20

ELECTROCHEMISTRY

20.1 INTRODUCTION

Electrochemistry is the study of interchange between chemical energy and electrical energy. Many significant chemical reactions are electrochemical in nature. Electrochemical reactions are chemical reactions in which electrons are transferred. To understand electrochemical reactions, it is necessary to understand the terms and concepts of electricity and extend these to apply to electrochemical relationships.

OBJECTIVES

After reading this lesson, you will be able to:

- describe the basic concepts of Oxidation and Reduction
- explain Electrochemical cells
- describe Electrochemical potentials
- describe the application of Electrochemistry

20.2 BASIC CONCEPTS OF OXIDATION AND REDUCTION

Electrons are always transferred from one atom or molecule to another in an electrochemical reaction. There are three different types of electrochemical reactions based on the changes in oxidation state that occur in them. They are

1. **Oxidation reactions:** atoms of the element(s) involved in the reaction lose electrons. The charge on these atoms must then become more positive.

   Eg: Fe^{2+} (aq) $\longrightarrow$ Fe^{3+}(aq) + e^-

2. **Reduction reactions:** In reduction reactions, atoms of the elements involved gain electrons.

   Eg: $Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$

3. **Redox reactions :** A redox reaction is an electrochemical reaction in which both reduction and oxidation take place together. The electrons lost in an oxidation component are gained in a reduction component.

   Eg: $Fe^{3+} + Cu^{+} \longrightarrow Fe^{2+} + Cu^{2+}$

These redox reactions are of two types they are:

(a) **Direct redox reaction:** In a direct redox reaction, both oxidation and reduction reactions take place in the same vessel. Chemical energy is converted to heat energy in a direct redox reaction.

(b) **Indirect redox reaction:** In indirect redox reactions, oxidation and reduction take place in different vessels. In an indirect redox reaction, chemical energy is converted into electrical energy.

20.3 ELECTROLYTE AND ELECTRODES

Compounds, molecules, and atoms that do not carry any charge are referred to as neutral species. Eg KCl, $O_{2.}$

- **Ion** is an atom or molecule that has an electrical charge.
- **Cation:** An ion that carries a positive charge is called a cation.
- **Anion:** An ion that carries a negative charge is called an anion.
- **Electrolyte:** A solution that contains ions is called an electrolyte solution, or an electrolyte. They conduct electricity as charged ions can move through them.
- **Electrodes:** A solid electric conductor through which an electric current enters or leaves an electrolytic cell or other medium. In electrochemical reactions oxidation or reduction reaction takes place at the electrodes. These are called electrode reactions, or half-reactions.
- A half-reaction can be either a reaction in which electrons appear as products (oxidation) or a reaction in which electrons appear as reactants (reduction). A combination of two half reaction forms the complete reaction.
- **Cathode:** An electrode in which reduction takes place.
- **Anode:** An electrode where oxidation takes place.

20.4 ELECTROCHEMICAL CELLS

Electrochemical cell is a device which converts chemical energy into electrical energy in an indirect redox reaction.

An electrochemical cell can either drive an external electrical device (load) or be driven by it (power supply), depending upon the relative electromotive forces applied by the cell and the device. It is of three types galvanic, reversible, or electrolytic:

- A galvanic cell is a cell in which current flows, power is produced, and the cell reaction is proceeding spontaneously.
- An electrolytic cell is a cell in which current flows, power is consumed,and the cell reaction being driven is the reverse of the spontaneous cell reaction.
- A reversible cell is a cell in which no current flows (and therefore no power is involved, because $P = EI$. The cell reaction in a reversible cell is neither spontaneous nor nonspontaneous; it is called reversible because an infinitesimal change in the cell potential can cause it to proceed in either direction.

In an electrochemical cell, the half cell where oxidation takes place is known as oxidation half cell and the half cell where reduction takes place is known as reduction half cell. Oxidation takes place at anode which is negatively charged and reduction takes place at cathode which is positively charged. During this process transfer of electrons takes place from anode to cathode while electric current flows in the opposite direction. An electrode is made by dipping the metal plate into the electrolytic solution of its soluble salt. A salt bridge is a U shaped tube containing an inert electrolyte in agar-agar and gelatine.

A salt bridge maintains electrical neutrality and allows the flow of electric current by completing the electrical circuit.

20.4.1 Representation of an electrochemical cell

While representing an electrochemical cell Anode is written on the left while the cathode is written on the right.

Anode represents the oxidation half cell and is written as:

Metal/Metal ion (Concentration) Cathode represents the reduction half cell and is written as: Metal ion (Concentration)/Metal. Salt bridge is indicated by placing double vertical lines between the anode and the cathode. The physical state of all components like solid, liquid, gas, aqueous (s, l, g, aq, etc.) should be mentioned.

Example: An aqueous cell that operates spontaneously using the following reaction:

$$2\mathrm{Cu(s)} + \mathrm{Zn}^{2+} \longrightarrow 2\mathrm{Cu}^{+} + \mathrm{Zn(s)}$$

would be written in cell notation as

$$Cu(s)/Cu^{+}//Zn^{2+}/Zn(s)$$

The Zn^{2+} is being reduced at the cathode, so the Zinc electrode couple is written on the right.

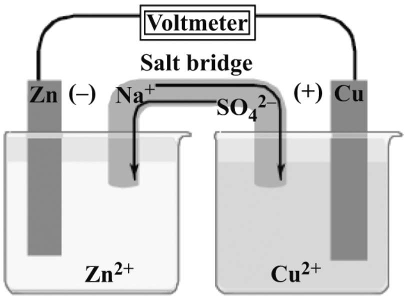

Fig. 20.1

20.5 ELECTROCHEMICAL POTENTIALS

It is the potential difference measured between two electrodes. Voltmeters can be used to measure the potential differences across electrochemical cells but cannot measure directly the actual potential of any single electrode.

20.5.1 Electrode potential

Electrode potential is the potential difference that develops between the electrode and its electrolyte. The separation of charges at the equilibrium state results in the potential difference between the metal and the solution of its ions. It is the measure of tendency of an electrode in the half cell to lose or gain electrons.

There are 2 types of electrode potentials: Oxidation potential and reduction potential. Oxidation potential is the tendency of an electrode to lose electrons or get oxidized. Reduction potential is the tendency of an electrode to gain electrons or get reduced. Oxidation potential is the reverse of reduction potential. The electrode having a higher reduction potential has a higher tendency to gain electrons. So, it acts as a cathode. The electrode having a lower reduction potential acts as an anode.

20.5.2 Standard electrode potentials

When the concentration of all the species involved in a half cell is unity, then the electrode potential is known as standard electrode potential. It is denoted as

$E^{\text{È}}$. For solid or liquid compounds or elements, standard conditions are the pure compound or element; for gases they are 100 kiloPascal (kPa) pressure, and for solutes they are the ideal 1 molar (mol/liter) concentration.

The standard electrode potential of an electrode cannot be measured in isolation. Tables of standard electrode potentials can be obtained for all elements if any one electrode, operated under standard conditions, is designated as the standard electrode or standard reference electrode with which all other electrodes will be compared. According to convention, the Standard Hydrogen Electrode, abbreviated SHE is taken as a reference electrode and it is assigned a zero potential at all temperatures.

The potential difference across a reversible cell made up of any electrode and a SHE is called the reversible potential of that electrode, *E*. If this other electrode is also being operated under standard conditions of pressure and concentration, the reversible potential difference across the cell is the standard electrode potential E^{Θ} of that electrode.

In many practical potential measurements, the standard hydrogen electrode cannot be used because hydrogen reacts with other substances in the cell or because other substances in the cell react with the catalytic platinum electrode surface upon which the H^+/H_2 potential is established. It is often much more convenient to use alternative electrodes whose potentials are precisely known with respect to the SHE.

Two of the electrodes most commonly used as reference electrodes are the silver/silver chloride electrode with $E^{\Theta} = +0.2224$ V, and the saturated calomel electrode (SCE) at 0.241 V. The effect of changing the reference electrode is to change the zero of a potential scale while leaving the relative positions of all of the potentials unchanged.

20.5.3 Standard hydrogen electrode

Standard hydrogen electrode consists of a platinum wire sealed in a glass tube and carrying a platinum foil at one end. The electrode is placed in a beaker containing an aqueous solution of an acid having 1 Molar concentration of hydrogen ions. Hydrogen gas at 1 bar pressure is continuously bubbled through the solution at 298 K. The oxidation or reduction takes place at the Platinum foil. The standard hydrogen electrode can act as both anode and cathode.

If the standard hydrogen electrode acts as an anode:

$$H_2\,(g) \longrightarrow 2H^+\,(aq) + 2e^-$$

If the standard hydrogen electrode acts as a cathode:

$$2H^+\,(aq) + 2e^- \longrightarrow H_2\,(g)$$

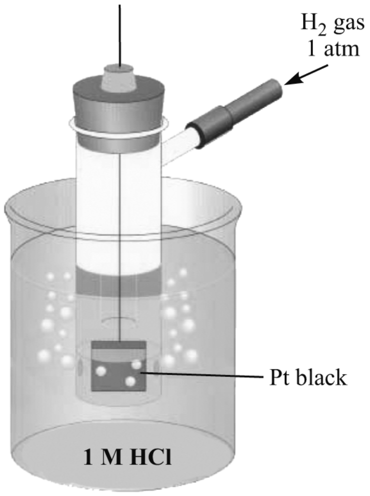

Fig. 20.2

In the electrochemical series, various elements are arranged as per their standard reduction potential values. A substance with higher reduction potential value means that it has a higher tendency to get reduced. So, it acts as a good oxidising agent. A substance with lower reduction potential value means that it has a higher tendency to get oxidised. So, it acts as a good reducing agent. The electrode with higher reduction potential acts as a cathode while the electrode with a lower reduction potential acts as an anode. The potential difference between the 2 electrodes of a galvanic cell is called cell potential and is measured in Volts.

The cell potential is the difference between the reduction potential of cathode and anode.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

Cell potential is called the electromotive force of the cell (EMF) when no current is drawn through the cell.

20.5.4 Electrode potential at Non-Standard conditions

Nernst studied the variation of electrode potential of an electrode with temperature and concentration of electrolyte. Nernst formulated a relationship between standard electrode potential $E^{\ominus}$ and electrode potential E.

When cell is not at standard conditions, use **Nernst Equation**:

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

R = Gas constant 8.315 J/K•mol

F = Faraday constant

Q = reaction quotient [products] $^{\text{coefficient}}$/[reactants] $^{\text{coefficient}}$

E = Energy produced by reaction

T = Temperature in Kelvins

n = number of electrons exchanged in BALANCED redox equation

Electrode potential increases with increase in the concentration of the electrolyte and decrease with decrease in temperature.

Nernst equation when applied to a cell:

$$E_{\text{cell}} = E^{\Theta}{}_{\text{cell}} - \frac{2.303\ RT\ \log}{nF}\ \frac{[\text{Anode ion}]}{[\text{Cathode ion}]}$$

This helps in calculating the cell potential. At equilibrium, cell potential E_{cell} becomes zero

20.6 APPLICATION OF ELECTROCHEMISTRY IN BIOCHEMISTRY

Based on the electrochemical principle several analytes of biochemical importance can be detected. Some of the devices are explained below

20.6.1 Ion selective electrodes: (I.S.E.)

Principle

An ideal I.S.E. consists of a thin membrane across which only the ion to be measured can be transported. The transport of ions from a high conc. to a low one through a selective binding with some sites within the membrane creates a potential difference. This forms the basis of ion selective electrode.

Types of I.S.E.

A wide variety of analytes can be detected using ISE by varying the membrane as given below:

1. Glass membrane (i.e. H^+ electrode)
2. Solid-state electrode (e.g. F- electrode uses a Eu2 +-doped LaF3 crystal)
3. Liquid-based electrode (e.g. Ca2+ electrode uses a liquid chelator)
4. Compound electrode (e.g. CO_2 gas sensing electrode)

Advantages and limitations of I.S.E.

Advantages

1. Linear response: It shows linear response for wide concentration range of the analyte.
2. Non-destructive: The analyte is not consumed at the end of the reaction.
3. Non-contaminating.: The sample remains unchanged at the end of the reaction and can be used for other analysis
4. Short response time: The analyte can be determined within seconds or minutes
5. Unaffected by color or turbidity: Presence of color and turbidity does not affect the analysis as in spectrophotometry.

Limitations

1. Precision is rarely better than 1%.
2. Electrodes can be fouled by proteins or other organic solutes.
3. Interference by other ions.
4. Electrodes are fragile and have limited shelf life.
5. Electrodes respond to the activity of uncomplexed ion. So ligands must be absent or masked.

20.6.2 pH Electrodes

Principle: The H+ ions either diffuse out or into the gel layer of the glass membrane depending on the pH value of the measured solution. Since the glass electrode has an internal buffer with a constant pH value, the potential at the inner surface of the membrane is constant during the measurement. The total membrane potential is a result of the difference between the inner and outer charge. From the potential the H+ ions concentration can be determined using Nernst equation.

Instrumentation

The whole pH measuring circuit consists of a measuring electrode (glass electrode) and a reference electrode, which are both immersed in the same solution. In order to obtain a definite pH value the reference electrode must have a defined stable potential which is independent of the measured solution. Every reference electrode consists of a reference element which is immersed in a defined electrolyte.

This electrolyte must be in contact with the measured solution. This contact most commonly occurs through a porous ceramic junction. Of the many reference systems, only the mercury/calomel and the silver/silver chloride systems, along with certain modifications of them, have attained practical importance.

Due to environmental considerations, however, the mercury electrode is rarely used today. The potential of the reference electrode system is defined by the reference electrolyte and the reference element (e.g. silver/silver chloride). Here it is important that the reference electrolyte has a high ion concentration which results in a low electrical resistance. Ideally no reaction between the reference electrolyte and the measuring solution should occur over a wide temperature range.

Combination electrodes

Since the combination electrode is much easier to handle than the separate electrodes, the former is used almost exclusively today. In the combination electrode the glass electrode is concentrically surrounded by the reference electrolyte.

Only when the different parts of the electrode are expected to have very different life expectancies is the use of separate electrodes recommended instead of a single combination electrode.

Three-in-one electrodes A recent innovation is the addition of a temperature sensor to the pH combination electrode. By housing the temperature sensor in the same body as the pH and reference elements, temperature compensated readings can easily be made with a single probe.

Application

Most of the biochemical reactions are pH dependent.

Eg. Enzyme assays

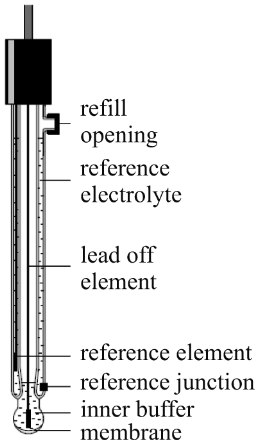

Fig. 20.3

20.6.3 pO_2 (Clark) Electrode

Principle

Binding of oxygen to the polypropylene membrane creates a potential which is directly propotinal to pO_2

Instrumentation

This electrode is known as “Clark Type” after their inventor, Dr. Leland Clark. The Clark electrode consists of an anode and cathode in contact with an electrolyte solution. It is covered at the tip by a semi-permeable membrane usually polypropylene membrane, which is permeable to gases but not contaminants and reducible ions of the sample. The cathode is in a glass envelope in the body of the electrode. The anode has a larger surface that provides stability and guards against drift due to concentration of the pO_2 electrolyte (usually potassium chloride, 0.1 M). This silver/ silver chloride (Ag/ AgCl) anode provides electrons for the cathode reaction. The Clark (pO_2) electrode measures oxygen tension amperometrically. That is the pO_2 electrode produces a current, at a constant polarizing voltage (usually -0.6 V vs. Ag/AgCl) which is directly proportional to the partial pressure of oxygen (pO_2) diffusing to the reactive surface of the electrode. Silver at the anode becomes oxidized.

$$\text{Ag anode : } 4Ag + 4\,Cl^- \; 4AgCl + 4e^-$$

$$\text{Pt cathode : } O_2 + 4H^+ + 4e^- \; 2H_2O$$

Reduction of oxygen occurs at the surface cathode which is exposed at the tip of the electrode. Oxygen molecules diffuse through the semi-permeable membrane and combine with the KCl electrolyte solution. The current produced is a result of the following reduction of oxygen at the cathode.

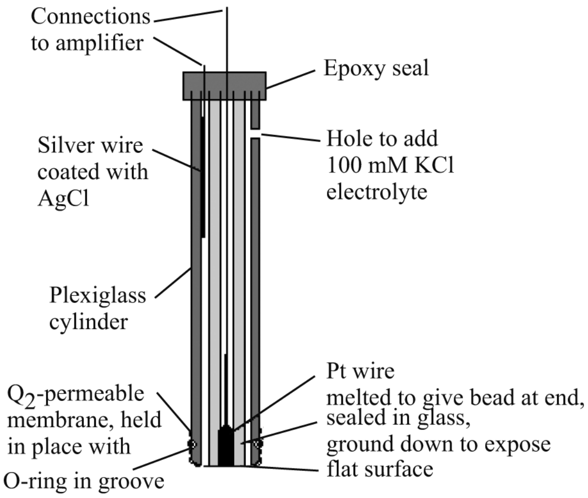

Fig. 20.4

Production of four electrons accompanies each molecule reduced. The pO_2 channel measures this flow of electrons and the resulting microvoltage is displayed as pO_2. Therefore, pO_2 is measured amperometrically; the pO_2 electrode produces a current at a constant polarizing voltage (0.6 V) which is directly proportional to the partial pressure of oxygen diffusing to the reactive surface of the electrode.

20.6.4 Biosensors

Principle

Biosensors are analytical instruments that convert biochemical signal into quantifiable electrical signal.

Instrumentation

It consists of a biocatalyst which can be an enzyme, cell or tissue. This is immobilized on a membrane or gel. It is held in close contact with a transducer which converts biochemical signal into quantifiable electrical signal.

Advantages

1. Highly specific & sensitive
2. Detect wide range of molecules

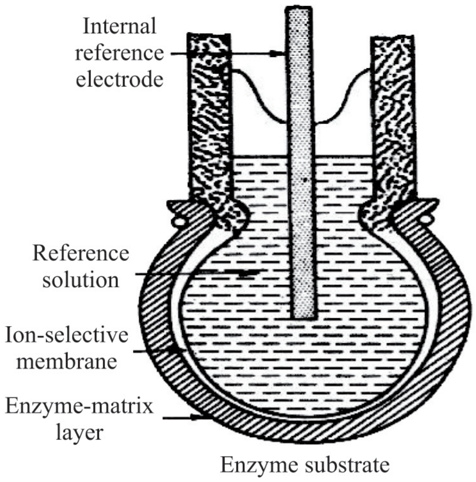

Fig. 20.4

Uses

1. It has wide range of uses in clinical, environmental and Industrial fields

   Eg. Glucose sensors used in the detection of blood glucose for diabetes management

Types

Based on the intimacy between the biocatalyst and the transducer. They are classified into

1. First generation
2. Second generaion
3. Third generation sensors

In first generation, the biocatalyst and transducer can be separated easily. Both can function separately without the other.

In second generation, the biocatalyst and transducer cannot function separately.

In third generation, biochip is used.

Analyte	Biocatalyst	Transducer
Alcohol	Alcohol oxidase	O_2
Glucose	Glucose oxidase	O_2
Urea	Urease	NH_4^+
Glutamate	Glutamate decarboxylase	CO_2

20.6.4.1 Micro-potentiometric sensors

- These sensors are very small and are used to measure analytes in micro litre volumes of sample.
- These are initially developed for studying pH in living cells.
- These units are also used for monitoring organ perfusion.
- It can measure ions like H^+, Na^+, K^+, Ca^{2+} in 10 μL volumes as in 96-well microtiter plates
- It can be used in flow-through systems, such as HPLC detector with 50 μL volumes.

20.6.5 Electrochemical Detectors

Introduction

Electrochemical detection (ECD) technique used for High Performance Liquid chromatography (HPLC) is an extremely selective and sensitive detection technique.

Detection principle

In amperometric electrochemical detection the electrical current is measured resulting from oxidation or reduction reactions. A sample is introduced in HPLC and separated on the chromatographic column. The column is connected to an ECD cell, an electrochemical sensor where a reaction takes place at an electrode. Electrochemically active substances that elute from the column undergo an electrochemical reaction, electrons are transferred resulting in an electrical current. The electrodes are connected to an electronic circuitry with a powerful -low noise- amplifier that converts a pico- or nanoampere current in a signal in the range of ± 1 Volt which is commonly used in data acquisition.

Uses

- It is useful in analyses of several compounds such as aromatic substances, drugs, catechol amines, neurotransmitters etc.
- Concentrations as low as 50 pmole/L and as high as 100 μmole/L or more can be detected using this technique.

INTEXT QUESTIONS 20.1

1. Fill in the blanks
    1. Oxidation is .... of electrons
    2. Reduction is .... of electrons
    3. Both reduction and oxidation takes place in .... reactions.
    4. The potential of Standard Hydrogen electrode is ....
    5. In cathode .... reaction takes place.
2. State True or false:
    1. In pH electrode polypropylene membrane is used.
    2. Silver/ Silver chloride electrode can be used as standard electrode.
    3. Micropotentiometric sensors use larger volume for detection of ions.
    4. Glutamate detection biosensor uses CO_2 as transducer
    5. First generation biosensors, the biocatalyst and the transducer cannot be separated.

WHAT YOU HAVE LEARNT

- Oxidation is defined as a loss of electrons while reduction is defined as a gain of electrons.

- In a redox reaction, both oxidation and reduction reaction takes place simultaneously.
- In an electrochemical cell: Oxidation takes place at anode which is negatively charged and reduction takes place at cathode which is positively charged. Transfer of electrons takes place from anode to cathode while electric current flows in the opposite direction. An electrode is made by dipping the metal plate into the electrolytic solution of its soluble salt. A salt bridge is a U shaped tube containing an inert electrolyte in agar-agar and gelatine.
- Electrode potential is the potential difference that develops between the electrode and its electrolyte. The separation of charges at the equilibrium state results in the potential difference between the metal and the solution of its ions. It is the measure of tendency of an electrode in the half cell to lose or gain electrons.
- According to convention, the Standard Hydrogen Electrode is taken as a reference electrode and it is assigned a zero potential at all temperatures. Standard calomel electrode can also be used as a reference electrode**.**
- The cell potential is the difference between the reduction potential of cathode and anode. $E_{cell} = E_{cathode} - E_{anode}$
- Ion selective electrodes are useful for detecting wide range of bioanalytes.

TERMINAL QUESTIONS

1. What is Redox reaction?
2. Write short notes on redox potential.
3. Write about electrode potential and Nernst equation
4. Write about biosensors, its types and applications
5. What is an electrochemical cell and how to represent it?
6. Write a note on Standard hydrogen electrode
7. Write about different types of ion sensitive electrodes and its uses
8. Write a note on Clarks oxygen electrode
9. Write a note on pH electrode
10. What are electrochemical detectors and its applications?