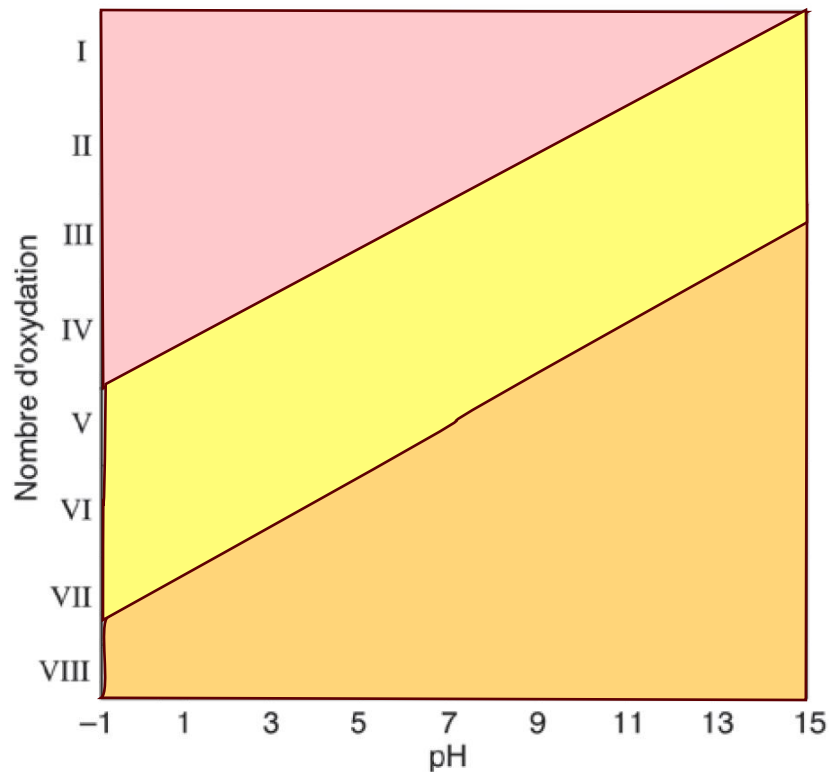


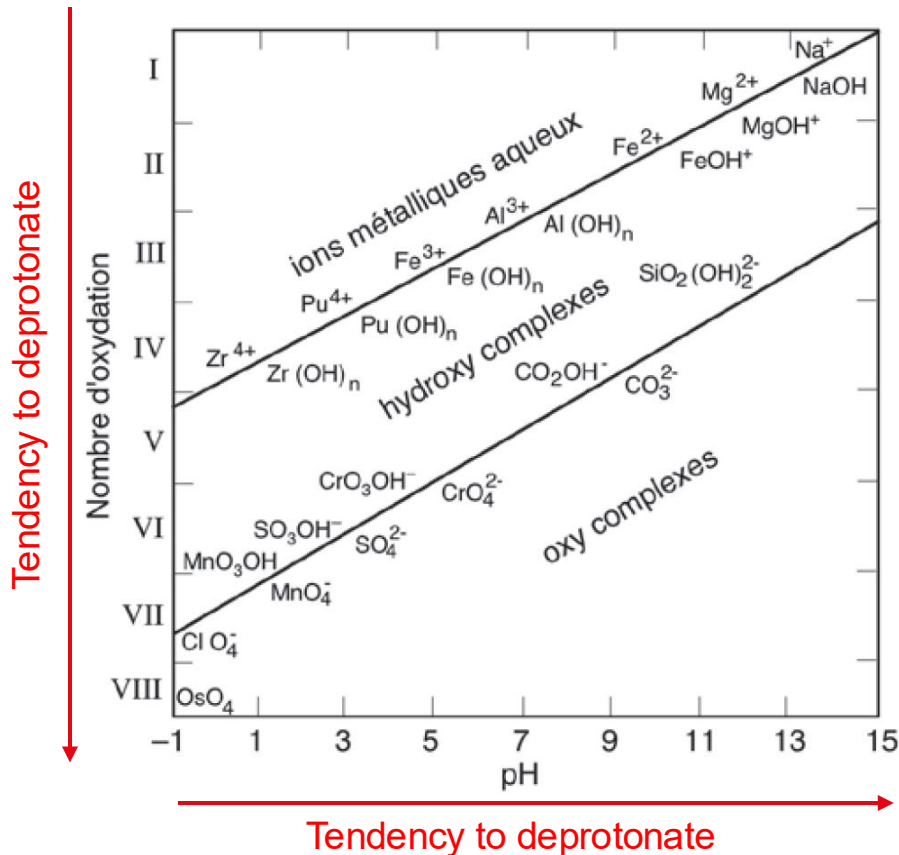
Exercise 1: Complex formation with water



Which color refers to

- Aquo-metal ions (fully protonated)?
- Hydroxo (OH⁻) complexes?
- Oxy (-O) complexes (fully deprotonated)?

Exercise 1: Solution



For most natural waters,

- metals in valence states I and II will be present as “free ions”, that is, aquo-complexes
- valence III metals will be present as aquo- and hydroxo-complexes (depending on pH)
- and those with higher charge will be present as oxo-complexes.

Exercise 2: pH - $p\beta_i$ relationships for hydrolysis



Consider a system with Cu in water.

- What is the pH in solution when the concentration of Cu^{2+} equals the concentration of $\text{Cu}(\text{OH})_2$?
- At pH 8, is Cu^{2+} or $\text{Cu}(\text{OH})_2$ the dominant species in solution?

The following constant is available:

$$*\beta_2 = \frac{[\text{Cu}(\text{OH})_2][\text{H}^+]^2}{[\text{Cu}^{2+}]} = 10^{-13.8}$$



- a. Take negative logs on both sides of the equation

$$13.8 - 2 \text{ pH} = \log[\text{Cu}^{2+}] - \log [\text{Cu}(\text{OH})_2]$$

Here, $[\text{Cu}^{2+}] = [\text{Cu}(\text{OH})_2]$

$$13.8 = 2 \text{ pH}$$

$$\underline{\text{pH} = 6.9}$$

- b. $\text{p}^*\beta_2 = 13.8$

$$\text{m pH} = 2 * 8 = 16$$

m pH > $\text{p}^*\beta_2$: $\text{Cu}(\text{OH})_2$ is dominant in solution

Exercise 3: Hydroxo complexes



Consider the following equations:



- Is the acidity of Cu^{2+} or Mg^{2+} higher? (In this context, acidity is the tendency to hydrolyse water.)
- At pH 7, which fraction of the Cu(II) of a pure Cu-salt solution will occur as hydroxo complex?
- At pH 7, which fraction of the Mg(II) of a pure Mg-salt solution will occur as hydroxo complex?

Exercise 3: Solution



- a. Cu^{2+} has higher acidity than Mg^{2+} (higher $\log *K_1$ value)
- b. Fraction of hydrolysed species, α , is expressed as:

$$\alpha_{\text{CuOH}^+} = \frac{[\text{CuOH}^+]}{\text{Cu}_T} = \frac{[\text{CuOH}^+]}{[\text{Cu}^{2+}] + [\text{CuOH}^+]}$$

$$*K_1 = \frac{[\text{CuOH}^+][\text{H}^+]}{[\text{Cu}^{2+}]}, \text{ i.e., } [\text{Cu}^{2+}] = \frac{[\text{H}^+][\text{CuOH}^+]}{*K_1}$$

$$\alpha_{\text{CuOH}^+} = \frac{[\text{CuOH}^+]}{\frac{[\text{H}^+][\text{CuOH}^+]}{*K_1} + [\text{CuOH}^+]} = \frac{1}{\frac{[\text{H}^+]}{*K_1} + 1} = \underline{0.091}$$

- c. Analogous calculation to b.

$$\alpha_{\text{MgOH}^+} = \frac{1}{\frac{[\text{H}^+]}{*K_1} + 1} = \underline{0.00004}$$

Exercise 4: Hydrolysis of iron



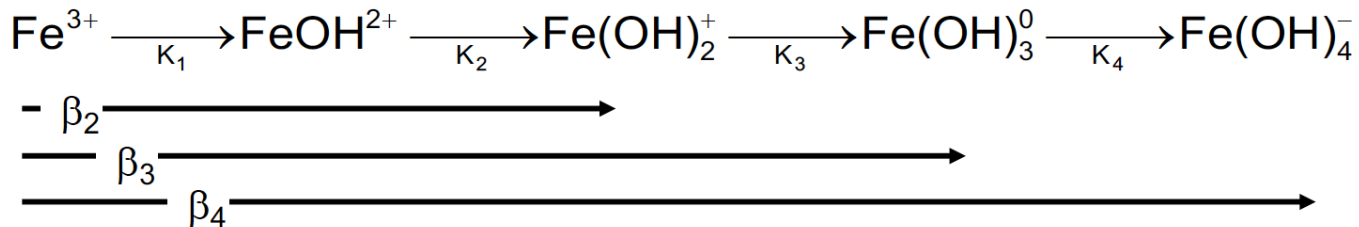
Construct a distribution diagram for iron species as a function of pH. Follow the guidelines for constructing distribution diagrams (note that we consider all hydrolysis species here). Use the following constants for your calculations and a total Fe(III) concentration of 10^{-9} M.

$$\log *K_1 = -3.05$$

$$\log * \beta_2 = -6.31$$

$$\log * \beta_3 = -13.8$$

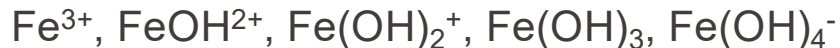
$$\log * \beta_4 = -22.7$$



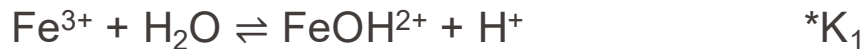
Exercise 4: Solution



1. Identify species present at equilibrium



2. Write our equilibrium equations and list complexation constants



3. List mass balance equations



Exercise 4: Solution



4. Insert 2. into 3 to express $[\text{Fe(III)}]_{\text{T}}$ as a function of $[\text{Fe}^{3+}]$ and formation constants

$$\begin{aligned}
 [\text{Fe(III)}]_{\text{T}} &= 10^{-9} = [\text{Fe}^{3+}] \left(1 + \frac{{}^*K_1}{[\text{H}^+]} + \frac{{}^*K_1 \cdot {}^*K_2}{[\text{H}^+]^2} + \frac{{}^*K_1 \cdot {}^*K_2 \cdot {}^*K_3}{[\text{H}^+]^3} + \frac{{}^*K_1 \cdot {}^*K_2 \cdot {}^*K_3 \cdot {}^*K_4}{[\text{H}^+]^4} \right) \\
 &= [\text{Fe}^{3+}] \left(1 + \frac{{}^*K_1}{[\text{H}^+]} + \frac{{}^*\beta_2}{[\text{H}^+]^2} + \frac{{}^*\beta_3}{[\text{H}^+]^3} + \frac{{}^*\beta_4}{[\text{H}^+]^4} \right)
 \end{aligned}$$

5. Solve 4. for Fe^{3+}

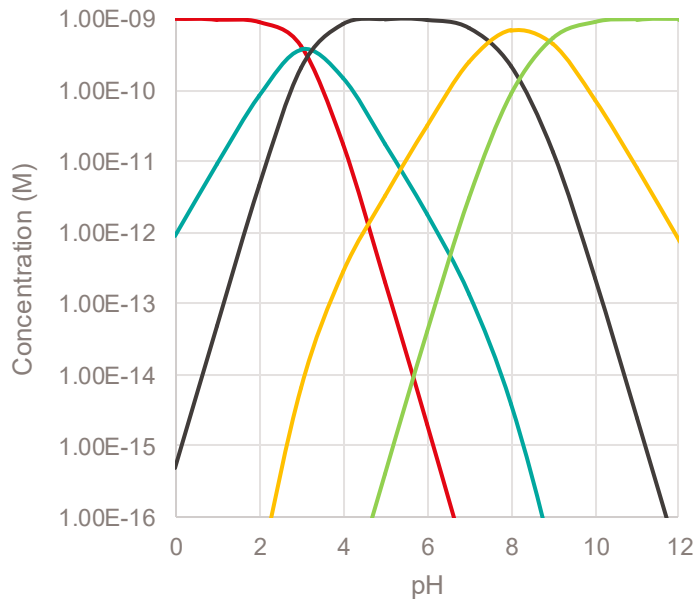
$$[\text{Fe}^{3+}] = [\text{Fe(III)}]_{\text{T}} / \left(1 + \frac{{}^*K_1}{[\text{H}^+]} + \frac{{}^*\beta_2}{[\text{H}^+]^2} + \frac{{}^*\beta_3}{[\text{H}^+]^3} + \frac{{}^*\beta_4}{[\text{H}^+]^4} \right)$$

6. Use the results of 5. to calculate the concentrations of hydroxo complexes using 2.

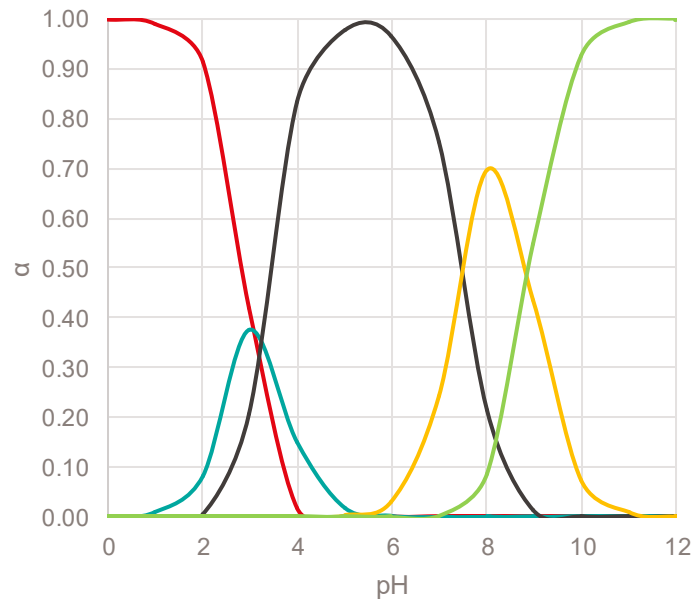
$${}^*K_1 = \frac{[\text{Fe(OH)}^+][\text{H}^+]}{[\text{Fe}^{3+}]}, \text{ thus } [\text{Fe(OH)}^+] = {}^*K_1 \frac{[\text{Fe}^{3+}]}{[\text{H}^+]}$$

Concentrations of other species can be calculated analogously using the eqs. in 2.

Exercise 4: Solution



— Fe³⁺ — FeOH₂⁺ — Fe(OH)₂⁺
— Fe(OH)₃aq — Fe(OH)₄⁻



— Fe³⁺ — FeOH₂⁺ — Fe(OH)₂⁺
— Fe(OH)₃aq — Fe(OH)₄⁻