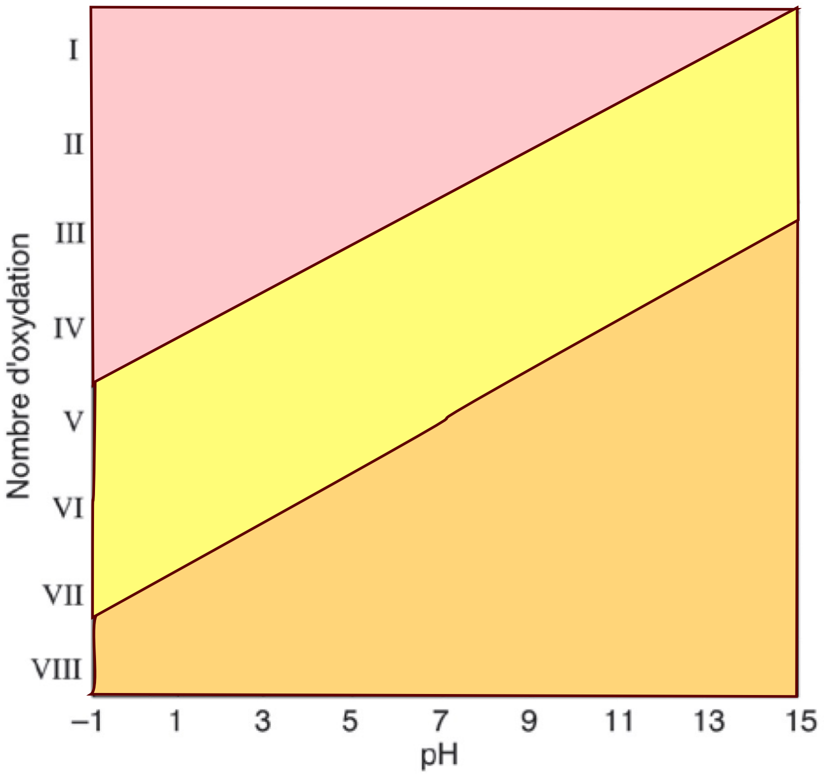
Exercise 1: Complex formation with water



Which color refers to

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

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Exercise 1: Solution

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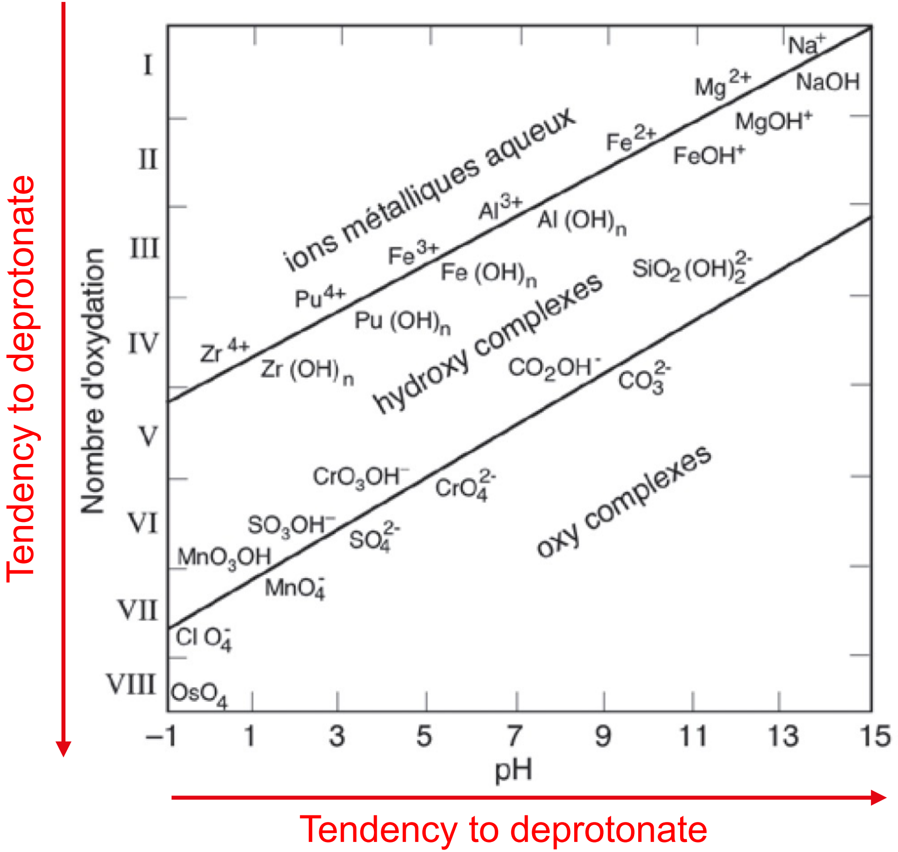

For most natural waters,

- 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 - pβ_i relationships for hydrolysis

Consider a system with Cu in water.

a. What is the pH in solution when the concentration of Cu^{2+} equals the concentration of $Cu(OH)_2$?

b. At pH 8, is Cu^{2+} or $Cu(OH)_2$ the dominant species in solution?

The following constant is available:

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

Exercise 2: Solution

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

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

$13.8 = 2\ pH$

<u>$pH = 6.9$</u>

b. $p^*\beta_2 = 13.8$

$m\ pH = 2 * 8 = 16$

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

Exercise 3: Hydroxo complexes

Consider the following equations:

$Cu^{2+} + H_2O = CuOH^+ + H^+$ $\quad\quad$ $\log {}^*K_1 = -8$

$Mg^{2+} + H_2O = MgOH^+ + H^+$ $\quad\quad$ $\log {}^*K_1 = -11.4$

a. Is the acidity of Cu^{2+} or Mg^{2+} higher?

b. At pH 7, which fraction of the Cu(II) of a pure Cu-salt solution will occur as hydroxo complex?

c. 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:

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

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

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

c. Analogous calculation to b.

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

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Exercise 4: Hydrolysis of iron

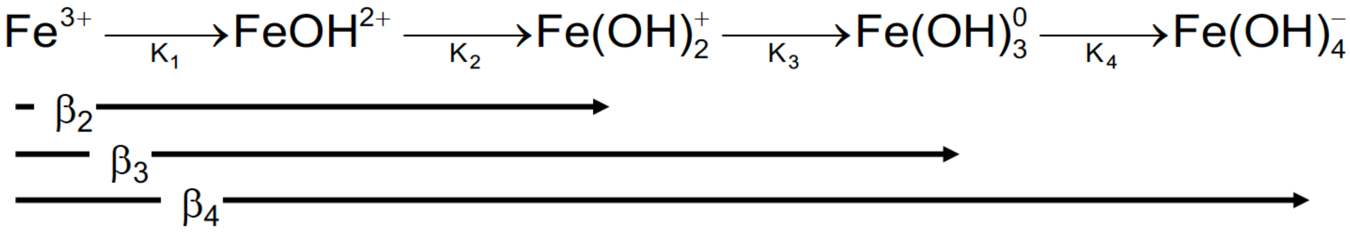
Construct a distribution diagram for iron species as a function of pH. Follow the guidelines for constructing distribution diagrams (note that we are considering all hydrolysis species here). Use the following constants for your calculations and a total Fe(III) concentration of 10^{-9} M.

$\log {}^*K_1 = -3.05$

$\log {}^*\beta_2 = -6.31$

$\log {}^*\beta_3 = -13.8$

$\log {}^*\beta_4 = -22.7$



Exercise 4: Solution

1. Identify species present at equilibrium

   Fe^{3+}, $FeOH^{2+}$, $Fe(OH)_2^{+}$, $Fe(OH)_3$, $Fe(OH)_4^{-}$

2. Write our equilibrium equations and list complexation constants

   $Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$ $\quad$ $^*K_1$

   $FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^{+} + H^+$ $\quad$ $^*K_2$

   $Fe(OH)_2^{+} + H_2O \rightleftharpoons Fe(OH)_3 + H^+$ $\quad$ $^*K_3$

   $Fe(OH)_3 + H_2O \rightleftharpoons Fe(OH)_4^{-} + H^+$ $\quad$ $^*K_4$

3. List mass balance equations

   $[Fe(III)]_T = [Fe^{3+}] + [FeOH^{2+}] + [Fe(OH)_2^{+}] + [Fe(OH)_3] + [Fe(OH)_4^{-}]$

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Exercise 4: Solution

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

$$[Fe(III)]_T = 10^{-9} = [Fe^{3+}]\left(1 + \frac{{}^*K_1}{[H^+]} + \frac{{}^*K_1{}^*K_2}{[H^+]^2} + \frac{{}^*K_1{}^*K_2{}^*K_3}{[H^+]^3} + \frac{{}^*K_1{}^*K_2{}^*K_3{}^*K_4}{[H^+]^4}\right)$$

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

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

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

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

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

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

Exercise 4: Solution

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