

3. ELECTROLYSIS

3.1 Introduction

Electricity is a household word. We use electricity for lighting, heating, cooling, etc.

Why are copper and aluminium wires used to conduct electricity? Why do we cover the wires with PVC or some other plastics? There are two divisions of matter: those that conduct electric current and those that do not. We shall return to this topic later, but let us first consider static electricity, and sources of electric current.

3.2 Electrostatics

Experiment 3.1: Investigating Static Electricity.

- (a) Cut some paper into tiny pieces, and place them on a table. Rub a ballpen hard on your dry hair and bring it near the pieces of paper. The pieces of paper stick to the ballpen. Plastic comb behaves similarly if rubbed on dry hair, so also a glass rod rubbed on silk. This indicates that charge can be induced on certain substances by rubbing them together.

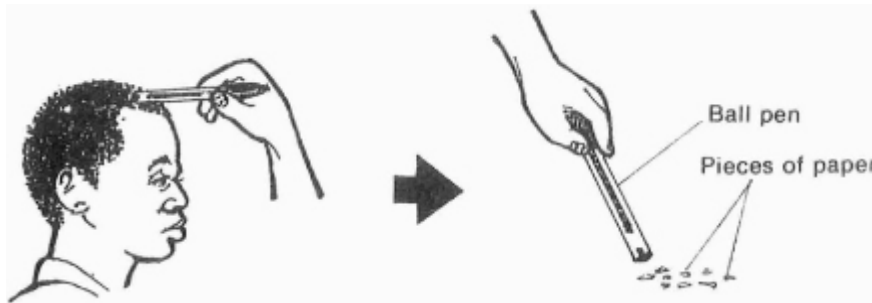


Figure 3.1 Effect of static electricity on pieces of paper

- (b) Place pieces of paper between two blocks of wood on a table. Place a sheet of glass on the blocks. Rub the top of the glass sheet with a piece of flannel. The pieces of paper will be observed to move up and down. The rubbing of the glass induces charges on the glass which induces opposite charges on the pieces of paper.

They get attracted to the glass but fall back on giving off the charges.

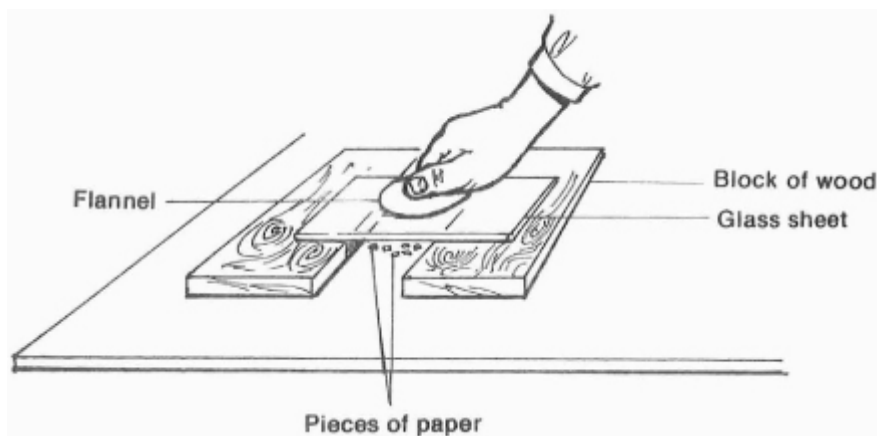


Figure 3.2 Effect of static electricity on paper

- (c) Roll up some paper foil, such as that from a cigarette packet, into a small ball. Pierce a hole through it, then pass a nylon or silk thread about 10 cm into it. Make a knob at the end of the thread, then hang the ball onto a ballpen. Clamp the ballpen onto a wooden burette holder as shown in Figure 3.3. Rub another ballpen hard on your dry hair and bring it near the ball of paper foil. The ball is attracted to the charged ballpen. Now rub the ballpen on a celluloid set square and bring both ballpen and celluloid in turns, near the ball of paper foil. Initially the paper foil is attracted to the ballpen, but later it is repelled. A similar thing happens with the set square. This shows that there are two types of charges.

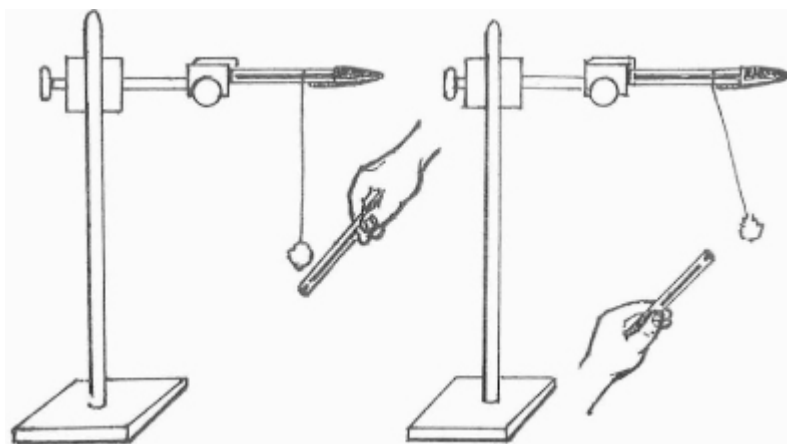


Figure 3.3 Effect of charged ballpen on paper foil

These experiments demonstrate the basic law of electrostatics.

Unlike charges attract; like charges repel one another.

But matter is made up of atoms which are made up of protons, electrons and neutrons. How then do the charges arise?

All the items such as the ballpen, plastic comb, glass rod, etc, which become charged on rubbing against the hair or fur are neutral to begin with. When rubbed against fur, they become positively charged

due to loss of electrons to the fur. The fur which receives the electrons becomes negatively charged. When brought near pieces of paper or the paper foil, the electrons on the pieces of paper or paper foil attract the positively charged ballpen. The neutral ballpen is shown in Figure 3.4 as having equal positive and negative charges (equal numbers of protons and electrons).

Only the excess positive charges are shown on the positively charged ballpen. The paper foil still has equal numbers of positive and negative charges, but the negative charges move to one side to attract the positive charges on the charged ballpen.

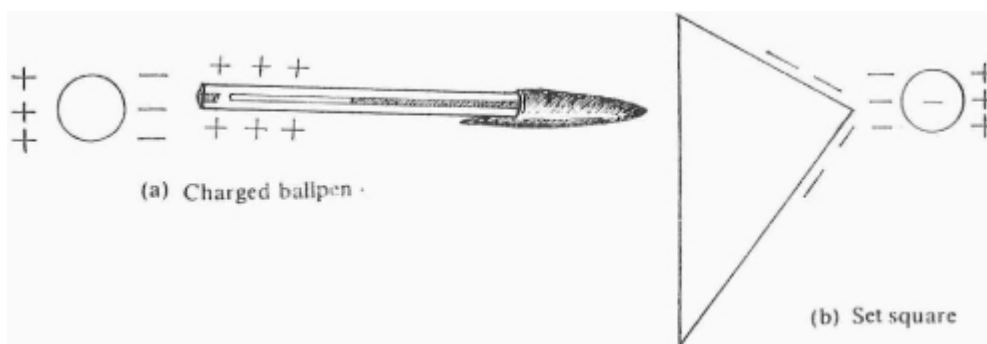


Figure 3.4 Transfer of static electricity between materials

To neutralise the positive charges on the ballpen, some electrons move from the neutral paper foil to the positively charged ballpen. The paper foil thus becomes positively charged. Hence, it repels the positively charged ballpen later. The celluloid set square accepts the electrons from the paper foil by rearranging its protons and electrons. But again, there is repulsion later when the paper foil has become negatively charged (Figure 3.4b).

The electroscope is an instrument used to detect static electricity. The simple electroscope consists of a conducting metal such as the copper alloy, brass, inside an earthed metal case. A gold leaf is attached to the brass plate inside the metal case (Figure 3.5). When a charged object is made to touch the metal cap, the gold leaf opens out but closes up when the charged object is removed. The charges move down from the charged body to the brass plate and gold leaf. Repulsion between the similar charges causes the opening up of the gold leaf. It falls back when the charge is removed.

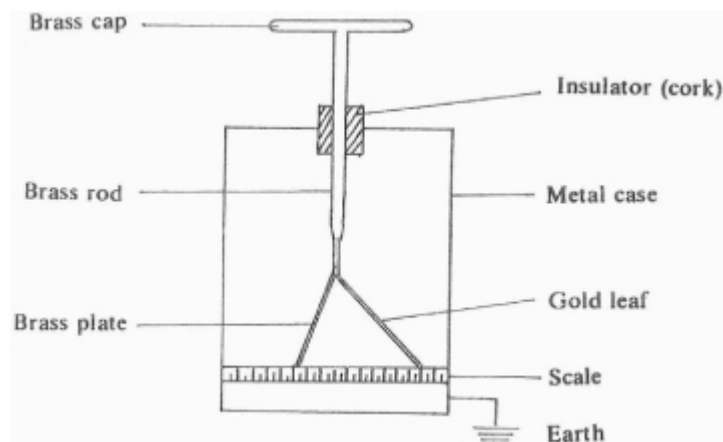


Figure 3.5 An electroscope

3.3 Generation of Electricity

Experiment 3.2 Generating Electricity from a Chemical Reaction.

Pour some copper(II) tetraoxosulphate(VI) solution into a beaker. Join a copper rod and a zinc plate with conducting wires to a voltmeter. Dip both metals into the solution (Figure 3.6). The voltmeter pointer is deflected. If a small electric bulb is connected at the position of the voltmeter, it lights, indicating a flow of current.

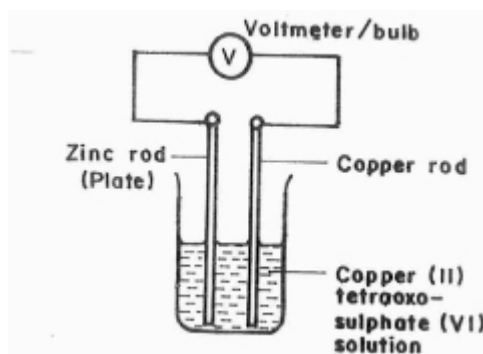


Figure 3.6 A simple cell

After a long time the blue colour of the copper(II) tetraoxosulphate(VI) solution fades, indicating that a chemical reaction has taken place. This reaction is responsible for the flow of current.

The reactions occurring in the cell are

- (1) Zinc atoms from the zinc rod lose electrons to become ions.

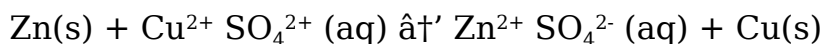
$$\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$$
- (2) Copper ions in solution gain the electrons lost by zinc atoms to become copper atoms.

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

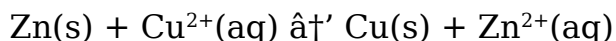
Copper is deposited on the copper rod dipping in the copper(II)

tetraoxosulphate(VI) solution. The electrons lost by zinc move over, from the zinc rod through the connecting wire, to the copper rod. **The moving electrons constitute electric current.**

The overall reaction can be represented as



OR



The heat of that reaction can be determined experimentally by measuring the temperature rise when zinc dissolves in copper(II) tetraoxosulphate(VI) solution.

Experiment 3.3: Determining the Heat of the Reaction in Experiment 3.2.

Make a glass calorimeter by packing an insulator such as cotton wool between a 250 cm³ beaker and a smaller beaker (150 cm³ say) (Figure 3.7). Put 100 cm³ of copper(II) tetraoxosulphate(VI) solution inside the inner beaker. Weigh out about 1g of powdered zinc. Insert a thermometer in the copper(II) tetraoxosulphate(VI) solution, and record the temperature of the solution. Then introduce the zinc powder. Stir the mixture with the thermometer and record the highest temperature reached during the reaction. The reaction is:

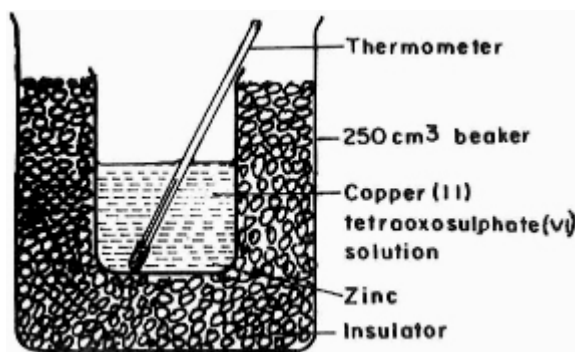
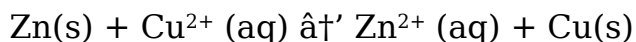


Figure 3.7 Determining the heat of reaction: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$

SPECIMEN RESULTS AND CALCULATION

Mass of zinc used = 1.0 g.

Mass of water used = 100 g.

Rise in temperature = 8°C.

Specific heat of water = 4.2 Joule g⁻¹

Take the specific heat of the resulting solution as equal to the specific heat of water.

$$\begin{aligned}
 \therefore \text{Heat absorbed by the solution} &= 4.2 \times 100 \times 8 \text{ Joules} \\
 \therefore \text{Heat of the reaction} &= 4.2 \times 100 \times 8 \text{ J g}^{-1} \text{ of Zn} \\
 &= 4.2 \times 100 \times 8 \times 65 \text{ J mol}^{-1} \\
 &\quad \text{of Zn} \\
 &= \frac{4.2 \times 100 \times 8 \times 65}{1000} \text{ kJ mol}^{-1} \text{ of Zn} \\
 &= 218.4 \text{ kJ mol}^{-1}
 \end{aligned}$$

If 1.1 volts is recorded on the voltmeter, the electrical energy due to the reaction can be calculated thus:

1 mole of Zn loses 2 Faradays of electrons.

$$\begin{aligned}
 \hat{\wedge}^{\wedge} \text{Electrical energy} &= 2 \times 96500 \times 1.1 \text{ joules} \\
 &= 212.3 \text{ kJ mol}^{-1}
 \end{aligned}$$

The heat of the reaction is represented by the symbol $\hat{\wedge}^{\wedge}\text{H}$. It is the energy of the reaction that is given to the surroundings by one mole of reactants. It is given out in the form of heat, hence the term heat of reaction. The electrical energy of 212.3 kJ mol⁻¹ is not given to the surroundings. It can be used to do work. It is called the free energy of the reaction and has the symbol $\hat{\wedge}^{\wedge}\text{G}$.

Any two different metals dipping into an electrolytic solution will produce electric current when connected externally. The voltage generated (and hence the free energy difference) will however differ according to the nature of the metals used.

3.4 Simple Cells

The arrangement of apparatus in Experiment 3.2 is known as a **Daniel Cell**. It can be made to produce electric current for a reasonable length of time by preventing the direct contact of the different ions in solution. This is achieved by immersing the zinc rod in a porous pot as shown in Figure 3.8. When the acid solution or zinc rod is used up, we cannot reverse the reactions. Such cells are called simple cells.

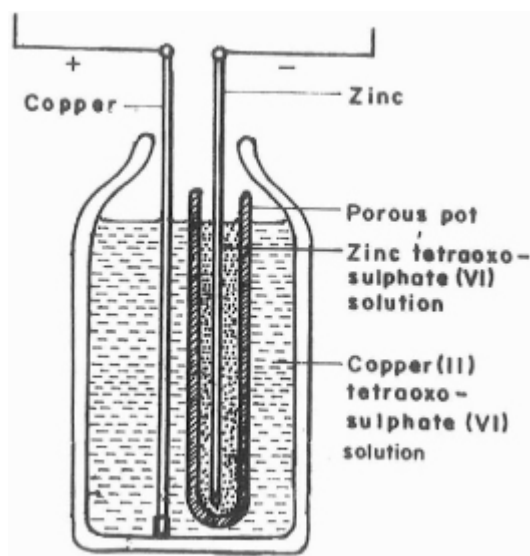


Figure 3.8 Daniel cell

The dry cell or torch-light battery is based on the same principle. The electrolytic solution is a paste of ammonium chloride while graphite and zinc are used as electrodes (Figure 3.9).

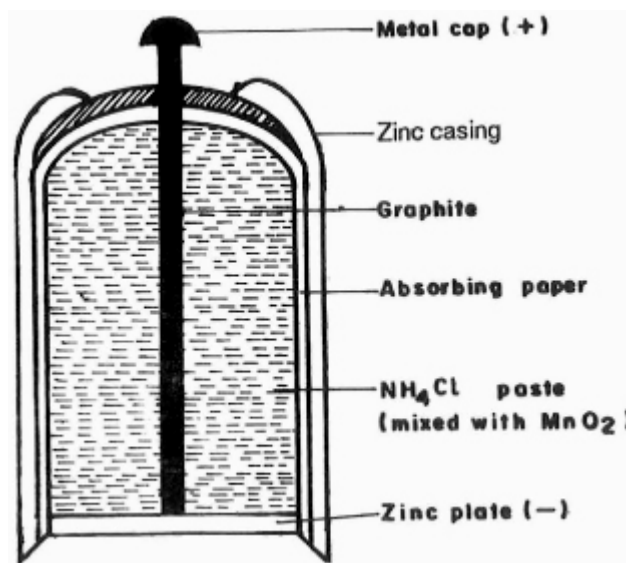


Figure 3.9 Leclanche dry cell

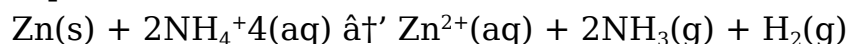
The reactions producing electricity in such a cell, known as the **Leclanche cell** are:

- (i) Zinc goes into solution by loss of electrons.

$$\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$$
- (ii) Ammonium ion gains an electron to become free ammonia gas and hydrogen.

$$2\text{NH}_4^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{NH}_3(\text{g}) + \text{H}_2(\text{g})$$

The equation for the overall reaction is



If the metallic cap and the zinc plate are joined by a conducting wire the electrons travel from the zinc plate, through the conducting wire to the metallic cap, (Figure 3.10).

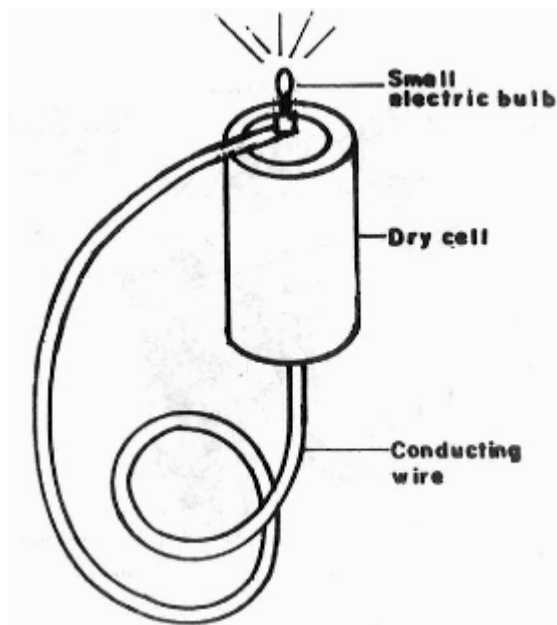


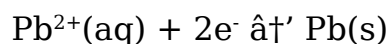
Figure 3.10 A dry cell lighting a bulb

3.5 Secondary Cells: Lead Accumulator

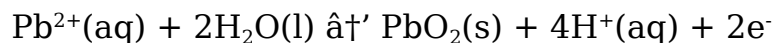
The lead accumulator or storage battery, used in cars has a lead-antimony alloy as both the anode and cathode (Figure 3.11), and tetraoxosulphate(VI) acid as electrolytic solution. Unlike the Daniel or Leclanche cells, the chemical reaction is not spontaneous. The cell first has to be charged, during which a set of reactions occur. When in use, it discharges by means of a second set of reactions during which electrons flow through an external conducting wire. The sets of reactions are as follows:

Charging

At the cathode:



At the anode:



Thus, the cathode becomes filled with spongy lead and the anode with lead(IV) oxide during charging. The electrons from the charging source drive the electrons from the anode to the cathode during the charging process.

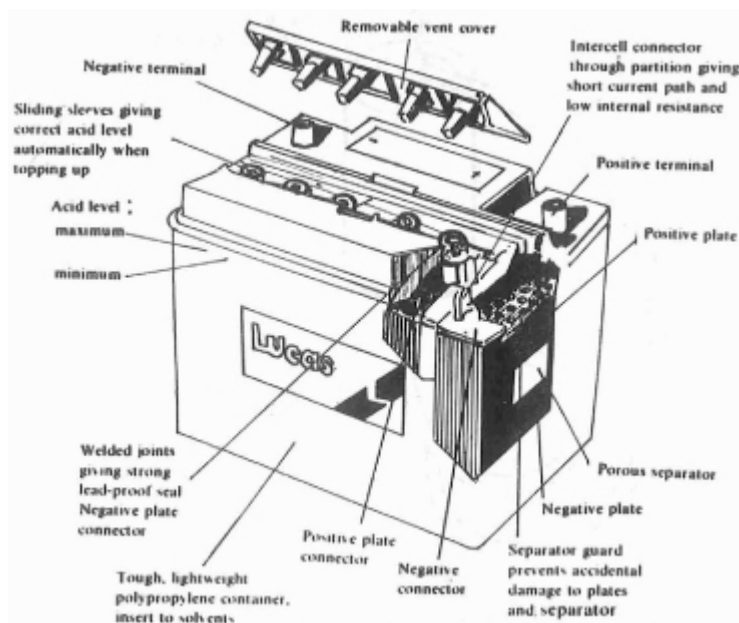
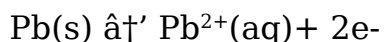


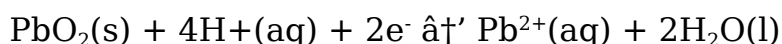
Figure 3.11 A lead-acid accumulator

Discharging

At cathode:



At anode:



Thus at both anode and cathode Pb^{2+} and SO_4^{2-} form a deposit of lead(II) tetraoxosulphate(VI). Electrons produced at the cathode migrate through an external wire to the anode, doing the necessary electrical work in the process.

A cell whose reactions can be reversed by charging and discharging is called a secondary cell.

3.6 Electrolytes and Non-electrolytes

Electrical conduction is one of the properties used to classify elements into metals and non-metals. Metals such as copper, silver and iron conduct electricity while non-metals, such as sulphur, phosphorus and iodine are non-conductors (insulators). Graphite, though a non-metal, however conducts electricity. The reason for this abnormal behaviour has been discussed in Book 1.

What about compounds? What kind of compounds conduct electricity, and in what form?

Experiment 3.4: Investigating Electrolytes and Non-electrolytes.

Connect a battery to an electric bulb and to two graphite rods as shown in Figure 3.12. Collect samples of the following compounds: sodium chloride, iron(II) tetraoxosulphate(VI), sugar, candle wax,

camphor, calcium trioxocarbonate(IV), bleaching powder, potash alum and copper(II) oxide. Put each of these compounds, in turn, into an evaporating dish, immerse the graphite rods into it, then switch on the current. The bulb does not light with any of these compounds in the evaporating dish.

Heat to melt each substance, and put the graphite rods in the molten compounds. The bulb lights when the graphite rods are immersed in the molten metallic compounds, but not when they are immersed in organic compounds such as sugar, camphor and candle wax. Those compounds which cause the bulb to light are called electrolytes. The others are non-electrolytes.

Experiment 3.5: Investigating Electrolytes (Conduction by Aqueous Solutions).

Repeat Experiment 3.4, this time dipping the graphite rods into aqueous solutions of the compounds in turn (Figure 3.13). If the bulb does not light in any of the cases, replace the bulb with a galvanometer (an instrument for detecting flow of small currents), and note whether the galvanometer needle is deflected or not. Include dilute solutions of the following in the investigation: ethanoic acid, unripe orange juice, lime water, hydrogen chloride acid (hydrochloric acid), trioxonitrate(V) acid, and tetraoxosulphate(VI) acid.

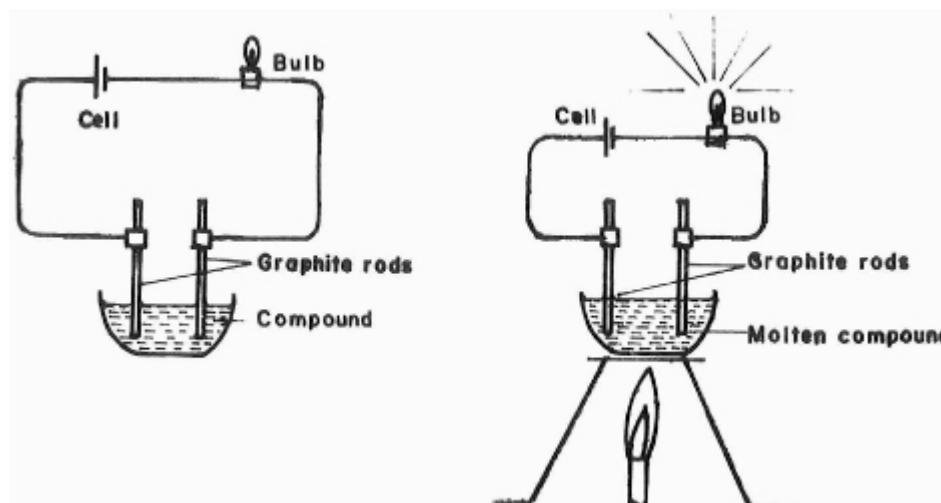


Figure 3.12 Investigating electrolytes

Those solutions which cause the bulb to light in the above experiment are strong electrolytes. They include the mineral acids, solutions of sodium chloride, and most other soluble metallic salts, oxides or hydroxides. Those which do not cause the bulb to light, but cause deflection of the galvanometer needle, are weak electrolytes. In this group are ethanoic acid and unripe orange juice. Slightly soluble ionic compounds which cause slight deflections, are strong electrolytes. They conduct well in the molten state. The compounds whose aqueous solutions do not allow the passage of current, and therefore do not cause a deflection of the galvanometer needle or

cause the bulb to light, are called non-electrolytes. Sugar solution belongs to this group.

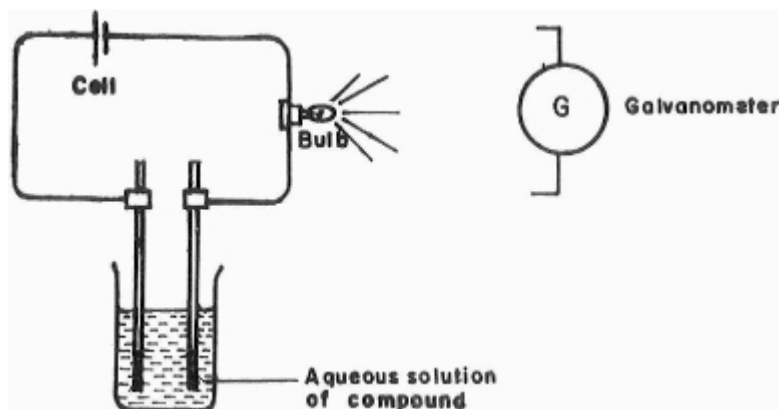


Figure 3.13 Conduction of electricity by aqueous solution

An electrolyte is a compound which in aqueous solution or in the molten state allows the passage of electric current through it with decomposition at the electrodes.

Electrodes are the poles through which electric current enters or leaves an electrolyte.

Anode is the positive electrode.

Cathode is the negative electrode.

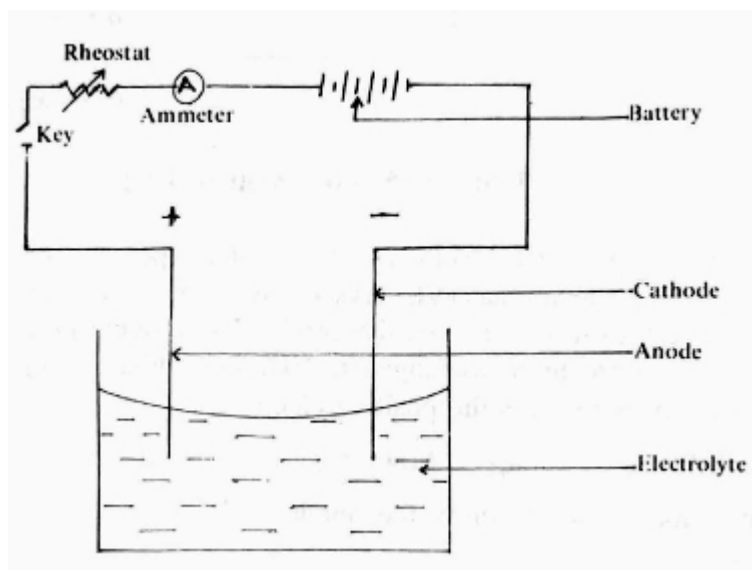


Figure 3.14 Electrolytic cell

What carries the current through electrolytes? Does it not exist in non-electrolytic solutions?

Experiment 3.6: Investigating the Movement of Ions in Solution.

Set up the apparatus shown in Figure 3.15. Soak a piece of filter paper cut to fit a microscope slide, in aqueous ammonia. Place a crystal of

copper(II) tetraoxosulphate(VI) at the centre of the filter paper, then switch on the current. A patch of blue colour is seen moving towards the cathode. As copper ions from the copper(II) tetraoxosulphate(VI) migrate towards the cathode they form the blue copper(II) tetraamine complex ion which is blue in colour.

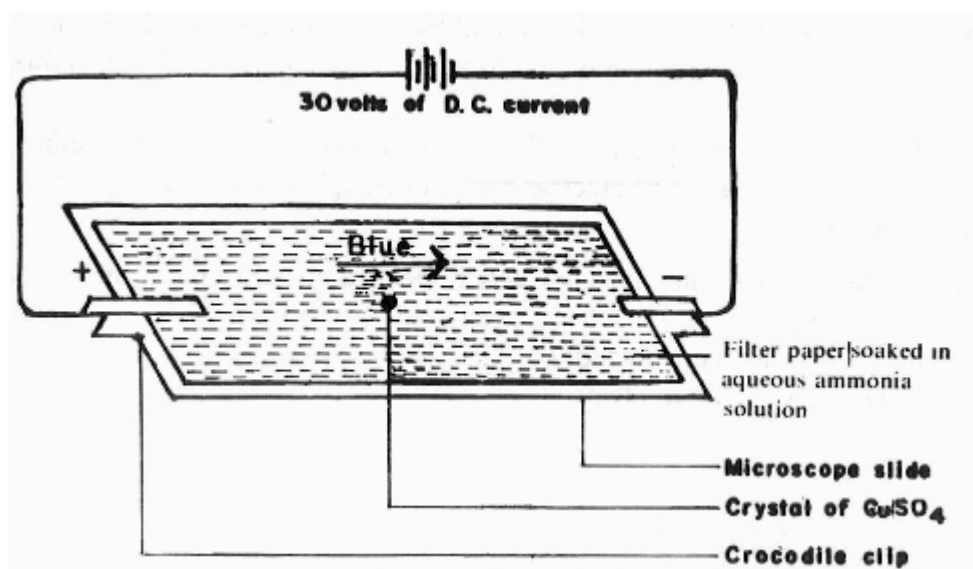
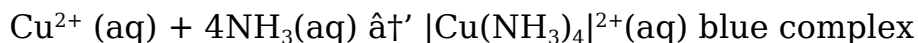
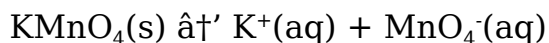


Figure 3.15 Movement of ions

Repeat the experiment by soaking another filter paper in water and placing potassium tetraoxomanganate(VII) crystal at the centre of the paper. A purple colour is seen to move towards the anode. The moving purple colour is due to the purple tetraoxomanganate(VII) ion which, being negatively charged, moves towards the positive electrode.



MnO_4^- ion moves towards the anode while K^+ moves towards the cathode.

Electrolytes can therefore be said to conduct electricity because they produce ions in the molten state or in solution. These ions migrate towards oppositely charged electrodes on application of electric current. The anions give up their electrons to the positive electrode (anode) and become neutral. The cations, on the other hand pick up electrons from the negative electrode (cathode), to become neutral also. The decomposition mentioned in the definition of electrolytes therefore arises from the ions becoming neutral at the electrodes.

Strong electrolytes produce many ions in solution because they are completely ionised. They therefore conduct electricity well. Weak electrolytes are poor conductors because they produce only a few ions in solution. They ionise only partially. Non-electrolytes do not form ions at all and so are non-conductors of electricity.

3.7 The Faraday as a Mole of Electrons

Ions carry one, two, three or even four charges. Table 3.1 shows the common ions and their charges.

TABLE 3.1 COMMON IONS AND THEIR CHARGES

Cations			Anions		
+1	+2	+3	-1	-2	-3
H ⁺	Ca ²⁺	Al ³⁺	OH ⁻	O ²⁻	N ³⁻
Na ⁺	Mg ²⁺	Cr ³⁺	Cl ⁻	S ²⁻	PO ₄ ³⁻
K ⁺	Ba ²⁺	Fe ³⁺	Br ⁻	CO ₃ ²⁻	
NH ₄ ⁺	Fe ²⁺		I ⁻	SO ₄ ²⁻	
Ag ⁺	Zn ²⁺		NO ₃ ⁻	SO ₃ ²⁻	
Cu ⁺	Cu ²⁺		MnO ₄ ⁻		

We should expect the singly charged cations to pick up only one electron each from the cathode, and the singly charged anions to give up only one electron each at the anode. Similarly the doubly charged cations should pick up two, and the doubly charged anions donate two electrons to the cathode and anode respectively. Therefore one mole of a doubly charged ion carries twice as much current as one mole of a singly charged ion, and one mole of a triply charged ion three times as much. In other words, an Avogadro number of ions of a doubly charged ion carries two Avogadro numbers of electrons, and an Avogadro number of a triply charged ion carries three Avogadro numbers of electrons.

An Avogadro number of electrons, or one mole of electrons, is known as the Faraday. Therefore one mole of a univalent ion carries one Faraday of electricity, one mole of a divalent ion carries two Faradays of electricity, and one mole of a trivalent ion carries three Faradays of electricity.

3.8 Electrolysis of some Compounds

When electric current is passed through electrolytes in the molten or solution state the component ions accept or lose electrons to form neutral atoms. The electrolytes are thereby decomposed. Some of the atoms may combine to form molecules. This decomposition is known as electrolysis.

Electrolysis is defined as the decomposition of electrolytes at electrodes when electric current is passed through them.

Experiment 3.7: Investigating the electrolysis of copper (II) tetraoxosulphate (VI) solution.

(a) Using inert electrodes:

Connect a 6 or 12 volt battery through a switch, to two graphite electrodes (or platinum electrodes). Dip the electrodes into copper(II) tetraoxosulphate(VI) solution in a beaker (Figure 3.16). Switch on the current and leave for about thirty minutes. The blue colour of the solution fades and brown copper metal deposits at the cathode.

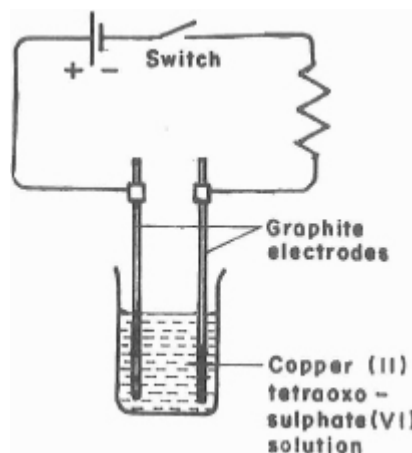
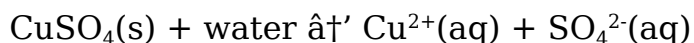
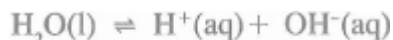


Figure 3.16 Electrolysis of copper(II) tetraoxosulphate(VI) solution

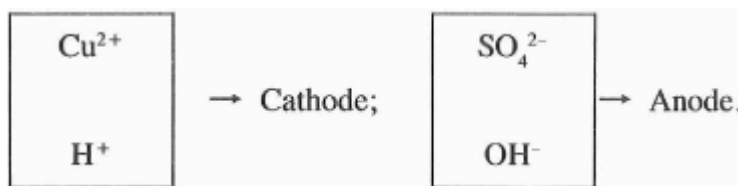
EXPLANATION OF THE OBSERVATIONS: In aqueous solution, copper(II) tetraoxosulphate(VI) exists as ions.



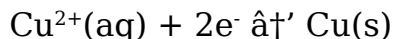
The water of the solution ionises partially:



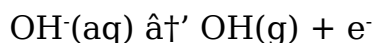
Since unlike charges attract each other, the Cu^{2+} and H^+ ions migrate to the cathode while the SO_4^{2-} and OH^- ions migrate to the anode.



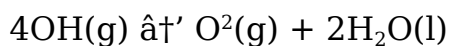
At the cathode, the Cu^{2+} ions pick up electrons and become discharged as free atoms. The atoms get deposited at the cathode.



At the anode (inert), OH^- ions give up their extra electrons to become discharged.



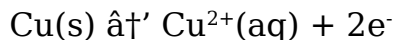
The OH group is not capable of independent existence, so four OH groups unite to form oxygen and water.



Thus, oxygen gas is given off at the inert anode.

(b) Using copper electrodes:

With the copper anode however, instead of a discharge of OH^- ions, copper atoms from the anode lose electrons and go into solution as Cu^{2+}



The overall effect is that copper from the anode passes into solution, while copper ions from the solution get discharged and deposited at the cathode. The concentration of copper ions in solution before and after electrolysis thus remains the same, as long as the copper anode is not used up. The blue colour, therefore, does not change.

(c) Comparison of results of use of inert and copper anodes:

A brown solid (copper) is deposited at the cathode in both experiments. Bubbles of a colourless, odourless gas, oxygen, are given off at the inert anode in the first experiment, but no gas is evolved at the copper anode in the second experiment. As electrolysis progresses in the first experiment with the inert electrodes, the blue colour of the electrolyte fades. The blue colour persists in the second experiment with copper electrodes. A close examination shows that "corrosion" of the copper anode occurs in this case.

Experiment 3.8: Investigating the electrolysis of sodium chloride.

Connect up the apparatus shown in Figure 3.17 and pour a saturated sodium chloride solution into it. Test the aqueous solution with litmus paper to confirm that it is neutral. Switch on the current and wait for about 30 minutes.

A colourless gas collects in the cathode compartment and a greenish-yellow in the anode. Bring a lighted taper near the gas in the cathode compartment and put a damp blue litmus paper into the gas in the anode compartment. A "pop" sound in the cathode compartment shows the gas to be hydrogen, while the litmus paper in the anode compartment is turned red, then bleached, indicating that the gas is chlorine. Test the solution again with litmus papers (blue and red). The solution is observed to have turned alkaline.

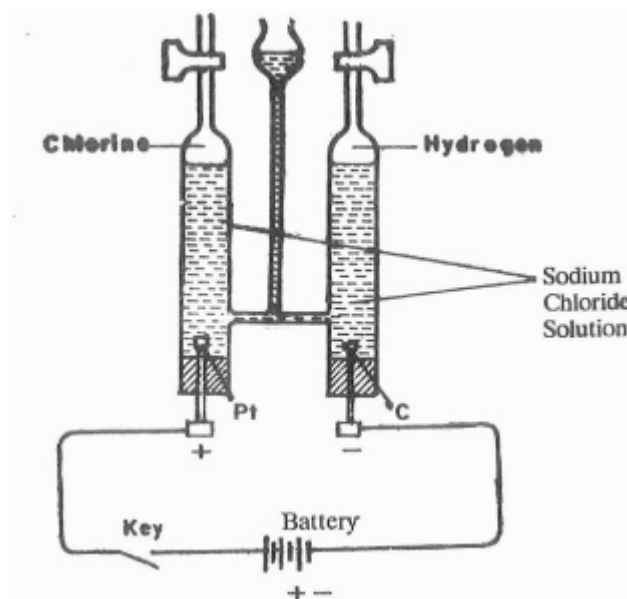
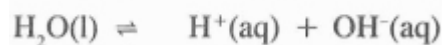
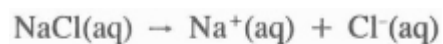


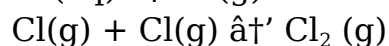
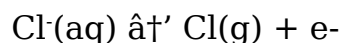
Figure 3.17 Electrolysis of sodium chloride solution

EXPLANATION OF OBSERVATIONS: Sodium chloride ionises completely in water, but water ionises partially.



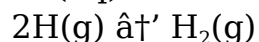
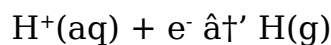
Na^+ and H^+ migrate to the cathode, while Cl^- and OH^- migrate to the anode.

At the anode, chloride ions give up electrons to become free atoms. The atoms pair up into molecules.



Chlorine gas is liberated.

At the cathode, hydrogen ions take up electrons to become free atoms, and the atoms pair up to form molecules.



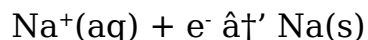
Hydrogen gas is thus liberated.

The discharge of H^+ causes further ionisation of water in the cathode compartment. Excess OH^- ions therefore accumulate. With incoming sodium ions, they form an alkaline solution of sodium hydroxide.

If Experiment 3.8 is repeated with very dilute sodium chloride solution, oxygen and chlorine are liberated simultaneously at the anode. The reason for this will become obvious when we discuss the preferential discharge of ions.

If fused sodium chloride is electrolysed, then there will be no hydrogen ions to discharge. Sodium ions should be discharged at the

cathode. But the reaction



is not spontaneous because sodium is an active metal. The spontaneous reaction is



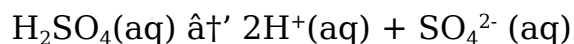
The extraction of sodium by the electrolysis of fused sodium chloride therefore uses the Keller cell which has mercury as the cathode. The discharge of sodium is enhanced by the formation of an amalgam with the mercury cathode.

Experiment 3.9: Investigating the electrolysis of dilute tetraoxosulphate (VI) acid.

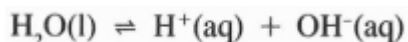
Using the apparatus in Figure 3.17, fill the container with dilute tetraoxosulphate(VI) acid. Switch on the current and watch for about thirty minutes. The ratio of the volume of gases in the anode and cathode areas is 2 : 1. Test the gases at the anode and cathode compartments with a glowing splint and a lighted taper respectively. The gas in the anode compartment rekindles the glowing splint while that in the cathode compartment makes a 'pop' sound with a lighted taper. The gases are oxygen and hydrogen respectively.

Withdraw samples of the acid from the anode and cathode compartments after electrolysis and match their colours with the universal indicator against a colour chart. The acidity is seen to decrease in the cathode area, but increases in the anode area.

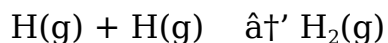
EXPLANATION OF OBSERVATIONS: Tetraoxosulphate(VI) acid ionises thus:



Water ionises partially.

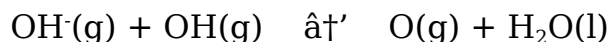


H^+ migrates to the cathode while SO_4^{2-} and OH^- migrate to the anode. At the cathode:



Hydrogen gas is given off. The discharge of H^+ reduces the acidity in the cathode compartment.

At the anode:



Thus, oxygen gas is evolved at the anode.

The discharge of OH^- leaves excess H^+ at the anode compartment. The acidity therefore increases in the compartment. The total acidity of the whole solution, however, remains constant.

Since the electrolysis leads to the decomposition of H^+ and OH^- ions, it is usually called the electrolysis of water rather than of tetraoxosulphate(VI) acid.

3.9 Preferential Discharge of Ions during Electrolysis

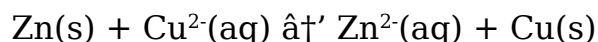
Hydrogen and metallic atoms form positive ions, but not with equal readiness. Some metals form positive ion much more readily than others. The position of ions in the electrochemical series, the concentration of the ions in solution, and the nature of the electrodes used in electrolysis, influence the discharge of ions.

Position of ions in the electrochemical series

Experiment 3.10: Investigating the relative readiness with which zinc and copper form ions.

Prepare 1 mol. dm^{-3} solution of zinc tetraoxosulphate(VI) and copper(II) tetraoxosulphate(VI) solutions in separate beakers. Place a zinc rod into the copper(II) tetraoxosulphate(VI) solution, and a copper rod into the zinc tetraoxosulphate(VI) solution. Keep both set-ups for about five minutes, then examine the rods and solutions.

The zinc rod is "eaten up". Zinc atoms from the metal pass into solution as zinc ions, Zn^{2+} , the rod becoming negatively charged. The copper rod, on the other hand is not affected. This shows that zinc can displace copper ions from its solution while copper cannot displace zinc ions from solution.



A measure of the readiness of metals to form positive ions in solution is known as the electrode potential.

The electrode potential of a metal is the potential difference, in volts, between the metal and 1 mol. dm^{-3} solution of its ions.

For example the electrode potential for zinc and copper are -0.8 volt and +0.3 volts respectively. The very active metals such as potassium, sodium, calcium, zinc, etc, have high negative electrode potentials. Their atoms readily give up electrons to form ions in solution. The less active metals such as copper, silver, gold, etc, have positive electrode potentials. Their ions readily take up electrons in solution to become

free atoms.

A solution containing active and less active ions will discharge the inactive ions in preference to the active ones. The electrochemical series is an arrangement of the ions in order of their activity, and hence order of preferential discharge.

An ion lower in the series is discharged in preference to one above it, (other factors being constant).

Electrochemical series exists for the negative ions also. Among them too, an ion lower in the series is discharged in preference to one above it.

TABLE 3.2 THE ELECTROCHEMICAL SERIES

Cations		Anions	
Least readily discharged	Li^+		
	K^+		
	Ca^{2+}		
	Na^+	SO_4^{2-}	Least readily discharged
	Mg^{2+}	NO_3^-	
	Al^{3+}	Cl^-	
	Zn^{2+}		
	Fe^{2+}	Br^-	
	Sn^{2+}		
	Pb^{2+}	I^-	
Most readily discharged	H^+	OH^-	Most readily discharged
	Cu^{2+}		
	Ag^+		
	Hg^{2+}		

Table 3.2 shows the arrangement of these ions in order of their readiness to be discharged, and is called the Electrochemical series.

EXERCISE 3A

Why were the following ions discharged in the electrolyses considered above?

- Cu^{2+} in preference to H^+ in the electrolysis of copper(II) tetraoxosulphate(VI) solution?
- H^+ in preference to Na^+ in the electrolysis of sodium chloride solution?

Concentration effect

In the electrolysis of sodium chloride solution we noted that chlorine is liberated at the anode if the sodium chloride solution is concentrated, but chlorine and oxygen are liberated if the sodium chloride solution is dilute. The implication of this observation is that **the higher the concentration of an ion in solution, the more likely it is to be discharged**. In the case of dilute sodium chloride solution we do not have an outright preferential discharge of hydroxide ions (and hence liberation of oxygen) because both chloride ions and hydroxide ions are present in small concentrations. Electrolysis of very dilute hydrochloric acid will give similar results.

Nature of electrodes

The electrolysis of sodium chloride solution with a platinum or graphite electrode liberates hydrogen at the cathode. This is expected because hydrogen ion is lower than sodium ion in the electrochemical series. If a mercury cathode is used for the electrolysis, sodium ions are discharged instead of hydrogen ions. The discharge of sodium, and the formation of sodium amalgam between the sodium atom and the mercury cathode, together require less energy than the discharge of hydrogen ions.

A second example of the nature of electrode determining the ion to be discharged, is found in the electrolysis of copper(II) tetraoxosulphate(VI) solution. With inert electrodes (platinum or graphite) hydroxide ions are discharged and oxygen gas liberated at the anode. But if copper anode is used, the copper anode ionizes and goes into solution. Hydroxide ion is not discharged and no oxygen is liberated.

3.10 Laws of Electrolysis

Michael Faraday studied the effect of electric current on electrolytes in great detail and discovered the Faraday's Laws of electrolysis.

Faraday's first law of electrolysis

The first law is concerned with the relationship between the amount of substance liberated or deposited during electrolysis and the quantity of electricity that passes through.

Experiment 3.11: Investigating Faraday's first law of electrolysis.

Connect a 6-volt battery to an ammeter, a variable resistance (rheostat) and a switch, all in series (Figure 3.18). Prepare 0.2 mol. dm^{-3} copper(II) tetraoxosulphate(VI) solution in a beaker. Weigh two copper rods to be used as electrodes. Connect the two ends of wires

from the battery to the two copper electrodes. Dip the electrodes into the copper(II) tetraoxosulphate(VI) solution.

Switch on the current and simultaneously start a stop-watch. Adjust the rheostat to get a current of about 0.5 ampere. If this amount of current fluctuates during the electrolysis, adjust the rheostat to maintain a steady current. Switch off the current after exactly ten minutes. Rinse both electrodes with water, then with ethanol. Dry and reweigh them.

Dip the electrodes in the electrolytes again. Switch on the current, and start the stop-watch at the same time. After another ten minutes switch off the current and stop the stop-watch. Rinse the electrodes once more, dry and weigh. Continue the process until you have obtained five sets of readings.

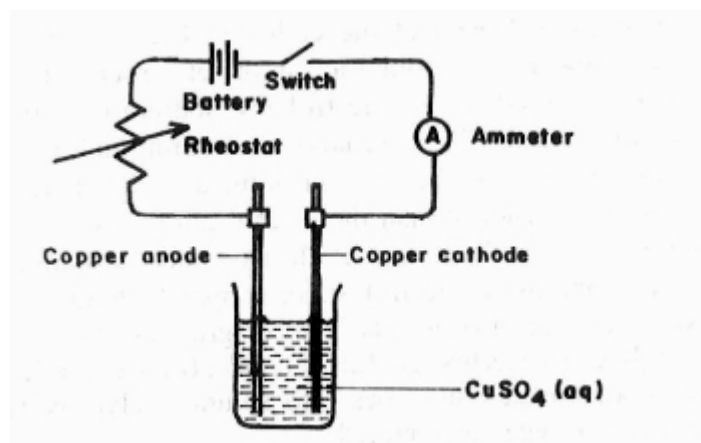


Figure 3.18 Faraday's first law of electrolysis

SPECIMEN RESULTS AND CALCULATIONS

Current (amps)	Time (secs)	Quantity of electricity (coulombs)	Increase in mass of cathode (g)	Decrease in mass of anode (g)	Average mass of Cu deposited or dissolved (g)
0.5	10 × 60	300	0.103	0.099	0.101
0.5	20 × 60	600	0.204	0.199	0.202
0.5	30 × 60	900	0.290	0.298	0.299
0.5	40 × 60	1200	0.397	0.398	0.398
0.5	50 × 60	1500	0.498	0.497	0.498

We expect the gain in mass of the cathode to be equal to the loss in mass of the anode because copper dissolved at the anode is deposited at the cathode. Experimental results show that they are nearly equal for each set of readings. To take care of the experimental errors, we add the increase and decrease in the cathode and anode respectively for each time interval, and find the average.

Plot a graph of average change in mass of electrodes against the

quantity of electricity flowing through the cell. A straight line graph passing through the origin is obtained (Figure 3.19), indicating that the mass of copper deposited at the cathode or liberated at the anode is proportional to the quantity of electricity that passes through the electrolyte. The quantity of current flowing through the cell is obtained from the expression:

$$\begin{array}{rclcl}
 Q & = & I & \times & t \\
 \text{Quantity} & = & \text{Current} & \times & \text{Time} \\
 \text{of} & & \text{(amp)} & & \text{(seconds)} \\
 \text{electricity} & & & & \\
 \text{(coulombs)} & & & &
 \end{array}$$

The same result can be obtained by measuring the masses of the electrodes when different levels of electricity measured in amperes flow for the same length of time.

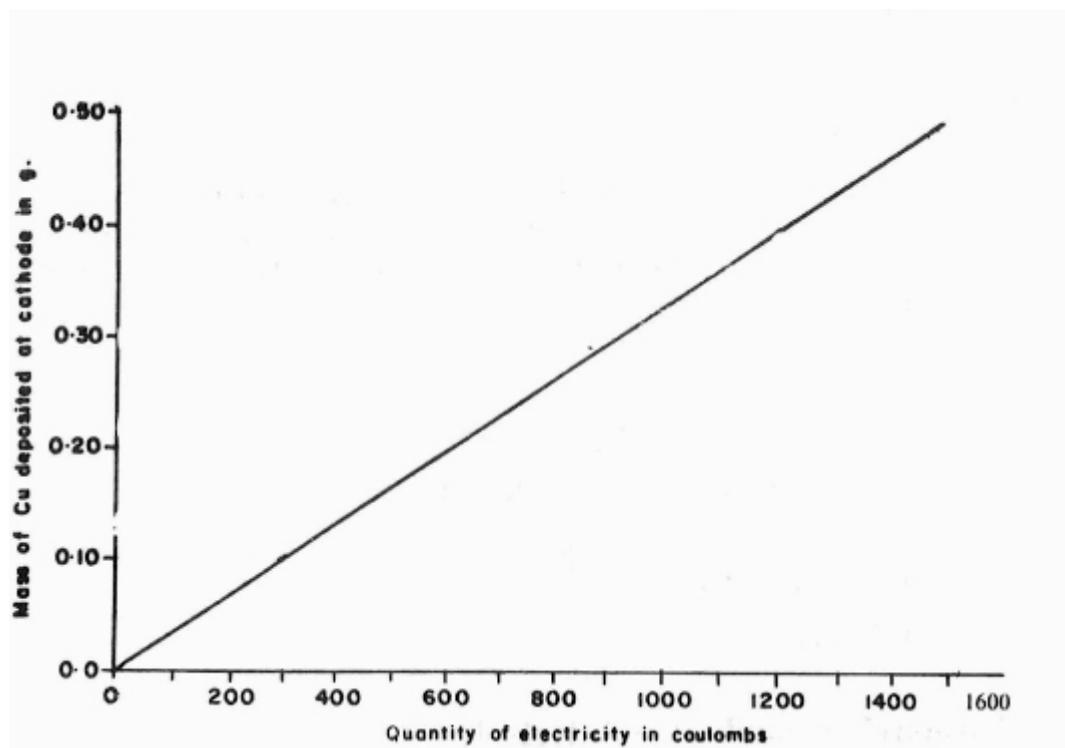


Figure 3.19 Graph of mass deposited vs quantity of current

The result of the above experiment proves Faraday's first law of electrolysis.

Faraday's first law of electrolysis states that the mass of a substance deposited on (or dissolved from) an electrode during electrolysis is proportional to the quantity of electricity which passes through the electrolyte.

WORKED EXAMPLES

- (1) A current of 10 amperes flowing for 20 seconds deposits 0.053g of copper. What mass of copper is deposited if the same amount of current flows for 1 minute?

SOLUTION:

Quantity of electricity flowing = $10 \text{ A} \times 20 \text{ coulombs} = 200 \text{ coulombs}$.
 200 coulombs deposit 0.053 g of copper

$$\begin{aligned} \therefore 10 \times 60 \text{ coulombs will deposit} \\ \frac{0.053 \times 10 \times 60}{200} \text{ g of copper} &= 0.159 \text{ g of copper} \\ &= 0.16 \text{ g of copper} \end{aligned}$$

= 0.16 g of copper

- (2) During the electrolysis of a salt solution, 0.38 g of a metal was deposited by a current of 0.5 ampere flowing for 40 minutes. Calculate the mass of the metal that will be deposited by a current of 0.6 ampere flowing for 30 minutes.

SOLUTION:

$$\begin{aligned} 0.5 \times 40 \times 60 \text{ coulombs deposited } 0.38 \text{ g.} \\ \therefore 0.6 \times 30 \times 60 \text{ coulombs will deposit} \\ \frac{0.38 \times 0.6 \times 60 \times 30}{0.5 \times 40 \times 60} \text{ g} \\ = 0.342 \text{ g.} \end{aligned}$$

Faraday's second law of electrolysis

The second law deals with the result of passing the same quantity of electricity through different electrolytes in series.

Experiment 3.12: Comparing the amounts of different substances liberated by the same quantity of electricity.

Weigh the clean copper and silver electrodes to be used as the cathodes. Connect up the circuit shown in Figure 3.20. Switch on the current and at the same time start a stop-watch. Keep the level of current constant by adjusting the rheostat, if need be. At the end of exactly thirty minutes, switch off the current and stop the stop-watch. Rinse, dry and weigh the cathodes.

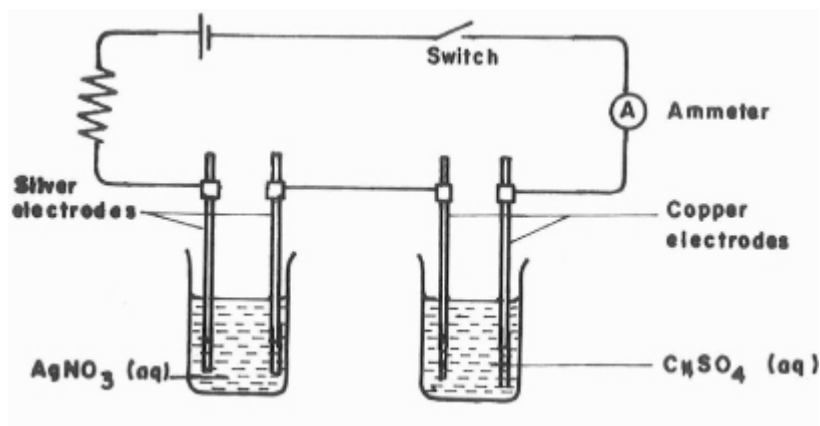


Figure 3.20 Faraday's second law

SPECIMEN RESULTS AND CALCULATION

Current flowing = 0.5 ampere

Time of flow = 30 minutes

Quantity of electricity = $0.5 \text{ A} \times 30 \times 60 = 900 \text{ coulombs.}$

Increase in mass of copper cathode = 0.30 g.

Number of mole of copper deposited $\frac{0.30}{63.5} \text{ mole} = 0.004724 \text{ mole}$

Increase in mass of silver cathode = 1.01 g

No. of mole of silver deposited $\frac{1.01}{108} \text{ mole} = 0.009352 \text{ mole}$

Ratio of the number of mole of copper : silver

= 0.004724: 0.009352

= 1: 2

That is, the same quantity of electricity deposits twice as many mole of silver as of copper.

The experiment can be repeated by connecting the copper voltameter in series with a Hoffmann voltameter as shown in Figure 3.21 The volume of oxygen liberated at the temperature and pressure of the experiment is changed to volume at s.t.p., then converted to mole of oxygen, using the fact that at s.t.p. one mole of every gas occupies 22.4 dm^3 .

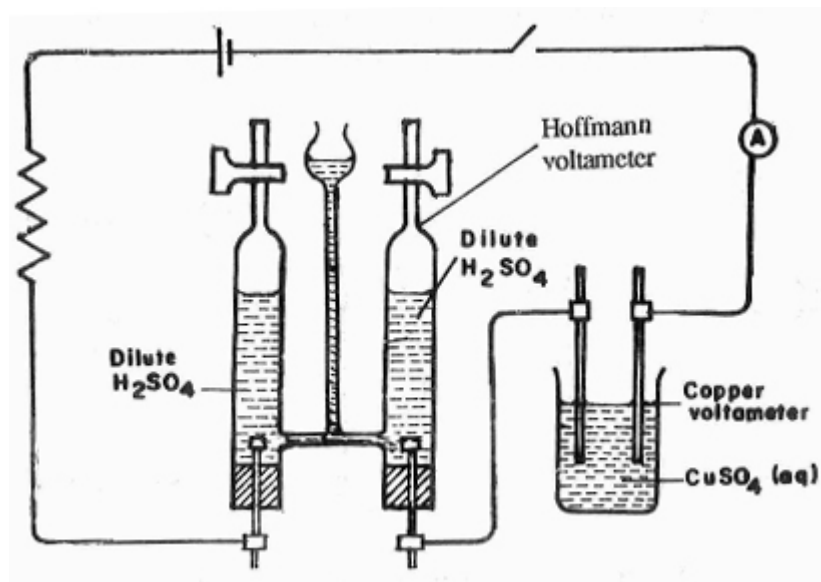


Figure 3.21 Hoffmann voltameter in series with a copper voltameter

SPECIMEN RESULT

A current of 0.5 ampere flowing for twenty minutes through a copper and a Hoffmann voltameter deposits 0.2 g of copper at the cathode of the copper voltameter, and 77 cm of oxygen at the anode of the Hoffmann voltameter. What is the mole ratio of copper to oxygen liberated?

Temperature of experiment = 25°C.

Pressure = 755 mm Hg.

Water vapour pressure at 25°C = 15 mm Hg.

∴ Partial pressure of oxygen produced
= (755 - 15) mm Hg = 740 mm Hg.

$$\begin{aligned} \therefore \text{Volume of oxygen at s.t.p.} &= \frac{740 \times 273 \times 77}{760 \times 298} \text{ cm}^3 \\ &= 68.68 \text{ cm}^3 \end{aligned}$$

22400 cm³ of oxygen at s.t.p. = 1 mole

$$\begin{aligned} \therefore 68.68 \text{ cm}^3 \text{ of oxygen at s.t.p} &= \frac{68.68}{22400} \text{ mole} \\ &= 0.003066 \text{ mole} \end{aligned}$$

$$\begin{aligned} \text{But 0.2 g of copper} &= \frac{0.2}{63.5} \text{ mole} \\ &= 0.00315 \text{ mole} \end{aligned}$$

∴ Mole ratio of copper to oxygen liberated = 0.003066: 0.00315, i.e. 1:1. Thus the relative number of mole of copper to oxygen liberated by

the same quantity of electricity is 1:1.

Note that copper ions carry two positive charges each while silver ions carry one positive charge. Also, equal number of moles of copper and oxygen are liberated, and they have equal, though opposite charges of +2 and -2 respectively. These results show that the number of mole of an element liberated during electrolysis depends on the charge on the ion of the element. This is expressed in Faraday's second law of electrolysis.

Faraday's second law of electrolysis states that the relative number of mole of elements dissolved, liberated or deposited by the same quantity of electricity are inversely proportional to the charges on the ions of the elements.

Recall that the Faraday is equal to a mole of electrons. One mole of electrons will discharge one mole of a unipositive ion, or half a mole of a dipositive ion, or one-third mole of a tripositive ion. Therefore, the ratio of the number of mole of uni-, di- and tri-positive ion discharged by one mole of electrons is 1:0.5:0.33, or 3:2:1.

The quantity of electricity required to discharge one mole of a univalent ion, is one Faraday. It is equal to 96, 500 coulombs of electricity. This is the quantity of electricity that passes when one Avogadro number (6.02×10^{23}) of electrons passes.

EXERCISE 3B

How many Faradays of electricity is required to liberate one mole of each of the following ions

- (i) Al^{3+} from fused aluminium chloride,
- (ii) Cu^{2+} from copper(II) tetraoxosulphate(VI) solution,
- (iii) Ag^{+} from silver trioxonitrate(V) solution?

WORKED EXAMPLES

- (1) Calculate the quantity of electricity (in coulombs) required to liberate the following masses of substances from their ions:
- (a) 8 g of oxygen
 - (b) 2.24 dm^3 of hydrogen at s.t.p.
 - (c) 10.8 g of silver
 - (d) 4.48 dm^3 of oxygen at s.t.p.
 - (e) 10.0 g of copper from Cu^{2+} compound.

SOLUTION

- (a) Oxygen carries double negative charge.
 $\hat{\wedge} \hat{\wedge} \hat{\wedge} 1 \text{ mole of oxygen atom is liberated by 2 Faradays.}$
 $\text{O}^{2-} \hat{\rightarrow} \text{O} + 2\text{e}^{-}$
 $2\text{O} \hat{\rightarrow} \text{O}_2$
Atomic mass of oxygen = 16
Molar mass of oxygen = 32 g.

$\therefore 8 \text{ g of oxygen} = \frac{8}{32} \text{ mole.}$

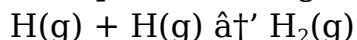
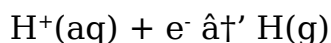
1 mole is liberated by 2 F — 96500 coulombs.

$$\therefore \frac{8}{32} \text{ mole is liberated by } \frac{2 \times 96500}{1} \times \frac{8}{32} \text{ coulombs}$$

$$= 48250 \text{ coulombs.}$$

- (b) 1 mole of hydrogen occupies 22.4 dm^3 at s.t.p. Hydrogen ion is unipositive.

\therefore 1 mole of H^+ is liberated by 1 Faraday of electricity. But 1 mole of hydrogen molecules is made up of 2 mole of hydrogen atoms, liberated by 2 Faradays of electricity. Now, two mole of hydrogen atoms is liberated by 2 Faradays of electricity.



$\therefore 22.4 \text{ dm}^3$ of H_2 is liberated by 2 Faradays of electricity.

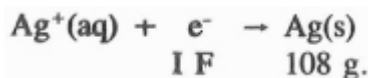
$\therefore 2.24 \text{ dm}^3$ of hydrogen at s.t.p. is liberated by

$$\frac{2}{22.4} \times 2.24 \text{ Faradays of electricity.}$$

$$= \frac{2}{22.4} \times 2.24 \times 96500 \text{ coulombs.}$$

$$= 19300 \text{ coulombs.}$$

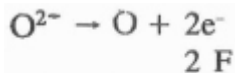
- (c) Silver ion is unipositive.



\therefore 1 mole of silver is liberated by 1 Faraday.

\therefore 108 g of silver is liberated by 96500 coulombs.

\therefore 10.8 g of silver is liberated by 9650 coulombs.



- (d) $2\text{O} \rightarrow \text{O}_2$

1 mole of oxygen molecules = 2 mole of atoms.

1 mole of oxygen atoms is liberated by 2 Faradays.

\therefore 2 mole of oxygen atoms is liberated by 4 Faradays.

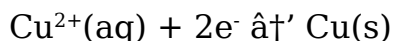
\therefore 1 mole of oxygen molecules is liberated by 4 Faradays, i.e. 22.4 dm^3 of oxygen at s.t.p. is liberated by 4 Faradays.

$$\therefore 4.48 \text{ dm}^3 \text{ of oxygen at s.t.p. is liberated by } \frac{4 \times 4.48}{22.4} \text{ F}$$

$$= \frac{4 \times 4.48}{22.4} \times 96500 \text{ coulombs}$$

$$= 77,200 \text{ coulombs.}$$

- (e) 1 mole of copper is deposited by 2 Faradays because copper ions are dipositive.



∴ 64 g of copper is deposited by 2. Faradays

∴ 10 g is deposited by $\frac{2}{64}$ ∴ 10 Faradays

$$= \frac{2 \times 10}{64} \times 96500 \text{ coulombs}$$

$$= 30,156 \text{ coulombs}$$

(2) A current of 0.5 ampere was passed through silver trioxonitrate(V) solution and the solution of a salt of a metal A in series for 16 minutes. If 0.54 g of silver and 0.28 g of A are deposited at the different cathodes. what is the oxidation state of A? [Ag = 108, A = 112]

SOLUTION

Ratio of the number of mole of A : Ag deposited is

$$\frac{0.28}{112} : \frac{0.54}{108}$$

$$= 0.0025 : 0.005$$

$$= 1 : 2$$

Since Ag^+ is unipositive, A is dipositive (A^{2+})

EXERCISE 3C

During the electrolysis of a Cu (II) salt solution, 0.4 mole of copper was deposited. This shows that the quantity of electricity passed was

- A. 0.2 Faradays
- B. 0.4 Faradays
- C. 0.8 Faradays
- D. 1.6 Faradays
- E. 3.2 Faradays

(WAEC)

3.11 Uses of Electrolysis

- (1) Purification of copper: Use is made of the fact that the

electrolysis of aqueous copper(II) tetraoxosulphate(VI), using copper electrodes, deposits copper at the cathode while the copper anode ionises and goes into solution. The impure copper rod is made the anode, and a thin plate of pure copper made the cathode of the electrolytic cell, with aqueous copper(II) tetraoxosulphate(VI) as electrolyte. During the electrolysis only pure copper from the impure anode goes into solution, and is deposited at the cathode. Any impurities remain behind at the anode or in solution.

(2) Electroplating: Metals that rust, such as iron, are coated with another metal to prevent rusting. The metal to be electroplated is made the cathode in an electrolysis of a salt of the metal to be used for coating. The protecting metal is evenly deposited on the cathode during electrolysis.

(3) Manufacture of some chemicals such as sodium hydroxide.

(4) Extraction of active metals such as sodium, aluminium, calcium, and isolation of active non-metals such as chlorine, oxygen.

(5) Estimation of the atomic mass of a metal.

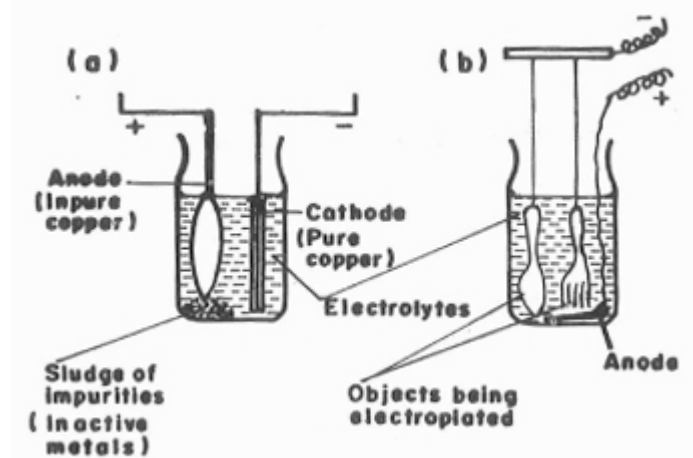


Figure 3.22 Uses of electrolysis (a) Purification of copper (b) Electroplating

WORKED EXAMPLE

0.53 g of copper is deposited by 4 amperes of current flowing for 6 minutes 40 seconds. If copper is known to be divalent, what is its atomic mass?

SOLUTION

Quantity of electricity that passed

$$= \text{time in seconds} \times \text{current in amperes}$$

$$= 400 \text{ s} \times 4 \text{ coulombs} = 1600 \text{ coulombs.}$$

1600 coulombs deposit 0.53 g of copper

$$\hat{\wedge} \text{ } 96,500 \text{ (1 Faraday) deposit } \frac{0.53}{1600} \times 96500 \text{ g} \\ = 31.97 \text{ g.}$$

But 1 Faraday should deposit $\frac{1}{2}$ mole of a divalent metal.
 $\hat{\wedge}$ 31.97 g is half a mole of copper.

$\hat{\wedge}$ One mole of copper = 2 \times 31.97 g = 63.94 g.
 i.e, Atomic mass of copper = 63.94 g.

3.12 Conductance of Strong and Weak Acids and Bases

The ease with which different solutions of acids, bases and salts conduct electricity is described as their conductance. Conductance can be likened to the resistance of electrical wires. Table 3.3 compares resistance with conductance.

TABLE 3.3 COMPARISON OF RESISTANCE AND CONDUCTANCE

Resistance	Conductance
1. A measure of the difficulty of flow of current through a conducting wire.	A measure of the difficulty of flow of current through an electrolyte.
2. Depends on the nature, thickness and the length of wire.	Depends on the nature, and concentration of electrolyte.
3. Measured in ohms.	Measured in reciprocal ohms (mhos).

For purposes of comparison, conductance is viewed in two ways. Conductance due to the nature of the electrolyte is referred to as **specific conductance**. Conductance due to the concentration of the electrolyte is the **molar conductance**. Specific conductance gets smaller as an electrolytic solution is diluted, but molar conductance increases with dilution. The increase in molar conductance with dilution is gradual for strong electrolytes, but very rapid with weak electrolytes. This is because the degree of ionisation of strong electrolytes is fairly constant (almost completely ionised in both concentrated and dilute solutions), whereas the degree of ionisation of weak electrolytes increases very rapidly with dilution. Tables 3.4 and 3.5 illustrate these points.

TABLE 3.4 SPECIFIC CONDUCTANCE OF AQUEOUS POTASSIUM CHLORIDE AT 25°C.

Concentration (mol dm ⁻³)	Specific Conductance (mhos cm ⁻¹)
1.0	0.11173
0.1	0.012886
0.01	0.0014114

TABLE 3.5 MOLAR CONDUCTANCE OF FOUR DIFFERENT ELECTROLYTES AT 25°C.

Concentration	Molar Conductance at 25°C (mhos)			
	HCl	KCl	NaOH	CH ₃ COOH
1.0	333	112	—	—
0.10	391	129	218.2	5
0.01	412	141	238	16
0.005	415.8	143.4	240.5	23
0.001	421	147	244.7	49
0.0005	422.7	147.8	245.6	101
0.00001	426	150	246.1	391

A comparison of the conductance of an electrolyte at any concentration with its conductance at infinite dilution, gives the degree of ionisation of the electrolyte at that concentration. **Infinite dilution** is the dilution attained when the ions are free from the influence of one another.

Chapter Summary

- Electrolysis is the decomposition of an electrolyte by electric current at the electrodes. Positive ions are discharged at the cathode, while negative ions are discharged at the anode.
- The preferential discharge of ions is governed by
 - concentration of the ions.
 - position of the ion in the activity series.
 - nature of the electrode.
- Faraday's laws of electrolysis can be used to determine the quantity of substances liberated during electrolysis.
 - First law: The mass of substances liberated at the electrodes during electrolysis is proportional to the quantity of electricity that is passed.
 - Second law: The relative amounts (number of mole) of elements liberated by the same quantity of electricity is inversely proportional to the charges on the ions of the

elements.

4. Quantity of electricity is measured in coulombs (current in amperes, multiplied by time in seconds).
5. One Faraday of electricity is 96,500 coulombs. This is the quantity of electricity passed when one Avogadro number of electrons (1 mole of electrons) flows through.
Thus, 1 Faraday liberates 1 mole of a univalent ion,
1 Faraday liberates $\frac{1}{2}$ mole of a divalent ion,
1 Faraday liberates $\frac{1}{3}$ mole of a trivalent ion.
6. Conductance is a measure of the flow of electric current through an electrolyte.
7. For strong electrolytes specific conductance decreases with dilution because there are fewer ions. Molar conductance is fairly constant.
8. For weak electrolytes molar conductance increases rapidly with dilution because their ionisation increases with dilution.
9. Electrolysis is employed in:
 - (a) purification of metals.
 - (b) extraction of very active metals.
 - (c) electroplating.
 - (d) manufacture of some chemicals.
 - (e) determination of the stoichiometry of some chemical reactions.

Assessment

1.
 - (a) Describe what happens when copper(II) tetraoxosulphate(VI) is electrolysed with carbon electrodes.
 - (b) How would you purify an impure copper rod?
 - (c) During the electrolysis of a copper(II) salt, the quantity of electricity passed was 9650 coulombs. Calculate
 - (i) the number of mole of copper metal deposited,
 - (ii) the mass of copper deposited.

(WAEC,)
2. Direct current was passed through a concentrated aqueous solution of sodium chloride in an electrolytic cell with platinum electrodes.
 - (a) Name the gas evolved at the cathode.
 - (b)
 - i. What ions were present in large amounts in the solution at the end of the electrolysis?
 - ii. What was the nature of the final solutions?
 - (c) Give one other product formed during the process.
 - (d) If a dilute solution of sodium chloride had been used instead of a concentrated solution, what gas would be evolved at the

anode?

(WAEC,)

3. (a) If two Faradays liberate 1 mole of atoms of a metallic element A, the formula of the oxide and chloride of A are _____ and _____.
(b) Explain why solid sodium chloride does not conduct electricity whereas its aqueous solution does.
(c) Describe an experiment to distinguish an electrolyte from a non-electrolyte.
4. If 75 cm^3 of oxygen is liberated at the anode during the electrolysis of aqueous copper(II) tetraoxosulphate(VI) solution, using inert electrodes, what mass of copper is deposited at the cathode?
5. If 96,500 coulombs of electricity is passed during the electrolysis of copper(II) chloride, how many mole of copper is liberated? Where is it deposited? What mass of copper will this be?
6. A solution of copper(II) tetraoxosulphate(VI) was electrolysed between copper electrodes and the following results were obtained:
Mass of anode before electrolysis = 14.40 g
Mass of anode after electrolysis = 8.00 g
Mass of cathode before electrolysis = 11.50 g
(a) What was the mass of cathode after electrolysis?
(b) Would you expect a change in the colour of the solution after electrolysis?
Explain your answer.
(c) If the electrolysis was carried out for 1 hour 20 minutes with a current of 4 A flowing, determine the value of the Faraday.
(WAEC,)
7. (a) Explain the following observations:
(i) Copper(II) tetraoxosulphate(VI) solution conducts electricity whereas glucose solution does not.
(ii) To protect iron against rusting, it is better to electroplate it with zinc than with tin.
(b) What products are obtained at the electrodes during the electrolysis of each of the following:
(i) concentrated sodium chloride solution, with carbon electrodes;
(ii) molten sodium chloride with a carbon anode and a mercury cathode?
(c) In an electrolytic experiment, 0.6 F of electricity is passed through solutions containing silver trioxonitrate(V) and aluminium tetraoxosulphate(VI) connected in series. Calculate the number of mole of metal deposited in each case. (WAEC,)

EXPERIMENTAL PROJECT

Electrolysis with Tin Can as Electrode

Cut out a strip of tin from an old tin can. Connect it to the positive end of a 6-volt battery with an electric wire. Connect the negative end of the battery to a graphite electrode from an old torch light battery. Dip the graphite and the strip of tin can into 1 M copper(II) tetraoxosulphate(VI) solution as shown in Figure 3P.1 below.

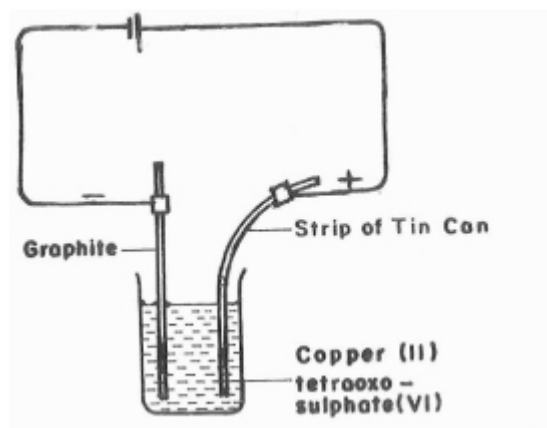


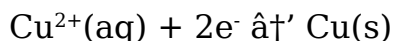
Figure 3P.1 Electrolysis with tin can as electrode

OBSERVATION

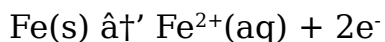
The blue colour of the solution changes to a light green solution after a long period. Copper metal is deposited on the cathode as a brown solid. The tin can is eaten up.

EXPLANATION

At the cathode, copper ions take up electrons to become copper atoms. The atoms are deposited at the cathode. The colour of the solution fades due to loss of Cu^{2+} .



At the anode, iron underneath the tin coating gives off electrons to form Fe^{2+} . Iron is more active than tin, and since it is exposed at the place of cutting, it is ionised in preference to tin.



The solution progressively becomes light green in colour as iron(II) ions go into solution. The tin can is eaten up, and if electrolysis goes on for a very long time, the can crumbles.

Remove the battery and replace it with a sensitive voltmeter (Figure 3P.2). A voltage of about 0.74 volt is recorded. This is a measure of the driving force for the reaction.

$\text{Fe(s)} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Cu(s)} + \text{Fe}^{2+}(\text{aq}); E^\circ = 0.74 \text{ V}$
 It is made up of the two reactions.

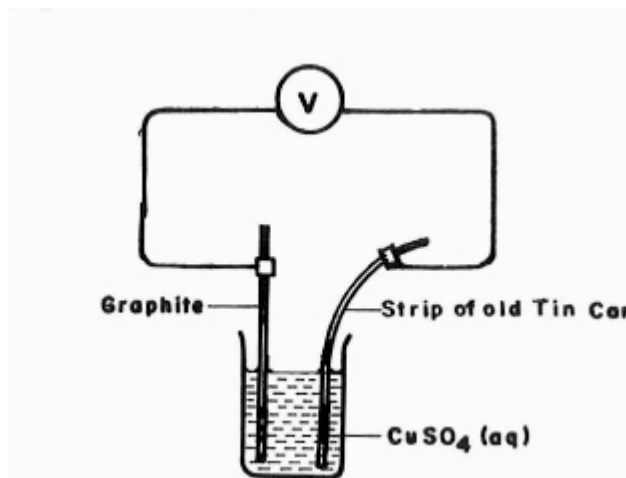
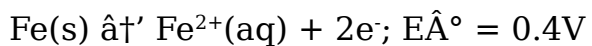


Figure 3P.2 Measuring the e.m.f. of a cell of tin can in CuSO_4 solution

Use other metals such as copper, aluminium, magnesium and tin as anode in the electrolysis, and different electrolytes. Offer explanations for your observations following the example above.