CHAPTER III. *Redox Reactions*

1. Definitions

1.1. An Oxidant (Oxidizing Agent)

An **oxidant**, is a chemical species that **gains one or more electrons** in a reaction, causing another species to lose electrons. When an oxidant gains electrons, it gets **reduced**.

Example

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

1.2. A Reductant (Reducing Agent)

A **reductor**, is a a chemical species that is capable of **donating one or more electrons** in a reaction, When a reductant loses electrons, it gets **oxidized**.

Example

$Al \rightarrow Al^{3+} + 3e-$

1.3. Redox Couple (Oxidant / Reductant)

A **redox couple** consists of an **oxidant** and a **reductant** that correspond to each other in a half-reaction. The species **Ox** and **Red** form a **redox couple**, written as **Ox/Red**.

Oxidant + ne− ↔ Reductant

Examples

Fe^{3+} / Fe^{2+} Couple

$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$

In this redox couple :

-**Fe^{3+}** (ferric ion) is the **oxidant** (it can gain an electron to become Fe^{2+}).

-**Fe^{2+}** (ferrous ion) is the **reductant** (it can donate an electron to become Fe^{3+}).

2. Redox Reaction

A redox reaction (oxidation-reduction reaction) involves **two redox couples**, where electrons are transferred between an **oxidant** from one redox couple and a **reductant** from another redox couple. The reaction can be written as :

$Ox_1 + Red_2 \leftrightarrow Red_1 + Ox_2$

Example

$Zn \rightarrow Zn^{2+} + 2e^-$ (**Oxidation Half-Reaction)**

$Cu^{2+} + 2e^- \rightarrow Cu$ (**Reduction Half-Reaction)**

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ (**Redox Reaction)**

Note : In a **basic** medium, **OH^-** ions are used to balance **oxygen** and **H_2O** molecules to balance **hydrogen**, whereas in an **acidic** medium, **H_2O** molecules balance oxygen and **H^+** ions balance hydrogen.

3. Oxidation Number (Oxidation State)

The **oxidation number (NO)** (also called the **oxidation state**) of an atom in a compound is the **number of electrons** an atom has gained or lost compared to its neutral (uncombined) state.

a. The oxidation number (NO) of an atom in its **free** or **elemental state** is always **zero**. This is because, there is no loss or gain of electrons in the neutral atom in this state.

Example

H, O, Cu, Co → **NO = 0**

b. When two atoms of the **same element** combine to form a molecule, and no charge is present on the molecule (neutral combination), the **oxidation number** of each atom in the molecule is **zero**.

Example

F_2, Br_2, Cl_2 → **NO = 0**

c. The **oxidation number (NO)** of an atom in a **monoatomic ion** is equal to the **charge** of the ion.

Example

Cl^- → **NO** (Cl) = **-I** ; Fe^{3+} → **NO** (Fe) = **+III**.

d. In a **neutral molecule**, the **sum of the oxidation numbers** of all the atoms within the molecule is always **zero**.

Example

NH_3 : ΣNO = N.O(N) + 3 × N.O(H) = 0

e. Oxygen is the most **electronegative** element after fluorine. In most compound, the oxidation number (NO) of oxygen is -2. However, there are exceptions depending on the specific bonding environment of oxygen.

Example

F2O → NO (F) = -I and NO (O) =+II

H2O2 → NO (H) = +I and NO(O) = -I

f. The oxidation number (NO) of **hydrogen** varies depending on the compounds it forms.

Example

H_2 : NO (H) = 0.

Hydrogen in compounds with non-metals (H_2O, HCl) : NO (H) = +1.

Hydrides (NaH, KH, LiH) : NO (H) = -1 (hydrogen is bonded to metals that are more electropositive).

g. For a **polyatomic ion**, the **sum of the oxidation numbers (NO)** of all the atoms within the ion is equal to the **total charge** of the ion.

Example

Sulfate ion (SO_4^{2-}) : ΣNO = NO(**S**) + 4×NO(**O**) = -2 → NO(**S**) = +6

4. 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 :

4.1. 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).

4.2. 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.

$Ox_1 + n_1e^- \rightarrow Red_1$

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

$Red_2 \rightarrow Ox_2 + n_2e^-$

Spontaneous reaction :

$n_2Ox_1 + n_1Red_2 \rightarrow n_2Red_1 + n_1Ox_2$

5. 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).

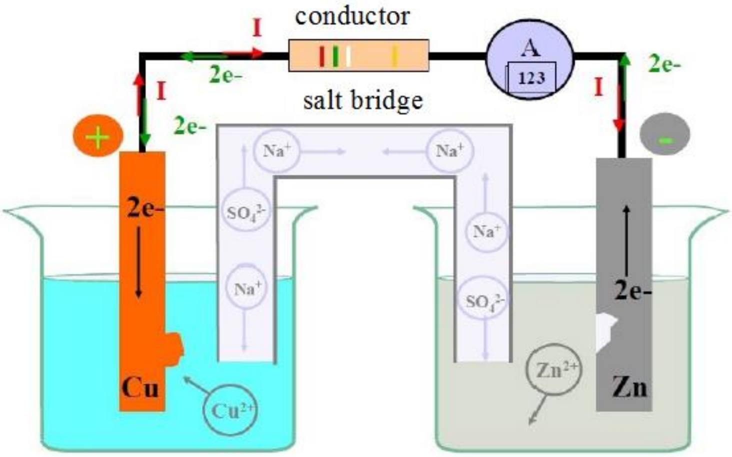


Fig 1. Shematic of a daniell cell

5.1. 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 :** $Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$

5.2. 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

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

5.3. 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).

5.4. 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 $t = 4\,\mathrm{hours} = 4 \times 3600\,\mathrm{seconds} = 14,400\,\mathrm{seconds}$

$$Q = I \times t$$

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

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

5.5. 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 :

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

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

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

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

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

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

6. Nernst equation and the concept of standard redox potential

6.1. 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

6.2. 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

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

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

The Nersnt équations for the two couple redox :

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

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

thus ,

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

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

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

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

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 is a half-cell with a constant and well-defined electrochemical potential, used in electrochemical measurements to provide a stable reference point.

It allows researchers to measure the potential of a second electrode, known as the working electrode, by forming a galvanic cell and focusing on the reaction occurring at the working electrode rather than on the entire cell.

Example

1. The Standard Hydrogen Electrode (SHE)

The Standard Hydrogen Electrode (SHE) is the primary reference electrode in electrochemistry, used to define the zero point of the electrode potential scale. All other electrode potentials are measured relative to it.

Composition and Structure:

The SHE consists of a platinum electrode coated with platinum black to increase (augmenter) surface area, immersed in a 1 M H^+ solution (usually HCl), and continuously bubbled with pure hydrogen gas at a pressure of 1 atm.

Half-Cell Reaction:

$$2H^+\ (aq, 1M) + 2e^- \rightarrow H_2(g), 1atm \quad E^0 = 0V$$

2. The Saturated Calomel Electrode (SCE)

The saturated calomel electrode (SCE) is a type of reference electrode commonly used in electrochemical measurements.

It consists of mercury (Hg) in contact with a paste of mercurous chloride (Hg_2Cl_2, or calomel) and a saturated potassium chloride (KCl) solution. This combination produces a stable and reproducible potential, making it ideal as a reference point for measuring other electrode potentials.

The half-cell reaction for the SCE is:

$$Hg_2Cl_2(s) + \ 2e^- \rightarrow 2Hg\ (l) + \ 2Cl^-(aq)$$

At 25 °C, the electrode potential of the SCE is approximately + 0.244 V/ SHE.

Because of its stability, reliability, and ease of preparation, the SCE is widely used in laboratory electrochemical experiments, though its use is being reduced in some settings due to the toxicity of mercury.

3. The Silver/Silver Chloride (Ag/AgCl) Electrode

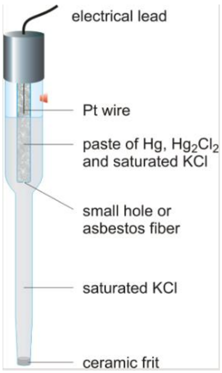
The silver/silver chloride (Ag/AgCl) electrode is a reliable reference electrode in electrochemistry, used to provide a stable and well-defined potential in aqueous solutions.

It consists of a silver wire coated with solid silver chloride, immersed in a potassium chloride (KCl) solution. This configuration ensures a stable and reproducible ionic contact between the solid and liquid phases.

Because of its simplicity, stability, and non-toxicity (compared to the saturated calomel electrode), the Ag/AgCl electrode is widely used in laboratories and field applications.

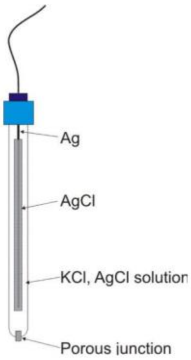
$$AgCl(s) + \ e^- \rightarrow Ag\ (s) + \ Cl^-(aq)$$

E = +0,222 V/ SHE (KCl 1 M).



Standard Hydrogen Electrode (SHE)

Saturated Calomel Electrode (SCE)



Silver/Silver Chloride (Ag/AgCl) Electrode

5.1.2 Working electrode

The working electrode is the main electrode in an electrochemical cell where the reaction of interest occurs—either oxidation or reduction. It is the electrode whose potential is controlled and measured relative to a reference electrode. It is an essential component of a three-electrode system, which also includes a reference electrode and a counter (auxiliary) electrode.

The working electrode allows the study of electron transfer reactions by applying a specific potential or current. It serves as the active surface where electrochemical reactions take place, such as metal dissolution, corrosion, deposition, or inhibitor adsorption.

Examples

1. Platinum electrode (Pt)

Frequently used in electrochemical studies where the reacting substance is non-conductive, such as during oxygen oxidation or hydrogen reduction. Platinum is chosen for its excellent chemical inertness, electrical conductivity, and resistance to corrosion, making it ideal for serving as an inert electrode in many redox systems.

2. Graphite electrode

Commonly employed in a wide range of applications because it is inexpensive, chemically stable, and mechanically robust. Graphite electrodes are especially suitable for experiments involving organic compounds or aqueous electrolytes, and are often used in battery research, electrocatalysis, and corrosion studies.

5.1.3 Auxiliary electrode (or counter electrode)

The auxiliary electrode, also known as the counter electrode, is an essential component of an electrochemical cell. It is used together with the working electrode and the reference electrode to complete the electrical circuit.

It allows the current to pass through the electrolyte while ensuring that the reaction of interest occurs only on the working electrode. Its main role is to balance the current flowing through the cell to maintain charge neutrality.

Examples

1.Platinum (Pt)

Widely used because of its high conductivity, chemical inertness, and corrosion resistance.

2. Graphite or glassy carbon

Cost-effective and stable alternatives, suitable for both aqueous and organic electrolytes.

3. Nickel or stainless steel

Commonly used in industrial or large-scale electrolysis systems.