EPFL

Metal Speciation

ENV-200 Weeks 3 and 4

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Organization of this part of the course

- Learning objectives and resources are provided at the beginning of each lecture.
- Each topic will have an environmental engineering challenge. This challenge will be introduced when we start the topic and we will address it in class at the end of the topic.
- We will solve exercises in class throughout the lectures.
- A summary of main points is provided at the closing of each lecture.

Learning objectives

You should be able to

1. describe the reactions involved in the speciation of metals in the environment.
2. identify which system properties impact the fate of metals.
3. address engineering challenges related to metals using the equilibrium approach for modelling metal speciation.

Resources

Aquatic Chemistry, Stumm

- Chapter 6 (complexation)
- Chapter 7 (precipitation and dissolution)

What are metals and why are they important?

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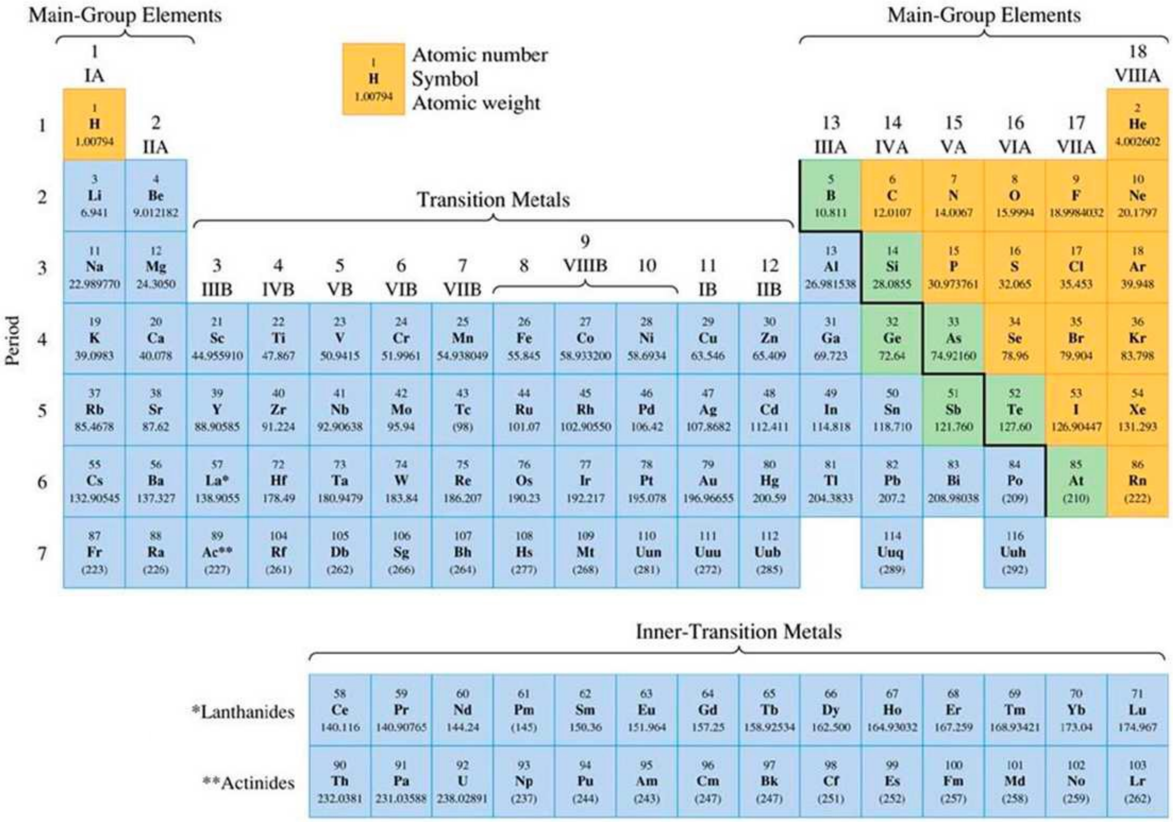


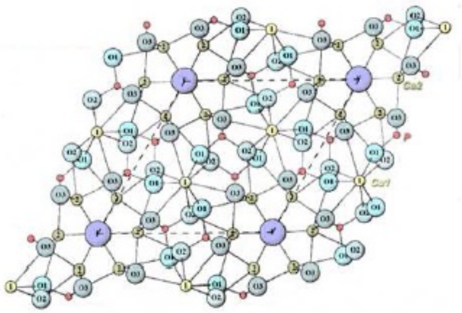
What are metals and why are they important?

- Naturally occurring metals
- Essential elements vs. elements that have toxic effects
- Transport and distribution: through water, air
- Anthropogenic fluxes of metals into natural waters
  - Burning of fossil fuels
  - Runoff from agricultural soils (metals in phosphate fertilizer, pesticides, manure)
  - Wastewater (industrial and household)
  - Metallurgy (mine waste, ore refinery by smelting, metal finishing)
  - Discarded technological products (e.g., batteries and computers)

Environmental problems related to metals

Some phosphate fertilizers used in agriculture contain elevated levels of metals

Phosphate fertilizers are chemical compounds produced from the acid treatment of apatite minerals ($Ca_5(PO_4)_3$ [F, OH or Cl]) that naturally contain minor amounts of trace metals



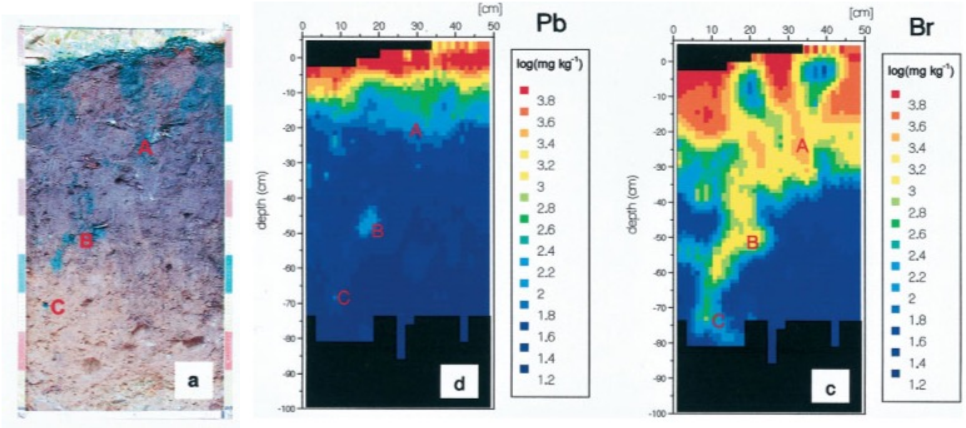
Element	Concentration in phosphate fertilizer[a] (ppm)		Concentration in phosphate rock[b] (ppm)	
	Range	Median	Range	Median
Cd	0–56.8	10.1	0.1–507.0	7.7
Cr	10.4–72.7	29.7	0.6–707.0	85.0
Cu	2.8–182.6	29.2	0.1–769.9	20.0
Zn	8.8–180.6	89.0	1.5–3400	89.2
Ni	7.0–26.9	17.9	0.7–511.0	28.0
Pb	5.1–30.7	12.2	0.3–1770	10.0
La		1000	2.1–8800	246.6
Ce		1000	1.8–4346	167.1
Pr		50	0.3–332.5	38.1
Nd		50	1.1–2202.0	191.0
U		37	0–390	57.0
V		38	0–2800.7	60.0

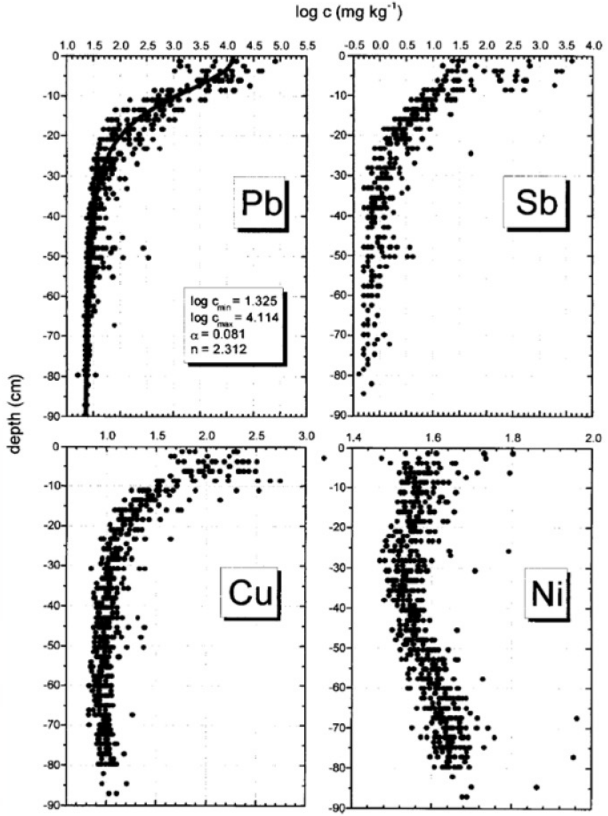
Chen and Graedel, 2015, J Clean Prod, 91, 337.

Environmental problems related to metals

Heavy metal contamination in shooting-range soils

- Pb has low mobility due to adsorption to Fe and Mn hydroxides
- However, decreased pH or preferential flow paths can lead to soluble Pb migration toward the groundwater





Knechthofer et al, 2004, J Plant Nutr Soil Sci, 166, 84.

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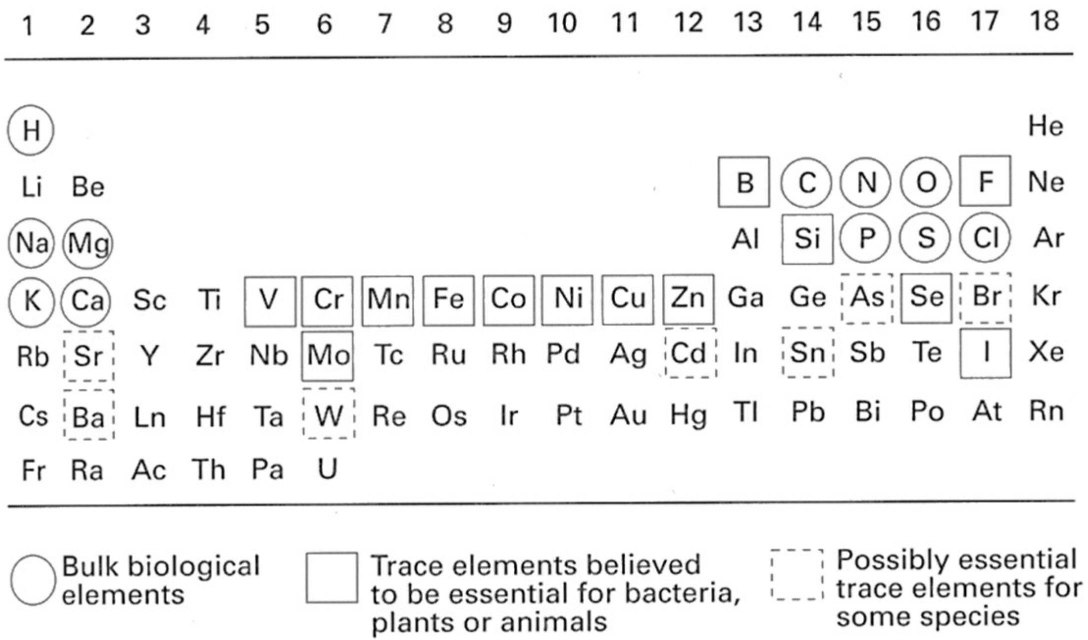
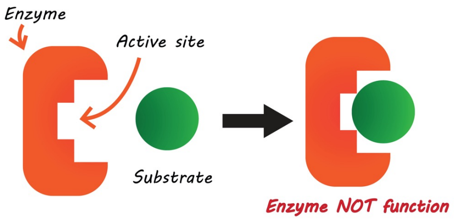
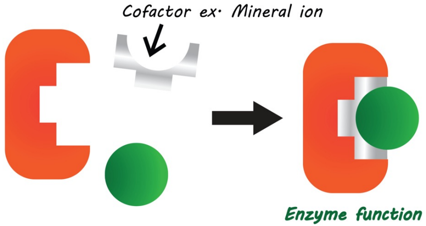
Biological function and toxicity of metals



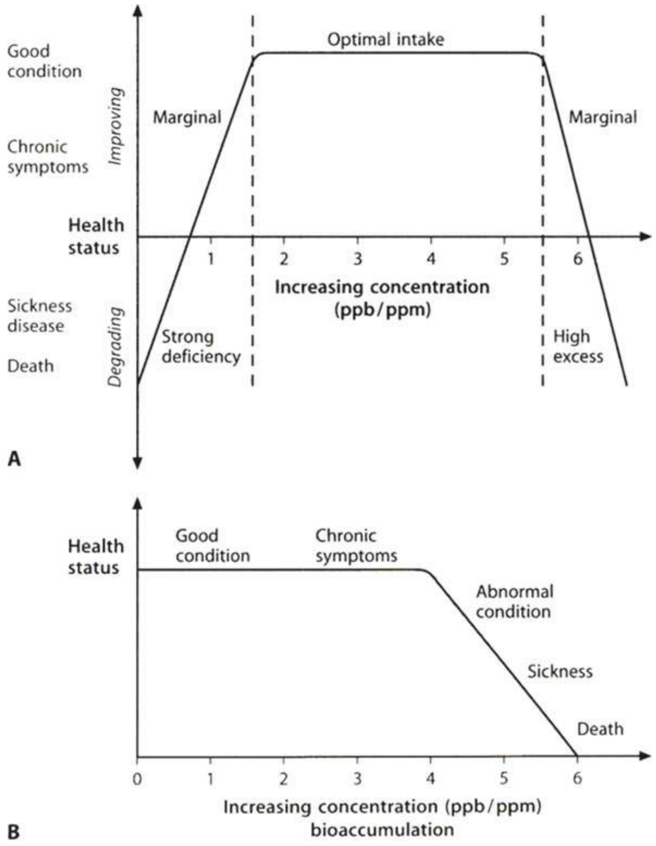




Biological function and toxicity of metals

A: essential micronutrient

B: non-essential micronutrient



Biological function and toxicity of metals

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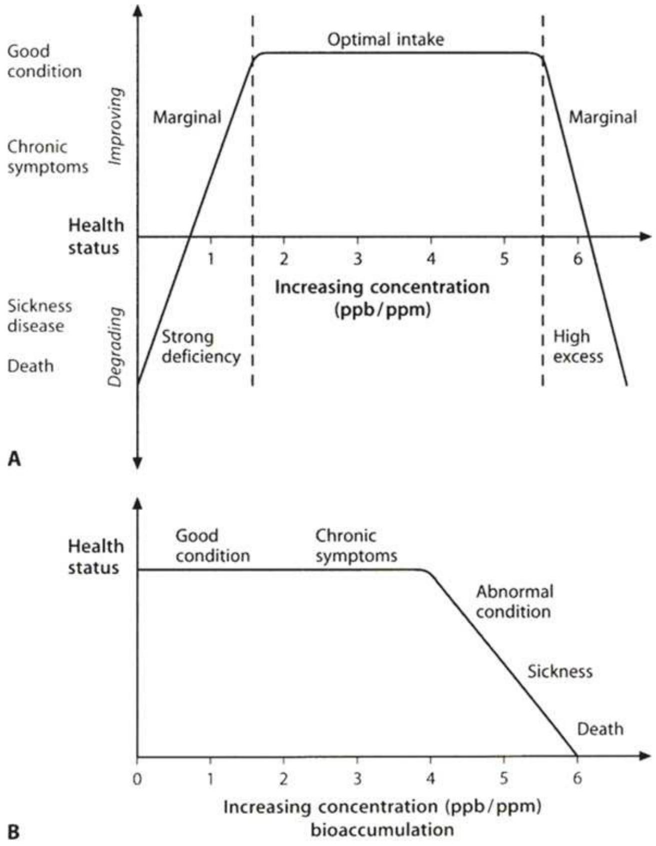
Metal toxicity can be caused by

- Displacement of an essential metal bound to a bioligand
- Complexation of a metal by a functional group
- Modification of the conformation of a biomolecule that is critical to its biochemical function

Toxicity mechanisms are related to complex formation between a metal ion and the functional group of a biomolecule.



What is metal speciation?

- Species refers to the chemical form of an element
- Speciation refers to the distribution between different chemical species (different chemical bonding)
- Mobility, toxicity and bioavailability of metals is governed by speciation

Free metal ion	Inorganic complexes	Organic complexes	Colloids, large polymers	Surface-bound metals	Solid bulk phase, lattice
Cu^{2+}	$CuCO_3$ $CuOH^+$ $CuSO_4$	$CuAc^+$ Cu-Humate	Inorganic Organic	≡Fe-Ocu R-COOCu	CuO $Cu_2[OH_2, CO_3]$

True solution

Dissolved | Particulate

Reactions involving metal species

1. Complexation to inorganic and organic ligands (today)
2. Precipitation and dissolution (next week)

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Metal speciation

Complexation

Learning objectives

You should be able to

1. explain what a complex is.
2. formulate equilibrium reactions and stability constants for complexation reactions.
3. calculate concentrations of different metal species in the presence of one or multiple ligands.
4. use the hard-soft classification scheme to qualitatively discuss the expected behavior of an element under given conditions.

Environmental engineering applications

Complexation is important for example in:

- Complexation agents such as phosphate, NTA, or EDTA are used in textile washing processes to minimize soap consumption by complexation of Ca^{2+}
- Biochar is used to remove heavy metals from environmental systems by complexation of metal cations on biochar
- Complexation agents are used on metal surfaces to avoid corrosion (i.e., the oxidation of metals and formation of metal oxides)

Other areas of relevance include medicine: e.g., detoxification of metal poisoning using EDTA or deferrisation of thalassemia patients by DFA

Environmental engineering challenge: Flint water crisis

Flint is a town in Michigan, US. In 2014, the drinking water for the city was contaminated with toxic levels of lead and possibly pathogenic microbes.

In early 2014, the city decided to use water from the local Flint river to save money. Previously, water from Detroit (sourced from Lake Huron and the Detroit River) was used.

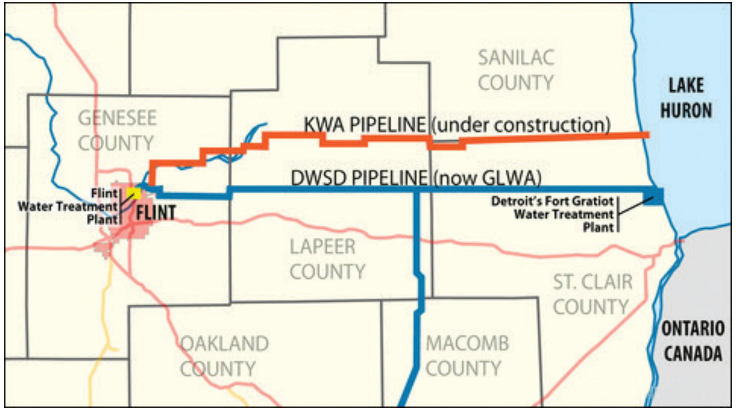

Image: The Flint Water Project; Map: Regina H. Boone/Detrois Free Press/Zuma Press

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Environmental engineering challenge

The switch in chemistry lead to a release of lead from the pipes.

Why did this happen and how can such catastrophes be avoided in the future?

Apparently, the city officials did not understand basic metal speciation!

We will come back to this challenge in our next class- after learning about metal complexation, dissolution and precipitation.

Pipes from the Flint water distribution after the city switched the water source to Flint River

Image: The Flint Water Project

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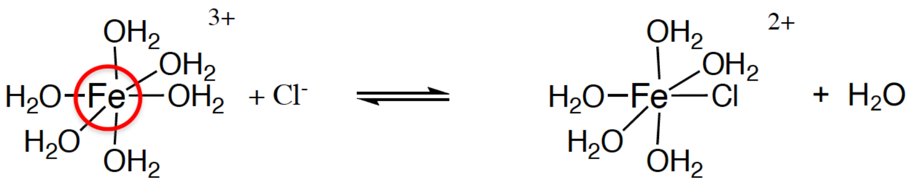
Why is complexation important?

- Complexes occur frequently in natural waters along with the free metal species
- The toxicity and bioavailability of metals depends on speciation in solution
- The adsorption of metals onto surfaces may be favored or disfavored in complexed form
- The complexation of a metal that forms part of a mineral increases the solubility of the mineral

Terminology

- Complex: Structure consisting of a central ion (typically metal) bonded to a surrounding array of molecules or anions (ligands)
  - ligands: can occupy one, two, three etc. coordination positions (unidentate, bidentate, tridentate etc. ligands)
  - chelation: complex formation with multidentate ligands; formation of ring structure (chelate complex)
  - multi- or polynuclear complexes: more than one central metal atom in a complex



- Coordination number: number of ligands around central ions (2, 4, 6)

$Ag(NH_3)_2^{+}$
Coordination number 2

$Cu(NH_3)_4^{2+}$
Coordination number: 4

$Fe(H_2O)_6^{2+}$
Coordination number: 6

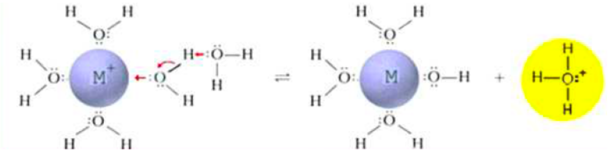
Complex formation with water

- All metal cations in water are hydrated (4 or 6 H_2O molecules around one metal cation)

  e.g, $Zn(H_2O)_6^{2+}$

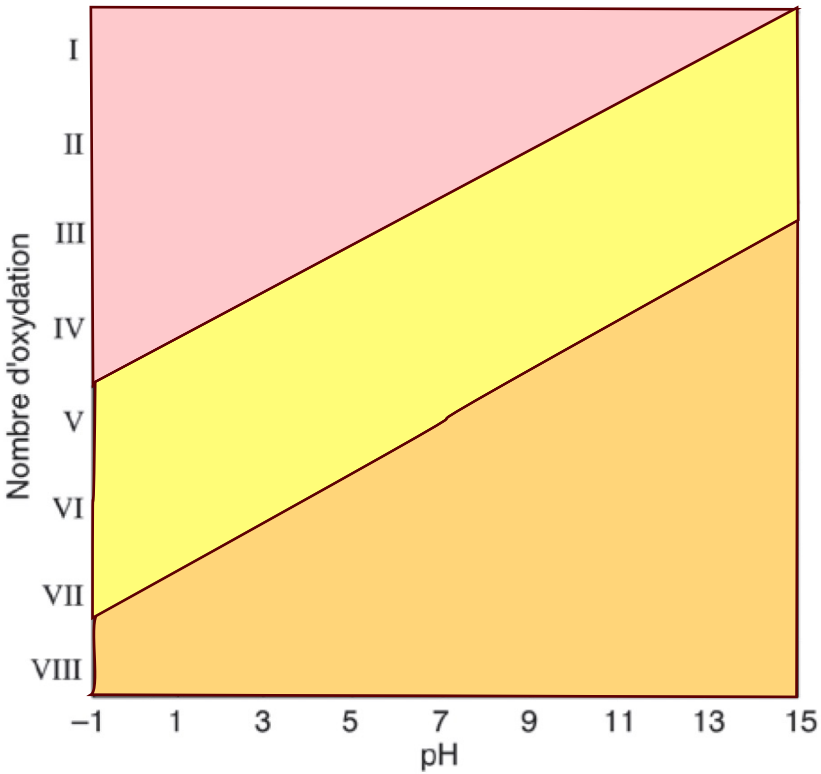
- Metal cations act as weak acids causing deprotonation of the water molecules: hydrolysis

  e.g., $Cu(H_2O)_6^{2+} \rightleftharpoons CuOH(H_2O)_5^{\ +} + H^+$



  Tendency to deprotonate increases with increasing charge of the central ion and decreasing radius (electrostatic repulsion of the protons of H_2O molecules by the positive charge of the metal ion)

Exercise 1: Complex formation with water



Which color refers to

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

Hydrolysis

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$M(H_2O)_m^n \rightleftharpoons M(H_2O)_{m-1}OH^{(n-1)+} + H^+$ $\quad {}^*K_1$

Brutto formation constant:

$${}^*\beta_2 = \frac{[M(OH)_m^{(m-n)+}][H^+]^m}{[M^{n+}]}$$

m: number of hydroxyl groups

n: valency of metal

Example:

$Cu(H_2O)_6^{2+} \rightleftharpoons Cu(H_2O)_5OH^+ + H^+$ $\quad {}^*K_1 = \frac{[CuOH^+][H^+]}{[Cu^{2+}]}$

$Cu(H_2O)_5OH^+ \rightleftharpoons Cu(H_2O)_4(OH)_2 + H^+$ $\quad {}^*K_2 = \frac{[Cu(OH)_2][H^+]}{[CuOH^+]}$

$Cu(H_2O)_6^{2+} \rightleftharpoons Cu(H_2O)_4\,(OH)_2 + 2H^+$ $\quad {}^*\beta_2 = {}^*K_1\,{}^*K_2 = \frac{[Cu(OH)_2][H^+]^2}{[Cu^{2+}]}$

$\log {}^*\beta_2 = \log {}^*K_1 + \log {}^*K_2$

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Hydrolysis

We know: $^*\beta_m = \dfrac{[M(OH)_m^{(m-n)+}][H^+]^m}{[M^{n+}]}$

Taking negative logs ("p"), we obtain:

$p^*\beta_m$ - m pH = log $[M^{n+}]$ - log $[M(OH)_m^{(n-m)+}]$

Comparing $p^*\beta_m$ and m pH allows us to easily see if the protonated (M^{n+}) or the deprotonated species ($M(OH)_m^{(n-m)+}$) is dominant in solution.

m pH > $p^*\beta_m$: deprotonated hydrolysis species is dominant in solution (left term of equation negative, i.e., log $[M(OH)_m^{(n-m)+}]$ > log $[M^{n+}]$)

m pH < $p^*\beta_m$: protonated hydrolysis species is dominant in solution (left term of equation positive, i.e., log $[M^{n+}]$ > log $[M(OH)_m^{(n-m)+}]$)

m pH = $p^*\beta_m$: both deprotonated and protonated species have the same activity in solution

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 3: Hydroxo complexes

Consider the following equations:

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

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

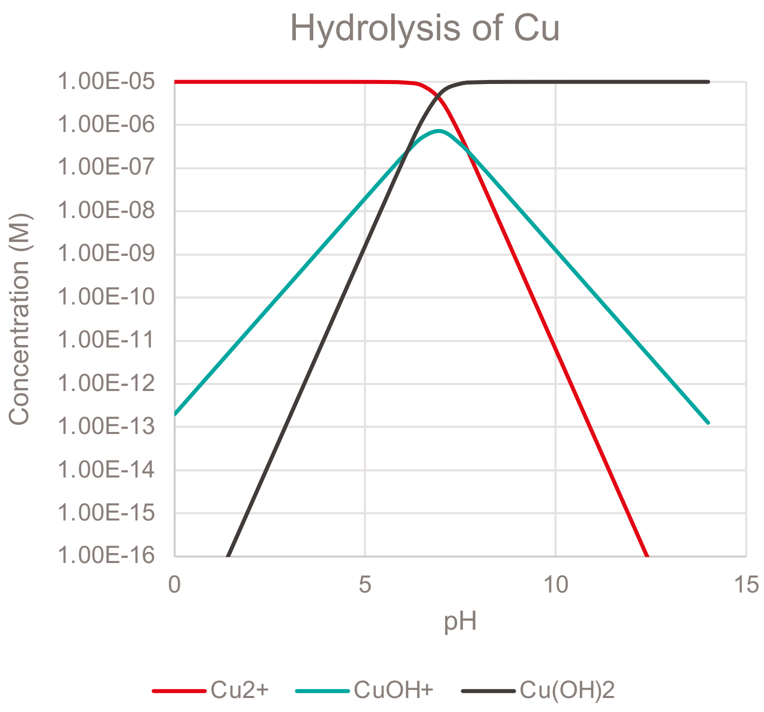
a. Is the acidity of Cu^{2+} or Mg^{2+} higher?

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?

Constructing distribution diagrams

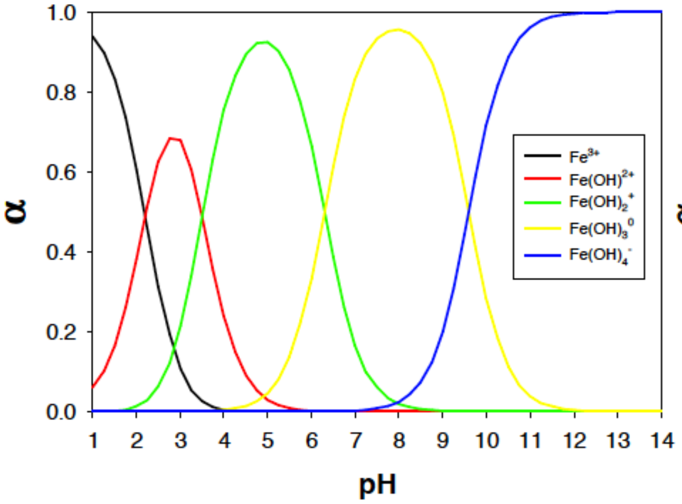
A distribution diagram is a visual representation of species present e.g., at different pH

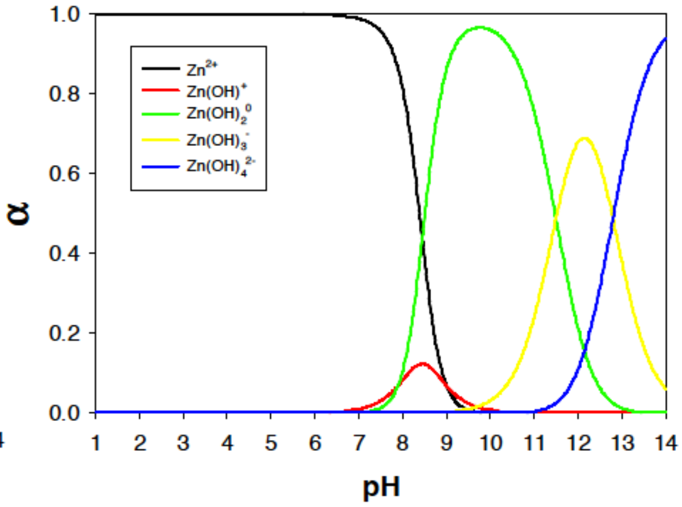


Distribution of hydrolysis products

Abundance (α) of hydrolysis products:

- All cations: free metal and hydrolysis products can coexist in solution, not all hydrolysis products are abundant
- Trivalent cations: hydrolysis species dominate at pH > 2 (Fe^{3+}) or > 5 (Al^{3+})
- Divalent cations: free metal ion dominates over broad pH range, decreases with increasing pH





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Constructing distribution diagrams

Example: Cu^{2+} in water with $[Cu]_T = 10^{-5}$ M

1. Identify species present at equilibrium

   Cu^{2+}, $CuOH^+$, $Cu(OH)_2$ (in this example, we are ignoring other minor hydrolysis species)

2. Write our equilibrium equations and list complexation constants

   $Cu^{2+} + H_2O \rightleftharpoons CuOH^+ + H^+$ $\quad$ $^*K_1 = 10^{-7.7}$

   $Cu^{2+} + 2\ H_2O \rightleftharpoons Cu(OH)_2 + 2H^+$ $\quad$ $^*\beta_2 = 10^{-13.8}$

3. List mass balance equations

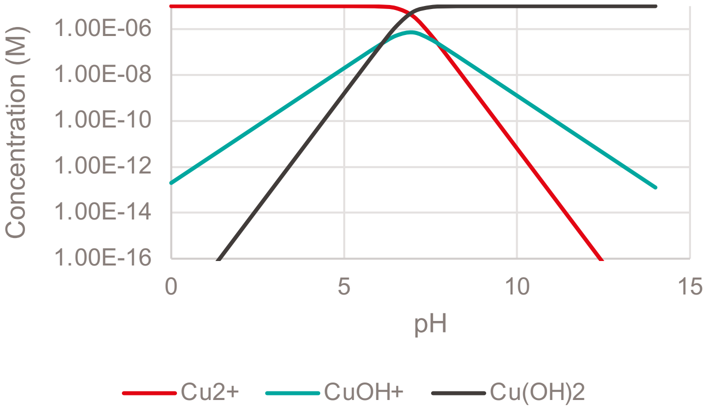
   $[Cu]_T = [Cu^{2+}] + CuOH^+ + Cu(OH)_2$

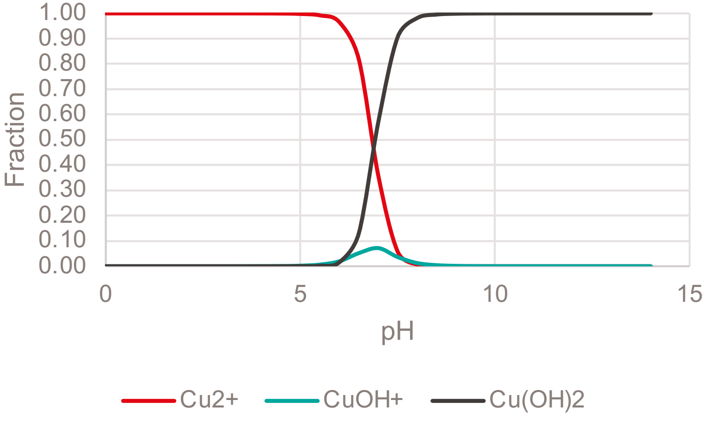
Constructing distribution diagrams

4. Insert 2. into 3 to express $[Cu]_T$ as a function of $[Cu^{2+}]$ and the formation constants

$$[Cu]_T = 10^{-5} = [Cu^{2+}]\left(1 + \frac{^*K_1}{[H^+]} + \frac{^*\beta_2}{[H^+]^2}\right)$$

5. Solve 4. for Cu^{2+}
6. Use the results of 5. to calculate the concentrations of hydroxo complexes using 2.





Exercise 4: Hydrolysis of iron

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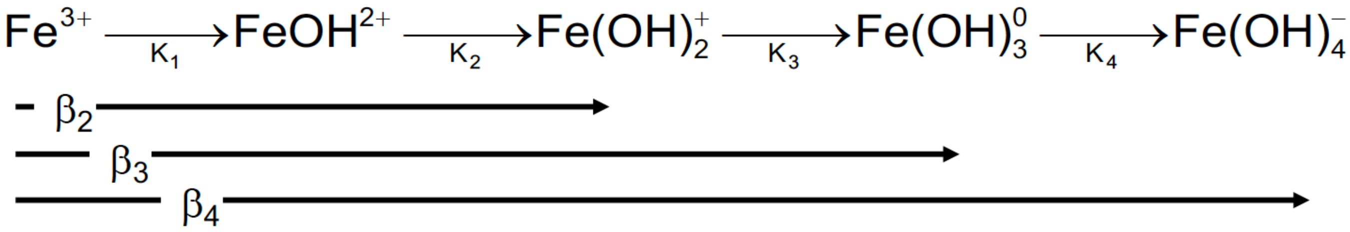
Construct a distribution diagram for iron species as a function of pH. Follow the guidelines for constructing distribution diagrams (note that we are considering all hydrolysis species here). Use the following constants for your calculations and a total Fe(III) concentration of 10^{-9} M.

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

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

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

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



Summary

- The mobility and toxicity of metals is governed by speciation.
- Complex formation is important for metal speciation and thus the fate of metals in environmental and engineered systems.
- Species distribution diagrams can be constructed from complexation constants and are useful to assess the speciation of a metal in a given environment.