



Metal Speciation II

ENV-200

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Last lecture recap

We learned what metal speciation is and why it is important.

We performed different speciation calculations for complexation reactions between metals and water.

Today, we will discuss complexation of metals cations with ligands other than water.

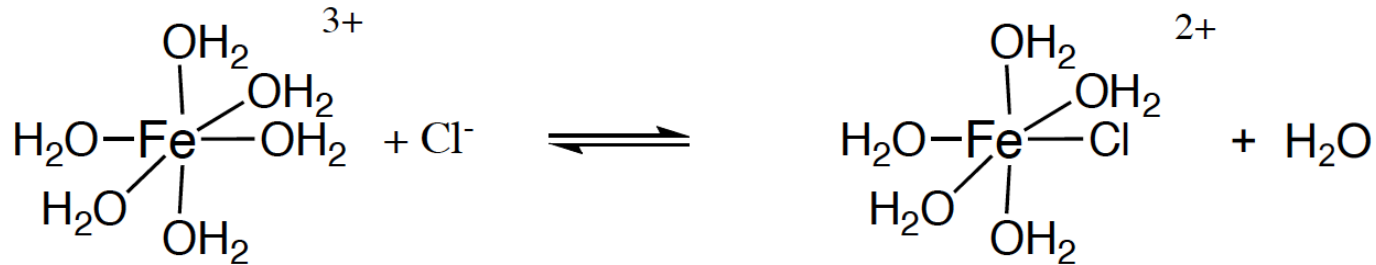


Metal speciation

Complexation

Complex formation with ligands

- Replacement of H₂O by (an)other ligand(s)
 - Inorganic ligands: CO₃²⁻, Cl⁻, SO₄²⁻, F⁻, S²⁻
 - Organic ligands: amino acids, phenols, acetic acid, macromolecular ligands, fulvic and humic acids
 - Synthetic ligands in wastewater (EDTA)
- Multistep reaction, equilibrium process

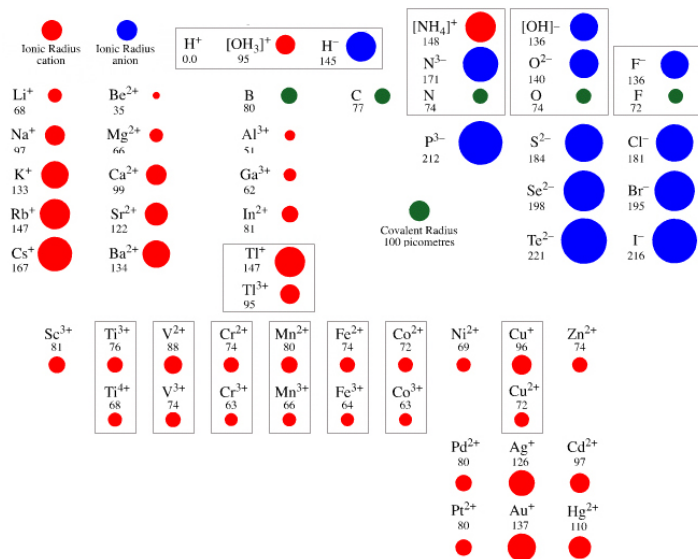


Factors influencing the stability of complexes

- Metal ion
 - charge density, polarisability, electronic structure
- Ligand
 - electron donor characteristics, polarisability, electronic structure, steric effects
- Concept of hard/soft metals/ligands

Factors influencing the stability of complexes

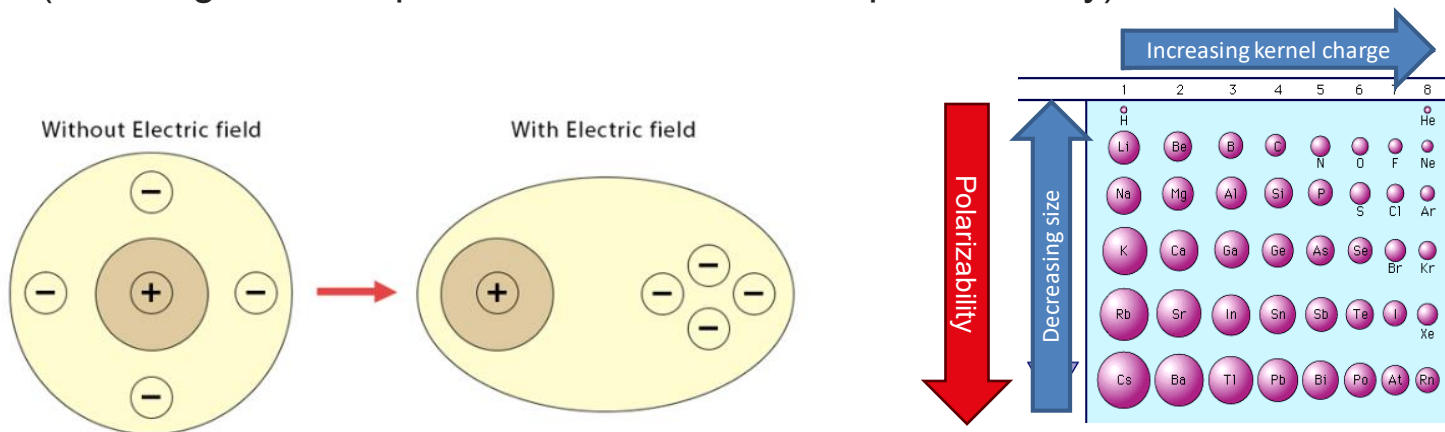
- Charge density of metals:
 - high charge and small ionic radius = high charge density
 - Low charge and large ionic radius = low charge density



Metal Ion	Charge	Ionic Radius (Å)	Charge Density (C·mm ⁻¹)
Fe ³⁺	3+	0.78	232
Pb ²⁺	2+	1.19	32
Cu ²⁺	2+	0.87	116
Co ²⁺	2+	0.88	108
Hg ²⁺	2+	1.02	49
Ni ²⁺	2+	0.83	134
Cr ³⁺	3+	0.52	261
Gd ³⁺	3+	0.94	91
Dy ³⁺	3+	0.91	99

Factors influencing the stability of complexes

- Polarizability of metals:
 - Tendency to “move around” electrons and form a dipole when an electric field is applied (i.e., an ion is nearby)
 - polarizability increases as the volume occupied by electrons increases
 - Large atoms with a low kernel charge are easily polarizable (downward on the periodic table increases polarizability)
 - Small atomic radius and high kernel charge decrease the polarizability (left to right on the periodic table decreases polarizability)



Hard-soft concept: metals

Classification of cations based on trends in complex formation constants (Ahrland 1958; Schwarzenbach 1961):

- A-cations/hard cations (e.g., Na^+ , Ca^{2+} , Al^{3+})
 - Only partly polarizable (high charge/diameter ratio), „hard spheres“
 - Mostly electrostatic metal-ligand interactions (ionic bond)
 - Often occur as free aquo-ions
 - For a given metal, the hardness increases with charge

- B-cations/soft cations (e.g., Ag^+ , Hg^{2+} , Cd^{2+})
 - Polarizable (electron cloud can be deformed, smaller charge/diameter ratio), „soft spheres“
 - Soft character increases with size (Hg^{2+} is softer than Cd^{2+})
 - Partially “covalent” metal-ligand interactions, often bound to S- or N-ligands

- Transition metal/intermediate cations (e.g., Fe^{2+} , Ni^{2+} , Cu^{2+})
 - Stability of organic complexes follows the Irving-Williams series
 $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+}$

27 Co	28 Ni	29 Cu	30 Zn
45 Rh	46 Pd	47 Ag	48 Cd
77 Ir	78 Pt	79 Au	80 Hg

Hard-soft concept: ligands

- Hard ligands: small, little polarizability
 - Examples: F^- , OH^- , $O(-II)$ in PO_4^{3-} , SO_4^{2-} , CO_3^{2-} and carboxyl-type ligands
- Soft ligands: large, polarizable
 - Examples: I^- , CN^- , S^{2-} , $S(-II)$ in $S_2O_3^{2-}$

Some ligands can undergo acid-base reactions- we will discuss this later

Hard metal cations preferentially form complexes with hard ligands
Soft metal cations preferentially form complexes with soft ligands

Exercise 1: Contaminated wetland



Consider a contaminated wetland soil containing Sr^{2+} , Co^{2+} , and Hg^{2+} . Soil flooding results in soil reduction and in the release of bicarbonate (HCO_3^-) and sulfide (HS^-) into soil solution.

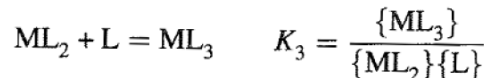
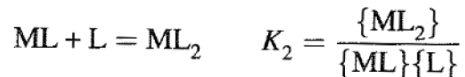
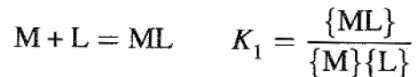
- a. Which of the metals would you expect to mainly interact via complexation and precipitation with bicarbonate and which one predominantly with sulfide?
- b. For which trace metal is it most difficult to anticipate its preference for one of the two anions?



Formulation of stability constants

Stability constants for each ligation step

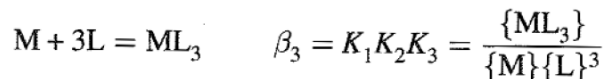
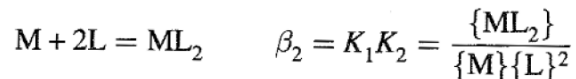
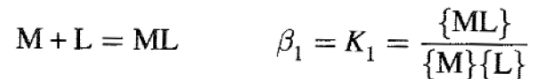
Unprotonated ligand



etc.

Stability constants for brutto reactions = brutto stability constants

Unprotonated ligand

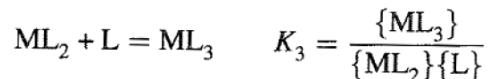
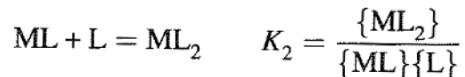
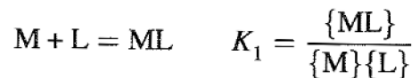


etc.

- K_i are individual complexation constants (stability constants) and characterize the equilibria and the stepwise complexation
- Analogous formulation to protonation/deprotonation processes

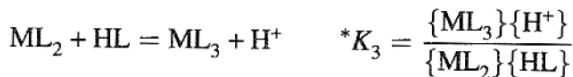
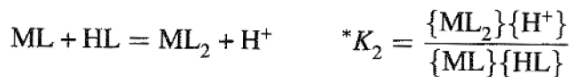
Stability constants for each ligation step

Unprotonated ligand



etc.

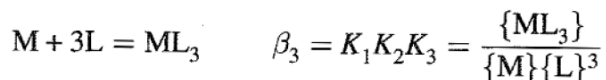
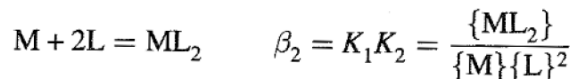
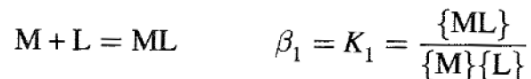
Protonated ligand



etc.

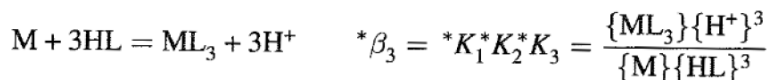
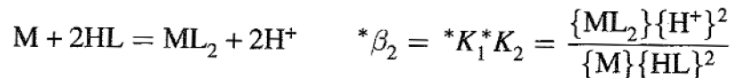
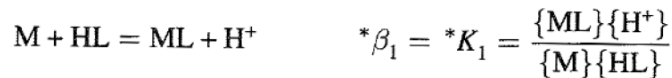
Stability constants for brutto reactions = brutto stability constants

Unprotonated ligand



etc.

Protonated ligand



etc.

You can work with either K or *K values, depending on what is available.

Complex formation with basic ligands

- L, e.g.: NH_3 , F^- , CN^- , PO_4^{3-}
- L undergoes acid-base equilibrium- we have a system with coupled reactions



- During complexation the metal ion promotes the release of the proton
Example: $2 \text{NH}_4^+ + \text{Ag}^+ \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+ + 2\text{H}^+$

In the presence of M and L, various complexes are possible (mixture):

$$\begin{aligned}
 [M]_{\text{tot}} &= [M] + [ML] + [ML_2] + \dots [ML_i] \\
 &= [M] + [M] [L] K_1 + [M] [L]^2 \beta_2 + \dots [M] [L]^i \beta_i \\
 &= [M] (1 + [L] K_1 + [L]^2 \beta_2 + \dots [L]^i \beta_i)
 \end{aligned}$$

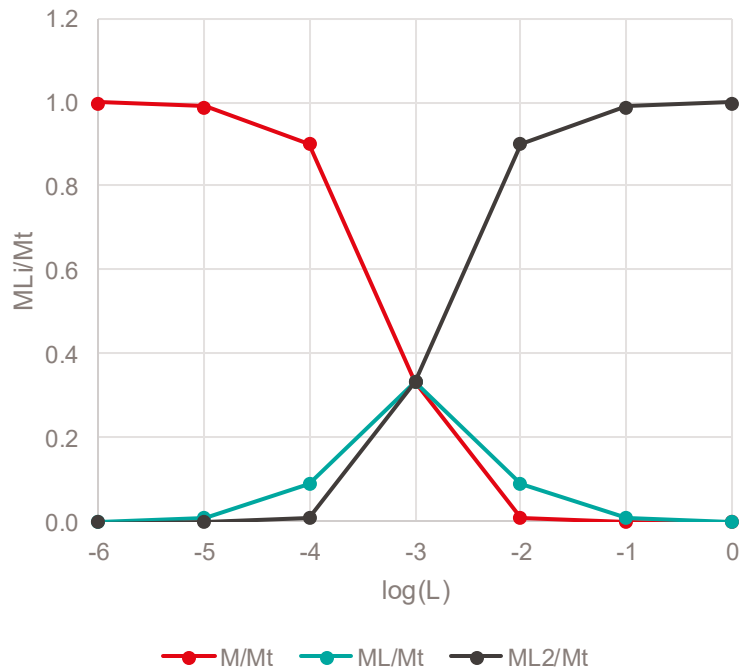
$$\alpha_i = \frac{[ML_i]}{[M]_{\text{tot}}} = \frac{[L]^i \beta_i}{1 + \sum [L]^i \beta_i} \quad \text{and} \quad \beta_i = \frac{[ML_i]}{[M][L]^i}, \text{ hence } [ML_i] = [M] [L]^i \beta_i$$

- α_i = distribution coefficient (function of [L] and β_i)
- relative distribution of M is independent of $[M]_{\text{tot}}$

These equations are analogous to the ones for hydrolysis

Example distribution function

Distribution of complexes as a function of ligand concentration



Given: $K_1 = 10^3$, $K_2 = 10^3$ ($\beta_2 = 10^6$)

Calculated: $[M]$, $[ML]$ and $[ML_2]$ as a function of ligand concentration

Recipe for speciation calculation

1. Identify species present at equilibrium

M, L, ML, ML₂, ... , ML_i, HL, H⁺, OH⁻

2. Write our equilibrium equations and list complexation constants (note that for basic ligands, you could also write these in terms of *K_i and *β_i)



3. List mass balance equations

$$[\text{M}]_{\text{T}} = [\text{M}] + [\text{ML}] + \dots [\text{ML}_i]$$

$$[\text{L}]_{\text{T}} = [\text{L}] + [\text{HL}] + [\text{ML}] + \dots [\text{ML}_i]$$

Recipe for speciation calculation

4. Solve equations (x unknowns require x equations)

$$[M]_T = [M] (1 + [L] + \beta_1 [L] + \dots + \beta_i [L]^i)$$

$$[L]_T = [L] + [H^+] K_a^{-1} [L] + \beta_1 [M][L] + \dots + \beta_i [M][L]^i$$

5. Apply simplification, if warranted, e.g., if ligand is in excess

$$[L]_T \sim [L] + [HL]$$

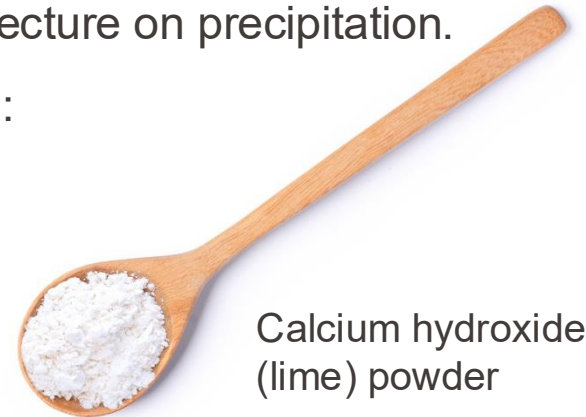
6. Calculate unknown parameter(s)

Polynuclear hydroxocomplexes

- The equations on the previous slide are for mononuclear complexes (i.e., a single central metal atom)
- Multiple metal atoms (and their surrounding ligands) can aggregate to form polynuclear complexes
- These complexes can form solid phase hydroxides when the solubility product is exceeded – we will discuss this in the lecture on precipitation.
- The formulas for a polynuclear complex M_mL_n are:

$$\beta_{nm} = \frac{[M_mL_n]}{[M]^m[L]^n} \text{ for a deprotonated ligand (L)}$$

$$*\beta_{nm} = \frac{[M_mL_n][H^+]^n}{[M]^m[HL]^n} \text{ for a protonated ligand (HL)}$$



Calcium hydroxide
(lime) powder

Exercise 2: Silver speciation



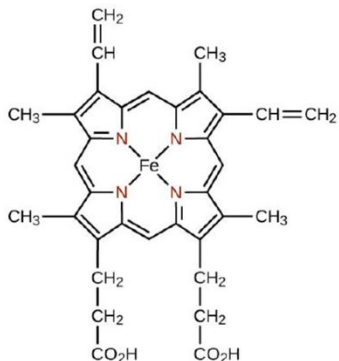
For a system with Ag^+ and NH_3 , what is the silver speciation at pH 7?

We know: $[\text{Ag}^+]_{\text{tot}} = 10^{-6} \text{ M}$, $[\text{NH}_4^+]_{\text{tot}} = 10^{-2} \text{ M}$, $K_1 = 10^{3.2}$, $K_2 = 10^{3.83}$, $K_a = 10^{-9.3}$

1. Identify species present at equilibrium
2. Write out equilibrium equations
3. List mass balance equations
4. Solve equations
5. Apply simplifications
6. Calculate silver speciation

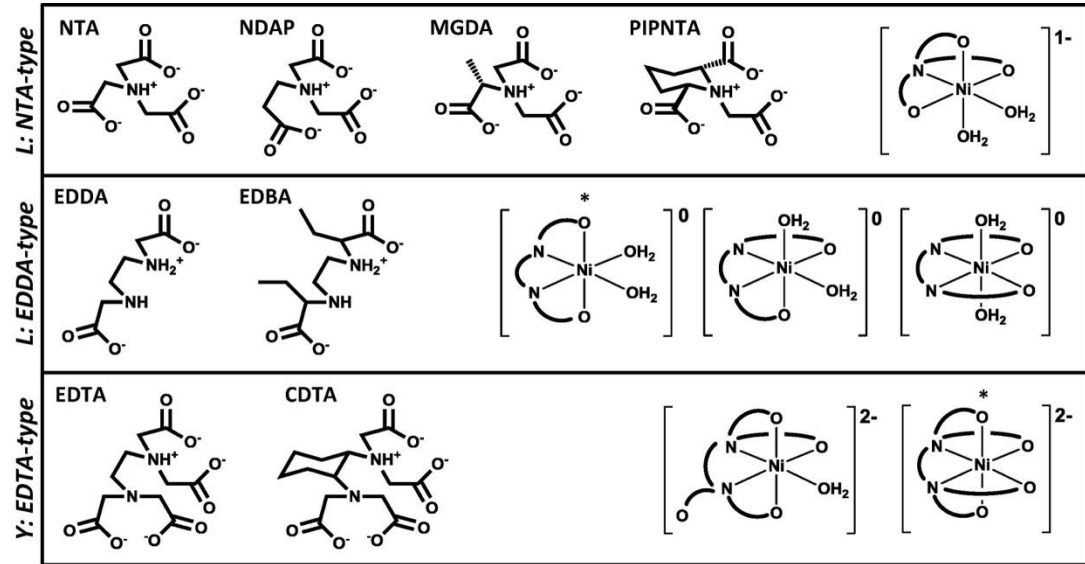
Chelating ligands

- The word chelation is derived from Greek χηλή, chelè, meaning claw; the ligands lie around the central atom like the claws of a lobster.
- The chelate effect produces increased stability for the complexes of chelating ligands as compared with open chain analogues
- Chelates remain remarkably stable even at very dilute concentrations

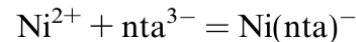


A famous chelating ligand: heme (in hemoglobin)

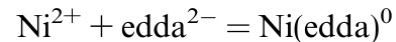
- Denticity refers to the number of atoms with which a ligand binds to a metal ion
 - monodentate = single atom
 - Bidentate = two different atoms
 - etc
- What is the denticity of NTA^{3-} , EDDA^{2-} , and EDTA^{4-} ?
- Which ligand will form the strongest complex?



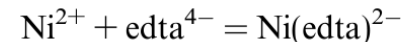
Equation

Log K 

12.30

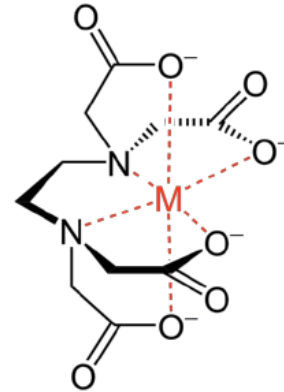
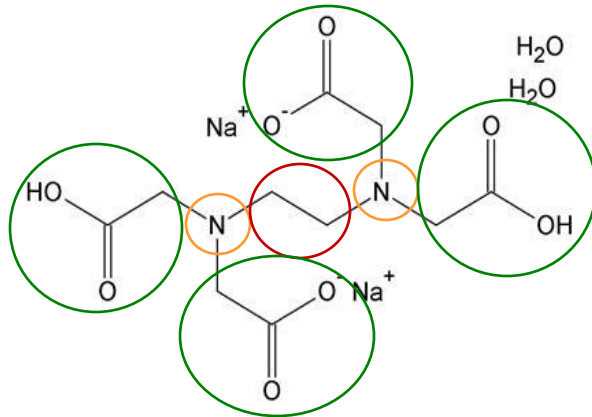


14.1



19.5

- EDTA (**E**thylene**d**iamine**t**etra**a**cetic**a**cid) is a 6 dentate ligand that
 - forms strong complexes with major divalent metal ions Ca^{2+} and Mg^{2+} as well as many heavy metal ions
 - is commercially used to prevent precipitation of these ions (e.g., in food and shampoos to prevent calcium or magnesium from precipitating)
 - is often used to determine the hardness of water.



6 dentate ligand

In-class experiment: water hardness



Water hardness arises from divalent and multivalent metal ions: Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , etc., which can precipitate out with carbonate: $\text{CaCO}_3(\text{s})$, $\text{MgCO}_3(\text{s})$, etc. "Hard" water contains more metal ions than "soft" water.



High concentrations of metal ions reduces the effectiveness of detergent substances



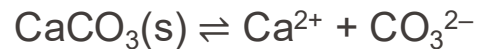
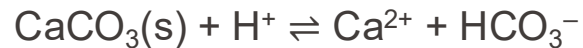
Rising water temperature reduces the solubility of lime and it precipitates.



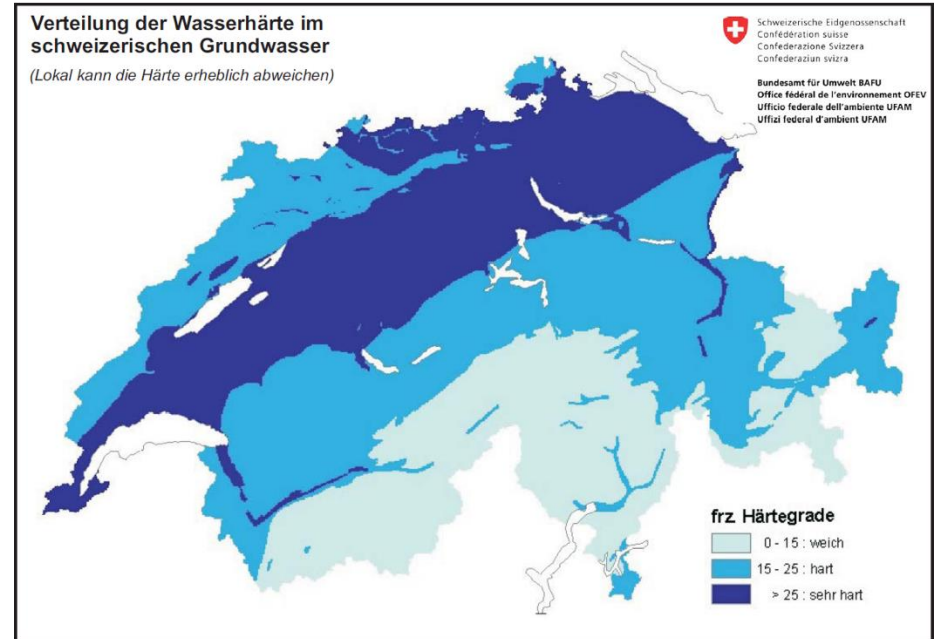
How do the ions get into the water?



Reactions of acids with calcite (CaCO_3) increase the concentration of ions in groundwater (analogous reactions with dolomite $[\text{Ca},\text{Mg}(\text{CO}_3)_2]$ also occur):



Is groundwater or surface water (lakes, streams) harder?



In-class experiment: water hardness

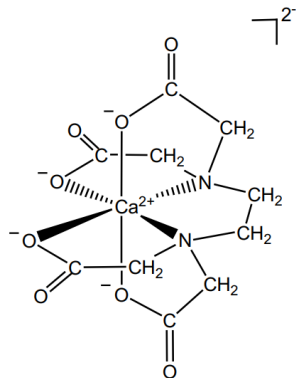


Water hardness can be determined by reacting metal cations with chelating ligands, such as EDTA.



From the amount of EDTA used to complex all Ca^{2+} , we can determine the concentration of Ca^{2+} in our sample.

However, the $[\text{CaEDTA}]^{2-}$ complex is colorless and cannot be observed directly- this is why we are using a color indicator in the experiment.



Complex formed by EDTA and calcium ions

Bürette



Standard EDTA solution

Sample with unknown metal content

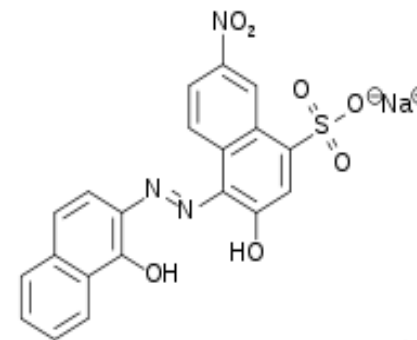
In-class experiment: water hardness



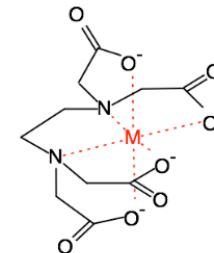
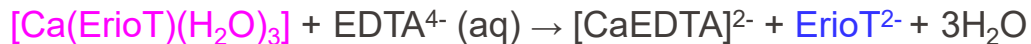
Reaction 1



Reaction 2



Reaction 3



Which of the three complexes, $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ca}(\text{ErioT})(\text{H}_2\text{O})_3]$, or $[\text{CaEDTA}]^{2-}$ is the most stable?

In-class experiment: water hardness



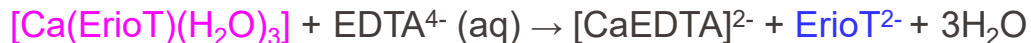
Reaction 1



Reaction 2



Reaction 3



To quantify the water hardness, we need to know

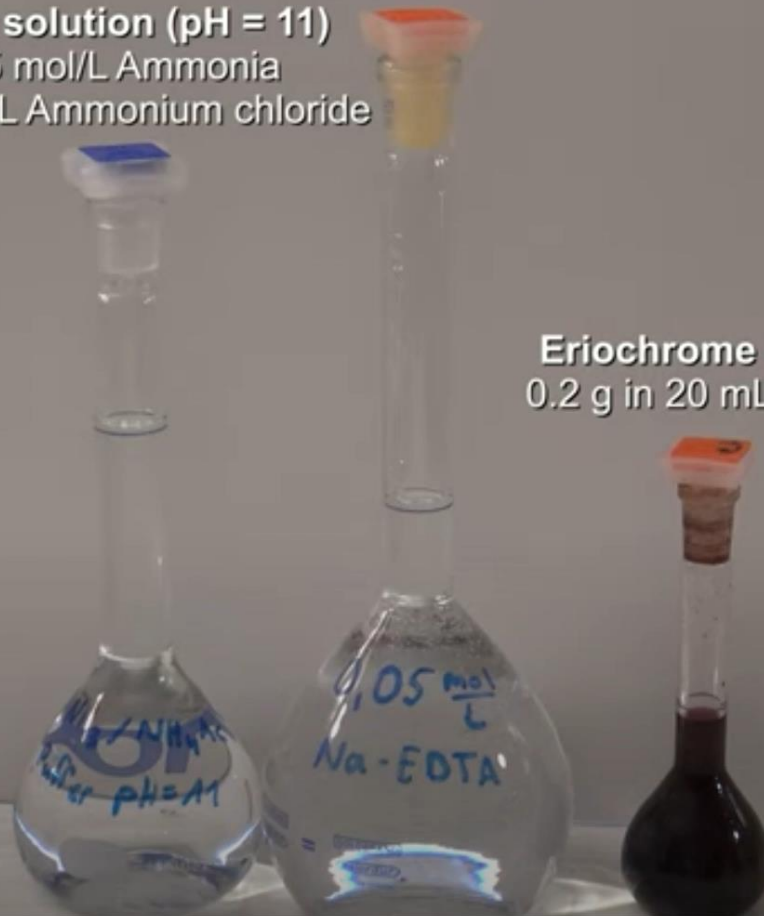
1. Volume of water sample
2. Initial burette reading
3. Final burette reading

Collect these parameters during the demonstration

Na-EDTA (0.05 mol/L)*

Buffer solution (pH = 11)
0.75 mol/L Ammonia
0.17 mol/L Ammonium chloride

Eriochrome black T
0.2 g in 20 mL Ethanol



*The sodium salt of ethylenediaminetetraacetic acid.

In-class experiment: water hardness



	Run 1	Run 2	Run 3
Volume of water sample (mL)			
Initial burette reading (mL)			
Final burette reading (mL)			
Volume of EDTA solution used (mL)			

Fill out the table. You will need the data for Homework. (Link to clip on [YouTube](#))

- Experimental conditions
 - Buffer: ammonia (0.75 mol/L)/ammonium chloride (0.17 mol/L)
 - Indicator ErioT (0.2 g in 20 mL Ethanol)
 - EDTA solution (0.05 M)

Speciation in natural waters

Concentration range of some ligands in natural waters (log conc (M))

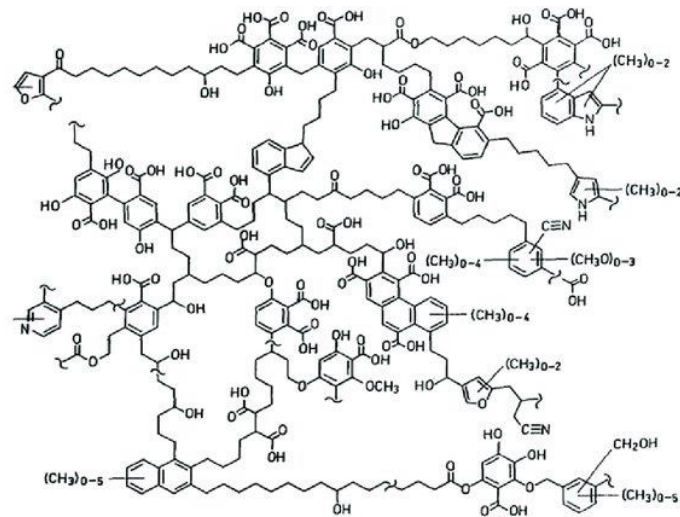
Domaines de concentration dans les eaux douces et l'eau de mer (log C (M))		
	Eaux douces	Eau de mer
HCO ₃ ⁻	-4 - -2.3	-2.6
CO ₃ ²⁻	-6 - -4	-4.5
Cl ⁻	-5 - -3	-0.26
SO ₄ ²⁻	-5 - -3	-1.55
F ⁻	-6 - -4	-4.2
HS ⁻ /S ²⁻ 1)	-6 - -3	-
Acides aminés	-7 - -5	-7 - -6
Acides organiques	-6 - -4	-6 - -5

1) Ces deux espèces sont seulement présentes en milieu anoxique.

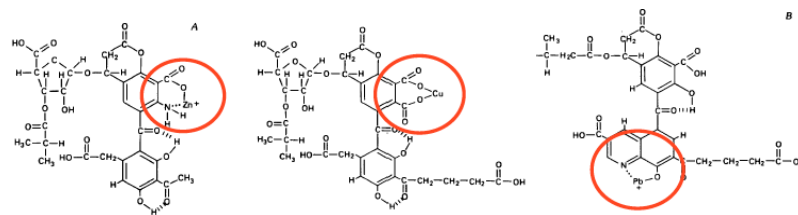
- Inorganic ligands are well known
- Organic ligands are usually only known as collective partners
- Anthropogenic ligands (EDTA, NTA) often occur in waters

- Natural organic matter (NOM) contains numerous functional groups that complex metal ions. It acts as a mixture of many ligands because it has many sites with different properties, meaning that there is no simple equilibrium constant but instead a distribution of equilibrium constants
- NOM does not have a single, known structure. The structure of NOM differs across space and time and is extremely difficult to characterize due to its complexity
- Acidic functional groups have different affinities towards metal cations; the stability decreases in the following sequence:

$$\text{Cu(II)} > \text{Ni(II)} > \text{Zn(II)} > \text{Co(II)} > \text{Cd(II)} > \text{Ca(II)} > \text{Mg(II)}$$



Hypothetical structure of NOM



anthranilic acid

phthalic acid

8-hydroxyquinoline

Acidic functional groups

Natural organic matter

NOM is an assembly of various colloidal breakdown products of living organisms. It includes fractions of lipids, nucleic acids, proteins, cellulose, lignin, cutin, etc. It covers most surfaces in the environment, and acts as a sorbent for organic substances

There is no single chemical formula to describe organic matter, but it can be characterized in terms of:

- Composition (typically 45-55% C, 35-45% O, 3-5% H, 1-4% N, traces of other elements)
- Spectral properties (yellow-brown-black appearance)
- Aromaticity (how many rings)
- Functional groups (phenol, carboxylic acid content, etc.)



The color of beer stems from dissolved organic carbon

Some roles of NOM in environmental chemistry

- NOM is ubiquitous in water!
- Covers (almost) all surfaces and provides a hydrophobic layer that contaminants can adsorb to
- Complexes metals and adsorbs organic contaminants
- NOM-associated contaminants can be protected from degradation processes
- Shields light and thereby protects contaminants from photolytic degradation
- Reacts with light to form oxidants
- Can interfere with water treatment processes (membrane fouling, disinfection byproducts)

Surface Waters



Marine Waters



Sediment Pore Waters



Simple model for metal speciation in natural waters

- Model considers only inorganic species (organic matter is not represented).
- Although model output gives incomplete picture of metal speciation in natural waters, it can show important trends.

$$\frac{[\text{Me}^{n+}]}{[\text{Me}]_T} = \frac{1}{1 + \sum \beta_{i,\text{OH}}[\text{OH}^-]^i + \sum \beta_{i,\text{CO}_3}[\text{CO}_3^{2-}]^i + \sum \beta_{i,\text{Cl}}[\text{Cl}^-]^i + \sum \beta_{i,\text{SO}_4}[\text{SO}_4^{2-}]^i}$$

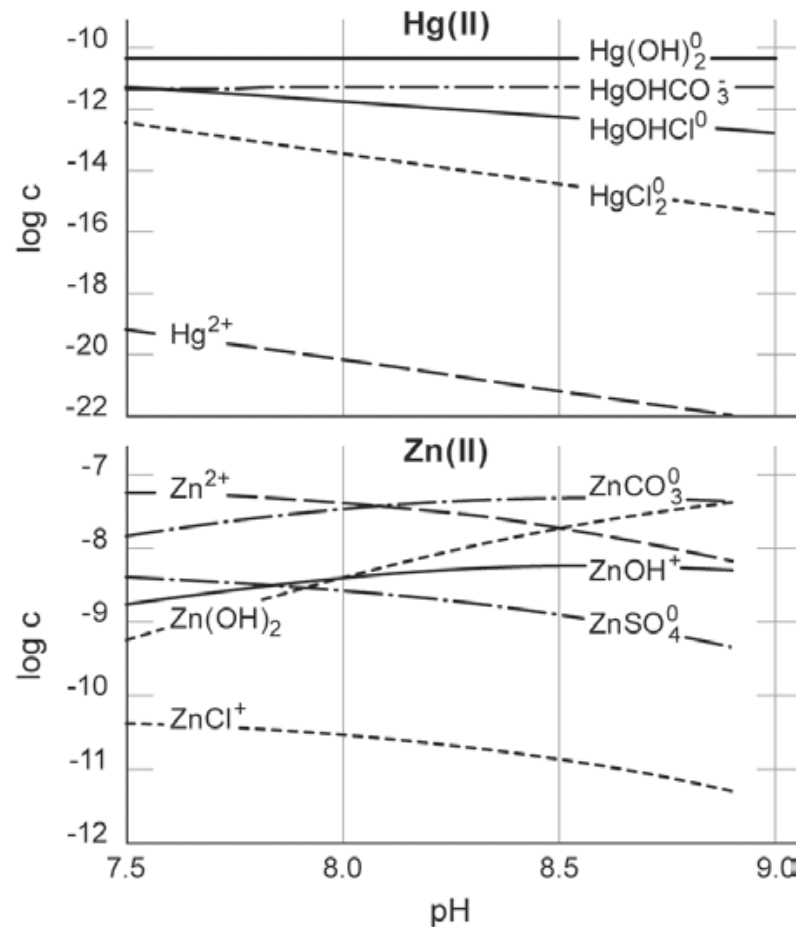
Simple model for metal speciation in natural waters

Metal speciation in freshwater system

- Hydroxo- and carbonato complexes are dominant for most metals
- Chloride complexes are not significant (with the exception of Ag^+)

Complexation with inorganic ligands keeps free metal ion concentrations at low levels in the pH range around 8.

Decreasing pH, however, increases the concentrations of free metal ions



Exercise 3: Zn(II) speciation in the presence of several ligands



Consider a system with Zn(II). Zn forms both hydroxo-complexes and carbonato-complexes. You have the following information:

- pH 8.5
- $Zn_{\text{tot}} = 10^{-8} \text{ M}$
- Total carbonate: $C_{\text{tot}} = 2 * 10^{-3} \text{ M}$

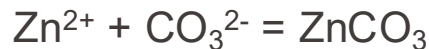
Calculate the concentrations of Zn^{2+} , $Zn(OH)^+$, $Zn(OH)_2$ and $ZnCO_3$



$$K_1^* = 10^{-9.1}$$



$$\beta_2^* = 10^{-17}$$



$$K_2 = 10^{4.52}$$



$$K_a = 10^{-10.2}$$

- 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.
- The hard-soft classification scheme allows to qualitatively assess the expected behavior of an element under given conditions.
- The equilibrium approach for modelling metal speciation can be used to assess the fate of different metals in different systems.