Exercise

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:

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

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**,

Calculation

1. The oxidation number of iron in the different species.

o.n. of Fe	Elements	
0	Fe(s)	
+ II	Fe^{2+}(aq)	$Fe(OH)_2$(s)
+ III	Fe^{3+}(aq)	$Fe(OH)_3$(s)

2. pH_1 an pH_2 at which precipitation begins for: $Fe(OH)_3$(s) and $Fe(OH)_2$(s), respectively

$$\boldsymbol{Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2}$$

$$\boldsymbol{K_{S1} = [Fe^{2+}][OH^-]^2 = [OH^-] = \sqrt{\frac{K_{S1}}{[Fe^{2+}]}} = \sqrt{\frac{10^{-15.1}}{10^{-2}}} = 2.81 \times 10^{-7}}$$

$$\boldsymbol{K_e = [H^+][OH^-] = 10^{-14} \rightarrow [H^+] = \frac{10^{-14}}{2.81 \times 10^{-7}} = 3.558 \times 10^{-8}}$$

$$\boldsymbol{pH_1 = -log[OH^-] = 7.45}$$

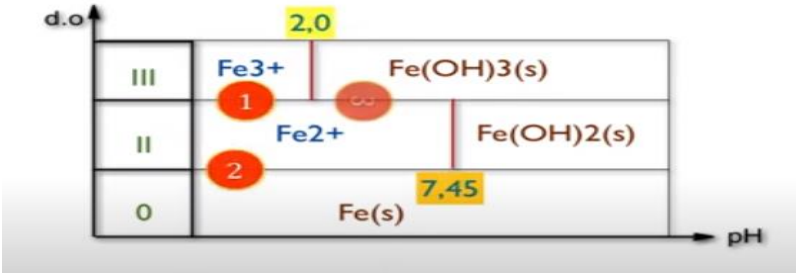
$$\boldsymbol{Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3}$$

$$K_{S2} = [Fe^{3+}][OH^-]^3 = [OH^-] = \sqrt[3]{\frac{K_{S1}}{[Fe^{2+}]}} = \sqrt{\frac{10^{-38}}{10^{-2}}} = 10^{-12}$$

$$K_e = [H^+][OH^-] = 10^{-14} \rightarrow [H^+] = \frac{10^{-14}}{10^{-12}} = 0.01$$

$$pH_2 = -log[OH^-] = 2$$

3. Draw the initial (speciation) diagram for the iron element.



4. **Derive the equilibrium (boundary) equations** between the different iron species

- Equation between $Fe^{3+}(aq)$/ $Fe^{2+}(aq)$

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

$$E_1 = E_{Fe^{3+}/Fe^{2+}} = E^{\circ}_{Fe^{3+}/Fe^{2+}} + \frac{R.T}{n.F}.\log\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$\rightarrow E_1 = 0.77V$$

- Equation between $Fe^{2+}(aq)$/Fe(s)

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$$

$$E_2 = E_{Fe^{2+}/Fe} = E^{\circ}_{Fe^{2+}/Fe} + \frac{R.T}{n.F}.\log[Fe^{2+}]$$

$$E_2 = -0.04 + \frac{0.059}{2}.\log[10^{-2}]$$

$$\rightarrow E_2 = -0.499\ V$$

- Equation between $Fe(OH)_3$ (s)/ Fe^{2+}(s)

$$Fe(OH)_3(s) + 3H^+(aq) + 1e^- \rightarrow \mathbf{Fe^{2+}}(aq) + 3H_2O$$

$$E_3 = E_{Fe(OH)_3/\mathbf{Fe^{2+}}} = E^{\circ}_{Fe(OH)_3/\mathbf{Fe^{2+}}} + \frac{0.059}{1}.\log\frac{[H^+]^3}{[Fe^{2+}]}$$

$$E_3 = E^{\circ}_{Fe(OH)_3/\mathbf{Fe^{2+}}} - 0.18\,pH - 0.059\log[Fe^{2+}]$$

At pH = 2 $\rightarrow$ $E_1 = E_3$ $\rightarrow E^{\circ}_3 = E^{\circ}_{Fe(OH)_3/\mathbf{Fe^{2+}}} = 1.13\ V$

$$\rightarrow E_3 = 1.13 - 0.18\,pH$$

- Equation between $Fe(OH)_3$ (s)/ $Fe(OH)_2$ (s)

$$Fe(OH)_3(s) + H^+(aq) + 1e^- \rightarrow Fe(OH)_2(s) + H_2O$$

$$E_4 = E_{Fe(OH)_3/Fe(OH)_2} = E^\circ_{Fe(OH)_3/Fe(OH)_2} + 0.059 \cdot \log[H^+]$$

At pH = 7.45 → $E_3 = E_4 \rightarrow E_4^\circ = E^\circ_{Fe(OH)_3/Fe(OH)_2} = 0.23\ V$

$$\rightarrow E_4 = 0.23 - 0.059\ pH$$

- Equation between $Fe(OH)_2$ (s)/ Fe (s)

$$Fe(OH)_2(s) + 2H^+(aq) + 2e^- \rightarrow Fe(aq) + 2H_2O$$

$$E_5 = E_{Fe(OH)_2/Fe} = E^\circ_{Fe(OH)_2/Fe} + \frac{0.059}{2} \cdot \log[H^+]^2$$

$$E_5 = E^\circ_{Fe(OH)_2/Fe} - 0.059\ pH$$

At pH = 7.45 → $E_2 = E_5 \rightarrow E_5^\circ = E^\circ_{Fe(OH)_2/Fe} = -0.02\ V$

$$\rightarrow E_5 = -0.053 - 0.059\ pH$$

5. **Plot and annotate the E–pH diagram**, showing:

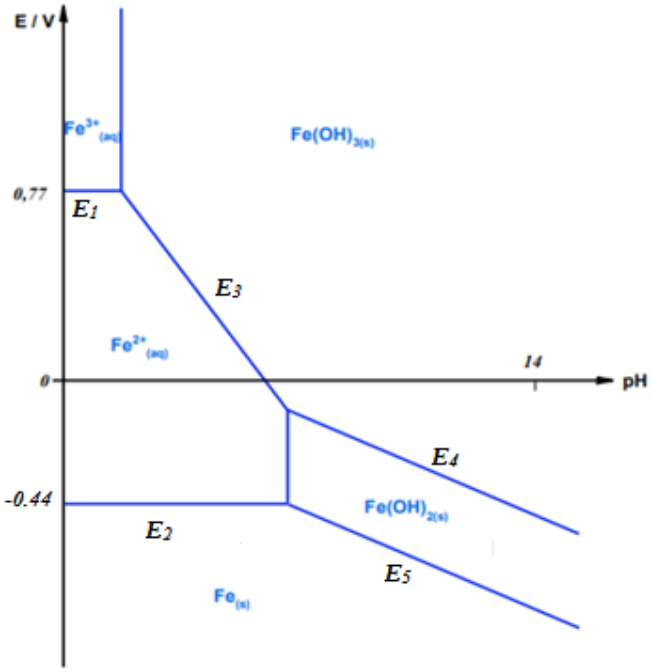


Figure II.3. Potential-pH diagram of iron at 25°C for $C_{tr} = 10^{-2}$ mol/L.