



People's Democratic Republic of Algeria
Ministry of Higher Education and Scientific Research
Mohamed Khider University– Biskra - Algeria
Exact Sciences

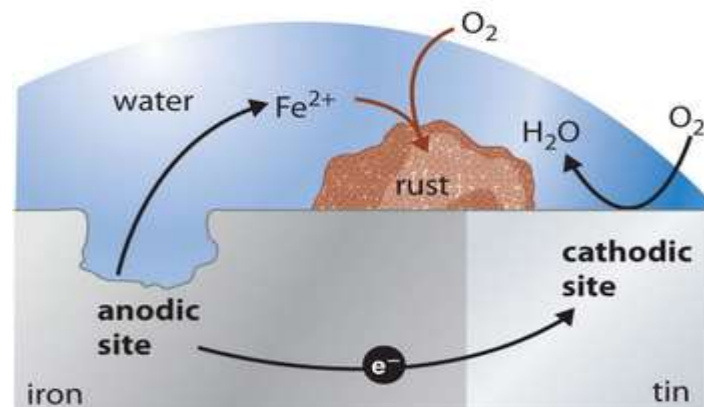


Department of Material Sciences

Course handout

Electrochemistry and corrosion.

(Lessons and Solved Exercises)



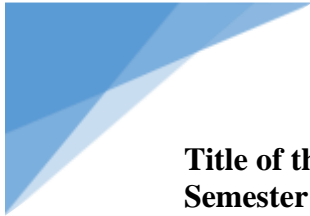
Courses intended for third-year undergraduate students in the Materials Chemistry
Bachelor's program.

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Title of the License: Materials Chemistry
Semester: 5
TU title: fundamental (UEF13)
Course Title: Electrochemistry and Corrosion
Credits: 6
Coefficient: 3

Teaching objectives:

Get the fundamentals of thermodynamics and electrochemical kinetics. Study the stability of metallic materials and their protection against oxidation in an aqueous environment. Know the industrial uses of electrochemistry for the treatment of metal surfaces and the refining or obtaining of metals.

Evaluation method: Continuous assessment: **33%**. Final exam: **67%**

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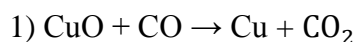
Chapter I: Oxidation-Reduction

I.1 Oxidizing Agents, Reducing Agents, and Redox Reactions

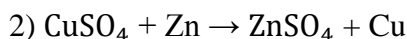
- **Definitions**

- ❖ **An oxidizing agent** is a chemical species capable of accepting electrons. When an oxidizing agent accepts electrons, it undergoes reduction. Thus, **reduction** refers to a gain of electrons.

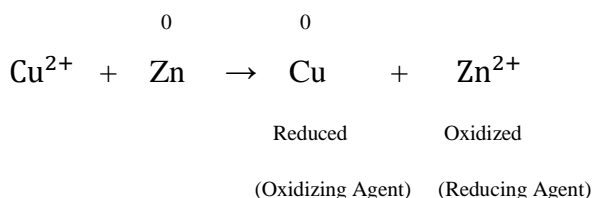
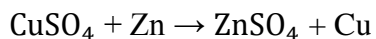
- ❖ **A reducing agent** is a chemical species capable of donating electrons. When a reducing agent donates electrons, it undergoes oxidation. Therefore, **oxidation** is defined as the loss of electrons. Illustration.



In this reaction, copper undergoes reduction, making it the oxidizing agent, while carbon, which is oxidized, acts as the reducing agent.



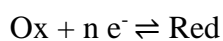
In this reaction, copper undergoes reduction and therefore acts as the oxidizing agent, whereas zinc is oxidized and serves as the reducing agent.



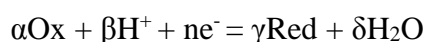
- ❖ **Oxidation and reduction** occur concurrently and cannot be separated, as they jointly constitute a **redox reaction**.

When an oxidizing agent, denoted as « Ox 1 » gains electrons, it is converted into its reduced form, « Red 1 ». Conversely, a reducing agent, « Red 2 », loses electrons and transforms into its oxidized form, « Ox 2 ». These pairs, represented as « Ox 1/Red 1 » or « Ox 2/Red 2 », are referred to as redox couples.

A redox couple is defined by the half-equation:

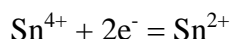


Where **n** represents the number of electrons: (i) either accepted by the oxidizing agent (Ox) from the reducing agent of another redox couple or from an electrode to convert into its reduced form (Red); or (ii) donated by the reducing agent (Red) to the oxidizing agent of another couple or to an electrode to convert into its oxidized form (Ox). In aqueous solutions, some redox couples involve hydronium ions (H⁺) and water molecules (H₂O). The corresponding half-reaction follows the general formulation:

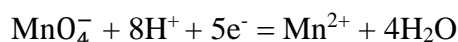


Example:

❖ For the redox couple Sn⁴⁺/Sn²⁺ :



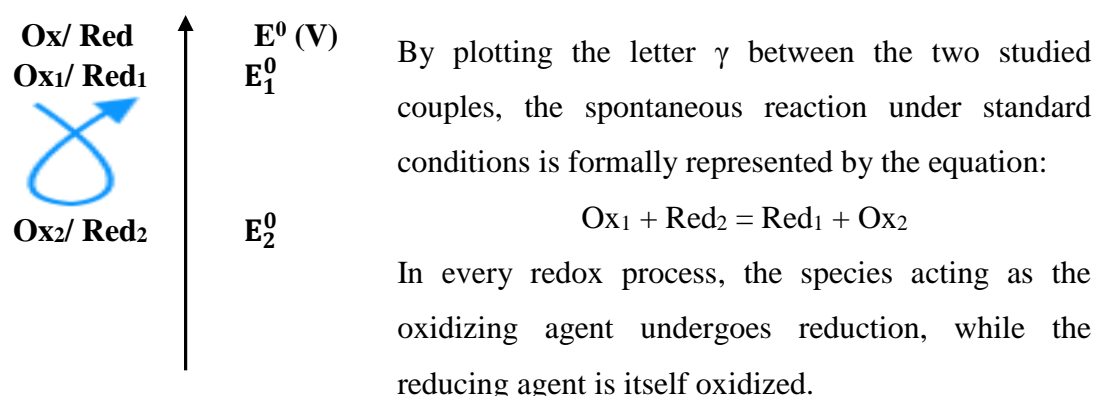
❖ For the redox couple MnO₄⁻/Mn²⁺ :



❖ **Redox Reaction**

A redox reaction involves the interaction of two redox couples. Under standard conditions at a given temperature T, the strongest oxidizing agent from one couple reacts with the strongest reducing agent from the other couple.

The reaction, whether balanced or complete, is formulated according to the "gamma rule":



By plotting the letter γ between the two studied couples, the spontaneous reaction under standard conditions is formally represented by the equation:

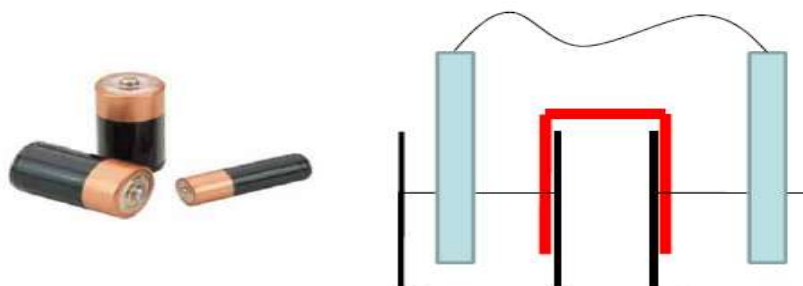
$$\text{Ox}_1 + \text{Red}_2 = \text{Red}_1 + \text{Ox}_2$$

In every redox process, the species acting as the oxidizing agent undergoes reduction, while the reducing agent is itself oxidized.

I.2 Galvanic Cell

A **galvanic** or **voltaic cell** is an electrochemical system capable of producing an electric current through a spontaneous chemical reaction. It functions as an

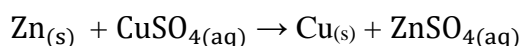
electrochemical generator, fundamentally linked to the process of a redox (oxidation-reduction) reaction.



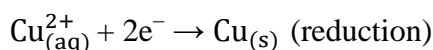
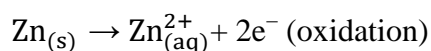
The standard 1.5-volt cell, a common electrochemical cell, is widely employed to supply energy to various appliances like clocks and television remotes. A **voltaic cell** is composed of two distinct compartments known as half-cells. The electrode at which oxidation occurs is designated as the **anode**, whereas the electrode where reduction takes place is known as the **cathode**. The reactions taking place in each half-cell are described as half-cell reactions, and the overall reaction combining these two processes is known as the cell reaction. In an electrochemical cell, the cathode functions as the positive electrode, while the anode corresponds to the negative electrode. To aid in remembering these roles, the acronyms «**An Ox**» and «**Red Cat**» (indicating **Anode Oxidation** and **Reduction Cathode**) can be used. They emphasize that oxidation takes place at the anode, whereas reduction occurs at the cathode.

I.2.1 Functioning of an Electrochemical (Galvanic) Cell

When a zinc plate is immersed in a copper sulfate solution, the following reaction occurs:



This overall reaction can be expressed in ionic form as two half-reactions:



For this system to function as a galvanic cell, the electrons released by the oxidation of zinc must be directed through an external circuit before being transferred to the copper ions. To achieve this, the two half-reactions are physically separated into distinct compartments, as illustrated in **Figure I-1**. One compartment contains a plate of

copper metal immersed in an aqueous solution of Cu^{2+} and SO_4^{2-} ions, prepared by dissolving copper sulfate (CuSO_4) in water. The other compartment consists of a plate of zinc metal placed in a solution of Zn^{2+} and SO_4^{2-} ions, obtained by dissolving zinc sulfate (ZnSO_4) in water.

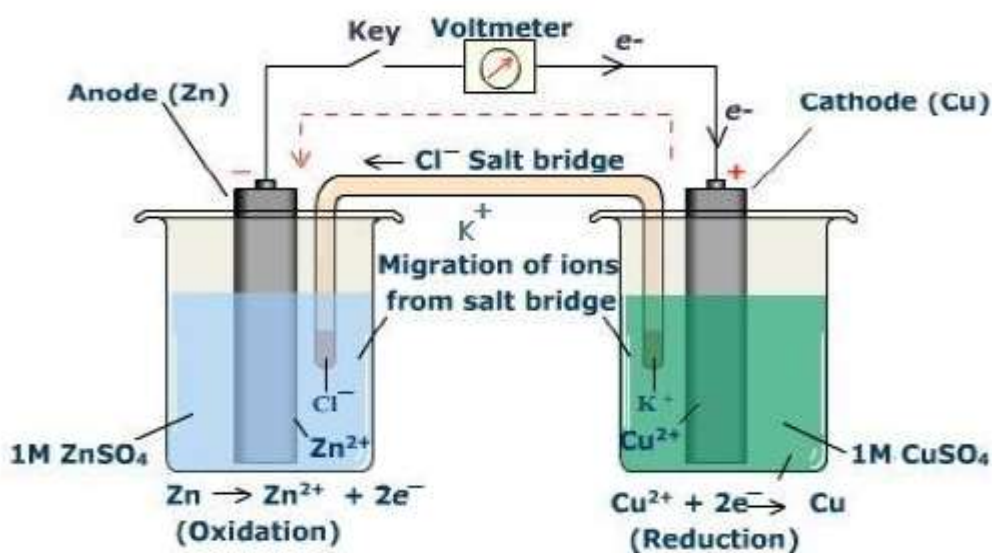
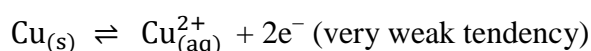
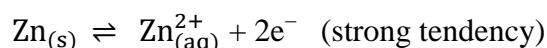


Figure I-1 An electrochemical cell: The Daniell cell, or copper-zinc cell.

This setup prevents direct interaction between zinc atoms and copper ions, as separating the compartments ensures that the ions do not come into direct contact with the metals. The system is characterized by the different tendencies of the metals to lose electrons, which can be represented as:



In this system, zinc atoms from the zinc plate oxidize, each releasing two electrons and entering the solution as zinc ions. This process leads to an accumulation of electrons on the zinc electrode, resulting in a negative charge. When the two plates are connected via an external conductor, the electrons accumulated on the zinc electrode are now able to flow. Copper ions (Cu^{2+}) in the solution, which have a strong tendency to gain electrons, are reduced at the surface of the copper electrode. Consequently, electrons flow from the zinc plate through the external circuit to the copper plate, driven by this difference in electron affinity. This electron flow generates an electric current, which can be utilized to power devices such as an electric bulb connected to the circuit.

Note:

- The spontaneous flow of electrons determines which electrode acts as the cathode and which as the anode, as well as the force that drives the electrons through the external circuit.
- Thus, since the zinc electrode loses electrons, it serves as the anode, while the copper electrode, which gains electrons, acts as the cathode.
- The electrons released by the anode accumulate on its surface, imparting a negative charge. The electrons subsequently flow through the wire from the anode to the cathode.
- Additionally, copper ions (Cu^{2+}) in the solution are reduced and deposited onto the copper electrode (cathode). The consumption of electrons at the cathode gives it a positive charge relative to the anode, which pulls the electron flow through the circuit.

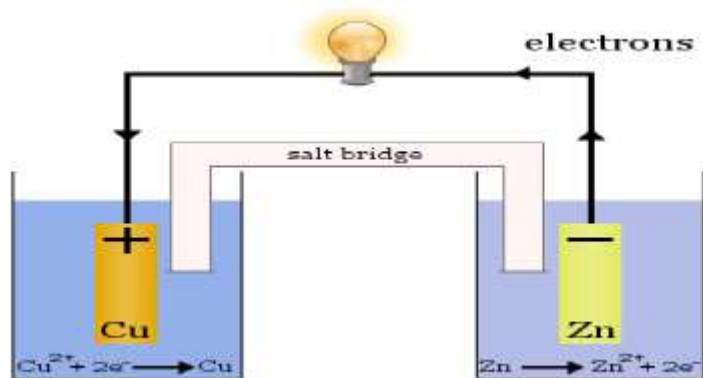


Figure I-2 Electrochemical Cell as a Source for Electric Bulb Lighting.

As the reaction progresses, the zinc electrode (anode) gradually becomes smaller as it is consumed, while the copper electrode (cathode) increases in size due to the deposition of copper. To preserve charge balance within the cell, a salt bridge is essential. Without it, the electrons generated at the anode would accumulate at the cathode, halting the redox reaction. For a galvanic cell to work, the two half-cells must have different electrochemical properties, in particular different abilities to carry out oxidation and reduction reactions. A difference in the reactivity of the electrodes is necessary to permit the spontaneous redox process between the two half-cells.

The Daniell cell is a classic example of a galvanic (or voltaic) cell. It was named in honour of the British chemist and meteorologist John Frederic Daniell, who invented it. This cell is analogous to the zinc-copper cell previously described, with a key distinction: in the Daniell cell, a porous pot replaces the salt bridge. The porous pot allows

Zn^{2+} ions and SO_4^{2-} ions to migrate toward the cathode and anode, respectively, thus facilitating the flow of ions without direct mixing of the electrolytes. Despite this structural difference, the cell diagram (or cell notation) remains unchanged.

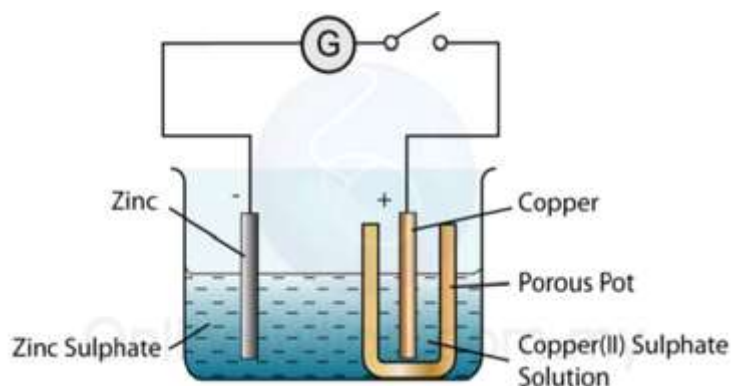



Figure I-3 Schematic Representation of the Daniell Cell.

I.2.2 Salt Bridge

A salt bridge serves as an ionic conductor positioned between the oxidation and reduction half-cells of a galvanic cell. Structurally, it is typically an inverted U-shaped tube filled with a strong electrolyte such as Na_2SO_4 , KNO_3 , K_2SO_4 , KCl , or NaCl . At both ends of the salt bridge, cotton plugs are placed to prevent the uncontrolled flow or excessive mixing of the electrolyte with the solutions in the half-cells. However, ions from the salt bridge can gradually diffuse through these plugs, maintaining electrical neutrality in both compartments. This prevents the electrochemical reaction from prematurely reaching equilibrium. In the absence of a salt bridge, the anodic half-cell would rapidly accumulate positive charge due to the loss of electrons (oxidation), while the cathodic half-cell would accumulate negative charge from the gain of electrons (reduction). Such charge imbalance would interrupt the redox process and halt the production of electrical current. Therefore, for a galvanic cell to operate efficiently, it is essential that both half-cells remain electrically neutral throughout the reaction.

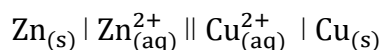
An electrochemical cell that lacks a salt bridge cannot sustain electrical current for an extended period. This limitation arises because, as electrons flow from the anode to the cathode, negative charge progressively accumulates in the cathodic half-cell. On the other hand, the anodic half-cell develops an excess of positive charge due to the ongoing loss of electrons through oxidation. This accumulation of charge leads to an imbalance in the distribution of ions, disrupting the electrical neutrality within both half-cells. As a result, the cell ceases to produce electrical energy.



To prevent the effects of charge separation, anions from the salt bridge gradually flow into the oxidation half-cell (anode) to maintain electrical neutrality, while cations enter the reduction half-cell (cathode) for the same purpose. This ion flow occurs in the reverse direction of electron flow, ensuring that charge balance is maintained throughout the cell. The electrochemical cell continues to operate until one of the reactants, either the zinc metal or the copper ions, is entirely depleted.

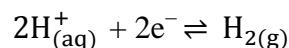
I.2.3 Cell Notation

In electrochemical studies, it is standard practice to represent the reactions of electrochemical cells in a concise, shorthand format rather than illustrating the entire setup. This abbreviated representation is referred to as cell notation or a cell diagram. An electrochemical cell comprises two half-cells, each of which can be succinctly described using this notation. Following the 1953 IUPAC conventions, and with specific reference to the Zinc-Copper cell, the recommended format for cell notation is as follows:

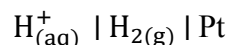


On the left: the anode; on the right: the cathode. The double vertical line (\parallel) symbolizes a separation between the two half-cells—such as a salt bridge or porous barrier—that allows ions to pass through while preventing the mixing of the electrolytes. A single vertical line (\mid) is used to represent the interface or boundary between a metal electrode and its corresponding ions in solution.

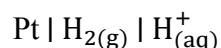
In cases where a half-reaction involves a gaseous species, an inert material such as platinum is employed as both a terminal and an electrode surface, facilitating the occurrence of the half-reaction. Platinum acts as a catalyst for the reaction but does not participate chemically in the process. For instance, **Figure I-4** illustrates a hydrogen electrode, where hydrogen gas is bubbled over a platinum plate immersed in an acidic solution. The corresponding cathode half-reaction is represented as:



The notation for the hydrogen electrode, when functioning as a cathode, is expressed as:



To denote the same electrode operating as an anode, the notation is simply reversed:



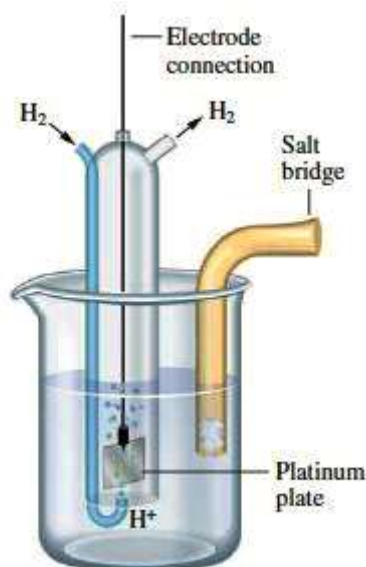
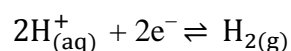


Figure I-4 A hydrogen electrode.

In the illustrated setup (**Figure I-4**), hydrogen gas is bubbled over a platinum surface, which acts as the electrode. The platinum facilitates the half-reaction:




I.3 Electrode Potential and Standard Electrode Potential

The **redox (electrode) potential** is the voltage of a cell in which the electrode under study forms the right half-cell, while the standard hydrogen electrode (SHE) serves as the left half-cell

Example: In a cell, the right half-cell consists of a pure silver strip in contact with a solution containing silver ions, while the left electrode is the standard hydrogen electrode (SHE). Since the potential of the SHE is arbitrarily set to 0.000 V, we can express the cell potential as:

$$E_{\text{cell}} = E_{\text{Right}} - E_{\text{Left}} = E_{\text{Ag}} - E_{\text{SHE}} = E_{\text{Ag}} - 0.000 = E_{\text{Ag}}$$

Here, E_{Ag} represents the potential of the silver electrode. This electrode potential (which would be more formal and accurately termed «relative electrode potential») corresponds to the voltage exhibited by a complete electrochemical cell that contains a rigorously defined reference electrode. The potential of an electrode, such as the silver electrode, is sometimes denoted as E_{Ag} versus SHE to emphasize that it represents the voltage measured in a cell where the standard hydrogen electrode (SHE) serves as the reference.



The **standard electrode potential**, E^0 , of a half-reaction refers to the voltage measured when the activities of all reactants and products are unity under standard conditions.

I.4 Electromotive Force (emf)

The electromotive force (emf), also referred to as the open-circuit voltage of the cell (i.e., the voltage measured when no current is flowing), is denoted by E . It corresponds to the positive difference between the electrode potentials of the half-cells, as determined by the Nernst equation.

The cell potential (E_{cell}), in volts, is obtained by linking the electrodes of an electrochemical cell to a voltmeter. This measurement assigns a specific voltage value to the cell, as different chemical combinations in electrochemical cells generate distinct voltages. A **positive cell voltage** indicates that the reaction proceeds spontaneously and is thermodynamically favorable in the forward direction. As a result, the electrons flow clockwise through the external circuit. Conversely, a negative voltage implies that the reaction is not spontaneous and the reverse direction is favored.

A negative cell voltage means that the reaction does not occur spontaneously in the specified direction (thermodynamically unfavorable), but becomes feasible in the opposite direction. Non-spontaneous reactions can be induced to proceed by applying an external energy source. In addition, the cell potential, or electromotive force (emf), can be obtained by subtracting the anode half-cell potential from that of the cathode, as expressed by the following equation:

$$E_{\text{cell}} = E_{\text{Right}} - E_{\text{Left}}$$

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

Here, E_{cathode} and E_{anode} represent the potentials of the cathode and anode, respectively. Thermodynamically feasible reactions are characterized by **positive cell potential** (E_{cell}) values, while non-feasible reactions exhibit negative E_{cell} values. The cell potentials measured under standard conditions are referred to as the **standard cell potential** (E^0). Standard conditions are defined as follows: the concentrations of all reactants and products are 1 M, the temperature is 25°C (298 K), and for gaseous species, a pressure of 1 atm is used in place of concentration.

I.5 Influence of Concentration on Electrochemical Cell Potential: An Analysis Based on the Nernst Equation

The cell potential of an electrochemical system depends on the concentrations of ions in solution and the partial pressures of gases involved in the redox reactions. Consequently, cell potentials can be used to determine ion concentrations. A pH meter, for example, operates by measuring changes in cell potential as a function of hydrogen-ion concentration. The quantitative relationship between cell potential, ion concentration, gas pressure, and standard electrode potential is described by the Nernst equation, formulated by the German chemist Walther Nernst (1864–1941).

❖ Nernst Equation

The relationship between the free-energy change, ΔG , and the standard free-energy change, ΔrG^0 is expressed by the following equation

$$\Delta G = \Delta rG^0 + RT \ln Q$$

In this equation:

R is the ideal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$),

T is the absolute temperature in kelvin (K),

Q is the thermodynamic reaction quotient, which is defined analogously to the equilibrium constant K . However, unlike K , which is evaluated at equilibrium, Q is calculated using the instantaneous concentrations of reactants and products or the partial pressures of gaseous species present in the reaction mixture at a specific point in time. This relationship is particularly relevant in the context of electrochemical cells, such as voltaic cells. For such systems, the concentrations of species in solution and the partial pressures of gases correspond to their values in the cell at a given moment. By substituting the expressions $\Delta G = -nFE_{\text{cell}}$ and $\Delta rG^0 = -nFE_{\text{cell}}^0$ into the Gibbs free energy equation, we obtain:

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^0 + RT \ln Q$$


Where:

n : The number of moles of electrons transferred in the redox reaction,

F : Faraday's constant ($96485 \text{ C} \cdot \text{mol}^{-1}$),

E_{cell} : The cell's potential under non-standard conditions,

E_{cell}^0 : The standard cell's potential,



Rearranging this equation yields the **Nernst equation**, which establishes a quantitative relationship between the cell potential, the standard cell potential, and the reaction quotient:

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln Q \text{ or } E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303 RT}{nF} \log Q$$

When the temperature is set to 298 K (25°C), and the values of the universal gas constant R and Faraday's constant F are substituted into the Nernst equation, the expression can be simplified further. Using common logarithms (base 10); the equation takes the following form:

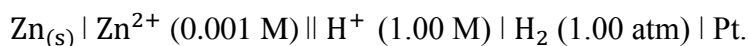
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{n} \log Q \quad (\text{values in volts at } 25^\circ\text{C})$$

The Nernst equation provides a quantitative framework for understanding how the cell potential (E_{cell}) varies as the electrochemical cell operates. During the progression of the redox reaction, the concentration of reactants gradually diminishes, while that of the products increases. This shift in composition causes the reaction quotient, Q, to increase over time. Since Q appears in the logarithmic term of the Nernst equation:

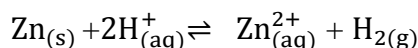
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{n} \log Q$$

An increase in Q leads to a corresponding increase in $\log Q$. Consequently, the term $\frac{RT}{nF} \ln Q$ becomes larger, causing the overall value of $E_{\text{cell}}^0 - \frac{RT}{nF} \ln Q$ to decrease. This results in a gradual reduction of E_{cell} as the reaction progresses. Eventually, the system reaches a state of equilibrium, at which point the cell potential, E_{cell} becomes zero. At equilibrium, the reaction quotient Q equals the equilibrium constant K.

To demonstrate the application of these principles, consider the following example of a voltaic cell:



The cell reaction under consideration is:



The equilibrium constant, K, for this reaction is expressed as:

$$K = \frac{[\text{Zn}^{2+}] P_{\text{H}_2}}{[\text{H}^+]^2}$$

Here, $[Zn^{2+}]$ and $[H^+]$ represent the molar concentrations of the zinc ion and hydrogen ion, respectively.

It is important to note that the concentration of hydrogen gas is expressed here in terms of its partial pressure (measured in atmospheres). The reaction quotient maintains the same structural form as the equilibrium constant K ; however, it utilizes the actual ion concentrations and hydrogen gas pressures present within the electrochemical cell. Hence,

$$Q = \frac{[Zn^{2+}] P_{H_2}}{[H^+]^2} = \frac{0.01 \times 1.00}{(1.00)^2} = 0.01$$

I.6 Examples of Electrodes

The term electrode should be specifically used to describe the interface at which the redox half-reaction occurs. Generally, it refers to the entire device, which includes the electronic conducting material, its support, and the electric connexion.

Electrodes are essential components of electrochemical systems, with their structure and function tailored to the specific measurement or application. The figure I-5 below illustrates several types of electrodes commonly used in electrochemical measurements:

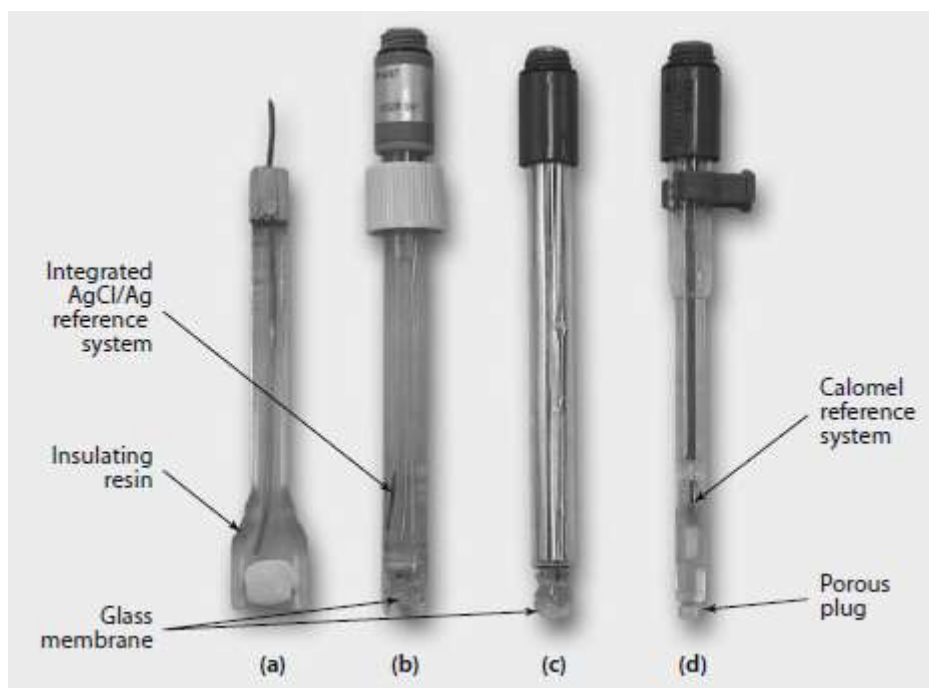



Figure I-5 Examples of Electrodes in Electrochemical Systems.



Device (a) shown above consists of a metal electrode enclosed in an insulating resin that also serves to define a precise surface area exposed to the electrolyte.

A reference electrode is typically more elaborate. It contains an electrochemical system characterized by a known and stable potential, provided it is immersed in a suitable solution. Electrical contact with the cell's electrolyte is established through a porous material. A common example of such a reference electrode is the calomel electrode (device d).

More generally, the term "electrode" refers to any half-cell that includes an electrical connection. This broad definition encompasses specialized electrodes in which the electrochemical system is separated from the solution by an ionic membrane separating. For instance, device (c) employs a glass membrane selective proton (other ion-selective membranes also exist). Additionally, commercially available electrodes may incorporate both the measuring and reference systems into a single unit. These integrated electrodes are often coaxial in structure and make contact with the solution through a porous element located laterally. The combined pH electrode (device b) is a representative example of this configuration.

Electrode materials exhibit a wide range of behaviors. Depending on their nature and their interaction with the contacting solution, they are commonly classified into four main categories.

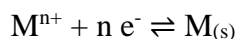
1. An electrode in contact with a solution containing its own ions can be divided into two main cases:

(a) A metal in contact with a solution of its corresponding cations, such as $\text{Cu}^{2+} | \text{Cu}$, where

$$E = E^0 + \frac{RT}{nF} \ln a_{\text{M}^{n+}}$$

$a_{\text{M}^{n+}}$ is the activity of the ion (approximately equal to its molar concentration, $[\text{M}^{n+}]$, in a dilute solution).

and the half-reaction is



❖ **Review of Activities:**

The activity of the solvent H_2O is $a_{\text{solvent}} \approx 1$ and therefore does not appear in the logarithmic term.

For a species dissolved in solution, its activity is equal to the numerical value of its concentration expressed in $\text{mol} \cdot \text{L}^{-1}$.

For a gas, its activity is equal to the numerical value of its pressure expressed in bar.

Example: Silver Electrode

This type of electrode consists of a silver wire immersed in a solution containing Ag^+ ions, typically a silver nitrate solution

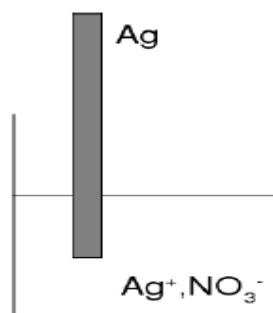
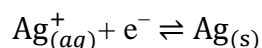


Figure I-6 Schematic representation of a silver wire immersed in silver nitrate solution.

The redox couple involved is Ag^+/Ag , represented by the half-reaction:



By applying the Nernst equation, the electrode potential is expressed as:

$$E(\text{Ag}^+/\text{Ag}) = E^0(\text{Ag}^+/\text{Ag}) + \frac{RT}{F} \ln [\text{Ag}^+]$$

(b) A non-metal in equilibrium with its ions, for example $\text{H}_2 | \text{H}^+$ or $\text{Cl}_2 | \text{Cl}^-$, on the surface of an inert conductive material such as platinum. For the first example,

$$E = E^0 + \frac{RT}{2F} \ln \frac{a_{\text{H}^+}^2}{P_{\text{H}_2}}$$

where P_{H_2} represents the partial pressure of hydrogen gas. In such electrodes, the electrode potential originates from electron transfer processes between the ion and the neutral species.

2. An electrode consisting of a metal in contact with a solution containing anions capable of forming a sparingly soluble salt with the metal's ions. A typical example is the calomel electrode, $\text{Hg} | \text{Hg}_2\text{Cl}_2 | \text{Cl}^-$ (see Figure I-5)

In such systems, the salt remains predominantly in the solid phase, allowing its activity to be considered effectively constant (approximated as unity). As a result, the electrode potential depends solely on the activity of the anion in solution,

$$E = E^0 - \frac{RT}{F} \ln a_{\text{Cl}^-}$$

Such systems are widely employed as reference electrodes due to the very low solubility product of the salt, which ensures a highly stable and reproducible electrode potential. An additional example is the silver–silver chloride electrode ($\text{Ag} | \text{AgCl} | \text{Cl}^-$).

3. This type of electrode functions as an electron source or sink, enabling electron transfer between redox species in solution without the electrode itself directly participating in the chemical reaction—as is the case with the first and second types. For this reason, such electrodes are referred to as redox or inert electrodes. Platinum is commonly used in this context, immersed in a solution containing both the oxidized and reduced forms of the redox couple. For example, consider an electrode composed of a platinum wire immersed in a solution containing Fe^{2+} and Fe^{3+} ions. The redox couple involved is $\text{Fe}^{3+} / \text{Fe}^{2+}$, and the corresponding half-reaction is: $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$.

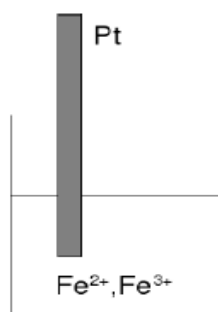


Figure I-7 Schematic representation of a platinum wire electrode immersed in a solution containing Fe^{2+} and Fe^{3+} ions.

The electrode potential is given by the Nernst equation:

$$E(\text{Fe}^{3+}/\text{Fe}^{2+}) = E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) + \frac{RT}{F} \ln \left(\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right)$$

4. Electrodes that do not fall into any of the previously defined categories include, for example, modified electrodes.

I.7 Prediction of Redox Reactions

I.7.1 Standard Electrode Potential Scale

The redox couples are classified according to their standard electrode potential, $E_{\text{Ox/Red}}^0$ as schematically represented in the following figure:

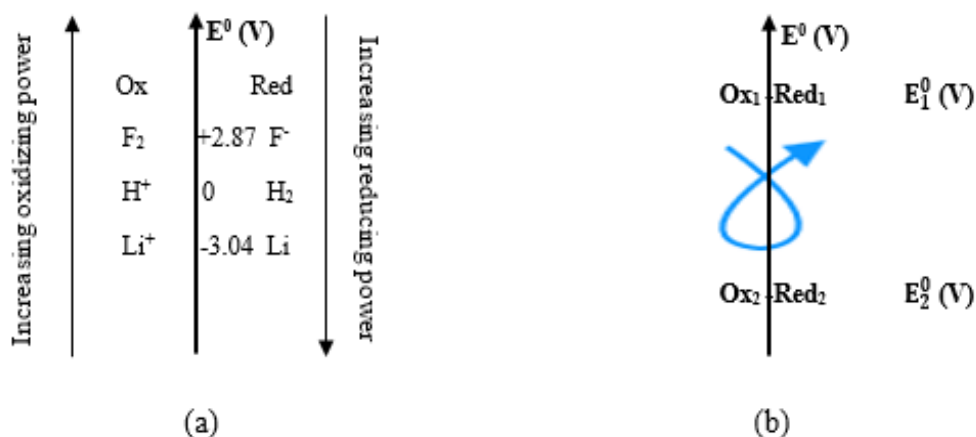
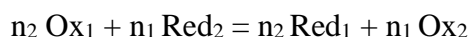


Figure I-8 (a) Principle of the standard electrode potential scale. (b) Gamma rule.

For the redox couples located at the top of the scale, the oxidized form (Ox) is a strong oxidizing agent, while the reduced form (Red) is a weak reducing agent. At the bottom of the scale, these properties are reversed.

I.7.2 Thermodynamically Favorable Redox Reactions

The reaction:



is thermodynamically favorable if:

$$E_1(Ox_1 / Red_1) > E_2(Ox_2 / Red_2)$$

To make a general prediction, it is assumed that the reaction is likely to occur if $E_1^0 > E_2^0$, in which case it proceeds according to the **gamma rule**.

A thermodynamically favorable reaction ($\Delta rG < 0$) may not be observed due to kinetic factors. The condition $E_1(Ox_1 / Red_1) > E_2(Ox_2 / Red_2)$ is necessary but not sufficient for a redox process to occur.

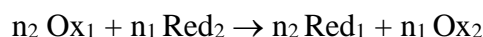
I.7.3 Quantitative Study of System Evolution and the Equilibrium Constant

The electromotive force (emf) of a galvanic cell is the maximum value of the potential difference between the cathode and the anode: $\varepsilon = E_C - E_A$, i.e., the open-circuit voltage (when the cell is not discharging).

We have the relation:

$$\Delta_r G = -nF \varepsilon$$

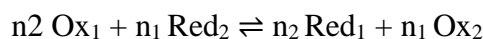
For the following galvanic cell reaction, considered at 25 °C, and with Q as the reaction quotient:



The cell potential is given by $\varepsilon = \frac{-\Delta_r G}{nF}$ which leads, in volts: $\varepsilon = \varepsilon^0 - \frac{0.0592}{n} \log_{10} Q$

Where: $\varepsilon^0 = \frac{-\Delta_r G^0}{nF}$ is the standard emf of the cell.

When the cell is "dead" (i.e., the system has reached equilibrium), the reaction becomes:



At equilibrium, $Q = K$ (the equilibrium constant), and it is related to the standard emf ε^0 by:

$$K = 10^{\frac{n\varepsilon^0}{0.0592}}$$

To predict whether a redox reaction proceeds quantitatively or not, the equilibrium constant can be calculated by replacing ε^0 in the previous equilibrium expression with $(E_1^0 - E_2^0)$.

$$K = 10^{\frac{n(E_1^0 - E_2^0)}{0.0592}}$$

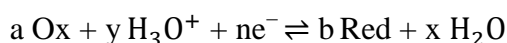
I.8 Influence of the Environment, Apparent Potential.

I.8.1 Influence of pH

The potential of a redox system is sensitive to the pH of the medium as soon as H_3O^+ ions or OH^- ions are involved in the redox reactions.

In such cases, for each specific pH value, an apparent standard potential—also referred to as the conditional standard potential—is defined and denoted as E'^0 .

When $\text{pH} = 0$, we have: $E'^0 = E^0$



$$E = E^0 + \frac{0.0592}{n} \log \frac{[\text{Ox}]^a [\text{H}_3\text{O}^+]^y}{[\text{Red}]^b}$$

$$E = E^0 + \frac{0.0592}{n} \log \frac{[\text{Ox}]^a}{[\text{Red}]^b} + \frac{0.0592}{n} \log [\text{H}_3\text{O}^+]^y$$

Now, $\text{pH} = -\log [\text{H}_3\text{O}^+]$

Hence, the electrode potential can be expressed as:

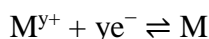
$$E = E^0 + \frac{0.0592}{n} \log \frac{[\text{Ox}]^a}{[\text{Red}]^b} - y \frac{0.0592}{n} \text{pH}$$

We define: $E'^0 = E^0 - y \frac{0.0592}{n} \text{pH}$, which is called the apparent standard potential.

One significant use of the relationship E as a function of pH is the ability to determine the pH of a solution by merely measuring its electrode potential. This dependence can be represented graphically by plotting the $E = f(\text{pH})$ curve.

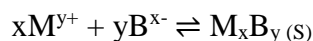
I.8.2 Influence of the Solubility Product Constant (K_{sp}) on the Electrode Potential

The direction of a redox reaction can also be influenced by the formation of precipitates. Thus, the electrode potential can be expressed as a function of the solubility product constant (K_{sp}) of the salt in question. For example, consider a metal strip M immersed in a solution containing M^{y+} ions.



$$E(M^{y+}/M) = E^{\circ}(M^{y+}/M) + \frac{0.0592}{y} \log [M^{y+}]$$

If B^{x-} ions are added to the solution in such a way as to induce the precipitation of the salt M_xB_y , this gives:



$$K_{sp} = [M^{y+}]^x [B^{x-}]^y \Rightarrow [M^{y+}] = \left(\frac{K_{sp}}{[B^{x-}]^y} \right)^{\frac{1}{x}}$$

$$E(M^{y+}/M) = E^{\circ}(M^{y+}/M) + \frac{0.0592}{y} \log \left(\frac{K_{sp}}{[B^{x-}]^y} \right)^{\frac{1}{x}}$$

$$E(M^{y+}/M) = E^{\circ}(M^{y+}/M) + \frac{0.0592}{xy} \log K_{sp} - \frac{0.0592}{x} \log [B^{x-}]$$

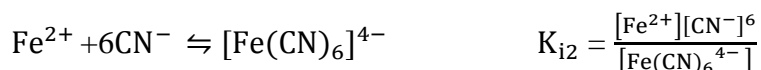
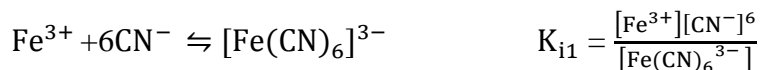
$$pK_{sp} = -\log K_{sp}$$

$$E(M^{y+}/M) = E^{\circ}(M^{y+}/M) - \frac{0.0592}{xy} pK_{sp} - \frac{0.0592}{x} \log [B^{x-}]$$

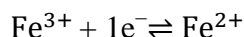
$$E(M^{y+}/M) = E^{\circ} - \frac{0.0592}{x} \log [B^{x-}]$$

I.8.3 Influence of the Formation Constant (K_f) on the Electrode Potential


The direction of a redox reaction can be influenced by the formation of coordination complexes. Consider, for instance, the redox couple Fe^{3+}/Fe^{2+} . In the presence of cyanide ions (CN^{-}), the following complexes are formed: $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$.



The corresponding redox equilibrium is:



The Nernst equation for this redox couple is:


$$E(\text{Fe}^{3+}/\text{Fe}^{2+}) = E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.0592 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

By substituting the expressions derived from the complexation equilibria, we obtain

$$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = \frac{K_{i1} [\text{Fe}(\text{CN})_6^{3-}]}{K_{i2} [\text{Fe}(\text{CN})_6^{4-}]}$$

Therefore:

$$E(\text{Fe}^{3+}/\text{Fe}^{2+}) = E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.0592 \log \left(\frac{K_{i1}}{K_{i2}} \right) + 0.0592 \log \left(\frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}(\text{CN})_6^{4-}]} \right)$$

We can write this as:

$$E(\text{Fe}^{3+}/\text{Fe}^{2+}) = E'^0 + 0.0592 \log \left(\frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}(\text{CN})_6^{4-}]} \right)$$

Where:

$$E'^0 = E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.0592 \log \left(\frac{K_{i1}}{K_{i2}} \right)$$

Exercises

Exercise 1.

What happens if zinc is placed in a solution containing tin (IV) ions (Sn^{4+})?

Given that: $E_1^0(\text{Sn}^{4+}/\text{Sn}^{2+}) = +0.14 \text{ V}$ and $E_2^0(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$

Exercise 2.

- Calculate the standard cell potential for the Daniell cell represented by the following cell notation:

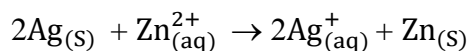
$\text{Zn}_{(s)} \mid \text{Zn}_{(aq)}^{2+} \parallel \text{Cu}_{(aq)}^{2+} \mid \text{Cu}_{(s)}$ Given that:



- Comment on the thermodynamic feasibility of the electrochemical cell under standard conditions.

Exercise 3.

Calculate the standard emf and assess the feasibility of the following redox reaction:



Given that: $E^\circ(\text{Ag}^+/\text{Ag}) = 0.80 \text{ V}$; $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$

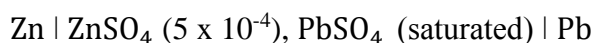
Exercise 4.

Calculate the redox potential in each of the following cases:

- $\text{Al} \rightleftharpoons \text{Al}^{3+} (0.01 \text{ M}) + 3e^- \quad E^\circ = -1.67 \text{ V}.$
- $\text{Fe}^{2+} (10^{-4} \text{ M}) \rightleftharpoons \text{Fe}^{3+} (10^{-2} \text{ M}) + e^- \quad E^\circ = +0.77 \text{ V}.$
- $2\text{SO}_4^{2-} (1 \text{ M}) \rightleftharpoons \text{S}_2\text{O}_8^{2-} (10^{-4} \text{ M}) + 2e^- \quad E^\circ = +2.05 \text{ V}.$
- $2\text{Cr}^{3+} (0.1 \text{ M}) + 21\text{H}_2\text{O} \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} (10^{-3} \text{ M}) + 14\text{H}_3\text{O}^+ (10^{-3} \text{ M}) + 6e^- \quad E^\circ = +1.36 \text{ V}.$

Exercise 5.

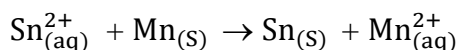
Calculate the cell potential of the following electrochemical cell:



Given that: $E^\circ(\text{PbSO}_4/\text{Pb}) = -0.350 \text{ V}$; $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.763 \text{ V}.$

Exercise 6.

The functioning of a galvanic cell relies on the following redox reaction:



Calculate the cell potential at 25 °C under each of the following sets of conditions:

- Standard conditions
- $[\text{Sn}^{2+}] = 0.01 \text{ mol/L}$; $[\text{Mn}^{2+}] = 2.00 \text{ mol/L}$.
- $[\text{Sn}^{2+}] = 2.0 \text{ mol/L}$; $[\text{Mn}^{2+}] = 0.01 \text{ mol/L}$.

Given that: $E^\circ(\text{Sn}^{2+}/\text{Sn}) = -0.14 \text{ V}$; $E^\circ(\text{Mn}^{2+}/\text{Mn}) = -1.18 \text{ V}$;

Exercise 7.

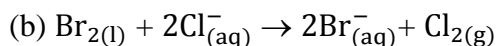
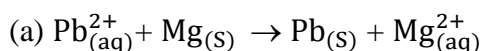
An electrochemical cell is composed of two compartments:

- The first contains a platinum wire immersed in a solution with a concentration of 10^{-2} M of Fe^{2+} ions and $2 \cdot 10^{-3} \text{ M}$ of Fe^{3+} ions.
 - The second consists of metallic thallium immersed in a 10^{-2} M solution of Tl^+ ions.
- Determine the potential of each electrode.
 - Identify the negative electrode and calculate the electromotive force (emf) of the cell.
 - Write the half-reactions at each electrode and the overall cell reaction.
 - Determine the equilibrium constant of the reaction. What can be concluded?

Given that: $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}$ and $E^\circ(\text{Tl}^+/\text{Tl}) = -0.34 \text{ V}$

Exercise 8.

- Calculate the standard Gibbs free energy change (ΔG°) at 25°C for each of the following redox reactions:



- Are these reactions spontaneous under standard conditions?
- Calculate the equilibrium constant (K°) for each reaction.

Given: $E^\circ(\text{Mg}^{2+}/\text{Mg}) = -2.37 \text{ V}$; $E^\circ(\text{Pb}^{2+}/\text{Pb}) = -0.13 \text{ V}$; $E^\circ(\text{Br}_2/\text{Br}^-) = 1.09 \text{ V}$;
 $E^\circ(\text{Cl}_2/\text{Cl}^-) = 1.36 \text{ V}$; $R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.



Exercise 9.

Given the standard potential of the $\text{Mn}^{7+}/\text{Mn}^{2+}$ redox couple:

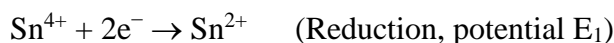
- a. Calculate the apparent standard potential of this system at $\text{pH} = 3.0$, $\text{pH} = 4.0$, and $\text{pH} = 7.0$, assuming that no precipitation occurs at these pH values.
- b. What conclusion can be drawn from the comparison of these results?

$$E^\circ(\text{Mn}^{7+}/\text{Mn}^{2+}) = +1.50 \text{ V.}$$

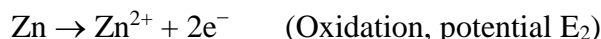
Solutions

Exercise 1.

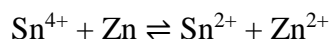
- Since $E_1^0 > E_2^0$, electrons flow from zinc to Sn^{4+} , leading to the following reduction reaction:



- Zinc loses electrons and is therefore oxidized:



When zinc is introduced into the tin solution, the following overall redox reaction takes place:



Since E_1 is greater than E_2 , the reaction is spontaneous in the forward direction, and zinc dissolves as it is oxidized to Zn^{2+} .

Exercise 2

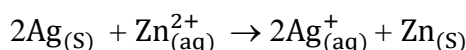
Anode (oxidation): $\text{Zn}_{(s)} \rightarrow \text{Zn}_{(aq)}^{2+} + 2e^- \quad E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$

Cathode (reduction): $\text{Cu}_{(aq)}^{2+} + 2e^- \rightarrow \text{Cu}_{(s)} \quad E^\circ(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$

$$E^\circ_{\text{Cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.34 - (-0.76) = 1.10 \text{ V.}$$

A positive standard emf confirms that the cell reaction is thermodynamically spontaneous (feasible) under standard conditions.

Exercise 3.



Anode (oxidation): $2\text{Ag}_{(s)} \rightarrow 2\text{Ag}_{(aq)}^+ + 2e^- \quad E^\circ(\text{Ag}^+/\text{Ag}) = 0.80 \text{ V}$

Cathode (reduction): $\text{Zn}_{(aq)}^{2+} + 2e^- \rightarrow \text{Zn}_{(s)} \quad E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$

$$E^\circ_{\text{Cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.76 - 0.80 = -1.56 \text{ V.}$$

A negative standard emf indicates that the cell reaction is not spontaneous (non-feasible) under standard conditions.

Exercise 4.

a) $\text{Al} \rightleftharpoons \text{Al}^{3+} (0.01 \text{ M}) + 3e^- \quad E^\circ = -1.67 \text{ V.}$

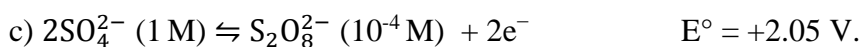
$$E(\text{Al}^{3+}/\text{Al}_{(s)}) = E^\circ(\text{Al}^{3+}/\text{Al}_{(s)}) + \frac{0.0592}{3} \log [\text{Al}^{3+}]$$

$$E(\text{Al}^{3+}/\text{Al}_{(s)}) = -1.67 + \frac{0.0592}{3} \log(0.01) = -1.709 \text{ V} \approx -1.71 \text{ V}$$

b) $\text{Fe}^{2+} (10^{-4} \text{ M}) \rightleftharpoons \text{Fe}^{3+} (10^{-2} \text{ M}) + e^- \quad E^\circ = +0.77 \text{ V.}$

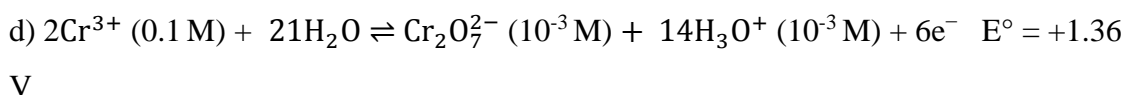
$$E(\text{Fe}^{3+}/\text{Fe}^{2+}) = E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.0592 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$E(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 + 0.0592 \log\left(\frac{10^{-2}}{10^{-4}}\right) = 0.888 \text{ V} \approx 0.89 \text{ V}$$



$$E(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}) = E^0(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}) + \frac{0.0592}{2} \log \frac{[\text{S}_2\text{O}_8^{2-}]}{[\text{SO}_4^{2-}]^2}$$

$$E(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}) = +2.05 + \frac{0.0592}{2} \log\left(\frac{10^{-4}}{1}\right) = 1.93 \text{ V}$$



$$E(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = E^0(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) + \frac{0.0592}{6} \log \frac{[\text{Cr}_2\text{O}_7^{2-}][\text{H}_3\text{O}^+]^{14}}{[\text{Cr}^{3+}]^2}$$

$$E(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = +1.36 + \frac{0.0592}{6} \log\left(\frac{10^{-3} \times (10^{-3})^{14}}{(10^{-1})^2}\right) = 0.9357 \text{ V} \approx 0.94 \text{ V}$$

Exercise 5.

In a neutral solution, the formation of HSO_4^- is negligible, and we can reasonably assume:

$$C_{\text{ZnSO}_4} = [\text{SO}_4^{2-}] = [\text{Zn}^{2+}] = 5 \times 10^{-4} \text{ M}$$

Potential of the lead electrode:

$$E_{\text{PbSO}_4/\text{Pb}} = E_{\text{PbSO}_4/\text{Pb}}^0 - \frac{0.0592}{2} \log [\text{SO}_4^{2-}] = -0.35 - \frac{0.0592}{2} \log (5 \times 10^{-4}) = -0.252 \text{ V}.$$

$$E_{\text{PbSO}_4/\text{Pb}} = -0.252 \text{ V}.$$

Potential of the zinc electrode:

$$E_{\text{Zn}^{2+}/\text{Zn}} = E_{\text{Zn}^{2+}/\text{Zn}}^0 + \frac{0.0592}{2} \log [\text{Zn}^{2+}] = -0.763 + \frac{0.0592}{2} \log (5 \times 10^{-4}) = -0.860 \text{ V}.$$

$$E_{\text{Zn}^{2+}/\text{Zn}} = -0.860 \text{ V}.$$

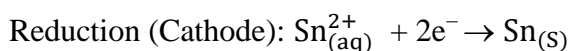
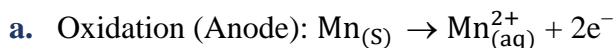
Cell potential:

$$E_{\text{Cell}} = E_{\text{Right}} - E_{\text{Left}}.$$

$$E_{\text{Cell}} = E_{\text{PbSO}_4/\text{Pb}} - E_{\text{Zn}^{2+}/\text{Zn}} = -0.252 - (-0.860) = 0.608 \text{ V}.$$

$$E_{\text{Cell}} = 0.608 \text{ V}.$$

Exercise 6.



$$E_{\text{Cell}}^0 = E_{\text{cat}}^0 - E_{\text{an}}^0 = -0.14 + 1.18 = 1.04 \text{ V}$$

b. $E_{\text{Right}} = E_{\text{Sn}^{2+}/\text{Sn}}^0 + \frac{0.0592}{2} \log [\text{Sn}^{2+}] = -0.14 + \frac{0.0592}{2} \log (0.01) = -0.199 \text{ V}$

$$E_{\text{Left}} = E_{\text{Mn}^{2+}/\text{Mn}}^0 + \frac{0.0592}{2} \log [\text{Mn}^{2+}] = -1.18 + \frac{0.0592}{2} \log (2.0) = -1.17 \text{ V}$$

$$E_{\text{Cell}} = E_{\text{Right}} - E_{\text{Left}} = -0.199 + 1.17 = 0.971 \text{ V} \approx 0.97 \text{ V}.$$

c. $E_{\text{Right}} = E_{\text{Sn}^{2+}/\text{Sn}}^0 + \frac{0.0592}{2} \log [\text{Sn}^{2+}] = -0.14 + \frac{0.0592}{2} \log (2.0) = -0.131 \text{ V}$

$$E_{\text{Left}} = E_{\text{Mn}^{2+}/\text{Mn}}^0 + \frac{0.0592}{2} \log [\text{Mn}^{2+}] = -1.18 + \frac{0.0592}{2} \log (0.01) = -1.239 \text{ V}$$

$$E_{\text{Cell}} = E_{\text{Right}} - E_{\text{Left}} = -0.131 + 1.239 = 1.108 \text{ V} \approx 1.11 \text{ V}.$$

Exercise 7.

a) Electrode potentials

Platinum electrode ($\text{Fe}^{3+}/\text{Fe}^{2+}$ system):

$$E_{\text{Pt}} = E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.0592 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = 0.7286 \text{ V} \approx 0.729 \text{ V}$$

Thallium electrode (Tl^+/Tl system):

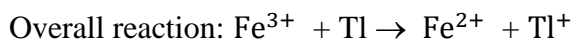
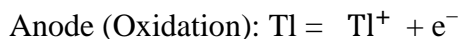
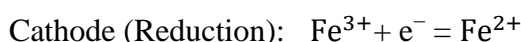
$$E_{\text{Tl}} = E^0(\text{Tl}^+/\text{Tl}) + 0.0592 \log [\text{Tl}^+] = -0.458 \approx -0.46 \text{ V}.$$

b) Electrode polarity and electromotive force

Since the platinum electrode has the higher potential, it acts as the positive electrode (cathode). The thallium electrode is the negative electrode (anode).

$$E = E_{\text{Right}} - E_{\text{Left}} = \text{emf} = 1.189 \text{ V}.$$

c) Half-cell reactions and overall cell reaction



d) Equilibrium constant

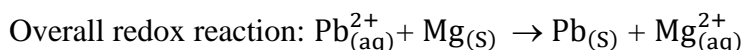
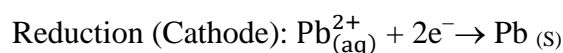
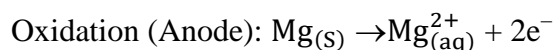
From the relation:

$$\log k = \frac{0.77 + 0.34}{0.0592} = 18.75 \quad k = 10^{18.75}$$

The value of the equilibrium constant indicates that the reaction is essentially complete.

Exercise 8.

(a) Half-reactions:



Standard cell potential:

$$E_{\text{Cell}}^0 = E_{\text{cat}}^0 - E_{\text{an}}^0 = E_{\text{Pb}}^0 - E_{\text{Mg}}^0 = -0.13 + 2.37 = 2.24 \text{ V}$$

Standard Gibbs free energy change:

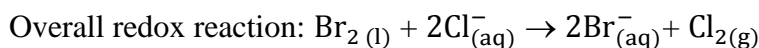
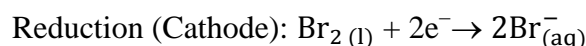
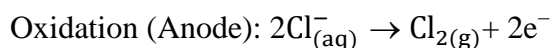
$$\Delta G^\circ = -n F E_{\text{Cell}}^0 = -2 \cdot 96485 \cdot 2.24 = -4.32 \times 10^5 \text{ J}\cdot\text{mol}^{-1} \approx -432 \text{ KJ}\cdot\text{mol}^{-1}.$$

Since $\Delta G^\circ < 0$, the reaction is spontaneous under standard conditions.

Equilibrium constant (K°):

$$K^\circ = e^{\frac{-\Delta_r G^\circ}{RT}} = e^{\frac{-(-432 \times 10^3)}{8.314 \times 298}} = 5.314 \times 10^{75} \approx 5.31 \times 10^{75}$$

(b) Half-reactions:



Standard cell potential:

$$E_{\text{Cell}}^0 = E_{\text{cat}}^0 - E_{\text{an}}^0 = 1.09 - 1.36 = -0.27 \text{ V}$$

Standard Gibbs free energy change:

$$\Delta G^\circ = -n F E_{\text{Cell}}^0 = -2 \cdot 96485 \cdot (-0.27) = 52101.9 \text{ J} = +5.21 \times 10^4 \text{ J}\cdot\text{mol}^{-1} \approx +52.1 \text{ KJ}\cdot\text{mol}^{-1}.$$

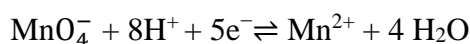
Since $\Delta G^\circ > 0$, the reaction is non-spontaneous under standard conditions.

Equilibrium constant (K°):

$$K^\circ = e^{\frac{-\Delta_r G^\circ}{RT}} = e^{\frac{-(+52.1 \times 10^3)}{8.314 \times 298}} = 7.368 \times 10^{-10} \approx 7.4 \times 10^{-10}$$

Exercise 9.

a. Redox equilibrium involved and Nernst equation expression:



The corresponding Nernst equation is:

$$E = E^0 + \frac{0.0592}{5} \log \left(\frac{[\text{MnO}_4^-] \times [\text{H}^+]^8}{[\text{Mn}^{2+}]} \right)$$

This can be rearranged to:

$$E = 1.5 - 0.0947 \text{ pH} + 0.0118 \log \left(\frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} \right) \quad (1)$$

Expression for the apparent standard potential

By definition, the **apparent standard potential** E'^0 is the cell potential where:

$$[\text{MnO}_4^-] = [\text{Mn}^{2+}] = 1 \text{ M} \quad (2)$$

Substituting (2) into equation (1) simplifies the expression to:

$$E'^0 = 1.5 - 0.0947 \text{ pH} \quad (3)$$

Calculations of E'^0 at different pH values

- At **pH = 3.0**:
 $E'^0 = +1.2159 \approx + 1.216 \text{ V}$
- At **pH = 4.0**:
 $E'^0 = +1.1212 \approx + 1.121 \text{ V}$
- At **pH = 7.0**:
 $E'^0 = +0.8371 \approx + 0.837 \text{ V}$

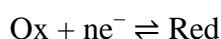
Conclusion: As the pH increases, the apparent standard potential E'^0 **decreases**. This means that the redox system becomes **less oxidizing** at higher pH values. The linear relationship between E'^0 and pH has a **negative slope** equal to - 0.0947.



Chapter II: Electrolysis

II.1 Electrochemical Reaction

An electrochemical reaction refers to a chemical transformation that is directly associated with the transfer of charge across an interface. The most typical example involves the movement of electrons across the boundary between a solid electrode and a liquid electrolyte. At its most fundamental level, this process may involve either the gain of electrons by a species in solution (reduction) or the loss of electrons from a species (oxidation), with the electrode serving as either the donor or acceptor of electrons. This can be generally represented by the following equation



This expression highlights that charge transfer at the electrode–electrolyte interface is intrinsically linked to chemical change—specifically, the interconversion between oxidized and reduced species. Moreover, the flow of electrons during this transfer constitutes an electric current. Consequently, monitoring this current can yield valuable insights into the underlying chemical processes. The direction of electron flow across an electrode interface determines the sign of the resulting electrical current. Two electrode reactions may co-occur with equal but opposite electrical currents, resulting in no net current being measured. More generally, a net current I_{net} may be measured, representing the excess charge transfer not balanced by the opposite process:

$$I_{\text{net}} = I_{\text{Ox}} + I_{\text{Red}}$$

Where:

I_{Ox} is the electrical current associated with oxidation (positive contribution).

I_{Red} is the electrical current associated with reduction (negative contribution).

In an electrical system, electrons transport the electrical current. In contrast, in a solution, charge transfer occurs through the movement of ions rather than electrons. Establishing electrical contact with an electrode is straightforward when using an electron-conducting electrode, but making contact with the solution requires immersing the conductor, thereby creating a second interface between the conductor surface and the solution. A preliminary conclusion is that electrochemical measurements always require at least two electrodes to perform and study an electron-transfer reaction.

An electrochemical cell requires a minimum of two electrodes, which are illustrated schematically in Figure II-1. These metallic electrodes are placed in an electrolyte solution and linked to a direct current (DC) source or an applied potential difference.

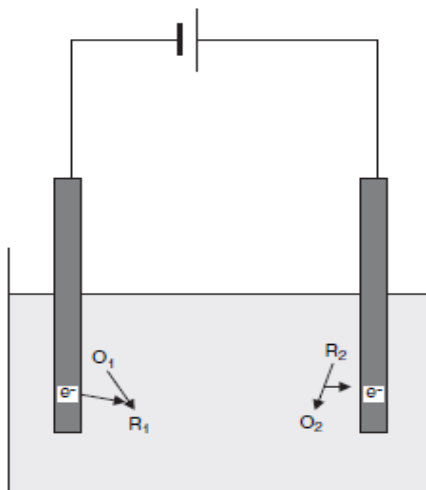


Figure II-1 Illustration of a potentiometric cell configuration with the anode on the right where oxidation occurs and the cathode on the left where reduction takes place.

Electrons flow from the negative terminal of the power source toward the electrode at that side, where they are accepted by chemical species in the solution (reduction). At the opposing electrode, oxidation occurs as electrons are released from chemical species and transferred to the electrode, continuing on to the positive terminal of the source.

This entire process ensures that:

Electrons enter the system at one electrode,

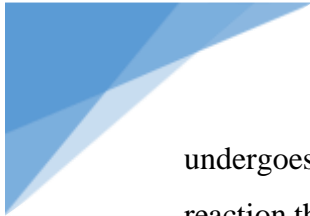
Electrons exit at the other electrode.

However, within the electrolyte, it is ions that mediate the transport of charge between the electrodes. As such, the overall electrochemical reaction is composed of two half-reactions:

A reduction reaction at one electrode ($Ox_1 + ne^- \rightleftharpoons Red_1$) and an oxidation reaction ($Red_1 \rightleftharpoons Ox_2 + ne^-$) at the other. Consequently, every electrochemical process involves two distinct steps, with each taking place at one of the two electrodes.

II.2 Electrolysis

Electrolysis is the process by which electrical energy is employed to initiate chemical transformations in a conductive medium, typically an aqueous solution or molten ionic solution. Under the influence of an externally applied current, the compound



undergoes decomposition into its elemental constituents. Since electrolysis involves a reaction that is not thermodynamically favorable ($\Delta_r G > 0$), it requires a continuous input of energy—commonly supplied by an external power source—to proceed.

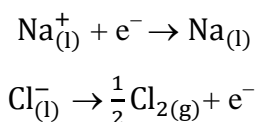
II.3 Electrolytic Cells

An electrolytic cell is a type of electrochemical system in which an external electric current is applied to drive a chemical reaction that would not occur spontaneously. This process, known as **electrolysis**, is fundamental to the large-scale production of various industrial substances such as aluminum and chlorine. A typical electrolytic setup consists of a container holding the electrolyte, two electrodes (anode and cathode), and an external power source connected via conductive wiring. This system is also referred to as a **voltmeter**, as it measures the voltage at its terminals.

II.4 Illustrative Examples of Electrolysis

II.4.1 Electrolysis of Molten Salts

Figure II-2 illustrates a basic electrolytic cell in which a battery supplies current to two electrodes immersed in molten sodium chloride (NaCl), which melts at 801°C. Metallic sodium appears at the cathode connected to the battery's negative pole, while chlorine gas is produced at the anode. The half-cell reactions involved in this process are:



As previously defined (see Chapter I), oxidation occurs at the anode, and reduction takes place at the cathode—a convention that applies to both electrolytic and voltaic cells. Accordingly, in the electrolysis of molten NaCl, sodium ions are reduced to sodium metal at the cathode, while chloride ions are oxidized to chlorine gas at the anode.

This process is applied industrially to extract sodium metal from sodium chloride. A commercially used cell for this purpose is the Downs cell, as shown in Figure II-3. This cell is specifically designed to keep the reaction products—sodium and chlorine—separated, as they would otherwise react with one another. Calcium chloride is mixed with sodium chloride to reduce the melting point from 801°C (for NaCl) to approximately 580°C. (This reflects the general principle that adding of a solute lowers the melting or freezing point of a substance.)

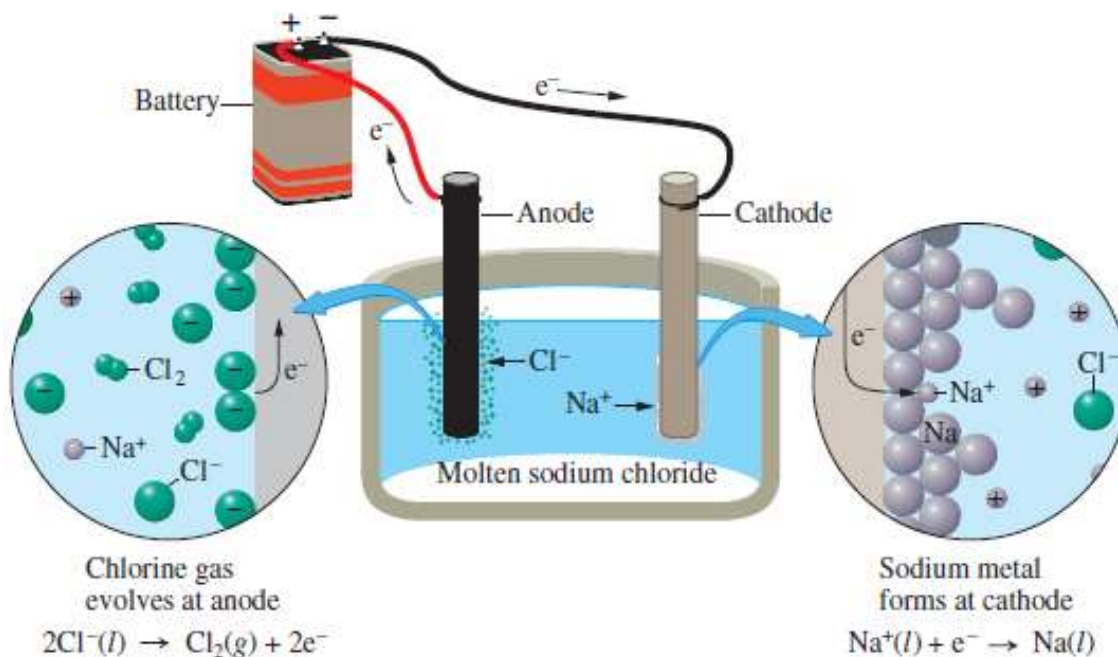


Figure II-2 Electrolysis of molten sodium chloride.

At the cathode, sodium metal is generated through the reduction of Na^{+} ions, while at the anode, chlorine gas is produced by the oxidation of Cl^{-} ions. This method is used industrially for sodium metal production, though commercial cells are specifically engineered to collect the products separately and prevent their interaction.

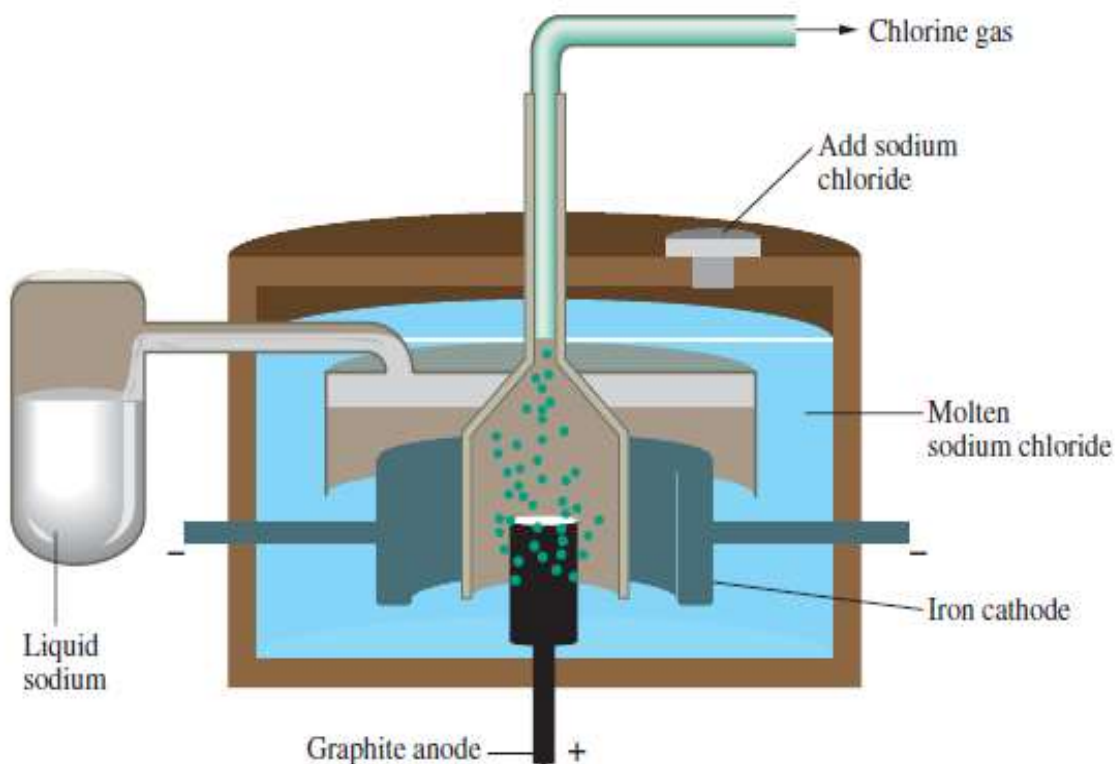
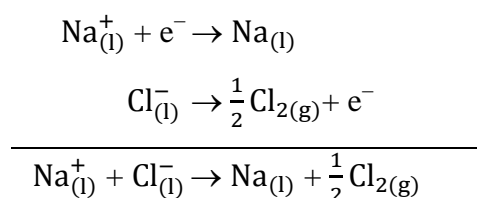


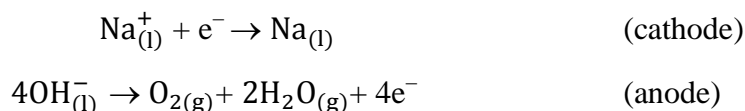
Figure II-3 Downs cell used for the production of sodium metal.

In this industrial electrolytic cell, sodium is obtained through the electrolysis of molten sodium chloride. Calcium chloride is incorporated into the mixture to reduce its melting point. At the cathode, liquid sodium forms and rises to the surface of the molten salt, where it is collected in a designated reservoir. Chlorine gas is simultaneously generated as a by-product.

The overall cell reaction results from combining the two half-reactions:



Other reactive metals, such as lithium, calcium, and magnesium, are similarly obtained through the electrolysis of molten chlorides. Historically, the first method for producing metallic sodium on a commercial scale was developed based on Humphry Davy's work in 1807, when he discovered sodium by electrolyzing molten sodium hydroxide (NaOH), which has a relatively low melting point of 318°C. The half-reactions for that process are:



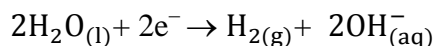
A significant number of industrial applications of electrolysis are based on aqueous solutions.

II.4.2 Aqueous Electrolysis

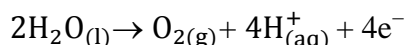
During the electrolysis of a molten salt, the half-reactions are typically restricted to the ions present in the salt. However, when an aqueous solution of an ionic compound is electrolyzed, water may also be involved in the reactions occurring at one or both electrodes.

Water may undergo oxidation or reduction during electrochemical reactions, resulting in distinct half-reactions. To determine these reactions, it is important to identify the species that may be involved. In this context, the relevant species are H₂O, H₂, O₂, H⁺, and OH⁻. Among these, only H₂ and O₂ reflect a change in oxidation state. In H₂, hydrogen has an oxidation state of 0, whereas in H₂O, it is +1. For oxygen, the oxidation state is 0 in O₂ and -2 in H₂O. This means that water can be reduced to H₂ or oxidized to O₂.

Focusing on the reduction half-reaction, the process involves the transformation of water into hydrogen gas by reduction. To balance this half-reaction, an oxygen-containing species must appear on the right side. Only the hydroxide ion (OH^-) presents oxygen in the same oxidation state as it has in water. The resulting balanced reduction half-reaction is:



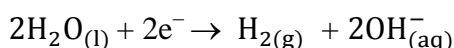
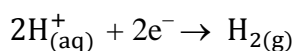
The oxidation half-reaction of water can be derived in a similar manner. It corresponds to the transformation of H_2O into O_2 by oxidation. To balance the equation, a chemical species providing hydrogen must be included among the products. Only H^+ maintains the same oxidation state for hydrogen as in water. The balanced oxidation half-reaction is:



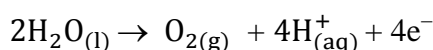
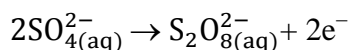
To illustrate the application of electrochemical principles, the following examples present typical half-reactions involved in the electrolysis of various aqueous solutions.

❖ Electrolysis of Sulfuric Acid Solutions

Understanding the electrolysis of a sulfuric acid (H_2SO_4) solution requires considering all possible half-reactions involving both the acid-derived ions and water to predict what may occur in this process. H_2SO_4 ionizes completely, producing H^+ and hydrogen sulfate ions (HSO_4^-). Due to its acidic nature, HSO_4^- is comparatively strong and, in most cases, dissociates into sulfate ions (SO_4^{2-}) and H^+ . As a result, the key species to consider in the system are H^+ , SO_4^{2-} and H_2O . At the cathode, the feasible reduction half-reactions are as follows:

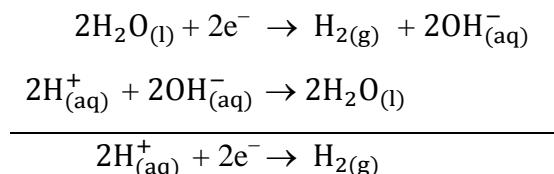


At the anode, the feasible oxidation half-reactions are as follows:



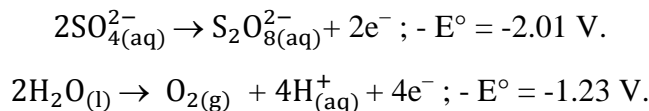
In the initial half-reaction, the sulfate ion (SO_4^{2-}) undergoes oxidation to form the peroxydisulfate ion ($\text{S}_2\text{O}_8^{2-}$). The $\text{S}_2\text{O}_8^{2-}$ ion includes a peroxy group ($-\text{O}-\text{O}-$), in which the oxygen atoms exhibit an oxidation state of -1. Consequently, within this half-reaction, oxygen is oxidized as its oxidation state increases from -2 to -1.

Let us analyze the cathode reaction. As can be readily demonstrated, in an acidic medium, the two possible reduction half-reactions—namely, the reduction of H^+ ions and that of H_2O —are fundamentally equivalent. When water is reduced, it produces hydrogen gas (H_2) and hydroxide ions (OH^-). In acidic solution, these OH^- ions react with H^+ ions to form water. The result is obtained by combining the two reactions.



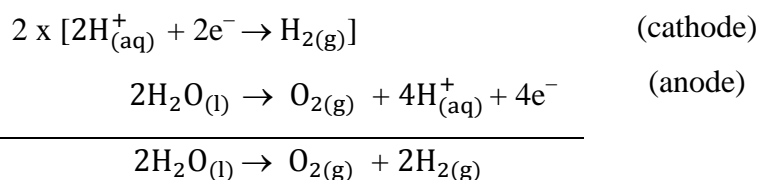
As can be seen, the cathodic process corresponds to the reduction of H^+ ions.

For the anode, it is necessary to consider the relevant oxidation half-reactions and their associated oxidation potentials, which are numerically equal to the corresponding electrode potentials but with reversed signs.:



The species with the higher (i.e., less negative) oxidation potential is more readily oxidized. Consequently, under standard conditions, H_2O is expected to undergo oxidation more readily than SO_4^{2-} .

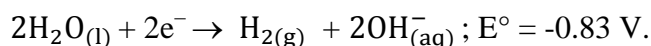
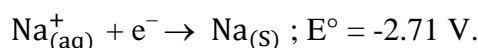
It is important to note a point of caution. Electrode potentials are determined under conditions where the half-reactions are at or near equilibrium. However, during electrolysis, the half-reactions may occur far from equilibrium, and as a result, a higher voltage than that predicted by electrode potentials may be required. This additional voltage, known as overvoltage, can be considerable—often amounting to several tenths of a volt—especially when a gas is produced. Therefore, when attempting to determine which of two half-reactions actually takes place at an electrode, particular attention must be paid if their electrode potentials differ by less than several tenths of a volt. For instance, although the standard oxidation potential for O_2 is -1.23 V , the actual potential required may be several tenths of a volt lower due to overvoltage. Nevertheless, the sulfate ion is extremely difficult to oxidize ($-E^\circ = -2.01 \text{ V}$), so the conclusion regarding the anode half-reaction during the electrolysis of aqueous sulfuric acid remains valid. The cell reaction is obtained by combining the half-reactions that occur at the electrodes.



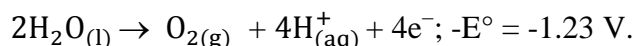
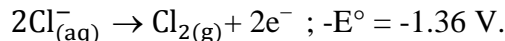
The overall cell reaction corresponds to the electrolysis of water. Where electricity is inexpensive, hydrogen can be commercially produced through this process. In this case, H_2SO_4 served as the electrolyte; however, a range of other electrolytes, such as NaCl , can also be employed.

❖ Electrolysis of Sodium Chloride Solutions

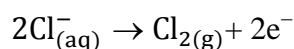
During the electrolysis of an aqueous solution of sodium chloride (NaCl), the species that may participate in the half-reactions include Na^{+} , Cl^{-} , and H_2O . The half-reactions occurring at the cathode are as follows:



Under standard conditions, H_2O is expected to be reduced rather than Na^{+} , which aligns with what is observed. Hydrogen gas is evolving at the cathode. The possible oxidation half-reactions at the anode are as follows:

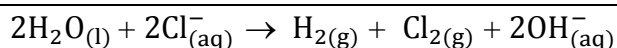
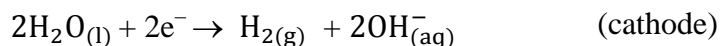


Although H_2O is expected to be oxidized rather than Cl^{-} , under standard-state conditions, the closeness of their potentials and the effect of overvoltages at the electrodes may affect this expectation. Nonetheless, a general remark can be made regarding the product predicted at the anode. Since electrode potentials depend on concentrations, Cl_2 is produced when the solution is sufficiently concentrated in Cl^{-} , whereas O_2 is formed in dilute solution. This can be shown by applying the Nernst equation to the $\text{Cl}^{-}/\text{Cl}_2$ half-reaction.



When beginning with highly dilute NaCl solutions, the oxidation potential of Cl^{-} is highly negative, resulting in the preferential reduction of H_2O rather than Cl^{-} . However, as the NaCl concentration increases, the oxidation potential of Cl^{-} also increases, until eventually the oxidation of Cl^{-} occurs in preference to H_2O —consequently, the product shifts from O_2 to Cl_2 . The half-reactions and the overall cell reaction involved in the

electrolysis of aqueous sodium chloride to produce chlorine and hydroxide ions are as follows:



Since the electrolysis process begins with sodium chloride, the cation present in the electrolyte solution is Na^+ . When the electrolyte solution is evaporated at the cathode, sodium hydroxide (NaOH) is obtained. A comparable process is shown in Figure II-4, which illustrates the electrolysis of aqueous potassium iodide (KI).



Figure II-4 Electrolysis of an aqueous solution of potassium iodide.

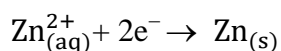
At the anode, iodine is formed by the oxidation of iodide ions (I^-). This iodine then reacts with iodide ions to produce the red-brown triiodide ion (I_3^-). At the cathode, hydrogen gas and hydroxide ions (OH^-) are formed through the reduction of water.

The industrial-scale electrolysis of aqueous sodium chloride forms the basis of the chlor-alkali industry, a key commercial method for producing both chlorine and sodium hydroxide. Although different types of commercial electrolysis cells are used, they all face the same primary challenge: preventing interaction between the products, as chlorine readily reacts with aqueous sodium hydroxide.

❖ Electroplating of Metals

To protect metals from corrosion, they are often plated with other metals that act as protective barriers. Steel is commonly coated with zinc because it provides cathodic

protection, which remains effective even when the zinc layer is scratched. A thin coating of zinc can be formed on steel by electrogalvanizing, also known as zinc electroplating. (In comparison, galvanized steel possesses a thicker zinc coating, which is achieved by immersing the object in molten zinc.) The steel object is submerged in a bath of zinc salts and serves as the cathode within an electrolytic cell. The cathodic half-reaction involved is:



Electrolysis is also employed for the purification of certain metals. For instance, copper intended for electrical applications requires a very high level of purity. The purification process involves using impure copper slabs as anodes and pure copper sheets as cathodes, with CuSO_4 serving as the electrolyte bath (Figure II-5). Throughout the electrolysis, copper(II) ions are released from the anode and are plated onto the cathode. Less reactive elements such as silver, gold, and platinum, which exist as impurities in the anode, accumulate as valuable mud at the bottom of the electrolytic cell. In contrast, metals that are more reactive than copper remain dissolved as ions in the electrolyte bath. After approximately one month of operation, the cathodes—now substantially thickened with deposited pure copper—are withdrawn from the electrolyte bath.

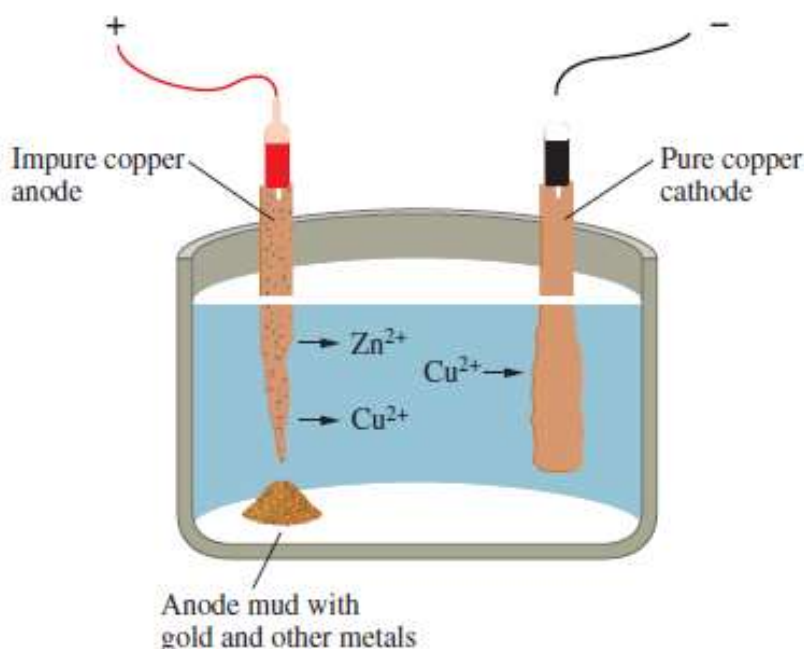


Figure II-5 Purification of copper by electrolysis

On the left, Cu^{2+} ions leave the impure copper anode and are plated onto the cathode. More reactive ions, such as Zn^{2+} , remain in solution, whereas less reactive elements,

including gold, accumulate beneath the anode as a mud. On the right, pure copper sheets are alternated with impure copper slabs inside the electrolytic tank. In about one month, the pure copper sheets gradually increase in size and are then removed.

II.5 Faraday Laws

II.5.1 First Law of Electrolysis

According to this law, the mass of a substance deposited or dissolved at an electrode during electrolysis is directly proportional to both the duration of electrolysis and the intensity of the electric current.

$$m \propto Q \quad \text{and} \quad Q = I.t$$

$$m \propto I.t$$

$$\Rightarrow m = Z. I.t$$

Where:

m is the mass of the substance deposited or liberated at the electrode

I is the electric current (in amperes),

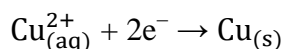
t is the time (in seconds) for which the current flows,

Z is the electrochemical equivalent of the ion,

Q is the total electric charge passed through the electrolyte, or the quantity of electricity.

II.5.2 Second Law of Electrolysis

This law asserts that the mass of a substance liberated or formed by the same amount of electric charge is directly proportional to its equivalent weight. For instance, in an electrolytic solution containing Cu^{2+} ions, the reduction process at the cathode follows the half-reaction:

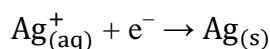


Since two electrons are involved and copper exhibits a valency of two, its equivalent weight is determined by dividing its atomic mass by the valency:

$$\text{Equivalent weight} = \frac{\text{atomic weight}}{\text{charge on ion}} = \frac{\text{atomic weight}}{\text{valency}}$$

Thus, for copper: $\frac{63.56}{2} = 31.78$

For silver, the relevant half-reaction is:



Here, the equivalent weight is equal to its atomic weight, 107.89, because only one electron participates in the reaction.

The electric charge carried by a single electron is 1.602×10^{-19} coulombs. Using this, the number of electrons corresponding to one Faraday (96500 C) can be calculated as:

$$\frac{96500}{1.602 \times 10^{-19}} = 6.03 \times 10^{23}$$

This value represents Avogadro's number. In other words, passing one Faraday of electricity through a solution delivers one Avogadro's number of electrons to the anode, provided by the oxidation of one equivalent of a substance, and these electrons subsequently cause a reduction at the cathode.

II.6 Comparison between the Galvanic Cell and the Electrolytic Cell

S/No	Electrolytic Cell	Galvanic Cell
1	Electrical energy is utilized during the process.	Electrical energy is produced during the process
2	The system converts electrical energy into chemical energy	The system transforms chemical energy into electrical energy.
3	Electrons flow from the anode to the cathode via an external electrical circuit	Electrons flow from the metal with higher electropositivity to the one with lower electropositivity
4	The electrodes may consist of either identical or different metallic elements	The electrodes must be made of two different metals.
5	The reaction does not occur spontaneously and requires an external energy source	The electrochemical reaction proceeds without external energy input
6	Oxidation takes place at the positively charged electrode (anode) whereas reduction occurs at the negatively charged electrode (cathode)	The reduction process takes place at the positive electrode (cathode) whereas the oxidation process takes place at the negative electrode (anode)
7	Both half-cell reactions occur within a single compartment containing either a solution or a molten electrolyte, eliminating the need for a salt bridge	The half-cells are arranged in separate compartments and linked via a salt bridge or a porous barrier
8	In this cell, the anode is positively charged and the cathode is negatively charged	In this cell, the anode carries a negative charge, while the cathode is positively charged
9	An external power source delivers electrons; they enter the system through the cathode and exit via the anode	Electrons flow from the anode to the cathode through the external circuit

Exercises

Exercise 1.

An aqueous solution of nickel(II) chloride is subjected to electrolysis at $\text{pH} = 0$, using graphite electrodes. The applied potential difference between the electrodes is 1.8 V.

- What is the sign of the Gibbs free energy change (ΔG) for an electrolytic reaction?
- For the system described, write the four-redox half-reactions that could, in principle, occur at the electrodes.
- In practice, chlorine gas is observed to evolve at one electrode, while metallic nickel is deposited at the other. Write the overall redox equation for the electrolysis process.

Data (Standard electrode potentials at $\text{pH} = 0$):

$E^\circ(\text{H}^+/\text{H}_2) = 0 \text{ V}$; $E^\circ(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V}$; $E^\circ(\text{Ni}^{2+}/\text{Ni}) = -0.26 \text{ V}$; $E^\circ(\text{Cl}_2/\text{Cl}^-) = 1.36 \text{ V}$.

Exercise 2.

Determine the likely half-reactions involved in the electrolysis of an aqueous copper(II) sulfate solution?

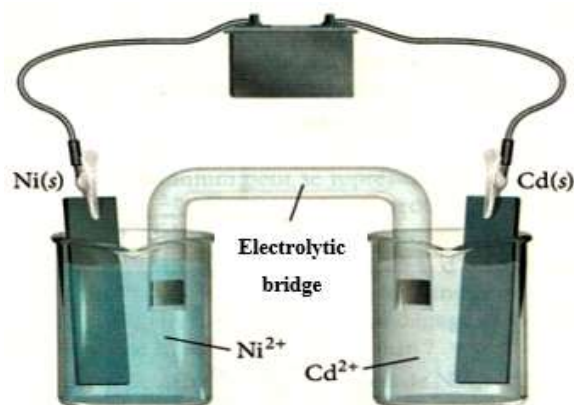
Exercise 3.

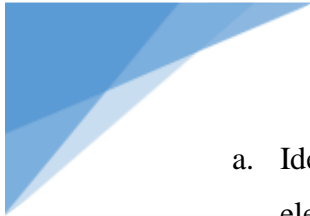
Draw an electrolytic cell in which Mn^{2+} is reduced to Mn and Sn is oxidized to Sn^{2+} . Identify the anode and the cathode, indicate the direction of electron flow, and write the half-equation occurring at each electrode. What is the minimum voltage required to drive the reaction?

Given: $E^\circ(\text{Mn}^{2+}/\text{Mn}) = -1.18 \text{ V}$; $E^\circ(\text{Sn}^{2+}/\text{Sn}) = -0.14 \text{ V}$.

Exercise 4.

Consider the following electrolytic cell:

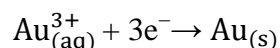


- 
- Identify the anode and the cathode, and write the half-reaction that occurs at each electrode.
 - Indicate the direction of electron flow.
 - Specify the sign (positive or negative) of each terminal of the power supply, and calculate the minimum voltage required for the reaction to proceed.

Given: $E^\circ(\text{Ni}^{2+}/\text{Ni}) = -0.23 \text{ V}$; $E^\circ(\text{Cd}^{2+}/\text{Cd}) = -0.40 \text{ V}$;

Exercise 5.

A solution containing Au^{3+} ions can be used to plate gold according to the following half-reaction:

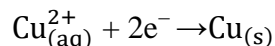


What mass of gold (in grams) can be deposited onto an object if a current of 5.5 A is applied for 25 minutes?

Given: $M_{\text{Au}} = 196.97 \text{ g/mol}$.

Exercise 6.

Copper electroplating can be carried out at the cathode of an electrolytic cell according to the following half-reaction:



How long would it take to plate 225 mg of copper if a current of 7.8 A is applied?

Exercise 7.

A constant electric current was applied to a solution containing AuCl_4 ions using gold electrodes. After 10 minutes, the mass of the cathode increased by 1.394 g.


Determine the total charge passed and the current intensity.

Given: atomic mass of gold, $\text{Au} = 197 \text{ g/mol}$.

Exercise 8.

A rechargeable concentration cell is composed of two half-cells, each containing a silver electrode (Ag^+/Ag) with a volume of 2.0 L. The concentration of Ag^+ ions is 1.25 mol. L^{-1} in one half-cell and $10^{-3} \text{ mol. L}^{-1}$ in the other.

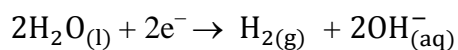
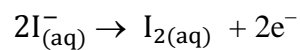
- What mass of silver is deposited on the cathode if the cell delivers a constant current of 3.5 A for 5.5 hours?
- During the recharging process, how much time would be required to dissolve exactly 100 g of silver using a current of 10 A?



Given that: $E^\circ(\text{Ag}^+ / \text{Ag}) = 0.80 \text{ V}$; $M_{\text{Ag}} = 107.868 \frac{\text{g}}{\text{mol}}$; $F = 96485 \frac{\text{C}}{\text{mol e}^-}$

Exercise 9.

During the electrolysis of an aqueous potassium iodide (KI) solution using platinum electrodes, the electrode half-reactions are as follows:



Calculate the mass of iodine (I_2) formed when a current of 8.52 mA is passed through the cell for a duration of 10.0 min.

Solutions

Exercise 1.

- a. Electrolysis is a reaction that is not thermodynamically favorable ($\Delta rG > 0$), but is made possible through the input of external energy supplied by a power source.
- b. In an aqueous solution at $\text{pH} = 0$, the species that can be oxidized are: H_2O and Cl^- , while those that can be reduced are: H^+ and Ni^{2+} .

Half-reactions:

<i>Oxidation half-reactions theoretically possible at the anode (positive terminal)</i>	<i>Reduction half-reactions theoretically possible at the cathode (negative terminal)</i>
(1) $\text{H}_2\text{O}_{(l)} = \frac{1}{2} \text{O}_{2(g)} + 2\text{H}_{(aq)}^+ + 2e^-$	(3) $2\text{H}_{(aq)}^+ + 2e^- = \text{H}_{2(g)}$
(2) $2\text{Cl}_{(aq)}^- = \text{Cl}_{2(g)} + 2e^-$	(4) $\text{Ni}_{(aq)}^{2+} + 2e^- = \text{Ni}_{(s)}$

- c. The decreasing order of the standard potentials of the four couples is:

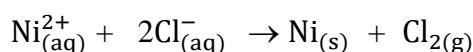
$$E^\circ(\text{Cl}_2/\text{Cl}^-) > E^\circ(\text{O}_2/\text{H}_2\text{O}) > E^\circ(\text{H}^+/\text{H}_2) > E^\circ(\text{Ni}^{2+}/\text{Ni})$$

According to this thermodynamic order, H_2O should be oxidized according to (1), and H^+ ions should be reduced according to (3), at potentials lower than those required for the oxidation of Cl^- ions and the reduction of Ni^{2+} ions, according to (2) and (4) respectively. With an applied electrolysis voltage of **1.8 V**, which exceeds the potential difference between the two most extreme standard potentials:

$$E^\circ(\text{Cl}_2/\text{Cl}^-) - E^\circ(\text{Ni}^{2+}/\text{Ni}) = 1.36 \text{ V} - (-0.26 \text{ V}) = 1.62 \text{ V}$$

All four half-reactions listed above are theoretically expected. However, experimentally, only **chlorine gas evolution** and **nickel deposition** are observed.

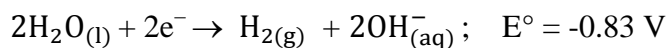
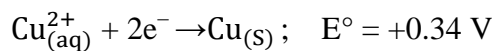
Overall reaction (electrolysis):



Exercise 2.

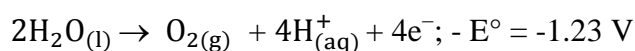
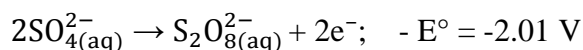
The relevant species to consider are: $\text{Cu}_{(\text{aq})}^{2+}$, $\text{SO}_{4(\text{aq})}^{2-}$, and H_2O .

At the cathode, the possible reduction half-reactions are:



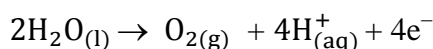
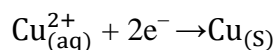
Since the standard electrode potential of copper is considerably more positive than that of water, the reduction of Cu^{2+} is expected to occur at the cathode

At the anode, the possible oxidation half-reactions include:



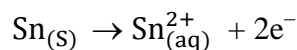
Given these values, water is more likely to undergo oxidation at the anode.

Therefore, the expected overall half-reactions are:

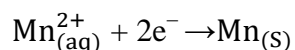


Exercise 3.

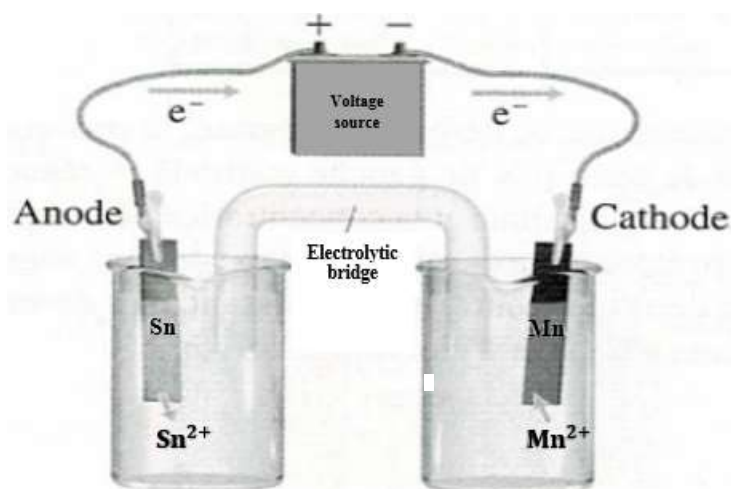
Tin (Sn) serves as the anode, where oxidation occurs:



Manganese (Mn^{2+}) is reduced at the cathode:



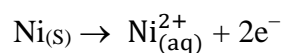
Electrons flow from the anode to the cathode through the external circuit.



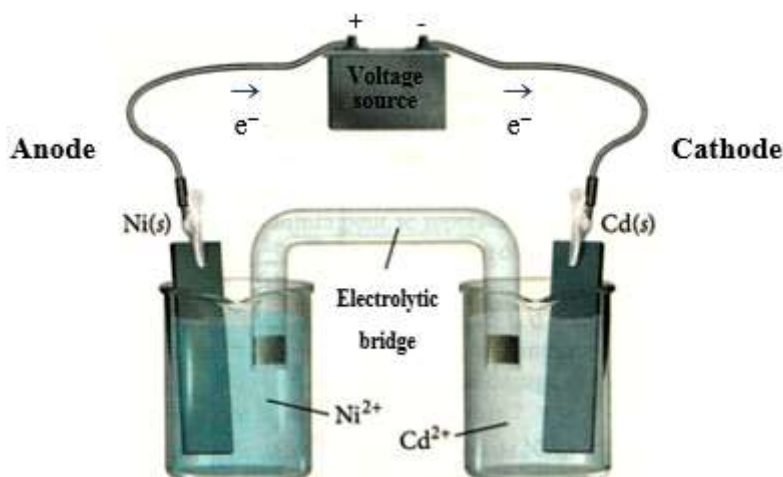
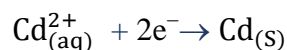
The minimum voltage that must be applied by the power supply is: 1.04V

Exercise 4.

a. Ni forms the anode, and the oxidation reaction is:



Cd forms the cathode, and the reduction reaction is:



b. Electrons flow from the anode (Ni) to the cathode (Cd) through the external circuit.

c. The anode is connected to the **positive** terminal of the power supply, and the cathode is connected to the **negative** terminal.

The **minimum voltage** that must be applied is 0.17 V.

Exercise 5.

$$t = 25 \text{ mn} = 25 \times 60 = 1500 \text{ S.}$$

Using the electrolysis mass formula:

$$m = \frac{M \cdot Q}{n \cdot F} = \frac{196.97 \times 1500 \times 5.5}{3 \cdot 96485} = 5.6 \text{ g Au.}$$

Exercise 6.

To determine the required time, we use the relation:

$$m = \frac{M \cdot Q}{n \cdot F} = \frac{M \times I \times t}{n \times F}$$

$$\Rightarrow t = \frac{m \times n \times F}{M \times I} = \frac{225 \times 10^{-3} \times 2 \times 96485}{63.55 \times 7.8} = 87.59 \text{ s} \approx 88 \text{ s.}$$

Approximately 88 seconds are required to deposit 225 mg of copper under a current of 7.8 A.

Exercise 7.

Relevant half-reaction: $\text{Au}_{(\text{aq})}^{3+} + 3\text{e}^{-} \rightarrow \text{Au}_{(\text{s})}$

We use the relation:

$$m = Zit \Rightarrow I = \frac{m}{Zt}$$

Where the electrochemical equivalent Z is calculated as:

$$Z = \frac{\text{Atomic mass}}{\text{No of Faraday}} = \frac{197}{3 \times 96485} \approx 6.8 \times 10^{-4} \text{ g/C}$$

Now substituting values:

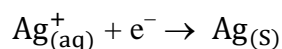
$$I = \frac{1.394}{Z \times 600} = 3.4166 \approx 3.42 \text{ A}$$

$$Q = I \times t = 3.42 \times 600 = 2052 \text{ C}$$

The total charge passed through the solution was approximately 2052 C, and the current applied was about 3.42 A.

Exercise 8.

a. Mass of silver deposited at the cathode:



Using Faraday's law:

$$m = \frac{M \cdot Q}{n \cdot F} = \frac{M \times I \times t}{n \times F}$$

$$m = \frac{107.868 \times 3.5 \times 5.5 \times 3600}{1 \times 96485} = 77.4757 \approx 77.476 \text{ g}$$

b. Time required to dissolve 100 g of silver during recharging:

$$t = \frac{m \times n \times F}{M \times I} = \frac{100 \times 1 \times 96485}{107.868 \times 10} = 8944.7287 \text{ s} = 2.48 \text{ h.}$$

Exercise 9.

First, calculate the total electric charge transferred:

$$Q = I \times t = (8.52 \times 10^{-3} \text{ A}) \cdot (10.0 \text{ min} \times 60 \text{ s/min}) = 5.11 \text{ C}$$

It is important to recognize that the formation of 1 mole of iodine (I_2) requires the transfer of 2 moles of electrons. Therefore,

$$m = \frac{M \cdot Q}{n \cdot F}$$

$$m = \frac{254 \times 5.11}{2 \times 96485} = 6.726 \times 10^{-3} \approx 6.73 \times 10^{-3} \text{ g I}_2$$

Approximately 6.73 mg of iodine (I_2) is produced under these conditions.



Chapter III: Electrochemical thermodynamics

III.1 Construction of E-pH diagrams

III.1.1 Diagrams in Electrochemistry

Predominance diagrams provide thermodynamic information in a visual form, enabling rapid prediction of the possible chemical evolutions of a system. It must, however, be emphasized with great care that these are purely thermodynamic data. All kinetic aspects are therefore completely disregarded. Since electrochemical kinetics can be very slow, some predicted reactions might either not occur at all or proceed only very slowly.

III.1.2 Pourbaix Diagrams (E-pH)

The potential-pH diagram (or Pourbaix diagram), plotted for a given element, shows a predominance domain for each dissolved species and an existence domain for each solid species. Horizontal, vertical, or sloping boundary line segments separate the different domains. The molar concentration used for plotting, denoted C_T , of the dissolved species is fixed, and along a boundary line segment, the atomic concentrations of the element are equal.

In practical applications, Pourbaix diagrams serve as valuable tools in fields such as corrosion science, electroplating, electrowinning, electrolysis, hydrometallurgy, electrochemical cells, and water treatment. These diagrams act as electrochemical maps that delineate the stability domains of ions, oxides, and hydroxides. This diagram represents the oxidizing strength within an electrochemical system, expressed in terms of potential, together with the acidity and alkalinity of the species, expressed as pH. Consequently, reactions involving hydroxyl ions (OH^-) are conventionally expressed in terms of proton concentration $[\text{H}^+]$, which is directly related to pH via $\text{pH} = -\log[\text{H}^+]$.

In addition to predicting the reactions likely to occur within a given electrochemical environment, simplified Pourbaix diagrams highlight three fundamental regions used in the interpretation and design of electrochemical systems: corrosion, passivation, and immunity. Nevertheless, a Pourbaix diagram does not provide information on the corrosion rate, which remains a key parameter in kinetic investigations.

III.1.2.1 Principles of Construction

Potential-pH diagrams are intended to illustrate the influence of pH on the apparent potentials of half-reactions involving the same element. Their value lies in providing a concise summary of the predominant or existing species. The construction of these diagrams, however, is based on several conventions that allow their plotting:

1. The temperature is taken as 25 °C unless otherwise specified;
2. Activities are assumed to be equal to concentrations;
3. Only oxides or hydroxides are considered;
4. Solids are assigned a unit activity, as they exist alone in their phase;
5. The concentration of the element is fixed.

It is essential to always specify the plotting concentration C , as the overall shape of the diagrams depends strongly on it. The convention adopted at the boundaries must also be stated. Several conventions exist, but the most common are:

1. At the boundary, the concentrations of the oxidant and reductant are equal, and both are equal to the plotting concentration, C ;
2. The total concentration of the element is equal to the plotting concentration. In this case, for the I_2/I^- couple at the boundary: $2 [I_2] = [I^-]$ and $2 [I_2] + [I^-] = C$.

For gases, the standard-state pressure is generally taken as 1 bar. A given diagram should allow for the location of the different species, which is achieved by following a two-step procedure:

1. Classify the species according to the oxidation state of the element and place them on a vertical axis: species with the highest oxidation state at the top, the most reduced at the bottom;
2. For species with the same oxidation state, arrange their acid–base forms: the most acidic to the left, the most basic to the right.

The table thus constructed provides a preliminary view of the general appearance of the diagram. To proceed with the complete construction of the diagram, it is necessary to:

1. Calculate the positions of the vertical boundaries (between acid–base species);
2. Write the half-reactions for all half-couples (for each horizontal boundary);
3. Plot the boundaries as a function of pH. The slope is generally negative and is given, in most cases, by $-\frac{0.06 \bar{v}_{H^+}}{n}$ pH, where n is the number of electrons

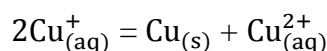
exchanged and $\bar{\nu}_{H^+}$ is the stoichiometric number of protons in the redox half-equation written in the direction of oxidation;

4. Check whether there are domains in which the plotted line indicates a disproportionation reaction; in such a case, the correct half-couple with the stable species must be rewritten.
5. Throughout this chapter, the value 0.06 V is used in the Nernst equation as a simplified approximation of the constant $\frac{2.303RT}{F}$ at 25 °C, which is more precisely 0.0592 V. This simplification is made to facilitate clearer calculations and graphical constructions in an educational context. For precise thermodynamic calculations, the value 0.0592 V should be used.

▪ **Note – Disproportionation Reaction**

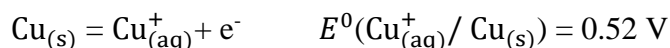
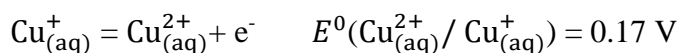
A **disproportionation** reaction occurs when the same species acts simultaneously as the oxidant in one half-couple and as the reductant in another half-couple, with the predominance domains for each half-couple being separate. There is then disproportionation, producing both higher and lower oxidation states.

The simplest example is that of copper(I):



Here, copper in the +I oxidation state disproportionates into one species in the 0 oxidation state and another in the +II oxidation state.

For the half-couples $\text{Cu}_{(\text{aq})}^{2+}/\text{Cu}_{(\text{aq})}^+$ and $\text{Cu}_{(\text{aq})}^+/\text{Cu}_{(\text{s})}$, the corresponding half-reactions (written as oxidations) and their standard potentials are:

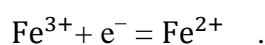


A) Predominance Domains

❖ Redox couple

Example:

Redox couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ ($E^0 = 0.77 \text{ V}$ at 298 K):

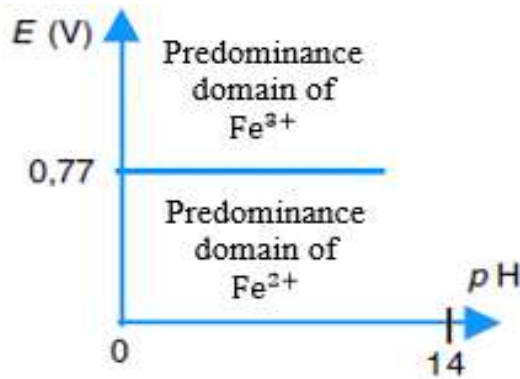


The Nernst equation is written as:

$$E = E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.06 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$E > 0.77 \text{ V} \Leftrightarrow [\text{Fe}^{3+}] > [\text{Fe}^{2+}]$: the Fe^{3+} ion predominates over the Fe^{2+} ion.

$E < 0.77 \text{ V} \Leftrightarrow [[\text{Fe}^{2+}] > [\text{Fe}^{3+}]]$: the Fe^{2+} ion predominates over the Fe^{3+} ion.



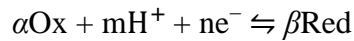
We have: $[\text{Fe}^{3+}] + [\text{Fe}^{2+}] = C_T$

On the boundary line segment separating the two domains, the equality of the atomic concentrations of the element Fe is written as:

$$[\text{Fe}^{3+}] = [\text{Fe}^{2+}]$$

Therefore $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = \frac{C_T}{2} \Rightarrow E = 0.77 \text{ V}$.

Consider a redox couple Ox/Red, whose half-equation is:



We then have:

$$E = E^0 + \frac{0.06}{n} \log \frac{a_{\text{Ox}}^\alpha}{a_{\text{Red}}^\beta} + m \frac{0.06}{n} \log [\text{H}^+].$$

The potential of the Ox/Red couple therefore depends on the pH.

The expression of the potential becomes:

$$E = E^0 + \frac{0.06}{n} \log \frac{a_{\text{Ox}}^\alpha}{a_{\text{Red}}^\beta} - 0.06 \frac{m}{n} \text{pH}$$

Suppose the ratio of the activities of the oxidant and the reductant is fixed such that:

$$\frac{a_{\text{Ox}}^\alpha}{a_{\text{Red}}^\beta} = K$$

Where K is a constant. The expression of the potential of the redox couple then becomes:

$$E_K = E^0 + \frac{0.06}{n} \log K - 0.06 \frac{m}{n} \text{pH}$$

This is the equation of a straight line ($y = ax + b$) in the (E, pH) plane, with:

- A slope: $a = -0.06 \frac{m}{n}$
- An intercept: $b = E^0 + \frac{0.06}{n} \log K$
- **Note:**

In general, the slopes are negative (m is positive).

In the case where $m = 0$, this line is horizontal.

As shown in the following figure (Figure III-1), this line divides the (E, pH) plane into two domains:

- **Above the line ($E > E_K$):**

This corresponds to a ratio of redox species activities such that:

$$\frac{a_{\text{Ox}}^\alpha}{a_{\text{Red}}^\beta} > K$$

The oxidant is said to predominate.

- **Below the line ($E < E_K$):**

This corresponds to a ratio of redox species activities such that:

$$\frac{a_{\text{Ox}}^\alpha}{a_{\text{Red}}^\beta} < K$$

The reductant is said to predominate.

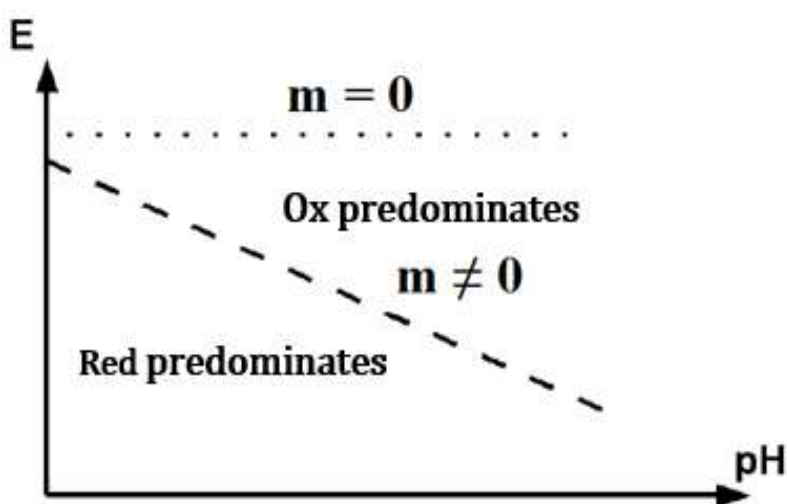


Figure III-1 Representation of the redox potential of a couple in the (E, pH) plane.

For a given redox couple, we can thus define two predominance domains in the (E, pH) plane. The boundary between these two domains is a straight line whose equation requires specifying a condition on the ratio of the activities of the Ox and Red species, known as the boundary convention.

The predominance domain of the oxidant lies above the line, and that of the reductant lies below it.

- ❖ **Acid/Base Couple**

The predominance domains of the species in an acid–base couple AH/A^- do not depend on the potential (since the oxidation number of the elements is identical in both species). On an E–pH diagram, a vertical line (vertical boundary) at $pH = pK_a$ therefore separates the predominance domains of AH and A^- (see Figure III-2).

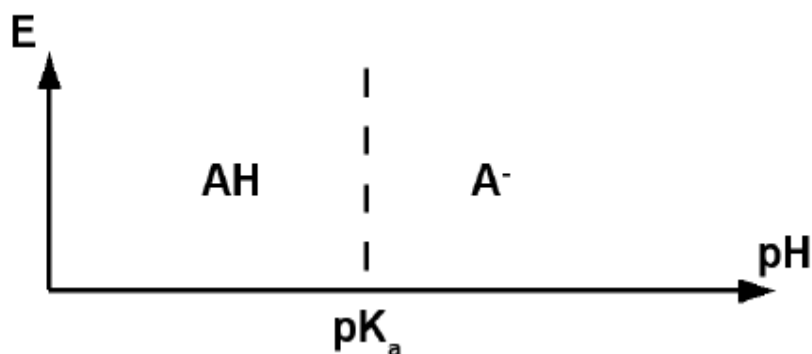
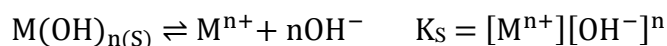


Figure III-2 Schematic predominance diagram of the species in an acid–base couple.

❖ Precipitate/Cation

We consider here hydroxides of the form $M(OH)_{n(S)}$, whose dissociation equilibrium is written as:



If the total quantity of element M is fixed—corresponding to a concentration $[M^{n+}]_0$ when no precipitate is present—the condition for the existence of a hydroxide is given by:

$$Q \geq K_S \quad \text{or equivalently} \quad [OH^-] \geq \left(\frac{K_S}{[M^{n+}]_0} \right)^{\frac{1}{n}}$$

The hydroxide thus exists if:

$$pH \geq pH_0 = pK_i - \frac{pK_S}{n} - \frac{\log [M^{n+}]_0}{n}$$

(where pK_i is the negative logarithm of the ion product of water, i.e., pK_w)

The (E, pH) plane can therefore be divided into two domains by a vertical line at $pH = pH_0$. To the left of this boundary, only the cation M^{n+} exists with concentration $[M^{n+}]_0$. To the right, we enter the domain of existence of the hydroxide $M(OH)_{n(S)}$.

Remark:

- The position of the boundary depends on the total concentration $[M^{n+}]_0$ of element M.
- In the case where a precipitate forms, we define a **domain of existence** rather than a **domain of predominance**.

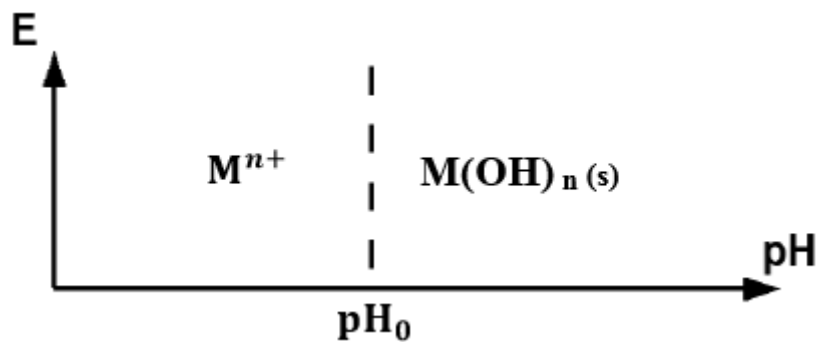
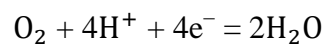


Figure III-3 Schematic predominance diagram of species: hydroxide precipitate/metal cation couple.

B) Potential–pH Diagram of Water

In an aqueous medium, it is essential to consider the action of water on the species present.

- **Case of the $O_2(g)/H_2O$ couple ($E^0 = 1.23$ V):**



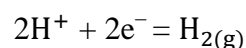
which corresponds to the oxidation of water into O_2 (reaction written from right to left).

The Nernst relation is expressed as:

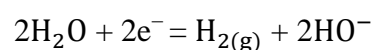
$$E = 1.23 - 0.06 \text{ pH (for } pO_2 = 1 \text{ bar)}$$

If $E < 1.23 - 0.06 \text{ pH}$, the oxidation of water does not occur.

- **Case of the $H^+/H_2(g)$ couple ($E^0 = 0$ V):**



or equivalently,



which corresponds to the reduction of water to H_2 .

The Nernst relation is given by:

$$E = - 0.06 \text{ pH (for } pH_2 = p^0 = 1 \text{ bar)}$$

If $E > -0.06$ pH, the reduction of water does not occur.

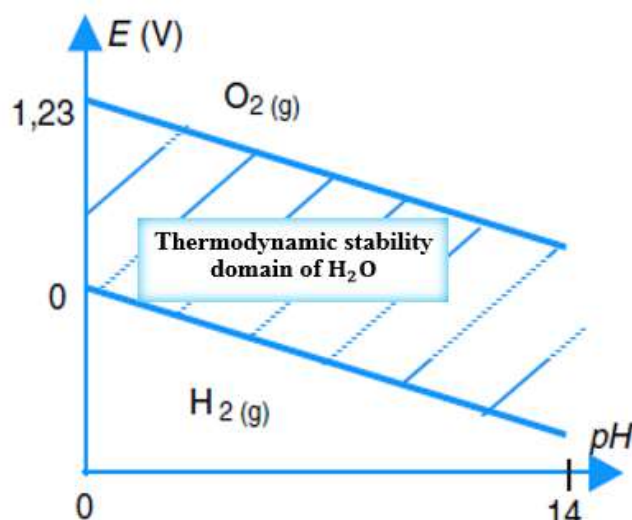


Figure III-4 Potential-pH diagram of water: thermodynamic stability domain of H₂O.

The two lines $E = f(\text{pH})$ are parallel (having the same slope).

The thermodynamic stability domain of water lies between these two lines.

C) Use of a Potential–pH Diagram


- If the stability domain of a species from a redox couple Ox/Red overlaps with the thermodynamic stability region of water, no reaction occurs between this species and H₂O. Conversely, if no such overlap exists, a reaction will take place (involving either oxidation or reduction of water).
- By superimposing the potential–pH diagrams of two elements, it is possible to predict, on thermodynamic grounds, whether two species will react with each other depending on whether they have a common domain or not.

D) Applications of Potential–pH Diagrams

1. Calculation of Thermodynamic Constants

From an E–pH diagram, it is possible to determine the values of the thermodynamic constants that were employed in its construction:

- Standard potential E^0 of a redox couple, obtained from the intercept of the boundary line separating the predominance or existence domains of the species belonging to that couple. It is important to exercise caution, since the equations of



certain boundary lines depend on the plotting parameter, such that the intercept does not directly provide the value of E^0 . Furthermore, in Pourbaix's work, the pH range considered extends from -2 to 16, and the ordinate axis is omitted from all figures. It is therefore necessary to reconstruct this axis, defined by the equation $\text{pH} = 0$, which is indispensable for determining the intercepts.


- Acidity constant of a weak acid, obtained from the vertical line separating the predominance domains of the two species AH and A^- . The equation of this line does not depend on the plotting parameter, provided that both species are soluble. The pK_a of the acid–base couple can thus be determined directly.
- Solubility product of a hydroxide, obtained from the vertical boundary line separating the predominance domain of the metallic ion M^{y+} from the **existence** domain of the hydroxide $\text{M}(\text{OH})_y$. The equation of this line depends on the plotting parameter. The relation $\text{pH}_A = \frac{1}{y}\text{pC}_i + \text{pK}_i - \frac{1}{y}\text{pK}_S$ allows the calculation of the pH at which the precipitate first appears.
- Other equilibrium constants.

It must be remembered that chemical equilibria do not involve the potential; as a result, the corresponding boundary lines are always vertical. This applies, for example, to the equilibrium corresponding to the re-dissolution of a hydroxide precipitate in an alkaline medium.

2. Prediction of Reactions

When two redox couples are brought into contact, the stronger oxidant reacts with the stronger reductant of the other couple. The reaction proceeds more or less quantitatively depending on the difference between the standard potentials of the two couples, as outlined by the gamma rule described in Chapter I. However, the predictions derived from this empirical rule remain approximate. Indeed, most redox potentials depend not only on the activity of the redox species involved but also on the pH. Therefore, experimental conditions must be taken into account to determine the redox potentials.

An E-pH diagram makes it possible to predict the direction of displacement of a redox equilibrium, provided that the representative lines of the two redox couples involved have been plotted.



At a given pH, let us denote by **A** the point on the diagram corresponding to the initial experimental conditions for couple (1), and by **B** that corresponding to couple (2). Points **A** and **B** lie on a vertical line. If point **A** lies above point **B**, the redox equilibrium $Ox_1 + Red_2 = Red_1 + Ox_2$ is displaced in direction (1): $Ox_1 + Red_2 \rightarrow Red_1 + Ox_2$. In this case, Ox_1 reacts with Red_2 to produce Ox_2 and Red_1 . The greater the potential difference between points **A** and **B**, the more the equilibrium is shifted in the direction (1). Conversely, if point **B** lies above point **A**, the equilibrium is displaced in the direction (2).

In general, to predict whether two species can coexist, there must exist a boundary line separating the two domains corresponding to these species; this boundary being the manifestation of a chemical or redox equilibrium.

The use of an E-pH diagram is therefore essential to determine whether a species is thermodynamically stable in an aqueous medium. Any redox species whose predominance domain (for dissolved species) or existence domain (for solid species) lies within the thermodynamic stability domain of water is stable in aqueous solution.

If point **A**, with coordinates $(pH_{(A)}, E_{(A)})$, which represent the experimental conditions of the system, lies below the thermodynamic stability domain of water, the reduced form (Red) of the redox couple in question reduces the solvent, releasing dihydrogen.

Conversely, if point **A** lies above the thermodynamic stability domain of water, the oxidized form (Ox) of the redox couple under consideration oxidizes the solvent, resulting in the release of dioxygen.

3. Application to the Study of Corrosion in aqueous media

E-pH diagrams may be used to make predictions concerning the behavior of metals with respect to corrosion in aqueous media.

For a given metal, the E-pH diagram is constructed for a low plotting parameter C_i (for example, $C_i = 10^{-4}$ or $10^{-6} \text{ mol L}^{-1}$). It is reasonable to assume that a total concentration of dissolved species lower than 10^{-4} or $10^{-6} \text{ mol L}^{-1}$ does not correspond to significant corrosion of the metal.

The **immunity domain** coincides with the existence domain of the metal in oxidation state 0.

The predominance domain(s) of the dissolved species (metal ions) constitute(s) the **corrosion domain**.

Finally, the existence domain(s) of solid species other than the metal in oxidation state 0 constitute(s) the **passivation domain**. This domain is so named because, in aqueous media, if a metal becomes covered with a layer of insoluble hydroxide or oxide, this layer may prevent further in-depth corrosion of the metal.

III.2 Electrochemical kinetics

Electrochemical reactions occur at the electrode/electrolyte interfaces, where charge transfer (CT) takes place with a characteristic rate that depends on the redox system, the electrode material, and the applied potential. For electron transfer to proceed, the electroactive species must be transported from the bulk solution to the interface, and the reaction products must be removed, as illustrated in the Figure III-5, where mass transport is denoted (MT). In this figure, a reduction reaction is considered: the oxidized species (Ox) migrates from the bulk solution (denoted by an asterisk) toward the interface (at $x = 0$). The reduced species (Red), generated by the electrochemical reaction, is then transported back into the bulk solution.

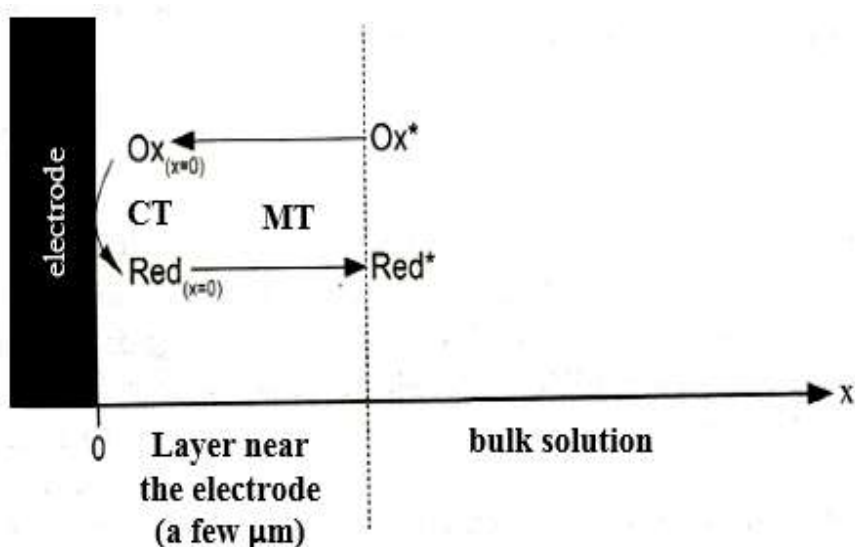


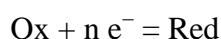
Figure III-5 Charge transfer (CT) and mass transport (MT) in an electrochemical reaction.

Consequently, in electrochemical kinetics, it is always necessary to take into account two competing phenomena: electron transfer and mass transport. The slower of the two determines the overall rate of the reaction. In electrochemical systems, mass transport can occur through three distinct mechanisms:

- A) **Migration**: the movement of charged species induced by an electric potential gradient, that is, within an applied electric field.
- B) **Diffusion**: the spontaneous movement of species from regions of higher concentration toward regions of lower concentration, driven by the concentration gradient.
- C) **Convection**: the transport of species resulting either from fluid motion caused by density differences within the medium (natural convection) or from externally induced forces such as stirring or pumping (forced convection).

III.2.1 Rate of an Electrochemical Reaction

Let us consider the redox half-equation:



involving two soluble species, Ox and Red. According to Faraday's law, the amount of species X formed (Ox or Red), denoted n_X , is proportional to the total electric charge passed, Q :


$$n_X = \frac{Q}{nF} \quad (1)$$

It is important to recall that we are dealing with a heterogeneous reaction that takes place at the surface of an electrode. Consequently, the electrode area S must be taken into account in the expression of the rate of an electrochemical reaction. This rate—defined as the number of moles formed or consumed per unit time and per unit surface area—can be deduced from Faraday's law by differentiating equation (1) with respect to time:

$$v = \frac{1}{S} \frac{dn_X}{dt} = \frac{1}{nFS} \frac{dQ}{dt} = \frac{I}{nFS} = \frac{J}{nF} \quad (2)$$

Since the current, I, passing through the electrode, is defined as the rate of charge flow with respect to time, we can see that the rate of an electrochemical reaction is directly proportional to the current. This makes it a quantity that is readily measurable using a simple ammeter.

The rate of an electrochemical reaction is expressed in $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, which is the same unit as a material flux. Moreover, the definition of v can be conveniently expressed in terms of the current density, $J = \frac{I}{S}$.



By convention, anodic currents are assigned positive values, while cathodic currents are taken as negative, in accordance with the recommendations of the International Union of Pure and Applied Chemistry (IUPAC).

Thus, studying the kinetics of an electrochemical reaction essentially amounts to examining the intensity of the current that flows.

III.2.2 Tafel's Empirical Law

In 1905, Tafel established an experimental relationship between the overpotential and the observed current in the simple case of an electrochemical reaction where mass transport does not intervene (e.g., the electrolysis of water). This law, which can be generalized to many systems, is written as:

$$\eta = a + b \log |I| \quad (3)$$

It expresses the variation of the overpotential as a function of the decimal logarithm of the current intensity. In practice, it is often preferable to use the current density, J , in the logarithmic term.

Tafel's law applies to reactions occurring either at the anode or at the cathode. In such cases, the overpotentials are expressed as:

$$\eta_a = a_a + b_a \log |I_a| \quad (4)$$

$$\eta_c = a_c + b_c \log |I_c| \quad (5)$$

The parameters a_a and a_c represent the intercepts in the linear Tafel plot, in which the electrode potential (or the overpotential) is plotted on the abscissa and the decimal logarithm of the absolute value of the current intensity on the ordinate. The parameters b_a and b_c (expressed in volts) are called the anodic and cathodic Tafel slopes, respectively. In many cases, b_a is close to +120 mV and b_c is close to -120 mV.

III.2.3 Fick's Laws of Diffusion

Diffusion is the phenomenon in which the mass of matter is transferred as a result of random motion. According to **Fick's** postulate, the matter flux J across a specified plane is directly proportional to the concentration gradient across that plane. In a finite volume of a conductive medium—such as a silicon substrate or an electrolyte—this

concentration gradient ($\partial C/\partial x$) decreases as the transferred matter redistributes uniformly within the finite volume. Consequently, if the matter is chemically inactive, concentration homogeneity can be attained throughout the finite volume.

For an isotropic and homogeneous medium with a diffusion coefficient (diffusivity) D ($10^{-6} \frac{\text{cm}^2}{\text{s}} \leq D < 10^{-4} \frac{\text{cm}^2}{\text{s}}$ for most cations), the rate of transfer of matter (ions, atoms, or molecules) is described by **Fick's First Law**. Although diffusion is fundamentally a three-dimensional process, it is often sufficient to consider its description within isotropic media.

The general forms of **Fick's laws** distinguish between steady-state conditions ($\frac{\partial C}{\partial t} = 0$) and non-steady, or transient, conditions ($\frac{\partial C}{\partial t} \neq 0$).

$$J_n = - \sum_{n=1}^3 D_{nn} \frac{\partial C}{\partial x_n} \quad (\text{first law})$$

$$\frac{\partial C}{\partial t} = \sum_{n=1}^3 D_{nm} \frac{\partial^2 C}{\partial x_{nm}^2} = - \frac{\partial J_n}{\partial x_n} \quad (\text{second law})$$

Here, $\frac{\partial C}{\partial t}$ denotes the concentration rate ($\text{mol} \cdot \text{cm}^{-3} \text{s}^{-1}$). The indices $n, m = 1, 2, 3$ correspond to the spatial coordinates, with $x_1 = x, x_2 = y$, and $x_3 = z$. Because mixed partial derivatives are equal, one has $\frac{\partial^2 C}{\partial x_{nm}^2} = \frac{\partial^2 C}{\partial x_{mn}^2}$. By symmetry, the diffusivity satisfies $D_{nm} = D_{mn}$.

Fick's laws provide the theoretical foundation for determining diffusivity in both isotropic and anisotropic systems. In most cases, a one-dimensional treatment is sufficient to approximate diffusion behavior. Under this assumption, Fick's laws can be simplified to describe diffusion along the x -direction in isotropic media:

$$J_x = -D \frac{\partial C}{\partial x} \quad (\text{first law}) \quad (6)$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} = - \frac{\partial J_x}{\partial x} \quad (\text{second law}) \quad (7)$$

These expressions indicate that both the molar flux and the concentration rate depend exclusively on the concentration gradient along the x -direction, since $\partial C/\partial y = \partial C/\partial z = 0$. Consequently, the diffusion flow is oriented perpendicular to the moving plane of the

solute. General solutions of Fick's second law can be found in the literature for specific diffusion problems in two-component systems, for instance an electrode sheet placed in or suspended within a liquid solution. In natural diffusion involving ionic mass transport, the current density (i) is a fundamental kinetic parameter, as it represents the rate of oxidation (corrosion) or reduction (electrodeposition). In this case, together with $J_d = J$ (where J_d denotes the diffusion molar flux driven by the concentration gradient dC/dx ($\text{mol}\cdot\text{cm}^{-2}\text{s}^{-1}$)), the current density may also be expressed as a function of the concentration gradient:

At the anode (oxidation)

$$i_a = + zFD \frac{\partial C}{\partial x} \quad (8)$$

At the cathode (reduction)

$$i_c = -zFD \frac{\partial C}{\partial x} \quad (9)$$

Another important kinetic parameter in electrochemical systems is the exchange current density (i_0), which plays a key role in describing electrochemical processes. It represents the common current density for both the oxidation and reduction reactions occurring within a given electrochemical cell. By definition, i_0 corresponds to the current density in the absence of an applied electric field, where the overpotential is zero ($\eta = 0$). Thus


$$i_{0,a} = + \frac{RTD}{\eta} \frac{\partial C}{\partial x} \quad \text{for oxidation} \quad (10)$$

$$i_{0,c} = - \frac{RTD}{\eta} \frac{\partial C}{\partial x} \quad \text{for reduction} \quad (11)$$

This indicates that, at equilibrium, $i_{0,a} = -i_{0,c}$, confirming that the anodic and cathodic current densities are equal in magnitude but opposite in direction when $\eta \rightarrow 0$. Furthermore, in the preceding expressions, the diffusion coefficient, or the diffusivity (D) is considered to be independent of the concentration (C). It can be expressed in the form of an Arrhenius-type relation (Svante Arrhenius, 1889):

$$D = D_0 \exp\left(-\frac{U^*}{RT}\right) \quad (12)$$

In this context, D_0 denotes the diffusion constant (cm^2/s), and U^* represents the activation energy ($\text{J}\cdot\text{mol}^{-1}$).



The Arrhenius equation is formulated for the rate constant (K_c) of chemical reactions at absolute temperature T . It is expressed in the generalized form:

$$K_c = A \exp\left(-\frac{E_A}{RT}\right) = A \exp\left(-\frac{E_A}{K_B T}\right) \quad (13)$$

where A is the pre-factor (reaction constant), which depends on the order of the reaction; E_A is the activation energy, assumed to be temperature-independent over an appropriate range of T ; R is the universal gas constant; and K_B is the Boltzmann constant. The Arrhenius relation is widely applicable, as expressed in Eq. (12).

Exercises

Exercise 1.

Draw the E–pH diagram of the iron system considering the following species: Fe^{3+} , Fe^{2+} , Fe(s) , $\text{Fe(OH)}_3\text{(s)}$, and $\text{Fe(OH)}_2\text{(s)}$,

The working concentration is set as:

$$[\text{Fe}]_{\text{tot}} = C_0 = 10^{-2} \text{ mol.L}^{-1}$$

The following thermodynamic data are provided:

$$K_S(\text{Fe(OH)}_3) = K_{S1} = 10^{-38} \quad E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) = E_1^0 = 0,77 \text{ V}$$

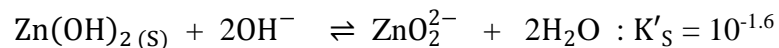
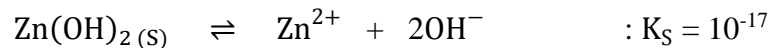
$$K_S(\text{Fe(OH)}_2) = K_{S2} = 10^{-15} \quad E^0(\text{Fe}^{2+}/\text{Fe(s)}) = E_2^0 = -0,44 \text{ V}$$

Exercise 2.

Draw the E–pH diagram of the zinc systems for $[\text{Zn}]_{\text{dissolved}} = 10^{-2} \text{ mol/L}$.

Given data:

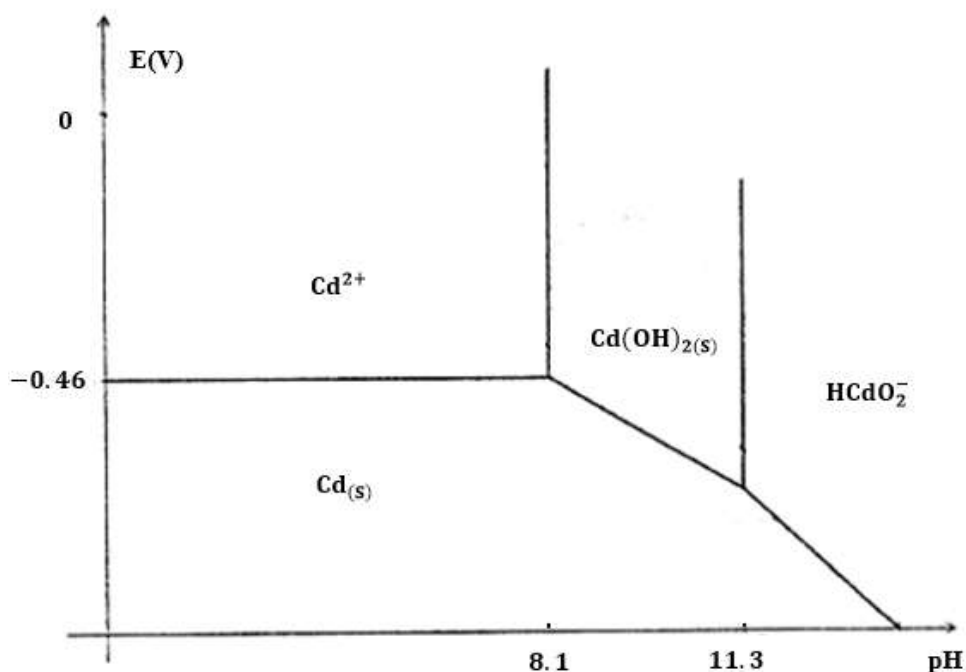
$$\text{Zn}^{2+}/\text{Zn} : E^0 = -0.76 \text{ V.}$$



Exercise 3.

The following potential–pH diagram is given for a dissolved cadmium concentration of

$[\text{Cd}]_{\text{dissolved}} = 10^{-2} \text{ mol.L}^{-1}$.



1. Determine E^0 ($\text{Cd}^{2+}/\text{Cd}_{(s)}$).
2. Calculate the solubility products associated with $\text{Cd}(\text{OH})_2$ (s).
3. Derive the equations of the straight lines represented in the diagram.
4. Discuss what would theoretically occur if cadmium were placed in water.

Data: $E^0(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V}$; $E^0(\text{H}^+/\text{H}_{2(\text{g})}) = 0 \text{ V}$

Exercise 4.

Given the standard potential of the redox system $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ à $\text{pH} = 0.0$:

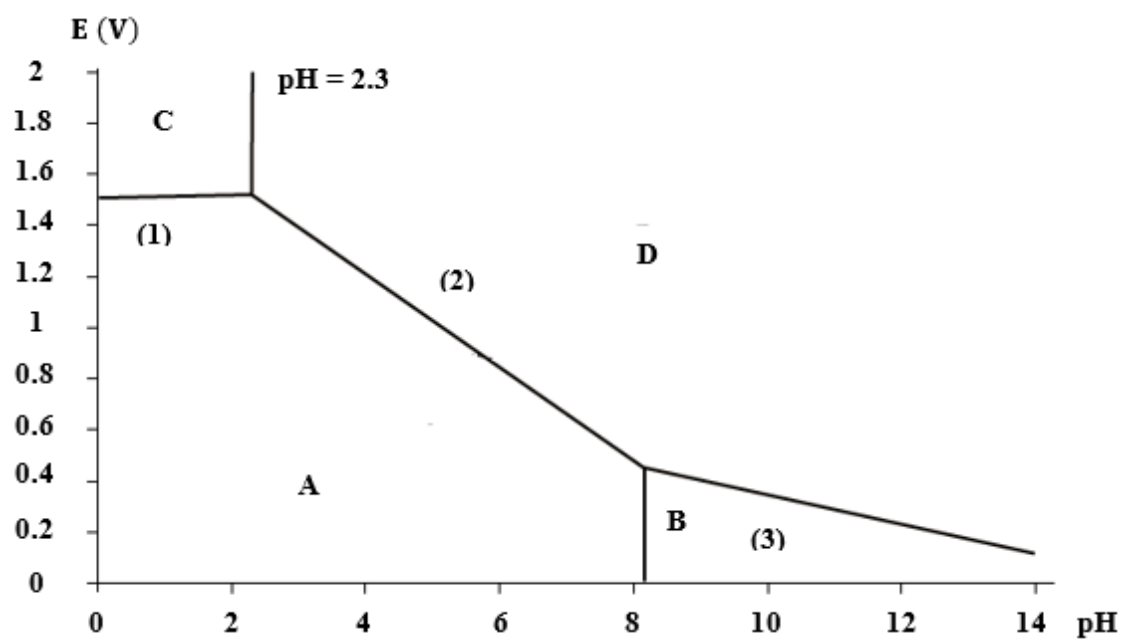
- a. Plot the potential–pH diagram for $0 \leq \text{pH} \leq 5.0$, assuming concentrations of 10^{-2} M for both the oxidized and reduced species.
- b. Calculate the potential of this system at $\text{pH} = 3.0$ and at $\text{pH} = 4.0$.

Data: $E^0_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = +1.35 \text{ V}$; $\text{Cr}(\text{OH})_3$: $\text{p}K_S = 30.0$

Exercise 5.

This diagram (given below) is constructed for the following species: Mn^{2+} , Mn^{3+} , $\text{Mn}(\text{OH})_2$, and the hydrated oxide Mn_2O_3 , denoted as $\text{Mn}(\text{OH})_3$. The plotting convention adopted is as follows: dissolved manganese species are assigned a total concentration of $0.10 \text{ mol} \cdot \text{L}^{-1}$, and at any boundary, only the two forms of the corresponding redox couple are taken into account.

1. Assign, with justification, the different domains of the diagram to the corresponding species, specifying whether they represent domains of existence or of predominance.
2. Calculate the slope of the boundary (2).
3. Which boundaries would be modified if the total concentration were changed?



Solutions

Exercise 1.

❖ **Classification of species by oxidation number and acid–base character**

As a first step, we draw up a simple table classifying the species according to their oxidation number (O.N.) and their acid–base behavior.

Initial Classification

O.N. (Fe)	Species	
+III	Fe^{3+}	$\text{Fe}(\text{OH})_3(\text{s})$
+II	Fe^{2+}	$\text{Fe}(\text{OH})_2(\text{s}),$
0	$\text{Fe}(\text{s})$	

Vertical separations

In the same row of the previous table, species with the same oxidation number coexist, but they correspond to acid–base couples. The first thing to do is therefore to determine the predominance (or existence) domains of these species before considering the redox couples, in order to avoid unnecessary work.

In our example, depending on the respective values of K_{S1} and K_{S2} , two possible cases may arise:

Case a:

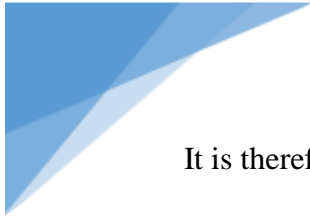
O.N.(Fe)	Species	
+III	Fe^{3+}	$\text{Fe}(\text{OH})_3(\text{s})$
+II	Fe^{2+}	$\text{Fe}(\text{OH})_2(\text{s}),$
0	$\text{Fe}(\text{s})$	

Case b:

O.N.(Fe)	Species	
+III	Fe^{3+}	$\text{Fe}(\text{OH})_3(\text{s})$
+II	Fe^{2+}	$\text{Fe}(\text{OH})_2(\text{s}),$
0	$\text{Fe}(\text{s})$	

The boundaries to be determined between the oxidation states +II and +III of iron are not identical in the two cases:

- Case a: $\text{Fe}^{3+}/\text{Fe}^{2+}$; $\text{Fe}(\text{OH})_3(\text{s})/\text{Fe}^{2+}$; $\text{Fe}(\text{OH})_3(\text{s})/\text{Fe}(\text{OH})_2(\text{s})$
- Case b: $\text{Fe}^{3+}/\text{Fe}^{2+}$; $\text{Fe}^{3+}/\text{Fe}(\text{OH})_2(\text{s})$; $\text{Fe}(\text{OH})_3(\text{s})/\text{Fe}(\text{OH})_2(\text{s})$



It is therefore essential to first establish which of these two situations applies.

In this context, the vertical separations correspond to the precipitation limits of the two iron hydroxides, $\text{Fe}(\text{OH})_2(\text{s})$ and $\text{Fe}(\text{OH})_3(\text{s})$. They are defined as follows:

- For $\text{Fe}(\text{OH})_2(\text{s})$:

$$[\text{Fe}^{2+}][\text{OH}^-]^2 = K_{S2}$$

At the precipitation limit, $[\text{Fe}^{2+}] = C_0$, thus:

$$[\text{OH}^-] = \sqrt{\frac{K_{S2}}{C_0}} \Rightarrow \text{pH} = 7.5$$

- For $\text{Fe}(\text{OH})_3(\text{s})$:

$$[\text{Fe}^{3+}][\text{OH}^-]^3 = K_{S1}$$

At the precipitation limit, $[\text{Fe}^{3+}] = C_0$, thus:

$$[\text{OH}^-] = \left(\frac{K_{S1}}{C_0}\right)^{\frac{1}{3}} \Rightarrow \text{pH} = 2$$

Therefore, the system corresponds to case (a).

❖ Boundary Equations

To construct the complete diagram, it remains necessary to determine the equations of five boundaries:

$\text{Fe}^{3+}/\text{Fe}^{2+}$; $\text{Fe}(\text{OH})_3(\text{s})/\text{Fe}^{2+}$; $\text{Fe}(\text{OH})_3(\text{s})/\text{Fe}(\text{OH})_2(\text{s})$; $\text{Fe}^{2+}/\text{Fe}(\text{s})$; and $\text{Fe}(\text{OH})_2(\text{s})/\text{Fe}(\text{s})$

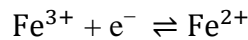
The order in which these boundaries are determined has no influence on the final diagram. However, it is recommended to proceed in the following sequence:

upper left corner \rightarrow lower left \rightarrow upper right \rightarrow lower right.

This approach allows for a stepwise construction of the diagram while avoiding possible disproportionation reactions, which would otherwise require reconsideration of the redox couples involved.

- **Fe³⁺/Fe²⁺:**

For this couple (pH ≤ 2)



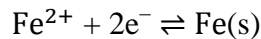
$$E_1 = E_1^0 + 0.06 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

At the boundary, $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = \frac{C_0}{2}$, hence:

$$E_1 = E_1^0 = \mathbf{0.77 \text{ V}}$$

- **Fe²⁺/Fe(s):**

For this couple (pH ≤ 7.5)



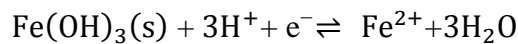
$$E_2 = E_2^0 + 0.03 \log [\text{Fe}^{2+}]$$

At the boundary, $[\text{Fe}^{2+}] = C_0$, thus:

$$E_2 = E_2^0 + \mathbf{0.03 \log C_0 = -0.50 \text{ V}}$$

- **Fe(OH)₃(s)/Fe²⁺:**

For this couple (2 ≤ pH ≤ 7.5)



$$E_3 = E_3^0 + 0.06 \log \frac{[\text{H}^+]^3}{[\text{Fe}^{2+}]}$$

The boundary for this couple can be written as:

$$E_3 = A_3 - \mathbf{0.18 \text{ pH}}$$

A_3 is a constant that depends on E_3^0 , the standard redox potential of the Fe(OH)₃(s)/Fe²⁺ couple (which is not known), and on the boundary convention. Although E_3^0 could in principle be calculated to determine A_3 , it is also possible to proceed by reasoning through continuity. At pH = 2, the redox potential calculated from the Fe³⁺/Fe²⁺ couple and from the Fe(OH)₃(s)/Fe²⁺ couple must coincide, which implies:

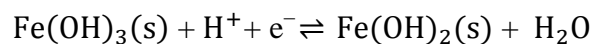
$$E_1(\text{pH} = 2) = E_3(\text{pH} = 2) \Rightarrow A_3 - 0.18 \times 2 = 0.77$$

Finally, we obtain:


$$E_3 = \mathbf{1.13 - 0.18 \text{ pH}}$$

- **Fe(OH)₃(s)/Fe(OH)₂(s):**

For this couple (pH ≥ 7.5), we have:



$$E_4 = E_4^0 + 0.06 \log [\text{H}^+]$$



The boundary for this couple can therefore be expressed as:

$$E_4 = A_4 - 0.06 \text{ pH}$$

The constant A_4 is obtained by continuity at $\text{pH} = 7.5$, for which $E_3 = E_4$, i.e.:

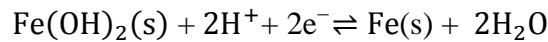
$$A_4 - 0.06 \times 7.5 = 1.13 - 0.18 \times 7.5$$

Hence, we deduce:

$$\mathbf{E_4 = 0.23 - 0.06 \text{ pH}}$$

▪ **Fe(OH)₂(s)/Fe(s):**

For this couple ($\text{pH} \geq 7.5$), we have:



$$E_5 = E_5^0 + 0.03 \log [\text{H}^+]^2$$

The boundary for this couple can therefore be written as:

$$E_5 = A_5 - 0.06 \text{ pH}$$

The constant A_5 is obtained by continuity at $\text{pH} = 7.5$, for which $E_2 = E_5$, i.e.:

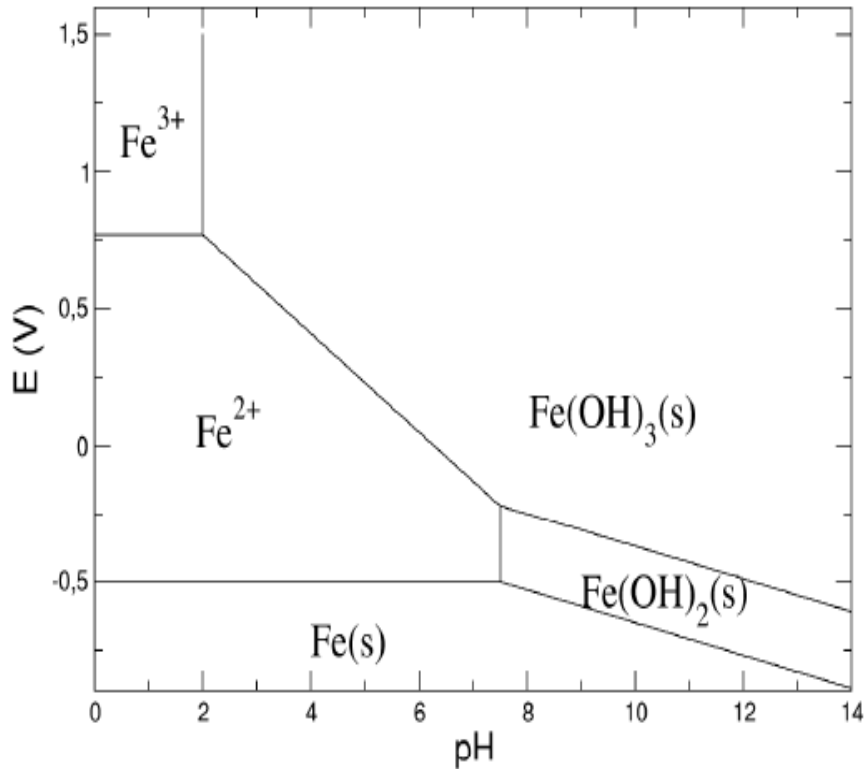
$$A_5 - 0.06 \times 7.5 = -0.50$$

Thus, we obtain:

$$\mathbf{E_5 = -0.05 - 0.06 \text{ pH}}$$

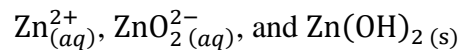
❖ **Construction of the Diagram**

The complete E–pH diagram is constructed progressively by plotting each boundary equation within its corresponding pH domain.



Exercise 2.

Zinc in the oxidation state (+II) may exist in three different forms:



The compound zinc hydroxide $\text{Zn(OH)}_{2(s)}$ is described as an **amphoteric hydroxide**.

- Its **basic character** is reflected by the equilibrium constant K_S .
- Its **acidic character** is demonstrated by the equilibrium constant K'_S .

Method for Constructing the E–pH Diagram of the Zn (II) / Zn (0) System

1. Determine the pH values at which the hydroxide precipitates, respectively from $\text{Zn}_{(aq)}^{2+}$ and $\text{ZnO}_{2(aq)}^{2-}$. From this, deduce the predominance domains of the ions and the existence domain of the solid.
2. Express the Nernst potential of the Zn (II) / Zn (0) redox couple in each of the pH domains thus determined.
3. Using the above results, construct the required E– pH diagram.

❖ Solution

a. Predominance or Existence Domains of the Species

- In acidic medium, where $[\text{Zn}^{2+}] \gg [\text{ZnO}_2^{2-}]$, the system contains almost exclusively dissolved Zn^{2+} . Thus:

$$[\text{Zn}^{2+}] \approx 10^{-2} \text{ mol.L}^{-1}.$$

The precipitation of $\text{Zn}(\text{OH})_2(\text{s})$ occurs when the solubility product K_S is reached, i.e.:

$$[\text{Zn}^{2+}] [\text{OH}^-]^2 = 10^{-17}$$

Substituting $[\text{Zn}^{2+}] = 10^{-2} \text{ mol.L}^{-1}$, we obtain:

$$[\text{OH}^-] = 10^{-7.5} \Rightarrow \text{pH} = 6.5$$

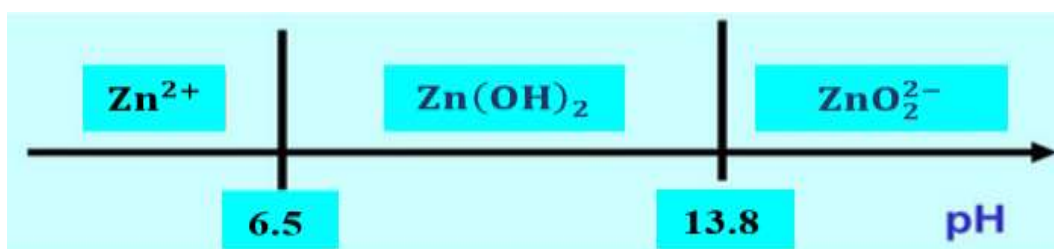
The complete redissolution of $\text{Zn}(\text{OH})_2(\text{s})$ takes place when the solubility product K'_S is reached with $[\text{ZnO}_2^{2-}] \approx 10^{-2} \text{ mol.L}^{-1}$:

$$\frac{[\text{ZnO}_2^{2-}]}{[\text{OH}^-]^2} = 10^{-1.6} \Rightarrow [\text{OH}^-] = 10^{-0.2}$$

Hence:

$$\text{pH} = 13.8$$

Thus, the sought domains can be plotted on a pH axis

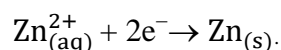


b. Establishing the Expressions $E = f(\text{pH})$

Three distinct pH regions must be considered:

1. For $\text{pH} < 6.5$: System $\text{Zn}^{2+} / \text{Zn}_{(\text{s})}$.

The half-reaction for the redox couple $\text{Zn}^{2+} / \text{Zn}_{(\text{s})}$ is:

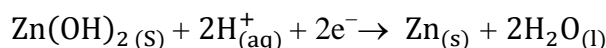


Thus, the potential is:

$$E = E_{\text{Zn}^{2+}/\text{Zn}}^0 + \frac{0.06}{2} \log [\text{Zn}^{2+}] \text{ with } [\text{Zn}^{2+}] \approx 10^{-2} \text{ mol.L}^{-1}.$$
$$E = -0.82 \text{ V}$$

2. For $6.5 \leq \text{pH} \leq 13.8$: System $\text{Zn(OH)}_2(\text{s})/\text{Zn}(\text{s})$

The half-reaction for the redox couple $\text{Zn(OH)}_2(\text{s})/\text{Zn}(\text{s})$ is:



Thus:

$$E = E'^0 + 0.03 \log [\text{H}^+]^2 \text{ or equivalently } E = E'^0 - 0.06 \text{ pH.}$$

The value of E'^0 (the standard potential of the $\text{Zn(OH)}_2(\text{s})/\text{Zn}(\text{s})$ couple at $\text{pH} = 0$) can be obtained by ensuring continuity of the potential at $\text{pH} = 6.5$:

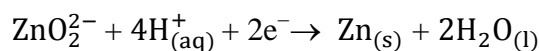
$$-0.82 = E'^0 - 0.06 \times 6.5$$
$$E'^0 = -0.43 \text{ V}$$

Therefore:

$$E = -0.43 - 0.06 \text{ pH. (Volt.)}$$

3. For $\text{pH} > 13.8$: System $\text{ZnO}_2^{2-}/\text{Zn}(\text{s})$

The half-reaction is:



Thus:

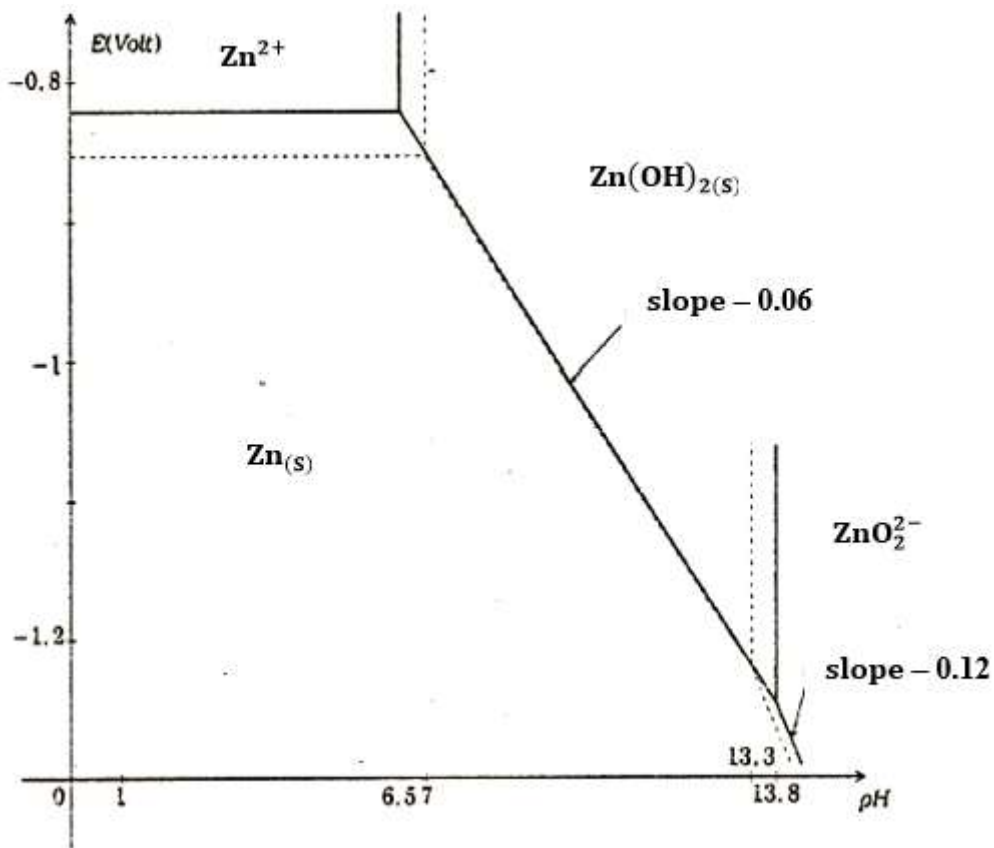
$$E = E''^0 + 0.03 \log [\text{H}^+]^4 \Rightarrow E = E''^0 - 0.12 \text{ pH.}$$

Again, E''^0 is determined by ensuring continuity at $\text{pH} = 13.8$:

$$E = 0.398 - 0.12 \text{ pH. (Volt.)}$$

c. Construction of the Diagram and Domains of Existence/Predominance

From the above expressions, the E–pH diagram can be drawn, showing the respective predominance domains of Zn^{2+} , $\text{Zn(OH)}_2(\text{s})$ and ZnO_2^{2-} .

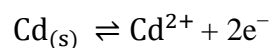


The domains represented on the diagram above are **existence domains** for $\text{Zn}_{(s)}$ and $\text{Zn}(\text{OH})_2(s)$. In other words, outside these domains, these phases do not exist.

For Zn^{2+} and ZnO_2^{2-} , these are **domains of predominance**; that is, both ions exist everywhere, but they predominate only within the domains specified above.

Exercise 3.

1. The **horizontal line** at ordinate $E = -0.46 \text{ V}$ corresponds to the Nernst law for the redox couple:



That is:

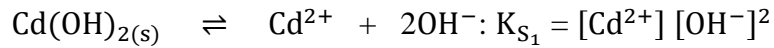
$$E = E_{\text{Cd}^{2+}/\text{Cd}_{(s)}}^0 + \frac{0.06}{2} \log [\text{Cd}^{2+}] = E_{\text{Cd}^{2+}/\text{Cd}_{(s)}}^0 + \frac{0.06}{2} \log (10^{-2}) = E_{\text{Cd}^{2+}/\text{Cd}_{(s)}}^0 - 0.06 = -0.46 \text{ V}.$$

Hence:

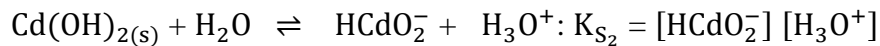
$$E_{\text{Cd}^{2+}/\text{Cd}}^0 = -0.40 \text{ V}$$

2. There are two equilibria related to the cadmium hydroxide precipitate:

▪ **In acidic medium:**



▪ **In basic medium:**



The precipitation of $\text{Cd(OH)}_{2(s)}$ from a $10^{-2} \text{ mol.L}^{-1}\text{Cd}^{2+}$ solution occurs, according to the diagram, at $\text{pH} = 8.1$. Thus:

$$K_{S_1} = [\text{Cd}^{2+}] [\text{OH}^-]^2 = 10^{-2} \times (10^{-5.9})^2 = 10^{-13.8}$$

Hence:

$$K_{S_1} = 10^{-13.8} \approx 1.58 \times 10^{-14} = [\text{Cd}^{2+}] [\text{OH}^-]^2$$

Similarly, the precipitation of $\text{Cd(OH)}_{2(s)}$ from a $10^{-2} \text{ mol.L}^{-1}\text{HCdO}_2^-$ solution occurs, according to the diagram, at $\text{pH} = 11.3$. Thus:

$$K_{S_2} = [\text{HCdO}_2^-] [\text{H}_3\text{O}^+] = 10^{-2} 10^{-11.3} = 10^{-13.3}$$

Hence:

$$K_{S_2} = 10^{-13.3} = 5 \times 10^{-14} = [\text{HCdO}_2^-] [\text{H}_3\text{O}^+]$$

3. Here, we will consider only the lines corresponding to the redox equilibria.

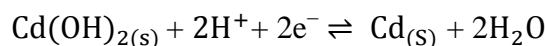
▪ **Line separating the domain of Cd^{2+} from that of $\text{Cd}_{(s)}$**

As established in Question 1, this corresponds to a line with the equation:

$$E = E_{\text{Cd}^{2+}/\text{Cd}_{(s)}}^0 + 0.03 \log [\text{Cd}^{2+}] = -0.46 \text{ V.}$$

▪ **Line separating the domain of $\text{Cd(OH)}_{2(s)}$ from that of $\text{Cd}_{(s)}$**

The Nernst law for the half-reaction:



is written as:

$$E = E_{\text{Cd(OH)}_2(\text{s})/\text{Cd}(\text{s})}^0 + 0.03 \log [\text{H}^+]^2$$

$$E = E_{\text{Cd(OH)}_2(\text{s})/\text{Cd}(\text{s})}^0 - 0.06 \text{ pH}$$

The value of $E_{\text{Cd(OH)}_2(\text{s})/\text{Cd}(\text{s})}^0$ may be determined in two ways:

✓ **First method: Continuity of potential at pH = 8.1.**

$$-0.46 = E_{\text{Cd(OH)}_2(\text{s})/\text{Cd}(\text{s})}^0 - 0.06 \times 8.1$$

$$E_{\text{Cd(OH)}_2(\text{s})/\text{Cd}(\text{s})}^0 = 0.026\text{V}$$

✓ **Second method: Uniqueness of the potential.**

In the presence of $\text{Cd(OH)}_2(\text{s})$, the Nernst potential can be expressed equivalently as:

$$E = E_{\text{Cd(OH)}_2(\text{s})/\text{Cd}(\text{s})}^0 - 0.06 \text{ pH}$$

$$E = E_{\text{Cd}^{2+}/\text{Cd}(\text{s})}^0 + \frac{0.06}{2} \log [\text{Cd}^{2+}] \text{ with } K_{S_1} = [\text{Cd}^{2+}] [\text{OH}^-]^2$$

Thus:

$$E_{\text{Cd(OH)}_2(\text{s})/\text{Cd}(\text{s})}^0 - 0.06 \text{ pH} = E_{\text{Cd}^{2+}/\text{Cd}(\text{s})}^0 + 0.03 \log \frac{K_{S_1}}{[\text{OH}^-]^2}$$

Which simplifies to:

$$E_{\text{Cd(OH)}_2(\text{s})/\text{Cd}(\text{s})}^0 = E_{\text{Cd}^{2+}/\text{Cd}(\text{s})}^0 - 0.03 \text{ p}K_{S_1} + 0.06 \text{ p}K_i$$

Substituting $\text{p}K_{S_1} = 13.8$ and $\text{p}K_i = 14$:

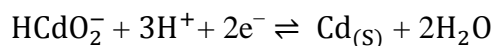
$$E_{\text{Cd(OH)}_2(\text{s})/\text{Cd}(\text{s})}^0 = 0.026\text{V}$$

Hence, the equation of the line is:

$$E = 0.026 - 0.06 \text{ pH (Volt.)}$$

▪ **Line separating the domain of HCdO_2^- from that of $\text{Cd}(\text{s})$**

The Nernst law for the half-reaction:



is written as:

$$E = E_{\text{HCdO}_2^- / \text{Cd}_{(s)}}^0 - 0.09 \text{ pH} + 0.03 \log [\text{HCdO}_2^-]$$

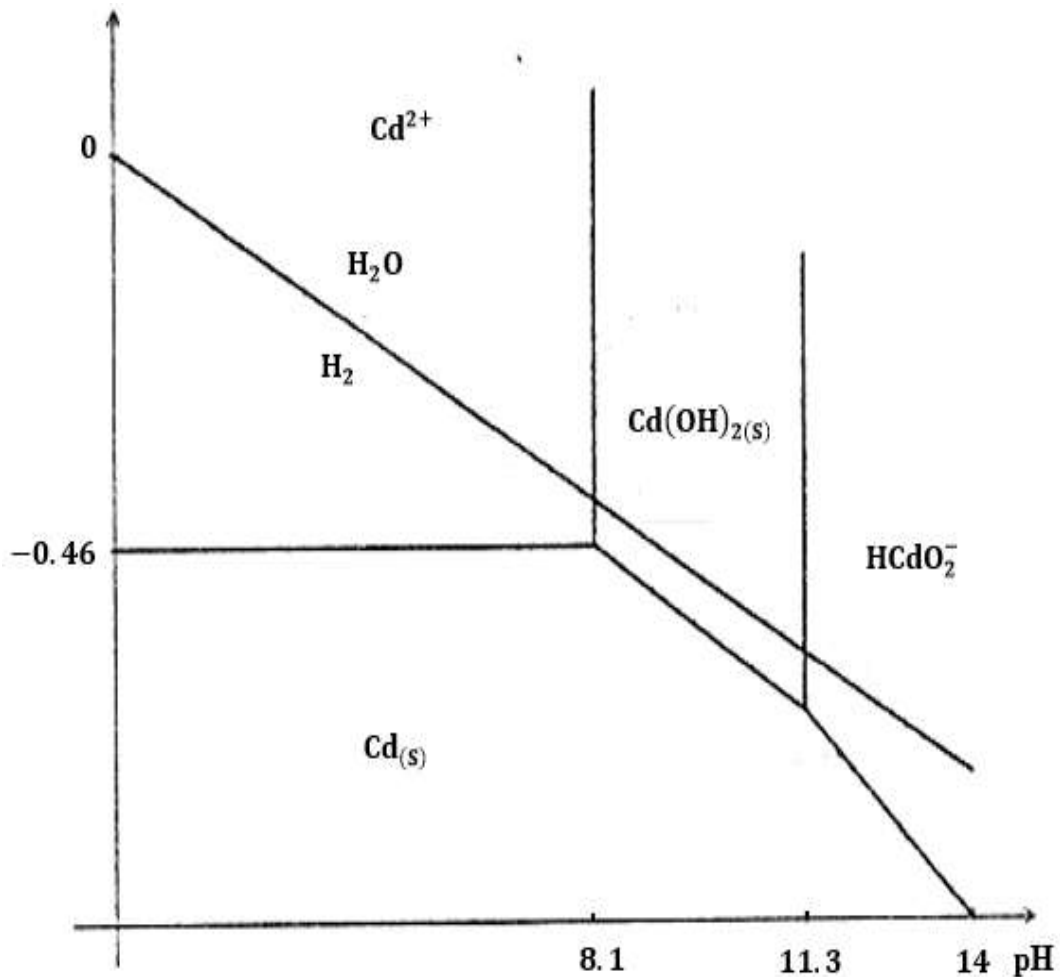
Using one of the above methods, we obtain:

$$E_{\text{HCdO}_2^- / \text{Cd}_{(s)}}^0 = 0.425\text{V}$$

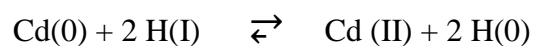
Thus, the line equation is:

$$E = 0.365 - 0.09 \text{ pH (Volt.)}$$

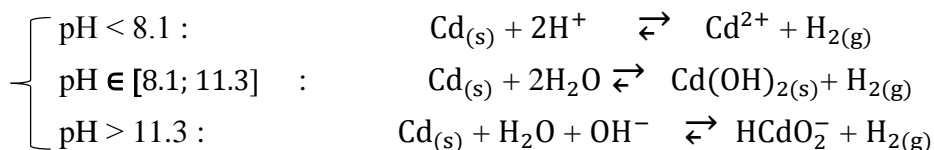
4. To address this question, we may superimpose the potential–pH diagram of cadmium with that of the water systems (restricted here to the H(I)/ H(0) system).



As can be seen above, regardless of the pH, we have in principle:



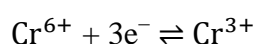
More precisely:



Exercise 4.

$\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+} : E^0 = + 1.35 \text{ V} ; \text{Cr}(\text{OH})_3 : \text{p}K_S = 30.0.$

This system corresponds to the redox couple ($\text{Cr}^{6+}/\text{Cr}^{3+}$) of chromium:

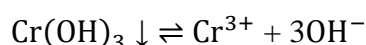


a. Potential–pH diagram between pH = 0 and pH = 5 for a solution containing 10^{-2} M of each form ($\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$)

- **pH at the onset of $\text{Cr}(\text{OH})_3$ precipitation:**

The Cr^{3+} ions involved in the redox equilibrium may precipitate as chromium hydroxide $\text{Cr}(\text{OH})_3$ when the pH increases. It is therefore necessary to determine the pH at which this precipitate first appears under the given conditions.

The precipitation equilibrium of $\text{Cr}(\text{OH})_3$ is:



with

$$K_S = [\text{Cr}^{3+}] [\text{OH}^-]^3 = 10^{-30.0}$$

Since:

$$\text{p}K_i = \text{pH} + \text{pOH}$$

$$\text{p}K_S = \text{pCr}^{3+} + 3 \text{pOH} = \text{pCr}^{3+} + 3 \text{p}K_i - 3 \text{pH} = 30.0 \quad (1)$$

or equivalently:

$$3 \text{pH} = \text{pCr}^{3+} - \text{p}K_S + 3 \text{p}K_i \quad (2)$$

Given that the concentration of Cr^{3+} in the solution is 10^{-2} M ($\text{pCr}^{3+} = 2.0$), $\text{Cr}(\text{OH})_3$ begins to precipitate when the solubility product is reached, i.e., from equation (2):

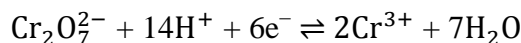
$$\text{pH} = \frac{\text{pCr}^{3+} + 3 \text{p}K_i - \text{p}K_S}{3} = \frac{2 + (3 \times 14) - 30.0}{3} \approx 4.67 \approx 4.7$$

- **Redox equilibria as a function of pH:**

Since Cr^{3+} begins to precipitate at $\text{pH} \approx 4.67$, two distinct redox equilibria can be considered depending on the pH range.

a) pH < 4.67

As Cr^{3+} has not yet precipitated, the redox equilibrium is:



The equilibrium potential is:

$$E(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = E^0(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) + \frac{0.06}{6} \log \left(\frac{[\text{Cr}_2\text{O}_7^{2-}] \times [\text{H}^+]^{14}}{[\text{Cr}^{3+}]^2} \right)$$

In logarithmic notation:

$$E(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = E^0(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) + \frac{0.06}{6} \times (2 \text{pCr}^{3+} - \text{pCr}_2\text{O}_7^{2-} - 14 \text{pH}) \quad (3)$$

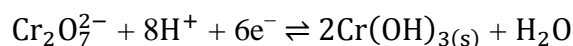
Thus, the equilibrium potential is a function of pH.

Assuming that $[\text{Cr}_2\text{O}_7^{2-}] = [\text{Cr}^{3+}] = 10^{-2} \text{ M}$ and that $E^0 = +1.35 \text{ V}$, substitution into (3) gives:

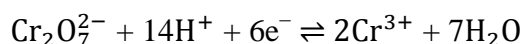
$$E \approx +1.37 - 0.14 \text{ pH} \quad (4)$$

β) pH > 4.67

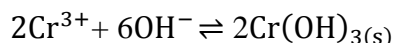
Cr^{3+} precipitates as $\text{Cr}(\text{OH})_{3(s)}$. The redox system becomes:



This process can be decomposed into:



and



The equilibrium potential remains defined by equation (3), but now $[\text{Cr}^{3+}]$ is governed by the solubility product (pK_S) of $\text{Cr}(\text{OH})_{3(s)}$ and the pH. Combining (3) with (2):

$$E \approx E^0 + \frac{0.06}{6} \times (2 \text{pK}_S - 6 \text{pK}_i + 6 \text{pH} - \text{pCr}_2\text{O}_7^{2-} - 14 \text{pH})$$

$$E \approx E^0 + \frac{0.06}{6} \times (2 \text{pK}_S - 6 \text{pK}_i - 8 \text{pH} - \text{pCr}_2\text{O}_7^{2-})$$

Substituting $pK_S = 30.0$, $pK_i = 14$, and $pCr_2O_7^{2-} = 2.0$:

$$E \approx +1.09 - 0.08 \text{ pH} \quad (6)$$

Numerical values:

- **At pH = 0.0:**

$$E \approx +1.37 - (0.14 \times 0) \approx +1.37 \text{ V}$$

- **At pH = 4.67:**

$$E \approx +1.37 - (0.14 \times 4.67) \approx +0.716 \text{ V}$$

or from (6):

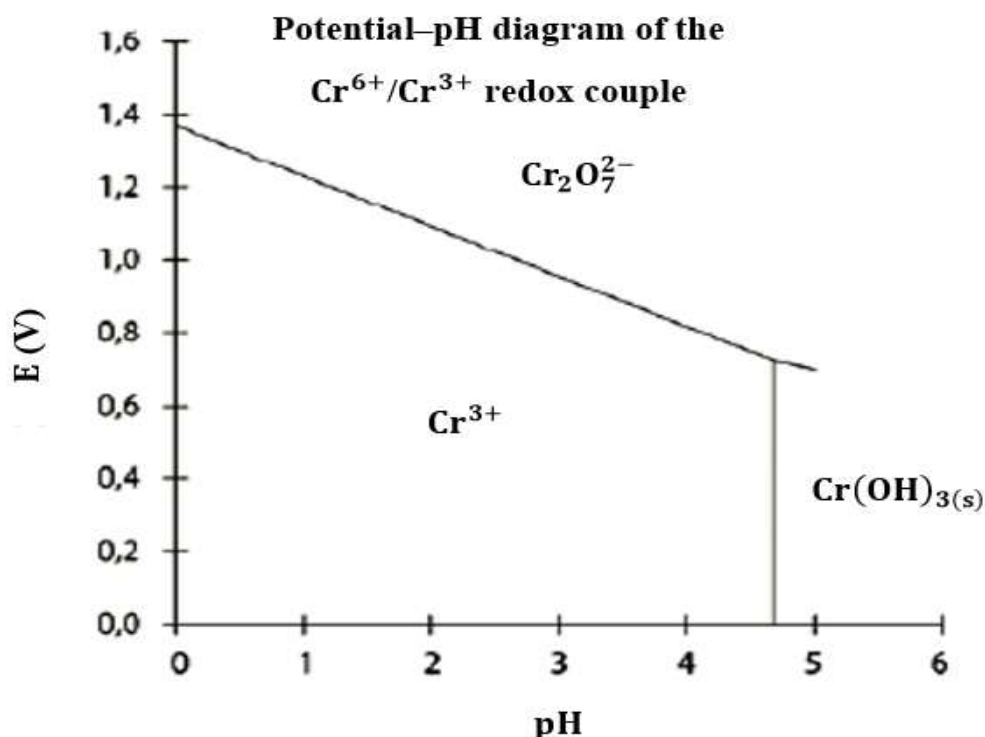
$$E \approx +1.09 - (0.08 \times 4.67) \approx +0.716 \text{ V}$$

- **At pH = 5.0:**

$$E = + 1.09 - (0.08 \times 5.0) = + 0.69 \approx +0.700 \text{ V}$$

Thus, between pH = 0 and pH = 4.67, and between pH = 4.67 and pH = 5.0, the plots of **E** as a function of pH are straight lines with slopes of -0.14 and -0.08 , respectively.

The potential–pH diagram in the range $0 \leq \text{pH} \leq 5$ is shown in the figure below.



It should be noted that above the curve lies the domain corresponding to the oxidized form, whereas below it are the domains corresponding to the reduced forms.

b. Potential at pH = 3.0 and pH = 4.0

Since these pH values are lower than 4.67, the equilibrium potentials can be calculated directly using expression (4):

- **At pH = 3.0:** $E \approx +1.37 - (0.14 \times 3.0) \approx +0.950 \text{ V}$
- **At pH = 4.0:** $E \approx +1.37 - (0.14 \times 4.0) \approx +0.810 \text{ V}$

Exercise 5.

- a. We know that the species represented in potential–pH diagrams are arranged as follows:
 - According to the increasing value of their oxidation state along the vertical potential axis;
 - Precipitates in the form of hydroxides are obtained at increasing hydroxide ion concentrations, that is, at progressively higher pH values

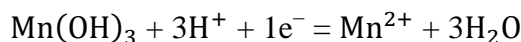
Since the relevant species are specified in the problem statement, we can assign to each its corresponding domain:

- **Oxidation state +II:** Mn^{2+} (domain A) and $\text{Mn}(\text{OH})_2$ (domain B);
- **Oxidation state +III:** Mn^{3+} (domain C) and $\text{Mn}(\text{OH})_3$ (domain D).

For the solid species ($\text{Mn}(\text{OH})_2$, $\text{Mn}(\text{OH})_3$), these domains correspond to **exclusive existence domains**, whereas for the aqueous species (Mn^{2+} , Mn^{3+}) they represent **predominance domains**.

- a. **Boundary (2)** separates domain A (Mn^{2+} ions) from domain B ($\text{Mn}(\text{OH})_3$).

These two species are connected by the following redox equilibrium:



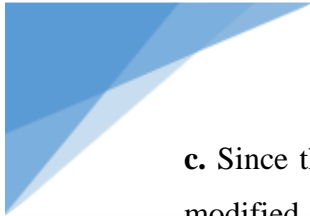
Applying the Nernst relation to this equilibrium:

$$E_2 = E^0(\text{Mn}(\text{OH})_3/\text{Mn}^{2+}) + 0.06 \log \frac{[\text{H}^+]^3}{[\text{Mn}^{2+}]}$$

$$E_2 = E^0(\text{Mn}(\text{OH})_3/\text{Mn}^{2+}) - 0.18 \text{ pH} - 0.06 \text{ Log}(0.10)$$

$$E_2 = \text{constant} - 0.18 \text{ pH}$$

Thus, the slope is **−0.18**.



c. Since the total concentration only affects soluble species, **boundary (3)** will not be modified, as it separates two solid species. Likewise, **boundary (1)** will remain unchanged, even though it separates two soluble species, because the total concentration is modified for both species simultaneously (so the concentration ratio remains the same).

However, **boundary (2)**, which separates a soluble from an insoluble species, will be affected.

In the same way, the **vertical boundaries**, which also separate soluble from insoluble species, will be modified.

Chapter IV: Corrosion

IV.1 Description of Corrosion Processes in Metallic Materials

IV.1.1 Introduction to Corrosion

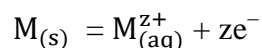
Corrosion refers to the deterioration of metals due to environmental exposure through chemical or redox reactions. It constitutes a major harmful chemical phenomenon that has received worldwide attention from scientists. Unlike corrosion, physical damages such as erosion, galling, or wear are distinct processes. However, when chemical and physical mechanisms act together, they give rise to corrosion and erosion, often termed fretting corrosion. Although non-metals may also deteriorate, they do not rust in the same way as metals. Rusting occurs exclusively in iron and its alloys, producing hydrous ferric oxides as the principal corrosion products. Corrosion, often-referred to as cancer of metals, is an irreversible process that progressively deteriorates metal structures, leading to lasting damage and significant financial losses through chemical or electrochemical reactions. It is a naturally occurring process in which metals deteriorate under the influence of environmental agents such as moisture, oxygen, acids, bases, salts, and pollutants, ultimately resulting in oxidation and possible failure of infrastructure, machinery, and equipment. Corrosion is a surface phenomenon driven by factors such as ionic species, temperature, ambient contaminants, and humidity. When the surface is damaged, the deterioration advances into the structure, a process further exacerbated by acidic elements in the environment, thereby reducing the metal's durability. Corrosion can occur in several forms—pitting, galvanic, intergranular, and stress corrosion—all of which affect metallic structures such as rods, wires, pipes (potentially causing leakage), bases, and electrical systems, as illustrated in Figure IV-1.



Figure IV-1 Effects of corrosion on different metallic structures

IV.1.2 Nature and Types of Corrosion

Corrosion is a redox reaction that occurs between a metal and its environment when the latter contains oxidizing agents. During this reaction, the metal M is oxidized into a dissolved species $M_{(aq)}^{z+}$:



Corrosion is referred to as **dry** when the oxidizing agents are in the gaseous phase (for example, corrosion caused by atmospheric dioxygen), and **wet** when the oxidizing agents are in the aqueous phase (for example, corrosion of steel in a marine environment).

In **wet** corrosion, dissolved oxygen and protons are the two principal oxidizing agents. For instance, metallic iron ($Fe_{(s)}$) passes from oxidation state zero to oxidation state +II (as Fe^{2+} ions or $Fe(OH)_2$, depending on the pH), and then to +III (as Fe^{3+} ions or $Fe(OH)_3$). Since the system must remain electrically neutral, a reduction reaction occurs simultaneously in the solution: dissolved oxygen is reduced to H_2O , or $H_{(aq)}^{+}$ is reduced to hydrogen ($H_{2(g)}$).

It is shown that the wet corrosion of a metal occurs essentially in the simultaneous presence of dissolved oxygen and water. Furthermore, the intensity of corrosion increases when the medium contains a large quantity of ions (chloride, sulfate, etc.). The corrosion of iron, for example, leads to the formation of iron oxides (Fe_2O_3 and Fe_3O_4). A corrosive (or oxidizing) medium therefore contains:

- dissolved oxygen ($O_{2(aq)}$)
- water (H_2O),
- ions in large quantity (e.g., $Na_{(aq)}^{+}$, $Cl_{(aq)}^{-}$, $SO_{4(aq)}^{2-}$),
- possibly bacteria, algae, microorganisms...

Other oxidants may also take part, such as NO_3^{-} , CrO_4^{2-} , ClO^{-} , Cl_2 , SO_3 , etc. In the absence of oxygen, iron can also be oxidized in an acidic medium by protons: it then goes into solution in the form of Fe (II) ions, but no iron oxides are formed. A metal is considered to undergo corrosion when the concentration of its ions in solution exceeds $10^{-6} \text{ mol. L}^{-1}$.

There are two modes of wet corrosion (Figure IV-2): known as **uniform** corrosion, in which the metal is corroded in a perfectly homogeneous manner over the entire surface (a rare case), and **differential** corrosion, which is due to the existence of a gradient (of composition, concentration, etc.). This gradient induces a potential difference and therefore creates an anode and a cathode (a corrosion cell).

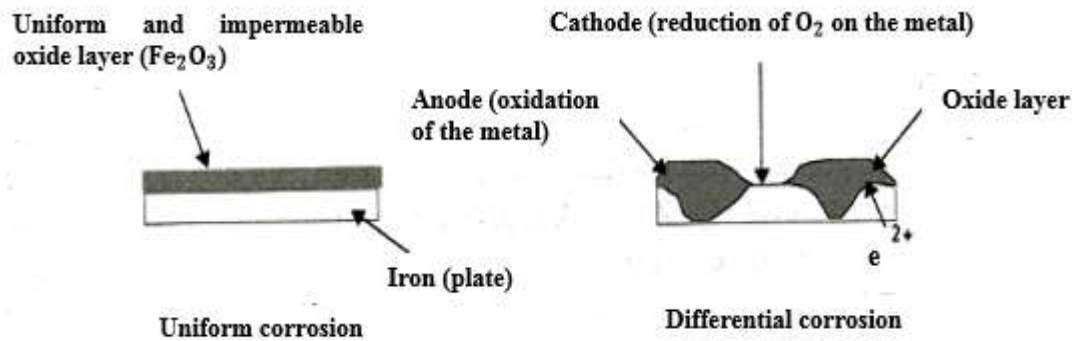


Figure IV-2 Representations of the two modes of corrosion in wet corrosion.

IV.1.3 Classification of Corrosion

Corrosion can be categorized in various ways, for example as high-temperature and low-temperature corrosion or as wet corrosion and dry corrosion. However, the primary classification considered here is between uniform corrosion and localized corrosion. Uniform corrosion is the most common form, progressing uniformly over the exposed surface of a metal. It usually occurs when a protective coating or barrier film fails, resulting in progressive thinning of the metal through chemical or electrochemical reactions at the metal surface. Initially, this process damages the surface and can eventually lead to structural failure. Because it is predictable, uniform corrosion is relatively easy to control and prevent, making it the least damaging type. Common examples include oxidation, tarnishing and atmospheric or immersed corrosion of metals. Protection can be achieved by methods such as cathodic protection, anodic protection, or the application of paints. In contrast, localized corrosion develops at selective sites on the metal surface and causes more severe degradation than uniform corrosion. It is particularly hazardous because it is difficult to detect and usually occurs without warning. The extent of damage at localized sites depends on several factors, including exposure duration, defects in protective coatings, and variations in the electrolyte. Localized corrosion can be further divided into the following forms.

IV.1.3.1 Pitting Corrosion

Pitting is considered the most severe form of localized corrosion. It produces small pits or cavities in the substrate, as shown in Figures IV-3 and IV-4.

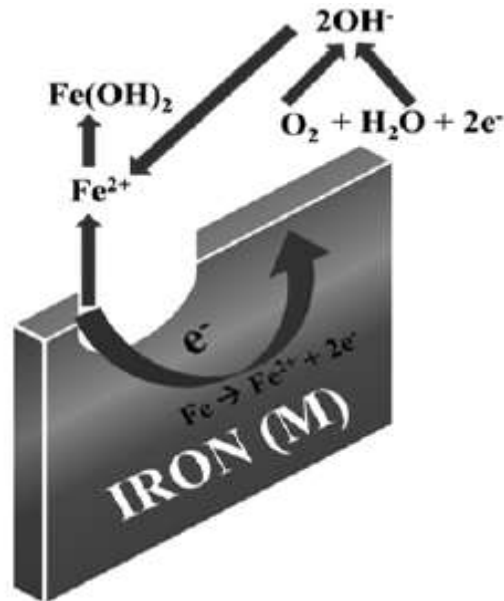


Figure IV-3 Schematic illustration of pitting corrosion.

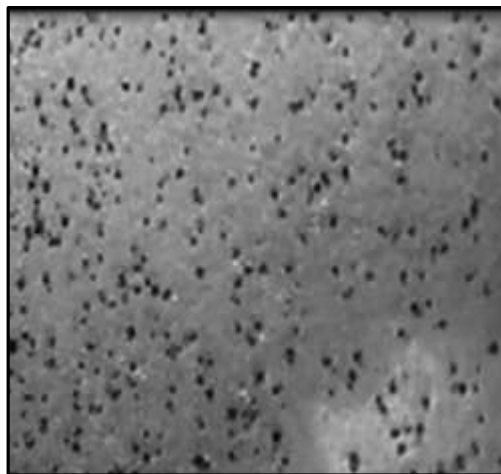


Figure IV-4 Pitting corrosion resulting from atmospheric exposure.

This phenomenon occurs when the protective barrier coating breaks down in the presence of aggressive anions. The attack is confined to a very limited area of the metal surface, while the surrounding areas are not affected. Within the pit, the area becomes anodic, whereas the remaining surface acts cathodically, initiating a galvanic reaction that changes the pH value within the pit. The acidified electrolyte within the pit inhibits repassivation of the metal and accelerates pit propagation.

Because pits are extremely small and often hidden under corrosion products, predicting them is a major challenge. Although pitting corrosion often causes only minimal weight loss in the metal substrate, it can ultimately result in complete structural failure. Pitting corrosion is thought to have caused the 1967 collapse of the U.S. Highway 35 bridge connecting Point Pleasant, WV, and Kanauga, OH, which suddenly fell into the Ohio River. Jane Alexander (2017) reports that investigators traced the origins of the failure to a small crack that had formed decades earlier during the casting of the bridge's I-beams. Over time, the affected I-bar fractured under the compounding stress from the corrosive environment and the increased loads from heavier vehicles using the bridge.

IV.1.3.2 Crevice Corrosion

It is a distinct form of pitting corrosion with a crevice-type geometry, generally occurring near the gap or crevice between two joined metal surfaces. Such corrosion is typically observed in engineering structures, for example between the bolted joints, beneath or between flanges, and around nuts and rivet heads (see Figure IV-5).



Figure IV-5 Crevice Corrosion of steel die mold.

The crevice is sufficiently narrow to maintain a stagnant zone, yet wide enough to permit liquid access. Its initiation depends on several factors, including variations in oxygen concentration, pH, and concentration of constituents. In the bulk solution, the oxygen concentration and pH are higher than inside the crevice, leading to the establishment of an electrochemical cell. Within the crevice, iron undergoes oxidation, producing Fe^{2+}

ions. At the cathode, oxygen reduction occurs, resulting in the formation of a passive $\text{Fe}(\text{OH})_2$ layer at the mouth of the crevice. After initiation, the propagation mechanism proceeds like that of pitting corrosion.

IV.1.3.3 Galvanic Corrosion

Galvanic corrosion, also referred to as bimetallic corrosion, occurs when two different metals are coupled in the presence of an electrolyte or under corrosive conditions. For this phenomenon to occur, three fundamental conditions must be satisfied: the metals must be electrochemically different, they must be in electrical contact, and both must be exposed to the electrolyte. This corrosion is driven by the potential that develops between the two dissimilar metals (Figure IV-6). The less noble, or more active, metal functions as the anode and undergoes accelerated corrosion, whereas the less active or noble metal functions as the cathode and undergoes corrosion at a slower rate. The electrolyte provides the medium through which ions are transferred from the anode to the cathode. Bimetallic corrosion occurs predominantly in marine environments, where salt water is highly effective as an electrolyte. Acting as a pathway for ion migration, the electrolyte transports metal ions from the anode toward the cathode. Consequently, the anode metal undergoes accelerated corrosion, whereas the cathode metal corrodes more slowly, and in some cases, the corrosion rate is negligible. The relative position of metals within the galvanic series determines the tendency for galvanic corrosion. Thus, by selecting metals whose positions are adjacent in the galvanic series, we can reduce the impact of galvanic corrosion. Common examples of galvanic corrosion include the corrosion of the body of the ship in contact with bronze or brass propellers; in the heat exchangers between the tubes and tube sheet; defects in the copper coating on the surface of steel coated with copper; steel pipe fitted with brass fittings, etc.

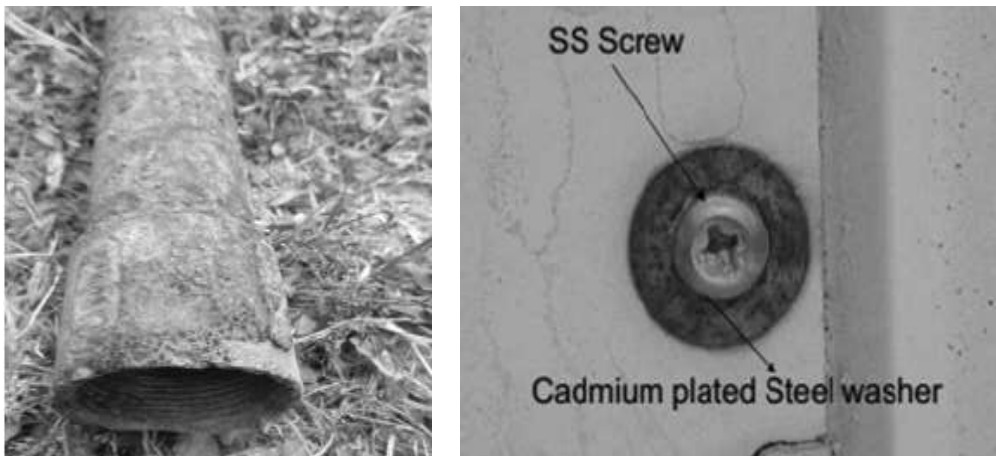


Figure IV-6 Galvanic corrosion in water pipelines and SS screw fixed on steel washer.

IV.1.3.4 Erosion Corrosion

Erosion corrosion is the combined action of corrosion or erosion that takes place due to the relative movement between a fluid and a metal surface. It commonly develops in pipelines, where fluid turbulence is the primary factor driving material deterioration. The rate of erosion–corrosion is influenced by the velocity and the physical condition of the fluid. The combined effects of corrosion and erosion typically result in severe pitting in the substrate, accompanied by high shear stresses. Abrasive particles in the fluid deplete the outer layer due to the relative motion of the solid with respect to the surface. Cavitation is a particular case of erosion corrosion, arising from the collapse of vapor bubbles in a liquid contacting a metal surface.

IV.1.3.5 Intergranular Corrosion

Intergranular corrosion is a distinct form of corrosion that typically occurs along grain boundaries or in the regions adjacent to them. It is also referred to as intergranular attack or interdendritic corrosion. The primary causes of this type of corrosion are the formation of precipitates and segregate in specific areas of the grain boundaries. These precipitates and segregates alter the physical and chemical characteristics of the boundaries compared to the grains, leading to the selective dissolution of the grain boundaries or the regions nearby. Intergranular corrosion typically remains confined to a small region; however, in some cases, an entire grain may detach due to the total destruction of the boundaries. This form of attack significantly affects the mechanical properties of metallic substrates. A well-known example is the sensitization of stainless steels, commonly referred to as weld decay. In this process, chromium precipitates form along the grain boundaries, which depletes chromium concentrations in the adjacent regions to these precipitates and renders these areas susceptible to corrosive attack. Identification of this form of corrosion is usually carried out by microscopic examination, although in certain cases it can also be observed with the naked eye.

Intermetallic compounds, such as Mg_5Al_8 , when formed at grain boundaries, establish a galvanic cell with the alloy matrix in marine environments, leading to severe intergranular corrosion. Various alloy systems, such as stainless steel, nickel alloys, and aluminum alloys, also exhibit this phenomenon. Even small amounts of iron in aluminum have been shown to segregate at grain boundaries and promote intergranular corrosion. Depletion of chromium in stainless steel (SS) directly leads to intergranular corrosion (IC). When the chromium content in steel falls below 10%, its corrosion resistance is

markedly reduced. In SS 304, which typically contains 0.06–0.08% carbon, carbon combines with chromium to form chromium carbide, as illustrated in Figure IV-7. This process occurs when the steel is heated in the sensitization temperature range of 950–1450 °F. If the metal is cross-sectioned and examined under a scanning electron microscope, the regions affected by CrC_3 formation appear as deep, narrow trenches.

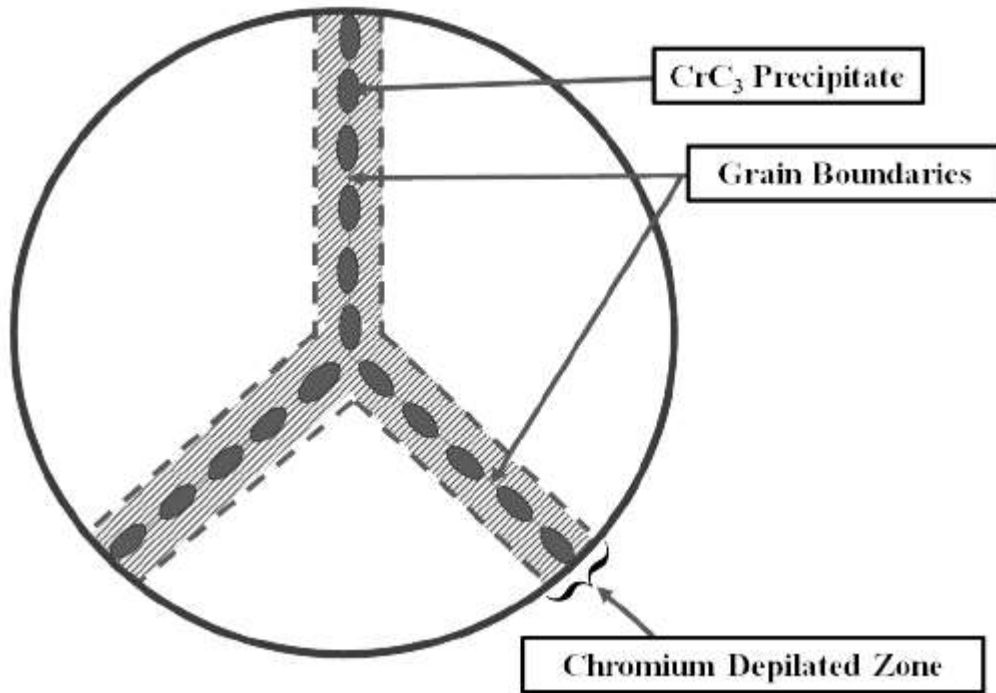


Figure IV-7 Intergranular corrosion in SS.

IV.1.3.6 Cracking Corrosion

Cracking corrosion represents another category of corrosion that can cause abrupt structural failure. It typically develops when ductile metallic substrates are subjected to stress at elevated temperature. This form of corrosion encompasses stress corrosion cracking, corrosion fatigue, and hydrogen-damage types of corrosion.

IV.1.3.7 Stress Corrosion Cracking

Stress corrosion cracking occurs as a result of the combined influence of tensile stress and a corrosive environment. Stress corrosion cracking may be caused by either external stress or residual stress within the material, as demonstrated in Figure IV-8. This phenomenon leads to unforeseen failure of metallic structures. It is most frequently observed in regions of high stress, pressure vessels, pipelines, and reactors buried under the earth.

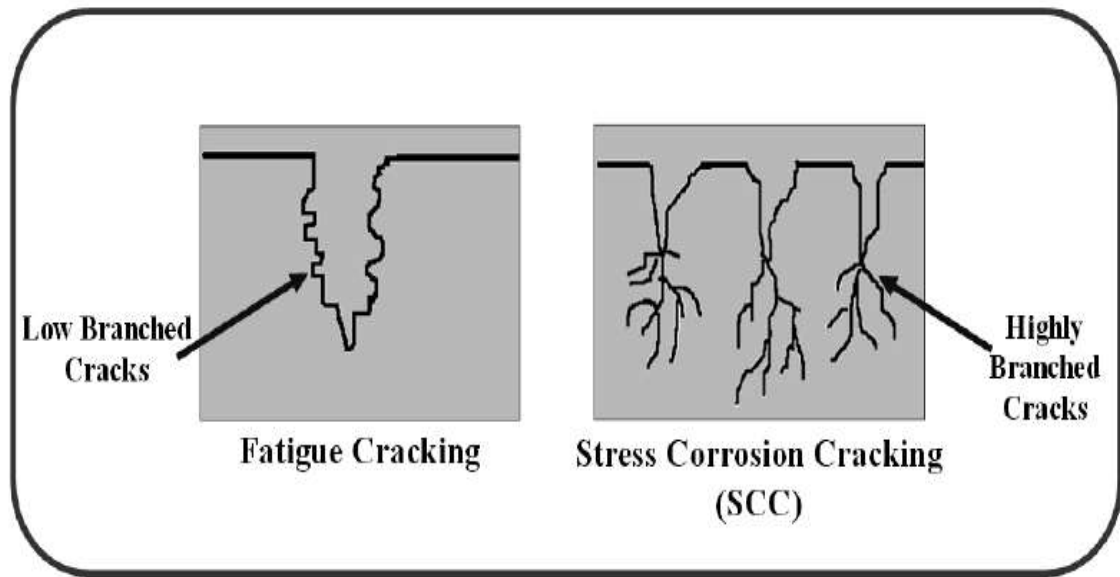


Figure IV-8 Schematic representation of propagation of fatigue cracking and stress corrosion cracking.

Besides metals, materials such as ceramics, pure materials and polymeric materials are also susceptible to stress cracking corrosion under certain corrosive environments. Environments that initiate cracking typically contain aggressive corrosive ions such as Cl^- and NH_3 . The mechanism of stress corrosion cracking, as illustrated in Figure IV-9, remains not fully understood; nevertheless, it is thought to result from stress, aggressive corrosive media, and susceptible microstructures, and may be correlated as indicated.

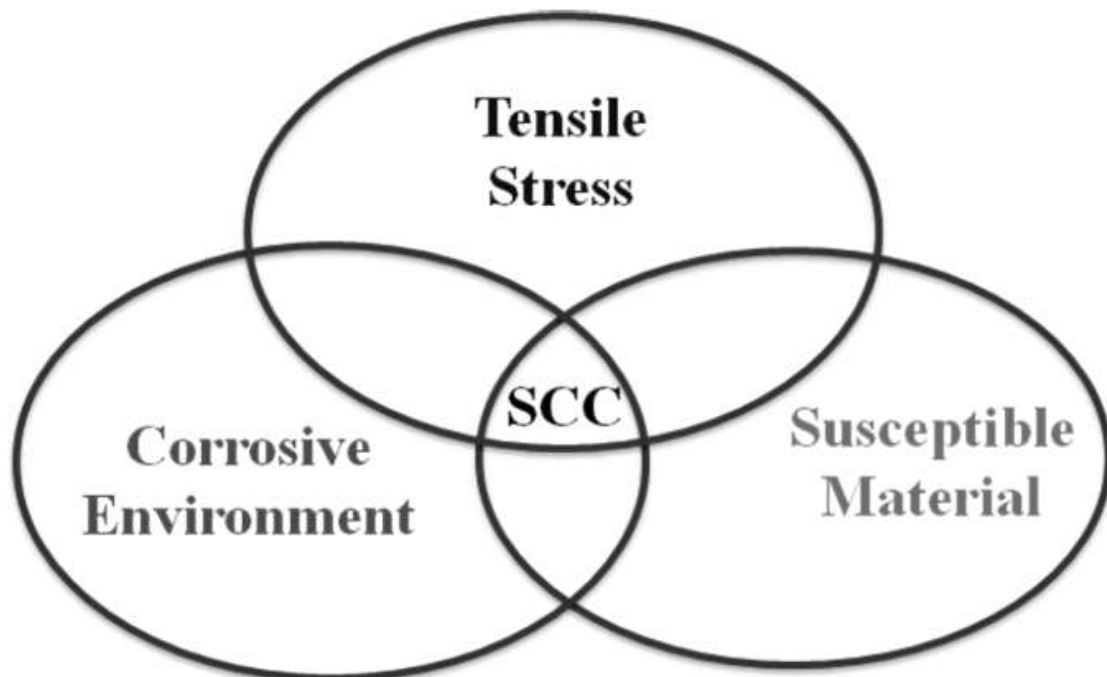



Figure IV-9 Mechanism of stress corrosion cracking.



In certain cases, the initiation of cracking may be linked to the formation of a brittle film on the material's surface, which reduces ductility because its metal composition differs from that of the bulk material. The most obvious distinguishing feature of stress corrosion cracking in pipelines, irrespective of pH, is the manifestation of patches or colonies of parallel cracks on the pipe's external surface. Pitting is often linked to the phenomenon of stress corrosion cracking (SCC). Among the metals most vulnerable to SCC are aluminum and steel. In buried pipelines, this phenomenon typically initiates with the development of small cracks on the external surface, which, under severe conditions, may end in a structural failure.

IV.1.3.8 Fatigue Corrosion

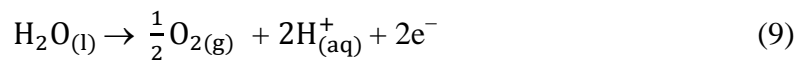
Fatigue corrosion occurs through the combined action of cyclic stress and corrosive environments, producing a more severe effect than either factor alone. This phenomenon typically initiates at pits, surface defects, or irregularities. Fatigue corrosion shares many features with stress corrosion cracking; however, unlike SCC, it can occur in any environment. In such cases, transgranular propagation is generally observed, without exhibiting the branched propagation that is characteristic of stress corrosion cracking (Figures IV-3 and IV-4). The extent of fatigue corrosion is related to environmental, loading, and metallurgical conditions. Crack morphology and dimensions depend on the stress frequency: high-frequency stresses generate fine cracks, while low-frequency stresses produce broad cracks.

IV.1.4 Thermodynamic Aspect of Corrosion (Pourbaix Diagrams)

The Pourbaix diagram, also known as the potential-pH diagram, illustrates the thermodynamic principles underlying corrosion reactions. Pourbaix (1966) demonstrated the correlation between pH and electrode potential upon the electrode condition. This diagram represents the behavior of a metal in an aqueous solution, identifying whether it is corroding, non-corroding, or passivated. The diagram is divided into three distinct domains: **immunity**, **corrosion**, and **passivation**. Each of these domains designates the region where a particular species is thermodynamically most stable. When a metal exists in its most stable form, it is regarded as immune to corrosion. Conversely, if the most stable state corresponds to a soluble ionic species, the metal undergoes corrosion. On the other hand, if the insoluble product represents the most stable species within a given region, the system is regarded as passive. Figure IV-10 presents the potential-pH diagram for iron exposed to water. During iron corrosion in water, the possible reactions are:

$\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2\text{e}^{-}$	(1) Corrosion reaction
$\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{e}^{-}$	(2) Oxidation reaction
$2\text{Fe}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2\text{O}_3 + 6\text{H}^{+} + 6\text{e}^{-}$	(3) Precipitation reaction
$\text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + \text{H}^{+}$	(4) Hydrolysis reaction
$2\text{Fe} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2\text{O}_3 + 6\text{H}^{+} + 6\text{e}^{-}$	(5) Corrosion reaction
$\text{Fe} + 2\text{H}_2\text{O} \rightleftharpoons \text{HFeO}_2^{-} + 3\text{H}^{+} + 2\text{e}^{-}$	(6) Corrosion reaction
(Hypoferrite)	
$\text{HFeO}_2^{-} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + \text{e}^{-}$	(7) Precipitation reaction
$\text{Fe}^{2+} + 2\text{OH}^{-} \rightleftharpoons \text{Fe}(\text{OH})_2$	(8) Precipitation reaction

Reactions (1), (2), and (7) are independent of pH and therefore appear as straight horizontal lines. In contrast, reactions (3), (5), and (6) depend on both pH and potential and are represented on the potential–pH diagram as sloped lines. Reactions (4) and (8), which vary with pH, are shown as vertical lines. The evolution of oxygen occurs above the line “cd”, but not below it, in accordance with the reactions.



Hydrogen evolution can occur below, but not above, the line “ab” in accordance with the reaction.



Figure IV-10 shows that the redox potential of the hydrogen electrode (line ab) lies above the immunity region across the entire pH scale. This indicates that dissolution accompanied by hydrogen evolution can occur in aqueous solutions at all pH values. However, within the pH range of 9.4 to 12.5, a passivating layer of $\text{Fe}(\text{OH})_2$ forms (reaction (8)). At low pH values, iron corrodes with the formation of Fe^{2+} ions (reaction (1)), while at higher pH values, soluble hypoferrite ions can form within a restricted active potential range. At higher redox potentials in a corroding medium, the passivating layer can consist of $\text{Fe}(\text{OH})_3$, $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, or Fe_2O_3 , or Fe_3O_4 . In alkaline solution, soluble ferrate ions (FeO_4^{2-}) can form at a very noble potential. Although the potential–pH diagram is valuable for illustrating the conditions of potential and pH under which the metal will corrode, its application to practical corrosion problems is subject to certain limitations. As the data presented in the potential–pH diagram are thermodynamic, they do not convey any information concerning the rate of the reactions.

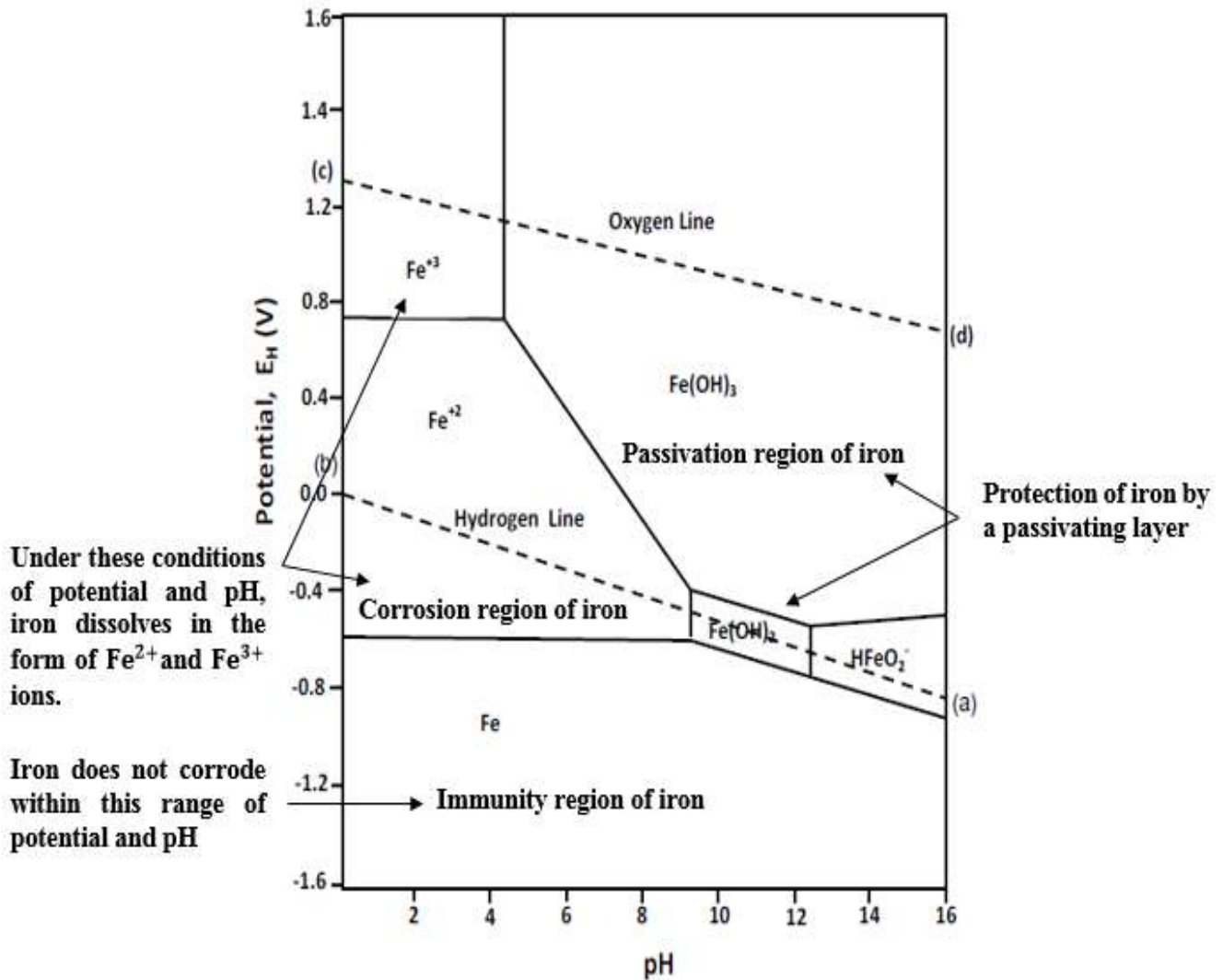


Figure IV-10 Potential–pH (Pourbaix) diagram for iron exposed to water.

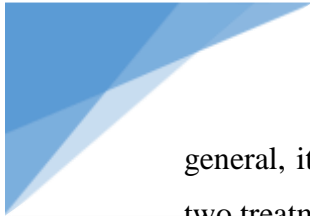
IV.2 Methods of Protection against Corrosion

There are several methods of protection against corrosion. These methods can be divided into two categories: passive methods (various coatings, the action of corrosion inhibitors), which are costly in terms of raw materials, and active methods (electrochemical methods using a generator), which are costly in terms of energy.

IV.2.1 Application of Protective Coatings on Metal (Passive Methods)

Metals and alloys can be protected by coatings such as paints, varnishes, or coatings with other metals, whose main properties are impermeability and resistance to time and water.

The surface to be protected must first undergo treatment. This treatment depends on the nature of the metal, its metallurgical history, and its condition upon delivery. In



general, it consists of pickling, degreasing, and then polishing of the surface. The first two treatments serve to clean the metal, while the third serves to improve the state of the metallic surface and thus the adhesion of the future coating. A paint or varnish coating makes it possible to isolate the material from its environment (water, dissolved oxygen). For the protection to be effective, the paint must be applied in several successive layers: the primary layers (impermeable), which ensure adhesion and protection against corrosion itself (they are often orange in color); the intermediate and finishing layers, which are intended to protect the primary layers and to give the metallic structures an agreeable appearance (color, texture, etc.). Metallic coatings can be obtained by electrolysis of a solution containing the cation of the metal to be deposited (electro-galvanizing, chromium plating, nickel plating, etc.). In certain cases (notably for zinc), the piece to be protected can be immersed directly in a bath of molten metal: this is galvanization.

The protection against corrosion of parts on which a metallic layer is deposited depends fundamentally on the relative tendency to oxidation of the metal to be protected and of the protective metal:

- When the protective metal is more easily oxidized (a better reducing agent) than the metal to be protected (as in the case of zinc on iron, for example), the latter will remain protected as long as it is in contact with the protective layer. Thus, a defect in the coating has no consequence for corrosion. However, the relatively rapid consumption of the protective metal requires that sufficiently thick layers be deposited in order for the protection to remain effective over a long period.
- When the protective metal is less easily oxidized (a poorer reducing agent) than the metal to be protected (as in the case of nickel on iron, for example), the slightest defect in the protective layer will give rise to galvanic corrosion. Therefore, it is essential to ensure that the protective layer contains no defects. On the other hand, its relatively slow consumption means that a small thickness (10–100 nm) is generally sufficient to ensure protection over a long period.

IV.2.2 Metals Naturally Protected Against Corrosion

The rust layer (ferric oxides and hydroxides) that forms during the natural corrosion of iron is friable and highly permeable, allowing the corrosion to reach deeper areas. There are, however, metals that are naturally protected against corrosion by their oxide layer: aluminum is a classic example. It becomes covered with a very thin protective

layer of aluminum oxide Al_2O_3 (called alumina), which is transparent and impermeable. Stainless steel is a steel that passivates at the surface. It contains a minimum of 13% chromium (by mass). Other elements are frequently added, in particular nickel. The latter, having the same face-centered cubic structure as iron, facilitates the incorporation of chromium (body-centered cubic structure) into iron. Corrosion resistance is therefore, paradoxically, due to the ability of chromium to oxidize upon contact with the oxidizing medium like air, forming a very thin, protective surface layer of chromium oxide (Cr_2O_3).

IV.2.3 Use of a Sacrificial Anode

Iron can be protected by using a sacrificial anode, that is, by electrically connecting iron with a metal (denoted M) more reducing than iron ($E_{\text{Fe}^{2+}/\text{Fe(s)}}^0 > E_{\text{M}^{n+}/\text{M(s)}}^0$). In this way, the metal M serves as the anode, while iron functions as the cathode (there is a reduction of dissolved oxygen on the iron).

Example:

When iron and zinc are connected (short-circuited, see Figure IV-11), only zinc undergoes oxidation. At the same time, oxygen is reduced to H_2O at the surface of the iron.

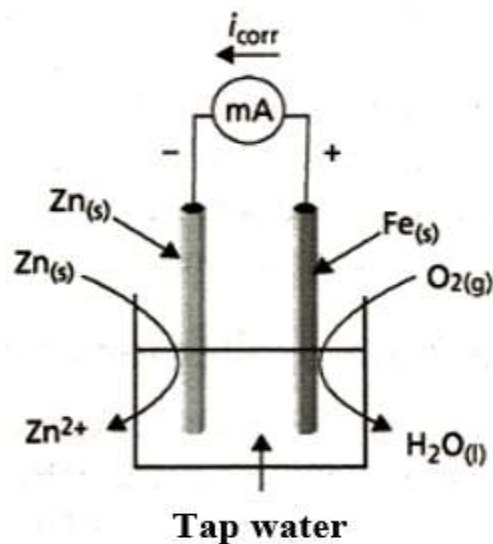



Figure IV-11 Cathodic protection of iron by sacrificial anode.

This method, known as sacrificial anode protection, is very commonly used on ships, pipelines, and steel tubes. Pieces of zinc or magnesium are regularly attached to



the plate (e.g., every 100 meters in the case of pipelines). Once these pieces are nearly completely dissolved, they are replaced with new ones.

IV.2.4 Impressed Current Cathodic Protection (Active Method)

Within a certain potential range, iron is in its immunity zone. At these potentials, iron is not attacked, because the metal is the stable form of the element. By connecting the steel plate to a generator and imposing the desired voltage or current, iron is brought into its immunity zone and is thus protected against corrosion. In cathodic protection, the metal to be protected is connected to the negative pole (cathode) of a direct current generator. The positive pole is connected to either an inert anode (platinum) or a sacrificial anode (zinc, magnesium, etc.). This technique is used for the protection of buried pipelines.

IV.2.5 Anodic Protection

Anodic protection (or passivation) consists of forming, by electrochemical means (or possibly by chemical means), a protective oxide layer on the surface of the metal to be protected, using a generator supplying a current that enables the formation of the passivation layer. This method is particularly applied in the protection of aluminum: by electrolysis of an acidic solution between an aluminum anode and a steel cathode, a layer of alumina a few microns thick is generated, which is then treated thermally and with a solution of dyes to seal its pores; thus, anodized aluminum is obtained.

IV.2.6 Use of Corrosion Inhibitors

Corrosion inhibitors are chemical compounds added in small quantities to the corrosive medium to slow down, or even stop, the corrosion process of a metal. These molecules form a barrier, preventing the transfer of corrosive molecules towards the metal. They may also reinforce a pre-existing barrier, such as an oxide. In certain cases, a protective compound is formed by a reaction between the metal cation and the inhibitor. Anodic inhibitors are generally alkaline reagents or phosphates that form a precipitate in the presence of metal cations. Corrosion inhibitors are also organic molecules that adsorb on the metal.

Exercises

Exercise 1.

Are the following statements true or false?

1. The wet corrosion of a uniform, defect-free metallic piece occurs primarily in the areas where the oxidizing agent is least concentrated.
2. From a purely thermodynamic perspective, a metal becomes more easily oxidizable as the pH decreases.
3. The comparative corrosion rate of two metals in an aqueous acidic medium can be predicted by comparing their respective oxidation potentials.
4. A metal can be protected from corrosion by electrochemically oxidizing it.

Exercise 2.

A conductor connects an underground iron tank to a block of pure zinc with a mass of $m = 100$ g. The whole system is placed in a medium assumed to be humid and neutral.

1. Indicate the polarities of the electrochemical cell formed.
2. The corrosion current of this cell is $I = 2$ mA. How long would it theoretically take the zinc block to disappear completely?

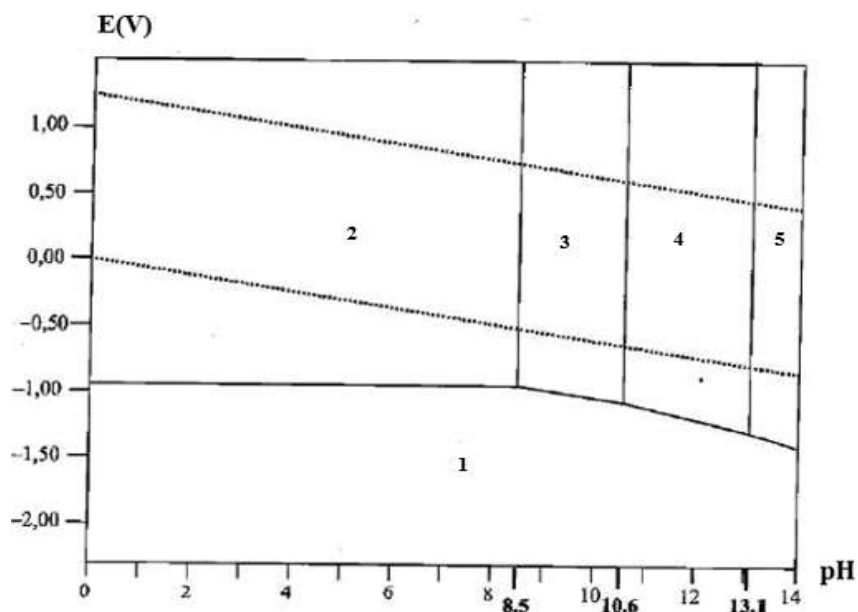
Given that: $M_{\text{Zn}} = 65.4 \frac{\text{g}}{\text{mol}}$; $F = 96500 \frac{\text{C}}{\text{mol e}^-}$

Exercise 3.

Corrosion refers to the deterioration of a material through chemical reaction with an oxidant, such as water or the oxygen in the air. It is of considerable importance: about one quarter of the world's iron production is used merely to replace corroded iron. Galvanizing an iron part provides relatively effective protection against corrosion, since the part is coated with metallic zinc. The thermodynamic aspects of corrosion can be studied using potential-pH diagrams (Pourbaix diagrams).

In this exercise we consider the corrosion of zinc. Its potential-pH diagram is shown in the following figure, plotted for a concentration $C_0 = 10^{-6} \text{ mol} \cdot \text{L}^{-1}$. The species taken into account are $\text{Zn}_{(s)}$, HZnO_2^- , $\text{Zn}(\text{OH})_2$, ZnO_2^{2-} , and $\text{Zn}_{(aq)}^{2+}$. The boundary conventions are as follows:

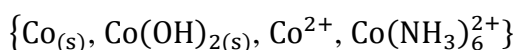
- At the boundary between two dissolved species their concentrations are equal.
- At the boundary between a dissolved species and a solid species, the concentration of the dissolved species is taken equal to the plotting concentration C_0 .



1. Propose an explanation for the choice of such a low plotting concentration.
2. Show that the species HZnO_2^- (aq), Zn(OH)_2 (s), ZnO_2^{2-} (aq), and Zn^{2+} (aq). Are linked by acid–base equilibria. Write the equations of the corresponding reactions and arrange these species in order of increasing basicity.
3. Assign to each species its domain of stability. Specify whether these are domains of predominance or domains of existence.
4. The thermodynamic stability domain of water has been superposed on the diagram. Indicate the corresponding redox couples and establish the equations of the two bounding lines. Assume the partial pressure of gaseous species equals 1 bar at the boundary. Standard potentials are $E^0(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V}$; $E^0(\text{H}^+/\text{H}_2(\text{g})) = 0 \text{ V}$.
5. From the diagram, does a layer of metallic zinc in a deaerated aqueous solution undergo corrosion? Write the associated reaction(s).
6. Propose an explanation for the use of zinc to protect iron from corrosion.

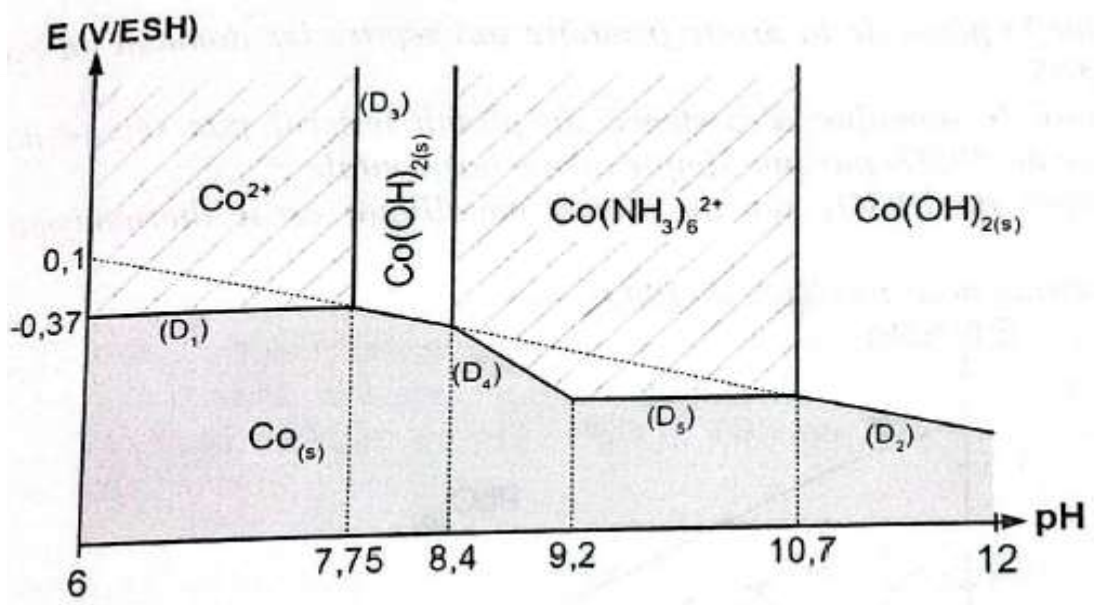
Exercise 4.

The simplified E–pH diagram of cobalt at 25°C in the presence of ammonia has been plotted for $C_i = 10^3 \text{ mol.L}^{-1}$ and $C_L = 2 \text{ mol.L}^{-1}$, considering the system:



1. Calculate the slopes of the lines (D_4) and (D_5).
2. What is the impact of complexation on the corrosion of the metal?

Recall that for the acid–base couple $\text{NH}_4^+/\text{NH}_3$, $\text{pK}_a = 9.2$.





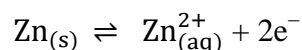
Solutions

Exercise 1.

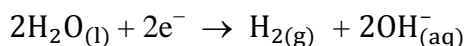
1. TRUE: Although paradoxical at first glance, this statement is a consequence of the fact that wet corrosion is an electrochemical process (a galvanic cell...) and not simply a redox reaction. The oxidizing agent does not react directly with the metal but through a concentration cell. The area of higher concentration (corresponding to the higher reduction potential) acts as the cathode, and thus the area of lower concentration becomes the anode, i.e., the area of corrosion.
2. FALSE: Although corrosion is usually promoted in acidic media, the oxidation potential of a metal (its tendency to oxidize) actually decreases as the pH increases. This can be seen from Pourbaix diagrams, or directly from the Nernst equation, where protons appear in the numerator.
3. FALSE: The corrosion rate of a metal depends primarily on the reduction rate of the oxidizing agent (oxygen, water) on that metal. When this reaction is slow (high overpotential), corrosion will also be slow—even if the metal has a very low oxidation potential (as in the case of zinc, for example). Coupling two different metals generally leads to accelerated corrosion of the more oxidizable one (galvanic corrosion), simply because the reduction of the oxidizing agent no longer occurs on this metal but on the other.
4. TRUE: This is the principle of anodic protection. It requires passivation through the formation of a protective oxide layer, as in the anodizing of aluminum.

Exercise 2.

1. The zinc block constitutes the anode (negative pole) and will therefore be oxidized:



The reduction of water is written as:



The iron tank thus plays the role of the cathode (positive pole).

2. The oxidation of n moles of zinc releases an electron amount:

$$n(e^-) = 2 \times n$$

The corresponding quantity of charge is:

$$Q = n(e^-) \times F$$

Also:

$$Q = I \times t \text{ and } n = \frac{m}{M(\text{Zn})}$$

Hence:

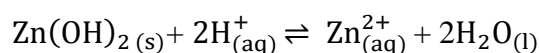
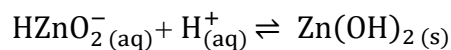
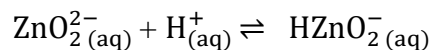
$$I \times t = 2 \times \frac{m}{M(\text{Zn})} \times F$$

Therefore:

$$t = \frac{2m \times F}{I \times M(\text{Zn})} = \frac{2 \times 100 \times 96500}{2 \times 10^{-3} \times 65.4} = 1.48 \times 10^8 \text{ s, which corresponds to approximately } \mathbf{4 \text{ years}} \\ \mathbf{\text{and } 8 \text{ months.}}$$

Exercise 3.

1. Corrosion occurs under the action of external agents, such as rainwater, and it is a slow phenomenon. Ions therefore do not have time to accumulate before being naturally removed, which justifies the use of a very low plotting concentration.
2. The successive acid-base couple equations are as follows. To find them, we reason that a species is all the more basic the more negatively charged it is. Thus,



3. The oxidation state of Zn in $\text{Zn}(\text{s})$ is 0. The oxidation state of Zn in each of the species investigated in the previous question is +II. Since we have already classified these species by increasing basicity, we can then deduce their relative

positions on the diagram. As this directly reproduces the shape of the diagram provided in the problem statement, we may conclude:

O.N. = +II	(2) $\text{Zn}_{(\text{aq})}^{2+}$	(3) $\text{Zn}(\text{OH})_{2(\text{s})}$	(4) $\text{HZnO}_2^{-}(\text{aq})$	(5) $\text{ZnO}_2^{2-}(\text{aq})$
O.N. = 0	(1) $\text{Zn}_{(\text{s})}$			

The stability domains of the ions ((2), (4), and (5)) are domains of predominance, whereas the stability domains of the solids ((1), (3)) are domains of existence.

Note

In such a simple case, we can conclude directly without going through the situation diagram.

4. The first redox couple is $\text{H}^+ / \text{H}_{2(\text{g})}$. The Nernst law and the boundary equation of this redox couple are:

$$E = E^0(\text{H}^+ / \text{H}_{2(\text{g})}) + 0.03 \log \frac{[\text{H}^+]^2}{P_{\text{H}_2}}$$

which simplifies, for $P_{\text{H}_2} = 1$ bar, to:

$$E = 0 - 0.06 \text{ pH}$$

The second redox couple is $\text{O}_2 / \text{H}_2\text{O}$, with the half-equation $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$.

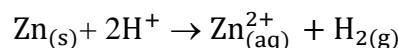
From which we deduce:

$$E = E^0(\text{O}_2 / \text{H}_2\text{O}) + \frac{0.06}{4} \log [\text{H}^+]^4 \cdot P_{\text{O}_2}$$

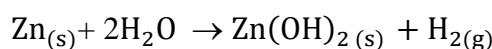
$$E = 1.23 - 0.06 \text{ pH (for } p\text{O}_2 = 1 \text{ bar)}$$

5. According to the diagram, the stability domains of metallic zinc and of water are disjoint: zinc is unstable in water; therefore a layer of zinc immersed in aqueous solution will normally be corroded.

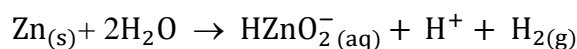
In acidic medium ($\text{pH} < 8.5$), the reaction is:



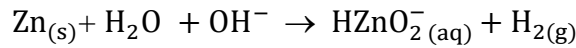
For $8.5 < \text{pH} < 10.6$, the product is no longer Zn^{2+} but $\text{Zn}(\text{OH})_2$, the reaction is:



For $10.6 < \text{pH} < 13.1$, the product is $\text{HZnO}_2^{-}(\text{aq})$:

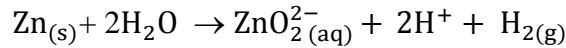


Thus

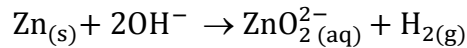


which, because it is necessary to respect the basicity of the medium in writing the reaction.

For $\text{pH} > 13.1$,



that is:



According to this diagram, zinc should not be able to protect iron from corrosion, since it is thermodynamically unstable in water. The phenomenon of **passivation** resolves this apparent contradiction. In practice, a protective layer of zinc oxide forms on the surface of metallic zinc. This layer is sufficiently impermeable to isolate the zinc from water and air, thereby halting further corrosion and enabling its sacrificial protective function.

Exercise 4.

1. Line (D₅) separates the predominance domain of $\text{Co}(\text{NH}_3)_6^{2+}$ and the existence domain of $\text{Co}_{(s)}$.

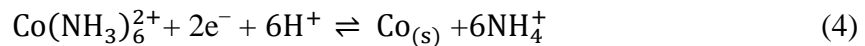


$$E = E_5^0 + \frac{2.3RT}{2F} \log \frac{[\text{Co}(\text{NH}_3)_6^{2+}]}{[\text{NH}_3]^6};$$

On (D₅): $[\text{Co}(\text{NH}_3)_6^{2+}] = C_i$ and $[\text{NH}_3] = C_L$.

$$(D_5) E = E_5^0 - 0.03\text{p}C_i + 0.18\text{p}C_L. \text{ (Horizontal line).}$$

The half-reaction (5) applies only for $\text{pH} > \text{p}K_a$. For $\text{pH} < \text{p}K_a$, NH_3 must be replaced by the predominant species NH_4^+ :



$$E = E_4^0 + \frac{2.3RT}{2F} \log \frac{[\text{Co}(\text{NH}_3)_6^{2+}][\text{H}^+]^6}{[\text{NH}_4^+]^6};$$

On (D₄): $[\text{Co}(\text{NH}_3)_6^{2+}] = C_i$ and $[\text{NH}_4^+] = C_L$.


$$(D_4) E = E_4^0 - 0.03\text{p}C_i + 0.18\text{p}C_L - 0.18\text{pH}.$$

2. The area of the corrosion domain is larger in the presence of the complex ion, at the expense of the passivation domain and (slightly) the immunity domain of the metal.



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