



Metal Speciation

ENV-200 Weeks 3 and 4

Meret Aeppli

meret.aeppli@epfl.ch

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

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

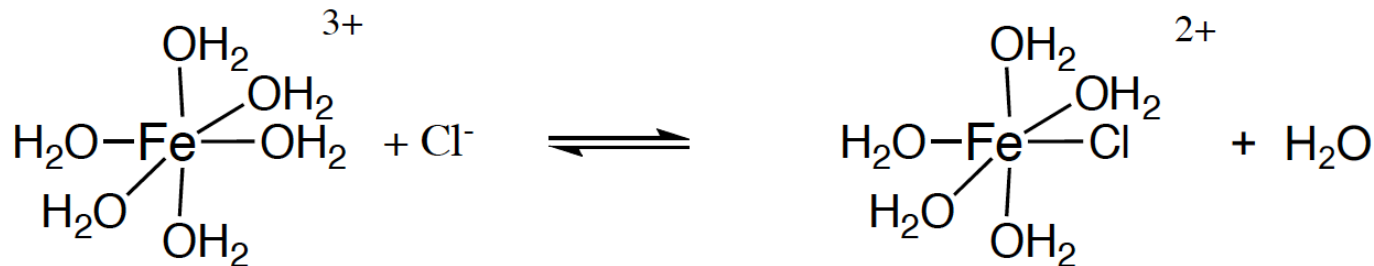
Today, we will discuss complexation of metals cations with ligands other than water.



Metal speciation

Complexation

- Replacement of H_2O by (an)other ligand(s)
 - Inorganic ligands: CO_3^{2-} , Cl^- , SO_4^{2-} , F^- , S^{2-}
 - Organic ligands: amino acids, phenoles, 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

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 $S_2O_3^{2-}$

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

Ligands

 hard  intermediate  soft

C	N	O	F
	P	S	Cl
	As	Se	Br
	Sb	Te	I

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.

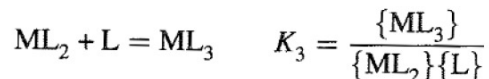
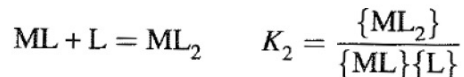
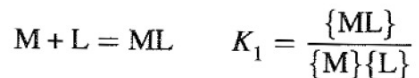
- a. Which of the metals would you expect to mainly interact via complexation and precipitation with bicarbonate and which one predominantly with sulfide?
- b. For which trace metal is it most difficult to anticipate its preference for one of the two anions?



Formulation of stability constants

Stability constants for each ligation step

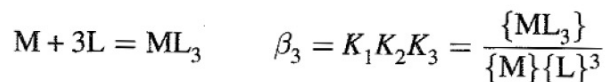
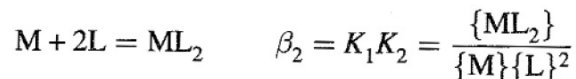
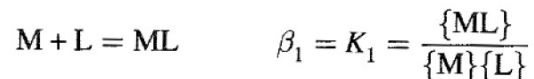
Unprotonated ligand



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

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

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

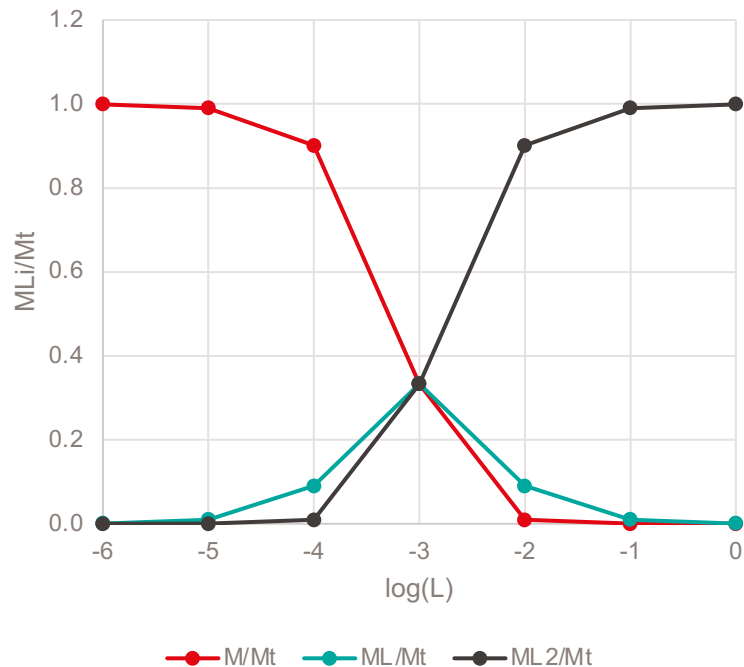
$$\alpha_i = \frac{[ML_i]}{[M]_{\text{tot}}} = \frac{[L]^i \beta_i}{1 + \sum [L]^i \beta_i} \quad \text{and} \quad \beta_i = \frac{[ML_i]}{[M][L]^i}, \text{ hence } [ML_i] = [M] [L]^i \beta_i$$

- 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



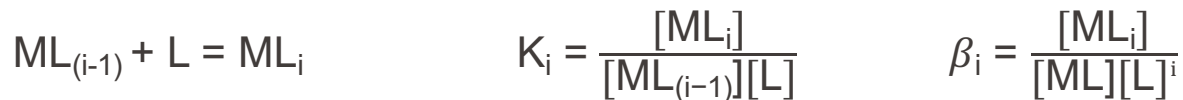
Given: $K_1 = 10^3$, $K_2 = 10^3$ ($\beta_2 = 10^6$)

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

1. Identify species present at equilibrium

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

2. Write our equilibrium equations and list complexation constants



3. List mass balance equations

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

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

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)

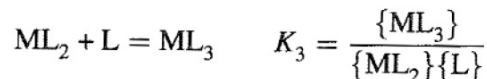
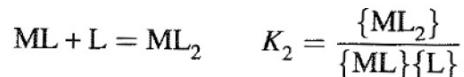
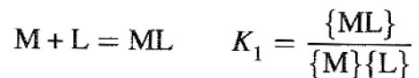
- L, e.g.: NH_3 , F^- , CN^- , PO_4^{3-}
- L undergoes acid-base equilibrium- we have a system with coupled reactions



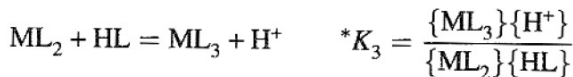
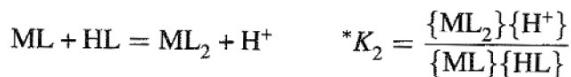
- During complexation (in presence of a metal ion), HL reacts more acidic than in a pure HL solution



Stability constants for each ligation step

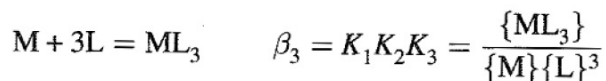
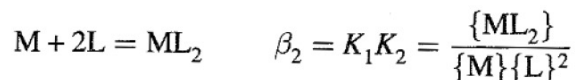
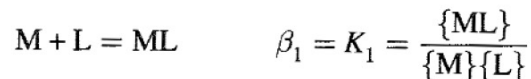
Unprotonated ligand

etc.

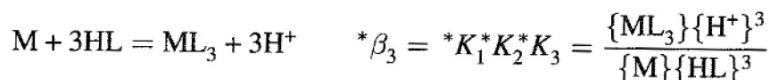
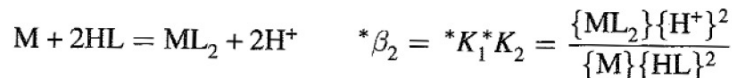
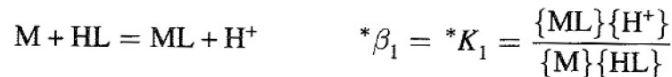
Protonated ligand

etc.

Stability constants for brutto reactions = brutto stability constants

Unprotonated ligand

etc.

Protonated ligand

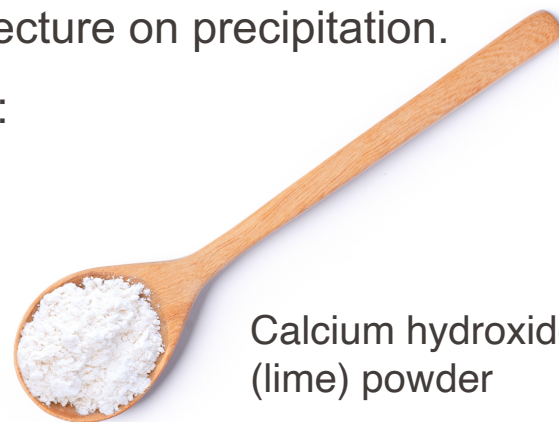
etc.

You are familiar with
*K_i and *β_i from the
hydrolysis class

- 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?

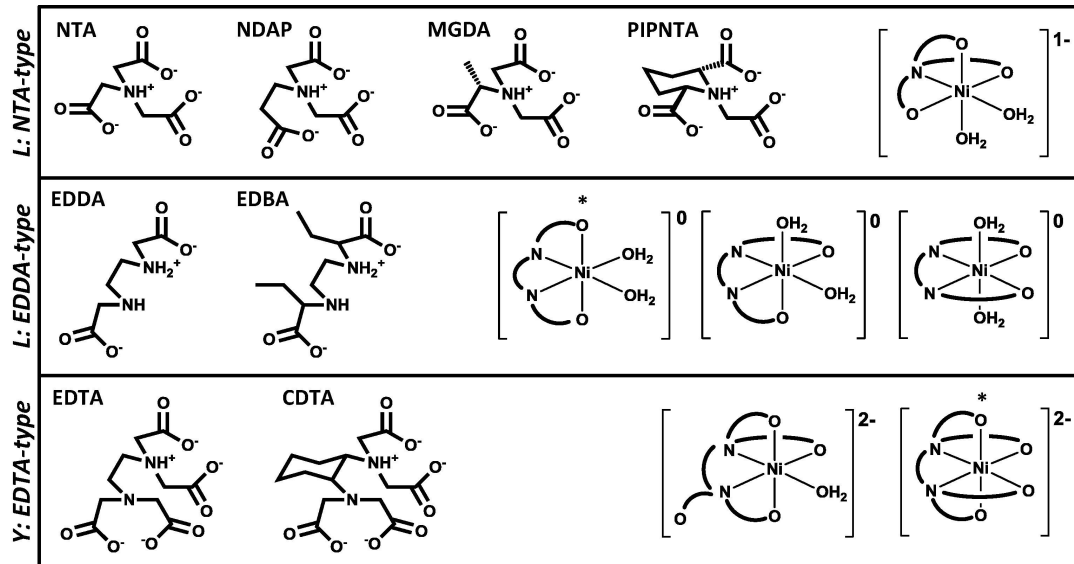
We know: $[\text{Ag}^+]_{\text{tot}} = 10^{-6} \text{ M}$, $[\text{NH}_4^+]_{\text{tot}} = 10^{-2} \text{ M}$, $K_1 = 10^{3.2}$, $K_2 = 10^{3.83}$, $K_a = 10^{-9.3}$

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

- The word chelation is derived from Greek $\chiηλή$, *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

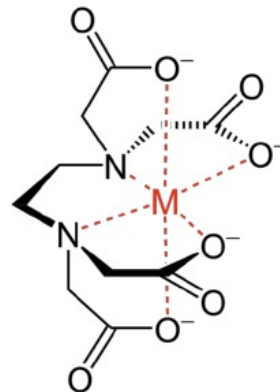
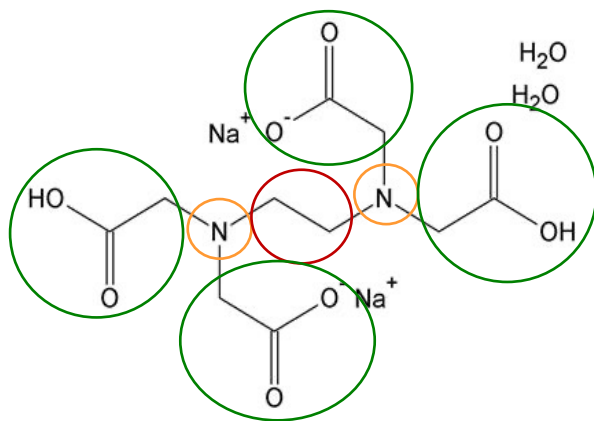


- Denticity refers to the number of atoms with which a ligand binds to a metal ion
 - monodentate = single atom
 - Bidentate = two different atoms
 - etc
- What is the denticity of NTA^{3-} , EDDA^{2-} , and EDTA^{4-} ?
- Which ligand will form the strongest complex?



Equation	Log K
$\text{Ni}^{2+} + \text{nta}^{3-} = \text{Ni}(\text{nta})^{-}$	12.30
$\text{Ni}^{2+} + \text{edda}^{2-} = \text{Ni}(\text{edda})^0$	14.1
$\text{Ni}^{2+} + \text{edta}^{4-} = \text{Ni}(\text{edta})^{2-}$	19.5

- EDTA (**E**thyl**e**di**a**min**e****t**etra**a**ce**t**ic**a**c**i**d) 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



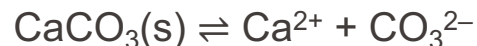
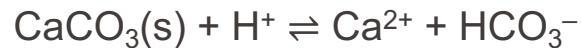
Rising water temperature reduces the solubility of lime and it precipitates.



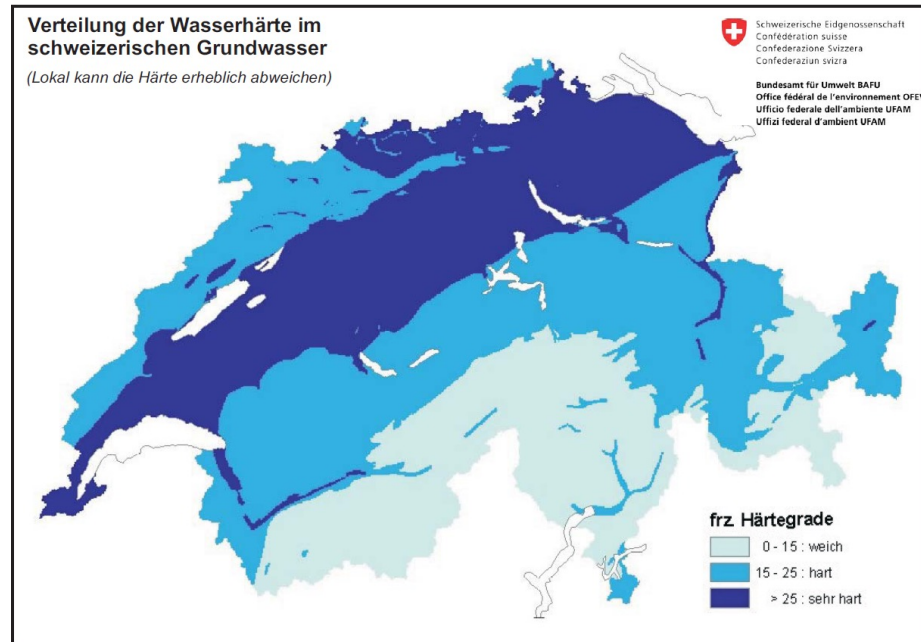
How do the ions get into the water?



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

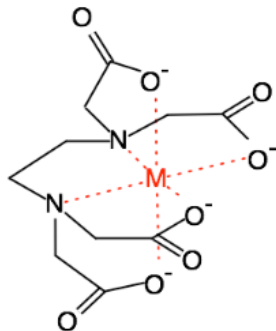


Water hardness can be determined by reacting metal cations with chelating ligands, such as EDTA.

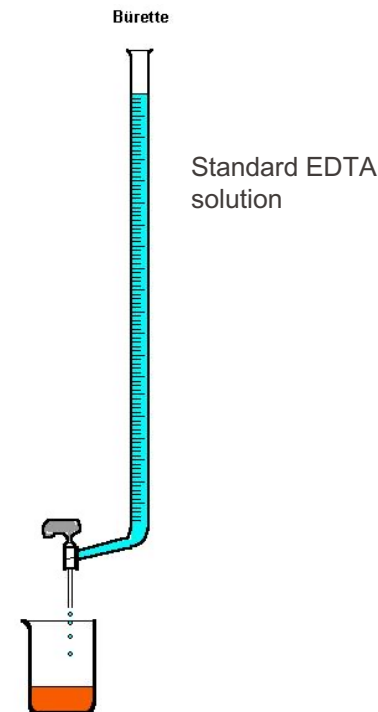


From the amount of EDTA used to complex all Ca^{2+} , we can determine the concentration of Ca^{2+} in our sample.

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.



Sample with
unknown
metal content



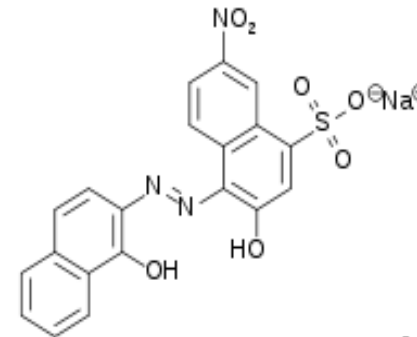
In-class experiment: water hardness



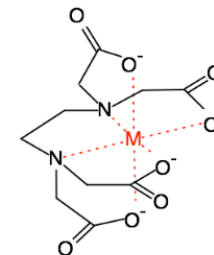
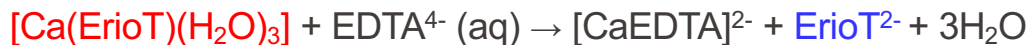
Reaction 1



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



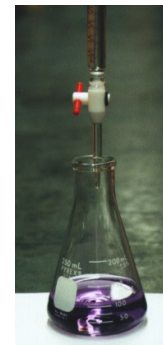
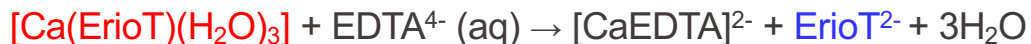
Reaction 1



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

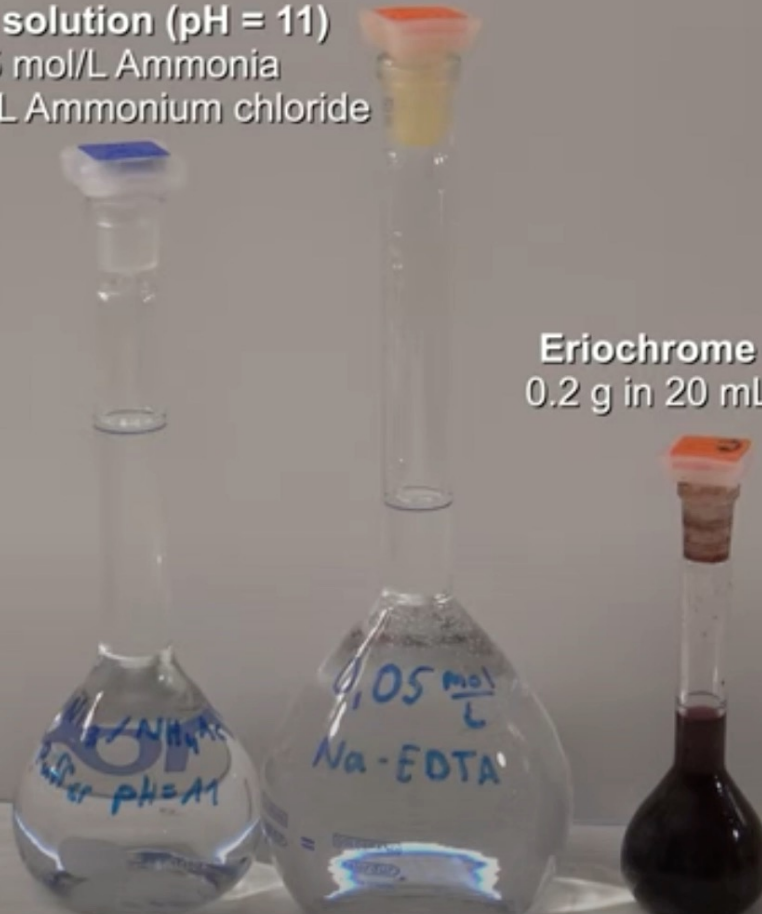
Na-EDTA (0.05 mol/L)*

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 3. (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)

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

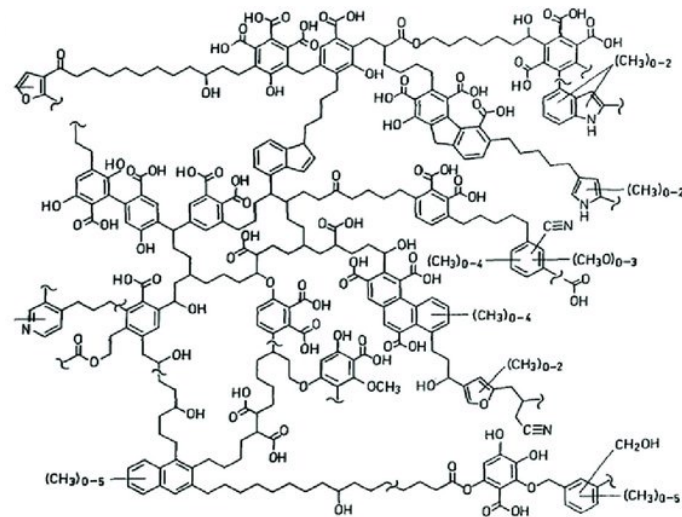
Domaines de concentration dans les eaux douces et l'eau de mer (log C (M))		
	Eaux douces	Eau de mer
HCO_3^-	-4 - -2.3	-2.6
CO_3^{2-}	-6 - -4	-4.5
Cl^-	-5 - -3	-0.26
SO_4^{2-}	-5 - -3	-1.55
F^-	-6 - -4	-4.2
$\text{HS}^-/\text{S}^{2-}$ ¹⁾	-6 - -3	-
Acides aminés	-7 - -5	-7 - -6
Acides organiques	-6 - -4	-6 - -5

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

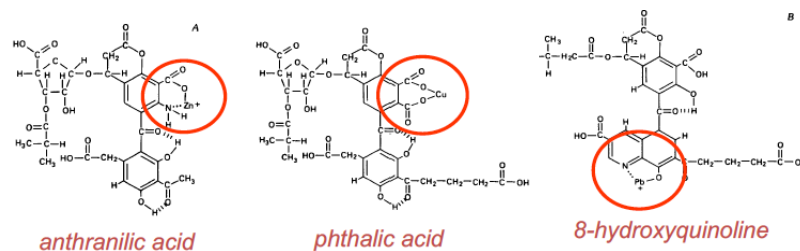
- Inorganic ligands are well known
- Organic ligands are usually only known as collective partners
- Anthropogenic ligands (EDTA, NTA) often occur in waters

- 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



Acidic functional groups

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.

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

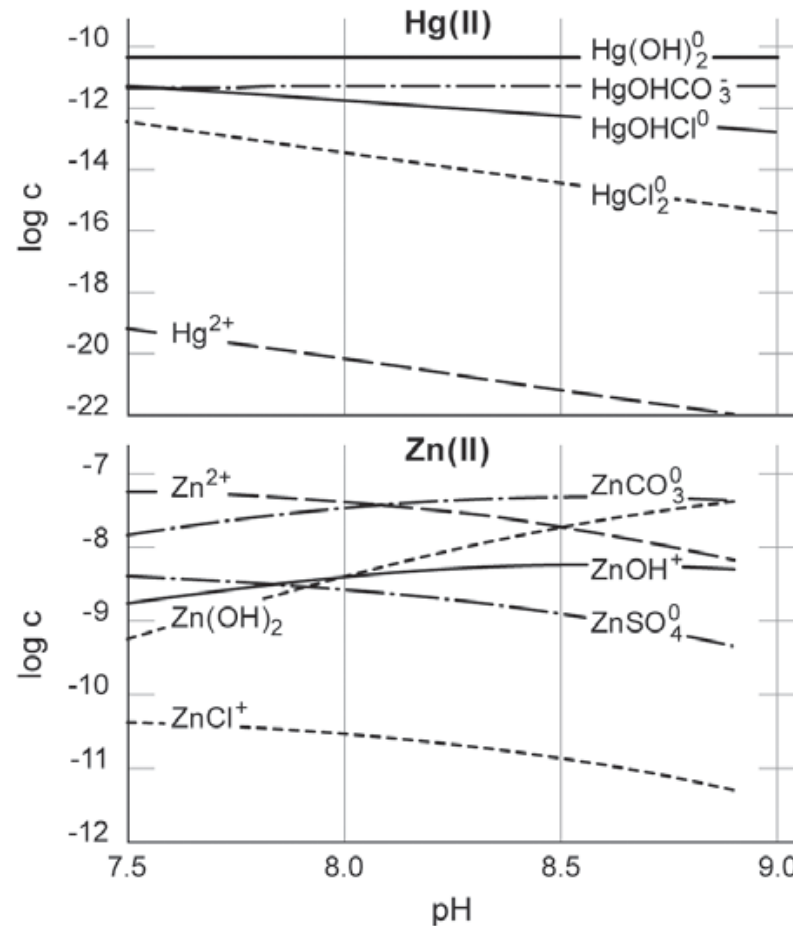
Simple model for metal speciation in natural waters

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

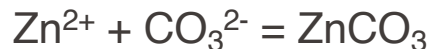
Calculate the concentrations of Zn^{2+} , $Zn(OH)^+$, $Zn(OH)_2$ and $ZnCO_3$



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



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



$$K_2 = 10^{4.52}$$



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

- 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.