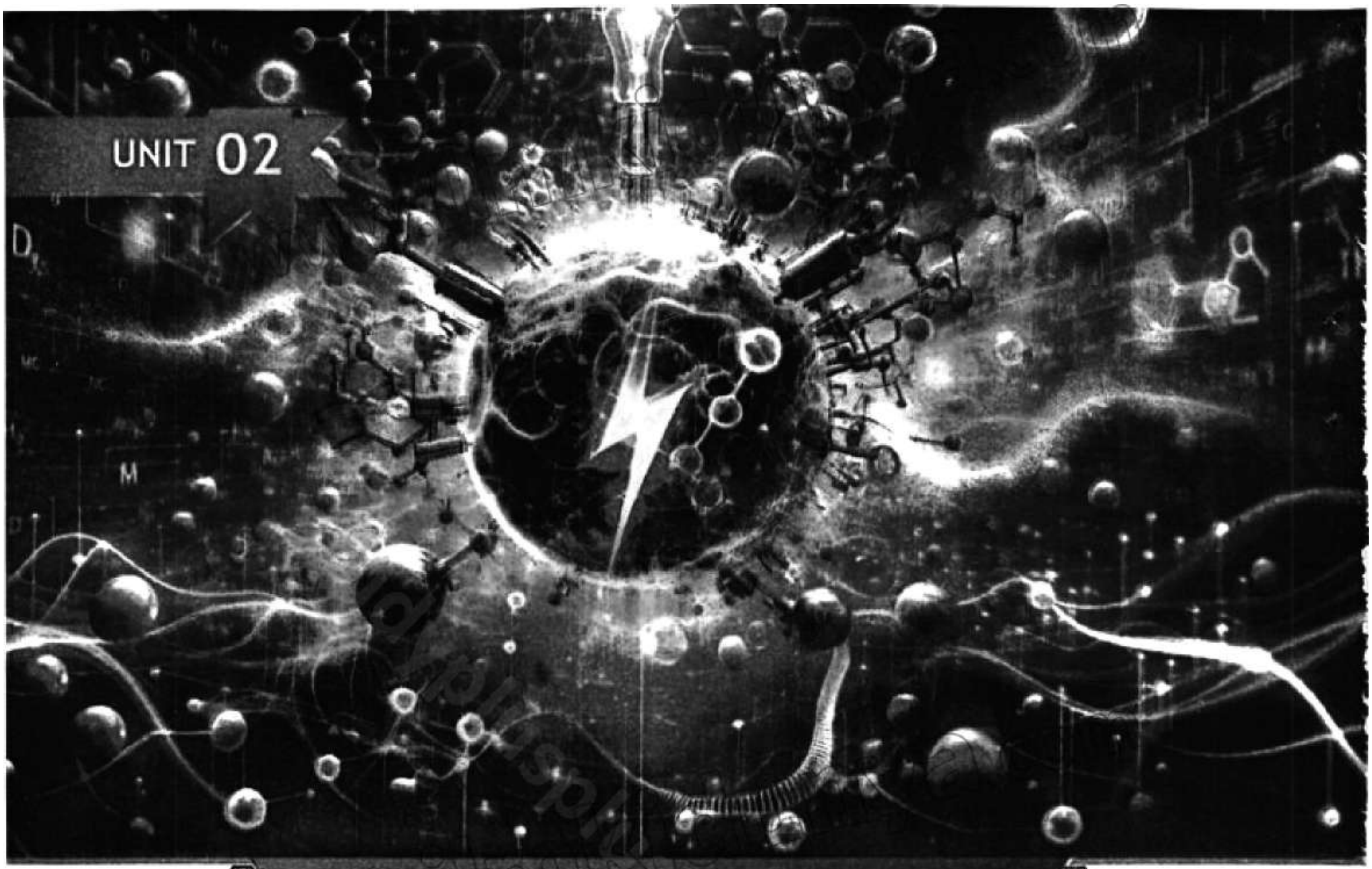


UNIT 02

ELECTROCHEMISTRY

Student Learning Outcomes (SLOs)

- Apply the concept of oxidation numbers in identifying oxidation and reduction reactions.
- Apply the concept of changes in oxidation numbers to balance chemical equations.
- Define the terms redox, oxidation, reduction, and disproportionation (in terms of electron transfer and changes in oxidation number).
- Identifying the oxidizing and reducing agents in a redox reaction.
- Describe the role of oxidizing and reducing agents in the redox reaction.
- Explain the concept of the activity series of metals and how it relates to the ease of oxidation.
- Deduce the feasibility of redox reactions from activity series or reaction data.
- Explain the use of the Winkler Method to measure biochemical oxygen demand(BOD) and its use as a measure of water pollution.
- Explain how electrolytic cells convert electrical energy to chemical energy, with oxidation at the anode and reduction at the cathode.

- Predict the identities of substances liberated during electrolysis based on the electrolyte, position in the redox series, and concentration.
- Apply the relationship between the Faraday constant, Avogadro constant, and the charge on the electron to solve problems.
- Calculate the quantity of charge passed during electrolysis and the mass or volume of substance liberated during electrolysis.
- Deduce the Avogadro constant by an electrolytic method.
- Define the terms standard electrode potential and standard cell potential.
- Describe the standard hydrogen electrode and methods used to measure standard electrode potential.
- Calculate the standard cell potentials by combining the potentials of two standard electrodes and then use these to predict the feasibility of a reaction and the direction of electron flow in a simple cell.
- Deduce the relative reactivity of elements, compounds, and ions as oxidizing agents or reducing agents from their electrode potential values.
- Construct redox equations using relevant half-equations.
- Explain how electrode potential varies with the concentrations of aqueous ions and use the Nernst equation to predict this quantitatively.
- Explain how voltaic (galvanic) cells convert energy from spontaneous, exothermic chemical processes to electrical energy, with oxidation at the anode and reduction at the cathode.
- Explain how voltaic cells convert chemical energy from redox reactions to electrical energy using Cu-Zn galvanic cells as an example.

Electrochemistry is concerned with a wide range of significant processes, many of which are dependent on the exchange of electrons from one chemical to another. Electrochemical processes include redox (oxidation-reduction) reactions, where the energy released during spontaneous reactions is converted into electricity, or in which the electricity is used to induce a non-spontaneous reaction. Redox reactions involve the transfer of electrons between two or more substances. Electrochemistry deals with energy sources that are highly efficient, such as batteries, and fuel cells. The chemistry of these devices is discussed here.

2.1 Oxidation - Reduction Concepts

Recall the definition of oxidation and reduction in terms of transfer of oxygen or hydrogen or electrons. Here we will discuss oxidation and reduction in terms of loss or gain of electrons by a chemical reaction.

Example 2.1

When a piece of zinc metal is dipped in an aqueous solution of $CuSO_4$, it is observed that a dark brown layer of copper begins to form at the zinc surface. At the same time, the blue colour of the solution is discharged. If we analyse this solution we find that Zn^{++} ions are present in the solution. The change can be described by the following chemical equation.

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

This reaction can be described in terms of two-half reactions.

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

In this reaction, zinc metal loses two electrons and changes into Zn^{2+} ions while Cu^{2+} ions gain two electrons and give copper metal. The two processes taking place simultaneously are called oxidation-reduction reactions.

"A reaction in which a substance loses electrons is called oxidation. The reaction in which a substance gains electrons is called reduction. Oxidation-reduction reactions are also known as redox reactions. In a redox reaction, elements undergo a change in their oxidation number.

2.1.1 Oxidation Number

The oxidation number (oxidation state) is defined as the apparent charge, positive or negative, which an element would have in a compound.

2.1.2 Oxidation-Reduction in Terms of Change in Oxidation Number

We have already defined oxidation and reduction in terms of the transfer of one or more electrons. We can also define oxidation and reduction in terms of change in oxidation number. An increase in oxidation number is called oxidation and a decrease in oxidation number is called reduction. For example;

$$2Na_{(g)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$$

Assign oxidation numbers to all the atoms involved in this reaction and write it over their symbols.

$$2\overset{0}{Na}_{(g)} + \overset{0}{Cl}_{2(g)} \longrightarrow 2Na^{1+}Cl^{1-}_{(s)}$$

Note that the oxidation number of Na is zero because it is in its elemental form. In this reaction, the oxidation number of Na changes from zero to +1 when it loses one electron, which is called oxidation.

$$2\overset{0}{Na}_{(g)} \longrightarrow 2\overset{1+}{Na}_{(g)} + 2e^-$$

On the other hand, each Cl atom in the Cl_2 molecule changes its oxidation number from zero to -1, gains one electron, and is called reduction.

$$\overset{0}{Cl}_{2(g)} + 2e^- \longrightarrow 2Cl^{1-}_{(g)}$$

So we can also define oxidation and reduction in terms of change in oxidation number.

Oxidation is an increase in oxidation number (loss of electrons).

Reduction is a decrease in oxidation number (gain of electrons).

Example 2.2

Identify the elements undergoing oxidation or reduction in terms of change in oxidation number in the following reaction which takes place in the combustion of natural gas.

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$$

Solution

Assign oxidation number to all the atoms involved in this reaction.

$$\overset{4-}{C}\overset{(1+)4}{H}_{4(g)} + 2\overset{0}{O}_{2(g)} \longrightarrow \overset{+4}{C}\overset{(2-)2}{O}_{2(g)} + 2\overset{2(1+)}{H_2}\overset{2-}{O}_{(l)}$$

The C changes its oxidation number from -4 in CH_4 to +4 in CO_2 whereas oxygen changes its oxidation number from 0 to -2. This means C undergoes an increase in oxidation number. On the other hand, O changes its oxidation number from zero in O_2 to -2 in H_2O and CO_2. Each oxygen atom gains two electrons and therefore it is reduced.

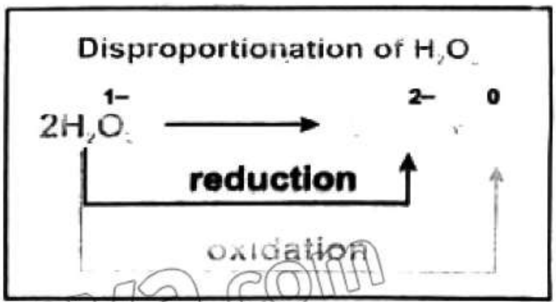
We can say that,

i) C is oxidized because there has been an increase in its oxidation number.

ii) O is reduced because there has been a decrease in its oxidation number.

2.1.3 Disproportionation Reaction

In some redox reactions, the same element is oxidised and reduced simultaneously. Such reactions are called self-oxidation-reduction reactions or disproportionation reactions. For example, consider the decomposition of hydrogen peroxide. In this reaction, oxygen is oxidized to 0 in O_2 and reduced to 2- in H_2O.



CONCEPT ASSESSMENT EXERCISE 2.1

Use the oxidation number change method to identify the atoms undergoing oxidation or reduction in the following redox reactions.

$$Cl_{2(g)} + 2NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + NaClO_{(aq)} + H_2O_{(l)}$$

$$4Fe_{(s)} + 3O_{2(g)} \longrightarrow 2Fe_2O_{3(s)}$$

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(l)}$$

2.2 Balancing of Equations

i. Redox Method (Oxidation Number Method)

ii. Ion Electron Method

i. Redox Method (Oxidation Number Method)

It is based on the principle that in any redox reaction, the total number of electrons lost by one element must be equal to the total number of electrons gained by another element. This method can be understood by the following example.

Example 2.3

Balance the following equation by the oxidation number method.

$$P + HNO_3 + H_2O \longrightarrow H_3PO_4 + NO$$

Solution

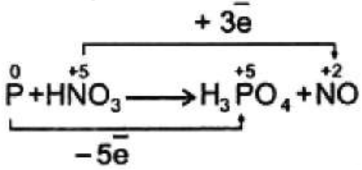
Step 1: **Assign oxidation numbers to all the atoms involved in the equation.**

$$\overset{0}{P} + \overset{+1\,+5\,(-2)3}{HNO_3} + \overset{(+1)2-2}{H_2O} \longrightarrow \overset{3(+1)+5(-2)4}{H_3PO_4} + \overset{+2\;-2}{NO}$$

Step 2: **Identify the elements changing oxidation number.**

The P goes from zero to +5 oxidation state in H_3PO_4. This is 5 electrons change. N in HNO_3 goes from +5 to +2 oxidation state in NO. This is 3 electron change.

Step 3: **Draw a bridge between the same atoms whose oxidation numbers have changed, Indicate this change by the number of electrons gained or lost by each element.**



Step 4: **Equalize the number of electrons lost and gained by multiplying the two numbers, by a small whole number which produces a common number. Use these multiples as coefficients of the respective substance.**

To balance a $3e^-$ gain against a $5e^-$ loss, we need to multiply $3e^-$ gain by 5 and $5e^-$ loss by 3. This will equalize the number of electrons gained and lost.

$$+3\bar{e} \times 5 = +15\bar{e}$$

$$\overset{0}{P} + H\overset{+5}{N}O_3 \longrightarrow H_3\overset{+5}{P}O_4 + \overset{+2}{N}O$$

$$-5\bar{e} \times 3 = -15\bar{e}$$

Multiply the coefficients of P and that of H_3PO_4 by 3. Whereas multiply the coefficients of HNO_3 and NO by 5.

$$3P + 5HNO_3 + H_2O \longrightarrow 3H_3PO_4 + 5NO$$

Now the coefficient of H_3PO_4 and NO should not be changed hereafter it.

Step 5: **Balance the rest of the equation by inspection method. Balance the atoms other than oxygen and hydrogen first, then oxygen atoms and finally hydrogen atoms.**

To balance oxygen atoms, multiply coefficient of H_2O by 2.

$$3P + 5HNO_3 + 2H_2O \longrightarrow 3H_3PO_4 + 5NO$$

Inspect the equation, it is balanced.

CONCEPT ASSESSMENT EXERCISE 2.2

Using the oxidation number method balance the following equation.

1. $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$
2. $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

2.2.1 Construction of Redox Equations

There are two half-reactions in any given oxidation and reduction reaction: the oxidation-half reaction and the reduction-half reaction. The oxidation and reduction reaction is the sum of the two half-reactions.

We can balance the half-reaction by the ion-electron method. Equalise the number of electrons lost and gained in the two half-reactions and combine them. The rest of the equation is balanced by the inspection method. The steps involved in this method can be understood by considering the following example.

Example 2.4

Construct a redox equation using the following half-equations.

Reduction half-reaction:

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

Oxidation half-reaction:

$$H_2SO_3 \longrightarrow HSO_4^-$$

Step 1:

Balance each half-reaction. First, consider reduction half-reaction. Two Cr atoms on the left require 2 before Cr^{+3}

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

There are seven O atoms on the left and none on the right. We will add 7 H_2O on the right side.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

There are 14 H atoms on the right and none on the left, so we will add 14 H^+ on the left side.

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

Now balance charges. The left side has one di-negative and 14 mono-positive charges, corresponding to -2 +14 = +12. The right side has two tri-positive charges corresponding to +3 × 2 = +6. Thus left side needs $6e^-$.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \qquad ---(1)$$

In the other half-reaction (Oxidation half-reaction), S atoms are already balanced.

$$H_2SO_3 \longrightarrow HSO_4^-$$

Balance O - atoms. As there are three O - atoms on the left and four on the right, we will add one H_2O to the left.

$$H_2SO_3 + H_2O \longrightarrow HSO_4^-$$

There are four H-atoms on the left and one on the right. We will add $3H^+$ to the right.

$$H_2SO_3 + H_2O \longrightarrow HSO_4^- + 3H^+$$

For charge, the left side is neutral, but the right side has a net charge of (-1) + (+3) = +2.

Thus, we will add $2e^-$ to the right side.

$$H_2SO_3 + H_2O \longrightarrow HSO_4^- + 3H^+ + 2e^- \qquad -----(2)$$

Step 2:

Equalize the number of electrons transferred in the two half-reactions and add half-reactions. Reduction half-reaction uses up $6e^-$ and oxidation half-reaction produces $2e^-$. Therefore, multiplying equation (1) by one and equation (2) by three and adding two equations we get.

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

$$3H_2SO_3 + 3H_2O \longrightarrow 3HSO_4^- + 9H^+ + 6e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 3H_2SO_3 + 3H_2O + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O + 3HSO_4^- + 9H^+ + 6e^-$$

Step 3:

Cancel the duplication. Duplications are $6e^-$, $3H_2O$ and $9H^+$. Strike these out from both sides.

$$Cr_2O_7^{2-} + 5H^+ + 3H_2SO_3 \longrightarrow 2Cr^{3+} + 4H_2O + 3HSO_4^-$$

(-2) (+5) (+6) (-3)

= +3 = +3

Result:

Since LHS charges are equal to RHS charges, therefore the equation is balanced.

CONCEPT ASSESSMENT EXERCISE 2.3

Use the half-reaction method to balance the following redox reactions.

(i) $Co + Cr^{3+} \longrightarrow Co^{2+} + Cr^{2+}$ (ii) $Au^{3+} + H_2 \longrightarrow H^+ + Au$

(iii) $Cl_2 + I^- \longrightarrow I_2 + Cl^-$

CONCEPT ASSESSMENT EXERCISE 2.4

Construct a redox equation from the following half-equations.

1. $MnO_4^- \rightarrow Mn^{2+}$ and $H_2O_2 \rightarrow O_2$
2. $NO_3^- \rightarrow NO$ and $Br^- \rightarrow Br_2$
3. $MnO_4^- \rightarrow Mn^{2+}$ and $C_2O_4^{2-} \rightarrow CO_2$

2.3 Oxidizing and Reducing Agents

An oxidizing agent is a substance that accepts electrons and causes oxidation, therefore, its oxidation state decreases. A reducing agent is a substance that causes reduction through the loss of electrons; therefore, its oxidation state increases. This means an oxidizing agent is a substance that causes the oxidation of another substance. On the other hand, a reducing agent is the substance that causes another substance to reduce.

An oxidizing agent contains an element that is being reduced (gaining electrons). The reducing agent contains an element that is being oxidized (losing electrons). Consider the following reaction.

$$3\overset{0}{P} + 5\overset{+1}{H}\overset{+5}{N}\overset{(-2)3}{O_3} + \overset{(+1)2-2}{2H_2O} \longrightarrow \overset{3(+1)+5(-2)4}{3H_3PO_4} + 5\overset{+2}{N}\overset{-2}{O}$$

P is undergoing oxidation, so it is reducing agent. Whereas N present in HNO_3 is undergoing reduction HNO_3 is an oxidising agent. Similarly,

$$\overset{+4}{Mn}O_2 + 4H\overset{-1}{Cl} \longrightarrow \overset{+2}{Mn}Cl_2 + 2H_2O + \overset{0}{Cl_2}$$

Mn present in MnO_2 is undergoing reduction, therefore MnO_2 is an oxidising agent. Cl of HCl is oxidised, so HCl is a reducing agent.

How can you identify oxidising and reducing agents in a chemical reaction?

CONCEPT ASSESSMENT EXERCISE 2.5

Identify the oxidising and reducing agents in the following reaction.

$$CuO + H_2 \rightarrow Cu + H_2O$$

Activity 2.1: Identifying Oxidizing and Reducing Agents

Prepare solutions of ferrous sluphate ($FeSO_4$) and potassium permanganate ($KMnO_4$) in separate beakers. Transfer about $10cm^3$ of ferrous sulphate solution in a test tube. Add about $10cm^3$ of dil. H_2SO_4 in it. Now add a few drops of $KMnO_4$ the solution in the test tube. What happens?

$FeSO_4$ reduces $KMnO_4$, so its purple colour is discharged. $KMnO_4$ oxidizes $FeSO_4$ in this reaction. $FeSO_4$ is a reducing agent whereas $KMnO_4$ is an oxidizing agent.

How can you identify oxidizing and reducing agents in a chemical reaction?

Consider the following reaction that takes place in the manufacture of steel.

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

To identify the oxidizing and reducing agents, work out the oxidation states of all the elements involved in the reaction.

$$\overset{2(+3)(-2)3}{Fe_2O_3} + \overset{+2\ -2}{3CO} \longrightarrow \overset{0}{2Fe} + \overset{+4(-2)2}{3CO_2}$$

(i) Carbon is being oxidized because there is an increase in its oxidation state.

(ii) Fe is being reduced because there is a decrease in its oxidation state.

(iii) The reactant CO contains the C that is being oxidized, so CO is a reducing agent.

(iv) The reactant Fe_2O_3 contains the Fe that is being reduced. So Fe_2O_3 is an oxidizing agent.

Oxidizing or reducing agent is the whole molecule or formula unit and not the atom that has undergone a change in oxidation number. The oxidizing agent facilitates oxidation by accepting electrons, while the reducing agent promotes reduction by donating electrons.

2.4 Electrode, Electrode Potential and Electrochemical Series

2.4.1 The Galvanic Cell (Daniel Cell)

When a Zn rod is dipped into a copper(II) sulphate solution, zinc atoms are oxidized to zinc ions, and copper (II)ions are reduced to copper metal, which deposits on the zinc rod. The following reaction occurs:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

In this reaction, electrons flow directly from the zinc rod to Cu^{2+} ions in solution. However, if the electrons transfer from the zinc rod to the copper ions in solution could be directed through an external circuit, the spontaneous redox reaction could be used to generate an electric current. But when a zinc rod dipped in zinc sulphate solution in one container is connected by a copper wire to the copper rod dipped in copper (II) sulphate solution in a separate container, no current flows through the external circuit. However, when the two solutions are connected with a tube **(salt bridge)** filled with a solution of an electrolyte such as KCl, KNO_3 or Na_2SO_4, the current flows through the external circuit.

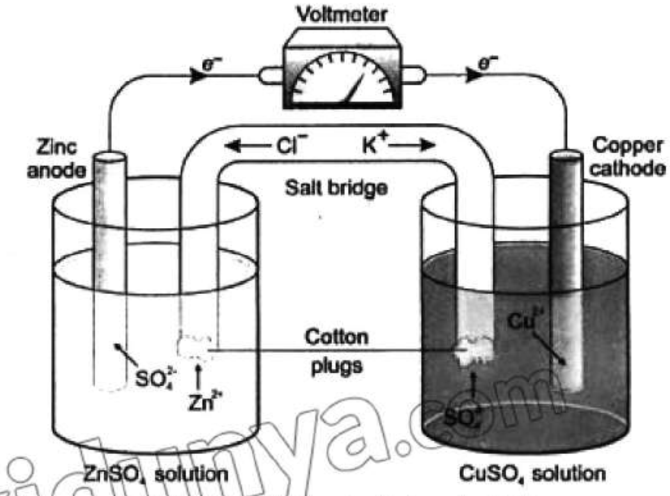


Fig 2.1: A simple Galvanic Cell

The salt bridge allows the movement of ions from one solution to the other without mixing the two solutions. It maintains electrical neutrality within the internal circuit of the cell by allowing ions to flow between the two half-cells. This flow of ions prevents the buildup of charge in either half-cell, which would otherwise stop the reaction and the flow of electricity. (See Fig. 2.1)

Half-cell, in which oxidation occurs is called an oxidation half-cell or anode half-cell. The other half-cell, in which reduction occurs is called a reduction half-cell or cathode half-cell. The reaction taking place in the oxidation half-cell is called the oxidation half reaction and the reaction taking place in the reduction half-cell is called the reduction half reaction. The electrode at which oxidation occurs is called the anode. The electrode at which reduction occurs is called the cathode.

Zn has a greater tendency to lose electrons than Cu. Therefore, the Zn electrode acquires a negative charge relative to the Cu electrode. The electrons flow from the Zn electrode through the external circuit to the Cu electrode. The following half-cell reactions occur at the two electrodes.

At anode: $Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^-$ (Oxidation half-reaction)

At cathode: $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ (Reduction half-reaction)

Overall cell reaction

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

An electrochemical cell in which a spontaneous redox reaction produces an electric current is known as a galvanic or voltaic cell.

2.4.2 Cell Potential

The cell potential for a galvanic cell is literally the potential of the cell to do work on its surroundings by driving an electric current through a wire. The work that can be accomplished when electrons are transferred through a wire depends upon the push or force behind the electrons.

The force with which electrons are pushed to flow through the wire from the anode to the cathode is called the electromotive force or emf. It is measured in **volts (V).**

The emf produced by the galvanic cell is called cell potential (E^0 cell). It depends upon the difference in the electrode potentials of the two half-cells joined in series. Thus the electrode with a more negative reduction potential acts as the anode and the electrode with a more positive reduction potential acts as the cathode. Thus under standard conditions (1 mol dm^{-3} concentration at 25 °C and 1 atm pressure), the reaction with a more negative E° value occurs as oxidation (anode reaction). The reaction with a more positive E° value occurs as reduction (cathode reaction). The voltage of any cell under standard conditions can be calculated using tabulated standard reduction potentials (see Table 2.1).

The combination of two half-cells will produce a complete cell. The overall cell reaction is obtained by suitably combining the equations for the two half-reactions. Standard cell potential E°_{cell} or emf of the cell is the algebraic difference between the respective standard reduction potentials of the two half-cells.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

The cell potential has a positive value for any spontaneous redox reaction. The potential of a galvanic cell can be measured with a voltmeter. However, a single half-cell potential or the **electrode potential** cannot be measured directly. This is because one half-cell reaction cannot occur without a simultaneous reaction in another half-cell. However, the relative half-cell potential (electrode potential) can be determined by coupling it with the **standard hydrogen electrode (SHE)** as a reference electrode, with a standard potential of 0.00 volt.

The standard electrode potential is defined as the tendency of a half-cell reaction to undergo reduction relative to the standard hydrogen electrode. Its potential difference developed when an electrode of an element is placed in a solution containing ions of that element when all the components are in their standard state i.e. 1 atm. for gases, 1M for solutions, pure solid for electrode, and at 25 °C.

2.4.3 Standard Hydrogen Electrode

A standard hydrogen electrode (SHE) consists of a platinum foil coated with finely divided platinum, surrounded by hydrogen gas at 1atm pressure in contact with 1M HCl solution at 298K, as shown in Fig. 2.2. Its electrode potential is arbitrarily chosen as zero at all temperatures.

By convention, the half-cell potential for reduction of $H^+_{(aq)}$ to H_2 gas or the potential for the oxidation of H_2 to $H^+_{(aq)}$ in standard hydrogen, a half-cell is defined as exactly 0.00V.

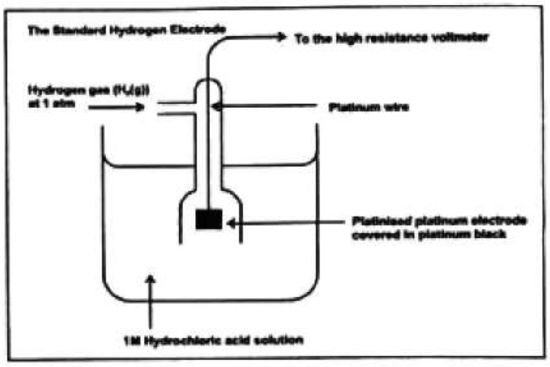


Fig 2.2: Standard Hydrogen Electrode

Reduction: (act as cathode)

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)} \qquad E^o_{H^+/H_2} = 0.00V$$

Oxidation: (act as anode)

$$H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^- \qquad E^o_{H_2/H^+} = 0.00V$$

S.H.E. can act as a cathode or anode depending upon the nature of the electrode with which it is connected to complete an electrochemical cell.

The symbol E^o designates a standard potential i.e., the potential measured under standard conditions (1M concentration, 1 atm pressure, and 25 °C).

2.4.4 Method to measure the electrode potentials

The Standard Hydrogen Electrode (SHE) is the primary reference electrode used to measure the standard electrode potentials of other half-cells, such as copper and zinc. It has a standard electrode potential of 0 V by definition.

Determination of Standard Electrode Potential of Zn^{2+}/Zn Electrode

An Electrochemical Cell is Setup in which a zinc rod is dipped in 1 M zinc Sulphate solution. This half-cell is combined with a standard hydrogen electrode through a salt bridge. The deflection of the voltmeter indicates that current is flowing from the zinc electrode to the hydrogen electrode or the electrons are moving from the zinc rod to the hydrogen electrode. Hence the zinc electrode acts as an anode and the SHE acts as a cathode. In this case, the reading (E^o) by the voltmeter is 0.76 V. The cell can be represented as

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$$

Calculations

The E^o_{Cell} is 0.76 volt

$E^o_{Cell} = E^o_{Anode} + E^o_{Cathode}$

$0.76 = E^o_{Anode} + 0$ or $E^o_{Anode} = +0.76\ V$

Hence oxidation potential of zinc is 0.76 V and the reduction potential of zinc will be − 0.76 V.

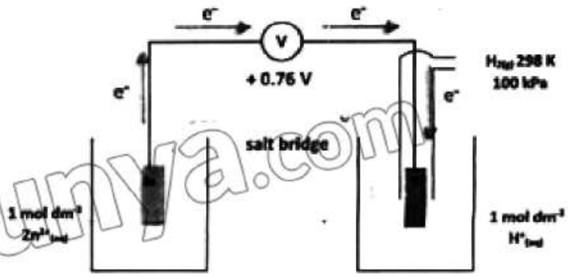


Fig 2.3: Measurement of Standard Electrode Potential of Zn/Zn^{2+} Electrode

Determination of Standard Electrode Potential of Cu^{2+}/Cu Electrode

An Electrochemical Cell is set up in which a copper rod is dipped in 1 M copper sulphate solution. This half-cell is combined with a standard hydrogen electrode through a salt bridge. The deflection of the voltmeter indicates that current is flowing from the hydrogen electrode to the copper electrode or the electrons are moving from the hydrogen rod to the copper electrode. Hence the copper electrode acts as a cathode and the hydrogen electrode acts as an anode. In this case, the reading (EMF) by the voltmeter is 0.34 V. The cell can be represented as

$$Cu^{2+}_{(aq)} + H_{2(g)} \rightarrow 2H^{+}_{(aq)} + Cu_{(s)}$$

Calculations

The E^{o} of the cell is 0.34 volt

$E^{o}_{Cell} = E^{o}_{Anode} + E^{o}_{Cathode}$

$0.34 = 0.0 + E^{o}_{Cathode}$ or $E^{o}_{Cu2+/Cu} = +0.34$ V

Hence reduction potential of copper is 0.34 V and the oxidation potential of copper will be -0.34V.

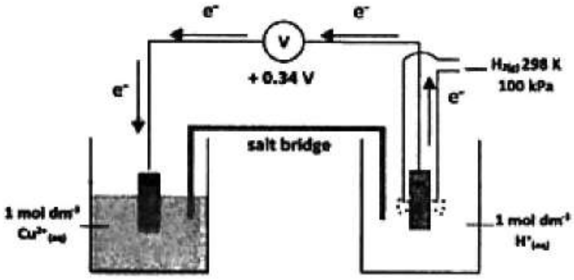


Fig 2.4: Measurement of Standard Electrode Potential of Cu^{2+}/Cu Electrode

Table 2.1: Reduction potentials of some elements, ions and compounds

Reduction Half-reaction	E^{0} (Volts)
$Li^{+} + \bar{e} \rightleftharpoons Li$	-3.05
$K^{+} + \bar{e} \rightleftharpoons K$	-2. 92
$Ba^{2+} + 2\bar{e} \rightleftharpoons Ba$	-2.90
$Ca^{2+} + 2\bar{e} \rightleftharpoons Ca$	-2.76
$Na^{1+} + 1\bar{e} \rightleftharpoons Na$	-2.71
$Mg^{2+} + 2\bar{e} \rightleftharpoons Mg$	-2.38
$Al^{3+} + 3\bar{e} \rightleftharpoons Al$	-1.67
$Mn^{2+} + 2\bar{e} \rightleftharpoons Mn$	-1.03
$2H_2O + 2\bar{e} \rightleftharpoons H_2 + 2OH^{-}$	-0.83
$Zn^{2+} + 2\bar{e} \rightleftharpoons Zn$	-0.76
$Cr^{3+} + 3\bar{e} \rightleftharpoons Cr$	-0.74
$Fe^{2+} + 2\bar{e} \rightleftharpoons Fe$	-0.44
$PbSO_4 + 2\bar{e} \rightleftharpoons Pb + SO_4^{2-}$	-0.36
$Ni^{2+} + 2\bar{e} \rightleftharpoons Ni$	-0.25
$Sn^{2+} + 2\bar{e} \rightleftharpoons Sn$	-0.14

$Pb^{2+} + 2\bar{e} \rightleftharpoons Pb$	-0.13
$Fe^{3+} + 3\bar{e} \rightleftharpoons Fe$	-0.04
$2H^{+} + 2\bar{e} \rightleftharpoons H_2$	0.00
$AgCl + \bar{e} \rightleftharpoons Ag + Cl^{-}$	+0.22
$Hg_2Cl_2 + 2\bar{e} \rightleftharpoons 2Hg + 2Cl^{-}$	+0.27
$Cu^{2+} + 2\bar{e} \rightleftharpoons Cu$	+0.34
$Cu^{+} + 1\bar{e} \rightleftharpoons Cu$	+0.52
$I_{2(aq)} + 2\bar{e} \rightleftharpoons 2I^{-}$	+0.54
$Fe^{3+} + \bar{e} \rightleftharpoons Fe^{2+}$	+0.77
$Ag^{+} + \bar{e} \rightleftharpoons Ag$	+0.80
$Br_{2(aq)} + 2\bar{e} \rightleftharpoons 2Br^{-}$	+1.09
$O_2 + 4H^{+} + 4\bar{e} \rightleftharpoons 2H_2O$	+1.23
$MnO_2 + 4H^{+} + 2\bar{e} \rightleftharpoons Mn^{2+} + 2H_2O$	+1.28
$Cr_2O_7^{2-} + 14H^{+} + 6\bar{e} \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cl_{2(g)} + 2\bar{e} \rightleftharpoons 2Cl^{-}$	+1.36
$2ClO_3^{-1} + 12H^{+} + 10\bar{e} \rightleftharpoons Cl_2 + 6H_2O$	+1.47
$8H^{+} + MnO_4^{-} + 5\bar{e} \rightleftharpoons Mn^{2+} + 4H_2O$	+1.49
$PbO_2 + SO_4^{-2} + 4H^{+} + 4\bar{e} \rightleftharpoons PbSO_4 + 2H_2O$	+1.69
$H_2O_2 + 2H^{+} + 2\bar{e} \rightleftharpoons 2H_2O$	+1.7
$S_2O_3^{-2} + 2\bar{e} \rightleftharpoons 2SO_4^{-2}$	+2.00
$F_2 + 2\bar{e} \rightleftharpoons 2F^{-}$	+2.87

2.4.4 Determination of Cell Potential

A cell reaction consists of two half-reactions. Reduction takes place in the half-cell having greater value of reduction potential. Oxidation takes place in the half-cell having the smaller value of reduction potential. The equation of the half-cell reaction having a smaller value of reduction potential is reversed and added to the equation of the half-cell having a greater value of reduction potential. The sum of these two equations represents cell reaction.

Standard cell potential E^{o}_{cell} or emf of the cell is the algebraic difference between the respective standard reduction potentials of the two half-cells.

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

Example 2.5

Calculate E° cell for the Zn-Cu cell and write cell reactions. Predict the direction of electron flow.

Solution

Half Cell-reaction	Reduction potential
i) $Zn^{++}_{(aq)} + 2\bar{e} \longrightarrow Zn_{(s)}$	- 0.76V
ii) $Cu^{++}_{(aq)} + 2\bar{e} \longrightarrow Cu_{(s)}$	+ 0.34V

Data indicates that the reduction potential of the second half-cell is greater than the first. Hence reduction reaction will occur in the second half-cell and oxidation in the first half-cell. Reverse the first equation and add it to the second equation to get the cell reaction.

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2\bar{e} \quad \text{(Oxidation half-reaction)}$$

$$Cu^{2+}_{(aq)} + 2\bar{e} \longrightarrow Cu_{(s)} \quad \text{(Reduction half-reaction)}$$

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)} \quad \text{(Cell reaction)}$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = E^0_{Cu} - E^0_{Zn}$$

$$E^0_{cell} = +0.34 - (-0.76)$$

$$E^0_{cell} = +1.10V\ s$$

Since E^0_{cell} is positive, the electrons will flow from the anode to the cathode i.e., from the Zn electrode to the Cu electrode.

Example 2.6

The standard reduction potentials for the following half-reactions are:

$Ni^{2+}_{(aq)} + 2e^- \longrightarrow Ni_{(s)}$ $E^0 = -0.25V$

$Mg^{2+}_{(aq)} + 2e^- \longrightarrow Mg_{(s)}$ $E^0 = -2.38V$

Calculate E^0_{cell} for Ni-Mg cell, write cell reaction, and direction of electron flow, and identify the anode of the cell.

Solution:

Data indicates that the reduction potential of the first reaction is greater than that of the second reaction. Hence reduction will occur in the first reaction and oxidation in the second reaction. Reverse the second reaction and add it to the first reaction to get the cell reaction.

$$Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2e^- \quad \text{(Anode reaction)}$$

$$Ni^{2+}_{(aq)} + 2e^- \longrightarrow Ni_{(s)} \quad \text{(Cathode reaction)}$$

$$Mg_{(s)} + Ni^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Ni_{(s)} \quad \text{(Cell reaction)}$$

Thus Mg will act as the anode and Ni as the cathode. Electrons will flow from Mg to Ni.

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = E^0_{Ni} - E^0_{Mg}$$

$$= -0.25 \quad -(-2.38)$$

$$= 2.13\text{ V}$$

Since E^0_{cell} is positive, the Electrons will flow from the anode to the cathode i.e., from the Mg electrode to the Ni electrode.

CONCEPT ASSESSMENT EXERCISE 2.6

The standard reduction potentials for the following half-reactions are:

$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ $E = +0.34V$

$F_2(g) + 2e^- \rightarrow 2F^-$ $E = +2.87V$

Estimate E^0_{cell} for $Cu\text{-}F_2$ cell, write cell reactions, choose cathode and show the direction of electron flow.

2.4.5 Feasibility of a Chemical Reaction

Whether a chemical reaction is feasible or occurs spontaneously or not, can be inferred from the sign of the sum of E^o values of the two half-cell reactions. If this value is positive, a reaction occurs spontaneously or will be feasible. The negative value indicates that the reaction is not feasible.

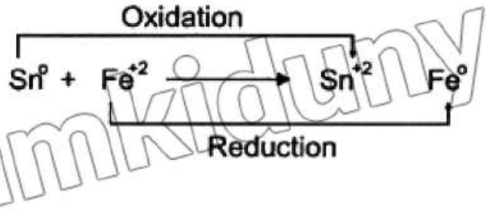
Example 2.7

Is the following reaction feasible?

$$Sn + Fe^{2+} \longrightarrow Sn^{2+} + Fe$$

The standard reduction potential values are $E^0_{Sn} = -0.14V$, $E^0_{Fe} = -0.44V$

Solution



It is clear from the above equation that oxidation of Sn and reduction of Fe is taking place. Sn is acts as an anode and Fe as the cathode. The above reaction consists of the following two half-cell reactions.

$Sn \longrightarrow Sn^{2+} + 2\bar{e}$ (oxidation half-reaction)

$Fe^{2+} + 2\bar{e} \longrightarrow Fe$ (reduction half-reaction)

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = -0.44V - (-0.14V)$$

$$= -0.30V$$

As E^0_{cell} is negative, therefore the given reaction is not feasible. However reverse reaction would be spontaneous.

CONCEPT ASSESSMENT EXERCISE 2.7

1. Using emf data, argue on the following:
   (i) Can Mg displace Cu from a solution of Copper(II) sulphate.?
   (ii) Can Iodine displace chlorine from an aqueous solution of Potassium chloride?
2. Is the following reaction feasible?

$$Al + Mn^{2+} \rightarrow Al^{3+} Mn$$

The standard reduction potential values are $E^0_{Al} = -1.66V$, $E^0_{Mn} = -1.18V$

2.5 Nernst Equation

The relationship between concentration and electrode potential is given by the Nernst equation.

The electrode potential is influenced by the concentrations of the ions involved in the redox reaction. The Nernst equation is a mathematical expression that relates the standard electrode potential (E°) to the actual electrode potential (E) under non-standard conditions, considering the concentrations of the reactants and products.

Mathematically Nernst equation is:

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

Where n = No. of electron transferred from the reduced species to oxidised species.

R = the universal gas constant. Its value is 8.314J/mol.

T = Kelvin temperature

F = Charge of a mol of electron and the charge of 1 mol of electron is 9.648×10^4 Cmol^{-1})

[oxidized species] = Conc. of species with higher oxidation state.

[reduced species] = Conc. of species with lower oxidation state.

$$E = E^0 + \frac{2.303\ RT}{nF} \log \frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

Remember that *lnx* = 2.303logx

$$E = E^0 + \frac{0.059}{n}\log\frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

$$\frac{2.303RT}{F} = \frac{2.303 \times 8.314 JK^{-1}mol^{-1} \times 298K}{9.648 \times 10^4 Cmol^{-1}}$$

$= 0.059JC^{-1} = 0.059V$ since $1J/C = 1V$

2.5.1 Electrode potentials and concentration

We have already discussed copper half-equation; it has the following standard electrode potential.

$$Cu^{2+} + 2e^- \rightarrow Cu \quad +0.34V$$

For this value of E^o the Cu^{2+} ions should have a concentration of 1 mol/dm^3. What will happen if the concentration of Cu^{2+} ions is decreased by adding water? If you decrease the concentration of any species in an equilibrium reaction, then according to Le Chatelier`s Principle the position of equilibrium shifts in such a way as to counter-act or nullify the change. The position of equilibrium will shift to the left, increasing the concentration of Cu^{2+} ions again. Since E^o measures the position of the equilibrium. The electrode potential would become less positive. So, it will no longer be a standard potential.

Electrode potential measures how easily a species gains or losses electrons. It depends on the concentration of the ions in the redox reaction.

When the concentration of ions changes:

1. An increase in the concentration of ions (e.g., Cu^{2+} ions for copper electrodes) makes reduction easier because more ions are available to gain electrons. This increases electrode potential.
2. A decrease in the concentration of ions makes reduction harder because fewer ions are available to accept electrons. This decreases the electrode potential.

The Nernst equation quantitatively predicts these changes.

Example: The standard electrode potential of the Cu^{2+}/Cu system is +0.34V. What is the electrode potential of a solution containing 0.5M Cu^{2+} ions?

Solution:

$$E = E^0 + \frac{0.059}{n}\log\frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

Nernst equation for Cu^{2+}/Cu system is:

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} + \frac{0.059}{n}\log\frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

$$E_{Cu^{2+}/Cu} = 0.34 + \frac{0.059}{2}\log\frac{0.5}{1}$$

$$= 0.34 + 0.0295 \times (-0.301)$$

$$= 0.34 - 0.0089$$

$$= 0.331V$$

CONCEPT ASSESSMENT EXERCISE 2.8

The standard electrode potential of Fe^{3+}/Fe^{2+} is 0.77V. What is the electrode potential of the system containing 1.0 mol/dm^3 of Fe^{3+} and 0.2 mol/dm^3 of Fe^{2+} ions? **Ans: 0.811V**

2.6 Electrochemical Series

Under the recommendation of the International Union of Pure and Applied Chemistry (IUPAC) the half-cell reactions are given in the reduction reactions (Table 2.2) therefore E° values are known as reduction potentials. However, the value of oxidation potential for an electrode can be obtained by reversing the sign of reduction potential for that electrode. Note that the given reduction potential values relate to standard conditions only. i.e., 1M solution of ions, 25 °C (298K) and 1 atm. pressure. Changes in conditions will alter these values.

Such a list of arrangement of elements in the order of their standard electrode potential with reference to standard hydrogen electrode is called an electrochemical series (Table 2.1).

2.6.1 Activity Series of Metals

A displacement or replacement reaction occurs when an element displaces another element that is a part of a compound. The general equation,

$$A + XY \longrightarrow X + AY$$

In this reaction, atom A replaces atom X in the compound XY. When Zn metal is placed in a blue solution of copper (II) sulphate, the blue colour slowly fades away and grey metal is replaced by red-orange Cu metal. In this reaction Cu ions in the solution are reduced to Cu metal and Zn atoms are oxidized to Zn ions (for details see section 2.1).

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

However, when copper metal is placed in a zinc sulphate solution, no replacement reaction occurs. Table 12.1 shows that the standard reduction potential of copper is greater than that of zinc. This means that it is easy to oxidize Zn to its ions and reduce Cu^{2+} ions to its atoms. Thus, Zn can replace Cu^{2+} ions from its solution. For the same reason Mg and Al can also displace Cu^{2+} ions, but Ag cannot displace Cu^{2+} ions.

Similarly, it is observed that metals like Na, and K can displace H_2 from water but metals like Cu, and Ag cannot displace H_2 from water. Metals are, therefore, ranked according to their ability to replace other metals and hydrogen from their compounds. In this ranking **metals and hydrogen are arranged in order of decreasing ease of oxidation to their respective ions in aqueous solution.** This arrangement is called **activity series** (see Table 2.2).

Table 2.2 Activity series of common metals

Increase in Reactivity	Li K Ba Sr Ca Na	Very Active metals; React with cold water with the liberation of hydrogen gas; (K and Na react violently with water), They also react violently with acids
	Mg Al Mn Zn Cr Fe Cd	Metals of intermediate activity: React with steam or with acids such as HCl with the liberation of H_2
	Co Ni Sn Pb	Moderately active metals React slowly with HCl Do not react with water
	H_2	
	Cu Ag Hg	Moderately noble metal; Do not react with water, or HCl but react with oxidizing acids such as HNO_3
	Pt Au	Very noble metals; React only with aqua regia

1. Metals higher on the list transfer electrons to metal cations lower on the list. The greater the separation between the species the more vigorous will be the reaction. For example, when powdered barium is heated with lead (II) oxide, a replacement reaction occurs. This is because Ba is more active than Pb. Barium is oxidized to form barium oxide and lead is reduced to elemental lead.

$$Ba_{(s)} + PbO_{(s)} \longrightarrow BaO_{(s)} + Pb_{(s)}$$

On the other hand, when iron pellets are added to a solution of $MgCl_2$ no reaction will occur. This is because Fe is below Mg in the activity series.

CONCEPT ASSESSMENT EXERCISE 2.8

Predict whether a replacement reaction will occur in the following instances. Defend your conclusion.

a) Magnesium ribbon is in a solution of silver nitrate.
b) A copper plate is dipped in iron(II) sulphate ($FeSO_4$) solution.
c) Lead(II) oxide is heated with powdered zinc.
d) Nickel wire is placed into a solution of silver nitrate.

2.7 The Relative Reactivity of Species as Oxidizing Agents or Reducing Agents

Electrode potential values, also known as reduction potentials, provide insight into the relative reactivity of elements, compounds, and ions as oxidizing or reducing agents. By comparing reduction potentials, you can determine the relative reactivity of species as oxidizing or reducing agents. Those with higher reduction potentials are stronger oxidizing agents, while those with lower reduction potentials are stronger reducing agents.

For Example

Consider the reaction reduction potentials for the following half-reactions.

$$Cu^{2+} + 2e^- \longrightarrow Cu \quad E^0 = +0.34V$$

$$Zn^{2+} + 2e^- \longrightarrow Zn \quad E^0 = -0.76V$$

Note that Cu^{2+} ions have a higher reduction potential compared to Zn^{2+} ions. So, Cu^{2+} ions have a greater tendency to gain electrons and thus act as a stronger oxidizing agent than Zn^{2+} ions.

For Example

Consider the reaction between potassium permanganate ($KMnO_4$) and iron(II) sulphate ($FeSO_4$) in an acidic solution.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad E^0 = +1.52V$$

$$Fe^{2+} \longrightarrow Fe^{3+} + 1e^- \quad E^0 = +0.77V$$

Here, MnO_4^- ions have a higher value of reduction potential than Fe^{2+} ions. So, MnO_4^- ions act as a strong oxidizing agent and Fe^{2+} ions act as a strong reducing agent in this reaction.

2.8 Types of Electro-Chemical Cells

Devices, that convert electrical energy into chemical energy and vice versa, are known as electrochemical cells. There are two types of electrochemical cells.

1) Electrolytic cells.
2) Galvanic or voltaic cells. (see section)

2.8.1 Electrolytic Cells

An electrolytic cell is a device that converts electrical energy to chemical energy by electrolysis. Electrolysis is the process by which chemical reactions are stimulated by an external electrical current. In electrolytic cells, oxidation takes place at the anode (positive electrode) where electrons are lost. At the cathode (negative electrode), electrons are gained. The oxidation process results in the conversion of electrical energy into chemical energy by stimulation of a non-spontaneous reaction.

Electrolysis

Electrolysis is a process in which a chemical reaction occurs by means of an electric current in a molten state or in an aqueous state. The apparatus for electrolysis consists of an electrolytic cell containing the electrolyte either in a molten state or in an aqueous state. Two electrodes are placed in the solution. The electrodes are connected to a battery. The current is carried from the battery through the wires by means of electrons (metallic conduction). Within the cell, the current is carried by the anions and cations of the electrolyte (Electrolytic conduction). The electrodes serve as a point where conduction changes from metallic to electrolytic or vice versa. At each electrode, a chemical reaction takes place in which electrons are gained by the ions in solution at one electrode. Simultaneously electrons are released by some substance at the other electrode. These electrons are returned to the battery through the connecting wire. Thus, oxidation-reduction reactions occur at the electrodes. The electrode at which oxidation occurs is called an **anode**. The electrode at which reduction occurs is called as **cathode**. The changes, that occur at the electrodes, depend on the relative oxidation-reduction tendencies of the substances involved.

Units

The SI unit of charge is the **coulomb (C)**. It is the charge on 6.25×10^{18} electrons. Although the coulomb is the usual unit for measuring charge, the chemist finds that a more convenient unit is the **Faraday (F)**. It corresponds to the charge carried by one mole of electrons and amounts to 96487 C. The SI Unit of current is the ampere, which is the amount of current flowing when one coulomb passes a specific point in one second. Frequently, an ampere is referred to as "a coulomb per second".

2.8.2 Factors Influencing the Products of Electrolysis

Electrolysis involves the use of an electric current to drive a non-spontaneous redox reaction. The substances liberated during electrolysis depend on the following factors.

- The state of electrolyte
- Position in the electrochemical or redox series
- Concentration of the electrolyte

1. The state of electrolyte:

Electrolytes are substances that conduct electricity when dissolved in water or in their molten state. When molten electrolyte is used, its cations and anions are discharged at the electrodes. But aqueous solutions of electrolytes contain both ions from dissolved electrolytes and that of water. In this case, water molecules may produce H_2 at the cathode.

2. Position in the Electrochemical or Redox Series:

The position of substances in the electrochemical series can give an indication of their tendency to be reduced or oxidized during electrolysis. Generally, substances higher in the series tend to be reduced, while those lower in the series tend to be oxidized. In aqueous solutions, cations less reactive than hydrogen are preferentially discharged at the cathode e.g., Cu^{2+} ions. But cations more reactive than hydrogen do not discharge and remain in solution e.g., Na^+, Mg^{2+} etc. In this case, water molecules are discharged at the cathode to liberate hydrogen.

3. **Concentration of Electrolyte:**

The concentration of ions in the electrolyte solutions also affects the ease with which they are liberated during electrolysis. Higher concentrations can favour the liberation of certain ions. The ions with lower concentrations are not discharged, instead, water molecules are *discharged.*

The following examples show how the identities of substances liberated in electrolysis depend on specific electrolytes, their constituent ions as well as their position in the electrochemical series.

1. Electrolysis of fused NaCl

   At anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

   At cathode: $2Na^+ + 2e^- \rightarrow 2Na$

   Net reaction: $2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2$

2. Electrolysis of concentrated aqueous NaCl (brine)

   Since the solution contains a higher concentration of Cl^- ions. So, they are discharged at the anode instead of OH^- ions. Na^+ ions being more reactive than hydrogen remain in solution and are not discharged. Instead water molecules are discharged at the cathode.

   At anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

   At cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

   Net reaction: $2H_2O + 2Cl^- \rightarrow H_2 + Cl_2 + 2OH^-$

3. Electrolysis of dilute aqueous NaCl

   In dilute aqueous NaCl solution, Cl^- ions have a lower concentration. So, chloride ions are not discharged at the anode. Instead, OH^- ions are discharged at the anode. Here again, Na^+ ions being more reactive than hydrogen remain in the solution and water molecules are discharged at the cathode.

   At anode: $4OH^- \rightarrow O_2 + 4e^- + 2H_2O$

   At cathode $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

   Net reaction: $4H_2O \rightarrow 2H_2 + O_2$

2.9 Relation Between the Faraday Constant, Avogadro Constant, and the Change on the Electron

The amount of a substance produced at an electrode during electrolysis depends on the period of time for which a constant current is passed and the quantity of charge in coulombs that passes through the electrolyte. The relation between current and time is:

$$Q = I \times t$$

Where,

Q = Quantity of charge in coulombs (C)

I = Current in Ampere (A)

t = time of electrolysis in seconds(s)

The quantity of electricity can be expressed by Faraday constant (F). One faraday is the amount of electric charge carried by one mole of electrons.

Charge on one electron = $1.60217662 \times 10^{-19}$ C

Charge on one mole of electrons = $1.60217662 \times 10^{-19}$ C x 6.022×10^{23} per mol

= 96485.332 C/ mol

It is therefore concluded that 96485.332 C is the charge on one mole of electrons. This quantity of charge is referred to as one **Faraday**. Thus, the quantity of the change in electrolysis can be determined from the number of Faraday's of charge, which passes. For most calculations, the value of the Faraday will be taken as 96500 C.

The relationship between the Faraday constant (F), Avogadro constant (N_A), and the charge on the electron (e) can be expressed by the equation:

$$F = N_A \cdot e$$

where:

F = the Faraday constant (charge per mole of electrons),

N_A = the Avogadro constant (number of entities per mole) = 6.022141×10^{23} per mol

e = the elementary charge (charge on a single electron) = $1.60217662 \times 10^{-19}$ C

For example

$$Na^+ + e^- \rightarrow Na$$

To deposit one mole of Na, the amount of electricity needed is 1F (96500 C).

$$Cu^{2+} + 2e^- \rightarrow Cu$$

But to deposit one mole of Cu, 2 mole of electrons are required. So, the amount of electricity needed is 2F.

Example 2.8

In the electrolysis of molten $ZnCl_2$, how much Zn can be deposited at the cathode by the passage of 0.01-ampere current for one hour?

Solution

0.01 Amp. for one hour carries charge = $0.01 \times 1 \times 60 \times 60$

= 36 C

Since 1F = 96500 C

Therefore, 36 C = 3.7×10^{-4} Faraday

In molten Zinc chloride, the cathode reaction is

$$Zn^{+2} + 2e^- \longrightarrow Zn$$

2F current = 1 mol of Zn

$1F \text{ current} = \frac{1}{2} \text{ mol of Zn}$

$3.7 \times 10^{-4} F \text{ current} = \frac{1}{2} \times 3.7 \times 10^{-4}$

$= 1.85 \times 10^{-4} \text{ mol of Zn}$

Mass of zinc = n x molar mass

$= 1.85 \times 10^{-4} \times 63.37$

$= 0.012 \text{gm}$

Example 2.9

A constant current was passed through a solution of $AuCl_4^-$ ions between gold electrodes. After a period of 10.0 minutes, the cathode increased in weight by 1.314 grams.

i) How much charge was passed?

ii) What was the amount of current?

iii) What volume of Cl_2 was collected at the anode at 1 atm and 25 °C?

Solution

The reaction at the cathode is the reduction of Au (III) to Au metal

$$AuCl_4^- + 3e^- \longrightarrow Au + 4Cl^-$$

It means that for every 3 Faraday of electricity used up, 1 mole of Au is produced.

$$\text{Moles of Au} = \frac{1.314\text{gAu}}{197\text{g/mole of Au}} = 6.67\times10^{-3}$$

i) $$\text{Charge} = 6.67\times10^{-3} \text{ mole Au} \times \frac{3 \text{ Faraday}}{\text{mole of Au}}$$

$$= 2 \times 10^{-2} \text{ Faraday}$$

ii) $$\text{Current} = \frac{\text{Charge}}{\text{Time(s)}}$$

$$\text{Time} = 10 \text{ mins} = 10\times60 = 600\text{s}$$

$$\text{Current} = \frac{(2\times10^{-2}\text{F})(96500\text{C/F})}{600\text{s}} = 3.22 \text{ A.}$$

iii) The reaction at the anode is the oxidation of Cl^- ions.

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

For every 2 Faraday of electricity, 1 mole of Cl_2 was produced.

For 1 Faraday of electricity = 1/2 moles of Cl_2 was produced.

For $2x10^{-2}$ Faraday of electricity = $1/2 \times 2x10^{-2}$ moles of Cl_2 was produced.

= $1x10^{-2}$ moles of Cl_2 was produced.

n = 1×10^{-2} mol

P = 1atm

T = 25 + 273=298K

R = $0.0821 atm.dm^3 mol^{-1}$

V = ?

Volume of Cl_2 produced can be calculate by the following formula

$$V = \frac{nRT}{P}$$

$$= \frac{1x10^{-2} \times 0.0821 \times 298}{1} \quad = 0.245dm^3$$

2.10 Experimental Determination of Avogadro Constant By Electrolytic Method

Electrolysis provides a concrete way to measure the Avogadro Constant experimentally. In this experiment, a known electrolyte is electrolysed. The mass of metal deposited at the cathode is determined by passing known amperes of current for a known time. Suppose you electrolysed $AgNO_3$ using Ag electrodes. The experimental data shows that when 0.1 amperes is passed for exactly 30 minutes through the aqueous solution of silver nitrate solution, the amount of Ag deposited on the cathode is 0.201g. From this data, you can calculate the Avogadro Constant as follows;

I = 0.1amp

t = 30 min.= 30x 60= 1800s

Q = I x t

Q = 0.1 x 1800

Q = 180 Coulombs

Mass of Cu produced = 0.201g

This means 0.201g of Ag is produced by 180C of electricity.

So, 1 mol or 107.868g Ag would require = 180/0.201 x 107.868

= 96598.209 Coulombs

This charge must be present on electrons producing 1 mol of Ag

Cathode Reaction: $Ag^{+}_{(aq)} + 1e^{-} \rightarrow Ag_{(s)}$

This equation shows that 1 mole of electrons gives 1 mole of Ag.

So, the charge on 1 mole of electrons = 96598.209 C

As the charge on one electron is = 1.602×10^{-19}C

Therefore the number of electrons in one mole = $96598.209\ C/1.602 \times 10^{-19}C$

$= 6.0298 \times 10^{23}$

This value is very close to the accepted value of 6.02214×10^{23}

CONCEPT ASSESSMENT EXERCISE 2.10

1. An electrolytic cell is connected to a power source for two hours. If the current flowing through the cell is 0.5A during this time. Find the mass of the substance liberated during this time interval. (the molar mass of the substance is 107.9g/mol.)
2. Calculate the charge in coulombs when 3 moles of electrons flow through a circuit.
3. Calculate the mass of silver deposited at the cathode during electrolysis of $AgNO_3$ solution, if you use a current of 0.1A for 20 minutes.

2.11 Winkler Method for Biological Oxygen Demand

The biological oxygen demand (BOD) is the amount of oxygen used to decompose the organic matter in a sample of water over a specified time period, usually 5 days, at a specified temperature. A high BOD indicates a greater quantity of organic waste in the water, which means a lower level of dissolved oxygen. Dissolved oxygen is used as an indicator of the health of a water body, where higher dissolved oxygen concentrations are correlated with high productivity and little pollution.

The Winkler Method

The Winkler Method is a widely used redox technique to measure dissolved oxygen in freshwater systems.

The principle of the Winkler method

Oxygen present in a water sample is used to oxidize iodide ions into iodine. The amount of iodine produced is determined by titrating with a standard sodium thiosulphate solution. The amount of oxygen present in the original sample of water is determined from the titer.

ACTIVITY 2.2: DETERMINING OXYGEN PRESENT IN A WATER SAMPLE

Materials Required

- 300 BOD bottle
- Manganese(II) sulphate solution 2 cm^3
- Alkali iodide azide 2 cm^3
- Conc. H_2SO_4 2 cm^3
- Potassium iodide solution 2 cm^3.
- Sodium thiosulphate solution 0.1M
- Starch solution 2 cm^3

Procedure

- Collect sample water in a 300 cm^3 BOD bottle. To do this, the BOD bottle is immersed in water, remove the cap under water, fill the bottle with water and, put the cap under water.
- Add 2 cm^3 of alkaline iodide azide solution (an aqueous solution of 32.7% NaOH + 15% KI + 1% NaN_3) and close it with the cap. Then add 2 cm^3 of manganese(II) sulphate solution. Swirl the sample bottle a few times. Oxygen dissolved in the alkaline solution oxidizes the manganese(II) ions to manganese(IV) oxide, which appears as a brown precipitate.

$$2Mn^{2+}_{(aq)} + 4OH^-_{(aq)} + O_{2\,(aq)} \rightarrow 2MnO_{2\,(s)} + 2H_2O_{(l)}$$

- Add.2 cm^3 of conc. H_2SO_4 and then 2 cm^3 solution of potassium iodide, KI, to the solution. The precipitate will dissolve into a solution, so Mn(IV) is reduced back to Mn(II) liberating iodine in the process.

$$MnO_{2\,(s)} + 2I^-_{(aq)} + 4H^+_{(aq)} \rightarrow Mn^{2+}_{(aq)} + I_{2(aq)} + 2H_2O_{(l)}$$

- Start the titration process. Titrate 201 cm^3 of above water against standard sodium thiosulphate solution until the solution turns pale yellow. Now add 2 cm^3 starch solution as an indicator. The solution will turn blue. Continue to add sodium thiosulphate solution till the blue colour just disappears.

$$2S_2O_3^{2-}{}_{(aq)} + I_{2\,(aq)} \rightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-_{(aq)}$$

- The above stoichiometric equations show that:

  1 mole of $O_2 \rightarrow$ 2 moles of $MnO_2 \rightarrow$ 2 moles of $I_2 \rightarrow$ 4 moles of $S_2O_3^{2-}$

- Therefore, after determining the number of moles of iodine produced, you can work out the number of moles of oxygen molecules present in the original water sample.
- The oxygen content is usually presented as mg/dm^3 or ppm

KEY POINTS

1. Redox reactions i.e., oxidation and reduction reactions involve the transfer of electrons or change in oxidation numbers.
2. Redox equations can be balanced by using the oxidation number method and ion-electron method.
3. The driving force behind the spontaneous redox reaction is called the cell potential.
4. The magnitude of cell potential depends upon the conditions under which the measurement is made. Under standard conditions, all solutions have 1M concentration; all gases have a partial pressure of 1 atm. The standard potential for the reduction of H^+ to hydrogen gas is arbitrarily taken as zero volts.
5. In a galvanic cell, oxidation and reduction reactions take place at separate electrodes and electrons flow through the external circuit. These separate parts of the galvanic cell are half cells. The reactions which occur at these half cells are the half-cell reactions. A salt bridge allows the ions to flow between the half cells.
6. In a galvanic cell, oxidation occurs at the node, reduction occurs at cathode and the electrons flow in the external circuit from the anode to the cathode.
7. Voltaic cells use a spontaneous redox reaction to drive an electric current through a wire. Whereas, the electrolytic cells use an electric current to drive a redox reaction.
8. The quantity of electricity carried by 1mole of electrons is called a Faraday. It is equal to 96,500 coulombs.
9. In electrolysis, electric current from an external source drives a non-spontaneous chemical reaction. The amount of chemical reaction that takes place in electrolysis is directly proportional to the quantity of charge transferred at the electrode.
10. A battery is a galvanic cell or a group of galvanic cells connected in series. Some of the well-known batteries are the dry cell, the nickel-cadmium battery, the lead-storage battery used in automobiles, fuel cells, etc.
11. The corrosion of metals is an electrochemical phenomenon.

References for further learning:

- Bodener and Pardue, chemistry an experimental science 2/e
- Steven s. Zumdahl, Chemistry
- Zumdahl, introductory chemistry third edition
- Olmsted and Williams, chemistry, the molecular science
- Silberberg, chemistry, the molecular nature of matter and change

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which of the following elements is reduced in the reaction? $2Na+Cl_2 \rightarrow 2NaCl$

a) Na b) Cl c) Both Na and Cl d) Neither Na nor Cl

ii. In the reaction $Fe+CuSO_4 \rightarrow FeSO_4.Cu$, what is the reducing agent?

a) Fe b) Cu c) SO_4^{2-} d) $CuSO_4$

iii. What is the oxidation number of sulphur in H_2SO_4?

a) -2 b) 0 c) +2 d) +6

iv. Which of the following best describes the process of oxidation?

a) Gain of electrons b) Loss of electrons
c) Gain of protons d) Loss of protons

v. In the electrolysis of water, which substance is liberated at the cathode?

a) H_2 b) O_2 c) H_2O d) OH^-

vi. Which of the following metals would not react with HCl to produce H_2 gas?

a) Zn b) Fe c) Cu d) Mg

vii. The Winkler method measures the concentration of which substance to determine BOD

a) O_2 b) CO_2 c) N_2 d) H_2

viii. In a redox reaction, the oxidizing agent:

a) Loses electrons b) Gains electrons
c) Loses protons d) Gains protons

ix. The standard electrode potential of the hydrogen electrode is defined as:

a) 0 V b) 1 V c) -1 V d) 0.5 V

x. What is the relationship between the Faraday constant (F), Avogadro's number (NA), and the charge of an electron (e)?

a) $F=N_A \times e$ b) $F=e/N_A$ c) $F=N_A/e$ d) $F=e2 \times N_A$

2. Short Answer Questions

Explain the following with reasons.

i. The oxidation potential of Zn is +0.76V and its reduction potential is -0.76V

ii. A salt bridge maintains the electrical neutrality in the cell.

iii. Na and K can displace hydrogen from acids but Cu and Pt cannot.

iv. Define oxidation in terms of electron transfer.

v. What is the oxidation number of oxygen in H_2O_2?

vi. Identify the reducing agent in the reaction

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

vii. State the purpose of the Winkler method.

viii. Explain what happens at the anode during the electrolysis of aqueous sodium chloride.

ix. What does a positive standard electrode potential indicate about a substance's tendency to gain electrons?

x. Calculate the oxidation number of chromium in $K_2Cr_2O_7$

xi. Describe the role of the standard hydrogen electrode in electrochemistry.

xii. What is the significance of the activity series of metals?

xiii. How can you deduce the feasibility of a redox reaction using electrode potentials?

xiv. Bauxite ore is used for the commercial preparation of Al. For this purpose, bauxite ore is first purified to produce pure alumina, Al_2O_3. Alumina is then electrolyzed. The following reaction occurs:

$$2Al_2O_{3(s)} \longrightarrow 4Al_{(s)} + 3O_{2(g)}$$

Calculate the mass of Al, that collects at the cathode and the volume of oxygen that collects at the anode when Al_2O_3 is electrolyzed for 10 hours with a 15 ampere current at 1 atm and 25°C.

(Ans: mass of Al=50.36g, volume of oxygen=34.20dm^3)

xv. Which of the following compounds will give more mass of metal, when 15 ampere current is passed through a molten mass of these salts for 1 hr.

(a) NaCl (b) $CaCl_2$.

(Ans: NaCl will give more Na)

xvi. How many hours would electroplating have to be continued at the rate of 5 amperes if 75g of copper is to be deposited from $CuSO_4$ solution?

xvii. Differentiate between the following

(a) A galvanic and electrolytic cell

(b) Oxidation half-reaction and reduction half-reaction

xviii. An electroplating apparatus is used to coat jewellery with gold. What mass of gold can be deposited from a solution that contains $[Au(CN)_4]^{-1}$ ion if a current of 5.0 amperes flows for 30 minutes? The following half-reaction occurs;

$$[Au(CN)_4]^{-1}_{(aq)} + 3e^- \longrightarrow Au_{(s)} + 4CN^-_{(aq)}$$

(Ans: mass of gold =6.12g)

xix. Construct redox equations using the following half equations.

(a) $SO_2 \rightarrow HSO_4^-$

$MnO_4^- \rightarrow Mn^{2+}$

(b) $Cr_2O_7^{2-} \rightarrow Cr^{3+}$

$Cl^- \rightarrow Cl_2$
(c) $H_2O_2 \rightarrow O_2$
$MnO_4^- \rightarrow Mn^{2+}$
(d) $Sn^{2+} \rightarrow Sn^{4+}$
$Fe^{3+} \rightarrow Fe^{2+}$
(e) $IO_3^- \rightarrow I^-$
$AsO_3^{3-} \rightarrow AsO_4^{3-}$

xx. In the reaction between potassium permanganate and iron(II) sulphate in an acidic solution:

$$MnO_4^- + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+}$$

- a) Identify the oxidation states of manganese and iron before and after the reaction.
- b) Explain which species is oxidized and which is reduced.
- c) Balance the redox reaction using changes in oxidation numbers.
- d) Identify oxidising and reducing agents.

xxi. Explain why magnesium can displace zinc from zinc sulphate solution but copper cannot.

Predict the outcome of placing a zinc strip in a copper(II) sulphate solution, including the balanced chemical equation.

3. Long Answer Questions

i. Explain the process of balancing a redox equation using the oxidation number method. Include an example.

ii. Describe the Winkler method for measuring biochemical oxygen demand (BOD) and its importance in assessing water quality.

iii. Explain how the activity series of metals can be used to predict the outcome of displacement reactions.

iv. Describe the construction and function of an electrolytic cell.

v. Calculate the mass of copper deposited at the cathode during the electrolysis of CuSO4 solution when a current of 2 A flows for 30 minutes. (Faraday's constant = 96500 C/mol, Molar mass of Cu = 63.5 g/mol). **Ans: 1.18g**

vi. Balance the following equations by the oxidation number method.

- a. $MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2$
- b. $HNO_3 + HI \longrightarrow NO + I_2 + H_2O$
- c. $Ag + H_2S + O_2 \longrightarrow Ag_2S + H_2O$
- d. $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$
- e. $Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

vii. During the electrolysis of molten sodium chloride:

a) Describe the process occurring at the anode and the cathode.

b) Calculate the total charge passed through the cell if a current of 3 A is applied for 2 hours. **Ans: 21600 C**

viii. Consider the following half-reactions and their standard electrode potentials:

$Ag^+ + e^- \rightarrow Ag \quad E° = +0.80\,V$

$Zn^{2+} + 2e^- \rightarrow Zn \quad E° = -0.76\,V$

a) Calculate the standard cell potential for the galvanic cell constructed with these half-cells. **Ans: 1.56V**

b) Predict the direction of electron flow in the cell.

c) Using the calculated cell potential, discuss the feasibility of the redox reaction in this cell.

ix. A current of 1.0 A is passed through a solution of $AgNO_3$ for 965 seconds.

(a) How many Faradays of charge were passed? **Ans: 0.01F**

(b) How many moles of silver would be deposited? **Ans: .01 moles**

THINK TANK

1. Predict the outcome of mixing aqueous solutions of $FeSO_4$ and $AgNO_3$ with Cu based on their standard electrode potentials. Explain your reasoning.
2. Using the Nernst equation, calculate the cell potential of a galvanic cell with the following half-reactions: $Zn^{2+} + 2e^- \rightarrow Zn$ ($E° = -0.76$ V) and $Cu^{2+} + 2e^- \rightarrow Cu$ ($E° = +0.34$ V) if the concentration of Zn^{2+} is 0.1 M and Cu^{2+} is 1.0 M. **Ans: 1.39V**
3. A voltaic cell is constructed using a copper electrode in a 1 M copper(II) sulphate solution and a zinc electrode in a 1 M zinc sulphate solution:
   a) Calculate the cell potential under standard conditions using the given standard reduction potentials:

   $E°(Cu^{2+}/Cu) = +0.34\,V$

   $E°(Zn^{2+}/Zn) = -0.76\,V$ **Ans: 1.10V**

   b) Discuss how the Nernst equation can be used to predict the effect of changing the concentration of Cu^{2+} ions on the cell potential.

PROJECT

Discuss the environmental implications of high BOD levels in water bodies and the potential sources of this pollution.