UNIT 3

Electrochemistry

Unit Outcomes

After completing this unit, you will be able to:

- *understand how a chemical reaction produces an electric current and how electricity brings about chemical reactions in electrochemical cells;*
- *understand the differences between metallic conduction and electrolytic conduction;*
- *develop skills in writing the oxidation half-reaction, reduction half-reaction and cell reaction for the electrolysis of molten electrolytes that occur in electrolytic cells;*
- *know three types of voltaic cell;*
- *understand the difference between electrolytic cells and voltaic cells;*
- *appreciate the industrial applications of electrolysis in the production of certain metals, non metals and chemicals and electroplating, and purification of metals;*
- *demonstrate scientific inquiry skills: observing, comparing and contrasting, measuring, asking questions, designing experiment, interpreting data, predicting, classifying, communicating and problem solving.*

MAIN CONTENTS

3.1 INTRODUCTION

Competencies

By the end of this section, you will be able to:

- explain electrochemistry;

Activity 3.1

Discuss the following in groups and one of your group members will present your ideas to the class.

Dry cells which we use in portable radios and flashlights are energy converters.

a Peel the external cover of a dry cell battery and observe the components. How many different components do you see? What are they?

b What type of energy do we get from dry cells? How does the cell generate this energy?

Electrochemistry is a field of chemistry that deals with the relationship between electrical energy and chemical energy. It is a field of chemistry concerned with processes that bring about chemical reactions (*changes*) using electricity or generating electrical energy from chemical reactions. Thus, electrical energy and chemical energy are inter-convertible.

The devices that convert chemical energy to electrical energy or electrical energy to chemical energy are called electrochemical cells. These cells can be classified as electrolytic cells and galvanic or voltaic cells. Electrolytic cells use electrical energy to bring about chemical changes that produce many desirable substances in our daily lives. Galvanic or voltaic cells convert chemical energy to electrical energy. The cells we use in flashlight batteries, wrist watches, cameras and car batteries are examples of Galvanic cells. The reactions between the chemicals in these cells are responsible for the generation of electricity.

Electrochemistry has practical applications in our modern world and in everyday life. Electrolysis is used to manufacture metals like sodium, aluminium; non-metals like chlorine, hydrogen and compounds like sodium hydroxide and sodium hypochlorite. Electrochemistry also has a role in the production of dry cells and lead storage batteries used in the automotive industry.

3.2 ELECTRICAL CONDUCTIVITY

Competencies

After completing this subunit, you will be able to:

- define electrical conductivity;
- explain metallic conductivity;
- explain electrolytic conductivity;
- distinguish between metallic and electrolytic conduction;
- distinguish between weak and strong electrolytes;
- use conductivity apparatus to test the conductivity of substances.

Why do metals conduct electricity? Do you know any non-metal, which conducts electricity? Electrical conductivity is the capacity of a substance to transmit electricity. The materials that allow the passage of electricity through them are called electrical conductors.

Conductivity apparatus is used to test the conductivity of different solid substances or that of aqueous solutions of different compounds. The basic components of conductivity apparatus include electric wires, electrodes, a d.c. source or dry cells, a switch and light bulb. The components of the apparatus can be connected to one another as shown in Figure 3.1.

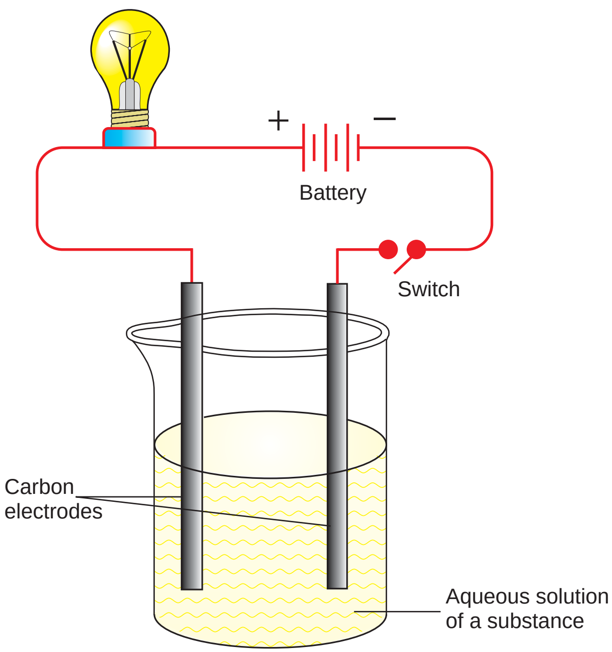


Figure 3.1 Conductivity cell.

Depending on the nature of the particles responsible for the flow of electric charges through conductors, electrical conductivity can be classified as metallic conductivity or electrolytic conductivity.

a) *Metallic conductivity*

Activity 3.2

1. With the help of your teacher collect pieces of iron bars, zinc metal, sodium chloride crystal, rubber stoppers, rubber bands, coins, stone, glass, pieces of dry wood, a spoon, a pencil, chalk and solid sulphur.
2. Identify the substances that conduct electricity and classify them as conductors and non-conductors.
3. From your observations above, (a) what type of solids conduct electricity, (b) why do you think some of the materials conduct electricity? (c) Does graphite have the same nature as the other conductors of electricity?

Discuss in groups and present it to the class

Why do metals transmit electric current? What are the charge carriers in metals? Metallic conductivity refers to the transmission of electric current through metals. This transmission is directly related to the structure of metals. In atoms of metals, the valence electrons are bounded very loosely to their respective nuclei and move very easily throughout the metal. This means metals contain electrons that do not have fixed positions and are relatively free to move. These electrons are called free electrons or mobile electrons or delocalized electrons. Thus, the structure of the metals can be regarded as a series of positively charged metal ions, or cations, in a sea of negatively charged electrons.

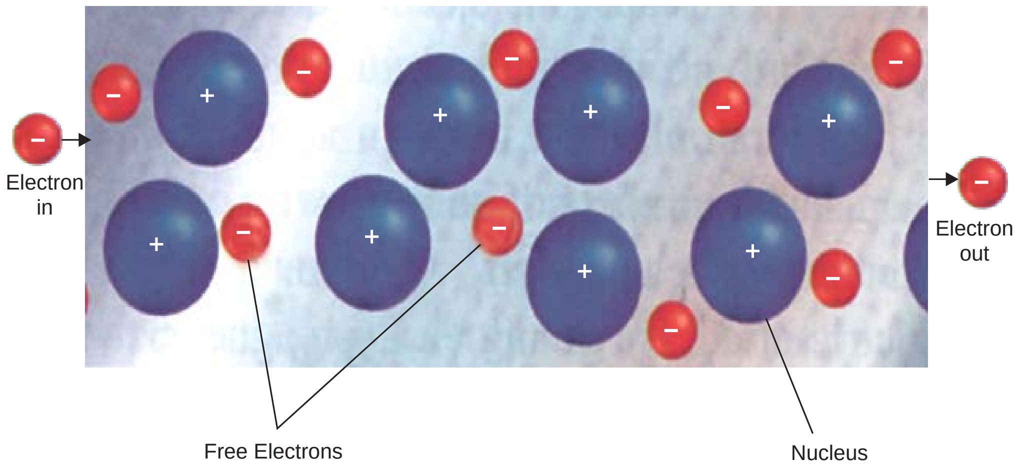


Figure 3.2 Electrical conductivity in metals.

The electrons entering the metal displace (repel) the freely moving electrons at the point of entry. The displaced electrons occupy new positions by pushing neighbouring electrons ahead. This will continue until electrons are forced out of the wire at the opposite end. So, metallic conductivity is caused by the flow of mobile electrons due to repulsion exerted on them from the electrons entering the metal from the source of electricity. The charge carriers in metallic conduction are electrons. Hence, metallic conductivity is also called electronic conductivity.

Non-metals are generally non-conductors of electricity, because they do not have freely moving electrons. Graphite is a form of carbon in which the carbon atoms are bonded in trigonal planar fashion to the three other carbon atoms, to form inter-connected hexagonal rings, as shown in Figure3.3. Electrons move freely through the hexagonal layers, making graphite a good conductor of electricity.

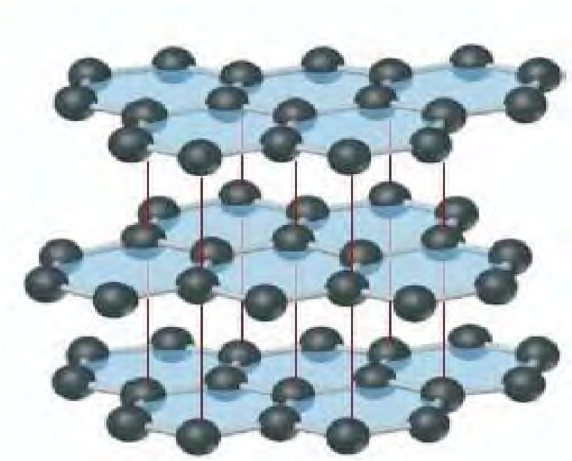


Figure 3.3 Structure of graphite (The blue colour is added to emphasize the planarity of the carbon layers.)

b) *Electrolytic conductivity*

Electrolytes are substances that transmit electricity in a molten state or in aqueous solution. Based on their degree of ionization or the extent to which they produce anions and cations, electrolytes can be classified as strong electrolytes or weak electrolytes. Strong electrolytes ionize almost completely in aqueous solutions. Weak electrolytes ionize only slightly. When electrical potential is applied through an electrolyte solution, the positive ions (*cations*) move in one direction and the negative ions (*anions*) move in the opposite direction. This movement of ions through the electrolyte, brought about by the application of electricity, is called electrolytic conductivity. Hence, the charge-carriers in electrolytic conductivity are ions (*anions and cations*).

Project 3.1

Construct a conductivity apparatus in your group. To construct the apparatus, you will need a light bulb, three dry cells, some electric wire, two graphite electrodes and a switch. You can get the graphite electrodes by peeling off two old dry cells. A graphite electrode is the long cylindrical black rod inside the cell. Ask your teacher for further assistance. Assemble the materials as shown in Figure 3.4. Demonstrate the experimental set-up to the class.

Experiment 3.1

Conductivity of electrolytes

Objectives: To test the conductivity of different electrolytes.

Materials required: Conductivity apparatus, distilled water, table salt, copper sulphate, hydrochloric acid, sodium hydroxide, acetic acid, ammonia solution, molten lead bromide and sugar solution.

Procedure:

1. Arrange the conductivity apparatus as shown in Figure 3.4.

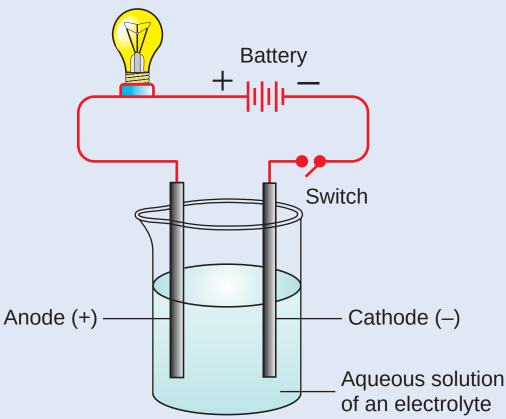


Figure 3.4 Conductivity of electrolytic solution.

2. Pour some distilled water in the beaker, dip the electrodes into the water and turn the switch on.
3. Repeat the experiment with separate solutions of table salt, copper sulphate, hydrochloric acid, sodium hydroxide, acetic acid, ammonia and sugar solutions (*use 1.0 M solutions of each*).

***Observations and Analysis*:**

a Does the bulb glow when the switch is turned on?

b Solutions of which substances make the bulb glow and not glow, when you turn on the switch?

c Solutions of which substances make the bulb to glow with a:

i bright light?

ii dim light?

d Classify the substances used in this experiment as strong conductors, weak conductors and non-conductors by completing the table below:

Strong conductors	Weak conductors	Non-conductors

e Which substances in the experiment are used as:

i strong electrolytes ii weak electrolytes

Write a laboratory report on what you have observed and submit to your teacher.

Exercise 3.1

1. Explain the difference between i) metallic and electrolytic conductivity ii) electrolyte and non-electrolyte.
2. Why do NaCl and $CaCl_2$ conduct electricity when they are dissolved in water or when they are in the molten form, but not in the solid state?
3. Why are solutions of strong electrolytes better conductors of electricity than weak electrolytes?

The substances that do not transmit electricity either in solution or in a molten state are called non-electrolytes. Ionic compounds are non-conductors of electricity in the solid state. This is because their ions are held at fixed positions and cannot move. Other examples of non-electrolytes include sugar, ethanol, oil, benzene, and liquid nitrogen.

3.3 ELECTROLYSIS

Competencies

After completing this section, you will be able to:

- define the term electrolysis;
- define the terms electrode, anode, cathode, electrolyte, anion and cation;

- describe an electrolytic cell;
- draw and label a diagram of an electrolytic cell;
- define the terms half-cell reaction and cell reaction;
- write the oxidation half-reaction, reduction half-reaction and cell reaction for the electrolysis of molten or fused electrolytes;
- perform an activity to show the electrolysis of molten electrolytes.

Activity 3.3

Give an opinion on the following questions and present your ideas to the class.

1. How do you identify whether an electrode is a cathode or an anode?
2. Can you suggest why positive and negative ions are named as cations and anions respectively?

Electrolysis is a process in which electrical energy is used to produce chemical changes. This process is carried out in an electrochemical cell known as an electrolytic or electrolysis cell. A typical electrolysis cell contains a source of direct electric current, an electrolyte and connecting wires that join the source to the electrodes.

Electrodes are strips of metal or graphite that allow electrons to leave or enter the electrolytes. They can be chemically active or inert. Active electrodes directly take part in reactions. Examples include zinc and magnesium. Inert electrodes do not directly take part in chemical reactions. They only serve to transfer electrons. Examples include platinum and graphite.

The electrode connected to the positive terminal of the source is positively charged and is called the anode. It is the electrode through which electrons leave the cell. The electrode connected to the negative terminal of the source is negatively charged and is called the cathode. It is the electrode through which electrons enter the cell.

During electrolysis, the ions of the electrolyte migrate to the electrodes of the opposite charge. The positive ions are attracted to the cathode and are called cations. Since the cathode has excess electrons, the cations will discharge by gaining electrons. This process of gaining electrons is called reduction. The negative ions are attracted by the positive electrode (*anode*) and are called anions. These ions are discharged by losing electrons at the anode. This process of losing electrons is called oxidation.

Thus, the cathode is the electrode at which reduction occurs and the anode is the electrode at which oxidation takes place.

The reaction that takes place at each electrode is known as a half-cell reaction. Oxidation half-reactions occur at the anode and reduction half reaction at the cathode. The net reaction that takes place in the electrolytic cell is known as a cell reaction. This overall reaction is also referred to as an oxidation-reduction reaction or redox reaction. So electrolysis is a process in which electric energy is used to bring about an oxidation-reduction reaction. It is also defined as the decomposition of an electrolyte, using electricity. The process of electrolysis includes electrolyzing aqueous solutions of electrolytes. However, at this level, electrolysis of molten electrolytes will be discussed.

Electrolysis of Molten (Fused) Electrolytes

When ionic solids melt, they dissociates into positive and negative ions that are not held in fixed positions. To understand the chemical reactions that occur during electrolysis, consider a hypothetical electrolyte, MX, that dissociate into M^+ and X^-.

$$MX \xrightarrow{\text{melting}} M^+ + X^-$$

During electrolysis, the cations, M^+ ions, move toward the cathode, gain one electron each and become M atoms. The anions, X^- ions, move toward the anode, lose one electron and become X atoms. The reaction at each electrode and the entire reaction in the electrolytic cell are represented by the following equations.

Cathode reaction: $M^+ + 1e^- \rightarrow M$ (*Reduction-half reaction*)

Anode reac tion: $X^- \rightarrow X + 1e^-$ (*Oxidation half-reaction*)

Cell reaction: $M^+ + X^- \xrightarrow{\text{electrolysis}} M + X$ (*Oxidation-reduction*)

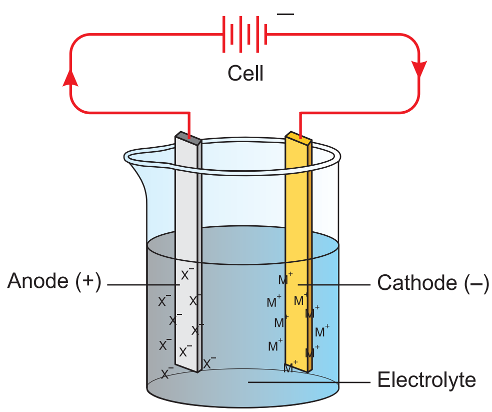


Figure 3.5 Electrolysis of fused Electrolyte, MX.

Here, it is very important to realize that the number of electrons gained by the cations at the cathode is exactly equal to the number of electrons lost by anions at the anode during electrolysis. This is true for any oxidation-reduction (*redox*) reaction. Moreover, oxidation and reduction reactions proceed simultaneously. Reduction and oxidation cannot occur separately. Oxidation is always accompanied by reduction and there cannot be reduction in the absence of oxidation, and vice versa.

Electrolysis of Molten (Fused) lead bromide

Experiment 3.2

Electrolysis of fused lead Bromide ($PbBr_2$)

Objectives: To observe substances produced at the electrodes during electrolysis.

Materials required: Stand and clamp, two graphite electrodes, wires, switch, light bulb, test tube (*bigger in size*), Bunsen burner, lead bromide crystals.

Precaution: Bromine causes very severe burn on the skin.

Procedure:

1. Assemble the materials as shown in Figure 3.6.

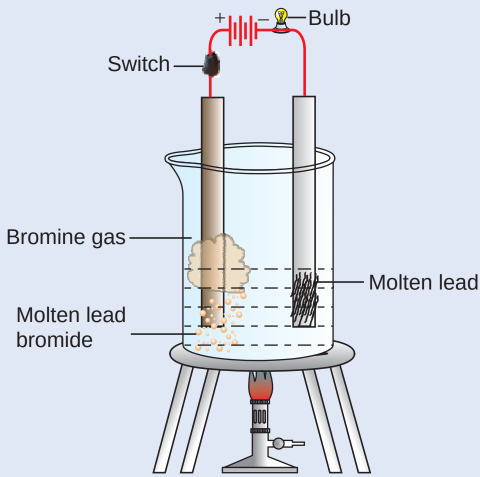


Figure 3.6 Electrolysis of Fused Lead Bromide.

2. Place small amount of lead bromide crystals in a beaker. Insert the two electrodes, as shown in Figure 3.6, until they are in contact with the lead bromide crystals. Then turn on the switch. Does the bulb glow?
3. Heat the lead bromide in a beaker gently, using a Bunsen burner. When the lead bromide melts, turn on the switch.

Observations and Analysis:

1. Does the bulb glow? If yes, what is the reason?
2. Write the dissociation reaction for $PbBr_2$.
3. Identify the ions which migrate to the respective electrodes.
4. Write the products formed at each electrode.
5. Identify the half reactions as oxidation and reduction.

Write a laboratory report on your observation and present to the class.

Exercise 3.2

Consider the electrolysis of KI and NaCl

a Identify ions which migrate towards the anode.

b Identify ions which migrate towards the cathode.

c Write down the half-reactions at the anode and cathode and cell reactions.

d Write the substances produced at the electrodes.

3.4 GALVANIC (VOLTAIC) CELLS

Competencies

After completing this section, you will be able to:

- construct a simple galvanic cell, using strips of zinc, copper, $ZnSO_4$ and $CuSO_4$ solutions;
- mention different types of voltaic cells;
- describe how voltaic cells can be used to make commercially useful batteries;
- distinguish between voltaic cell and an electrolytic cell;
- describe voltaic cells.

Activity 3.4

Discuss the following and present your ideas to the class:

1. Have you seen the expiry date written on dry cells? Can we get the expected amount of electric energy after the expiry date of the cell; why?
2. Do we throw away car batteries when they fail to generate electricity? Explain.
3. Galvanic cells available in the market have positive and negative terminals. Does this show that they also possess an anode and cathode?

In the previous section, electrolytic cells were defined as electrochemical cells in which electricity was used to bring about chemical reactions. The chemical reaction in an electrolytic cell is caused by electricity and is a non-spontaneous redox reaction. This means the reaction can proceed only in the presence of electricity. If we stop passing electricity through the electrolyte, the reaction will stop.

In a Galvanic cell, the reaction that occurs inside the cell is a spontaneous redox reaction. The reaction that occurs inside the cell will proceed on its own without any external influence. This reaction enables a galvanic cell to generate electricity. Therefore, Galvanic cells are electrochemical cells in which spontaneous redox reactions generate electricity. They convert chemical energy into electrical energy.

Galvanic or voltaic cells are classified into primary cells, secondary cells, and fuel cells. For this level, only primary and secondary cells will be discussed.

Primary Cells

Primary galvanic cells are those cells that are not rechargeable. This is because the electrode reaction as well as the entire cell reaction cannot be reversed on recharging. Once the chemicals in the cells that serve as reactants are completely used up, it is not possible to recover them by charging the cells. Examples of primary cells include Daniel's cell and zinc-carbon (*Leclanche*) dry cells. The common feature of all Galvanic cells is that they contain two electrodes in contact with an electrolyte. The electrolyte in a Galvanic cell can be in the form of a solution or a paste. The cells containing electrolytes in the form of solution are called wet cells, and those containing electrolytes in the form of paste are called dry cells.

An example of a wet primary cell is the Daniell cell. It consists of a zinc strip placed in $ZnSO_4$ solution in one compartment and a copper strip placed in copper sulphate, $CuSO_4$, solution in another compartment. Each compartment is called a half-cell, and the reactions occurring in each compartment are called half-cell reactions. The solutions in the two compartments are linked by a salt bridge as shown in Figure 3.7. The salt bridge consists of a delivery tube filled with warm mixture of conc. KCl solution and agar solution, which is then allowed to cool so that it sets in the form of a gel.

Alternately, a porous barrier is used to separate the solutions. The zinc atoms from the zinc electrode lose two electrons each and become zinc ions, Zn^{2+}. The ions enter into the solution, and the electrons remain on the electrode and flow through the external wire to the copper electrode. This situation causes the zinc electrode to be negative and the solution to have an overall positive charge.

On the other hand, in the compartment containing the copper electrode, copper ions, Cu^{2+}, from the solution move to the cathode and gain two electrons each, to become copper atoms and deposit on the surface of the copper electrode. This condition causes the electrode to be positive and the solution to have a negative charge.

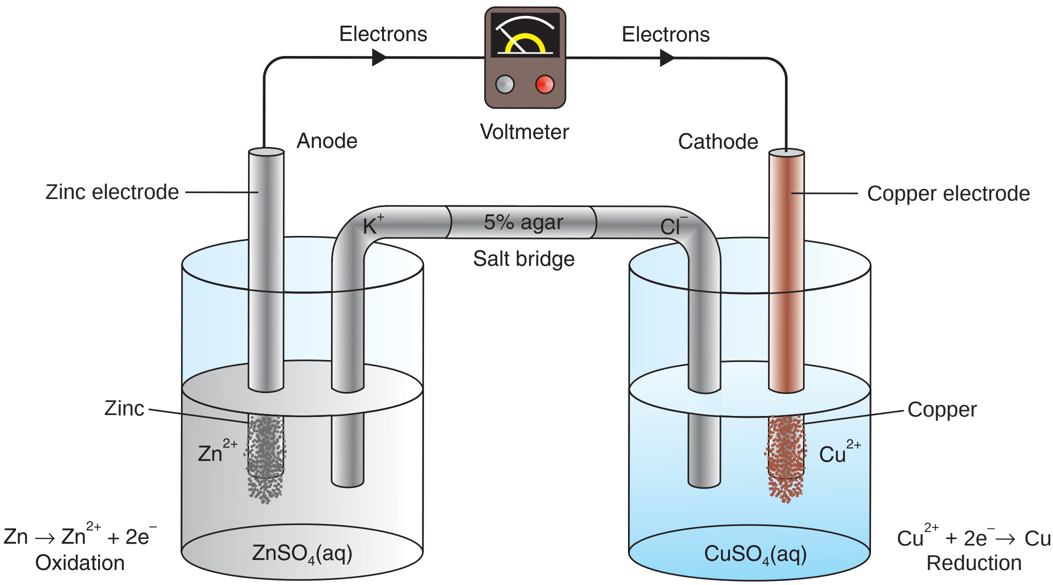


Figure 3.7 The Daniell Cell.

Note that the anode is the negative electrode and the cathode is the positive electrode in galvanic cells, as opposed to the situation in an electrolytic cell. But, it is always oxidation that occurs at the anode and reduction at the cathode.

The half-cell reactions and the cell reaction in Daniell cells are represented as

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

Cathode reaction: $Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$

Cell reaction: $Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$

Due to the oxidation-reduction reaction in the cell, the Daniell cell generates electricity.

What is the purpose of the salt bridge in Figure 3.7?

From the preceding discussion, it is clear that the solution in which the zinc electrode is placed has an overall positive charge while the solution in the copper compartment has a negative charge. Unless the two solutions are neutral, the cell cannot produce electricity. Thus, the purpose of the salt bridge is to:

a maintain electrical neutrality between the two solutions. In this process the anions (*negative ions*) from the salt bridge diffuse into the solution containing the zinc electrodes, and the cations (*positive ions*) diffuse into the solution containing the copper electrode to compensate for the excess positive and negative charges, respectively;

b allow electrical contact between the two solutions;

c prevent mixing of the electrode solutions.

Although, wet cells like the Daniell cell can serve as a source of electricity, they are not portable since they contain solutions. Due to this practical problem of using wet cells, dry cells were developed.

In a dry cell, a moist electrolyte paste is used instead of solutions. This cell was invented by Georges Leclanche, a French chemist.

A zinc-carbon dry cell, which is also called a Leclanche cell (Figure 3.8) is used in devices like portable radios and flashlights. The cell consists of a zinc cup that serves as the anode. The zinc cup is filled with a paste of manganese (IV) oxide, zinc chloride, ammonium chloride and powdered carbon. A graphite rod, immersed in this paste, serves as the cathode.

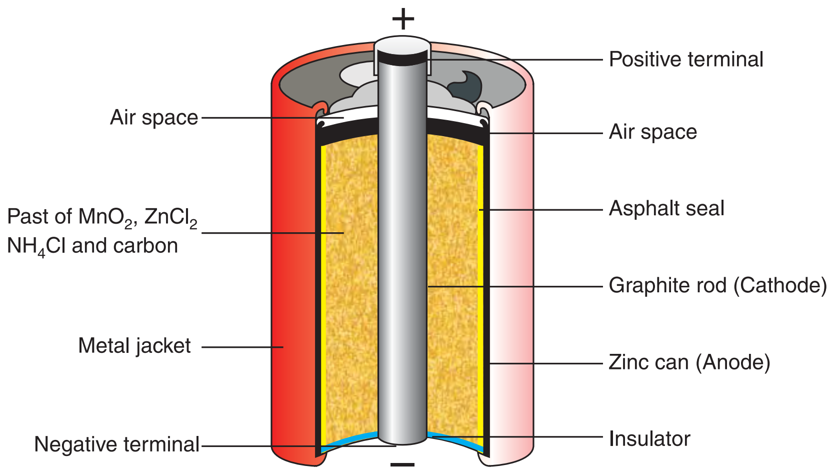


Figure 3.8 Zinc-carbon dry cell (Leclanche cell).

A zinc-carbon dry cell produces electricity as a result of a spontaneous redox reaction. Oxidation occurs at the zinc cup.

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

Reduction takes place at the graphite (*carbon*) electrode.

$$2MnO_2\ (s) + 2NH_4^+\ (aq) + 2e^- \rightarrow Mn_2O_3\ (s) + 2NH_3\ (aq) + H_2O\ (l)$$

A build up of ammonia gas around the cathode may disrupt the current. However, this is prevented by the reaction between Zn^{2+} and NH_3 to form a complex ion, $[Zn(NH_3)_2]^{2+}$ which crystallizes as a chloride salt.

$$Zn^{2+}\ (aq) + 2NH_3\ (g) + 2Cl^-\ (aq) \rightarrow Zn(NH_3)_2\ Cl_2\ (s)$$

The overall reaction occurring in a Leclanche cell is:

$$Zn\ (s) + 2MnO_2\ (s) + 2NH_4Cl\ (aq) \rightarrow Zn(NH_3)_2Cl_2\ (s) + Mn_2O_3\ (s) + H_2O\ (l)$$

There are other examples of dry cells, such as the alkaline dry cell, silver oxide cell, and copper oxide cell.

Exercise 3.3

1. In a Daniell cell, copper and zinc are used as electrodes. Which metal serves as an anode and which one as a cathode? Is the anode the positive or the negative terminal in this cell?
2. Which electrode is negative and which one is positive in the Leclanche cell? Is the polarity of the electrodes in Galvanic cells similar to that of the electrodes in electrolytic cells?
3. Why do we refer to the redox reactions in electrolytic and voltaic cells as non-spontaneous and spontaneous, respectively?

Experiment 3.3

Constructing Simple Galvanic Cells

Objectives: To design and construct a simple Galvanic cell.

Materials required: 1.0 M solutions of $ZnSO_4$, 1.0 M solutions of $CuSO_4$, concentrated KCl solution, zinc and copper strips, electric wires, beakers, a salt bridge, a tomato or lemon, magnesium ribbon, zinc, iron and aluminium metals.

Procedure:

1. Put about 150 mL of 1.0 M $ZnSO_4$ solution in one beaker and the same amount of 1.0 M $CuSO_4$ solution in another beaker. Immerse a zinc strip in the beaker containing the $ZnSO_4$ solution, and immerse a copper strip in the copper sulphate solution. Attach electric wires to the electrodes and a voltmeter as shown in Figure 3.7. Connect the solutions in the two beakers by yarn (*thread used in kerosene stoves*). Soak the yarn in concentrated KCl solution.
2. Insert a magnesium ribbon and a copper strip into a raw tomato or lemon. The two metals should be at least 0.5 cm apart and should not touch each other. Attach magnesium and copper strips to the negative and positive ends of a voltmeter, respectively, using electric wires.

3. Repeat the same procedure using metals like Fe, Al, Zn in place of Magnesium and see which of the metals gives the greatest voltage and which one the least.

Observations and Analysis:

A For the cell in procedure 1

1. What do you observe at each electrode in this cell?
2. What is the direction of electron flow in the external circuit?
3. Which metal serves as the a) anode b) cathode
4. At which electrode does a) oxidation b) reduction occur?
5. Write the a) anode b) cathode and c) cell reaction

B For the cell in procedure 2

1. Do you observe deflection of the pointer in the volt meter?
2. Which of the metals has the greatest voltage and which one the least when coupled with copper?
3. Is there any relationship between the voltage produced and the reactivity of the metals?

Write a laboratory report and submit to your teacher.

Secondary Cells

Unlike primary cells, secondary cells are rechargeable. The electrode reactions can be reversed, and the original reactants can be regenerated. This can be achieved by passing a direct current through the cell. The process is called charging or recharging.

A secondary cell needs to be recharged when it stops producing electricity. A lead storage battery is an example of a secondary cell.

A lead Storage Battery is the common automobile battery that usually delivers either 6 or 12 volts, depending on the number of cells used in its construction. The inside of the battery consists of galvanic cells connected in series. A fully-charged lead-acid cell is made up of a stack of alternating lead and lead (IV) oxide plates isolated from each other by porous separators. The individual cells contain a number of lead anodes connected together, plus a number of cathodes composed of PbO_2, also joined together. These electrodes are immersed in 35% sulphuric acid, which serves as an electrolyte.

A single lead-storage cell delivers 2 volts. Therefore, a 12 V battery contains six cells connected in series.

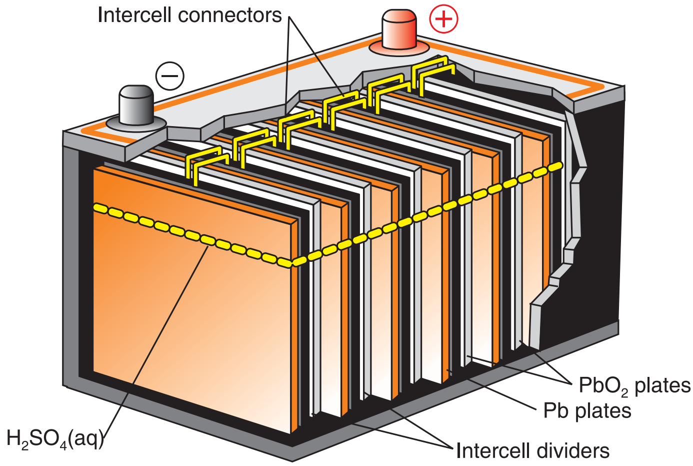


Figure 3.9 Lead - Storage Battery.

When a lead-storage battery is in operation (*on discharge*), the following reactions occur at the electrodes:

Anode reactions: $Pb\ (s) + SO_4^{2-}\ (aq) \rightarrow PbSO_4\ (s) + 2e^-$

Cathode reactions: $PbO_2\ (s) + 4H^+\ (aq) + SO_4^{2-}\ (aq) + 2e^- \rightarrow PbSO_4\ (s) + 2H_2O\ (l)$

and the overall reaction is:

$$Pb\ (s) + PbO_2\ (s) + 4H^+\ (aq)\ 2SO_4^{2-}\ (aq) \rightarrow 2PbSO_4\ (s) + 2H_2O\ (l)$$

From the electrode reactions it can be noticed that $PbSO_4$ is produced at both electrodes.

Unlike primary cells a lead-storage battery is rechargeable when the battery runs down. The electrode reactions can be reversed by placing a potential across the electrodes that is slightly larger than that which the battery can deliver. The reaction that takes place on recharging a lead storage battery is given by the following equation.

$$2PbSO_4\ (s) + 2H_2O\ (l) \rightarrow Pb\ (s) + PbO_2\ (s) + 2H_2SO_4\ (aq)$$

What are the differences between voltaic cells and electrolytic cells?

Activity 3.5

Compare and contrast between voltaic and electrolytic cells. List the differences between voltaic cells and electrolytic cells, and discuss with your classmates.

Exercise 3.4

1. Explain the differences between primary and secondary cells.
2. What substances are used as the anode, cathode and electrolyte in a lead storage battery?
3. What happens to the concentration of sulphuric acid when a lead storage battery is on discharge?
4. Write the overall reactions taking place in a lead storage battery when it is discharging.

3.5 INDUSTRIAL APPLICATIONS OF ELECTROLYSIS

Competencies

After completing this section, you will be able to:

- describe selected industrial applications of electrolysis;

Activity 3.6

1. The copper used for the transmission of electric current is supposed to be 100% pure. What happens if the copper is impure?
2. How many articles in your house are electroplated? Make a list. What is the purpose of electroplating?

Discuss in groups and share your opinions with your classmates.

Each day, our lives are touched directly or indirectly by the products of electrolysis. Electrolysis has important industrial applications. It is used for:

a) *The production of chemicals like sodium hydroxide, from electrolysis of brine (concentrated NaCl solution), using inert electrodes.*

The reactions that take place at the electrodes (*when graphite electrodes are used*) are as follows:

Anode reaction: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Cathode reaction: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

The overall cell reaction is:

$$2NaCl(aq) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + Cl_2(g) + H_2(g)$$

b) *For the production of metals and non-metals.*

The non-metals like H_2, Cl_2, F_2 etc are manufactured on an industrial scale by the process called electrolysis. The metal aluminium is extracted industrially by the Hall Process. This process involves the electrolysis of molten alumina (Al_2O_3) mixed with some amount of cryolite, Na_3AlF_6. The role of cryolite is to reduce the melting point of alumina from 2000°C to 1000°C. The vessel holding the molten mixture (Figure 3.8) is made up of iron lined with carbon, which serves as the cathode. Carbon (*graphite*) rods that serve as the anode are inserted into the melt. When the molten mixture is electrolyzed, pure aluminium is produced. The reactions at the electrodes are:

Anode reaction: $6O^{2-}(l) \rightarrow 3O_2(g) + 12e^-$

Cathode reaction: $4Al^{3+}(l) + 12e^- \rightarrow 4Al(l)$

Overall reaction: $4Al^{3+}(l) + 6O^{2-}(l) \rightarrow 3O_2(g) + 4Al(l)$

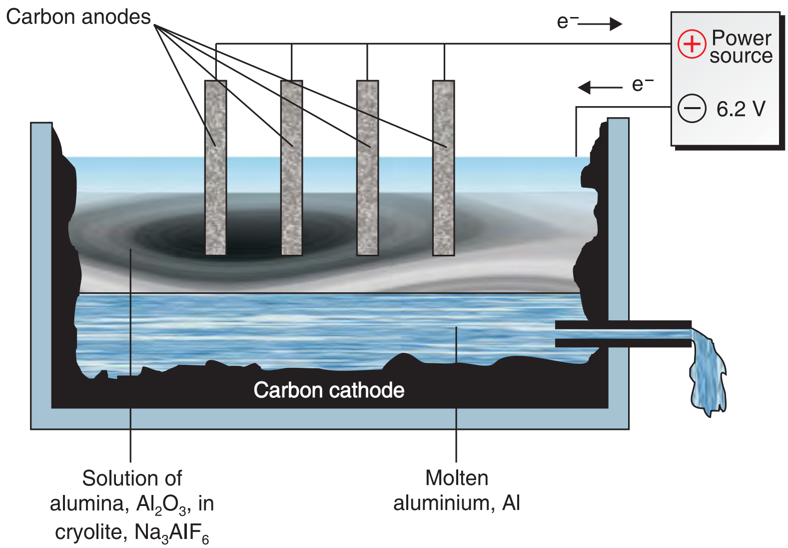


Figure 3.10 Production of Aluminium by Hall Process.

c) *For the Purification of Metals.*

Activity 3.7

For electrolytic and voltaic cells, the cell reaction is the sum of anode and cathode half-reactions. For electrolytic cell used to purify copper, there is no net (overall) reaction.

a Explain why this is so.

b Does this process mean wastage of time, labour and energy? Why? Discuss in groups and present your opinion o the rest of the class.

Another important application of electrolysis is the purification of metals like copper. When first separated from its ore, copper metal is about 99% pure with nickel, silver, gold and platinum as major impurities. In the refining process, the impure copper is used as the anode, copper metal of high purity used as cathode, and copper sulphate, $CuSO_4$ solution and aqueous H_2SO_4 as the electrolyte.

When electrolysis is carried out, copper and impurities that are more easily oxidized than copper, such as nickel, will go into the solution. Copper passes through the solution and deposits on the cathode, while the impurities remain in solution. Impurities like silver and gold are less easily oxidized and do not dissolve but fall away from the anode as 'sludge'. The electrode reaction in the purification of copper is the following:

Anode reaction: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Cathode reaction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

During the process, the size of the impure copper anode decreases and that of the pure copper cathode increases.

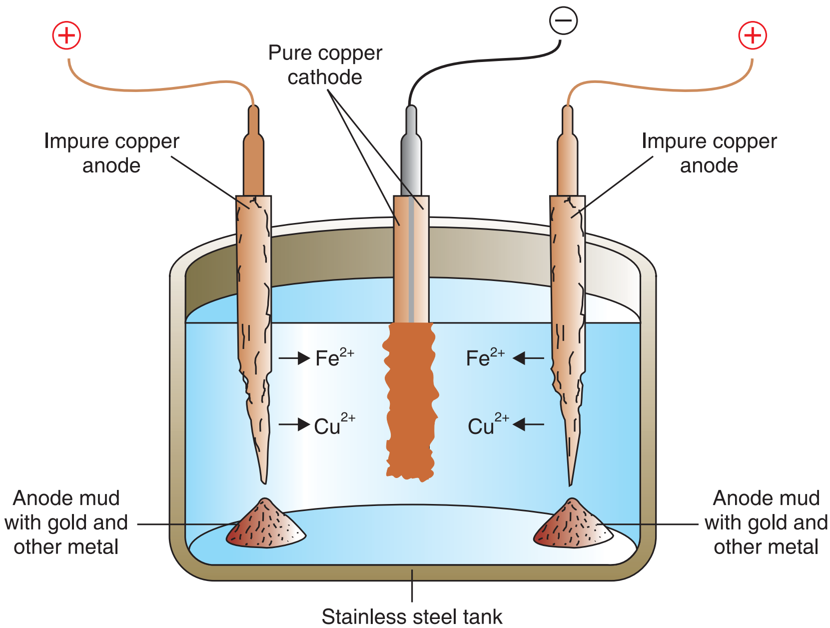


Figure 3.11 Purification of Copper by Electrolysis.

Always remember that, in the purification of metals by electrolysis, the impure metal should be used as the anode, the pure form of the metal as the cathode and an electrolyte should contain soluble salt (*ions*) of the metal to be purified. The process of purifying metals by electrolysis is called electrorefining.

d) *Electroplating*

Activity 3.8

When zinc electrode is dipped in copper sulphate solution, part of the electrode in the solution will be covered with a reddish brown layer of copper. Can this process be considered as electroplating? Explain. Discuss in groups and present your opinion to the class.

What is the purpose of electroplating?

Electroplating is a process of covering the surface of a metal (*metal article*) with a thin layer of another metal. Using this process, metals that easily corrode can be protected by a thin coating of another metal that resists corrosion. For example, tin cans are steel cans with a thin coating of tin, and chrome-plated bumpers are used for automobiles. Thus, the main objective of electroplating is to protect an article from corrosion and to give articles a beautiful appearance. In the process of electroplating, the pure plating metal should be used as the anode, the article (*metal*) to be plated the as cathode and a solution containing ions of the plating metal as the electrolyte. For example, to produce a silver-plated copper article, say, a medal, one should use silver as the anode, the copper medal as the cathode and silver nitrate solution as the electrolyte (Figure 3.12).

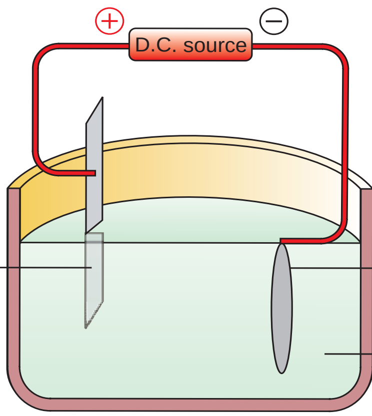


Figure 3.12 Electroplating Copper medal with Silver.

The reactions that occur at the electrodes during electroplating are:

Anode reaction: $Ag\,(s) \rightarrow Ag^{+}(aq) + 1e^{-}$

Cathode reaction: $Ag^{+}(aq) + 1e^{-} \rightarrow Ag\,(s)$

Check list

Key terms of the unit

- *anode*
- *cathode*
- *conductivity apparatus*
- *Daniel cell*
- *electrical conductivity*
- *electrochemical cell*
- *electrochemistry*
- *electrode*
- *electrolysis*
- *electrolyte*
- *electrolytic cell*
- *electroplating*
- *electrorefining*
- *half - cell*
- *half - reaction*
- *hall process*
- *primary cell*
- *salt bridge*
- *secondary cell*
- *voltaic (galvanic) cell*

Unit Summary

- *Electrochemistry is a field of chemistry that studies how chemical reactions produce electricity and how electricity is used to bring about chemical reactions in electrochemical cells.*
- *Electrochemistry deals with the relationship that exists between chemical energy and electrical energy.*
- *Electrochemical cells include electrolytic cells and Galvanic (voltaic) cells.*
- *Electrical conductivity is the ability of substances to conduct electricity.*
- *Metallic conductivity is the flow of electricity through metals, and the conduction of electricity through metals is due to the presence of freely moving (delocalized) valence electrons.*
- *Electrolytes are substances that conduct electricity, either in an aqueous solution or in a molten state.*
- *The conduction of electricity through electrolytes is due to the movement of anions and cations towards electrodes of opposite charge, and the charge-carriers in electrolytic conduction are ions.*
- *Electrolysis is a process in which electricity is used to bring about an oxidation- reduction reaction in an electrolytic cell.*
- *Electrolysis is also the process of decomposition of an electrolyte, using electrical energy.*

- *Electrodes are either metal strips or graphite rods.*
- *An anode is the electrode attached to the positive terminal of a direct current source, at which oxidation (loss of electrons) by anions occurs, and electrons leave the cell.*
- *A cathode is the electrode attached to the negative terminal of a dc source, the negative electrode at which reduction (gain of electrons) of cations occurs and electrons enter the cell (electric current enters the electrolyte).*
- *During electrolysis, anions move to the anode and cations move to the cathode.*
- *The reaction taking place at each electrode (cathode or anode) is said to be a half-cell reaction.*
- *Cell reaction is the reaction that takes place in the entire cell.*
- *Voltaic (Galvanic) cells are electrochemical cells in which a spontaneous redox reaction generates electricity. They convert chemical energy into electrical energy.*
- *Primary cells are voltaic cells that are not rechargeable, and the reactions taking place in them are irreversible.*
- *Secondary cells are voltaic cells that are rechargeable since the reactions taking place in them are reversible.*
- *Unlike electrolytic cells, the anode is negative and the cathode is positive in voltaic cells.*
- *Electrolysis has important industrial applications such as in the production of chemicals like NaOH, in the production of non-metals like Cl_2 and H_2, metals like Na, Al and in purification of metals and electroplating.*

REVIEW EXERCISE ON UNIT3

Part I: Choose the correct answer from the suggested options

1. Which one of the following solutions shows no current flow in an electrolytic cell?
   a water solution of table salt
   b molten sodium chloride
   c hydrochloric acid solution
   d sugar solution

2. Which of the following is not correct about voltaic cells?
   a the anode is negative
   b the cathode is positive
   c oxidation takes place at the cathode
   d redox reactions produce electricity in the cell
3. Which of the following conditions is not used to electroplate a tray made of iron with chromium?
   a using chromium as the anode
   b using an electrolyte containing iron (III) ions
   c using the tray as the cathode
   d using an electrolyte containing chromium ions
4. Electrolysis is not used for the:
   a purification of metals
   b production of metals
   c electroplating of metals
   d production of electricity
5. Which substance is not used in the Leclanche cell?
   a H_2SO_4
   b NH_4Cl
   c MnO_2
   d powdered carbon
6. Which one of the following is correct about automobile batteries?
   a the electrodes in the battery are graphite electrodes
   b each cell in the battery delivers 1.5 volts
   c the electrolyte is aqueous H_2SO_4 solution
   d lead (IV) oxide is used as anode
7. Which of the following occurs during electrolysis of the molten binary salt of a metal:
   a the metal in the salt will deposit on the cathode
   b reduction will take place at the anode
   c oxidation will take place at the cathode
   d no current will flow through the molten salt
8. Which substance does not conduct electricity?
   a solid $CaCl_2$
   b aqueous NaCl solution
   c dilute aqueous solution of HCl
   d molten $PbBr_2$

9. Two copper electrodes dipped in copper sulphate solution are connected to a 12 volt battery. The electrode connected to the end of the battery marked with a "–" is:

a anion
b cathode
c anode
d cation

10. The charge-carriers in electrolytic conduction are:

a anions only
b cations only
c cations and anions
d delocalized electrons

11. When electric current is applied externally, which of the following produces a redox reaction:

a wood
b electrolytic cells
c solid sugar
d diamond

12. During the electrolysis of fused sodium chloride, the anode half reaction involves:

a oxidation of sodium atoms to ions
b reduction of chlorine atoms to give chloride ions
c reduction of sodium ions to form free metal
d oxidation of chloride ions to elemental chlorine

13. Metals conduct electricity. This is because metals possess:

a freely moving ions
b all electrons held in fixed position
c delocalized electrons
d valence electrons that are strongly bound to the nucleus

14. Increasing the concentration of ions in an electrolyte solution:

a increases the extent of conduction of electricity through it
b decreases the extent of conduction of electricity through it
c has no effect on the conduction of electricity
d changes the direction of electron flow

15. Voltaic cells and electrolytic cells are similar in that:

a the anode is positive and cathode is negative in both types of cells
b oxidation half-reaction occurs at the cathode in both types of cells
c both types of cells contain two electrodes in contact with electrolytes
d reduction half-reaction occurs at the anode in both types of cells

16. The conduction of electricity through each of the following substances is caused by the migration of ions except in one case; the exception is:

a fused lead bromide
b aqueous solution of NaCl
c molten KCl
d graphite

17. Four different solutions of equal volume (1 L) were prepared by dissolving one mole of each of the following substances. The conduction of electricity is least in the solution containing:

a HCl
c HNO_3
b CH_3COOH
d KCl

18. Strong electrolytes differ from weak electrolytes in that strong electrolytes:

a are poorer conductors than weak electrolytes
b ionize to a smaller extent than weak electrolytes
c produce greater numbers of ions in aqueous solution as compared to weak electrolytes
d do not conduct electricity in aqueous solutions

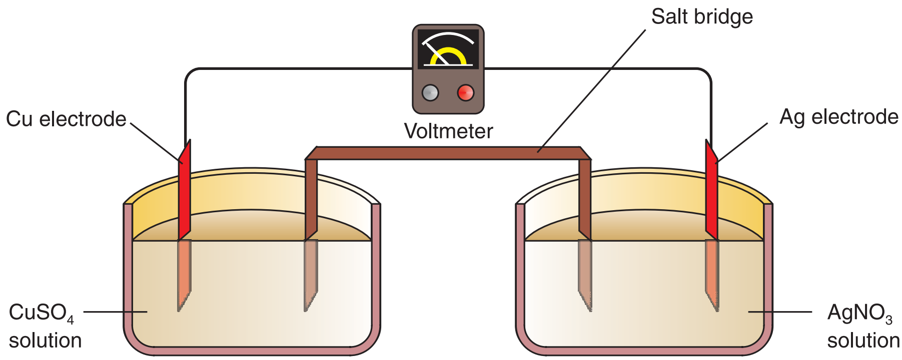
19. Which of the following is a wet voltaic cell:

a Leclanche cell
b cells used in electronic wrist watches
c cells used in mobile telephones
d lead-storage cell

Part II: Write the missing words in your exercise book

20. The type of electrical conductivity caused by the flow of freely moving electrons is known as__________________.

21. Consider the following galvanic cell:



Half-reaction: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Half-reaction: $Ag^+(aq) + 1e^- \rightarrow Ag(s)$

According to the information given in the above figure, a The anode of the galvanic cell is _______________.

b The cathode of the galvanic cell is ______________.

c The negative electrode is _____________________.

d The positive electrode is ______________________.

e The overall cell reaction is ____________________.

22. ________________ means two metal strips or graphite rods through which electrons enter and leave an electrolyte in electrolytic cells.

23. In an electrolytic cell, positive ions move to the ______________ and negative ions move to the _____________ and electrons flow from the _____________ to the __________ in the external circuit during electrolysis.

24. The process of covering one metal with a thin layer of another metal, using electricity, is known as ______________.

Part III: Give short answers to each of the following questions

25. Explain the differences between the following pairs of terms.

a Anode and cathode

b Metallic conduction and electrolytic conduction

c Inert and active electrodes

d Galvanic cell and electrolytic cell

e Cation and anion

f Wet cell and dry cell

g Primary and secondary voltaic cells

h Strong and weak electrolytes

26. Why are ionic compounds like NaCl, KCl, $CaCl_2$, $PbBr_2$, etc. non-conductors in the solid state but conductors in aqueous solutions?

27. During electrolysis of fused $CaCl_2$,

a Which ions are responsible for the conduction of electricity through the molten salt?

b What half-cell reactions occur at the anode and cathode?

28. How can a salt bridge maintain electrical neutrality in the solutions of the two half-cells of a galvanic cell?

29. A chemistry teacher in a chemistry laboratory asked two students, A and B, to perform an experiment. The teacher told student A to refine impure silver and told student B to produce a gold-plated medal from a medal made of copper. How can these students accomplish the tasks given to them?

30. What is the purpose of a salt bridge in a voltaic cell?