Chapter 2: Phase diagrams, Potential-pH diagram, Applications

Introduction

In the natural state most metals, with the exception of the noblest (gold), are not stable in their metallic state. Instead, they exist in oxidized form in ores. Consequently, metals have a natural tendency to oxidation, either through passivation or corrosion. The thermodynamic stability domains of these various forms can be represented on pH potential diagrams, or Pourbaix diagrams. These diagrams indicate the regions where various forms (ions, complexes, precipitates, metals) of the chemical element are present or dominant, as well as their regions of stability. The Nernst equation forms the basis of this concept, enabling us to understand how the change in the acidity of the medium might affect the redox properties of the pair. The water's potential-pH diagram is included in this graphic determine if redox reactions are possible with the water. Typically, redox reactions with water are often very slow. As a result, it is possible to prepare aqueous solutions of oxidant or reductant.

There are three main areas in Pourbaix diagram :

- Immunity domain: The metal is thermodynamically unassailable stable under the action of the surrounding environment. In practice, this is observed for noble metals, on other metals it is necessary to act on the potential to bring them to this area, this is the basis of cathodic protection.

- Passivation domain: It refers to a situation when the corrosion of a metal leads to the formation of a stable corrosion product that can act as a protective barrier.

- Corrosion domain: Where acidic or basic corrosion occurs, and the metal ions or complexes are stable.

Domains of predominance (DP) and domains of existence (DE)

Prior to commencing the construction of a Bourbet diagram, it is imperative to determine the areas of predominance and presence of the species being investigated. Hence, the presence and control of various species are determined by the horizontal, vertical, and diagonal lines. By understanding the systemic potential, we may accurately identify the regions of stability for the element and its compound. However, it is essential for us to be aware of the redox pairs and the oxidation number for each element.

Pourbaix diagrams necessitate the use of highly accurate rules.

A Pourbaix diagram pertains to a certain chemical element. Determine the specific species involved and establish the oxidation number of the element in each of them.

The chemical species are positioned on the diagram based on their increasing oxidation number along the axis of potentials.

Chemical species that have the same oxidation number will be separated by vertical boundaries.

To simplify matters, we make the assumption that the solutions and gases involved are perfect. Consequently, activities will be assimilated into concentrations (for dissolved species) or partial pressures (for gaseous species). The activitie of solid species will be equal to 1.

In order to apply Nernst's law or analyze acid-base balances, it is essential to have knowledge of the concentrations of specific chemical species.

The boundaries of oxidation-reduction equilibria can be described by Nernst's law, which provides the equation for these boundaries, and these boundaries can be either horizontal or oblique. In order to apply Nernst's law or analyze acid-base balances, it is essential to have knowledge of the concentrations of specific chemical species.

E-pH Diagram of Water

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 H2O 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

$2H^+ + 2e^- \rightarrow H_2$ (1)

Or $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (1)

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

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

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

$$E_1 = E_{H^+/H_2} = E^{\circ}_{H^+/H_2} + \frac{R.T}{n.F}.\log\frac{[H^+]^2}{P_{H2}}$$

$$E_1 = E^{\circ}_{H^+/H_2} - 0.059\,pH$$

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.

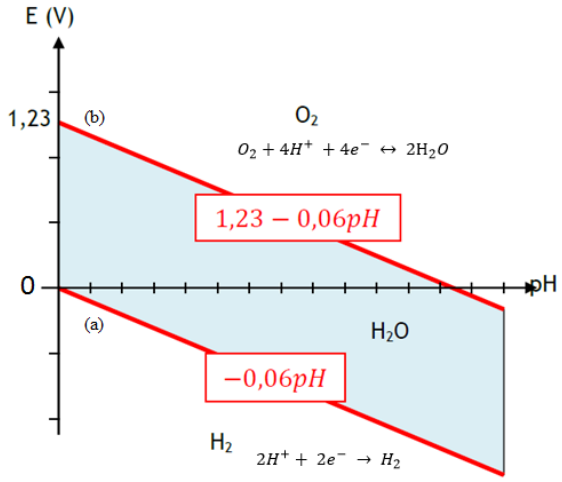


Figure .1. E-pH stability diagram of water at 25ºC

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.

Applications

1. Fe E-pH (Pourbaix) Diagram

Draw the Fe E-pH diagram under the conditions following :
+ Species considered : Fe (s), Fe^{2+}(aq), Fe^{3+}(aq), $Fe(OH)_2$ (s) and $Fe(OH)_3$ (s)
+ The total concentration of dissolved species is equal to Ctr = 10^{-2} mol/L

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

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

$$\boldsymbol{pK_{s1(Fe(OH)2} = 15.1}$$

$$\boldsymbol{pK_{s2(Fe(OH)3} = 38}$$

Calculation

b) Calcul des pH des deux précipités pH₁ et pH₂ :

$$\boxed{Fe^{2+} + 2\,OH^- \leftrightarrow Fe(OH)_2} \qquad \textbf{(32)}$$

$$K_{s1} = [Fe^{2+}][OH^-]^2 \Rightarrow [OH^-] = \sqrt{\frac{K_{s1}}{[Fe^{2+}]}}$$

$$[OH^-] = \sqrt{\frac{10^{-15,1}}{10^{-2}}} = \sqrt{10^{-13,1}} \Rightarrow pOH = -\frac{1}{2}\log\left(10^{-13,1}\right) = 6,55$$

$$\Rightarrow \boxed{pH_1 = 7,45} \qquad \textbf{(33)}$$

$$\boxed{Fe^{3+} + 3\,OH^- \leftrightarrow Fe(OH)_3} \qquad \textbf{(34)}$$

$$K_{s2} = [Fe^{3+}][OH^-]^3 \Rightarrow [OH^-] = \sqrt[3]{\frac{K_{s2}}{[Fe^{2+}]}}$$

$$[OH^-] = \sqrt[3]{\frac{10^{-38}}{10^{-2}}} = \sqrt{10^{-36}} \Rightarrow pOH = -\frac{1}{3}\log\left(10^{-36}\right) = 12$$

$$\Rightarrow \boxed{pH_2 = 2} \qquad \textbf{(35)}$$

c) Etude du couple $F^{2+}_{(aq)}/Fe_{(s)}$:

$$\boxed{Fe^{2+}_{(aq)} + 2e^{-} \rightarrow Fe_{(s)}} \qquad (36)$$

$$E_{Fe^{2+}/Fe} = E^{0}_{Fe^{2+}/Fe} + \frac{0{,}06}{2}\log\frac{\left[Fe^{2+}\right]}{\left[Fe\right]} \qquad (*)$$

Si on applique les concentrations de tracé, il vient :

$$E_{Fe^{2+}/Fe} = -\,0{,}44 + 0{,}03\log\left(10^{-2}\right)$$

$$\boxed{E_{Fe^{2+}/Fe} = -\,0{,}50\ V} \qquad (37)$$

d) Etude du couple $Fe^{3+}{}_{(aq)}/Fe^{2+}{}_{(aq)}$:

$$\boxed{Fe^{3+}_{(aq)} + 1e^{-} \rightarrow Fe^{2+}_{(aq)}} \qquad (38)$$

$$E_{Fe^{3+}/Fe^{2+}} = E^{0}_{Fe^{3+}/Fe^{2+}} + \frac{0{,}06}{1}\log\frac{\left[Fe^{3+}\right]}{\left[Fe^{2+}\right]} \qquad (**)$$

Si on applique les conventions de tracé, il vient :

$$\boxed{E_{Fe^{3+}/Fe^{2+}} = 0{,}77\ V} \qquad (39)$$

e) Etude du couple $Fe(OH)_{2\,(s)}/Fe_{(s)}$:

$$\boxed{Fe(OH)_{2(s)} + 2H^{+}_{(aq)} + 2e^{-} \rightarrow Fe_{(s)} + 2H_2O} \qquad (40)$$

Mais, comme le potentiel de la solution peut s'exprimer à partir de n'importe quel couple présent, il suffit de reprendre l'expression (*) et de remplacer $\left[Fe^{2+}\right]$ par son expression en fonction du K_{s1} :

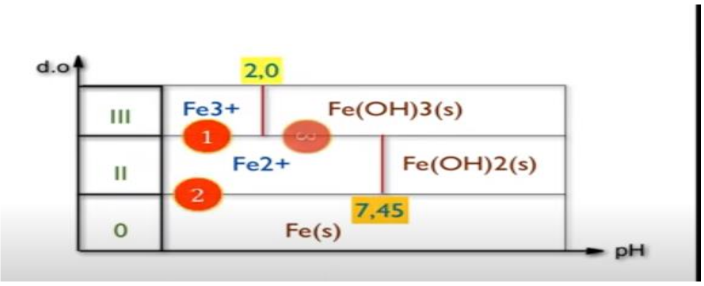
$$E = E^0_{Fe^{2+}/Fe} + \frac{0,06}{2}\log\frac{[Fe^{2+}]}{[Fe]}$$

$$E = E^0_{Fe^{2+}/Fe} + \frac{0,06}{2}\log\left(\frac{K_{s1}.[H^+]^2}{K_e^2}\right)$$

$$E = E^0_{Fe^{2+}/Fe} - 0,03pK_{s1} + 0,06pK_e - 0,06pH$$

$$E = -0,44 - 0,03\times15,1 + (0,06\times14) - 0,06pH$$

$$\boxed{E = -0,053 - 0,06pH} \qquad \textbf{(41)}$$



f) Etude du couple $Fe(OH)_{3\,(s)}/Fe^{2+}{}_{(aq)}$:

$$\boxed{Fe(OH)_{3(s)} + 3H^+ + 1e^- \rightarrow Fe^{2+}_{(aq)} + 3H_2O} \qquad \textbf{(42)}$$

Mais il est plus astucieux de reprendre l'expression (**) et de remplacer $\left[Fe^{3+}\right]$ comme suit :

$$E = E^0_{Fe^{3+}_{(aq)}/Fe^{2+}_{(aq)}} + 0,06\log\left(\frac{K_{s2}.[H^+]^3}{K_e^3.[Fe^{2+}]}\right)$$

Si on applique les conventions de tracé, il vient :

$$E = E^0_{Fe^{3+}_{(aq)}/Fe^{2+}_{(aq)}} + 0,06\log\left(\frac{K_{s2}.[H^+]^3}{K_e^3.[Fe^{2+}]}\right)$$

$$E = E^0_{Fe^{3+}_{(aq)}/Fe^{2+}_{(aq)}} - 0,06pK_{s2} + (3\times0,06)pK_e - 0,06\log C_0 - (3\times0,06)pH$$

$$E = 0,77 - 0,06\times38 + 3\times0,06\times14 - 0,06\log10^{-2} - 3\times0,06pH$$

$$\boxed{E = 1{,}13 - 0{,}18pH} \quad (43)$$

g) Etude du couple $Fe(OH)_{3\,(s)}/Fe(OH)_{2\,(s)}$:

$$\boxed{Fe(OH)_{3(s)} + H^+_{(aq)} + 1e^- \rightarrow Fe(OH)_2 + H_2O} \quad (44)$$

Mais il est plus astucieux de reprendre l'expression (**) et de remplacer $\left[Fe^{2+}\right]$ et $\left[Fe^{3+}\right]$

$$E = E^0_{Fe^{3+}_{(aq)}/Fe^{2+}_{(aq)}} + 0{,}06\log\left(\frac{K_{s2}.\left[H^+\right]}{K_e.K_{s1}}\right)$$

Si on applique les conventions de tracé, il vient :

$$E = E^0_{Fe^{3+}_{(aq)}/Fe^{2+}_{(aq)}} - 0{,}06\left(pK_{s2} - pK_{s1}\right) + 0{,}06pK_e - 0{,}06pH$$

$$E = 0{,}77 - 0{,}06\left(38 - 15{,}1\right) + 0{,}06 \times 14 - 0{,}06pH$$

$$\boxed{E = 0{,}23 - 0{,}06pH} \quad (45)$$

Le diagramme de Pourbaix de fer est présenté dans la figure suivante.

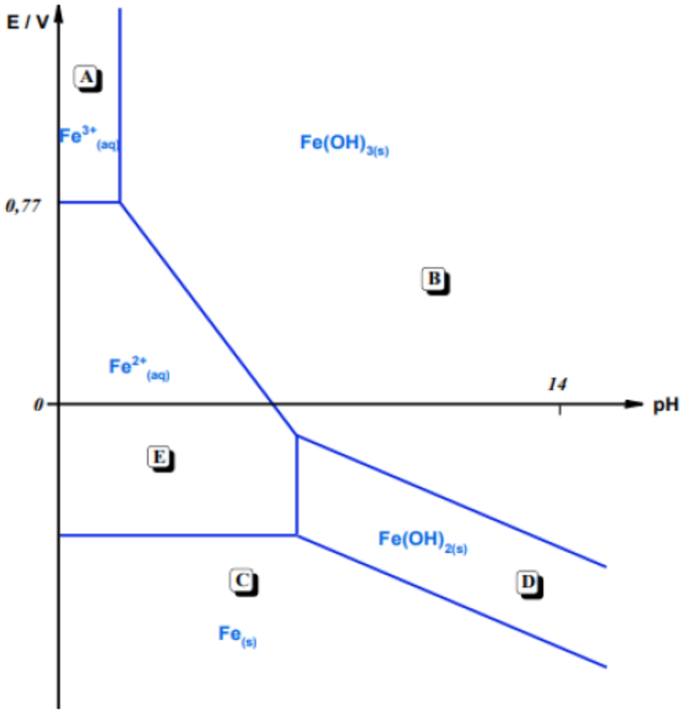


Figure 29 : Diagramme potentiel-pH simplifié du fer à 25 °C, pour $C_0 = 10^{-2}$ mol.L^{-1}.

Rapidement, nous voyons quels sont les domaines de prédominance des ions Fe^{3+} ou Fe^{2+} et quels sont les domaines d'existence des solides $Fe(OH)_2(s)$, $Fe(OH)_3(s)$ ou $Fe(s)$.

A : Domaine de prédominance de $Fe^{3+}(aq)$: Fe^{3+} n'est prédominant que dans les solutions de potentiel élevé et dans des solutions qui doivent être très acides.

B : Domaine d'existence de $Fe(OH)_3(s)$.

C : Domaine d'existence de $Fe(s)$

D : Domaine d'existence de $Fe(OH)_2(s)$

E : Domaine de prédominance de $Fe^{2+}(aq)$

2. Ni E-pH (Pourbaix) Diagram

Here, the E-pH diagram of nickel will be utilized to illustrate the construction of such diagrams based from basic principles. In the following discussion, the species containing the Nickel element will be Ni, Ni^{2+}, $Ni(OH)_2$, NiO_2, The concentration of Ni^{2+} used is 10^{-3} mol/L

$$\mathrm{E}^{\circ}_{Ni^{2+}/Ni} = 0.25\ \mathrm{V/ENH}$$

$$\mathrm{E}^{\circ}_{NiO2/Ni^{2+}} = 1.59\ \mathrm{V/ENH}$$

$$\boldsymbol{K_{s(Ni(OH)2} = 10^{-16}}$$

Questions

1. Calculate the oxidation number of the element nickel in the specified atoms.
2. Calculate the pH at which the precipitation of Ni^{2+} occurs in the form of $Ni(OH)_2$.
3. Create the preliminary diagram of Burpee, indicating simply the horizontal and vertical lines and arranging the elements in order of ascending oxidation number.
4. Determine the equations associated with each dividing term between the elements.

Calculations

1. Calculation of the oxidation number of the element nickel in the specified atoms.

Elements	Oxidation number of the element nickel
NiO_2	+IV
$Ni(OH)_2$	+II
Ni^{2+}	+II
Ni	0

2. The pH at which the precipitation of Ni^{2+} occurs in the form of $Ni(OH)_2$.

$$Ni^{2+}(\mathrm{aq}) + 2OH^-\ (\mathrm{aq}) \rightarrow\ Ni(OH)_2\ (s)$$

We have

$$Ks = [Ni^{2+}].[OH^-]^2$$

$$[OH^-] = \sqrt{\frac{K_S}{[Ni^{2+}]}} = 3.162.10^{-7}$$

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

$$[H^+] = 3{,}162.10^{-8}$$

$$pH = -log[H^+] = 7{,}5$$

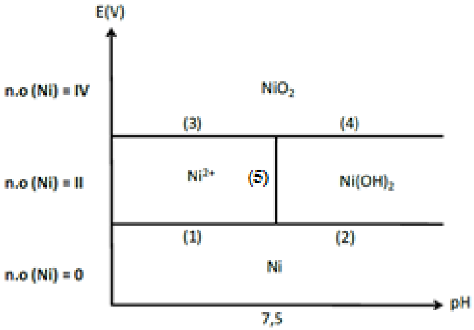


Figure 2. Preliminary E-pH diagram of Ni

The equations correspond to each line separating the elements.

$For\ pH < 7,5$

The border (1) between the $Ni^{2+}(\text{aq}) / Ni(s)$

$$Ni^{2+}(\text{aq}) + 2e^- \leftrightarrow Ni\ (\text{s})$$

$$E_1 = E_{Ni2+/Ni} = E^{\circ}_{Ni2+/Ni} + \frac{R.T}{n.F}.\log\frac{[Ni^{2+}]}{[Ni]}$$

$$E_1 = E^{\circ}_{Ni2+/Ni} + \frac{0.059}{2}.\log[Ni^{2+}]$$

$$E_1 = -0.34\text{V/ENH}$$

The border (3) between the $NiO_2(\text{s}) / Ni^{2+}(\text{aq})$

$$NiO_2(\text{s}) + 4H^+ + 2e^- \leftrightarrow Ni^{2+}(\text{aq}) + 4H_2O\ (l)$$

$$E_3 = E_{NiO_2/Ni^{2+}} = E^{\circ}_{NiO_2/Ni^{2+}} + \frac{0.059}{2}.\log\frac{[H^+]^4}{[Ni^{2+}]}$$

$$E_3 = E^{\circ}_{NiO_2/Ni^{2+}} + 4.\frac{0.059}{2}.log[H^+] - \frac{0.059}{2}.\log[Ni^{2+}]$$

$$E_3 = 1.68 - 0.059\,pH$$

$For\ pH > 7,5$

The border (2) between the $Ni(OH)_2(\text{s}) / Ni\ (\text{s})$

$Ni(OH)_2(\mathrm{s}) + 2H^+ + 2e^- \leftrightarrow Ni\ (\mathrm{s}) + 2H_2O\ (l)$

$E_2 = E_{Ni(OH)_2/_{Ni}} = E^{\circ}_{Ni(OH)_2/_{Ni}} + \frac{0.059}{2}\ .log[H^+]^2$

$E_2 = E^{\circ}_{Ni(OH)_2/_{Ni}} - 0.059\ pH$

Calculation of $E^{\circ}_{Ni(OH)_2/_{Ni}}$

The border between (1) and (2) meet in pH = 7.5

$E_1 = E_2 \leftrightarrow E_{Ni2+/_{Ni}} = E_{Ni(OH)_2/_{Ni}}$

$-0{,}34 = E^{\circ}_{Ni(OH)_2/_{Ni}} - 0.059\ pH$

$E^{\circ}_{Ni(OH)_2/_{Ni}} = 0{,}11\ \mathrm{V/ENH}$

$E_2 = 0{,}11 - 0.059\ pH$

The border (4) between the $NiO_2\ (\mathrm{s}) \Big/ Ni(OH)_2(\mathrm{s})$

$NiO_2\ (\mathrm{s}) + 2H^+ + 2e^- \leftrightarrow Ni(OH)_2(\mathrm{s})$

$E_4 = E_{NiO_2/_{Ni(OH)_2}} = E^{\circ}_{NiO_2/_{Ni(OH)_2}} + \frac{0.059}{2}\ .log[H^+]^2$

$E_4 = E^{\circ}_{NiO_2/_{Ni(OH)_2}} - 0.059\ pH$

Calculation of $E^{\circ}_{NiO_2/_{Ni(OH)_2}}$

The border between (3) and (4) meet in pH = 7.5

$E_3 = E_4 \leftrightarrow E_{NiO_2/_{Ni^{2+}}} = E_{NiO_2/_{Ni(OH)_2}}$

$E_3 = E_4 \leftrightarrow E_{NiO_2/_{Ni^{2+}}} = E_{NiO_2/_{Ni(OH)_2}}$

$1.68 - 0.059\ pH = E^{\circ}_{NiO_2/_{Ni(OH)_2}} - 0.059\ pH$

$E^{\circ}_{NiO_2/_{Ni(OH)_2}} = 1.23\ \mathrm{V/ENH}$

$E_4 = 1{,}23 - 0.059\ pH$

The border (5) is at pH = 7.5 and it is between the $Ni^{2+}(\mathrm{aq}) \Big/ Ni(OH)_2(\mathrm{s})$

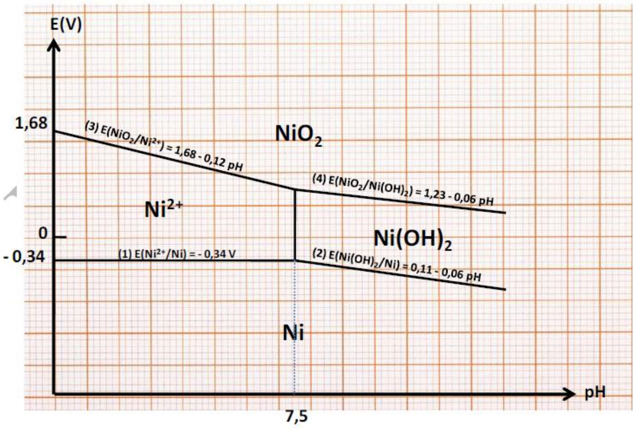


Figure 3. E-pH diagram of Ni

The stability of nickel in water

The E-pH diagram of Nickel incorporates the potential-pH diagram of water to determine if redox reactions are possible with water. Typically, redox reactions with water are often very slow, as a result, it is possible to create stable aqueous solutions oxidant or reducer. The thermodynamic stability region of water is delineated by two pink lines, as seen in figure 30.

3. Mg E-pH (Pourbaix) Diagram

Draw a Bourbet diagram for magnesium, limit the study at the elements Mg (s), Mg^{2+} and $Mg(OH)_2$ (s). The given practical concentration of Mg^{2+} ions is 10^{-2} mol/L.

$$E^{\circ}_{Mg^{2+}/Mg} = -2.37\ \mathrm{V/ENH}$$

$$E^{\circ}_{Mg(OH)2/Mg} = -2.69\ \mathrm{V/ENH}$$

$$K_{s\ (Mg(OH)2)} = 10^{-11}$$

1. Calculate the oxidation number of the magnesium element in the specified atoms.

2. Calculate the pH at which the precipitation of $\mathbf{Mg^{2+}}$ occurs in the form of $\mathbf{Mg(OH)_2}$.

3. Determine the equations associated with each dividing term between the elements.

4. Overlay this diagram upon the water diagram.

Calculations

1. Calculation of the Mg oxidation number in the specified atoms

Elements	no (Mg)
Mg	0
Mg^{2+}	+II
$Mg(OH)_2$	+II

2. Calculation of the pH precipitation of $\mathbf{Mg^{2+}}$ to $\mathbf{Mg(OH)_2}$.

$$Mg^{2+}(\mathrm{aq}) + 2OH^{-}\ (\mathrm{aq}) \rightarrow\ Mg(OH)_2\ (s)$$

We have

$$Ks = [Mg^{2+}].[OH^-]^2$$

$$[OH^-] = \sqrt{\frac{K_S}{[Mg^{2+}]}} = 3.162.10^{-5}\ mol/L$$

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

$$[H^+] = 3{,}162.10^{-8}$$

$$pH = \ -log[H^+] = 9{,}5$$

3. Determination of the equations associated with each dividing term between the elements

Therefore we have 2 borders

For pH $< 9,5$

Border (1) between the $^{Mg^{2+}(\text{aq})}/_{Mg(s)}$

$$Mg^{2+}(\text{aq}) + \ 2e^- \ \leftrightarrow \ Mg\ (\text{s})$$

$$E_1 = E_{Mg2+/_{Mg}} = E^{\circ}_{Mg2+/_{Mg}} + \frac{R.T}{n.F}.\log\frac{[Mg^{2+}]}{[Mg]}$$

$$E_1 = E^{\circ}_{Mg2+/_{Mg}} + \frac{0.059}{2}.\log\ [Mg^{2+}]$$

$$E_1 = -2.37\ + \frac{0.059}{2}.log(\ 10)^{-2}$$

$$E_1 = \ -2.43\ \text{V}$$

For pH $> 9,5$

Border (2) between the $^{Mg(OH)_2(\text{s})}/_{Mg\ (\text{s})}$

$$Mg(OH)_2(\text{s}) + 2H^+ + \ 2e^- \ \leftrightarrow \ Mg\ (\text{s})\ + 2H_2O\ (l)$$

$$E_2 = E_{Mg(OH)_2/_{Mg}} \ = \ E^{\circ}_{Mg(OH)_2/_{Mg}} + \frac{0.059}{2}.log[H^+]^2$$

$$E_2 = E^{\circ}_{Mg(OH)_2/_{Mg}} \ - \ 0.059\ pH$$

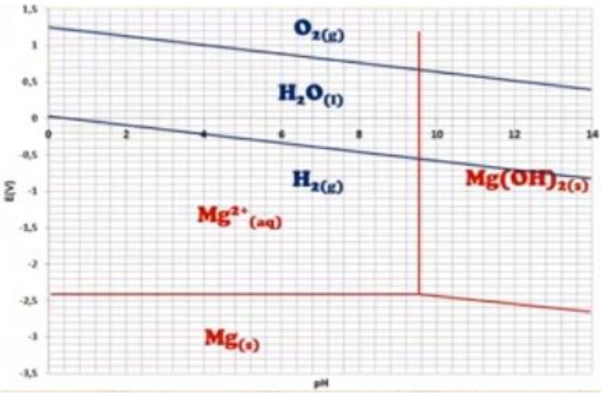


Figure 4. E-pH diagram of Mg