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POLYCOPY

Practical Work: Electrochemistry

Licence 3 Fundamental Chemistry

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Preface

This polycopied document is intended for third-year students in Fundamental Chemistry. It serves as a practical complement to theoretical courses, offering students the opportunity to apply key concepts of electrochemistry in a laboratory setting.

The experiments presented in this document have been carefully selected to cover essential aspects of electrochemistry, such as electrolyte conductivity, pH measurement, electrolysis phenomena, electrode design, and the electrochemical production of industrial compounds. These experiments are designed not only to enhance technical skills but also to develop scientific rigor, analytical thinking, and problem-solving abilities.

Through these practical sessions, students will gain valuable experience working with laboratory instruments, interpreting experimental data, and understanding how electrochemical reactions contribute to scientific and industrial advancements. This polycopy aims to provide a solid foundation for students to develop both theoretical knowledge and practical skills, essential for future research and professional careers.

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List of Abbreviations

Abbreviation	**Meaning**
HCl	Hydrochloric acid
NaOH	Sodium hydroxide
CH_3COOH	Acetic acid
BTB	Bromothymol blue (color indicator)
NaClO	Sodium hypochlorite (bleach)
$CuSO_4$	Copper (II) sulfate
$ZnSO_4$	Zinc sulfate
Ag/AgCl	Silver/silver chloride electrode
KCl	Potassium chloride
SCE	Saturated Calomel Electrode (SCE)
pH	Hydrogen potential
E	Electrode potential
E^0	Standard electrode potential
F	Faraday constant (96485 C/mol)
R	Gas constant (8.314 J/mol·K)
T	Temperature (in Kelvin)
Q	Electric charge (Coulombs)
I	Current intensity (Amperes)
t	Time (seconds)
G	Conductance
σ (sigma)	Conductivity
λ (lambda)	Molar ionic conductivity
ln	Natural logarithm (ln)
V	Volume

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Introduction

Electrochemistry is a key discipline in chemistry, focusing on the relationship between electrical energy and chemical changes. It plays a central role in various scientific and industrial processes, from the functioning of batteries and fuel cells to corrosion prevention, electroplating, and the synthesis of essential chemical compounds.

This polycopied document offers a series of experiments designed to help students deepen their understanding of electrochemical principles and their practical applications. The topics covered include :

1. **Electrolyte Conductivity and Its Role in Chemical Reactions:** Investigating how ions conduct electricity in solution and how this influences chemical reactions.
2. **pH Measurement and Acid-Base Properties of Solutions:** Using pH meters and indicators to study acid-base behavior and equilibria.
3. **Electrolysis Phenomena and Validation of Faraday's Laws:** Experimentally confirming the fundamental laws governing electrolysis.
4. **Design and Study of Electrodes, Especially Second-Kind Electrodes:** Exploring the properties and functions of specialized electrodes in electrochemical systems.
5. **Electrochemical Production of Compounds Such as Sodium Hypochlorite:** Demonstrating practical applications of electrochemical reactions in industrial processes.
6. **Experimental Determination of Standard Electrode Potentials:** Measuring and analyzing electrode potentials in various systems.

These practical experiments are essential for understanding the theoretical concepts discussed in lectures. They provide students with hands-on experience that is crucial for mastering electrochemical techniques and preparing for future scientific research or industrial work.

Lab 1

Electrolyte Conductivity and Conductometric Titration

Lab No. 1

Electrolyte Conductivity and Conductometric Titration

Conductometric Titration of an Acid with a Base

The conductivity of a solution (during a conductometric titration) varies either because the total number of ions changes or because ions are replaced by others with significantly different mobility.

1- Objective:

To determine the concentration of a substance by using the sudden change in conductance to identify the equivalence point.

2- Theoretical and Principle:

Electrochemistry is a discipline that studies the relationship between chemical transformations and the flow of electric current. Its field of application is broad: generation of electric current (electrochemical cells), energy storage (batteries and accumulators), electrolysis (production of hydrogen and oxygen, selective metal deposition, etc.).

The study of electrochemical reactions involves knowledge from various fields: thermodynamics, kinetics, transport phenomena, electricity, and hydrodynamics

2-1 Electrolyte:

An electrolytic substance is a substance that, when dissolved in solution, dissociates (partially or completely) to produce ions that can move in an electric field.
Examples of electrolytic substances include acids, bases…..etc.

A non-electrolytic substance is a substance that, when in solution, does not allow the passage of electric current.
Examples of non-electrolytic substances include sugar and alcohol.

There are two types of electrolytes: strong and weak:

- ✓ **Strong electrolytes:** Substances that dissociate completely in water, producing ions with high electrical conductivity. Examples: strong acids, strong bases.

- ✓ **Weak electrolytes:** Substances that dissociate partially in water, producing ions with low electrical conductivity. Examples: weak acids and weak bases.

2-2 Conductance of an Electrolytic Solution

The conductance of an electrolytic solution is equal to the inverse of the resistance of that same solution. It is expressed in Siemens (S) or ohm^{-1}.

To determine the conductance of an electrolyte solution, a low-frequency alternating voltage generator (LFG) is used (to avoid the electrolysis phenomenon) and connected to two conductive plates. The voltage (U) across the plates and the electric current (I) flowing through the circuit are measured (Figure 1).

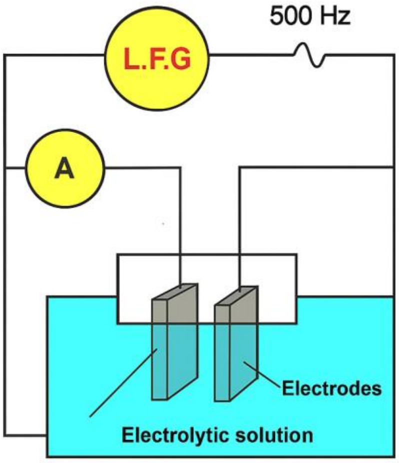


Figure 1: Conductance of an electrolytic solution.

2-3 Electrical Conductivity

Electrical conductivity is the ability of a material or solution to allow electric charges to move freely or to permit the flow of electric current.

Among the best conductors are metals (such as copper, aluminum, etc.), in which the charge carriers are “free electrons.” In the case of electrolyte solutions, the current is carried by ions. The conductivity of these solutions depends on the nature of the ions present and their concentrations. It can be measured using a **conductivity meter** (Figure 2). This device mainly consists of a measuring cell made of a rigid body with two parallel plates of surface area **S**, separated by a distance **L**.

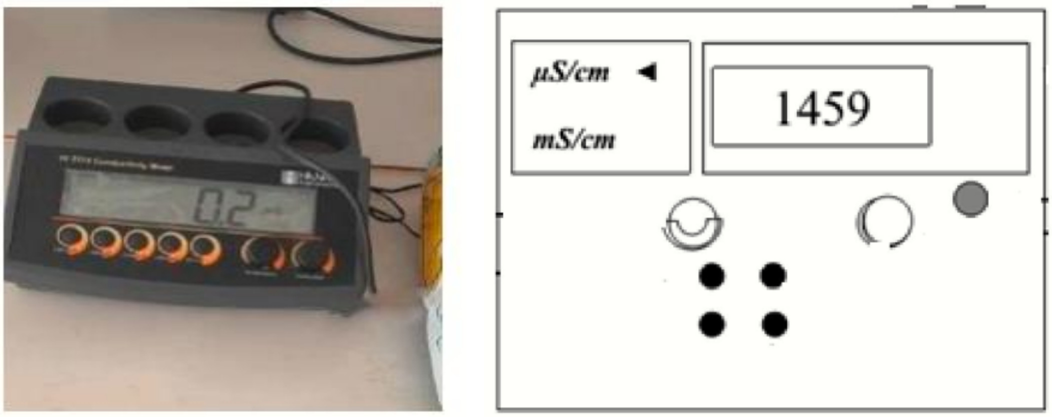


Figure 2: The conductometer**.**

This method relies on the presence of ions in solution and their ability to facilitate the flow of an electric current. In fact, the nature of the ions and their concentrations will modify the conductance G of the system, a quantity that is the inverse of resistance. The more the medium facilitates the flow of current, the higher the conductance. Conductance is related to three main parameters: the conductivity σ of the system, the length ℓ, and the cross-sectional area S of the cell, according to the following equation:

$$G = \frac{\sigma S}{l}$$

Conductance is expressed in ***Siemens*** (S), with 1 S=1 Ω−1. The unit of conductivity is thus $S{\cdot}m^{-1}$. The ratio $K = \ell/S$ is called the cell constant, so the equation becomes:

$$G = \frac{\sigma}{K}$$

Let us consider a solution containing, for simplicity, two ions A and B with arbitrary charges. Each ion is characterized by a molar ionic conductivity λ, expressed in $S{\cdot}m^{2}{\cdot}mol^{-1}$ and defined as:

$$\sigma = \lambda_A[A] + \lambda_B[B]$$

The total conductivity thus depends on the conductivity of each ion, which in turn depends on the concentration of the species and its molar ionic conductivity. The most general form of this relationship is given by **Kohlrausch's law**:

$$\sigma = \sum \lambda_i[A_i]$$

Thus, when a species disappears during a chemical reaction, its concentration decreases, and therefore its contribution to the conductivity decreases since conductivity coefficients are generally positive. At the same time, new ionic species may appear during the reaction, thereby changing G.

2-4 Conductometric Titration

Conductometric titration involves determining the ion concentration of a solution by measuring its conductivity. This method relies on the ability of ions to conduct electric current in an aqueous medium, where the solution's conductivity is measured using an electrode.

Since each ion conducts electricity differently, the conductivity changes during the titration. Conductivity is directly related to the concentration of ions in the solution.

A titration requires :

- An **analyte solution** containing the reagent whose concentration is to be determined.
- A **titrant solution** containing a reagent with a precisely known concentration.

In a titration, the goal is to determine the **equivalence point**, which is the exact volume of titrant solution needed to completely react with the analyte.

In **conductometric titration**, the conductivity of the analyte solution is monitored as the titrant is gradually added. This allows for the precise determination of the equivalence point.

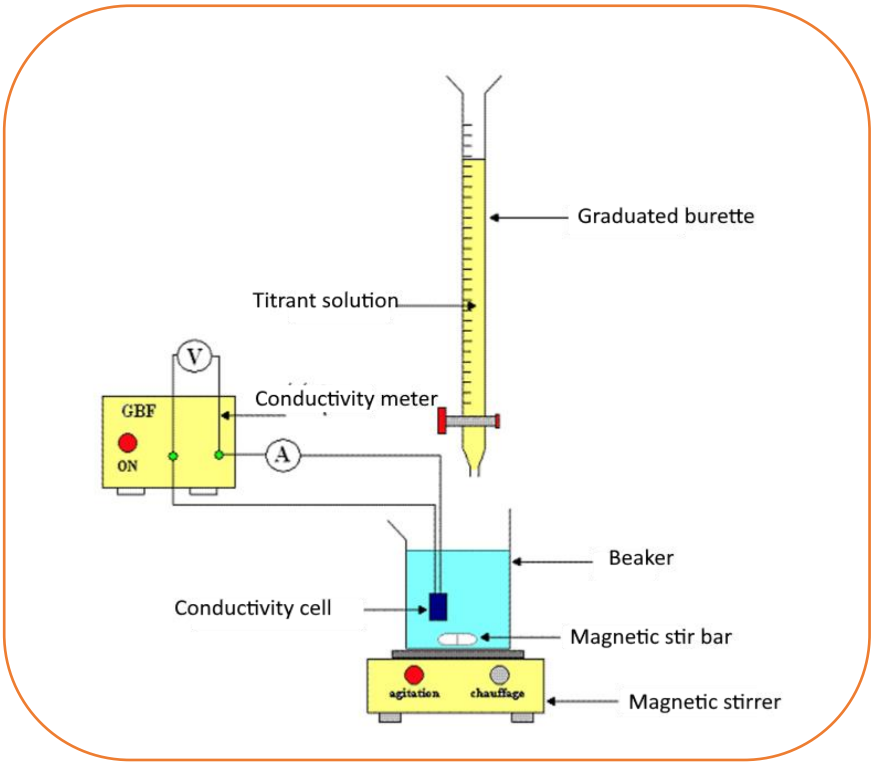


Figure 3: Conductometric titration.

Titration of a Strong Acid with a Strong Base

1- Theoretical:

During a titration between a strong acid (HCl) and a strong base (NaOH), the following reaction occurs:

$$\text{HCl (aq)+NaOH (aq)}\rightarrow\text{NaCl (aq)+H}_2\text{O} \qquad (1)$$

Initially, the solution contains only H^+ ions, which contribute to high conductivity. As NaOH is added, OH^- ions react with H^+ ions to form water, reducing the conductivity. After the equivalence point, the addition of extra OH^- ions from NaOH increases the conductivity again.

The point where conductivity stops decreasing and starts increasing indicates the equivalence point.

2. Materials and Chemical Product :

Materials	Product
• A conductometer • Graduated burette with stand • 150 ml beaker • 100 ml volumetric flask • Magnetic stirrer • Graduated cylinder	• HCl • NaOH (0.05N) • Acetic acid • Distilled water

3-Procedure :

- ✓ Calibrate the conductometer.
- ✓ Set up the electrical connections to measure the conductance G of a solution using the conductometric cell.
- ✓ Prepare a 250 mL beaker that is narrow enough to monitor the reaction; place a magnetic stir bar and a magnetic stirring device. Add 40 mL of HCl solution of unknown concentration; add 60 mL of distilled water; then add 3 drops of bromothymol blue (BTB).
- ✓ Place the 0.05N NaOH solution in the graduated burette.
- ✓ Titrate the HCl solution with NaOH, adding the same volume of NaOH (2 mL) each time.
- ✓ Record the conductance each time NaOH is added.

Given :

Ions	H_3O^+	OH^-	Na^+	Cl^-
λ ($S.m^2.mol^{-1}$)	350.10^{-4}	199.10^{-4}	$50.1.10^{-4}$	$76.2.10^{-4}$

4- Questions :

1. Identify the two acid-base pairs involved.
2. Write the two chemical equations and deduce the acid-base equation of the reaction.
3. Calculate the concentration of HCl.
4. Plot the graph **G = f(V)** (Conductance vs. Volume).
5. Indicate what the two parts of the curve represent.
6. Explain the evolution of the ionic conductivity of the mixture during the addition of the sodium hydroxide solution.
7. What is the purpose of adding water?
8. Conclusion.

Titration of a Mixture of Acids

1- Objective:

To determine the concentration of a mixture of two acids (a strong acid and a weak acid) using a conductometric titration with a strong base (NaOH).

2- Theoretical:

In a mixture of a strong acid (e.g., HCl) and a weak acid (e.g., acetic acid, CH_3COOH), the conductometric titration involves two successive reactions:

1- **Strong Acid Neutralization :**

$$HCl\ (aq) + NaOH\ (aq) \rightarrow NaCl\ (aq) + H_2O$$

First, NaOH neutralizes the strong acid (HCl) completely, causing a sharp decrease in conductivity due to the consumption of H^+ ions.

2- **Weak Acid Neutralization**

$$CH_3COOH\ (aq) + NaOH\ (aq) \rightarrow CH_3COONa\ (aq) + H_2O$$

After the strong acid is neutralized, NaOH begins to neutralize the weak acid. This reaction has a more gradual change in conductivity since CH_3COO^- ions contribute less to the solution's conductivity.

3- Procedure :

1. **Preparation of the Acid Mixture:**
   - Prepare 40 mL of a mixture of HCl and acetic acid in a 250 mL beaker.
   - Add 60 mL of distilled water.
   - Add 3 drops of bromothymol blue (BTB) as an indicator.
2. **Set Up the Equipment :**
   - Place the beaker on the magnetic stirrer and insert the conductometer probe.

3. **Titration :**
    - Fill the burette with 0.05N NaOH solution.
    - Add NaOH in increments of 2 mL
    - Record the conductance after each addition.

4- Questions :

1. Draw a diagram showing the chemical species present in the burette and the beaker solution. Indicate the known and unknown concentrations.
2. There are two acids in the solution to be titrated, so the $\mathbf{OH^-}$ base (present in the burette) will react successively with each of them—first with one until it is completely neutralized, then with the other, and so on. In what order does this occur? Write the corresponding reactions.
3. Plot the graph **G=f(V)** (Conductance vs. Volume).
4. Determine the equivalence volumes and calculate the concentrations of the acids.
5. Indicate what the three parts of the curve represent.
6. Conclusion.

Lab 2

Determination of the pH of Different Types of Solutions

Lab No. 2

Determination of the pH of Different Types of Solutions

1- Objective

- Learn to recognize whether a solution is acidic, neutral, or basic.
- Learn to predict and describe the evolution of pH through successive dilutions of a given solution.

2- Theoretical and Principles

2-1 Definition of the pH of an Aqueous Solution

pH, which stands for **"potential of hydrogen"**, is a parameter used to determine whether a medium is acidic or basic. This term was first introduced in 1909 by the Danish chemist **Søren Peder Lauritz Sørensen** while he was studying hydrogen ions.

The acidity of solutions is measured by the concentration of **H_3O^+ (hydronium) ions**. Typically, these concentrations are very low, ranging from **1.0×10^{-1} to 1.0×10^{-14} mol/L**.

Since this concentration range is extremely wide, it is more practical to use a **logarithmic scale** for easier interpretation. To achieve this, the mathematical operator **p = -log** is introduced, and pH is defined as:

$$\mathbf{pH = -\log[H_3O^+]}$$

where $[H_3O^+]$ is the molar concentration of hydronium ions (in mol/L).

The pH Scale

The pH scale generally ranges from 0 to 14:
- pH < 7: acidic solution
- pH = 7: neutral solution
- pH > 7: basic solution

This scale is based on the self-ionization of water.

-Self-Ionization of Water

Water is amphoteric: it can act as both an acid and a base. It self-ionizes slightly according to the following equilibrium:

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

At 25°C, the ionic product of water is:

$K_e = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

In a neutral solution: $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ mol/L, so pH = 7.

2-2 Calculation of pH

2-2-1. Strong Acid

A strong acid is completely dissociated in solution:

$HA \rightarrow H^+ + A^-$

If the initial concentration is C, then:

$[H_3O^+] = C \rightarrow pH = -\log C$

Example: HCl 0.01 mol/L → pH = 2

2-2-2. Strong Base

A strong base like NaOH fully dissociates:

$BOH \rightarrow B^+ + OH^-$

$[OH^-] = C \rightarrow pOH = -\log C$ and $pH = 14 - pOH$

Example: NaOH 0.001 mol/L → pOH = 3 → pH = 11

2-2-3. Weak Acid

A weak acid is only partially dissociated:

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$

We use the acidity constant Ka:

$Ka \approx [H_3O^+]^2 / C$ (if $[H_3O^+] << C$)

Then: $[H_3O^+] = \sqrt{(Ka \times C)} \rightarrow pH = -\log[H_3O^+]$

Example: Acetic acid $Ka = 1.8 \times 10^{-5}$, C = 0.1 mol/L → pH ≈ 2.87

2-2-4. Weak Base

Similar principle using the basicity constant Kb, or:

$pH = 14 - pOH$ with $pOH = -\log[OH^-]$

2-3. Influence of Dilution and Temperature

- Dilution decreases the concentration of H_3O^+ or OH^- ions, affecting the pH.
- Temperature affects the ionic product of water (K_e), so the pH of pure water is not always exactly7.

3-Measurement of pH

3-1. pH Meter

Principle:

The pH meter works based on the measurement of the potential difference between two electrodes: a glass electrode, which is sensitive to hydrogen ions (H^+), and a reference electrode, which provides a stable voltage. When the electrode is immersed in a solution, the difference in hydrogen ion activity creates an electric potential. This potential difference is measured and converted into a pH value using the Nernst equation:

$$\mathbf{pH = -\log[H_3O^+]}$$

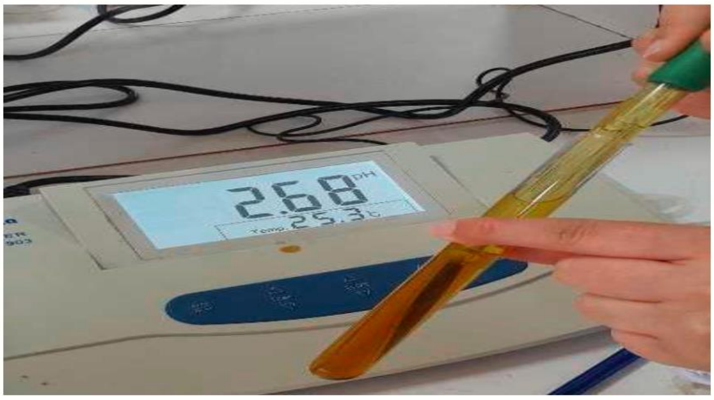


Figure 1: pH Meter.

Components of a pH meter:

- Combined electrode: glass + reference (e.g., Ag/AgCl)
- Electronic unit with digital display
- Buffer solution for calibration

3-2. Color Indicator

Principle:

Color indicators are organic chemical substances that change color depending on the pH of the aqueous solution in which they are dissolved. This color change corresponds to a structural transformation of the indicator molecule between its protonated (HInd) and deprotonated (Ind^-) forms.

The general equilibrium is as follows:

$$HInd \rightleftharpoons H^{+} + Ind^{-}$$

-Transition Range and Indicator Choice

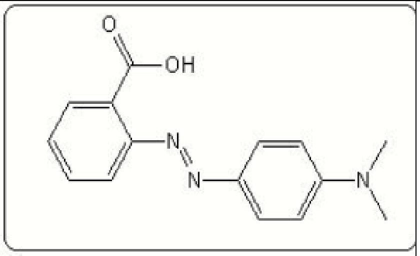
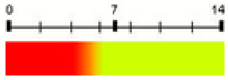
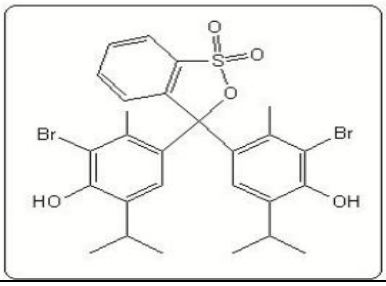
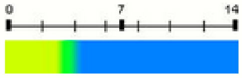
Each indicator has a pKa value around which its color changes. The transition range is typically defined as:

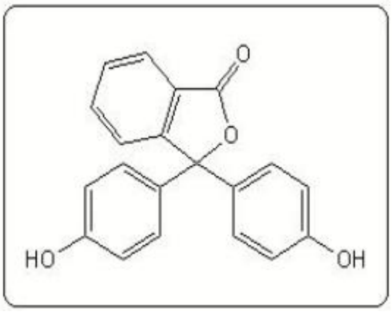
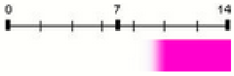
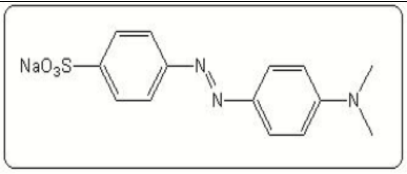
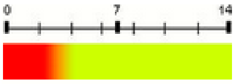
$$pKa \pm 1$$

Within this range, the indicator shifts from the color of its acidic form (HInd) to that of its basic form (Ind^-).

-Examples of Common Indicators

Table 1: Common Indicators:

Indicator	Chemical Formula / Structure	pH Range	Acid Color	Base Color
Methyl Red		4.4 – 6.2 	Red	Yellow
Bromothymol Blue		6.0 – 7.6 	Yellow	Blue

Phenolphthalein		8.2 – 10.0 	Colorless	Pink
Methyl Orange		2.4 – 4.4 	Red	Orange - Yellow

2-3. pH Paper (Indicator Strips)

pH paper is paper impregnated with one or more color indicators that allows for a quick estimation of the pH of an aqueous solution. It is a simple, fast, and cost-effective method for measuring the acidity or basicity of a solution without using electronic instruments.

Operating Principle

pH paper contains one or more color indicators that change color depending on the concentration of hydrogen ions (H^+) in the tested solution. When the paper is dipped into the solution or a few drops are placed on it, an acid-base reaction occurs with the indicator, causing a visible color change.

This color is then **compared to a reference color scale** provided with the pH paper, where each color corresponds to an approximate pH value (typically ranging from 0 to 14).

HCl 0,1 mol/L ; pH = 1.

NaOH 0,1 mol/L ; pH = 14.

vinaigre ; pH = 2.

Figure 2: pH Paper.

3-Materials and Chemical Products

- pH meter
- Color indicators (litmus solution, phenolphthalein, methyl orange)
- pH paper (indicator strips)
- Beakers (100 mL and 250 mL)
- Distilled water
- Solutions to test:
  - Sodium hydroxide (NaOH)
  - Tap water
  - Vinegar (acetic acid)
  - Bleach (sodium hypochlorite solution)
  - Liquid detergent (laundry soap)
  - Lemon juice
  - Hydrochloric acid (HCl)
  - Coca-Cola

4-Procedure:

4-1. pH Meter Method:

- Calibrate the pH meter using buffer solutions (pH 4, 7, and 10).
- Rinse the electrode with distilled water before each measurement.
- Immerse the probe into each solution and record the pH value.

4-2. Color Indicator Method:

- Add a few drops of the appropriate indicator to each solution.
- Observe the color change and compare it with the standard pH range of the indicator.

4-3. pH Paper Method:

- Dip a strip of pH paper into each solution.
- Compare the color obtained to the reference pH scale provided.

5- Observations

Fill in the following table with the recorded pH values for each solution using the three methods.

Solution	**pH Meter Value**	**Color Indicator Result**	**pH Paper Value**	**Expected pH Range**
Sodium hydroxide (NaOH)				12-14
Tap water				~7
Vinegar (acetic acid)				3-4
Bleach (NaClO)				11-13
Liquid detergent				9-11
Lemon juice				2-3
Hydrochloric acid (HCl)				1-2
Coca-Cola				2.5-3.5

6- Effect of Dilution, Evolution Of pH

The starting solutions, hydrochloric acid (HCl) and sodium hydroxide (NaOH), have the same concentration and are ready to use (**0.1 mol/L**).

- In a small beaker labeled **1**, pour a small amount of hydrochloric acid.
- Take the pH meter and immerse its probe into the hydrochloric acid solution in the small beaker.
- Then, pour the contents of **Beaker 1** into a larger beaker labeled **2**, which already contains a volume of distilled water equal to **5 times** the volume of the initial acid. Measure the pH again and record it in the table.
- Finally, pour the contents of **Beaker 2** into an even larger beaker containing **5 times more distilled water** than the total volume from **Beaker 2**. Perform a final pH measurement and record the value in the table.

Acidic Solutions	C = $[H_3O^+] = [Cl^-]$ (mol.L^{-1})	pH	-log $[H_3O^+]$
Solution A			
Solution A1			
Solution A2			

- How does the pH evolve during dilution ?
- What does this indicate ?
- Are the diluted acidic solutions still acidic?

Basic Solutions

Basic Solutions	C = $[HO^-] = [Na^+]$ (mol.L^{-1})	pH	$[H_3O^+]$ (mol.L^{-1})	$[H_3O^+] . [HO^-]$
Solution B				
Solution B1				
Solution B2				

7- Questions

1. What is the principle behind each of the three pH measurement methods?
2. Which method provides the most accurate result? Why?
3. Explain why the pH of tap water may not always be exactly 7.
4. Compare the sensitivity of color indicators and pH paper for acidic solutions.
5. Why is it important to calibrate the pH meter before use?
6. What could cause variations in pH measurement for the same solution across the three methods?
7. Discuss the impact of temperature on pH measurement using a pH meter.

Lab 3

Electrolysis - Verification of Faraday's Law

Lab No. 3

Electrolysis - Verification of Faraday's Law

1-Objective

- Demonstrate that electrolysis is a forced transformation.
- Measure Faraday's constant.

2-Principle

The experiment consists of performing an electrolysis and measuring the mass of the substance deposited on an electrode as a function of the amount of electricity that has passed through the electrolyte solution. By comparing the experimental results with the theoretical predictions of Faraday's Law, we can verify the relationship between the deposited mass, the current intensity, and the electrolysis duration.

3- Theoretical

3-1 Electrolysis

Electrolysis is a non-spontaneous process in which a chemical reaction is forced by the passage of electric current. It allows:

- Decomposition of chemical compounds
- Production or purification of metals
- Metal coating (electroplating)
- Manufacturing of chemical compounds (e.g., hydrogen, chlorine, NaOH)

3-2. Description of an Electrolytic Cell

An electrolytic cell is a device in which electrolysis takes place. It consists of:

- Anode (+): Site of oxidation (loss of electrons)
- Cathode (–): Site of reduction (gain of electrons)
- Electrolyte: Conductive medium containing mobile ions
- Power supply: Provides the electric current to force the reaction

Electron flow: from anode to cathode through the external circuit. Ion movement in the solution maintains electrical neutrality.

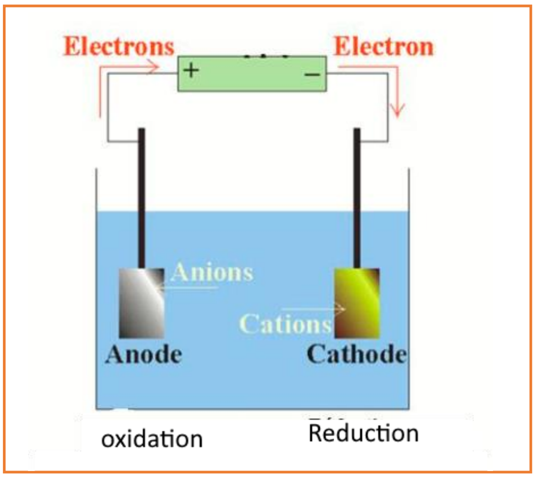


Figure 1: Electrolysis cell.

3-3 Electrolysis Reaction Principles

Electrode reactions depend on the ions present. Example with $CuSO_4$:

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

Overall: Cu^{2+} concentration remains nearly constant since deposit = dissolution.

3-4. Faraday's Laws of Electrolysis

Michael Faraday (1834) established two fundamental laws linking the quantity of transformed matter to the quantity of electricity passed.

- ***1st Faraday's Law***

The mass (m) of a substance deposited at an electrode is proportional to the amount of electricity (Q) passed through the electrolyte:

$$\mathbf{m = k \cdot Q}$$

where:

- m is the deposited mass (g),
- k is a proportionality constant (electrochemical equivalent),
- Q is the electric charge (Coulombs).

Since $Q = I \cdot t$, with:

- I being the current intensity (A),
- t the electrolysis duration (s),

we get: $\mathbf{m = k \cdot I \cdot t}$

- ***2nd Faraday's Law***

The constant k is given by:

$$\mathbf{k = M / (n \cdot F)}$$

where:

- M is the molar mass of the deposited element (g/mol),
- n is the number of electrons exchanged per ion,
- F = 96485 C/mol is the Faraday constant (the charge of one mole of electrons).

3-5 Comparison with Electrochemical Cells

Electrochemical Cell:

- Spontaneous reaction
- Produces electricity
- Example: Daniell cell

Electrolytic Cell:

- Non-spontaneous reaction
- Consumes electricity
- Example : Electrolysis of NaCl

3-6. Factors Influencing Electrolysis

- Current intensity (I): Higher I → faster reaction
- Duration (t): Longer t → more matter transformed
- Electrolyte concentration: Affects ion mobility
- Temperature: Moderate increase improves conductivity
- Electrode surface area: larger area enhances reaction

3-7. Industrial Applications

- Metallurgy: Copper refining, aluminum production
- Electroplating: Nickel, chromium, gold coatings
- Chemical industry: Cl_2, NaOH, H_2 production
- Energy storage: Rechargeable batteries

3-8. Advantages and Limitations

Advantages:

- High control over deposited mass
- Clean process
- Scalable to industry

Limitations:

- High energy cost
- Sensitive to purity
- Efficiency affected by side reactions

4-Materials and Chemicals

Materials :

- **Beaker** (50 mL)
- **Electronic balance** (to weigh the copper electrode)
- **Power supply** (to maintain a current intensity of 0.50 A)
- **Copper and zinc electrodes**
- **Connecting wires**
- **Switch**
- **Stopwatch**

Chemicals :

- Copper (II) sulfate solution ($CuSO_4$, C = 1.0 mol/L, 50 mL)
- Zinc sulfate solution ($ZnSO_4$)

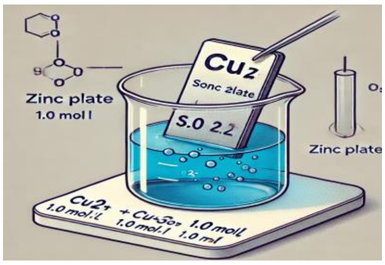
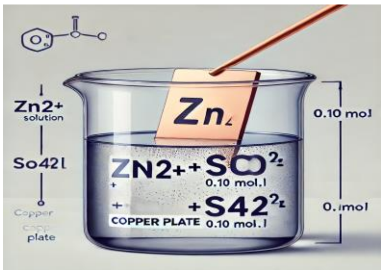
5. Spontaneous Evolution or Forced Transformation?

5.1 Spontaneous Transformations

We focus on the system formed by the redox pairs (Cu^{2+}/Cu) and (Zn^{2+}/Zn):

$$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s) \qquad (4)$$

The equilibrium constant (K) associated with this reaction is 4.0 × 10^{36}.

Experiment 1	**Experiment 2**
	

Questions

1. Based on the equilibrium constant, how will the two experiments evolve?
2. Conduct these two experiments and note your observations. Are they consistent with your previous predictions?
3. For Experiment 1, was the initial reaction quotient Qr less than, equal to, or greater than the constant K?
4. For Experiment 2, was the initial reaction quotient Qr less than, equal to, or greater than the constant K?

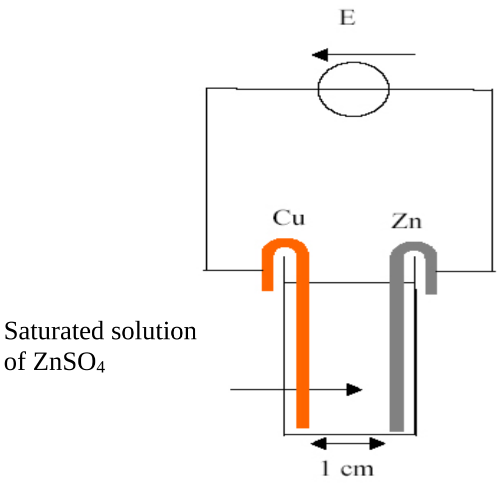
5.2 Forced Transformations: Electrolysis

1- Clean the zinc and copper plates using sandpaper.

2- Set up the circuit as shown and have it checked before turning on the power supply.

3- Adjust the current intensity to 1.0 A.

4- Operate the device for about 5 minutes and carefully observe the changes on the metal plates and in the solution.

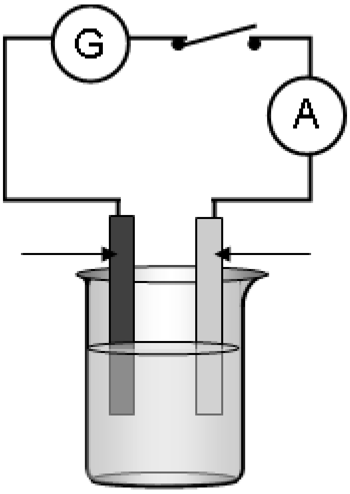


5. Complete your observations by marking them on the diagram.
6. Indicate on the diagram the direction of the current imposed by the generator and the movement

of free electrons in the metallic parts of the circuit.

7. Write the half-equation for the copper plate.
8. Write the half-equation for the zinc plate.
9. Label the anode and cathode on the diagram.
10. Does this system evolve spontaneously? What is the role of the power supply?

6. Measurement of Faraday's Constant



- Pour 50 mL of copper (II) sulfate solution (C = 1.0 mol/L) into a beaker.
- Weigh the copper electrode.
- Set up the circuit as diagrammed.
- Close the switch, start the stopwatch, and maintain a current intensity of I = 0.50 A for 15 minutes.
- Open the switch and stop the stopwatch.
- Record the mass of the copper electrode before and after electrolysis, along with the duration of electrolysis (Δt).
- Using a material balance, determine the quantity of exchanged electrons $n(e^-)$ during electrolysis.
- What is the relationship between the electric charge Q, the current intensity I, and the duration of electrolysis Δt?
- Derive an expression for Faraday’s constant and calculate its value.
- Dry the copper electrode and weigh it again.

Lab 4

Preparation and Study of a Second Kind Electrode

Lab No. 4

Preparation and Study of a Second Kind Electrode

1-Objectives:

- Prepare a second-kind electrode of type Ag/AgCl.
- Study the variation of its potential according to Cl^- ion concentration.
- Experimentally verify the Nernst equation.

2-Theoretical:

2-1. Definition of a Second-Kind Electrode

A **second-kind electrode** is a type of electrode whose potential is determined by the equilibrium between:

- A **metal (M)**,
- Its **sparingly soluble salt (MX)**, and
- The **anion (X^-)** in solution.

The general half-reaction for such an electrode is:

$$MX_{(S)} + e^- \leftrightharpoons M_{(S)} + X^-_{(aq)}$$

2-2 Examples of Second-Kind Electrodes

1- **Silver/Silver Chloride (Ag/AgCl)**:

$$AgCl \;\; + e- \rightleftharpoons Ag_{(s)} + Cl^-_{\;(aq)}$$

2- **Calomel Electrode (Hg/Hg_2Cl_2)**:

$$Hg_2Cl_{2(s)}+2e^-\rightleftharpoons 2Hg_{\;(l)}+2Cl^-_{(aq)}$$

3- **Lead/Lead Sulfate ($Pb/PbSO_4$)**:

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

2-3 Principle of Operation

The potential of a second-kind electrode depends on:

1. The **solubility product (K_{sp})** of the sparingly soluble salt (MX).
2. The **concentration** of the anion (X^-) in solution.

2-4 Nernst Equation for Second-Kind Electrodes

The electrode potential (E) is given by the Nernst equation:

Common Example: The **AgCl / Ag electrode**

$$E = E^{\circ}_{AgCl/Ag} - \frac{0,059}{n}\log[Cl^{-}]$$

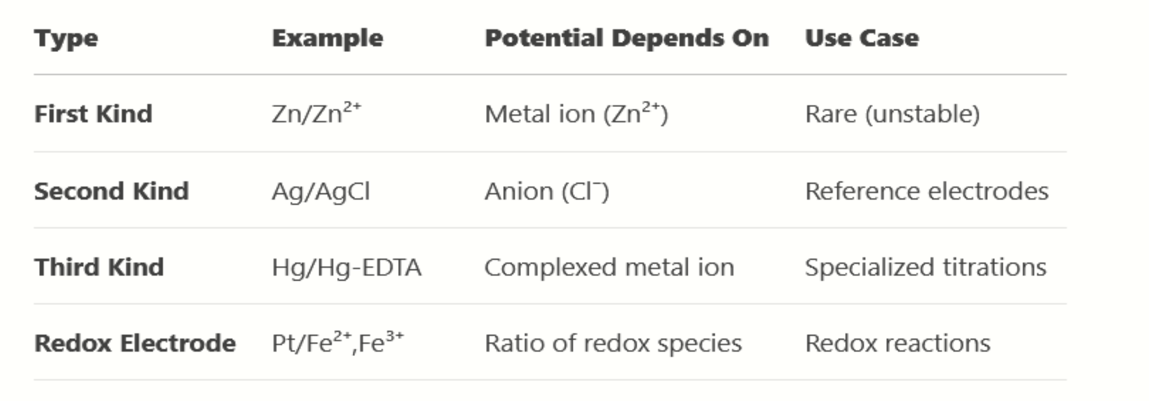
3- Why Are Second-Kind Electrodes Important?

1. **Stable and Reproducible Potential**:
    - The potential depends on the anion concentration, which can be fixed (e.g., saturated KCl in Ag/AgCl or calomel electrodes).
    - Used as **reference electrodes** in electrochemical measurements.

2. **Less Sensitive to Impurities** :
    - Unlike first-kind electrodes (e.g., Zn/Zn^{2+}), the potential is not affected by metal ion concentration fluctuations.
3. **Wide Applications** :
    - pH measurements (combined with glass electrode).
    - Potentiometric titrations.
    - Biosensors and medical devices.

4- Comparison with Other Electrodes

Table 1 : Comparison Electrodes



Type	Example	Potential Depends On	Use Case
First Kind	Zn/Zn^{2+}	Metal ion (Zn^{2+})	Rare (unstable)
Second Kind	Ag/AgCl	Anion (Cl^-)	Reference electrodes
Third Kind	Hg/Hg-EDTA	Complexed metal ion	Specialized titrations
Redox Electrode	$Pt/Fe^{2+},Fe^{3+}$	Ratio of redox species	Redox reactions

1- Materials and Solutions

Materials	Solutions
Silver wire (Ag)	0.01mol/L $AgNO_3$ solution
Sandpaper	Saturated KCl solution (~4.0 mol/L)
Potentiometer	KCl solutions at various concentrations
Reference electrode (SCE)	0.1mol/L HCl solution (optional)
Beakers, magnetic stirrer	Distilled water

6- Experimental Procedure

A. Preparation of the Ag/AgCl Electrode

1. **Cleaning:** Rub the silver wire with sandpaper to remove oxidation.
2. **Formation of AgCl deposit:**

    - ✓ Dip the electrode into a 0.01 mol/L $AgNO_3$ solution.
    - ✓ Add a drop of HCl to form a silver chloride precipitate.
    - ✓ Allow to dry in open air.

B. Potential Study

1. Immerse the prepared electrode in a KCl solution of known concentration.
2. Connect the electrode to a potentiometer in parallel with the reference electrode.
3. Measure and record the potential for various Cl^- ion concentrations.
4. Plot the graph E=f (log [Cl^-]).

Test No.	KCl Concentration (mol/L)	[Cl^-] (mol/L)	log[Cl^-]	Measured Potential (V)
1				
2				
3				
4				
5				

7-Questions

- What is the difference between a first-kind and a second-kind electrode?
- Why is a saturated KCl solution used around the Ag/AgCl electrode?
- Explain why the electrode's potential depends only on Cl^- ion concentration.
- What is the experimental value of the slope of your graph E=f (log [Cl^-])? Is it close to the theoretical value?
- What could cause deviations between theory and experiment (incomplete precipitation, impurities, etc.)?
- What happens if the temperature increases? How would it affect the measured potential?

Lab 5

Electrolytic Preparation of Sodium Hypochlorite ("Bleach")

Lab No. 5

Electrolytic Preparation of Sodium Hypochlorite ("Bleach")

1-Objective:

- Synthesize sodium hypochlorite ("bleach") through electrolysis.
- Understand the electrochemical principles behind the preparation of this solution.
- Measure the reaction parameters and calculate the yield.

2-Theoretical:

Sodium hypochlorite ($NaClO$), commonly known as bleach, is a widely used chemical for disinfection, bleaching, and water treatment. It can be easily prepared by the electrolysis of an aqueous sodium chloride solution (brine). This process relies on redox reactions driven by an external electric current.

2-1 Electrode Reactions

The electrolysis of an aqueous sodium chloride solution produces hypochlorite ions (ClO^-), which are responsible for the bleaching and disinfecting properties of bleach. The chemical equations are:

At the electrodes:

- Anode (+ electrode): $2Cl^- \rightarrow Cl_2(g) + 2e^-$
- Cathode (− electrode): $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$

Overall reaction in solution:

$$Cl_2(g) + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$$

2-2 Factors Influencing NaOCl Production

NaCl Concentration

✓ A saturated solution (~300 g/L) promotes better Cl_2 production.

Solution pH

✓ An alkaline pH (10–12) prevents chlorate (ClO_3^-) formation and stabilizes $NaOCl$.

Current Density

✓ Excessive current leads to overheating and NaOCl decomposition.

Temperature

✓ A temperature below 40 °C is ideal to avoid thermal decomposition:

$3NaOCl \rightarrow 2NaCl + NaClO_3$

2-3 Electrode Types

- **Anode**: Graphite or DSA (Dimensionally Stable Anodes, e.g., Ti/RuO_2)
- **Cathode**: Stainless steel or nickel

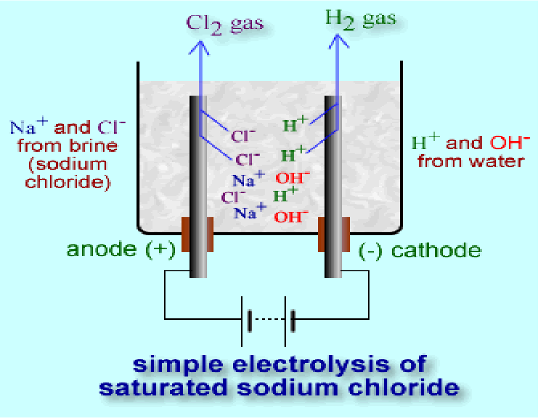


Figure 1: Electrolytic Cell for NaClO Production.

3-Materials and Reagents:

Materials:

- Electrolyzer (electrolytic cell with electrodes)
- Power supply (current generator)
- Ammeter
- Voltmeter
- Magnetic stirrer and stirring bar
- Beakers (100 mL and 250 mL)
- Graduated pipette
- Precision balance
- pH paper or pH meter

Products:

- Sodium chloride solution (NaCl) at 1 mol/L

- Distilled water
- Hypochlorite indicator (potassium iodide + sodium thiosulfate) at 0.1 mol/L concentrations

4- Experimental Procedure:

Preparation of the electrolyte:

- Prepare 200 mL of a 1 mol/L NaCl solution.
- Pour the solution into the electrolytic cell.
- Place a magnetic stirrer in the solution and start stirring.

Electrolysis setup:

- Insert two electrodes (graphite or titanium anode and stainless-steel cathode) into the solution.
- Connect the electrodes to the power supply.
- Measure the distance between the electrodes (avoid direct contact).

Electrolysis process:

- Set the current to 0.5 A and maintain a voltage of 4–6 V.
- Let the electrolysis run for 30 minutes.
- Observe the formation of gas bubbles (H_2 at the cathode and Cl_2 at the anode).

Analysis of the obtained solution:

- Measure the pH of the solution (should be high, indicating the presence of OH^-).
  - Detect the presence of hypochlorite ions (ClO^-):
  - Take a 10 mL sample of the solution.
  - Add a few drops of KI solution followed by sodium thiosulfate ($Na_2S_2O_3$).
  - Observe any color change.

Yield calculation:

- Record the amount of electricity supplied:
  $Q = I \times t$, where Q is in coulombs, I in amperes, and t in seconds.
- Calculate the theoretical amount of hypochlorite produced:
  $n_{ClO^-} = Q / (2F)$, with F = 96485 C/mol.
- Compare with the actual amount obtained through titration.

5- Questions:

- Why should the anode be made of graphite or titanium?
- What is the role of stirring during electrolysis?
- Explain why hypochlorite formation decreases if the pH is too low.
- Calculate the electrolysis yield by comparing theoretical and experimental values.
- Why is sodium hypochlorite an effective bleaching and disinfecting agen.

Lab 6

Determination of the Standard Electrode Potential

Lab No. 6

Determination of the Standard Electrode Potential

1- Objective:

- Determine the standard electrode potential of a given electrode by measuring its potential relative to a reference electrode using solutions of known concentrations.

2- Theoretical:

Electrochemical cells consist of two electrodes immersed in electrolyte solutions where oxidation and reduction reactions occur.

2-1 Electrode potentials and half-cells

When a metal, M is immersed into water, there is a **tendency** that it will lose electrons and enter the water as metal ions, M^{a+}. Soon, the water becomes a solution of the metal ions. This leaves the electrons on the metal and the metal becomes more and more negative.

$M(s) \rightarrow M^{a+}(aq) + ae^-$(electrons are left behind the metal)

The positive metal ions in the solution will be attracted towards the negative metal. Eventually some will accept the electrons and re-form the metal. $M^{a+}(aq) + ae^- \rightarrow M(s)$ (ions from solution deposited).

When the rate of these two reactions becomes equal, an equilibrium is established. At this equilibrium, the metal goes into the solution at a rate exactly same as the ions depositing.

$$M^{a+}(aq) + ae^- \rightleftharpoons M(s)$$

Different metals will have different tendencies of doing so. Some will lose electrons more readily than others. Reactive metals like magnesium prefer to stay as ions, therefore the position of equilibrium lies further to the left. Oppositely, unreactive metals like copper prefer to stay as metals, therefore the position of equilibrium lies further to the right.

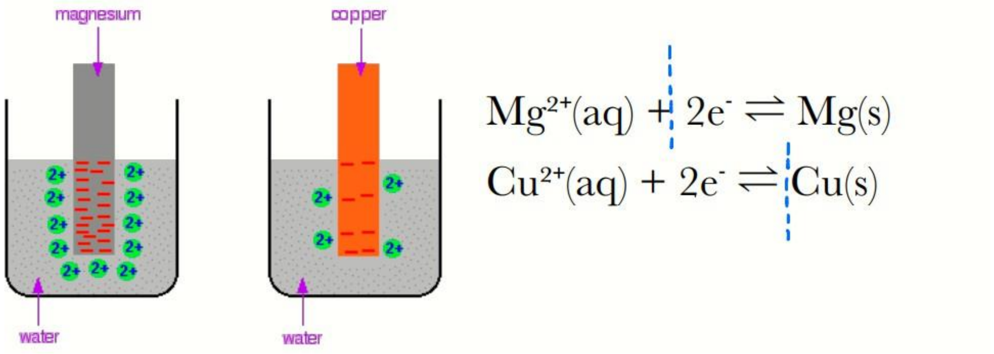


Figure 1: Half-cell.

This arrangement of a metal dipping into a solution of its ions is called a **half-cell**. The metal in a half-cell is called an electrode.

Since there is a **difference in charge** between the negative metal and the positive metal ion solution, a potential difference exists between them. This potential difference is called the **electrode potential, *E***. Electrode potential is measured in volts, V.

The electrode potential reflects the tendency of a metal to gain or lose electrons in these reactions. A standard electrode potential (E^0) is measured under standard conditions: 1 M ion concentration, 298 K temperature, and 1 bar pressure. The potential difference between two electrodes forms the basis for generating electrical energy or for driving chemical reactions, depending on the cell type (galvanic or electrolytic). The Nernst equation provides the relationship between the electrode potential, the concentration of ions, and other parameters:

$$E = E^0 + \frac{RT}{nF} ln [M^{n+}]$$

Where:

E is the electrode potential under non-standard conditions,

E^0 is the standard electrode potential,

R is the universal gas constant (8.314 J/mol·K),

T is the temperature in Kelvin (298 K),

n is the number of electrons exchanged,

F is the Faraday constant (96485 C/mol),

$[M^{n+}]$ is the concentration of metal ions in the solution.

The linear relationship between the measured potential (E) and the natural logarithm of the ion concentration ($\ln[M^{n+}]$) allows for the determination of E^0 by extrapolation.

2-2 Practical Reference Electrodes

A reference electrode provides a stable potential for calibration. It must be:

- **Reversible** (fast equilibrium).
- **Reproducible** (minimal sensitivity to external conditions).

2-2-1 The Standard Hydrogen Electrode (SHE)

A standard hydrogen electrode has hydrogen gas in equilibrium with hydrogen ions. The electrode potential of this half-cell is taken as **0 V**.

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)\ E = 0\ V$$

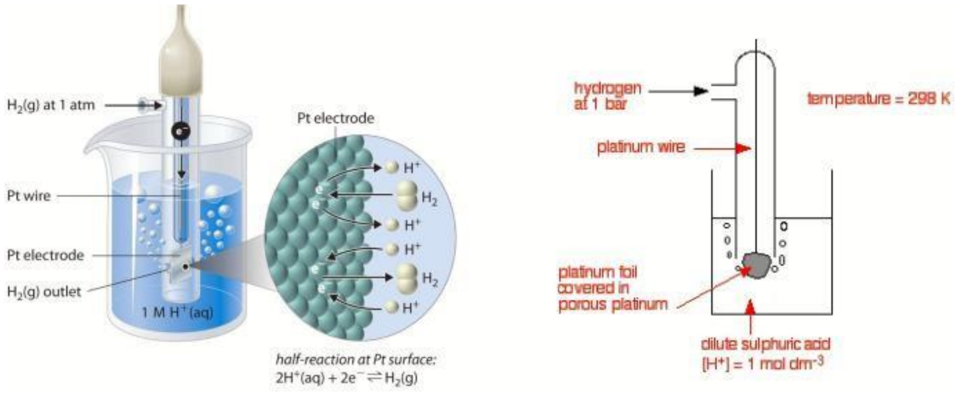


Figure 2: The Standard Hydrogen Electrode (SHE).

2-2-2 The Saturated Calomel Electrode (SCE)

The saturated calomel electrode (SCE) is the most prevalent reference electrode in electrochemical studies, valued for its stable and highly reproducible potential. It consists of a platinum wire immersed in pure mercury, which sits atop a paste mixture of mercurous chloride (Hg_2Cl_2) and mercury. This assembly is encased in a potassium chloride (KCl) solution that serves as both an electrolyte and salt bridge to complete the electrical circuit. The SCE is typically used with various KCl concentrations (0.1 M, 1.0 M, 3.5 M, or saturated), with the saturated solution being preferred to minimize liquid junction potential. At standard conditions (25°C), the SCE exhibits a well-defined potential of +0.241 V versus the standard hydrogen electrode, making it an indispensable tool for precise electrochemical measurements across numerous applications.

The overall equilibrium is expressed by:

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

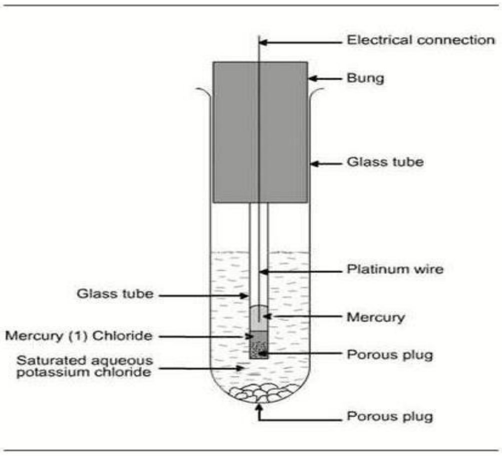


Figure 3: The Saturated Calomel Electrode (SCE)

2-2-3 Silver/Silver Chloride Electrode (Ag/AgCl)

The **Silver/Silver Chloride (Ag/AgCl) electrode** is a **reference electrode** widely used in electrochemistry, potentiometry, and biological measurements. It consists of a silver (Ag) wire or plate coated with a layer of silver chloride (AgCl) and immersed in a chloride ion (Cl^-) solution, typically potassium chloride (KCl).

The equilibrium electrochemical reaction is:

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

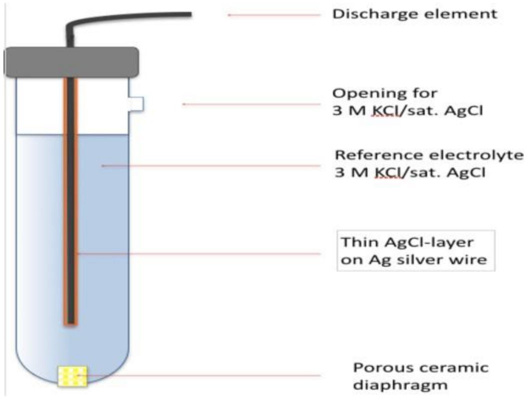


Figure 4: Silver/Silver Chloride Electrode (Ag/AgCl).

3- Materials:

- Metal electrode (e.g., Cu, Zn, Ag)
- Reference electrode (calomel electrode)
- Potentiometer or high-precision digital voltmeter
- Beakers (50 mL, 100 mL)
- Electrolytic solutions of known concentrations (e.g., $CuSO_4$, $ZnSO_4$, etc.)
- Connecting wires
- Electrode holder

Products:

- $CuSO_4$: Aqueous solution at 0.1 mol/L, 0.01 mol/L, 0.001 mol/L
- $ZnSO_4$: Aqueous solution at 0.1 mol/L, 0.01 mol/L, 0.001 mol/L
- Distilled or deionized water

4- Experimental Procedure:

Electrode Preparation:

- Rinse the metal electrode and the reference electrode with distilled water.

Use of the Reference Electrode

The reference electrode (often a saturated calomel electrode (SCE) or a silver/silver chloride electrode, Ag/AgCl) provides a stable and known potential during electrochemical measurements. To use it correct :

1. **Connection with the solution: use of a salt bridge or extension**

   - The reference electrode should **not** be placed directly into certain solutions (especially those that could react with KCl).
   - A **salt bridge** or **extension** (often a U-shaped tube or small pipe filled with saturated or gelled KCl solution) is used to establish **ionic contact** between the working solution and the reference electrode.
   - This prevents contamination of the electrode while maintaining good electrical contact.
   - The end of the salt bridge is typically sealed with a porous frit or porous wick to allow ion exchange without significant mixing of solutions.

2. **Electrode positioning**

   - The reference electrode should be placed **as close as possible** to the working electrode to minimize errors due to ohmic drop.
   - It should not be shaken or stirred vigorously to avoid damage to the internal salt bridge.

Potential Measurement:

- Place 50 mL of the electrolyte solution ($CuSO_4$ or $ZnSO_4$) in a beaker.
- Immerse the metal electrode in the solution and connect the reference electrode.
- Connect both electrodes to the potentiometer and record the measured potential value.

Repeat Measurements:

- Repeat the experiment for each concentration of the solutions (0.1 mol/L, 0.01 mol/L, 0.001 mol/L).

Data Analysis:

- Compare the results with the theoretical value of the standard electrode potential.

5- Questions:

- Why is a reference electrode used in this experiment?
- Explain the role of metal ion concentration in the solution on the measured potential.

- What is the difference between a standard potential and a measured potential?
- How do temperature variations affect potential measurements?
- What does the intercept potential represent on the $E = f(\ln [M^{n+}])$ graph?
- Why is it important to rinse the electrodes before each measurement?
- How can deposits on an electrode affect measurements?
- Explain the impact of measurement errors on the calculation of the standard electrode potential.

Conclusion

The electrochemistry practicals presented in this document provide an in-depth exploration of electrochemical phenomena and their applications. By combining hands-on experiments with critical analysis of the results, students develop essential skills for their future scientific careers. These practical sessions also underscore the importance of electrochemistry across various sectors, from energy to environmental sciences. I hope this material will serve as a solid foundation for acquiring both knowledge and practical skills in this fascinating field.

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Annex

Laboratory Safety Rules for Electrochemistry Practicals

Electrochemistry experiments involve the handling of corrosive chemicals, electrical devices, and sometimes the release of hazardous gases. Strict adherence to the following rules is essential to ensure personal safety, the safety of others, and the proper functioning of laboratory activities.

1. Personal Protective Equipment (PPE)

- ✓ Wearing a cotton lab coat, safety goggles, and appropriate gloves is mandatory.
- ✓ Long hair must be tied back, jewelry removed, and loose clothing avoided.

2. Handling of Chemicals

- ✓ Always read the hazard pictograms and safety data sheets (SDS) before using any reagent.
- ✓ Handle strong acids (HCl, H_2SO_4) and strong bases ($NaOH$, KOH) with great care.
- ✓ Never pour water into acid; always add acid slowly to water.
- ✓ In case of skin or eye contact, rinse immediately with plenty of water and inform the instructor.

3. Use of Electrochemical Devices

- ✓ Check the condition of cables, electrodes, conductometers, and power supplies before use.
- ✓ Never touch electrodes or electrical connections with wet hands.
- ✓ Follow strictly the current and voltage limits set by the instructor to prevent overheating or short circuits.

4. Gases and Electrochemical Reactions

- ✓ Some experiments generate gases such as H_2, O_2, or Cl_2, which may be flammable, irritating, or toxic.
- ✓ Always work under a fume hood or in a well-ventilated area.
- ✓ Never inhale gases or vapors directly.

5. General Laboratory Discipline

- ✓ Eating, drinking, or smoking in the laboratory is strictly forbidden.
- ✓ Mouth pipetting is prohibited; always use a pipette filler.
- ✓ Clearly label all prepared solutions.
- ✓ Keep the workbench clean, dry, and uncluttered.
- ✓ Dispose of chemical waste (acids, bases, metal salts, solvents) in the designated containers, never in the sink.

6. Emergency Procedures

- ✓ Report any accident, injury, or malfunction immediately to the instructor.
- ✓ Be familiar with the location and use of:
  - Emergency eyewash station
  - Safety shower
  - First-aid kit
  - Fire extinguishers
- ✓ In case of chemical spill, burn, or accidental inhalation, follow emergency protocols and alert the responsible staff without delay.