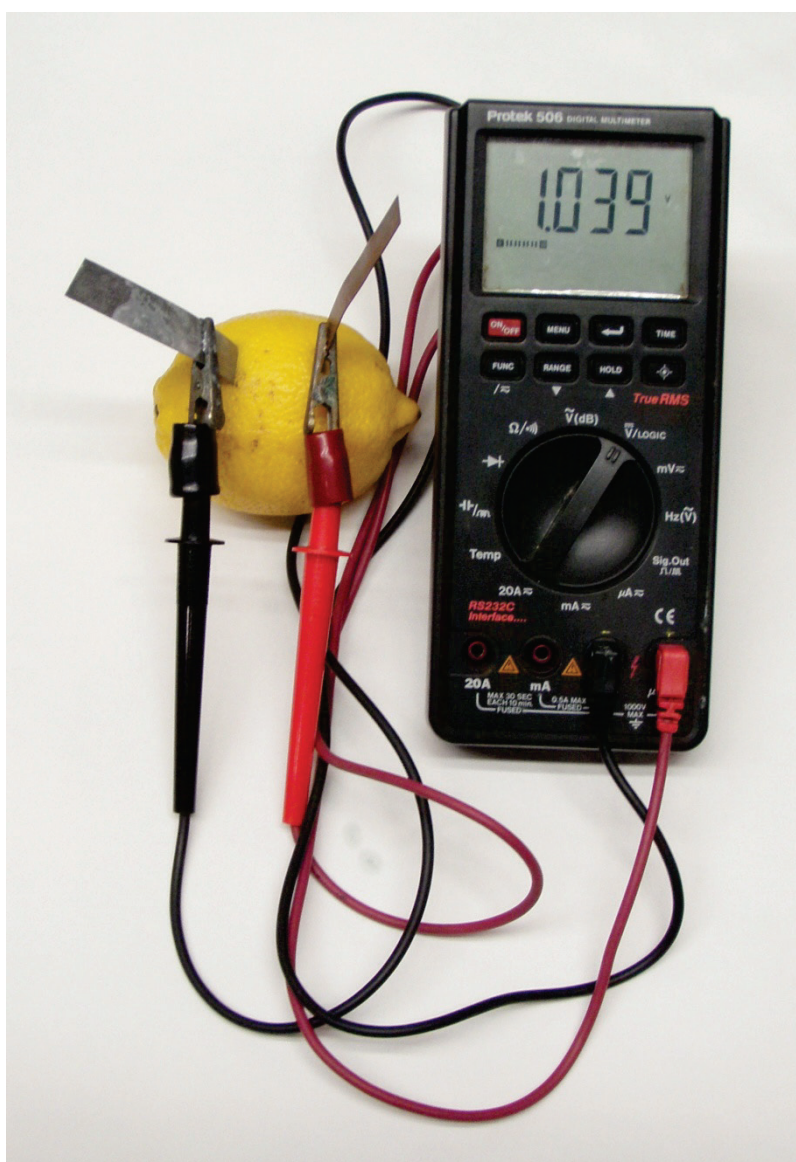# Experiment 13

The Electrical Control of Chemical Reactions

The Task

In this experiment you will explore the processes of oxidation and reduction, in which electrons flow between materials, and which can be used to generate voltages as a source of energy for driving other reactions (as in the case of a battery). You will also design strategies for the plating of electrodes with different metals.

Skills

At the end of the laboratory session you should be able to:
- dilute a stock solution,
- use a multimeter,
- extract simple mathematical relationships from graphical data.

Other outcomes

- You will develop an understanding of galvanic cells and how they are built.
- You will develop an understanding of how concentration differences can be used to generate a voltage.
- You will develop an understanding of metal electro-plating and dissolution.

The Assessment

You will be assessed on your use of the multimeter to identify the anode and cathode of an electrochemical cell.

Introduction

In this experiment you will look at a class of reactions where there is a transfer of electrons between different chemical species. These reactions are called reductions and oxidations and they can be either spontaneous or non-spontaneous. They occur spontaneously in batteries, in the protection of iron and other metals from corrosion, and sometimes in electroplating. Non-spontaneous reactions involving electron transfer are used for making gases (*e.g.* hydrogen and chlorine gas), purifying metals (*e.g.* magnesium, copper and aluminium) and in non-spontaneous electroplating. Many measuring devices (*e.g.* the pH meter) also rely on the transfer of electrons between species.

In general, a gain of electrons is termed *reduction* and a loss of electrons is termed *oxidation*. Electrons cannot just be created from nothing, so oxidation and reduction reactions always occur together and involve the transfer of electrons from one species to another.

You will use three different systems in this experiment to study the transfer of electrons: an electrochemical cell, an electrolytic cell and a concentration cell.

Safety

Chemical Hazard Identification

magnesium metal – Hazardous. Contact with acids liberates flammable hydrogen gas.

copper(II) sulfate – Hazardous. Moderate toxicity, irritant.

iron(II) sulfate – Hazardous. Moderate toxicity, irritant.

zinc sulfate – Hazardous. Low to moderate toxicity, irritant.

sodium sulfate – non-hazardous. Low to moderate toxicity, low irritant.

magnesium sulfate – non-hazardous. Low to moderate toxicity, low irritant.

Risk Assessment and Control

Minimal risk.

Avoid skin contact with solutions.

Waste Disposal

The **zinc**, **copper** and **iron** electrodes and the **iron nails** should be washed and placed back on the front desks, so that they can be reused. The **magnesium ribbon** should be placed in the container labelled "Magnesium Waste" in the fumehood. The **magnesium** and **iron sulfate** solutions can be poured down the sink with water. All **copper** and **zinc sulfate** solutions should be tipped into the "Heavy Metals" bucket in the fumehood. In Part E, use a 400 mL beaker on your desk to collect your waste **copper sulfate solution** as you make your dilutions. Then pour it into the Heavy Metal waste bucket in the fumehood.

Experimental

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This experiment is to be carried out in pairs.

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Part A   Depositing a metal from solution

Let's start with the spontaneous reduction of metal cations (*i.e.*, the addition of electrons to positively charged metal ions) to result in the solid metal (neutral charge) being deposited. The cations in this case will be Cu^{2+}.

(A1)   Choose one of the following metals and place it in a clean large test-tube.
   - zinc;
   - magnesium, cleaned with emery paper or steel wool;
   - iron nail, cleaned with emery paper or steel wool.

(A2)   Pour 5 mL of the 0.1 M copper sulfate solution into the test-tube so that approximately ¾ of the metal is covered.

(A3)   Pour the same volume of copper sulfate solution into a clean empty test-tube as a control.

(A4)   Leave for 15 minutes before making your final observations of both test-tubes. **Record your observations in your logbook**. (Continue with Part B while waiting for this reaction.)

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Some useful terminology for your logbook

The process by which copper(II) ions in solution are deposited as copper metal can be represented by the following *half-equation*.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
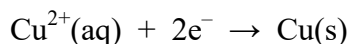
This half-equation shows that electrons are required for the copper(II) ions in solution to be converted to copper metal.

The process (half-equation) in which a species *gains* electrons is called **reduction**.

The other process, in which a species *loses* electrons, is called **oxidation**.

In Part A, both oxidation and reduction are occurring together, at the surface of the metal. In later parts of this experiment, the oxidation and reduction reactions will be separated from each other, occurring at the surface of separate **electrodes** in separate beakers. Such electrodes are given special names: reduction always occurs at the **cathode**, whilst oxidation always occurs at the **anode**.

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For your logbook:

Was copper deposited onto the metal?

What was the source of the electrons that reduced the Cu^{2+}?

If you put a piece of copper metal into the test-tube of copper sulfate, what half reaction(s) would you expect to occur? What would you expect to observe? (Feel free to try it out.)

Measuring the direction of electron flow using a multimeter

You are now going to use a multimeter to monitor the flow of electrons as they are transferred from one species to another. To measure the electron flow in a redox reaction, you first need to separate the reduction reaction from the oxidation. To do this you will make a galvanic cell, or battery, consisting of two 100 mL beakers joined by a piece of wire and a salt bridge. The idea is that the two half reactions, oxidation and reduction, occur at separate electrodes in separate beakers. For the reaction to proceed, the electrons must be transferred between the electrodes along the wire. This chemically-driven current can be measured by inserting a multimeter into the circuit. The salt bridge is necessary to complete the circuit to maintain electroneutrality and allow the current to flow. We will begin with a quick exercise to help you become familiar with the multimeter. Throughout this experiment, you may need to refer to this section so that you can work out the direction of electron flow in your electrochemical cells.
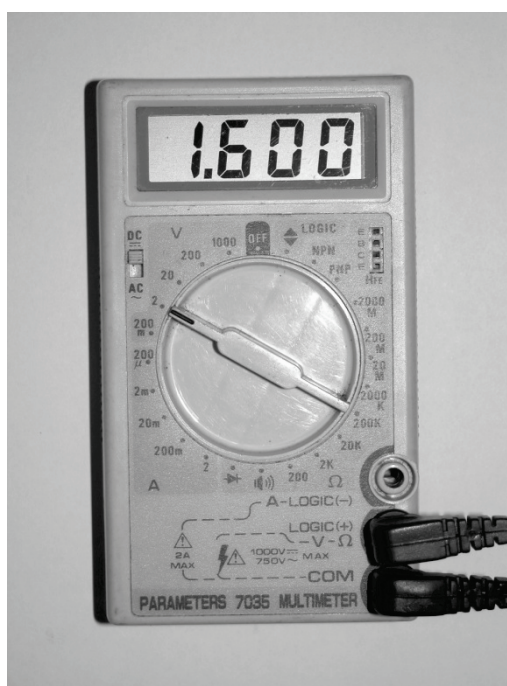

Figure 1: Photograph of a multimeter.

A multimeter is an instrument that measures the voltage (in volts, V), the current (in amperes, A) or the resistance (in ohms, Ω) depending on the setting. A multimeter is shown in Figure 1, giving a reading of +1.600 volts. Note the symbols V, A and Ω marked outside the setting numbers. You select the quantity to be measured and the scale that is appropriate by turning the central knob.

In this part of the experiment you will use the multimeter to measure the voltage of a battery. The point of this exercise is for you to be able to work out the direction of current flow from the sign of the voltage.

(A5)   Set the multimeter to "2V" and "DC" and measure the voltage of the battery provided. Take careful note of the sign of the voltage and which lead of the multimeter is attached to the battery anode - an electron source. (See Figure 2.) Try swapping the leads around. Record your results in your log book.

In a battery, the electrons flow from the negative to the positive terminal, *via* the device being powered. No electron flow occurs if the battery is not being used.
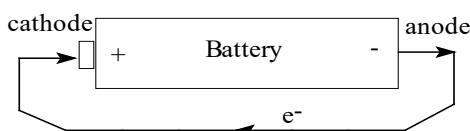

Figure 2: Diagram of a battery

Part B   Separating the half reactions in an electrochemical cell

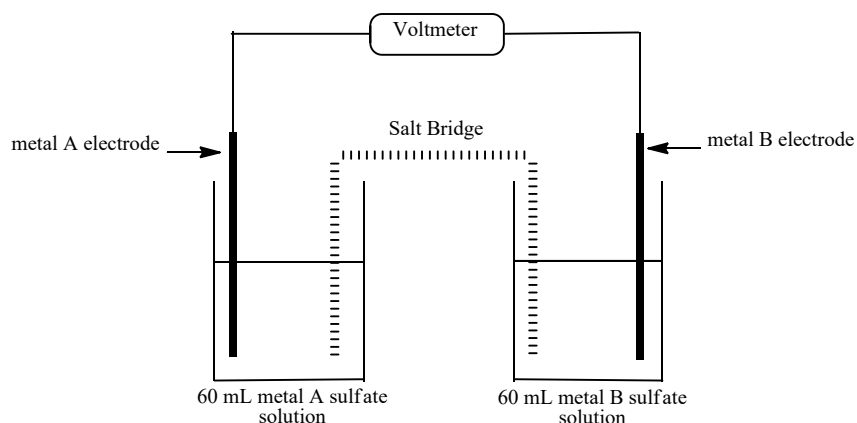| Materials and Chemicals |
|---|
| zinc metal |
| copper metal |
| magnesium metal – clean with emery paper or steel wool |
| iron metal - clean with emery paper or steel wool |
| 0.1 M $ZnSO_4$ |
| 0.1 M $CuSO_4$ |
| 0.1 M $MgSO_4$ |
| 0.1 M $FeSO_4$ |
| 0.1 M Na_2SO_4 |
| 12.5 cm filter paper |
| multimeter with wires and clips |
| 100 mL beakers |

Figure 3: Diagram of an electrochemical cell. If the two electrodes are made of different metals it is termed a galvanic cell, after Luigi Galvani, a pioneer in the field of electricity.

(B1)   Set up an electrochemical cell as shown in Figure 3. You have a choice of 4 metal electrodes: zinc, copper, magnesium or iron. Choose one of them and place it into a solution containing cations of the <u>same</u> metal, *e.g,* the copper electrode into the copper(II) sulfate solution. Choose a <u>different</u> metal/ion combination for the second beaker. NB. Each half-cell must contain the same metal *e.g.* Zn/Zn^{2+} or Cu/Cu^{2+}.

(B2)   **Copy Figure 3 into your logbook and record on it your choices of electrodes and solutions**. Make a salt bridge by folding a 12.5 cm filter paper into a strip about 1 cm wide, bend it in the middle, moisten with 0.1 M Na_2SO_4 and then insert the strip so that it links the solutions in both beakers.

(B3)   Switch the multimeter to "2V" and **record the magnitude and sign of the voltage in your logbook**.

(B4)   Remove the salt bridge and **record the voltage in your logbook**.

(B5)   Replace the salt bridge.

(B6)   Label each beaker with the metal ion solution it contains. Don't dispose of them until the end of the experiment because they will be reused throughout this practical. Take the metal electrodes out of the solutions when you are not using them.

For your logbook:

The salt bridge is necessary to complete the circuit and allow the current to flow. What species move through the salt bridge? Could you replace the salt-bridge with a wire?

Based on your observed direction of current flow write down the half reactions going on in each half-cell.

When making an electrochemical cell, what would happen if you were to use a different metal for the electrode than the metal ion in solution? (See Part A for an idea.)

Copy Table 1 into your logbook to record your data for the following experiments.

Table 1: Results from Part B.

Multimeter terminals connected to the following electrodes		Sign and magnitude of voltage	Electrons flowed from which metal?	Which metal ion is being reduced?
red	black			
Cu	Fe			
Cu	Zn			
Cu	Mg			
Fe	Zn			
Fe	Mg			
Zn	Mg			

(B7) Complete Table 1 by choosing different combinations of electrodes/solutions and repeating steps (B1) and (B3) for each pair. Determine the direction of electron flow and, therefore, which metal is being deposited. Remember to label your beakers and keep your solutions so that you can use them again.

For your logbook:

Using your results from Table 1, list the four metal ions in order from the one that most readily gains electrons to the one that least readily gains electrons. You have determined the electrochemical series. This series provides the direction of spontaneous current flow and reduction when any two of these half cells are combined in a galvanic cell.

Choose one of the galvanic cells that you made today, draw a diagram of it in your logbook (similar to Figure 3) and label the following:

> *the metals in the electrodes*
> *the metal ions in solution*
> *the anode and cathode*
> *the direction anions and cations are travelling through the salt bridge*
> *the direction of the electron flow in the wire*
> *the metal being deposited onto the electrode*
> *the electrode that is being eroded*

Write the half-equations for the reduction and oxidation reactions that are occurring.

Which two different metals would you use to make a cell with the largest voltage? What would its voltage be?

Which two different metals would you use to make a cell with the smallest voltage? What would its voltage be?

Part C   Voltages due to concentration differences

Up until now we have looked at reactions where there has been a transfer of electrons between two different substances. You are now going to investigate a cell where both of the electrodes are copper and both cells contain copper sulfate solution. This means that no net reaction can occur, since the reduction of Cu^{2+} ions to Cu metal in one cell will be exactly balanced by the oxidation of Cu metal to Cu^{2+} ions in the other cell. However, a voltage between the two half-cells can still be observed when there is a difference in the concentrations of the two copper sulfate solutions. This is an example of a special type of electrochemical cell called a *concentration cell*.

(C1) You need two copper electrodes and 90. mL of 0.10 M copper sulfate solution. Set up the concentration cell as shown in Figure 4. Fill one beaker with 60. mL of the 0.10 M copper sulfate solution. This half-cell remains unchanged for the duration of the experiment.

(C2) Dilute the remaining 30. mL of solution with 30. mL of deionised water to give 60. mL of 0.050 M copper sulfate solution and transfer it to another beaker. This half-cell undergoes a series of dilutions during the experiment.

(C3)   Prepare a new salt bridge as described in step (B2) and set up the cell and multimeter as shown in Figure 4.
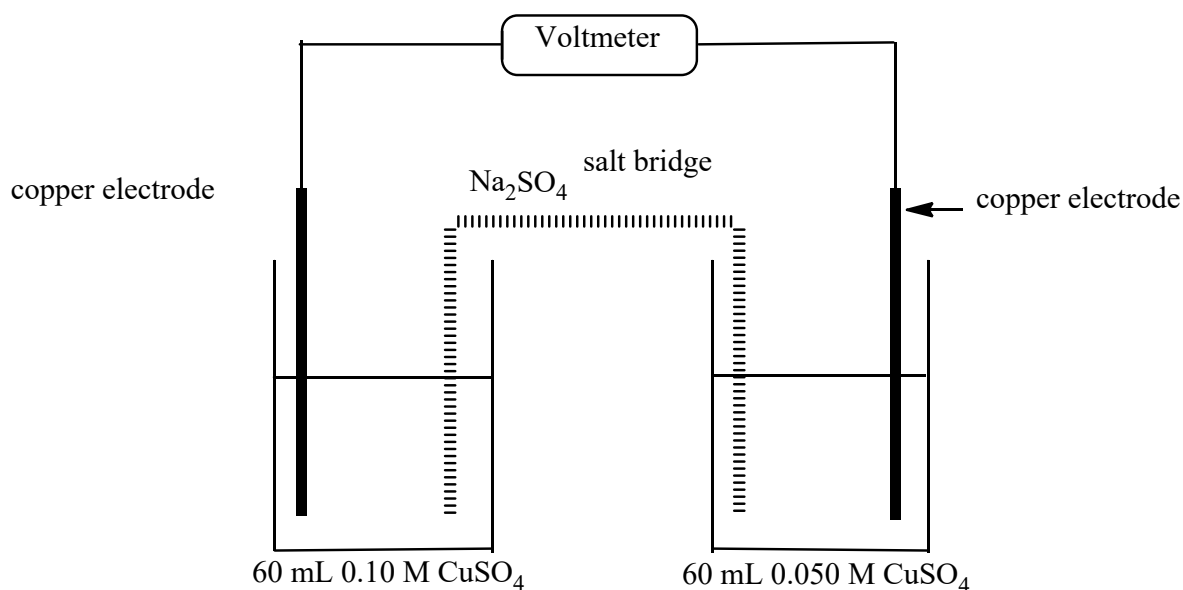
(C4)   Set the multimeter to "200 mV".

Figure 4: Concentration cell

(C5)   **Record the voltage and the concentration of CuSO$_4$ in both beakers in a Table in your logbook.**

(C6)   Now replace the 0.050 M solution with a 0.025 M solution, leaving the 0.1 M solution in the other beaker unchanged. (To halve the concentration, take 30. mL of your current solution in a measuring cylinder and make the volume up to 60. mL with deionised water.) **Record the concentrations of CuSO$_4$ in both beakers and the new voltage in the Table in your logbook. Make sure not to change the orientation of the salt bridge relative to the two beakers.**

(C7)   Continue to replace the diluted solution with one diluted by a further factor of 2, recording the voltage and concentrations for each successive dilution until you have collected 8 sets of readings. (The last concentration should be 0.00039 M.)

For your logbook:

On the graph paper provided plot a graph of voltage versus *–log[conc] for your concentration cell.*

Which of the following mathematical relationships between the voltage, V, and the concentration, C, best describes your graph? (Feel free to try make any other graphs which might help you decide.)

$V = a + bC$, $\qquad\qquad$ $V = ae^{bC}$, $\qquad\qquad$ $V = a + b\,logC$ $\qquad\qquad$ $V = a\,logC$

Describe how this could be used to measure an unknown concentration of copper(II) ions in solution.

From the observed sign of the voltage, in which beaker was oxidation occurring?

Part D   Plating

In Part A, the Cu^{2+} ions from solution received electrons from the metal electrode and became copper metal, *i.e.*, the copper metal was spontaneously plated onto the different metal electrodes.

In Part C, *via* the multimeter you detected the transfer of electrons from one species to the other *via* the wire. Although you could not observe it directly, this transfer of electrons results in the dissolution of one electrode and the plating of the metal at the other.

For your logbook:

Use your results from Parts A and C to determine the following. You have four solutions, each containing a different metal ion: i.e. Fe^{2+}, Cu^{2+}, Zn^{2+} and Mg^{2+}. Which metals would <u>*spontaneously*</u> *plate onto the following metal electrodes?*

$\qquad\qquad$ *Iron* $\qquad\qquad$ *Copper* $\qquad\qquad$ *Zinc* $\qquad\qquad$ *Magnesium*

Electrons can be made to flow in the opposite direction to that of the spontaneous flow in a galvanic cell by the application of a voltage from an external source, *i.e.* a power pack or battery. Such a cell no longer spontaneously produces its own voltage, in contrast to an electrochemical or galvanic cell. Instead, an applied voltage is used to drive a non-spontaneous reaction; this type of cell is termed an *electrolytic cell* (literally "splitting *via* electricity"). Cells of this type are used in the process of electroplating.

For your logbook:

You have a powerpack (to apply an external voltage) and four solutions, each containing a different metal ion: viz. Fe^{2+}, Cu^{2+}, Zn^{2+} and Mg^{2+}. Which metals would require a power supply in order to be plated onto the following metal electrodes?

$\qquad\qquad$ *Iron* $\qquad\qquad$ *Copper* $\qquad\qquad$ *Zinc* $\qquad\qquad$ *Magnesium*

(D1)   Set-up an electrolytic cell as shown in Figure 5. Use 60 mL of 1.0 M zinc sulfate solution and peg your electrodes to the opposite sides of the 100 mL beaker. Make sure the power pack terminals and the electrodes are the right way around and that the alligator clips are separated from each other,
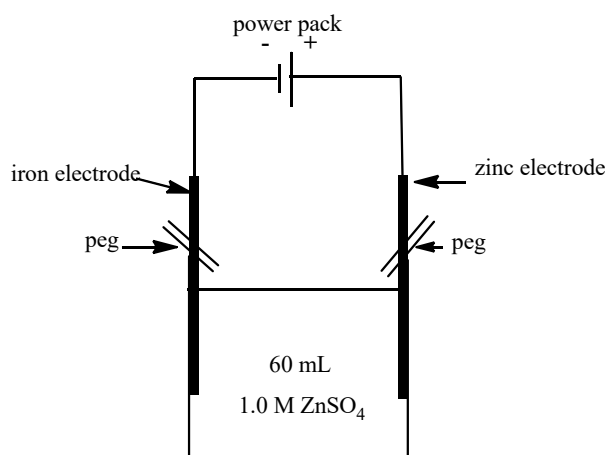

Figure 5: Diagram of an electrolytic cell.

(D2)   After 1-2 minutes disconnect your circuit (take off one of the alligator clips). **In your logbook**, describe what has happened to the iron electrode.

(D3)   Change over the positive and negative terminals on your electrolytic cell and re-connect the circuit for 1-2 minutes. **In your logbook**, describe what has happened to the iron electrode following the reversal of the current.

Group Discussion

Which choice did people make for the battery with the highest voltage?

What happened to the iron electrode when an external power source was applied?

Why does a concentration cell work? Put another way, why can we get electrical work out of a difference in concentration between the two half-cells? Why, do you think, the voltage depends on concentration?