must be removed to let the gases out; the gases are hydrogen and oxygen and naked lights near are dangerous. The water lost at the end of each charge must be made up by pouring in distilled water until the acid rises to the level marked on the case. If the specific gravity of the acid is then less than 1.25, the charging must be continued. Near the end of the charging, the back-e.m.f. of the cell rises sharply to about 2.6 volts (Fig. 34.26). It never gives a forward e.m.f. as great as this: as soon as it is put on discharge, its e.m.f. falls to about 2.2 volts.

Efficiency of Accumulator

The number of ampere-hours put into an accumulator on charge is greater than the number which can be got out of it without discharging it too far. The ratio

$$\frac{\text{ampere-hours on discharge}}{\text{ampere-hours on charge}}$$

is called the ampere-hour efficiency of the cell; its value is commonly about 90 per cent. However, to judge an accumulator by its ampere-hour efficiency is to flatter it; not only does it take in more ampere-hours on charge than it gives out on discharge, but it takes them in at a higher voltage. The electrical energy put into an accumulator on charge is the integral of current, e.m.f., and time:

$$W = \int I E dt.$$

For simplicity we may say

$$\begin{aligned} \text{energy put in} &= \text{quantity of electricity put in} \\ &\quad \times \text{average e.m.f. on charge.} \end{aligned}$$

If the quantity of electricity is measured in ampere-hours, the energy is in watt-hours instead of joules. Similarly, on discharge,

$$\text{energy given out} = \text{quantity of electricity given out} \\ \times \text{average e.m.f. on discharge.}$$

The energy efficiency of the cell is

$$\frac{\text{energy given out on discharge}}{\text{energy taken in on charge}} \\ = \frac{\text{amp-hours} \times \text{average e.m.f. on discharge}}{\text{amp-hours} \times \text{average e.m.f. on charge}} \\ = \text{amp-hour efficiency} \times \frac{\text{average e.m.f. on discharge}}{\text{average e.m.f. on charge}} \\ \approx \text{amp-hour efficiency} \times \frac{2.0}{2.2}.$$

The energy efficiency is more often called the watt-hour efficiency of the cell; it is about 80 per cent.

The Nickel-iron Accumulator

The nickel-iron (NIFE) accumulator has active materials of nickel hydroxide (positive), iron (negative) and caustic potash solution. Its e.m.f. varies from 1.3 volt to 1.0 on discharge; it has a higher internal resistance than a lead accumulator of similar size; and it is less efficient. Its advantages are that it is more rugged, both mechanically and electrically. Very rapid charging and discharging do not harm it, nor do overdischarging and overcharging. Vibration does not make the active materials fall out of the plates, as it does with a lead cell. Nickel-iron accumulators are therefore used in electric trucks and at sea.

EXAMPLES

1. A copper refining cell consists of two parallel copper plate electrodes, 6 cm apart and 1 metre square, immersed in a copper sulphate solution of resistivity 1.2×10^{-2} ohm metre. Calculate the potential difference which must be established between the plates to provide a constant current to deposit 480 g of copper on the cathode in one hour (e.c.e. of copper = 3.29×10^{-7} kg C^{-1}).

From $m = zIt$, since 480 g = 0.48 kg,

$$I = \frac{m}{zt} = \frac{0.48}{3.29 \times 10^{-7} \times 3600} \text{ A} \quad \dots \dots \dots (i)$$

$$\text{The resistance of the cell, } R, = \frac{\rho l}{A} \\ = \frac{1.2 \times 10^{-2} \times 6 \times 10^{-2}}{1^2}$$

$$\text{Hence, from (i), the p.d. } V = IR = \frac{0.48 \times 1.2 \times 10^{-2} \times 6 \times 10^{-2}}{3.29 \times 10^{-7} \times 3600 \times 1^2} \\ = 0.3 \text{ V (approx.).}$$

2. State Faraday's laws of electrolysis and show that the ionic dissociation theory offers an explanation of them. Acidulated water is electrolyzed between platinum electrodes. Sketch a graph showing the relation between the strength of the current and the reading of a voltmeter connected to the electrodes. Comment on the nature of the graph.

Give a circuit diagram showing how you would charge a series battery of 12 lead accumulators, each of e.m.f. 2 volts and internal resistance $1/24$ ohm, from 240-volt d.c. mains, if the charging current is not to exceed 3 amp. What percentage of the energy taken from the mains would be wasted? (L.)

First part (see text). When the water is electrolyzed, no current flows until the p.d. is greater than about 1.7 volts, when the back-e.m.f. of the liberated product is overcome. After this, a straight-line graph is obtained between V and I .

Second part. A series resistance R is required, given by

$$I = 3 = \frac{240 - 12 \times 2}{R + \frac{12}{24}}$$

$$\therefore 3R + 1.5 = 216.$$

$$\therefore R = \frac{214.5}{3} = 71.5 \text{ ohms.}$$

Energy taken from mains = $EIt = 240 \times 3t = 720t$, where t is the time.

$$\begin{aligned} \text{Energy wasted} &= (I^2R + I^2r)t = (3^2 \times 71.5 + 3^2 \times 0.5)t \\ &= 648t. \end{aligned}$$

$$\therefore \text{percentage wasted} = \frac{648t}{720t} \times 100\% = 90\%.$$

3. State Faraday's laws of electrolysis. How would you verify the laws experimentally? Discuss briefly the phenomenon of polarization in electrolysis and how it is overcome in the Daniell cell.

Calculate a value for the e.m.f. of a Daniell cell from energy considerations, using the following data: 1 g of zinc dissolved in copper sulphate solution liberates 3327 J (e.c.e. of zinc = $0.000340 \text{ g C}^{-1}$). (L.)

The e.m.f. E of a cell can be defined as the energy per coulomb delivered by the cell (p. 797).

When 1 g of zinc is dissolved, number of coulombs flowing, $Q = \frac{1}{0.00034}$

Energy liberated, $W = 3327 \text{ J}$.

$$\begin{aligned} \therefore \text{energy liberated per coulomb} &= \frac{W}{Q} \\ &= 3327 \times 0.00034 \text{ joules/coulomb} \\ &= 1.13 \text{ volts.} \end{aligned}$$

EXERCISES 34

1. State Faraday's laws of electrolysis and show how they can be interpreted in terms of the ionic theory.

A voltameter with large platinum plates contains dilute sulphuric acid in which 10^{-2} g of metallic copper has been dissolved. A constant current of 10^{-2} amp is then passed through the solution for 25 minutes. Calculate (a) the mass of copper deposited on the cathode, (b) the volume of oxygen liberated at the anode if the pressure is 750 mm Hg and the temperature is 20°C and (c) the additional time for which the same current must be passed before hydrogen is liberated at the cathode. (The chemical equivalents of copper and oxygen are 31.8 and 8

respectively; the Faraday is 95600 coulombs; 32 g of oxygen occupy 22.4 litres at S.T.P.) (O. & C.)

2. Describe the electrolytic processes which occur in a Daniell cell when its terminals are joined through a small resistance.

A steady current of 5 A is passed through a silver voltameter in series with a coil of wire of 10 ohms resistance immersed in 200 g of water. What will be the rise of temperature of the latter when 0.10 g of silver has been deposited? (Assume that the e.c.e. of silver = 1.118×10^{-6} kg C⁻¹; thermal capacity of the coil and vessel = 42 J K⁻¹.) (L.)

3. State Faraday's laws of electrolysis. Explain why it is necessary to have a potential greater than about 1.5 volts in order to maintain a large steady current through acidulated water.

In the electrolysis of water 83.7 cm³ of hydrogen were collected at a pressure of 68 cm of mercury at 25°C when a current of 0.5 A had been passed for 20 minutes. What is the electrochemical equivalent of copper in copper sulphate (CuSO₄)? (Atomic weight of copper = 63.57, atomic weight of hydrogen = 1.008, density of hydrogen at S.T.P. = 0.08987 kg m⁻³.) (L.)

4. What do you understand by (a) a *cathode*, and (b) an *ion*? Describe how the simple ionic theory accounts for the fact that the liberation of 1 g of hydrogen in the electrolysis of dilute sulphuric acid, using platinum electrodes, always requires the passage of a definite quantity of charge.

If the heat produced when 1 g of hydrogen burns to form water is 1.44×10^5 joules, calculate the minimum e.m.f. which must be applied in such electrolysis before a continuous current will flow. Justify and explain your calculation by reference to the principle of conservation of energy. (1 Faraday = 9.65×10^4 coulombs.)

Describe an experiment to determine the actual value of the back e.m.f. generated by a gas at the electrodes in such electrolysis. (C.)

5. State (a) Faraday's laws of electrolysis, (b) the main features of the theory of ionic dissociation, showing that the theory is in accordance with these laws.

A potential difference of 14 volts is applied to a water voltameter whose total thermal capacity is 2121 J K⁻¹. The temperature of the voltameter rises 1°C in the time taken to liberate 20 cm³ of hydrogen at S.T.P. Calculate the back e.m.f. of the voltameter and state the source of this e.m.f. (Assume the electrochemical equivalent of hydrogen to be 1.044×10^{-8} kg C⁻¹ and its density at S.T.P. to be 9×10^{-2} kg m⁻³.) (L.)

6. To answer this question you are asked to assume that no galvanometer of any kind is available and that you cannot take for granted that the same current flows continuously round a series circuit.

A circuit consists only of a straight horizontal length of wire and a copper voltmeter connected in series to a suitable d.c. supply. How would you show that a current is flowing through the wire as well as through the voltmeter?

How would you show that the direction of the current through the wire is the same as that of the current through the voltmeter?

Outline the measurements you would make to discover whether the strength of the current in the wire is the same as that of the current through the voltmeter.

Give an account of the actual physical processes by which a current passes through a metal wire. Explain briefly why the resistance normally increases as the temperature rises. (O.)

7. Explain the general nature of the chemical changes that take place in a lead accumulator during charging and discharging.

A battery of accumulators, of e.m.f. 50 volts and internal resistance 2 ohms, is charged on a 100-volt direct-current mains. What series resistance will be required to give a charging current of 2 A? If the price of electrical energy is 1d. per kilowatt-hour, what will it cost to charge the battery for 8 hours, and what percentage of the energy supplied will be wasted in the form of heat? (C.)

8. State the laws of electrolysis and give a concise account of an elementary theory of electrolysis which is consistent with the laws.

If an electric current passes through a copper voltameter and a water voltameter in series, calculate the volume of hydrogen which will be liberated in the latter, at 25°C and 78 cm of mercury pressure, whilst 0.05 g of copper is deposited in the former. (Take e.c.e. of hydrogen as 1.04×10^{-8} kg C⁻¹, e.c.e. of copper as 3.3×10^{-7} kg C⁻¹, density of hydrogen as 9×10^{-2} kg m⁻³ at S.T.P.) (L.)

9. State Faraday's laws of electrolysis and describe experiments to verify them.

A difference of potential of 60 volts is maintained between two electrodes 12 cm apart in a solution of common salt. How long will it take a chlorine ion to travel 3 cm in the solution? (The mobility of chlorine ions may be taken as 0.00053 cm s⁻¹ per V cm⁻¹.) (L.)

10. Explain what happens when an e.m.f. is applied to platinum electrodes immersed in dilute sulphuric acid. What is the relation between the e.m.f. and the current in such a cell?

If the electrochemical equivalent of hydrogen is 1.04×10^{-8} kg coulomb⁻¹, and if 1 g of hydrogen on burning to form water liberates 147000 joules, calculate the back-e.m.f. produced in a water voltameter when it is connected to a 2-volt accumulator. (C.)