CHAPTER III : *Redox Reactions*

2. Electrochemical Cells

An electrochemical cell is a device that produces electrical energy through redox reactions between two electrodes in separate half-cells, connected by a conductive solution, often a salt bridge. In each half-cell, the electrode reacts with ions to produce or consume electrons, which generates an electric current. There are two types :

2.1.Galvanic cell (battery) :

A galvanic cell, also known as a battery, is an electrochemical cell that generates electrical energy through spontaneous redox reactions. In this cell, electrons flow from the anode (where oxidation occurs) to the cathode (where reduction occurs).

2.2. Electrolytic cell :

It is an electrochemical cell where an external electrical energy source drives a non-spontaneous redox reaction. In this cell, electrical energy is supplied to force electrons to move in a direction opposite to that in a galvanic cell. Here, the positive electrode, called the anode, is where oxidation takes place, while the negative electrode, the cathode, is where reduction occurs.

The generator thus formed has two poles:

Positive pole (+) : The cathode, where reduction takes place.

$$Ox_1 + n_1e^- = \mathrm{Red}_1$$

Negative pole (-) : The anode, where oxidation occurs :

$$\mathrm{Red}_2 = Ox_2 + n2e^-$$

Spontaneous reaction :

$$\boxed{n_2Ox_1 + n_1\mathrm{Red}_2 = n_2\mathrm{Red}_1 + n_1Ox_2}$$

3. Daniell Cell

This cell was invented by British chemist John Daniell in 1836. It consists of an anode (a zinc strip immersed in a $ZnSO_4$ solution) and a cathode (a copper strip immersed in a $CuSO_4$ solution).

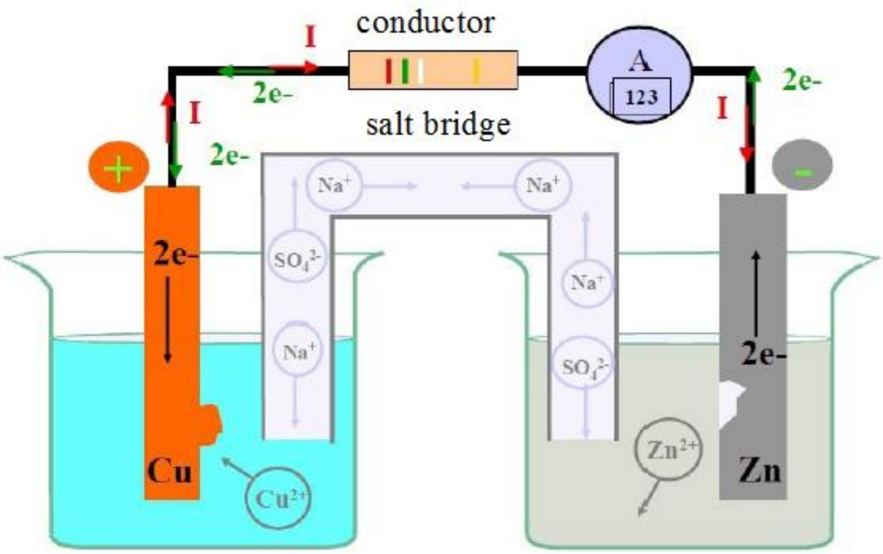

Fig 1. Shematic of a daniell cell

3.1. Operation of the Daniell cell

The two electrodes are linked by an external circuit made up of a resistive conductor in series with an ammeter. The ammeter measures the current that flows from the copper electrode (the positive terminal) to the zinc electrode (the negative terminal). This can also be described as electrons departing from the zinc electrode and traveling toward the copper electrode through the external circuit. Let’s now explore the source of this electrical current.

- **Negative Pole (Anode) :** $Zn \rightarrow Zn^{2+} + 2e^-$
- **Positive Pole (Cathode) :** $Cu^{2+} + 2e^- \rightarrow Cu$
- **Overall Reaction :** $Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$

3.2. Role of the Salt Bridge

- Allows the flow of current within the cell.
- Maintains electrical neutrality in the solutions (by the migration of Na^+ cations in the direction of the electric current within the bridge, and SO_4^{2-} anions in the opposite direction).

The formal representation of this cell is

$$\ominus \ \mathbf{Zn / Zn^{2+} // Cu^{2+} / Cu} \ \oplus$$

3.3. Electromotive Force (E.M.F.) of a Battery

The **E.M.F**, denoted as **E**, is the difference between the potentials of the two electrodes, and it is given by:

$EMF = E = E_{cathode} - E_{anode} = E_+ - E_-$

Where

- $E_{cathode}$ is the potential of the cathode (positive terminal).
- E_{anode} is the potential of the anode (negative terminal).

3.4. Amount of electricity Q delivered by a battery

When a battery delivers a constant current **I** over a period of time **t**, it circulates an amount of electricity **Q** given by:

$Q = I \times \Delta t$

Where

- Q is the amount of electricity delivered by the battery (**Coulombs**).
- I is the current intensity (**Amperes**).
- Δt is the duration of the battery's operation (**seconds**)

Example

Suppose you have a battery that delivers a current of **2 A** for **4 hours**. We want to calculate the total amount of electricity Q that the battery delivers.

- Current $I = 2\ \mathrm{A}$
- Time $t = 4\ \mathrm{hours} = 4 \times 3600\ \mathrm{seconds} = 14,400\ \mathrm{seconds}$

$$Q = I \times t$$

$$Q = 2\ \mathrm{A} \times 14,400\ \mathrm{s}$$

$$Q = 28,800\ \mathrm{C}$$

3.5. Battery Capacity

The battery capacity (**Q_{max}**), is the total amount of electric charge that can be transferred from the battery's electrodes during its operation before it reaches its equilibrium state (i.e., when the battery is "used up").

The formula for calculating the maximum amount of electricity is :

$$Q_{\mathrm{max}} = n_{\text{e-max}} \times F$$

Where

- Q_{max} is the maximum amount of electricity (in Coulombs).
- $n_{e\text{-}max}$ is the maximum number of moles of electrons that can be transferred between the electrodes.
- F is Faraday's constant, which is 96,500 C/mol, the charge of one mole of electrons.

Example

Calculate the maximum amount of electricity Qmax delivered by a battery, since the maximum number of moles of electrons that can be transferred $n_{e\text{-}max}$ = 0.5 mol

$$Q_{\max} = n_{\text{e-max}} \times F$$

$$Q_{\max} = 0.5\,\text{mol} \times 96,500\,\text{C/mol}$$

$$Q_{\max} = 48,250\,\text{C}$$

This means that the battery can transfer a total charge of 48,250 C before it reaches its equilibrium state.

4. Nernst equation and the concept of standard redox potential

4.1. Standard Potential

The standard redox potential (**E°**) characterizes the oxidizing or reducing ability of a chemical species. Measured under standard conditions (P = 1 atm, T = 25°C), it is represented as E° (Ox/Red).

Example

Redox Couple	H^+/H_2	Fe^{2+}/Fe	MnO_4^-/Mn^{2+}	Fe^{3+}/Fe^{2+}	Zn^{2+}/Zn	Cu^{2+}/Cu
E° (V/ENH)	0	- 0,44	1,51	0,77	-0,76	0,34

4.2. The Nernst Equation

The Nernst equation is a mathematical expression that determines the reduction potential of a redox reaction in non-standard conditions. For the reaction

$$a\,\text{Ox} + ne^- \leftrightharpoons b\,\text{Red}$$

The redox potential is given by the **Nernst equation**

$$E_{Ox/Red} = E^{\circ}_{Ox/Red} + \frac{RT}{nF}\log\frac{a_{Ox}}{a_{Red}}$$

Where

E: Cell potential under non-standard conditions (volts).

E°: Standard electrode potential (volts).

n: Number of electrons involved in the reaction.

R: Universal gas constant (8.314 J/mol)

T: Temperature (kelvins).

F: Faraday constant (96485 C/mol).

a_{Ox}: Activity of the oxidizing agent.

a_{Red}: Activity of the reducing agent.

At 25°C, the equation simplifies to :

$$E_{Ox/Red} = E^{\circ}_{Ox/Red} + \frac{0.059}{n}\log\frac{a_{Ox}}{a_{Red}}$$

Examples

1) Use the Nernst equation to calculate the cell potential $E_{Fe^{2+}/Fe}$. The following information about the Fe^{2+}/Fe half-reaction are given :

The standard electrode potential $E_{Fe^{2+}/Fe} = -0.44$ V/ ENH at 25°C and the concentration of Fe^{2+} is 0.01mol/L.

2) Give the Nernst equation for the couple (MnO_4^-/Mn^{2+})

4.3. Determination of the equilibrium constant for a redox reaction

Consider the redox reaction

$Ce^{4+} + Fe^{2+} \Longleftrightarrow Fe^{3+} + Ce^{3+}$

E°(Ce^{4+}/Ce^{3+})=1,44 V /ENH et E°(Fe^{3+}/Fe^{2+}) = 0,77 V/ENH

The redox couples involved are

$$Fe^{2+} \Longleftrightarrow Fe^{3+} + 1é \text{ (oxydation).....1}$$

$$Ce^{4+} + 1é \Longleftrightarrow Ce^{3+} \text{ (réduction)......2}$$

Global reaction $Ce^{4+} + Fe^{2+} \Longleftrightarrow Fe^{3+} + Ce^{3+}$

The Nersnt équations for the two couple redox :

- eq 1 : $\mathbf{E}_{Fe^{+3}/Fe^{2+}} = \mathbf{E}^{\circ}_{Fe^{+3}/Fe^{2+}} + \mathbf{0,06\,log}\,([Fe^{3+}]/[Fe^{+2}])$
- eq 2 : $\mathbf{E}_{Ce4+/Ce3+} = \mathbf{E}^{\circ}_{Ce4+/Ce3+} + \mathbf{0,06\,log}\,([Ce^{4+}]/[Ce^{3+}])$

When the reaction is complete; **$\Delta E = 0$ ==> $E_{Ce4+/Ce3+} - E_{Fe^{+3}/Fe^{2+}} = 0$**

thus ,

$$\mathbf{E}^{\circ}_{Fe^{+3}/Fe^{2+}} + \mathbf{0,06\,log}\,([Fe^{3+}]/[Fe^{+2}]) = \mathbf{E}^{\circ}_{Ce4+/Ce3+} + \mathbf{0,06\,log}\,([Ce^{4+}]/[Ce^{3+}])$$

$$\Longrightarrow \mathbf{E}^{\circ}_{Ce4+/Ce3+} - \mathbf{E}^{\circ}_{Fe^{+3}/Fe^{2+}} = 0.06\log k_c$$

$$\Longrightarrow \quad k_c = 10^{\Delta E°/0.06}$$

AN : $k_c = 1.47 \times 10^{11}$

5. Electrodes

Electrodes are conductors that allow the entry or exit of electrons during redox reactions. They are essential in electrochemical cells, where they physically separate the half-reactions (reduction and oxidation) and facilitate the flow of electrons through the external circuit.

5.1. Types of Electrodes

There are several types of electrodes used in electrochemistry, primarily distinguished by their role in the reaction and their material.

5.1.1 Reference Electrode

A reference electrode serves as a comparison point for measuring the potentials of other electrodes in a system. It must have a constant and well-defined potential.

Example

Standard Hydrogen Electrode (SHE)

The standard hydrogen electrode (H^+/H_2) is the most commonly used reference electrode. This electrode consists of a platinum wire coated with platinum black, immersed in a solution of H^+ (acid) and exposed to 1 atm hydrogen gas.

The half-reaction associated with this electrode is:

$2H^+ + 2e^- \leftrightarrow H_2 \qquad E°=0\ V$

Other Reference Electrodes

Saturated Calomel Electrode (SCE) : Made of mercury (Hg) in contact with a saturated KCl solution containing Hg_2Cl_2 (calomel).

Silver/Silver Chloride Electrode (Ag/AgCl) : Used in aqueous environments, this consists of a silver wire coated with silver chloride (AgCl) immersed in a chloride ion solution.

5.1.2 Working Electrode

The working electrode is where the redox reaction (either oxidation or reduction) takes place in an electrochemical cell. Its composition and potential are chosen based on the specific reaction being studied.

Examples

Platinum Electrode (Pt) : Often used for reactions where the substance is non-conductive (such as in oxygen oxidation or hydrogen reduction).

Graphite Electrode : Common in many applications because it is inexpensive and stable.

5.1.3 Auxiliary Electrode (or Counter Electrode)

The auxiliary electrode completes the external circuit and helps maintain charge balance in the electrochemical cell. It does not participate directly in the redox reaction but allows electrons to flow through the external circuit.

Example

A platinum or graphite electrode is often used as the auxiliary electrode in electrochemical cells.