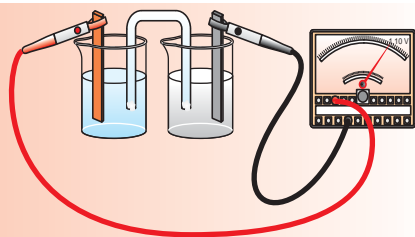# UNIT 4

Electrochemistry

Unit Outcomes

After completing this unit, you will be able to:

☛ *understand the fundamental concepts related to oxidation-reduction reactions;*

☛ *know the application of redox reactions in the production of new substances and electrical energy;*

☛ *demonstrate an understanding of fundamental concepts related to the interconversion of chemical and electrical energy;*

☛ *understand the difference between metallic conduction and electrolytic conduction;*

☛ *identify and describe the function of the components of Electrolytic and Galvanic cells;*

☛ *understand the difference between electrolytic and Galvanic cells;*

☛ *know how to solve problems based on Faraday's first and second laws;*

☛ *measure, through experimentation, the mass of the metal deposited by electroplating(example copper to copper (II) sulphate), and apply Faraday's Law to relate the mass of the metal deposited to the amount of charge passed;*

☛ *predict spontaneity of redox reactions and overall cell potentials by studying a table of half-cell reduction potentials;*

☛ *determine the emf of an electrochemical cell, experimentally or from given data;*

☛ *explain the application of electrochemistry in our daily lives and in industry;*

☛ *explain corrosion as an electrochemical process, and describe corrosion-inhibiting techniques (e.g. painting, galvanizing, cathodic protection);*

☛ *describe examples of common Galvanic cells and evaluate their environmental and social impact; and*

☛ *describe scientific enquiry skills: observing, classifying, comparing and contrasting, communicating, asking questions, measuring, relating cause and effect and problem solving.*

4.1 OXIDATION-REDUCTION REACTIONS

After completing this subunit, you will be able to:

- define a redox reaction;
- define oxidation, in terms of electron transfer and change in oxidation number;
- define reduction, in terms of electron transfer and change in oxidation number;
- describe the oxidizing and reducing agents;
- identify the species that are oxidized and reduced in a given redox reaction and determine the oxidizing and reducing agents;
- balance a given redox reaction, using the change in oxidation-number method; and
- balance a given redox reaction, using the ion-electron method.

Start-up Activity

Form a group and discuss the following questions,

1. What are oxidation-reduction (redox) reactions?
2. List the redox-reactions taking place in your body, and the surroundings.

After discussion, share your idea with other groups.

4.1.1 Oxidation

When do we say a substance is oxidized?

The term oxidation was originally used to describe reactions in which an element combines with oxygen. For example, the reaction between magnesium and oxygen involves the oxidation of magnesium: $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$. However, nowadays it has a broader meaning that includes reactions not involving only oxygen. Now, oxidation is the loss of electrons and is identified by an increase in oxidation number.

4.1.2 Reduction

When do we say a substance is reduced? Can oxidation occur without reduction and vice versa?

The term reduction was originally used to describe the production of a metal from an ore. The term has been modified through time to include other reactions. Now, reduction is the gain of electrons and is identified by a decrease in oxidation number.

Activity 4.1

In Grade 10 chemistry, you have learnt oxidation-reduction reactions. Form a group. Discuss the following questions and present your answers to the class.

1. Define each of the following terms.

    a Oxidizing agent   c Oxidation Number

    b Reducing agent

2. What will happen if a zinc rod is immersed in a solution of copper (II) sulphate?

3. Which of the following reactions are redox reactions? Explain your answer for each case.

    a $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$

    b $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

    c $Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$

    d $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

4. Use the given chemical equation to answer the following questions;

    $Mg(s) + Zn^{2+}(aq) \rightarrow Zn(s) + Mg^{2+}(aq)$

    identify the:

    a oxidized substance.   c oxidizing agent.

    b reduced substance.   d reducing agent.

5. Calculate the oxidation number of:

    a C in $C_2O_4^{2-}$

    b Cr in K_2CrO_4

    c N in N_2O_5

    d S in H_2SO_4

    e Cl in $HClO_4$

4.1.3 Balancing Oxidation-Reduction (Redox) Reactions

What scientific law is used in balancing chemical equations?

Because atoms are neither created nor destroyed in an ordinary chemical reaction, chemical equation must have an equal number of atoms of each element on the reactant and product sides. In addition, the net electrical charges in the reactant side must be equal to the net electrical charges in the product side.

Balancing Redox Reactions Using Change in Oxidation-Number Method

How do you balance redox reactions, using the change in the oxidation-number method?

In a redox reaction, the total number of electrons gained by the oxidizing agent is equal to the total number of electrons lost by the reducing agent. The change in oxidation number method for balancing redox reaction is based on this fact.

This method is used to balance redox reactions that do not occur in aqueous solutions, and also reactions that do not involve ions.

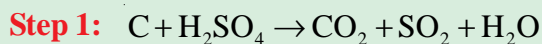Use the following steps to balance chemical equations, using the change in oxidation state method.

Step 1: Write an unbalanced chemical equation.

Step 2: Assign oxidation numbers to each atom, and determine which atoms are changing their oxidation numbers.

Step 3: Determine the number of electrons lost by each atom per molecule undergoing oxidation and the number of electrons gained by each atom per molecule being reduced.

Step 4: Balance the number of electrons lost in oxidation with those gained in reduction by adjusting the coefficients of substances being oxidized and reduced.

Step 5: Balance the remaining substances by counting atoms.

Step 6: Check the final equation to be sure that each atom as well as the net charges on either side is balanced.
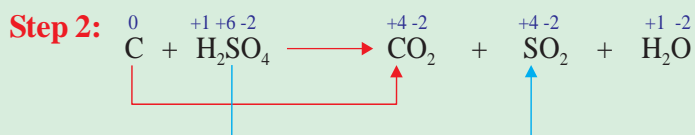

Example 4.1

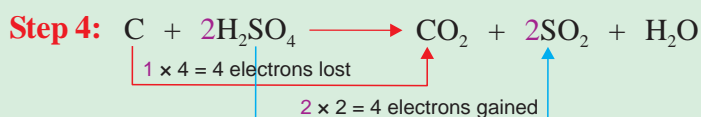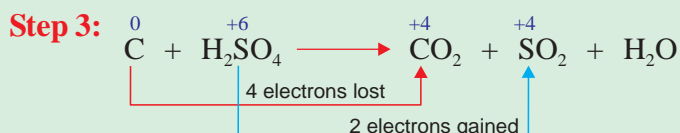Balance the following chemical equation, using the change in oxidation-number method.

$$C + H_2SO_4 \rightarrow CO_2 + SO_2 + H_2O$$

Solution:

Step 1: $C + H_2SO_4 \rightarrow CO_2 + SO_2 + H_2O$

Step 2:
$$\overset{0}{C} + \overset{+1\ +6\ -2}{H_2SO_4} \longrightarrow \overset{+4\ -2}{CO_2} + \overset{+4\ -2}{SO_2} + \overset{+1\ -2}{H_2O}$$

Changes in oxidation number are observed in carbon and sulphur.

Step 3:
$$\overset{0}{C} + \overset{+6}{H_2SO_4} \longrightarrow \overset{+4}{CO_2} + \overset{+4}{SO_2} + H_2O$$

4 electrons lost

2 electrons gained

Step 4: $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + H_2O$

1 × 4 = 4 electrons lost

2 × 2 = 4 electrons gained

Step 5: Balance hydrogen atoms by making the coefficient of water 2.

$$C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$$

Step 6:

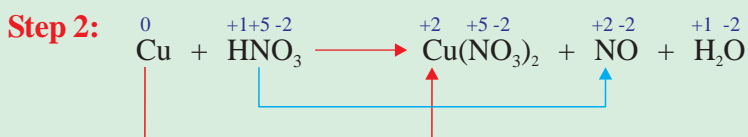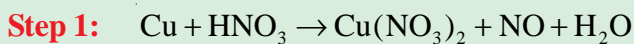| Reactants	Products
C (1)	C (1)
H (4)	H (4)
S (2)	S (2)
O (8)	O (8)

The chemical equation is balanced, because the number of atoms in the reactant side is equal to the number of atoms in the product side. It can also be confirmed that the net charge is zero on each side.

Example 4.2
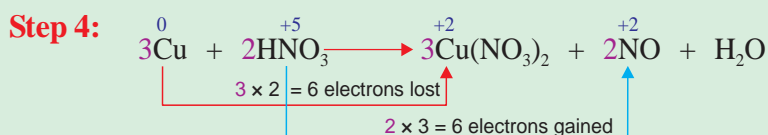
Balance the following chemical equation by using the change in oxidation-number method.

$$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$$

Solution:

Step 1: $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$

Step 2:
$$\overset{0}{Cu} + \overset{+1+5\ -2}{HNO_3} \longrightarrow \overset{+2\ +5\ -2}{Cu(NO_3)_2} + \overset{+2\ -2}{NO} + \overset{+1\ -2}{H_2O}$$
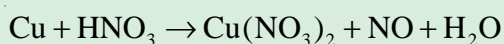
Changes in oxidation number are observed in copper and nitrogen.

Step 3: $\overset{0}{Cu} + \overset{+5}{HNO_3} \longrightarrow \overset{+2}{Cu(NO_3)_2} + \overset{+2}{NO} + H_2O$

2 electrons lost

3 electrons gained

Step 4: $3\overset{0}{Cu} + 2\overset{+5}{HNO_3} \longrightarrow 3\overset{+2}{Cu(NO_3)_2} + 2\overset{+2}{NO} + H_2O$

$3 \times 2 = 6$ electrons lost

$2 \times 3 = 6$ electrons gained
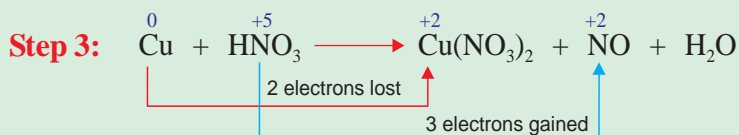
In this case, two NO_3^- ions are converted to two NO, but we need six NO_3^- to balance the six NO_3^- ions that are present in three $Cu(NO_3)_2$. Therefore, the coefficient of HNO_3 becomes 8.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + H_2O$$
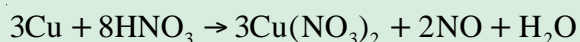
Step 5: Hydrogen atoms can be balanced by making the coefficient of water as 4.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$
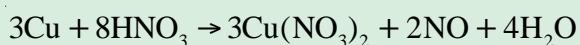
Step 6:

Reactants	Products
Cu (3)	Cu (3)
H (8)	H (8)
N (8)	N (8)
O (24)	O (24)

Is the chemical equation balanced?

Exercise 4.1

Balance each of the following chemical equations, using the change in oxidation number method.

a $Na_2Cr_2O_7 + FeCl_2 + HCl \rightarrow CrCl_3 + NaCl + FeCl_3 + H_2O$

b $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

c $H_2S + HNO_3 \rightarrow S + NO + H_2O$

d $Cu + H_2SO_4 \rightarrow CuSO_4 + SO_2 + H_2O$

e $P_4 + HNO_3 \rightarrow H_3PO_4 + NO_2 + H_2O$

4.1.4 The Ion-Electron Method for Balancing Redox Reactions

This method is useful if the net ionic equation is given or no spectator ions are present.

For example,

$$Na^+(aq) + S^{2-}(aq) + H^+(aq) + Cl^-(aq) + NO_3^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + S(s) + NO(g) + H_2O(l)$$

In this reaction, $Na^+(aq)$ and $Cl^-(aq)$ ions are spectator ions, because they appear on both the reactant and product sides. Therefore, the net ionic equation becomes:

$$S^{2-}(aq) + H^+(aq) + NO_3^-(aq) \rightarrow NO(g) + S(s) + H_2O(l)$$
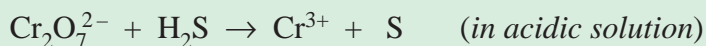
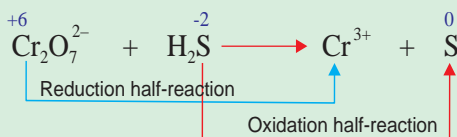Steps for balancing redox reaction using the ion-electron method:

Step 1: Identify the element undergoing oxidation and reduction; write separate equations for oxidation and reduction half-reactions.

Step 2: Balance the element oxidized or reduced.

Step 3: Determine the change in oxidation number of the element oxidized or reduced. Add the electrons gained or lost to the side on which the redox element has the higher oxidation number.

Step 4: Balance any elements other than hydrogen and oxygen that may be present.

Step 5: Balance charges by adding H^+ ions if the solution is acidic and OH^- ions if the solution is basic.

Step 6: Balance hydrogen by adding water molecules.

Step 7: Multiply each half-reaction by appropriate coefficients so that the number of electrons lost in oxidation equals the number of electrons gained in reduction.

Step 8: Add the two half-reactions together and eliminate anything that appears in identical form on both sides of the equation.

Example 4.3

Balance the following chemical equation using the ion-electron method.

$$Cr_2O_7^{2-} + H_2S \rightarrow Cr^{3+} + S \quad \text{(in acidic solution)}$$

Solution:

Reduction half-reaction

Step 1: $Cr_2O_7^{2-} \rightarrow Cr^{3+}$

Step 2: $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$

Step 3: $Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+}$

Step 4: There is no element other than oxygen.

Step 5: $Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+}$

Step 6: $Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

Here, the reduction half-reaction is balanced.

Oxidation half-reaction

Step 1: $H_2S \rightarrow S$

Step 2: Sulphur is already balanced.

Step 3: $H_2S \rightarrow S + 2e^-$

Step 4: There is no element other than hydrogen.

Step 5: $H_2S \rightarrow S + 2e^- + 2H^+$
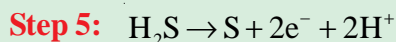
Step 6: Hydrogen is already balanced and the oxidation half-reaction is also balanced.

Step 7: *Oxidation half-reaction*

$(H_2S \rightarrow S + 2e^- + 2H^+) \times 3$

$3H_2S \rightarrow 3S + 6e^- + 6H^+$

Reduction half-reaction

$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+}$

Step 8: Add the two half-reactions.

$$3H_2S \rightarrow 3S + \cancel{6e^-} + \cancel{6H^+}$$
$$\underline{Cr_2O_7^{2-} + \cancel{6e^-} + \overset{8}{\cancel{14}}H^+ \rightarrow 2Cr^{3+} + 7H_2O}$$

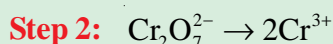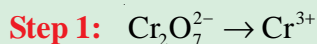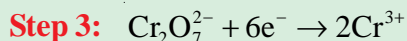Overall reaction : $Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 3S + 2Cr^{3+} + 7H_2O$
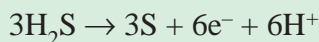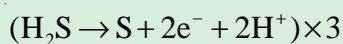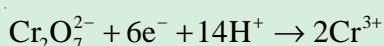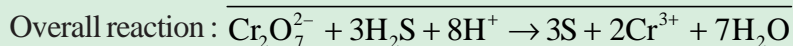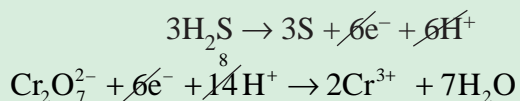
Exercise 4.2

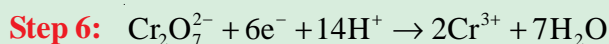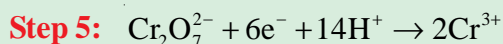Balance the following chemical equations, using the ion-electron method.

a $MnO_4^- + SO_3^{2-} \rightarrow Mn^{2+} + SO_4^{2-}$ (*in acidic solution*)

b $Sn^{2+} + Bi^{3+} \rightarrow [Sn(OH)_6]^{2-} + Bi$ (*in basic solution*)
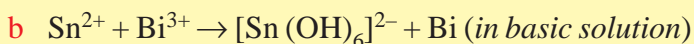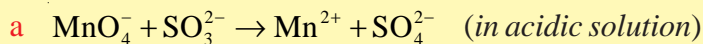
4.2 ELECTROLYSIS OF AQUEOUS SOLUTIONS

After completing this subunit, you will be able to:

- recall the concepts metallic conductivity, electrolytic conductivity and electrolysis of molten electrolytes;

- draw and label diagrams of electrolytic cell ;

- define preferential discharge;

- explain factors that affect preferential discharge;

- describe the effects of nature of ions on the electrolysis of aqueous solutions of dilute H_2SO_4 and NaOH;

- describe the effect of the concentrations of ions on the electrolysis of dilute and concentrated solutions of NaCl;

- describe the effects of types of electrodes on the electrolysis of $CuSO_4$ solution, using Ni and Cu electrodes;

- write the electrode half-reactions and overall reactions for the electrolysis of dilute H_2SO_4, dilute NaOH, dilute NaCl, concentrated NaCl and $CuSO_4$ solutions; and

- distinguish between molten electrolytes and aqueous solutions of electrolytes.

Before we study the electrolysis of aqueous solutions, let us consider some important concepts about conductivity. As you learned in Grade 10 Chemistry, electrical conductivity is the ability of a substance to transmit electricity. Generally, there are two major types of electrical conductors: metallic conductors and electrolytic conductors.

Activity 4.2

Form a group. Discuss the following points and present your answers to the class. Your teacher might help you to form groups.

1. How does conduction occur in metals and in electrolytes?
2. What do substances need in order to conduct electricity?
3. What are the physical states in which metals and electrolytes conduct electricity?
4. Can ionic compounds conduct electricity in the solid state? If your answer is "No", why?

Aqueous solutions can be tested for the presence of mobile ions by using an electric circuit like the one in Figure 4.1.
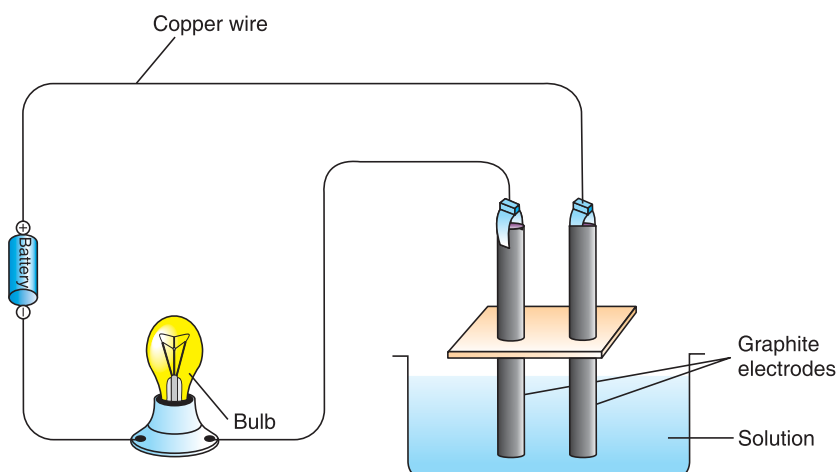
Figure 4.1 Electrical Conductivity Apparatus.

This circuit consists of a current source, a light bulb, and two graphite rods called electrodes that dip into the solution. If the solution contains ions, current flows through the circuit and the light bulb glows. The brightness of the bulb increases with current strength, which increases with the number of ions in the solution.

The ability of different solutes to provide ions can be compared by comparing the brightness of the light bulb at the same concentration.

Note that metallic conduction is a *physical process*, but electrolytic conduction causes *chemical changes* to occur on the surface of the electrodes.

Exercise 4.3

Which of the following substances are capable of conducting electricity? Give reason for your answer.

a   Iron   c   Solid sodium chloride

b   Sulphur   d   Molten calcium chloride

Experiment 4.1
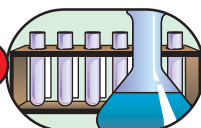
Electrical Conductivity Test

Objective: To classify substances as electrical conductors and insulators.

Apparatus: Copper wire, light bulb, power supply (DC) or dry cells, scotch tape, distilled water, 1M NaCl solution, 1 M H_2SO_4 solution, 1 M CH_3COOH solution, 1 M sugar solution, magnesium ribbon and an iron nail.
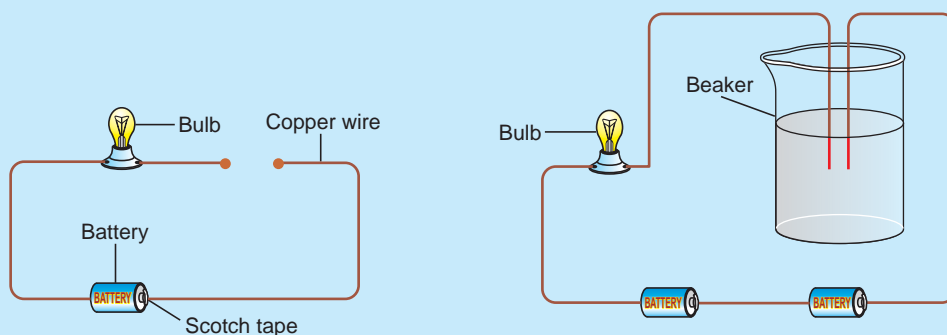
Figure 4.2 (a) Electrical conductivity apparatus for solid materials. **(b) Electrical conductivity apparatus for liquids and solutions.**

Procedure:

1. Polish the strip of magnesium and connect the two ends of the copper wire as shown in Figure 4.2a. Do the same thing for iron nail. Record your observations.

2. Rinse the 100 mL beaker thoroughly with distilled water and fill to the 50 mark and insert the two ends of the copper wire as shown in Figure 4.2b. Record your observations.

3. Clean the two ends of the copper wire in Figure 4.2b with distilled water and insert them into a beaker containing 50 mL of 1 M NaCl solution. Repeat the same thing for the 1 M H_2SO_4, 1 M CH_3COOH and 1 M sugar solutions. Record your observation.

Results and Discussion:

1. Why is it important to polish the magnesium ribbon and iron nail before use?

2. Classify the materials you used as conductors, strong electrolytes, weak electrolytes and nonelectrolytes.

3. Label the two ends of the wire in Figure 4.2b as cathode and anode.

4.2.1 Electrolytic cells

Activity 4.3

Form a group, and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. Describe the migration of ions during electrolysis?

2. Observe Figure 4.3 and answer the following questions.
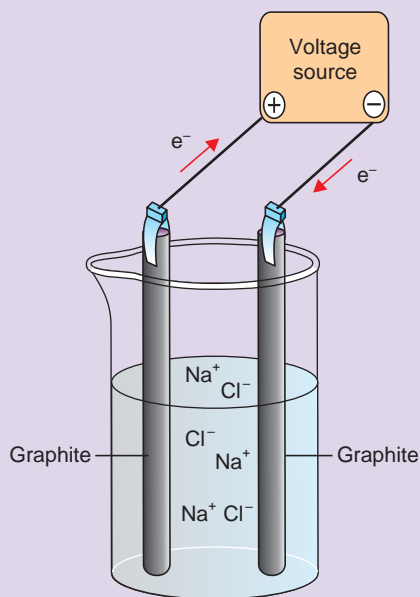
Figure 4.3 Electrolytic cell containing molten sodium chloride.

a Label the anode and the cathode.

b Indicate the migration of sodium ions and chloride ions.

c Write the reduction half-reaction, oxidation-half reaction, and the overall reaction.

d What are the products of electrolysis of molten NaCl?

4.2.2 Preferential Discharge

What does preferential discharge mean? What are the factors that affect preferential discharge of ions?

The preferential discharge of ions is affected by the nature of the electrodes, the positions of the ions in the electrochemical series and the concentration of the ions in the electrolyte. Let us discuss these factors one by one.

1. *Nature of the electrodes*

How do electrodes affect the preferential discharge of ions?

Inert electrodes, like graphite or platinum, do not affect the product of electrolysis, but reactive or active electrodes, like copper, can affect the product of electrolysis.

For example, in the electrolysis of copper sulphate solutions, using graphite electrodes,

oxygen gas is liberated at the anode and copper metal is deposited at the cathode, as shown below.

$$CuSO_4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

Anode : $4OH^-(aq) \longrightarrow O_2(g) + 2H_2O(l) + 4e^-$

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

However, if the electrolysis of copper sulphate is performed using copper electrodes, the copper electrode at the anode dissolves and copper metal will be deposited at the cathode, as indicated below.

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

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

2.   *The position of the ions in the electrochemical series*

The reactivity series or activity series is an empirical series of metals, in order of "reactivity" from highest to lowest. It is used to summarize information about the reactions of metals with acids and water, single displacement reactions and the extraction of m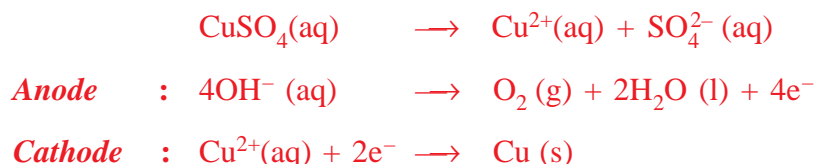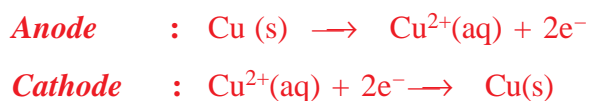etals from their ores. The electrochemical series is built up by arranging various redox equilibria in order of their standard electrode potentials (*redox potentials*). The values of standard electrode potentials are given in the Table 4.2 in volts relative to the standard hydrogen electrode. You will learn more about standard electrode potentials in this unit.

The reactivity series is sometimes quoted in the reverse order of standard electrode potentials:
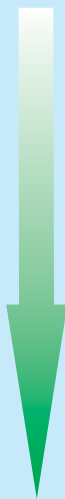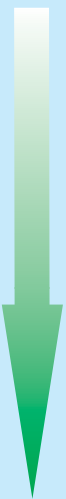
Li > K > Sr > Ca > Na > Mg > Al > Zn > Cr > Fe > Cd > Co > Ni > Sn > Pb > H > Cu > Ag > Hg > Pt > Au

The positions of lithium and sodium are changed on such a series; gold and platinum are also inverted, although this has little practical significance as both metals are highly unreactive.

Standard electrode potentials offer a quantitative measure of the power of a reducing agent, rather than the qualitative considerations of other reactivity series. However, they are only valid for standard conditions. In particular, they only apply to reactions in aqueous solution. Even with this provision, the electrode potentials of lithium and sodium, and hence their positions in the electrochemical series, appear anomalous. The order of reactivity, as shown by the vigor of the reaction with water or the speed at which the metal surface tarnishing in air, appears to be:

potassium > sodium > lithium > alkaline earth metals

Table 4.1 The ease of discharge of some common cations and anions.

Cations	Anions

The ease of discharge increase downward (Cations):

Li^+
K^+
Na^+
Mg^{2+}
Al^{3+}
Mn^{2+}
Zn^{2+}
Cr^{3+}
Fe^{2+}
Cd^{2+}
Pb^{2+}
Fe^{3+}
H^+
Cu^{2+}
Ag^+
Au^{3+}

The ease of discharge increase downward (Anions):

F^-
SO_4^{2-}
NO_3^-
CO_3^{2-}
Cl^-
Br^-
I^-
OH^-
S^{2-}

The ions that are lower in the electrochemical series get discharged in preference to those above them.

For example, if a solution has potassium ions and copper ions, the copper ions will accept electrons, and get discharged as copper atoms first. The potassium ions will not be affected.

In general, if two or more positive ions migrate to the cathode, the ion lower in the series is discharged preferentially. Similarly, if two or more negative ions migrate to the anode, the ion lower in the series is discharged preferentially.

3. *Concentration of the ions in the electrolyte*

If an electrolyte contains a higher concentration of ions that are higher in the electrochemical series than of those that are lower, then the higher ions get discharged in preference to the lower ones.

For example, a solution of sodium chloride in water contains two types of anions i.e., the chloride (Cl^-) ions and the hydroxide (OH^-) ions. The hydroxide ions are lower in the electrochemical series than the chloride ions. But if the concentration of chloride ions is much higher than that of the hydroxide ions, then the chloride ions get discharged first.

Exercise 4.4

1. Define the following terms:

   a   perferential discharge

   b   inert electrode

   c   reactive or active electrode.

2. What gases are liberated at the cathode and anode if concentrated hydrochloric acid is electrolyzed? Write the reduction half-reaction, oxidation half-reaction and the overall reaction.

4.2.3   Electrolysis of Some Selected Aqueous Solutions

Activity 4.4

Form a group, and discuss each of the following:

1. Prior to electrolysis, why sodium chloride must be in molten state?

2. Why water must be excluded in the electrolytic preparation of active metals such as potassium. What will happen if water gets into the cell?

3. For the electrolysis of molten KCl, write a balanced equation for the:

   a   anode reaction

   b   cathode reaction

   c   overall reaction

4. Why are H^+ and Cl^- ions discharged in preference to Na^+ and OH^- ions in concentrated sodium chloride solution?

After the discussion, share your ideas with the rest of the class.

Electrolysis of concentrated sodium chloride solution (brine solution)

Concentrated solution of sodium chloride (brine solution) contains Na^+, Cl^-, H^+ and OH^- ions. However, the concentrations of H^+ and OH^- are very small. Why? When a potential difference is established across the two electrodes, Na^+ and H^+ ions move towards the cathode, and Cl^- and OH^- ions move towards the anode. At the cathode, the H^+ ions are discharged in preference to the Na^+ ions. Similarly, Cl^- ions are discharged at the anode in preference to the OH^- ions because the concentration of Cl^- ions is very high.

Cathode (*reduction*) :	$2H^+(aq)$	+	$2e^-$	$\rightarrow$	$H_2(g)$	
Anode (*oxidation*) :			$2Cl^-(aq) \rightarrow$		$Cl_2(g)$	+ $2e^-$
Overall reaction :	$2H^+(aq)$	+ $2Cl^-(aq) \rightarrow$			$H_2(g)$	+ $Cl_2(g)$

Since the Na^+ and OH^- ions remain in the solution, the solution yields NaOH, as shown in Figure 4.4.
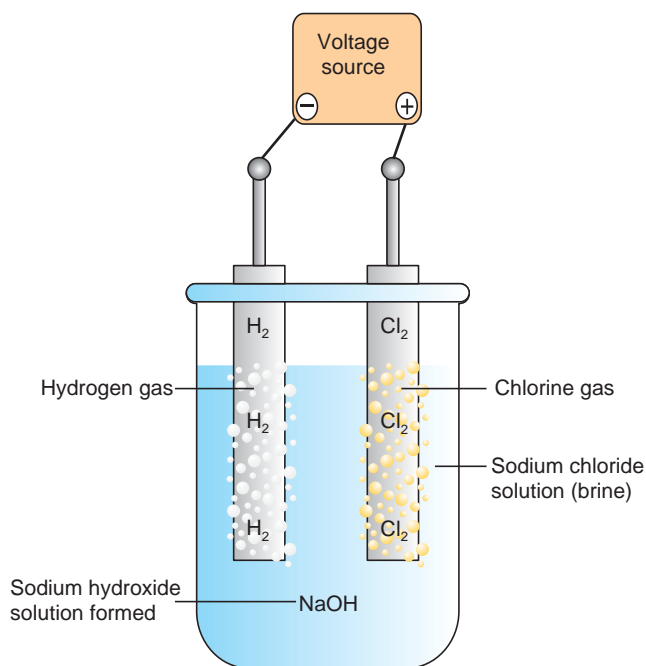
Figure 4.4 Electrolysis of brine solution.

Electrolysis of Dilute Sodium Chloride Solution

Activity 4.5

Form a group, and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. What is meant by dilute solution?

2. a   List all ions present in dilute sodium chloride solution.

    b   Identify ions that migrate towards the anode and the cathode.

    c   Which ions listed in (a) will discharge at the cathode and at the anode?

3. Write the electrode half-reactions and overall reaction for the electrolysis of dilute solution of sodium chloride.

Experiment 4.2
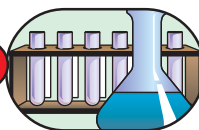
Investigating electrolysis of sodium chloride solution

Objective: To electrolyze sodium chloride solution and observe the reaction occurring at the electrodes.

Apparatus and Chemicals: Water, sodium chloride, beakers, measuring cylinder, graphite electrodes, batteries and connecting wires.
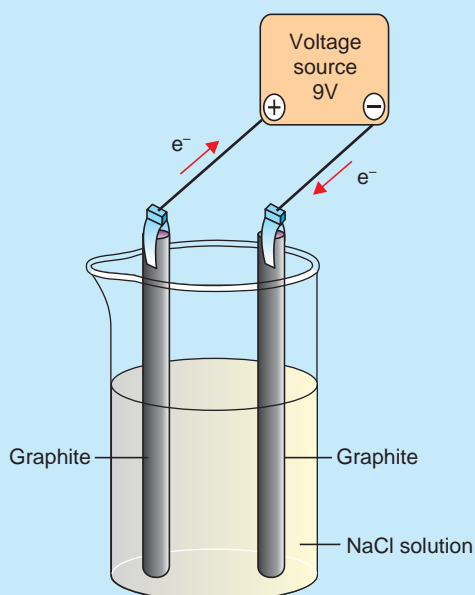
Figure 4.5 Electrolysis of sodium chloride solution

Procedure:

1. Prepare 0.1 M sodium chloride solution.
2. Transfer the solution to the beaker.
3. Immerse the graphite electrodes in the sodium chloride solution.
4. Arrange the setup as shown in the Figure 4.5.

Results and Discussion:

1. What do you observe at the surface of the electrodes?
2. Identify the cathode and anode in the Figure 4.5.
3. Name the gases evolved at the cathode and anode.
4. Write the equations for anode and cathode reactions.

Electrolysis of Dilute Sulphuric Acid Solution

Which ions are discharged at the cathode and anode?

Dilute sulphuric acid solution contains H^+, OH^- and SO_4^{2-} ions. When a potential difference is applied across the two electrodes (anode and cathode), only H^+ ions migrate towards the cathode, and OH^- and SO_4^{2-} ions migrate towards the anode.

At the cathode, H^+ ions are discharged, and at the anode, OH^- ions are discharged in preference to SO_4^{2-} ions because the hydroxide ion is below the SO_4^{2-} ion in the electrochemical series.

Anode (oxidation) : $4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$

Cathode (reduction) : $[2H^+(aq) + 2e^- \rightarrow H_2(g)] \times 2$

Overall reaction : $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

Note that the electrolysis of dilute $NaCl$ and dilute H_2SO_4 solutions results in the decomposition of water to oxygen and hydrogen gases.

Electrolysis of Copper (II) Sulphate, Using Inert Electrodes

Which ions are liberated at the cathode and anode if copper sulphate solution is electrolysed, using platinum (inert) electrodes?

Copper sulphate solution contains Cu^{2+}, H^+, SO_4^{2-} and OH^- ions. When a potential difference is established between the two electrodes, Cu^{2+} and H^+ ions migrate towards the cathode, and SO_4^{2-} and OH^- ions migrate towards the anode.

At the cathode, the Cu^{2+} ions are discharged in preference to the H^+ ions, because copper is below hydrogen in the electrochemical series. Similarly, at the anode, the OH^- ions are discharged in preference to the SO_4^{2-} ions.

Anode (oxidation) : $4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$

Cathode (reduction) : $[Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)] \times 2$

Overall reaction : $2Cu^{2+}(aq) + 4OH^-(aq) \rightarrow 2Cu(s) + 2H_2O(l) + O_2(g)$
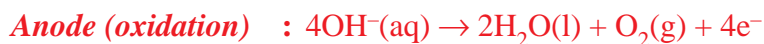
Since copper ions are deposited at the cathode, and hydroxide ions at the anode, the solution becomes acidic due to the formation of H_2SO_4.

## *Electrolysis of Copper (II) Sulphate Solution, Using Copper Electrodes*

Activity 4.6

Form a group, and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. What is the difference between inert electrodes and reactive electrodes?

2. Are the copper electrodes reactive or inert in the electrolysis of copper (II) sulphate solution?

3. a List all the ions present in copper (II) sulphate solution.

   b Identify the ions that migrate towards the anode and the cathode.

   c Which ions you listed in (a) will discharge at the cathode and at the anode?

4. Write the reactions ocurring at the anode and at the cathode during the electrolysis of copper (II) sulphate solution, using copper electrodes.

5. What is the net result of the electrolysis of copper (II) sulphate solution, using copper electrodes?

Exercise 4.5

1. For the electrolysis of dilute NaOH solution,

   a write the balanced chemical equations for the reduction half-reaction and oxidation half-reactions.

   b write the balanced overall cell reaction.

2. What happens to the concentration of the dilute H_2SO_4 solution after electrolysis?

3. Does the concentration of copper sulphate increase, decrease or remain the same after the electrolysis of copper sulphate, using inert electrodes? Explain.

4.3 QUANTITATIVE ASPECTS OF ELECTROLYSIS

After completing this subunit, you will be able to:

- state Faraday's first law of electrolysis;
- write the mathematical expressions for the Faraday's first law of electrolysis;
- do calculations related to Faraday's first law of electrolysis;
- state Faraday's second law of electrolysis;
- write the mathematical expressions for Faraday's second law of electrolysis; and
- do calculations related to Faraday's second law of electrolysis.

Is it possible to calculate the amount of product formed at the electrodes?

The quantitative treatment of electrolysis was developed primarily by Michael Faraday in the year 1834. His early research on electrolysis led him to propose a relationship between the amount of current passed through a solution and the amount of substance decomposed or produced by the current.

Biography
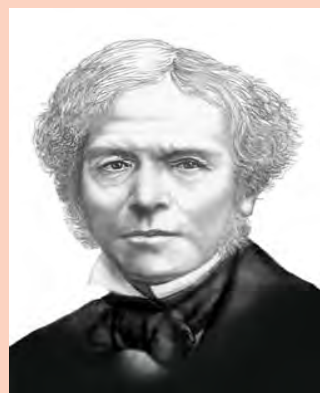
Faraday, Michael

Michael Faraday (1791-1867), was a British physicist and chemist, best known for his discoveries of electromagnetic induction and of the laws of electrolysis.

Faraday was born on September 22, 1791, in Newington, Surrey, England. He was the son of a blacksmith and received little formal education. While apprenticed to a bookbinder in London, he read books on scientific subjects and experimented with electricity. In 1812, he attended a series of lectures given by the British chemist Sir Humphry Davy and forwarded the notes he took at these lectures to Davy, together with a request for employment. Davy employed Faraday as an assistant in his chemical laboratory at the Royal Institution, and in 1813 took Faraday with him on an extended tour of Europe. Faraday was elected to the Royal Society in 1824, and the following year he was appointed director of the laboratory of the Royal Institution. In 1833, he succeeded Davy as professor of chemistry at the institution. Two years later he was given a pension of 300 pounds per year for life. Faraday was the recipient of many scientific honors, including the Royal and Rumford medals of the Royal Society; he was also offered the presidency of the society but declined the honour. He died on August 25, 1867, near Hampton Court, Surrey.

4.3.1   Faraday's First Law of Electrolysis

Faraday's First Law states that "the amount of substance consumed or produced at one of the electrodes in an electrolytic cell is directly proportional to the amount of electricity that passes through the cell".

If m is the mass of a substance librated or deposited at an electrode due to the passage of charge Q, then according to Faraday's first law of electrolysis,

$$m \propto Q \quad \text{or} \quad m = zQ$$

Where z is a constant of proportionality and is called electrochemical equivalent of the substance. It has the same charge which passes due to a steady current I flowing for time t, then the above equation can be written as:

$$m = z \times I \times t$$
$$= z \times Q$$

Show that the general formula of Faraday's first law is given by : $m = \dfrac{MIt}{nF}$. where, m is mass of the substance deposited or liberated, I is current in amperes, t is time in seconds, F is Faradays constant, n is the number of moles of electrons lost or gained, and M is the molar mass of the substance.

For example, in the electrolysis of molten NaCl, the cathode reaction tells us that one Na atom is produced when one Na^+ ion accepts an electron from the cathode. To reduce 1 mole of Na^+ ions, we must supply one mole of electrons (6.02×10^{23} electrons) to the cathode.

Example 4.4

How many moles of chlorine, magnesium and aluminium are formed when 2, 2 and 3 moles of charge are passed through three different solution containing chloride, magnesium and aluminium ions respectively?

Solution:

The stoichiometry of the anode reaction shows that oxidation of two Cl^- ions yields one chlorine molecule and releases two electrons. Therefore, the formation of 1 mole of chlorine results in 2 moles of electrons supplied by the Cl^- ions to the anode. Similarly, it takes 2 moles of electrons to reduce 1 mole of Mg^{2+} ions and 3 moles of electrons to reduce 1 mole of Al^{3+} ions:

$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

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

$Al^{3+}(l) + 3e^- \rightarrow Al(s)$
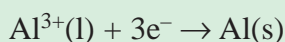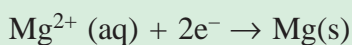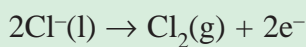
In an electrolysis experiment, we generally measure the current in amperes (A) that pass through an electrolytic cell in a given period of time. By definition, 1 coulomb of charge is transferred when a 1 ampere current flows for 1 second:

$1\ C = 1\ A \times 1\ s$

The charge on 1 mole of electrons is 96,500 C, which is obtained by multiplying 1 mol $(6.02 \times 10^{23}$ electrons) with the charge of electron $(1.602 \times 10^{-19}$ C).

Charge of 1 mol of electrons = 6.02×10^{23} electrons $\times 1.602 \times 10^{-19}$ C

$= 96,485\ C \approx 96,500\ C = 1\ F$ (one faraday)

Therefore, $1F = 96,500$ C.mol^{-1}.

Example 4.5

Calculate the mass of calcium metal and chlorine gas that can be produced when a current of 0.452 A is passed through molten $CaCl_2$ for 1.5 h.

Solution:

In solving electrolysis problems of this type, the first step is to determine which species will be oxidized at the anode and which species will be reduced at the cathode. Here the choice is straightforward because we only have Ca^{2+} and Cl^- ions in molten $CaCl_2$. Thus, we write the half and overall reactions as:

Anode (oxidation)   : $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Cathode (reduction) : $Ca^{2+}(l) + 2e^- \rightarrow Ca(l)$

_____

Overall reaction   : $Ca^{2+}(l) + 2Cl^-(l) \rightarrow Ca(l) + Cl_2(g)$
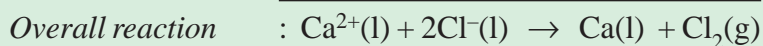
The quantities of calcium metal and chlorine gas formed depend on the number of electrons that pass through the electrolytic cell, which in turn depends on current $\times$ time or charge.

Charge (Q) = current (I) in A $\times$ time (t) in s

$$Q = I \times t = (0.452 \text{ A}) \times (1.5 \times 60 \times 60 \text{ s})$$

$$= 2.44 \times 10^3 \text{ A s} = 2.44 \times 10^3 \text{ C}$$

$$1 \text{ mol e}^- = 96,500 \text{ C}$$

$$x? = 2.44 \times 10^3 \text{ C}$$

$$\Rightarrow x = \frac{2.44 \times 10^3 \cancel{C} \times 1 \text{ mol e}^-}{96,500 \cancel{C}} = 0.0253 \text{ mol e}^-$$

2 moles of electrons are required to produce 1 mole, or 40 g, of calcium metal at the cathode. Hence, the mass of calcium formed is

$$2 \text{ mol e}^- = 1 \text{ mole Ca} = 40.08 \text{ g Ca}$$

$$0.0253 \text{ mol e}^- = x?$$

$$\Rightarrow x = \frac{0.0253 \cancel{\text{mol e}^-} \times 40.08 \text{ g Ca}}{2 \cancel{\text{mol e}^-}} = 0.507 \text{ g Ca}$$

The anode reaction indicates that 1 mole, or 71 g, of chlorine is produced by giving 2 moles of electrons to the anode. Hence, the mass of chlorine gas formed is

$$2 \text{ mol e}^- = 71 \text{ g Cl}_2 = 1 \text{ mole Cl}_2$$

$$0.0253 \text{ mol e}^- = x?$$

$$\Rightarrow x = \frac{0.0253 \cancel{\text{mol e}^-} \times 71 \text{ g Cl}_2}{2 \cancel{\text{mol e}^-}} = 0.898 \text{ g Cl}_2$$

Example 4.6

A current of 1.26 A is passed through an electrolytic cell containing an aqueous solution of H_2SO_4 for 7.44 h. Write the half-cell reactions and calculate the volume of the gases generated at STP (Note that at STP, $P = 1$ atm, and $T = 0°C$ or 273 K).

Solution:

Recall that, from the electrolysis of dilute H_2SO_4, we have:

Anode (oxidation) : $4OH^-(aq) \rightarrow 2H_2O\ (l) + O_2(g) + 4e^-$

Cathode (reduction) : $4H^+(aq) + 4e^- \rightarrow 2H_2(g)$

Overall reaction : $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$
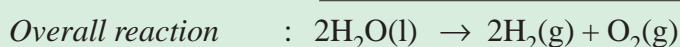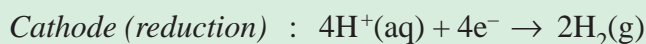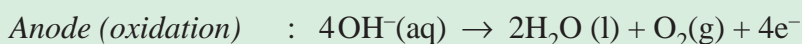
First let us calculate the total charge.

Given: $I = 1.26$ A

$t = 7.44\ h = 7.44 \times 60 \times 60\ s = 26{,}784\ s$

$Q = It = (1.26\ A) \times (26{,}784\ s) = 3.37 \times 10^4\ C$

The above balanced chemical equation shows that for 1 mole of O_2 formed at the anode, 4 moles of electrons are generated. Now let us calculate the number of moles of electrons.

$1\ \text{mol}\ e^- = 96{,}500\ C$

$x? = 3.37 \times 10^4\ C$

$$\Rightarrow x = \frac{1\ \text{mol}\ e^- \times 3.37 \times 10^4\ \cancel{C}}{96{,}500\ \cancel{C}} = 0.350\ \text{mol}\ e^-$$

The number of moles of oxygen becomes:

$4\ \text{mol}\ e^- = 1\ \text{mol}\ O_2$ (Observe the anode reaction)

$0.350\ \text{mol}\ e^- = x?$

$$\Rightarrow x = \frac{0.350\ \cancel{\text{mol}\ e^-} \times 1\ \text{mol}\ O_2}{4\ \cancel{\text{mol}\ e^-}} = 0.0875\ \text{mole of}\ O_2$$

The volume of 0.0875 mol O_2 at STP is given by

$$V = \frac{nRT}{P} = \frac{0.0875\ \cancel{mol} \times \left(0.0821\ \frac{L.\ \cancel{atm}}{\cancel{mol}\ .\ \cancel{K}}\right) \times (273\ \cancel{K})}{1\ \cancel{atm}}$$

$V = 1.96$ L or since the volume of 1 mol of a gas at STP is 22.4 L, the volume occupied by 0.0875 mol of O_2 can be obtained using the following relation.

1 mol = 22.4 L

0.0875 mol = x?

$$\Rightarrow x = \frac{0.0875 \text{ mol} \times 22.4 \text{ L}}{1 \text{ mol}} = 1.96 \text{ L}$$

Similarly, for hydrogen, we write

4 mol $e^- = 2$ mol H_2 (Observe the cathode reaction)

0.35 mol $e^- = x$?

$$x = \frac{0.35 \text{ mol } e^- \times 2 \text{ mol } H_2}{4 \text{ mol } e^-}$$

$$x = 0.175 \text{ mol } H_2$$

The volume of 0.175 mol of H_2 at STP is given by

$$V = \frac{nRT}{P} = \frac{0.175 \text{ mol} \times \left(0.0821 \frac{\text{L. atm}}{\text{mol . K}} \right) \times (273 \text{ K})}{1 \text{ atm}}$$

$V = 3.92$ L

Note that the volume of H_2 is twice that of O_2.

Exercise 4.6

1. Calculate the volume of H_2 and O_2 gases at 25°C and 1.00 atm that will be collected at the cathode and anode, respectively, when an aqueous solution of Na_2SO_4 is electrolyzed for 2 hours with 10 ampere current.

2. Calculate the mass of copper and volume of oxygen (at 25°C and 760 mmHg) that would be produced by passing a current of 0.5 A through a $CuSO_4$ solution between Pt electrodes for 3 hours.

3. What mass of aluminium is deposited electrolytically in 30 minutes by a current of 40 A?

4.3.2 Faraday's Second Law of Electrolysis

Faraday's second law of electrolysis states that "when the same quantity of charge (Q) is passed through different electrolytes, then the masses of different substances deposited ($m_1, m_2, m_3,...$) at the respective electrodes will be directly proportional to their equivalent masses ($E_1, E_2, E_3,...$)."

$$m \propto E$$

or, $\qquad m_1 \propto E_1,\ m_2 \propto E_2,\ \text{and}\ m_3 \propto E_3 \text{ etc.}$

Replacing the proportionality by a proportionality constant k, the equations become:

$$M_1/E_1 = M_2/E_2 = M_3/E_3 = \ \cdots\ = k$$

The law can be illustrated by passing the same quantity of electric current through three solutions containing H_2SO_4, $CuSO_4$ and $AgNO_3$, connected in series, as shown in Figure 4.6.
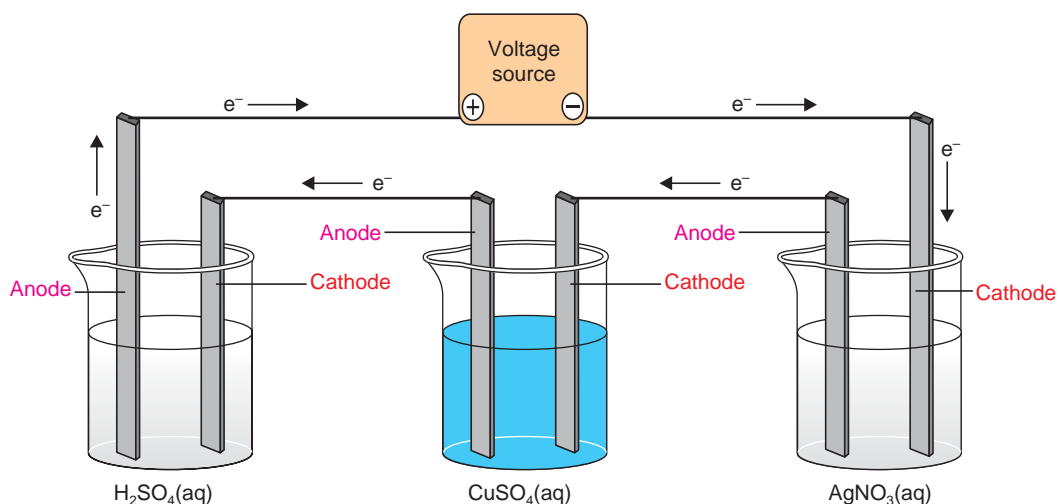
Figure 4.6 Solutions connected in series to a battery.

In the first solution, hydrogen and oxygen are liberated. In the second solution copper is deposited and in the third, silver is deposited.

$$\frac{\text{Mass of hydrogen}}{\text{Equivalent mass of } H_2} = \frac{\text{Mass of copper}}{\text{Equivalent mass of copper}} = \frac{\text{Mass of silver}}{\text{Equivalent mass of silver}}$$

Example 4.7

Calculate the mass of copper deposited by the electrolysis of copper (II) sulphate solution placed in series with a silver nitrate solution, when 0.108 g of silver is being deposited.

Solution:

The equivalent mass of silver and copper can be obtained from their reduction half-reaction:

$$Ag^+(aq) + 1e^- \rightarrow Ag(s), \ E_{Ag} = \frac{108 \ g/mol}{1} = 108 \ g/eq$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s), \ E_{Cu} = \frac{63.5 \ g/mol}{2} = 31.75 \ g/eq$$
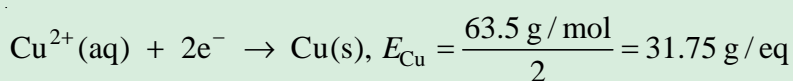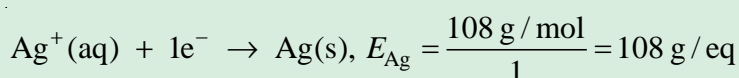
The mass of Ag is 0.108 g, and you are asked to find the mass of copper.

$$\frac{m_{Ag}}{E_{Ag}} = \frac{m_{Cu}}{E_{Cu}} \ \Rightarrow \ m_{Cu} = \frac{E_{Cu} \times m_{Ag}}{E_{Ag}}$$

$$= \frac{31.75 \ g/eq \times 0.108 \ g}{108 \ g/eq} = 0.032 \ g \ of \ Cu \ is \ deposited$$

Exercise 4.7

1. Two cells are connected in series. One contains $AlCl_3$, and the other contains $AgNO_3$ as the electrolytes. What mass of Ag is deposited when 18 g of Al is deposited at cathode?

2. 0.2 moles of electrons are passed through three electrolytic cells in series that contain silver ions, zinc ions and iron (III) ions. How many grams of each metal will be deposited at cathode?

4.4 INDUSTRIAL APPLICATION OF ELECTROLYSIS

After completing this subunit, you will be able to:

- mention the industrial applications of electrochemistry;
- explain electroplating and electrorefining;

- demonstrate copper refining; and

- explain how electrolysis is used in the production of some metals, nonmetals and compounds.

4.4.1 Electroplating and Electrorefining of Metals

Activity 4.7

Form a group. Discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. Define electroplating and electrorefining.

2. What are the purposes of electroplating and electrorefining?

3. Where do we put the plating metal and the metal to be plated, during electroplating?

4. Does the electrolyte contain dissolved ions of the plating metal or the metal to be plated?

5. What is chrome plating? How is it done?

6. Describe the electrorefining of copper. Include the appropriate chemical equations.

4.4.2 Extraction of Metals

Activity 4.8

Discuss each of the following questions. After the discussion, share your ideas with your classmates.

1. List active metals that can be extracted from their compounds by electrolysis.

2. Explain why electrolytic reduction rather than chemical reduction is often used to obtain active metals from their compounds.

3. Why are molten metal chlorides used as electrolytes rather than using other molten salts?

4.4.3   Manufacture of Nonmetals and Some Compounds

Activity 4.9

Form a group. Discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. List nonmetals and compounds that are prepared by electrolysis.

2. Write the cathode and anode reactions during the electrolysis of molten mixture of potassium fluoride and hydrogen fluoride.

3. Using chemical equations, write the preparation of:

    a   sodium hydroxide from the electrolysis of brine solution.

    b   hydrogen and oxygen from the electrolysis of dilute sodium chloride solution.

4. Why is a small amount of solute added in the electrolysis of water?

4.5 VOLTAIC (GALVANIC) CELLS

After completing this subunit, you will be able to:

*   define Voltaic cell and salt bridge;

*   draw and label Zn-Cu Voltaic cell;

*   define electrode potential and cell potential;

*   construct Zn-Cu Voltaic cell;

*   measure the cell potential of Zn-Cu cell using voltmeter;

*   explain how standard electrode potential is measured;

*   describe the reactivity of metal from its position in the activity series or electromotive series;

*   calculate cell potential;

*   decide whether a given redox reaction is spontaneous or not;

*   explain the effect of concentration on cell potential;

*   mention the different types of Voltaic cells;

*   give examples of each type of Galvanic cell;

*   describe how a hydrogen-oxygen fuel cell operates;

- distinguish between primary and secondary cells;

- identify the cathode, anode and electrolyte of a given Galvanic cell;

- compare and contrast electrolytic and Galvanic cells;

- explain metallic corrosion in terms of redox reactions;

- explain the negative effects of corrosion; and

- explain the different methods of the prevention of corrosion.

What makes a Galvanic cell different from an electrolytic cell?

A Galvanic cell is a device in which chemical energy is transformed into electrical energy.

4.5.1 Construction of Zn-Cu Galvanic Cell

Activity 4.10

Form a group. Discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. Describe the basic features of an electrochemical cell. Why are the two components of the cell separated from each other?

2. Given the following chemical reaction,

    $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$:

    a write equations for the oxidation and reduction half-reactions.

    b which half-reaction occurs in the anode compartment and which occurs in the cathode compartment?

What happens if zinc metal is immersed in copper (II) sulphate solution?

When zinc metal is immersed in copper sulphate solution, some zinc dissolves and some copper metal forms on the surface of the remaining zinc.

The net reaction,

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

is an oxidation-reduction reaction (redox reaction) in which electrons are transferred from zinc atoms to copper ions.

The half-reaction equations are:

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

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

Since the copper sulphate solution is in contact with the zinc metal, the electrons flow directly from the zinc metal atoms to the copper ions without doing useful work. If the half-reactions could be made to occur in separate compartments, and the electrons were transferred through an external wire from one compartment to the other, then we would have a Galvanic cell capable of doing electrical work.

A Galvanic cell was invented by the British Chemist John Daniell in 1836. It is called the Daniell cell. A diagram of this cell is as shown in Figure 4.7.
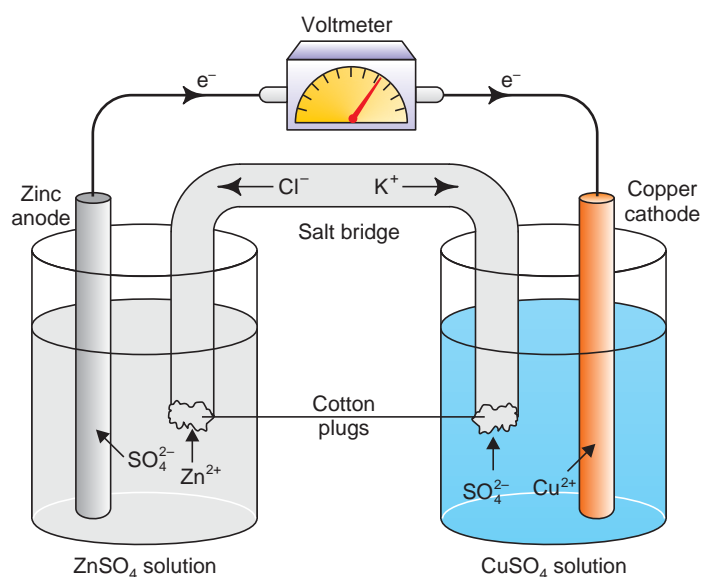
Figure 4.7 Daniell cell.

One compartment of the Daniell cell contains a zinc electrode immersed in a solution of zinc sulphate ($ZnSO_4$). The other compartment contains a copper electrode in a solution of copper sulphate ($CuSO_4$). When the two electrodes are connected by a wire, the zinc atoms give up electrons, forming positive ions:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$
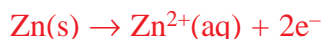
The zinc ions repel each other and enter the solution. The negative electrons also repel each other and travel through the external wire to the copper electrode, where they are accepted by copper ions from the surrounding solution:

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

The resulting copper atoms deposit as the copper metal on the surface of copper electrode. The Daniell cell reaction is identical to the reaction that occurs when zinc metal is dipped directly into copper sulphate solution (zinc atoms are oxidized and copper ions are reduced), but the cell is constructed so that the electrons pass through an external circuit where they can do useful work.

The solutions in the two halves of a Galvanic cell must be connected in order to complete the circuit, but they must not mix. The connection can be made through a salt bridge (see Figure 4.7).

A salt bridge is an inverted U-tube filled with an electrolyte, such as NH_4NO_3 or KCl, chosen so that it does not interfere with the operation of the cell. Regardless of how the cell is constructed, the solutions in each compartment remain more or less separated. Furthermore, because ions can move into and out of the salt bridge, the solutions remain electrically neutral.

How does the salt bridge maintain the electroneutrality of a solution?

Consider the zinc compartment. The oxidation of zinc atoms tends to build up the concentration of positive zinc ions in a solution around the zinc electrode. Some of the charge is neutralized by negative ions flowing out of the salt bridge and enter into the zinc compartment, and the rest of zinc ions flow out of the compartment into the salt bridge.

Now consider the copper compartment. The reduction of copper ions tends to decrease the concentration of positive copper ions around the copper electrode. The resulting negative charge is neutralized, partially by positive ions flowing from the salt bridge and enter into the copper compartment, and partially by negative sulphate ions flowing out of the compartment. If the flow of ions did not occur, a charge difference would build up between the compartments, and the reaction would stop. Every Galvanic cell has an oxidation half-reaction and a reduction half-reaction. The compartments in which these reactions occur (and their associated electrodes) are referred to as half-cells.

What are the anode and the cathode in a Galvanic cell?

The electrode where oxidation takes place is called the anode, and the electrode where reduction takes place is the cathode. In the Daniell cell, the zinc electrode is the anode and the copper electrode is the cathode. The anode sends electrons through the connecting wire (it is the electron source or negative terminal of the cell). The cathode receives electrons, so it is a positive terminal. When the terminals of a Galvanic cell are connected by an external circuit, there will always be a flow of electrons from anode to cathode through the external circuit.

Note that the electrode polarities in Galvanic cells are the reverse of those in an electrolytic cell.

	Cathode	Anode
Galvanic cell	+	–
Electrolytic cell	–	+

4.5.2 Cell Notation

How do you represent Galvanic cells without drawing a diagram?

A cell notation allows us to describe a Galvanic cell without drawing a diagram. It is a shorthand representation of a Galvanic cell. For example, a Daniell cell in which the electrolyte concentrations are each 1 molar is represented as

$$Zn(s) \mid Zn^{2+}(1\,M) \parallel Cu^{2+}(1\,M) \mid Cu(s)$$

The anode is written on the left. The cathode on the right and concentrations and other data are given in parentheses. The vertical line (|) indicates phase boundaries, and the double vertical line (||) indicates a salt bridge or a porous partition.

The cell notation for the Daniell cell tells us that the zinc anode is dipped into a 1 M solution of zinc ions, the copper cathode is dipped into a 1 M solution of copper ions, and the two half-cells are separated by a salt bridge or a porous partition. If the two half-cells were in direct contact, the double vertical line would be replaced by single line. The notation for any Galvanic cell has the following form:

anode | anode electrolyte (M) || cathode electrolyte (M) | cathode

Every redox reaction is the sum of an oxidation half-reaction and a reduction half-reaction written in such a way as to cancel out the electrons by suitably multiplying the half-reactions by the minimum integers.

Example 4.8

Write the cell notation for a Galvanic cell, based on this reaction:

$$Fe(s) + Hg_2^{2+}(aq) \rightarrow Fe^{2+}(aq) + 2Hg(l)$$
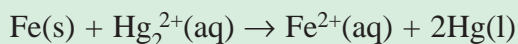
Assume that the solution concentrations are 0.10 M.

Solution:

Write the oxidation half-reaction and the reduction half-reaction separately.

Oxidation half-reaction (anode) : $Fe(s) \rightarrow Fe^{2+}(aq, 0.1\,M) + 2e^-$

Reduction half-reaction (cathode) : $Hg_2^{2+}(aq, 0.1\,M) + 2e^- \rightarrow 2Hg(l)$

The cell notation is : $Fe(s) \mid Fe^{2+}(0.10\,M) \parallel Hg_2^{2+}(0.10\,M) \mid Hg(l)$
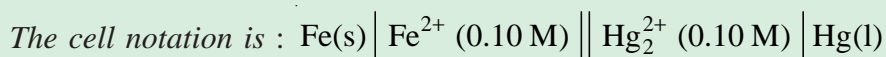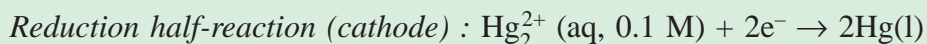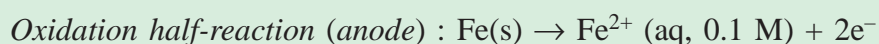
Exercise 4.8

1. Write the cell notation for a Galvanic cell consisting of an Al electrode placed in 1 M $Al(NO_3)_3$ solution and a Ag electrode placed in a 1 M $AgNO_3$ solution.

2. Explain the use of a salt bridge.

3. a Explain the difference between a Galvanic cell and an electrolytic cell.

   b Indicate the electrode polarity of each cell.

4.5.3 Standard Reduction Potentials

What is the difference between standard reduction potential and cell potential?

The cell potential is the difference between two electrode potentials, one associated with the cathode and the other associated with the anode.

By convention, the potential associated with each electrode is chosen to be the potential for reduction to occur at the electrode. Thus, standard electrode potentials (electrode potentials at a concentration of 1 M) are tabulated for reduction reactions and are denoted as E^o_{red}. The cell potential (E^o_{cell}) is E^o_{red} (*cathode*) minus the standard reduction potential of the anode reaction, E^o_{red} (*anode*):

$$E^o_{cell} = E^o_{red} \text{ (cathode)} - E^o_{red} \text{ (anode)}$$

Because every Galvanic cell involves two half-cells, it is not possible to directly measure the standard reduction potential of a half-reaction. However, if we assign a standard reduction potential to a certain reference half-reaction, we can then determine the standard reduction potentials of the other half-reactions, relative to that reference. The reference half-reaction is the reduction of $H^+(aq)$ to $H_2(g)$ under standard conditions, which is given a standard reduction potential of exactly 0.0 V.

$$2H^+ \text{ (aq, 1M)} + 2e^- \rightarrow H_2(g, 1 \text{ atm}); E^o_{red} = 0.0 \text{ V}$$

An electrode designed to produce this half-reaction is called a standard hydrogen electrode (SHE). As depicted in Figure 4.8, SHE consists of platinum wire connected to a piece of platinum foil covered with finely-divided platinum that serves as an inert surface for the reaction. The electrode is encased in a glass tube, so that hydrogen gas can bubble over the platinum, and the solution contains $H^+(aq)$ under standard (1 M) conditions.

Can you indicate the cathode and the anode in Figure 4.8?
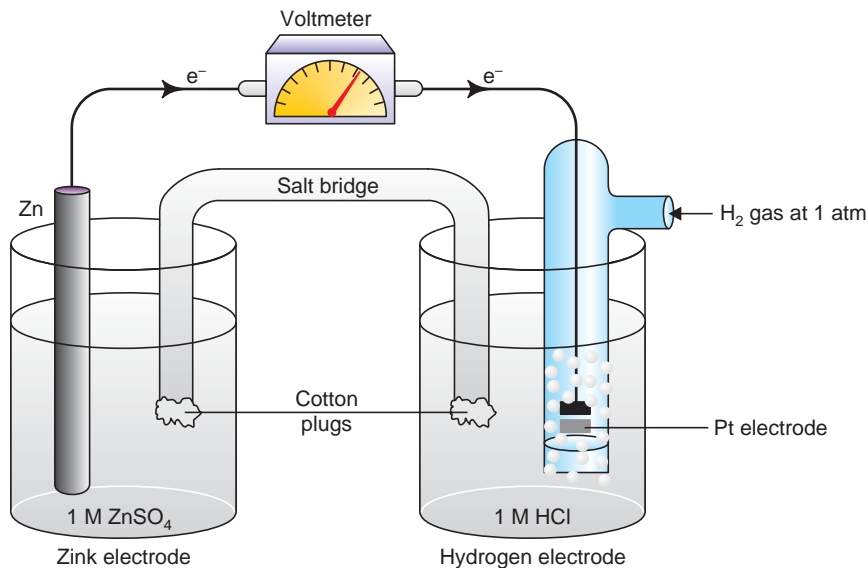
Figure 4.8 Standard Hydrogen Electrode

The spontaneous reaction in Figure 4.8, is the oxidation of zinc and the reduction of H^+ :

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

In the Figure 4.8, above;

i)   The Zn^{2+} | Zn electrode is the anode, and the SHE is the cathode.

ii)   The cell voltage is 0.76 V.

By using the defined standard reduction potential of H^+ , we can determine the standard reduction potential for Zn^{2+} | Zn half-reaction:

$$E^o_{cell} = E^o_{red} \text{ (cathode)} - E^o_{red} \text{ (anode)}$$

$$0.76 \text{ V} = 0.0 \text{ V} - E^o_{red} \text{ (anode)}$$

$\Rightarrow$ $E^o_{red} \text{ (anode)} = -0.76$ V

 Therefore, a standard reduction potential of –0.76 V can be assigned to the reduction of Zn^{2+} to Zn:

$$Zn^{2+} \text{ (aq, 1M)} + 2e^- \rightarrow Zn(s); E^o_{red} = -0.76 \text{ V}$$

Note that we write the reaction as a reduction, even though it occurs in reverse as oxidation. Whenever we assign a potential to a half-reaction, we write the reaction as a reduction.

The standard reduction potentials for other half-reactions are established in the way that we did for the $Zn^{2+} \mid Zn$ half-reaction. In Table 4.2, the standard reduction potentials of some of the half-reactions are given.

Table 4.2 Standard Reduction Potential in Aqueous Solution at 25°C.

Half-reaction	Volts
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	+1.70
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.07
$2Hg^{2+}(aq) + 2e^- \rightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$	+0.68
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+} + e^- \rightarrow Cu^+(aq)$	+0.15

Increasing strength as oxidizing agent

Increasing strength as reducing agent

Half-reaction	Volts
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	−0.41
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71
$Li^+(aq) + e^- \rightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent (left vertical label)

Increasing strength as reducing agent (right vertical label)

In your calculations, be sure to understand these points about the information in Table 4.2:

1. The E^o_{red} values apply to the half-cell reactions as read in the forward (*left to right*) direction.

2. The more positive E^o_{red} is the greater tendency for the substance to be reduced.

   For example, the reaction,

   $F_2(g, 1 \text{ atm}) + 2e^- \rightarrow 2F^-(1M)$, $E^o_{red} = +2.87$ V

has the highest E^o value for all of the half-cell reactions. Thus, F_2 is the strongest oxidizing agent because it has the greatest tendency to be reduced. At the other extreme is the reaction,

$$Li^+ (1M) + e^- \rightarrow Li(s), \; E^o_{red} = -3.05 \text{ V}$$

which has the most negative E^o_{red} value. Thus, Li^+ is the weakest oxidizing agent, because it is the most difficult species to be reduced. Alternatively, Li metal is the strongest reducing agent since it gets oxidized most readily.

3. Under standard state conditions, any species on the left of a given cell reaction reacts spontaneously with a species that appears on the right of any half-cell reaction that is located below it in Table 4.2. This principle is sometimes called the diagonal rule. In the case of the Daniell cell,

$$Cu^{2+} (1 \text{ M}) + 2e^- \rightarrow Cu(s); \quad E^o_{red} = +0.34 \text{ V}$$

$$Zn^{2+} (1 \text{ M}) + 2e^- \rightarrow Zn(s); \quad E^o_{red} = -0.76 \text{ V}$$

We see that the substance on the left of the first half-cell reaction is Cu^{2+}, and on the right in the second half-cell reaction is Zn. Therefore, Zn spontaneously reduces Cu^{2+} to form Zn^{2+} and Cu.

4. Changing the stoichometric coefficients of a half-cell reaction does not affect the value of E^o_{red}, because electrode potentials are intensive properties. This means that the value of E^o_{red} is unaffected by the size of the electrodes or the amount of solutions present but is dependent on the concentration of the solutions and the pressure of a gas (if any).

For example,

$$I_2(s) + 2e^- \rightarrow 2I^- (1M); \; E^o_{red} = +0.53 \text{ V}$$

but E^o does not change if we multiply the half-reaction by 2:

$$2I_2(s) + 4e^- \rightarrow 4I^- (1M); \; E^o_{red} = +0.53 \text{ V}$$

5. The sign of E^o_{red} changes, but its magnitude remains the same when we reverse a reaction.

6. The more positive the reduction potential, the greater the tendency to accept electrons. As a result, when two half-cells are coupled, the reaction with higher (more positive) reduction potential proceeds as reduction, while the other proceeds as oxidation.

Example 4.9

A Galvanic cell consists of a Mg electrode in 1.0 M $Mg(NO_3)_2$ solution and a Ag electrode in 1.0 M $AgNO_3$ solution. Calculate the standard cell potential (*emf*) of this cell at 25°C.

Solution:

Using Table 4.2, it can be noticed that Ag^+ will oxidize Mg:

Anode (oxidation) : $Mg(s) \rightarrow Mg^{2+}$ (1 M) + 2e$^-$; $E^o_{red} = $ +2.37 V

Cathode (reduction) : $2Ag^+$ (1 M) + 2e$^- \rightarrow 2Ag(s)$; $E^o_{red} = $ +0.80 V

Overall reaction : $Mg(s) + 2Ag^+$ (1 M) $\rightarrow Mg^{2+}$ (1 M) + 2Ag(s)
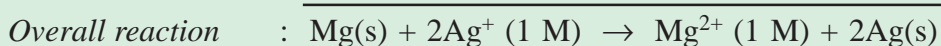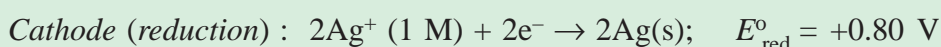
$$E^o_{cell} = 2.37 \text{ V} + 0.80 \text{ V} = +3.17 \text{ V}$$

Note that, in order to balance the overall reaction, we multiplied the cathode reaction by 2. We can do so because, E^o_{red} is an intensive property, which means it is not affected by this procedure. We can also find the E^o_{cell} by using the principle stated in number 6 above.

$Ag^+ (1.0 M) + e^- \rightarrow Ag^+(s), E^o_{red} = +0.80 V$ (*Cathode: higher reduction potential*)

$Mg^{2+} (1.0 M) + 2e^- \rightarrow Mg(s), E^o_{red} = -2.37 V$ (*Anode: lower reduction potential*)

$E^o_{red} = E^o_{red}$ (cathode) $- E^o_{red}$ (anode)
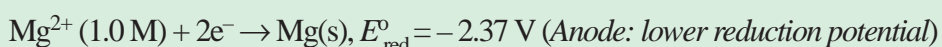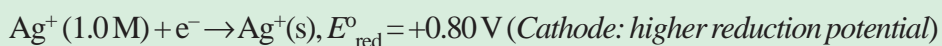
$\quad = E^o_{red}$ (Ag^+/Ag) $- E^o_{red}$ (Mg^{2+}/Mg)

$\quad = 0.80$ V $- (-2.37$ V) $= +3.17$ V

The positive value of E^o_{cell} shows that the forward reaction is favoured.

Experiment 4.3
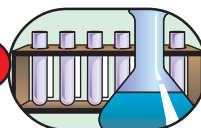
Determination of Cell Potential of Daniell Cell

Objective: To determine cell potential of Daniell cell and to identify the cathode and anode.

Apparatus: Voltmeter, copper strip, zinc strip, 1 M $ZnSO_4$, 1 M $CuSO_4$, saturated KCl solution, two 100 mL beakers, U-tube, a fine sandpaper or file and cotton.
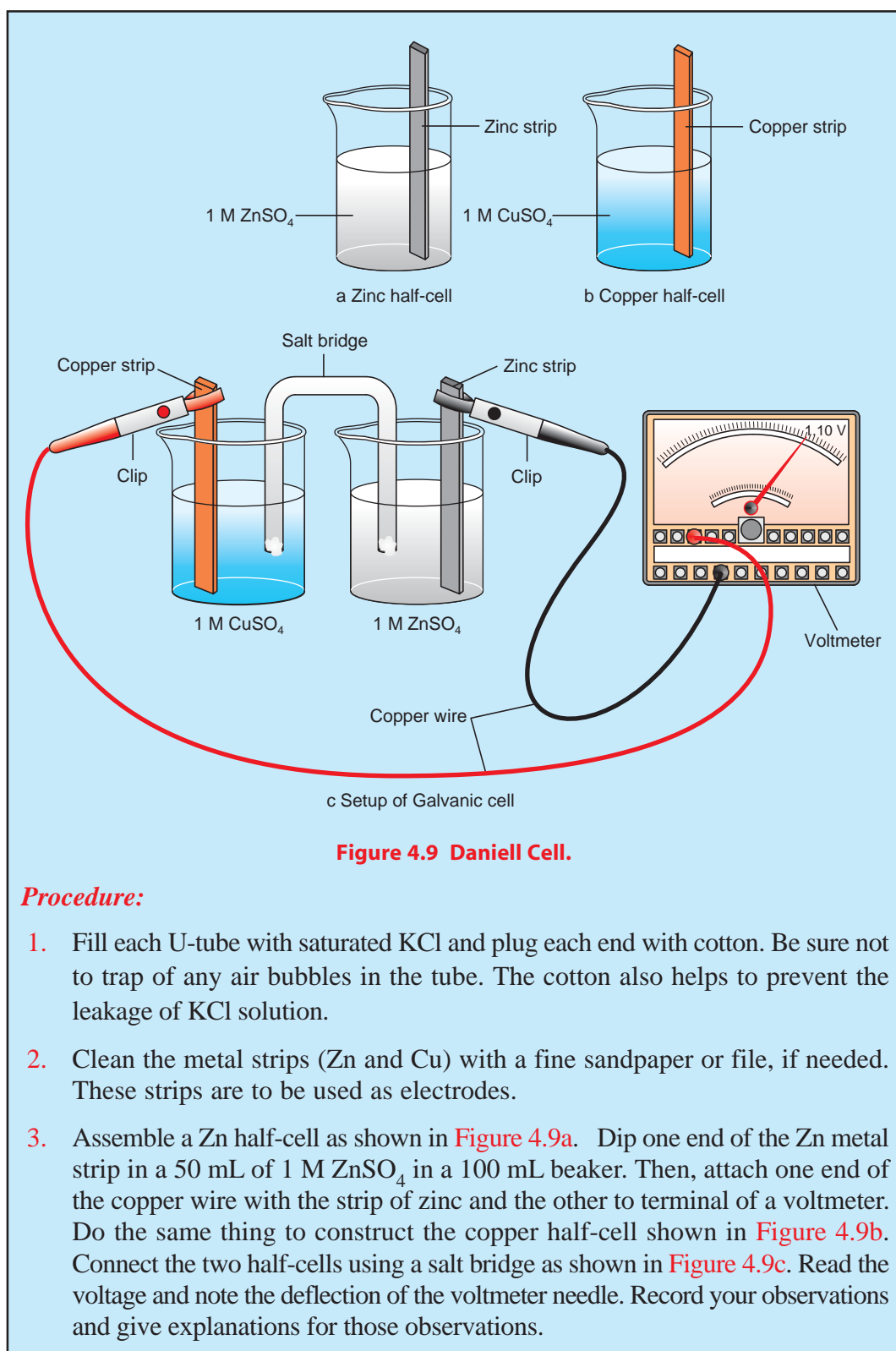
Figure 4.9 Daniell Cell.

Procedure:

1. Fill each U-tube with saturated KCl and plug each end with cotton. Be sure not to trap of any air bubbles in the tube. The cotton also helps to prevent the leakage of KCl solution.

2. Clean the metal strips (Zn and Cu) with a fine sandpaper or file, if needed. These strips are to be used as electrodes.

3. Assemble a Zn half-cell as shown in Figure 4.9a.   Dip one end of the Zn metal strip in a 50 mL of 1 M $ZnSO_4$ in a 100 mL beaker. Then, attach one end of the copper wire with the strip of zinc and the other to terminal of a voltmeter. Do the same thing to construct the copper half-cell shown in Figure 4.9b. Connect the two half-cells using a salt bridge as shown in Figure 4.9c. Read the voltage and note the deflection of the voltmeter needle. Record your observations and give explanations for those observations.

Results and discussion:

1. What happens to the needle in the voltmeter when current flows in the external circuit? What does the deflection of needle indicate? Label the cathode and anode.

2. Write the half-reactions at each half cells.

3. Is there any colour change in the intensity of copper sulphate solution?

4. What are the factors that affect cell potential?

Exercise 4.9

1. What is the standard emf (E^o_{cell}) of a Galvanic cell which is made of a Cd electrode in a 1.0 M $Cd(NO_3)_2$ solution and a Cr electrode in a 1.0 M $Cr(NO_3)_3$ solution at 25°C?

2. Given the following overall reaction,

   $$Cu^{2+}(1\ M) + Mg(s) \rightarrow Cu(s) + Mg^{2+}(1\ M)$$

   a Sketch the Galvanic cell based on the reaction.

   b Identify the cathode and anode.

   c Show the direction of electron flow through the external circuit.

4.5.4 Electromotive Force (emf)

Activity 4.11

Form a group. Discuss the following question.

Why does water in a river flow downhill rather than uphill? How do you relate this concept to the movement of electrons in a wire? After the discussion, share your ideas with the rest of the class.

When electrons move through a wire, they encounter resistance from localised atoms in their paths. The driving force that allows the electrons to overcome this resistance and move around the circuit is called electromotive force (emf).

The electromotive force in a Galvanic cell comes from the redox reaction that pushes electrons from the anode to a cathode through the external circuit. Electrons on the negative electrode repel each other and have more potential energy than electrons on

the positive electrode. This potential difference causes electrons to flow through the external circuit from the negative terminal (*anode*) to the positive terminal (*cathode*). The energy of the moving electrons is used to overcome resistance in the external circuit, and it can be used to do various forms of electrical work. Energy that overcomes resistance appears as heat or as light emitted by a glowing filament. Electrical work is used for starting cars, running watches, radios, and computers etc.

Electrical work (W) is the product of the emf of the cell and the total charge (in coulombs) that passes through the cell:

$$W = Q \times E$$

where Q is the charge and E is electrical potential.

Electrical energy = coulombs × volts = joules

The total charge is determined by the number of moles of electrons (n) that pass through the circuit.

By definition,

$$Q = nF$$

where F, the Faraday constant, is the total electrical charge contained in 1 mole of electrons.

$$1 \text{ F} = 96,500 \text{ C/mol e}^-$$

Because $1 \text{ J} = 1 \text{ C} \times 1 \text{ V}$,

We can also express the unit of Faraday as $1 \text{ F} = 96, 500 \text{ J/V. mol e}^-$.

The measured emf is the maximum voltage that the cell can achieve. This value is used to calculate the maximum amount of electrical energy that can be obtained from the chemical reaction. This energy is used to do electrical work (W_{ele}), so

$$W_{max} = W_{ele} = - nFE_{cell}$$

where, W_{max} is the maximum amount of work that can be done.

What does the negative sign indicate?

The change in free energy (ΔG) represents the maximum amount of useful work that can be obtained from a reaction.

$$\Delta G = W_{max}$$
$$\Rightarrow \quad \Delta G = W_{max} = - nFE_{cell}$$
$$\Delta G = - nFE_{cell}$$

Both n and F are positive quantities, and ΔG is negative for a spontaneous process, so E_{cell} must be positive. Therefore, a positive E_{cell} value corresponds to a negative ΔG value, which is the condition for spontaneity.

For standard state conditions,

$$\Delta G° = - nFE°_{cell}$$

Now we can relate $E°_{cell}$ to the equilibrium constant (K) of a redox reaction. The standard free energy change, $\Delta G°$, for a reaction is related to its equilibrium constant, as follows.

$$\Delta G° = - RT \ln K$$

If we substitute $\Delta G°$ by $- nFE°_{cell}$ it becomes $+ nFE°_{cell} = + RT \ln K$

$$\Rightarrow \quad nFE°_{cell} = RT \ln K$$

$$E°_{cell} = \frac{RT}{nF} \ln K$$

When $T = 298$ K, the equation can be simplified by substituting for R and F.

$$E°_{cell} = \frac{(8.134 \text{J/mol K}) \times (298 \text{ K})}{n \,(96,500 \text{J/V mol})} \ln K = \frac{0.0257 \text{ V}}{n} \ln K$$

The natural logarithm (ln) is related to the common logarithm (log) as follows:

$$\ln x = 2.303 \, \log x$$

$$\left(\frac{0.0257 \text{V}}{n}\right) \times 2.303 \, \log K = \frac{0.0592 \text{ V}}{n} \log K$$

Therefore, $E°_{cell} = \dfrac{0.0592 \text{ V}}{n} \log K.$

Thus, if any one of the three quantities $\Delta G°$, K or $E°_{cell}$ is known, the other two quantities can be calculated, using the equations $\Delta G° = - RT \ln K$, $\Delta G° = - nFE°_{cell}$

or $E°_{cell} = \dfrac{-\Delta G°}{nF}.$

Let us summarize the relationships among $\Delta G°$, K and $E°_{cell}$ and characterize the spontaneity of a redox reaction.

Table 4.3 Relationship among ΔG^o, K and E^o_{cell}

ΔG^o	K	E^o_{cell}	Reaction under standard state conditions
Negative	> 1	Positive	Favours the formation of products.
Zero	= 1	Zero	Reactants and products are equally favoured.
Positive	< 1	Negative	Favours the formation of reactants.

Example 4.10

Calculate the equilibrium constant for the following reaction at 25°C.

$$Sn(s) + 2Cu^{2+}(aq) \rightleftharpoons Sn^{2+}(aq) + 2Cu^{+}(aq)$$
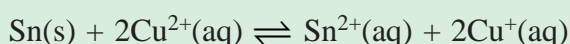
Solution:

The equilibrium constant (K) can be calculated, using the equation,

$$\ln K = \frac{nE^o_{cell}}{0.0257 \text{ V}} \implies K = e^{\left(\frac{nE^o_{cell}}{0.0257 \text{ V}}\right)}$$

The half-reactions are:

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

Cathode (reduction) : $2Cu^{2+}(aq) + 2e^- \rightarrow 2Cu^{+}(aq)$
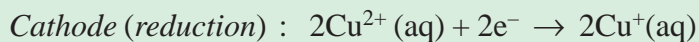
From the above reaction and using Table 4.2, we can calculate the cell potential,

$$E^o_{cell} = E^o_{red} \,(cathode) - E^o_{red} \,(anode)$$
$$= E^o_{red} \,(Cu^{2+}/Cu^{+}) - E^o_{red} \,(Sn^{2+}/Sn)$$
$$= 0.15 \text{ V} - (-0.14 \text{ V}) = +0.29 \text{ V}$$

E^o_{cell} is 0.29 V, and $n = 2$ (because 2 mol of electrons are consumed in the reaction), then,

$$\ln K = \frac{nE^o_{cell}}{0.0257 \text{ V}} = \frac{2 \times 0.29 \cancel{V}}{0.0257 \cancel{V}} = 22.6$$

$$\implies K = e^{22.6} = (2.72)^{22.6} = 7 \times 10^9$$

The reaction favours the products.

Example 4.11

Calculate the standard free-energy change for the following reaction at 25°C.

$2Au(s) + 3Ca^{2+} (1.0 \text{ M}) \rightarrow 2Au^{3+}(1.0 \text{ M}) + 3Ca(s)$
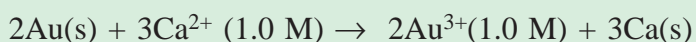
Solution :

The relationship between the standard free energy change and the standard cell potential is given by $\Delta G^\circ = -nFE^\circ_{cell}$. First, let us determine E°_{cell}

The half-reactions are:

Anode (oxidation) : $2Au(s) \rightarrow Au^{3+} (1.0 \text{ M}) + 6e^-$

Cathode (reduction) : $3Ca^{2+} (1.0 \text{ M}) + 6e^- \rightarrow 3Ca(s)$
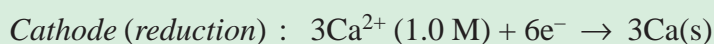
$E^\circ_{cell} = E^\circ_{red} (cathode) - E^\circ_{red} (anode)$

$E^\circ_{cell} = E^\circ_{red} (Ca^{2+}/Ca) - E^\circ_{red} (Au^{3+}/Au)$

$= -2.87 \text{ V} - 1.50 \text{ V} = -4.37 \text{ V}$

The overall reaction shows that n = 6 (6 moles of electrons are involved). Now we can calculate ΔG°, using the following equation:

$\Delta G^\circ = -nFE^\circ_{cell}$

$= -6 \times (96500 \text{ J/V mol}) \times (-4.37 \text{ V})$

$= 2.53 \times 10^6 \text{ J/mol} = 2.53 \times 10^3 \text{ kJ/mol}$

Therefore, the large positive value of ΔG° tells us that the reaction favours the reactants at equilibrium. The forward reaction is non-spontaneous, that is, gold cannot reduce calcium.

Exercise 4.10

By referring to Table 4.2, calculate ΔG° for the following reaction at 25°C.

$2Al^{3+}(aq) + 3Mg(s) \rightleftharpoons 2Al(s) + 3Mg^{2+}(aq)$
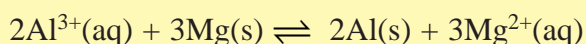
4.5.5   Dependence of emf on Concentration

What is the effect of changing the concentration of reactants on cell potential?

A change in concentration affects the change of cell potential which is a result of free energy change. According to chemical thermodynamics

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Where, Q is the reaction quotient, and Q was used to calculate the effect of concentration on ΔG. Since $\Delta G = -nFE_{cell}$ and $\Delta G^\circ = -nFE_{cell}^\circ$, the equation becomes

$$-nFE_{cell} = -nFE_{cell}^\circ + RT \ln Q$$

Dividing each side of the equation by $-nF$ gives

$$E = E_{cell}^\circ - \frac{RT}{nF} \ln Q$$

This equation gives the relationship between the cell potential and the concentrations of the cell components and is called the Nernst equation.

At 25°C:

$$E_{cell} = E_{cell}^\circ - \frac{(8.314 \text{ J/mol K}) \times (298 \text{ K})}{(n)\,(96,500 \text{ J/V mol})} \ln Q$$

$$E_{cell} = E_{cell}^\circ - \frac{0.0257 \text{ V}}{n} \ln Q \quad \text{or} \quad E = E_{cell}^\circ - \frac{0.0592}{n} \log Q$$

During the operation of a Galvanic cell, electrons flow from the anode to the cathode, resulting in product formation and a decrease in reactant concentration. Thus Q increases, which means that E_{cell} decreases. Eventually, the cell reaction reaches equilibrium. At equilibrium, there is no net transfer of electrons, so $E_{cell} = 0$ and $Q = K$, where K is the equilibrium constant.

The above equation enables us to calculate E_{cell} as a function of reactant and product concentrations in a redox reaction. For monovalent ions ten-fold changes in concentration of solution will cause a change of 0.0592 volts and bivalent a change of 0.0592/2 volts. For example, for the Daniell cell,

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s), \quad E^\circ_{cell} = 1.10 \text{ V}$$

The equation for this cell at 25°C can be written as:

$$E_{cell} = 1.1 \text{ V} - \frac{0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Note that the concentration of liquids and solids is constant and does not appear in the equilibrium constant expression. If the ratio $[\text{Zn}^{2+}]/[\text{Cu}^{2+}]$ is less than 1, then $\log ([\text{Zn}^{2+}]/[\text{Cu}^{2+}])$ is a negative number. Therefore, the second term on the right-hand side of the preceding equation is positive. Under this condition, E_{cell} is greater than the standard cell potential. If the ratio is greater than 1, E_{cell} is smaller than E^{o}_{cell}.

Example 4.12

Predict whether the following reaction would proceed spontaneously, as written at 298 K, given that $[\text{Co}^{2+}] = 0.15$ M and $[\text{Fe}^{2+}] = 0.68$ M :

$$\text{Co(s)} + \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Co}^{2+}(\text{aq}) + \text{Fe(s)}$$
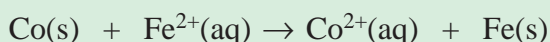
Solution :

Because the reaction is not run under standard state conditions (concentrations are not 1 M), we need the equation to calculate the emf (E_{cell}) of Galvanic cell. The standard emf (E^{o}_{cell}) can be calculated, using the standard reduction potentials in Table 4.2.

The half-cell reactions are

Anode (oxidation) : $\text{Co(s)} \rightarrow \text{Co}^{2+}(\text{aq}) + 2\text{e}^-$

Cathode (reduction) : $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe(s)}$

$E^{o}_{cell} = E^{o}_{red}(cathode) - E^{o}_{red}(anode)$

$\quad = E^{o}_{red} \text{ (Fe}^{2+}\text{/Fe)} - E^{o}_{red} \text{ (Co}^{2+}\text{/Co)}$

$\quad = -0.44 \text{ V} - (-0.28 \text{ V}) = -0.16 \text{ V}$

Using the equation,

$$E_{cell} = E^{o}_{cell} - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$= E^{o}_{cell} - \frac{0.0257 \text{ V}}{n} \ln \frac{\left[\text{Co}^{2+}\right]}{\left[\text{Fe}^{2+}\right]}$$

$$= -0.16 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln\left(\frac{0.15}{0.68}\right)$$

$$= -0.16 \text{ V} + 0.019 \text{ V} = -0.14 \text{ V}$$

The reaction is not spontaneous in the direction written. Why?

Exercise 4.11

1. Will the following reaction occur spontaneously at 25°C, given that $[Fe^{2+}] = 0.60$ M and $[Cd^{2+}] = 0.010$ M? (Hint: Use the Nernst equation)

   $$Cd(s) + Fe^{2+} \rightarrow Cd^{2+} \text{ (aq)} + Fe(s)$$
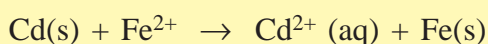
2. Complete the following table. State whether the cell-reaction is spontaneous, non-spontaneous, or at equilibrium.

E	ΔG	Cell reaction
> 0		
	> 0	
= 0		

4.5.6 Batteries

Activity 4.12

Form a group. Discuss the following questions, and share your idea with other groups.

1. What are the advantages of batteries?
2. When do we say a battery is "dead"?
3. Collect some used and disposed batteries;
   - i   classify them as:
     - a primary battery or secondary battery.
     - b dry cell or alkaline battery etc.
   - ii   Identify the parts of the batteries, which you have collected.
   - iii Describe the type of electrodes as well as physical and chemical nature of the electrolyte present in each battery.

Caution! Wear gloves while collecting the disposed batteries.

A battery is a Galvanic cell, or a series of combined Galvanic cells, that can be used as a source of direct current at a constant voltage.

The principal advantages offered by batteries are convenience and portability, rather than efficient use of energy.

Based on their rechargeability, we can classify batteries as primary and secondary. Primary batteries use redox reactions that cannot be returned to their original state by recharging, so when the reaction is complete, the batteries become "dead" and must be discarded. Secondary batteries are often called storage batteries, or rechargeable batteries. The reactions in these batteries can be reversed, which means that the batteries can be recharged. They have the advantage of being more cost-efficient in the long term although the individual batteries are more expensive.

PROJECT 4.1

Go to a nearby automobile garage and ask the garage mechanic:

1. about working of car battery;

2. how do they come to know whether a car battery needs recharging;

3. what components serve as electrolyte, anode and cathode in a car battery?

Write the project report and submit it to your teacher.

In this section, you will learn the various types of batteries that are widely used.

The Dry Cell Battery

Activity 4.13

In your Grade 10 chemistry, you have learnt about dry cell batteries. Form a group. Discuss the following questions, and share your idea with other groups.

1. What are the components that serve as electrolyte, anode and cathode in a dry cell?

2. For a dry cell, write the:

   a   oxidation half-reaction,

   b   reduction half-reaction, and

   c   overall reaction.
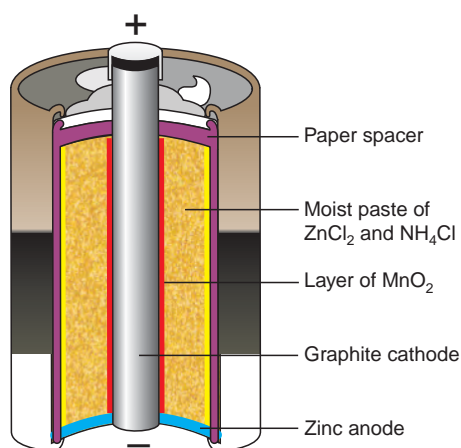
Figure 4.10 The interior section of a dry cell battery.

The voltage produced by a dry cell is about 1.5 V. The LeClanchè cells are widely used because of their low cost, but they have several disadvantages. If the current is drawn from the battery very rapidly, the gaseous products cannot be consumed immediately. As a result, the cell resistance increases and the voltage drop. In addition, since an ammonium ion is a weak conjugate acid, the zinc electrode and ammonium ion react very slowly. Because of this reaction, these voltaic cells cannot be stored indefinitely. You have probably learned from experience that, when the zinc outer cover deteriorates, the electrolyte can leak out and damage the flashlight or other appliances in which it contained.

Alkaline Battery

Alkaline batteries are more expensive than LeClanchè batteries. Why? They can generate current up to 50% longer than the same size of dry cell batteries. The chemistry of alkaline cells is quite similar to that of LeClanchè cells, except that the material inside the cell is basic or alkaline. Alkaline cells use the oxidation of zinc and reduction of MnO_2 to generate a current, but NaOH or KOH is used in the cell instead of the acidic salt NH_4Cl.

$$\textit{Anode} \quad : \; Zn(s) + 2OH^-(aq) \; \rightarrow \; ZnO(s) + H_2O(l) + 2e^-$$

$$\textit{Cathode} \; : \; 2MnO_2(s) \; + H_2O(l) \; + 2e^- \; \rightarrow \; Mn_2O_3(s) + 2OH^-(aq)$$

Write the overall balanced chemical equation.

The additional advantage of alkaline cells is that the cell potential does not decline under high current loads, because no gases are formed.

Mercury cells are alkaline cells that are typically used in calculators, cameras, watches and other devices. The anode in a mercury cell is again metallic zinc, but the cathode is mercury (II) oxide.

Anode : $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode : $HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(s) + 2OH^-(aq)$

Write the overall balanced chemical equation.

The cell produces 1.35 V. These cells are widely used, but their disposal is an environmental problem, and there are ongoing efforts to phase them out. Mercury and its compounds are poisonous. So, mercury batteries should be reprocessed to recover the metal at the end of their useful lives.

Nickel-Cadmium Battery

Because dry cells are not rechargeable, they have to be replaced frequently. The nickel-cadmium battery is rechargeable and especially is used in battery-operated tools and portable computers.

The cadmium metal serves as the anode, and the $NiO_2(s)$, which is reduced to $Ni(OH)_2(s)$, serves as the cathode. The cell reactions are:

Anode : $Cd(s) + 2OH^-(aq) \rightleftharpoons Cd(OH)_2(s) + 2e^-$

Cathode : $NiO_2(s) + 2H_2O(l) + 2e^- \rightleftharpoons Ni(OH)_2(s) + 2OH^-(aq)$

Overall reaction : $NiO_2(s) + Cd(s) + 2H_2O(l) \rightleftharpoons Ni(OH)_2(s) + Cd(OH)_2(s)$
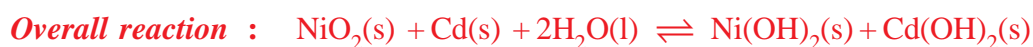
The solid reaction products, $Ni(OH)_2$ and $Cd(OH)_2$, adhere to the electrodes. This permits the reactions to be readily reversed during charging.

The Lead Storage Battery

The lead storage battery commonly used in automobiles consists of six identical cells joined together in series. This is an example of a secondary rechargeable cell. The reactions within the cell can be reversed. Each cell has a lead anode and a cathode made up of lead oxide (PbO_2) packed on a metal plate.

Both the cathode and the anode are immersed in an aqueous solution of sulphuric acid which acts as the electrolyte. Figure 4.11 depicted the typical lead storage battery. The cell reactions are:

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

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

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

Removable cap

Anode

Cathode

H_2SO_4 electrolyte

Negative plates
(lead grills
filled with
spongy lead)

Positive plates
(lead grills filled
with PbO_2)
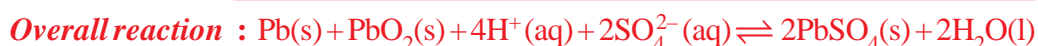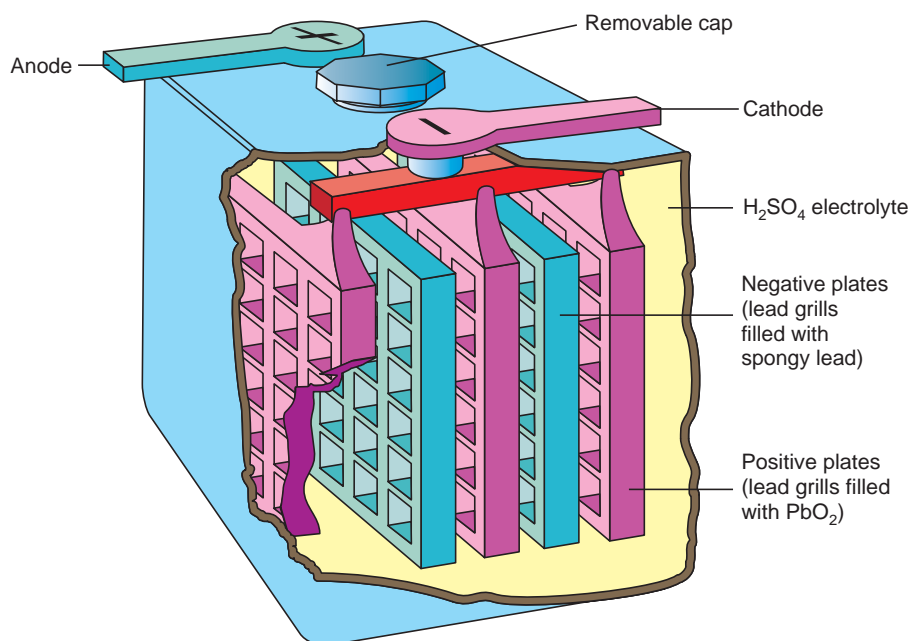
Figure 4.11 Interior section of a lead storage battery.

Under normal operating conditions, each cell produces 2 V. Therefore a total of 12 V is supplied by the six cells. Lead storage battery is used to power the ignition circuit of automobile and other electrical systems. The lead storage battery can deliver large amounts of current in short time, such as the time it takes to start up the engine. The lead storage battery is rechargeable.

Activity 4.14

Form a group. Discuss the chemical reactions occurring at the cathode and anode during the charging of the car battery. Do these reactions differ from the reactions occurring during discharge of the battery? Share your idea with the class.

Activity 4.15

Form a group. Discuss the following:

The electrolyte in a discharged lead storage battery freezes at higher temperature than a fully charged battery. Explain this observation to your class.

Fuel Cells

What makes a fuel cell different from other types of batteries?

Fossil fuels are major sources of energy, but the conversion of fossil fuel into electrical energy is a highly inefficient process.

Consider the combustion of methane:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) + Energy$$

To generate electricity, heat produced by the reaction is first used to convert water to steam, which then drives a turbine that drives a generator. A significant fraction of the energy released in the form of heat is lost to the surroundings at each step. Even the most efficient power plants convert only about 40% of the original chemical energy into electricity. Because combustion reactions are redox reactions, it is more desirable to carry them out directly by electrochemical means, thereby greatly increasing the efficiency of the power production. This objective can be accomplished by a device known as a fuel cell.

A fuel cell is a Galvanic cell that requires a continuous supply of reactants to keep functioning. In its simplest form, a hydrogen-oxygen fuel cell consists of an electrolyte solution such as sodium hydroxide solution, and two inert electrodes. The hydrogen and oxygen gases are bubbled through the anode and cathode compartments. See Figure 4.12.
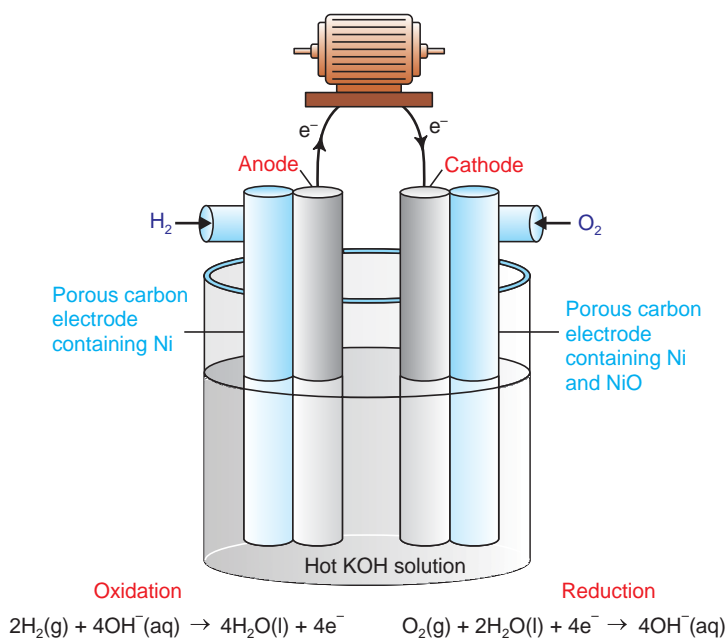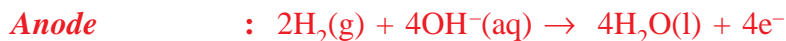

Oxidation
$2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

Reduction
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Figure 4.12 A Hydrogen-oxygen fuel cell.

The reactions are

Anode   : $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

Cathode   : $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Overall reaction : $2H_2(g) + O_2(aq) \rightarrow 2H_2O(l)$

The standard cell potential, can be calculated using the data from Table 4.2.

$$E^\circ_{cell} = E^\circ_{red} (cathode) - E^\circ_{red} (anode)$$
$$= 0.40 \text{ V} - (-0.83 \text{ V})$$
$$= +1.23 \text{ V}$$

Thus, the cell reaction is spontaneous under standard state conditions. Note that the reaction is the same as the hydrogen combustion reaction, except that the oxidation and reduction are carried out separately at the anode and the cathode. Unlike batteries, fuel cells do not store chemical energy. Reactants must be continuously supplied, and products must be continuously removed from a fuel cell.

Exercise 4.12

1. Explain the difference between a dry cell and a lead storage battery.

2. Write the reactions that occur at the cathode and anode during the charging of a lead storage battery.

3. a What is the electrolyte in a dry cell?

   b Write the half-reactions for the reducing and oxidizing agents in a dry cell.

4.5.7   Corrosion of Metals

What are the causes of corrosion?

Corrosion is the term usually applied to the deterioration of metals by an electrochemical process. It causes enormous damage to buildings, bridges, ships, and cars.

Can you give more examples of materials that can be damaged by corrosion from your environment?

Corrosion reactions are redox reactions in which a metal is attacked by some substance in its environment and is converted to an unwanted compounds. For nearly all metals, oxidation in air is a thermodynamically favourable process at room temperature. If the oxidation process is not inhibited, it can be very destructive. However, oxidation can also result in

the formation of an insulating protective oxide layer that prevents further reaction of the underlying metal. For example, on the basis of the standard reduction potential for Al^{3+}, we would expect aluminium metal to be readily oxidized. The exceptional stability of this metal in air is due to the formation of a thin protective coat of oxide (a hydrated form of Al_2O_3) on the surface of the metal. The oxide coat is impermeable to the passage of O_2 or water and so protects the underlying metal from further corrosion. Magnesium metal is similarly protected.

Corrosion of Iron

The most familiar example of corrosion is the rusting of iron. Oxygen gas and water must be present for iron to rust. Although the reactions involved are quite complex and not completely understood, the main steps are believed to be as follows:

A region of the metal's surface serves as the anode, where oxidation occurs.

$$\textit{Anode} : Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-;$$

The electrons given up by iron reduce atmospheric oxygen to water at the cathode, which is another region of the same metal surface.

$$\textit{Cathode} : O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l);$$

The overall reaction is

$$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

With data from Table 4.2, we find the standard emf for this process:

$$E^\circ_{cell} = E^\circ_{red}(\textit{cathode}) - E^\circ_{red}(\textit{anode})$$
$$= 1.23 \text{ V} - (-0.44 \text{ V})$$
$$= +1.67 \text{ V}$$

Note that this reaction occurs in an acidic medium, and the H^+ ions are supplied, in part, by the reaction of atmospheric carbon dioxide with water to form H_2CO_3.

Can you write the dissociation of carbonic acid in water?

The Fe^{2+} ions formed at the anode are further oxidized by oxygen:

$$4Fe^{2+}(aq) + O_2(g) + (4 + 2x) H_2O(l) \rightarrow 2Fe_2O_3 \cdot xH_2O(s) + 8H^+(aq)$$

This hydrated form of iron (III) oxide is known as rust. The amount of water associated with the iron oxide varies, so we represent the formula as $Fe_2O_3 \cdot xH_2O$. Figure 4.13 shows the mechanism of rust formation.

Why does rusting of iron occur rapidly in salt water?

Air

Water

Fe^{2+}
Fe^{3+}

O_2

Rust deposit
$(Fe_2O_3 \cdot xH_2O)$

Iron

e^-

Anode
$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

Cathode
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
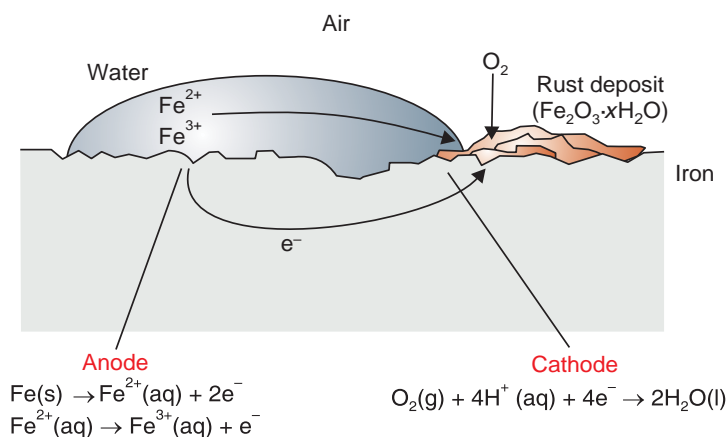
Figure 4.13 Corrosion of iron in contact with oxygen.

The electrical circuit is completed by the migration of electrons and ions.

Exercise 4.13

1. Define corrosion.
2. Explain the negative effects of corrosion.
3. Aluminium does not rust as iron does. Why?

Prevention of Corrosion

Activity 4.16

Form a group and discuss each of the following questions. After the discussion, share your ideas with the other groups.

1. List the methods that help to prevent the rusting of iron.
2. What is common in all methods of preventing the rusting of iron?

Activity 4.17

Form a group and discuss the following:

1. What does sacrificial anode mean?

2. Which of the following metals are suitable for uses as sacrificial anodes to protect against corrosion of underground iron pipes? If any are not suitable, explain why.

   Al, Pb, Mn, Mg and Cd.

3. What is the role of magnisum in the Figure 4.14?

4. Write chemical reactions occuring during protection of iron pipes, using magnisum as anode.

5. Would you advise to replace a section of damaged iron pipe with copper pipe? Explain?

6. Explain why galvanized iron, which contains a thin coating of zinc metal, corrodes much more slowly than iron.

After discussion, share your idea with rest of the class.
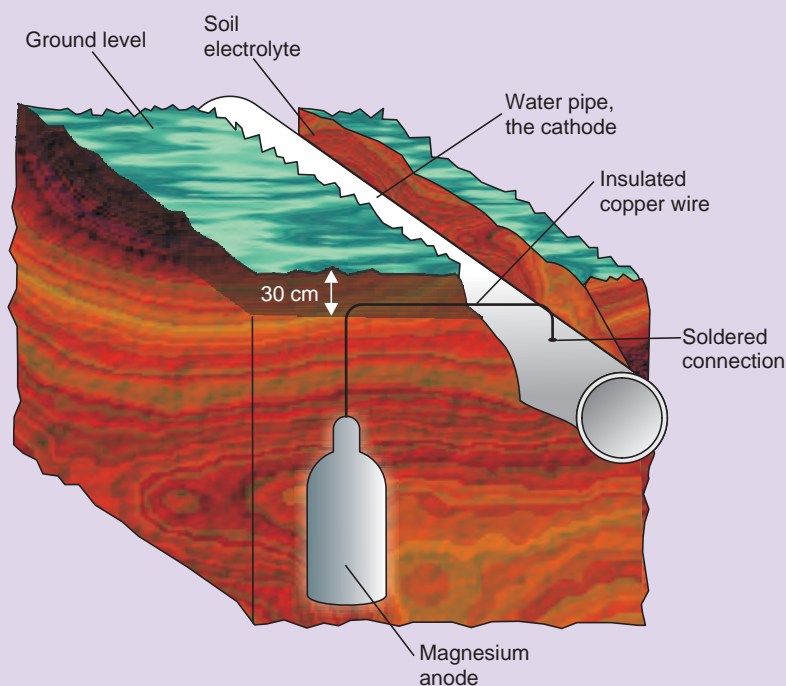

Figure 4.14 Protection of iron using magnesium.

Unit Summary

- *Oxidation is loss of electrons, and reduction is gain of electrons.*
- *A reduced substance is an oxidizing agent and an oxidized substance is a reducing agent.*

- *Redox reactions are balanced, using the oxidation number change method or the ion- electron method.*

- *Metals can conduct electricity because they have delocalized electrons, and electrolytes can also conduct electricity, due to the presence of free ions.*

- *In the electrolytic cell, electrical energy is used to bring about a chemical change.*

- *The cathode is the electrode at which reduction takes place and the anode is the electrode at which oxidation takes place.*

- *In an electrolytic cell, the anode is positive and the cathode is negative. In Galvanic cells, the electrode polarity is reversed.*

- *The preferential discharge of ions is affected by the nature of the electrodes, the position of the ions in the electrochemical series and the concentration of the ions in the electrolyte.*

- *In the electrolysis of molten sodium chloride, sodium is discharged at the cathode, and chlorine is released at the anode. But, in the electrolysis of concentrated brine solution, hydrogen is discharged at the cathode, and chlorine is discharged at the anode.*

- *In the electrolysis of dilute sodium chloride solution and dilute sulphuric acid solution, hydrogen gas discharges at the cathode and oxygen gas discharges at the anode.*

- *The Faraday's Laws are used to calculate the amount of substance deposited or liberated at the cathode or anode during electrolysis.*

- *Some of the applications of electrolysis are electroplating, electrorefining and extraction of metals and non-metals.*

- *A Galvanic cell is a device in which chemical energy is transformed to electrical energy.*

- *A salt bridge preserves the electroneutrality of a solution.*

- *A cell notation allows us to describe a Galvanic cell without drawing a diagram. The anode is written on the left and the cathode on the right.*

- *Cell potential is the difference between the electrode potentials of the cathode and anode.*

- *For spontaneous cell reactions, $\Delta G < 0$ and $E_{cell} > 0$.*

- *The Nernst equation enables us to calculate E_{cell} as a function of reactant and product concentrations in a redox reaction.*

- *A battery is a Galvanic cell that gives a direct current at a constant voltage.*

- *A battery can be either primary or secondary.*

- *Corrosion is the deterioration of metals by electrochemical processes. It is a redox reaction.*

- *Corrosion can be prevented by painting, electroplating and by way of cathodic protection.*

Check List

Key terms of the unit

- *Anion*
- *Anode*
- *Battery*
- *Brine solution*
- *Cathode*
- *Cation*
- *Cell notation*
- *Concentrated solution*
- *Conductivity*
- *Corrosion*
- *Daniell cell*
- *Dilute solution*
- *Dry cell*
- *Electrochemical series*
- *Electrolysis*
- *Electrolyte*
- *Electrolytic cell*

- *Electroplating*
- *Faraday's first law*
- *Faraday's second law*
- *Galvanic cell*
- *Galvanizing*
- *Nernst equation*
- *Oxidation*
- *Oxidation number*
- *Oxidizing agent*
- *Preferential discharge*
- *Primary batteries*
- *Redox reaction*
- *Reducing agent*
- *Reduction*
- *Salt bridge*
- *Secondary batteries*
- *SHE*
- *Standard electrode potential*

REVIEW EXERCISE ON UNIT 4

Part I: Multiple Choice Questions

1. What is the oxidation number of chromium in $(NH_4)_2Cr_2O_7$?

   a $+7$ c $+5$

   b $+3$ d $+6$

2. In the following half-reaction,

   $$C_2O_4^{2-} \rightarrow CO_2 + xe^-$$

   The value of 'x' is:

   a 1   c 4

   b 2   d 3

3. Balance the following equation, using the lowest possible whole number coefficients;

   $$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

   The sum of the coefficients is:

   a 8   c 12

   b 10   d 7

4. Which one of the following statements is not true regarding the electrolysis of concentrated sodium chloride solution?

   a chlorine gas is produced at the anode.

   b hydrogen gas is formed at the cathode.

   c oxygen gas is produced at the anode.

   d after the electrolysis, the remaining solution becomes basic.

5. Which one of the following statements about the Daniell cell is false?

   a zinc metal immersed in zinc sulphate solution acts as the anode.

   b copper metal dipped in copper sulphate solution acts as the cathode.

   c anode is the positive electrode and cathode is the negative electrode.

   d electrons flow from anode to cathode in the external circuit.

6. Given the following reaction:

$$Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Zn(s)$$

The correct cell notation for the reaction is:

a $Zn^{2+}(aq) \mid Zn(s) \| Mg(s) \mid Mg^{2+}(aq)$

b $Mg(s) \mid Mg^{2+}(aq) \| Zn^{2+}(aq) \mid Zn(s)$

c $Mg(s) \mid Mg^{2+}(aq) \| Zn(s) \mid Zn^{2+}(aq)$

d $Zn^{2+}(aq) \mid Zn(s) \| Mg^{2+}(aq) \mid Mg(s)$

7. Which of the following statements is correct about ΔG^o, K and E^o_{cell}?

a If K is less than one, ΔG^o is negative.

b If ΔG^o is zero, K is greater than one.

c If K is greater than one, the ΔG^o is negative.

d If a reaction is spontaneous, then ΔG^o is positive.

8. Which one of the following equations shows the relationship between standard Gibbs free energy and equilibrium constant?

a $K = \Delta G^o$ c $\Delta G^o = - RT \ln K$

b $K = RT \ln \Delta G^o$ d $\Delta G^o = RT \ln K$

9. Which of the following statements is true about E^o_{red}?

a When we reverse a reduction half-reaction, both the magnitude and sign of E^o_{red} change.

b The more positive the reduction potential, the higher the tendency to become a reducing agent.

c Its value does not change as we change the stochiometric coeffiecients of the half-reaction.

d All of the above

10. In the standard reduction potential table, the strongest oxidizing agent is:

a lithium   c ozone

b sodium   d fluorine

11. When does a spontaneous cell reaction occur:

    a $\Delta G < 0$ c $E_{cell} < 0$

    b $E_{cell} > 0$ d a and b

12. A battery is "dead" if:

    a reactants and products reach their equilibrium concentrations.

    b E_{cell} is equal to zero.

    c ΔG is equal to zero.

    d all of the above.

13. One of the basic differences between a fuel cell and a battery is:

    a a fuel cell is rechargeable, while a battery is not.

    b a fuel cell does not store chemical energy, but a battery can store chemical energy.

    c both a fuel cell and a battery are rechargeable.

    d a and c.

14. A metal corrodes if:

    a it serves as cathode in the corrosion process.

    b it serves as anode in the corrosion process.

    c it does not react with oxygen.

    d all of the above.

Part II: Short Answer Questions

15. Define each of the following terms:

    a oxidation   e electrolytic cell

    b reduction   f Galvanic cell

    c anode   g corrosion

    d cathode

16. How is corrosion of iron prevented?

17. Balance each of the following chemical equations, using oxidation state change method.

a $K_2CrO_4 + H_2O + S \rightarrow SO_2 + KOH + Cr_2O_3$

b $CuO + NH_3 \rightarrow Cu + N_2 + H_2O$

c $H_2SO_4 + NaBr \rightarrow Br_2 + SO_2 + Na_2SO_4 + H_2O$

18. Balance each of the following chemical equations in basic medium, using ion-electron method.

a $Mn^{2+} + BiO_3^- \rightarrow MnO_4^- + Bi$

b $H_2O_2 + Cl_2O_7 \rightarrow ClO_2^- + O_2$

19. Balance each of the following chemical equations in acidic medium, using ion-electron method.

a $MnO_4^- + CH_3OH \rightarrow Mn^{2+} + HCOOH$

b $NO_2^- + Cr_2O_7^{2-} \rightarrow Cr^{3+} + NO_3^-$

20. Calculate the standard free energy change for the following reaction at 25°C. (Hint use Table 4.2.).

$Mg(s) + Zn^{2+} (1.0\ M) \rightarrow Zn(s) + Mg^{2+} (1.0\ M)$

21. Calculate the volume of H_2 and O_2 gases that, at 25°C and 1.00 atm, will collect at the cathode and anode, respectively, when an aqueous solution of Na_2SO_4 is electrolyzed for 1.5 h with a 10 A current.