

CHAPTER 18 ELECTROCHEMISTRY

For a long time I have resisted writing a chapter on electrochemistry in these notes on electricity and magnetism. The reason for this, quite frankly, is that I am not a chemist, I know relatively little about the subject, and I am not really qualified to write on it. However, a set of notes on electricity and magnetism with no mention at all of this huge topic is not very satisfactory, so I should perhaps attempt a little. I shall do little, however, other than merely introduce and define some words.

We can perhaps think of two sorts of cell with rather opposite purposes. In an electrolytic cell, we pass an electric current through a conducting liquid through two electrodes, which may be of the same or of different metals. The object may simply be to see what happens (i.e. scientific research); or it may be to deposit a metal from a salt in the electrolytic solution on to one of the electrodes, as, for example, in silver plating, or in the industrial manufacture of aluminium; or it may be to break up the electrolyte into its constituent elements, as, for example, in a classroom demonstration that water consists of two parts of hydrogen to one of oxygen. The process is called *electrolysis*; the Greek etymology of the word electrolysis suggests "loosening" by electricity.

The other sort is what we commonly call a "battery", such as a flashlight battery or a car battery. In a "battery", we have an electrolyte and two metal poles (generally of different metals, or perhaps a metal and carbon). Because of chemical reactions inside the battery, there exists a small potential difference (usually about one or two volts) across the poles, and when the "battery" is connected to an external circuit, we can extract a continuous current from the battery. Strictly, we should call it a "cell" rather than a "battery". A "battery" is a battery of several cells in series. Usually a flashlight holds a battery of two or three cells. A car battery is genuinely a battery of several connected cells and can correctly be called a battery. Unfortunately in common parlance we often refer to a single cell as a "battery". In order to distinguish a cell in this sense from what I have called an "electrolytic cell", I shall refer to a cell from which we hope to extract a current as an "electrical cell". I hope these opposite terms "electrolytic cell" and "electric cell" do not prove too confusing. If they do, I'd be glad of suggestions. One suggestion that I have heard is to call an electric cell a "galvanic cell". Another is a "voltaic cell".

In an electrolytic cell, the *positive* electrode is called the *anode*, from a Greek derivation suggesting "up". The *negative* electrode is the *cathode*, from a Greek derivation suggesting "down". In the electrolyte, current is carried by positive ions and negative ions. The *positive ions*, which move toward the cathode, are called *cations*, and the *negative ions*, which move towards the anode, are called *anions*.

Do you find it confusing that the positive electrode is the anode, but the positive ion is the cation? And that the negative electrode is the cathode, but the negative ion is the anion? If you do, you are not alone. I find them confusing. Solution: I suggest that you call the positive electrode the *positive electrode*; the negative electrode the *negative electrode*; the positive ion the *positive ion*; and the negative ion the *negative ion*. That way there is no likelihood of your being misunderstood.

Now, when we come to electrical cells, it may be that the roles of the electrodes are reversed. What was a positive electrode in an electrolytic cell may be the negative side of an electrical cell. What are we going to call them? I suggest that, when we are talking about electrical cells we do not use the word "electrode" at all. We shall refer to the *positive pole* and the *negative pole* of an electrical cell.

Electrolysis of Water

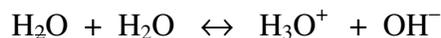
I vaguely remember my first impressions of what is supposed to happen when two platinum electrodes are dipped into water and a current is passed into the water. My guess is that, if the water were very pure water (which is quite difficult to come by) very little would happen. Pure water has very few ions in it (we'll discuss just how many a little later) and its electrical conductivity is quite small – about $5.5 \times 10^{-6} \text{ S m}^{-1}$. However, real water is not pure; it usually has enough impurities in it to supply plenty of ions and to make it a good conductor (and hence a danger in the presence of high-voltage equipment).

My early impression (not quite accurate) of what happens when an electric current passes through water was something like this. Water contains, in addition to billions of molecules of H_2O , a few ions formed through the partial dissociation of H_2O :



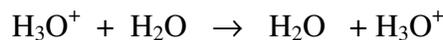
The hydrogen ions, which are the ~~eations~~ positive ions, move one way, and the hydroxyl ions, which are the negative ions, move the other way.

Well, I'm happy to believe in the existence (if not, maybe, the movement) of the hydroxyl ions, but not about the H^+ ions, which are bare protons with an enormous electrical field. I don't think bare protons exist in any liquid electrolyte, let alone water. I think the reaction is more like

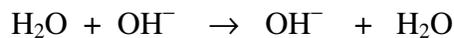


The positive ion is actually a hydrated proton, also known as "hydronium".

My other problem is that I have difficulty in imagining these great clumsy ions trying to barge their way (the H_3O^+ ions one way, and the hydroxyl ions the other way) through the milling crowd of H_2O molecules. If you imagine the positive electrode to be at the left and the negative electrode at the right, so that the electric field is from left to right, I think what happens when an ion bumps into a neutral water molecule is something like this:



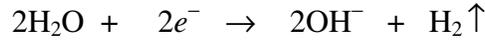
and



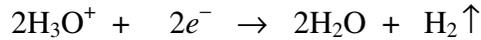
In either case, a proton is swapped between the jostling bodies, and so the proton moves from left to right.

Be that as it may, the following reactions occur at the negative electrode

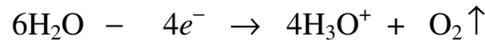
A fresh supply of hydroxyl ions is continuously being created while hydrogen molecules are being released in gaseous form



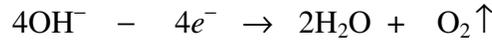
Also, arriving hydrated protons are neutralized:



At the positive electrode, a fresh supply of hydrated protons is continuously being created while oxygen molecules are being released in gaseous form. This happens by electrons from H_2O molecules being transferred to the positive electrode, in several stages, but with net result:



In addition, arriving hydroxyl ions are neutralized:



The whole process might seem a bit complicated, but, since we start off in water with twice as many hydrogen atoms as oxygen atoms, naturally the electrolysis results in hydrogen molecules being produced at twice the rate of oxygen molecules. Furthermore, the net result is the same as if we had supposed that there were indeed OH^- and H^+ ions moving through the water as in the simplest model.

One last point before we leave water. I mentioned that the electrical conductivity of pure water is very small, and the number of ions is very small, so that probably not much would happen if you tried to electrolyse pure water. Real water is rarely pure and it has enough impurity ions in it to allow an electrolysis experiment to proceed smoothly. In pure water at room temperature there are about 10^{-7} moles of hydrogen ions (hydrated protons) and a similar number of hydroxyl ions per litre. In SI units, that is also 10^{-7} kmole per m^3 . If you add a little bit of acid, you of course very much increase the number of hydrogen ions, and correspondingly the number of hydroxyl ions drops. (Don't worry – the solution remains electrically neutral! If, for example, the acid is HCl , there will be lots of Cl^- ions.) The number of hydrogen ions per litre might be, for example, 10^{-5} mole per litre, or kmole per m^3 . If you add a little alkali, you increase the number of hydroxyl ions and correspondingly decrease the number of hydrogen atoms, perhaps to 10^{-9} mole per litre, or kmole per m^3 . (Don't worry – the solution remains electrically neutral! If, for example, the alkali is NaOH , there will be lots of Na^+ ions.)

The absolute value of that exponent (7 for the neutral solution, 5 for the acidic solution, 9 for the alkaline solution) is called the *pH*. I think the symbol *p* was originally chosen from the German *Potenz*, or potential or power. The *pH* is commonly used to describe the acidity or alkalinity of a

solution. It is 7 for a neutral solution, less than 7 for an acidic solution, and greater than 7 for an alkaline solution. Actually, *pH* is just a rather rough indication of acidity, and there is often not much value in quoting a *pH* value to a large number of significant figures. For example, in hot water, more water molecules are dissociated, so there are more hydrogen ions (and of course more hydroxyl ions) so the *pH* value would nominally go down – though the hot water is no more acidic than it was when it was cold.

Electrolysis of silver nitrate.

There are countless examples of electrolysis that could be told in an encyclopaedia devoted to the subject, many of which are industrial applications. But I don't want to (indeed cannot) write a chemistry book. And indeed all that I need here is one example that is sufficient to introduce some scientific words. I choose the electrolysis of silver nitrate partly because it is simple; partly because at one time the practical definition of the amp was based on the rate of deposition of silver from silver nitrate solution; partly because it enables me to mention *Faraday's law* and the definition of the *faraday*, and even to mention *Avogadro's number*; partly because the electrolysis of silver nitrate can be used for very precise measurement of electric current, and partly because it is used in practice for silver plating.

The stoichiometric chemical formula for silver nitrate is AgNO_3 , though in fact, both in the crystalline state and in solution, it consists of Ag^+ and NO_3^- ions. During electrolysis of silver nitrate solution with silver electrodes, silver, of course, is deposited on the negative electrode. Oxygen is given off at the positive electrode. I mention this, because at one time (apart from the obvious practical use in silver plating), this was used as the practical definition of the unit the amp, or ampère. Indeed an "international amp" was that steady current which would deposit silver at a rate of 0.001118 grams of silver per second from a solution of silver nitrate. (This value is very close indeed to, though a tiny bit less than, the SI definition of the amp described in Chapter 6.) Oxygen is given off at the positive electrode.

Faraday measured the mass of many metals deposited from various electrolytes, and he enunciated what is now known as *Faraday's Law of Electrolysis*. In simple terms, and without using phrases that are more familiar to chemists than to physicists, Faraday's law could be stated as:

$$m \propto \frac{It\mu}{v}$$

That is to say, the mass m of a metal deposited on the cathode during electrolysis is proportional to the total quantity of electricity passed (that is It , where I is the current and t is the time), to the molar mass (i.e. the mass of a mole of the metal, popularly known as the "atomic weight") and inversely proportional to the "valence" or "valency" v , which is just the charge on the ion. For example aluminium has a valence of 3. Its ion has a charge of plus 3 electronic charges, and consequently it needs three times the amount of electricity to deposit a mole of Al than to deposit, say, a mole of univalent Ag. The molar mass of a metal divided by its valence is called the *electrochemical equivalent* of the metal. It is the *mass of metal that would be deposited by a*

coulomb of electricity. ($\frac{\mu}{v} = \frac{m}{It}$.) A silver nitrate electrolytic cell is in fact a very suitable instrument for the highly precise measurement of electric current. In this connection it is called a *voltmeter*, though I suppose “ammeter” would really be a better name!

So, how much electricity is required to deposit a mole of charge? (That is to say a mole of the metal ions times the charge on each.) The amount of electricity required to deposit a mole of charge (e.g. 108 grams of Ag, or $27 \div 3 = 9$ grams of Al) from solution is called a *faraday*. It is about 96,485 C, which is the charge of a mole (Avogadro's number) of electrons.

This is worth knowing, for a good examination question for physics students might be "How is Avogadro's number determined?" This is obviously a very important thing for a physicist to know, but a physics student with only a modest background in chemistry might not immediately think of the answer, which is: by measuring the size of the faraday by measuring the mass of silver deposited from silver nitrate solution. (Of course you have to use the SI definition of the amp for this – it wouldn't do to use the definition of the “international amp”!)