# Chapter II. Phase diagrams, Potential-pH diagram, Applications

## II.1. Introduction

In the context of corrosion, phase diagrams play a key role in determining the thermodynamic conditions required for a material to transition from a stable state to a corroded or degraded state. They provide information on the conditions under which a material can remain stable (non-corroded) or become vulnerable to corrosion due to specific environments such as water, acids, or bases. Furthermore, phase diagrams allow for the prediction of material durability when exposed to corrosive agents. By analyzing the stability zones on a diagram, it is possible to identify the environments where a material will resist corrosion and those where it is likely to degrade.

## II.2. Potential-pH diagram

The potential-pH diagram, also known as the Pourbaix diagram, is a crucial tool in studying electrochemical phenomena related to material corrosion. It analyzes the behavior of metals or alloys in a given environment based on two key variables: electrochemical potential and pH. This diagram helps visualize the evolution of material stability and predict potential corrosion reactions under varying conditions. It is particularly useful for identifying conditions where materials are either resistant to corrosion or prone to passivation, as well as for pinpointing regions where corrosion may occur due to aggressive ions, temperature changes, or pH fluctuations. Additionally, the diagram aids in selecting the most appropriate materials for specific applications by considering factors such as the environment and expected conditions.

### *II.2.1. Axes of the diagram*

#### II.2.1.1. Horizontal axis (pH)

This parameter represents the acidity or alkalinity of the environment. pH is measured on a scale from 0 to 14, where a pH of 0 is highly acidic, a pH of 7 is neutral, and a pH of 14 is highly alkaline.

#### II.2.1.2. Vertical axis (Electrochemical Potential, V)

This parameter represents a metal's tendency to lose or gain electrons in a specific environment. The potential is measured in millivolts (mV) and indicates whether a metal is more likely to corrode or protect itself by forming passive layers.

## *II.2.2. Stability zones on the diagram*

In a Pourbaix diagram, there are three main areas, each of these regions is determined by the electrochemical potential and the pH of the environment, and the boundaries between these areas are crucial for understanding the stability and corrosion behavior of materials in various environments.

### II.2.2.1. Immune (Stable) Area

This region represents the conditions under which the material is stable and immune to corrosion. In this area, the metal remains unreactive and does not undergo dissolution or corrosion. The material either forms a protective oxide layer or remains in its metallic form. The immunity area is typically found at high potentials and certain pH ranges where passivation occurs, preventing further degradation of the material.

### II.2.2.2. Active area

In this region, the metal tends to dissolve or undergo oxidation, leading to corrosion. The material is actively reacting with the environment, usually in the presence of aggressive ions or under certain temperature conditions. This region generally occurs at lower potentials or extreme pH values, where the material loses electrons and forms corrosion products.

### II.2.2.3. Passive area

The passive area is characterized by the formation of a protective oxide or passive film on the material's surface, which significantly reduces the corrosion rate. In this zone, the material may still be exposed to aggressive conditions, but the oxide layer prevents further degradation by isolating the metal from the surrounding environment. This passive layer acts as a barrier and is typically found in intermediate potential and pH ranges, especially for metals like stainless steel, which form stable oxide layers.

## *II.2.3. Domains of predominance (DP) and domains of existence (DE)*

- A Pourbaix diagram pertains to a specific chemical element, and it is necessary to identify the species involved and define the oxidation state of the element in each of these species.

- Chemical species are positioned on the diagram based on their increasing oxidation states along the potential axis. Species with the same oxidation state are separated by vertical boundaries.
- To simplify, we assume that the solutions and gases involved are ideal. Thus, activities are treated as concentrations (for dissolved species) or partial pressures (for gaseous species), and the activity of solid species is set to 1.
- In order to apply Nernst's law or analyze acid-base equilibria, it is crucial to know the concentrations of the specific chemical species.

## II.3. Electrode potential

When a metal is immersed in an electrolyte solution, it behaves as an electrode. It dissolves in the form of positively charged particles and, in exchange, receives an equal amount of negative charges, which alters its electrical potential. Depending on the nature of the solution, the potential that the metal can take is of two types:

- Equilibrium Potential
- Corrosion (or Dissolution) Potential

### *II.3.1. Equilibrium potential*

The equilibrium potential is the potential of a metal immersed in a non-corrosive solution containing its metal ions (such as a solution of one of its salts). This potential is a thermodynamic quantity and is independent of time. Its value is determined by applying Nernst's law to the considered redox system.

In general:

$$M \rightarrow \ M^{n+} + ne^-$$

The potential of metal M is given by the equation:

$$E_M = E^\circ_{M/_{M^{n+}}} + \frac{R.T}{n.F}.\ln[M^{n+}]$$

**Where**

$E^0_{M/M^+}$ : Standard potential

R: Ideal gas constant

T: Temperature

n: Number of electrons involved in the reaction

F: Faraday's constant (F = 96,500 coulombs)

$[M^{n+}]$: Concentration of the $M^{n+}$ ion in the solution.

The measured cell potentials only represent differences in electrical potential. It is therefore important to establish a reference point (or reference cell) to which other half-cells can be compared. The most commonly used reference cell is the standard hydrogen electrode (Figure II.1).

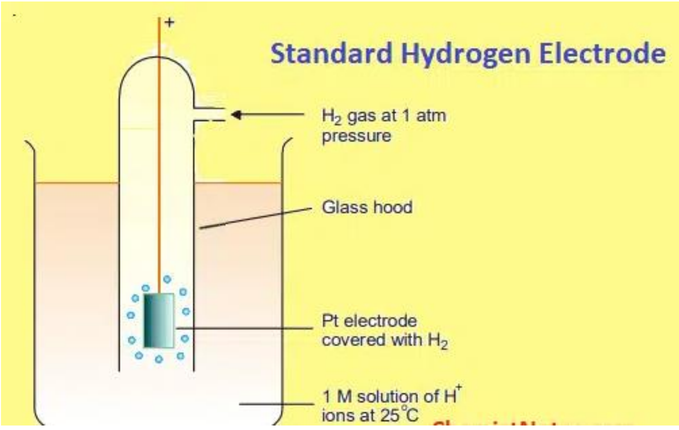


**Figure II.1.** Standard Hydrogen electrode

It consists of an inert platinum electrode immersed in a 1.0 M solution of $H^+$ ions, saturated with hydrogen gas bubbled into the solution at a pressure of $1.013 \times 10^5$ Pa and a temperature of 25°C. The platinum, which does not participate in the electrochemical reaction, serves only as a surface where hydrogen atoms can oxidize or hydrogen ions can reduce. The series of standard equilibrium potentials are presented in Table I.1.

**Table II.1.** Equilibrium potentials relative to the standard hydrogen electrode.

| Metal | Half-Cell Reaction | Standard Electrode Potential (E°) |
|---|---|---|
| Platinum (Pt) | $Pt^{2+} + 2e^- \rightarrow Pt$ | +1.22 V |
| Gold (Au) | $Au^{3+} + 3e^- \rightarrow Au$ | +1.50 V |
| Oxygen ($O_2$) | $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ | +1.23 V |
| Copper (Cu) | $Cu^{2+} + 2e^- \rightarrow Cu$ | +0.34 V |
| Silver (Ag) | $Ag^+ + e^- \rightarrow Ag$ | +0.799 V |
| Chlorine ($Cl_2$) | $Cl_2 + 2e^- \rightarrow 2Cl^-$ | +1.36 V |
| Iron (Fe) | $Fe^{2+} + 2e^- \rightarrow Fe$ | -0.44 V |

| | | |
|---|---|---|
| Zinc (Zn) | $Zn^{2+}$ + 2e- → Zn | -0.76 V |
| Magnesium (Mg) | $Mg^{2+}$ + 2e- → Mg | -2.37 V |
| Lithium (Li) | $Li^{+}$ + e- → Li | -3.04 V |

### *II.3.2. Corrosion potential ( dissolution potential)*

When a metal is immersed in any electrolyte, metal ions will dissolve into the solution, meaning the metal undergoes corrosion and thus acquires a potential relative to the solution. This potential changes over time until it stabilizes at a certain value, known as the corrosion or dissolution potential. This potential depends on factors such as the nature of the metal, the aggressiveness of the environment, the surface condition, the concentration, and the temperature.

The corrosion potential can be determined experimentally by plotting the curve E=f(t) until stabilization, or by plotting the curve I=f(E) or log (I) = f(E). The potentials measured in different environments are mixed potentials, which are non-reversible and involve both electrochemical reactions related to the metal (its oxidation) and the electrolyte (typically the reduction of a cation, such as $H^+$). The main reference electrodes are given in Table II.2.

**Table II.2.** Main Reference Electrodes

| Reference Electrode | Potential |
|---|---|
| Standard Hydrogen Electrode (SHE) | 0 V at 25°C, 1 atm, and 1 M $H^+$ |
| Saturated Calomel Electrode (SCE) | +0.241 V |
| Silver/Silver Chloride Electrode (Ag/AgCl) | +0.197 V |
| Saturated Copper Sulfate Solution ($CuSO_4$) | +0.318 V |
| Saturated Mercurous Sulfate Solution ($K_2SO_4$) | +0.615 V |

## II.4. Practical applications of the potential-pH diagram

### *II.4.1. E-pH diagram of water*

Water is a key factor in the corrosion of metallic materials. It facilitates electrochemical reactions, enables the formation of electrolyte solutions, and plays a role in galvanic corrosion, humidity, and the formation of protective films. Managing humidity and protecting against water are therefore essential to limit the effects of corrosion, particularly in marine or industrial environments.

Given that water is most common solvent, it is imperative to assess its thermodynamic stability by an examination of its potential acidity-potential diagram. We will systematically overlay the potential-pH diagram of water onto the diagram we are analyzing in order to predict the behavior of the species depicted in the diagram when exposed to water. The $H_2O$ molecule is amphiprotic, meaning it can function as both a reference or as an oxidant.

$$H_2O \leftrightarrow OH^- + H^+$$

$$[H3O^+].[OH^-] = 10^{-14} = Ke$$

$$pH = -log[H^+]$$

Water can decompose in electrolysis in a solution, resulting into hydrogen gas ($H_2$) and oxygen gas ($O_2$).

$$2H_2O \leftrightarrow 2H_2 + O_2$$

The following equation describes the equilibrium between hydrogen ions and hydrogen gas in an aqueous environment: .0

$$2H^+ + 2e^- \rightarrow H_2$$

$$\text{Or} \qquad 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^- \quad E^\circ = 1.24\, V/ENH$$

Since the concentrations of $[H^+]$ and $[OH^-]$ ions are related by the dissociation constant of water, these equations can be summarized in a Nernst equation.

$$H_2O \leftrightarrow OH^- + H^+$$

With

$$Ke = \frac{[OH^-].[H^+]}{H_2O} = 10^{-14} \quad at\ 25°C$$

$$E_1 = E_{H+/H2} = E^\circ_{H+/H2} + \frac{R.T}{n.F}.\log\frac{[H^+]^2}{P_{H2}}$$

$$E_1 = E^\circ_{H+/H2} - 0.059\,pH$$

Water can be decomposed into its other constituent, oxygen, as demonstrated by equations representing both the acidic and neutral/basic forms of the process.

$$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$$

$$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-$$

Again, we used the Nernst expression

$$E_2 = E_{O2}/_{H2O} = E^{\circ}_{O2}/_{H2O} + \frac{R.T}{n.F}.\log([H^+]^4.P_{O2})$$

$$E_2 = E^{\circ}_{O2}/_{H2O} - 0.059\,pH$$

The line labeled (**a**) in the Figure depicts the relationship between E and pH for the first equation, while the line labeled (**b**) in the Figure illustrates the relationship between E and pH for the second equation. Water's chemical behavior is categorized into three areas, encompassing all potential and pH values.

- In the top zone, water undergoes oxidation to generate oxygen.
- In the bottom region it undergoes reduction to produce hydrogen gas.
- Between lines (a) and (b) water is thermodynamically stable.

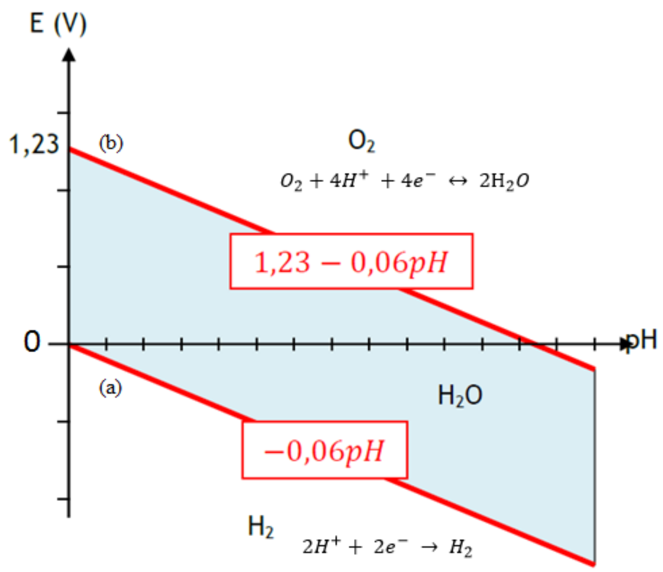


**Figure II.2.** E-pH stability diagram of water at 25°C

It is thermodynamically deduced that:

- Water is stable between the two lines on the plot.
- At potentials higher than the boundary line of the $O_2/H_2O$ couple, water oxidation occurs, accompanied by the release of gaseous oxygen.
- At potentials lower than the boundary line of the $H^+/H_2$ couple, water reduction takes place, accompanied by the release of gaseous hydrogen.

### *II.4.2. Fe E-pH diagram*

### *Exercise*

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The E–pH (Pourbaix) diagram of iron is constructed based on the following chemical species: Fe(s), $Fe^{2+}$(aq), $Fe^{3+}$(aq), $Fe(OH)_2$(s), and $Fe(OH)_3$(s). The total concentration of dissolved iron ($Fe^{2+}$ and $Fe^{3+}$) is : Ct = $10^{-2}$ mol/L.
The standard electrode potentials are:

$E^{\circ}_{Fe3+/Fe2+} = 0.77V/ENH$ and $E^{\circ}_{Fe2+/Fe} = -0.44V/ENH$

The solubility products are: $pK_{s1(Fe(OH)2} = 15.1$ and $pK_{s2(Fe(OH)3} = 38$

1. Determine the oxidation number of iron in each of the following species:
   Fe(s), $Fe^{2+}$(aq), $Fe^{3+}$(aq), $Fe(OH)_2$(s), and $Fe(OH)_3$(s).
2. Calculate the pH at which precipitation begins for: $Fe(OH)_3$(s) and $Fe(OH)_2$(s)
   (Assume $[Fe^{3+}] = [Fe^{2+}] = 10^{-2}$ mol/L)
3. Draw the initial (speciation) diagram for the iron element.
4. Derive the equilibrium (boundary) equations between the different iron species
5. Plot and annotate the E–pH diagram,