

Lecture 6

Aqueous Inorganic Geochemistry of Natural Waters

- ① *Lecture 5 left-over:*
 - a. Behavior of ions in aqueous solution – complexes
 - b. Quantifying aqueous solubility and total dissolved solids (TDS)
- ② Organic Chemistry Intro

Please read Manahan chapter 4 and chapter 29 (7th Ed) for this week

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The role of complexation/chelation reactions on solution chemistry

Definition

A **complex** is an association of molecules in solution or at a particle surface where electron sharing occurs through associations that are *weaker than true chemical bonds* but none the less *strong enough to make identifiable substances*.

The Lewis Acid-Base "donor/acceptor" concept is handy here, because complexes involve stabilization of charge (or partial charge) on ions (or polar molecules) through electron sharing.

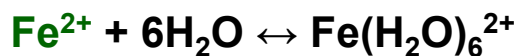
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complexation/chelation

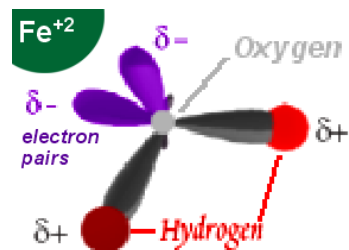
Complexes involve *ligands* and *host* ions.

We will mostly consider complexes of **cations** (M^{+n}) and electron donor ligands.

As discussed in lecture 3, *Hydration* is a specific type of complexation reaction where the ligands are all water:



Schematic depiction of water using its **lone pairs of electrons** to stabilize an Fe^{2+} ion in solution. The hydrate itself involves 5 other water molecules.



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ligands:

Other common natural ligands are Cl^- (chloride) and $:\text{NH}_3$ (ammonia).

These, along with water, are known as *unidentate*.

Unidentate ligands offer electrons from a single site to a complex.

In an aqueous Fe^{+3} solution with both Cl^- and $:\text{NH}_3$, many complexes are possible involving these two ligands and H_2O .

The charge on the complex remains unchanged relative to Fe^{+3} with H_2O and NH_3 ligands but each Cl^- ligand brings one negative charge.

All of the following complexes are possible in this solution:



The relative proportions of these complexes will vary with pH since $\text{NH}_3 + \text{H}^+ \leftrightarrow \text{NH}_4^+$. Thus $[\text{FeCl}_6]^{-3}$ would be favored at low pH

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ligands:

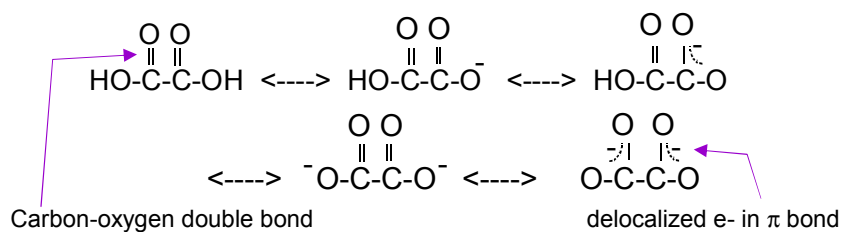
Chelation involves complexation by *multidentate* ligands.

Unidentate ligands are individual ligands that have more than one electron or electron pair to donate to a cation.

A *bidentate* ligand has two active binding sites for a cation

e.g., ethylene di-amine, **:NH₂-CH₂-CH₂-H₂N:**

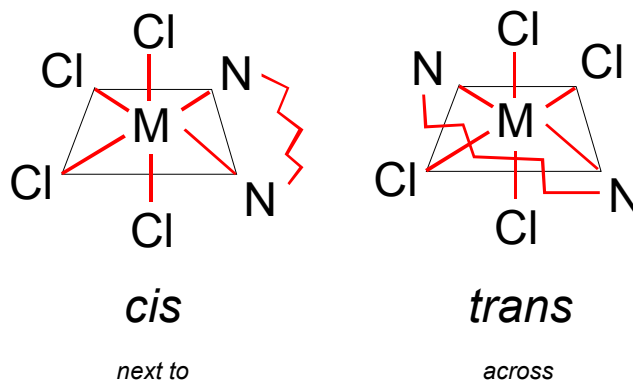
and **oxalic acid/oxylate anion**, which has the following forms in solution:



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ligands:

Bidentate ligands can bind in two ways:



a "small" bidentate ligand such as ethylene diamine can usually only bind *cis* for geometric reasons.

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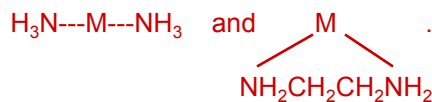
Why are Chelates favored over Complexes with similar electron donors in the ligands?

We can understand this phenomenon with thermodynamic reasoning (i.e., estimates of Gibbs free energy and K_{eq} should favor the chelate).

Example 1

Compare a metal di-amino complex (two ammonia ligands) vs a metal complex with ethylene di-amine (two ammonia molecules "fused" onto a single ethylene molecule, making it a bidentate ligand)

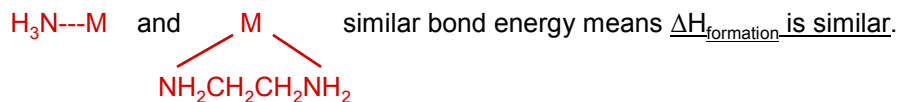
From a bond energy perspective, the M-N electron donor/acceptor relationship is very similar for



the M-N electron donor/acceptor relationship has **very similar bond energy**

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Energetics of Chelates vs. Complexes



But $\Delta S_{\text{formation}}$ differs for both...

because it takes 2 NH_3 ligands and 1 metal ion to come together to make $\text{H}_3\text{N}---\text{M}---\text{NH}_3$ (more order)

but it takes only 2 entities (1 ethylene diamine ligand and 1 metal ion) to come together to make the metal chelate (less order).

$\Delta S_{\text{reaction}}$ is positive for chelate formation relative to the ammonia.

$\Delta H^\circ \sim 0$, so $\Delta G^\circ = -T\Delta S^\circ$, @ constant T, $\Delta G^\circ = -\Delta S^\circ$.

Since ΔG° is negative, $K_{eq} > 1$ and products are favored as written.

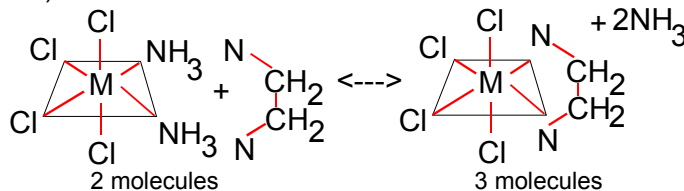
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Energetics of Chelates vs. Complexes

Example 2

What about a di-amino quadro-chloro metal complex vs an ethylene diamine quadro-chloro chelate?

Again, ΔS is positive for chelate formation relative to the di-unidentate ammonia metal complex. So $\Delta G_{\text{formation}}$ of the chelate is more negative (and thus favored)



$\Delta G^\circ = -\Delta S^\circ$, so products are favored as written.

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Chelates are an important control of ionic concentration in solution.

In cases where multidentate ligands are present in natural or waste waters, **they can actually leach metal ions from solids** (like pipes or rocks) **into solution**.

Humic Substances are an important class of naturally occurring organic chelating agents; We discuss them next week.

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④ Quantifying aqueous solubility

☞ *TDS, or total dissolved solids*

The dry weight of all solutes in solution per liter or kg of solution. TDS includes ionic and covalent solutes.

“high” TDS = lots of things in solution. “low” TDS ~ pure solvent.

TDS affects many properties of an aqueous solution

density

Pure water has a density of 1 kg/L at 4°C

Sea water (mean density of 1.034 kg/L) can be thought of as ~1 kg/L water and 0.034 kg/L TDS, or ~34 g TDS/L

Solubility

Specific solutes can be more or less soluble as in a natural water as a function of TDS

Usability

High TDS waters tend to be less useful for urban and industrial settings because precipitates can foul machinery and pipes.

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TDS in natural waters reflects a range of physical and chemical processes, such as:

- * precipitation and evaporation
- * weathering (dissolution/precipitation, incongruent reaction--such as leaching-- and ion-exchange)
- * temperature
- * pH
- * gas solubility
- * biological processes

| <u>Water "type"</u> | <u>TDS (mg/L)</u> | <u>Examples</u> |
|---------------------|-------------------|---|
| Fresh | <1000 | rain, river water, most lakes, drinking water |
| Brackish | 1000-10000 | estuaries, lagoons, near-shore aquifers, some inland seas |
| Saline | 10000-100000 | oceans, some inland seas, some geothermal waters |
| Brine | >100000 | shallow tidal basins, geothermal waters |

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Solubility refers to the equilibrium quantity of a substance that can be dissolved in a solution.

We can put lots of high solubility material but only a little of a low solubility material into a solute at saturation.

Saturation = maximum solute concentration in solution.

Concentrations are given in units of molarity (mole/L), molality (mole/kg), ppm by weight (or mg/kg = $\mu\text{g/g}$)

Before we can quantify saturation and use equilibrium constant expressions to predict solubilities of materials in water, we need to consider the dissolution process itself.

Two types of dissolution reactions exist:

1. **Congruent** – all of a material goes into solution, leaving nothing behind when it is dissolved
2. **Incongruent** – parts of a material go into solution, leaving a new, modified material behind.

These terms refer to the undissolved solid left behind

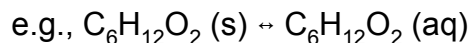
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There are also different type of solutes in solution:

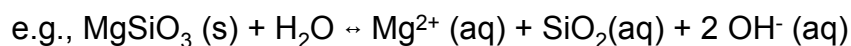
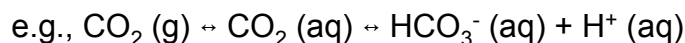
1. **ionically** bonded solids, which dissociate upon dissolution to form ions.



2. **covalently** bonded material which go into solution essentially unchanged, such as glucose .



3. covalently or ionically bonded **materials which undergo a reaction** with the solvent

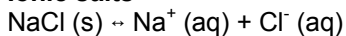


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We define **solubility** somewhat differently for each type of solute.

In general, solubility is a mole-for-mole measure of how much of a solid will go into a given volume of solution, regardless of what happens to it once it is there.

Ionic salts



each mole of halite, NaCl (s), that dissolves in a given volume of water produces one mole of Na⁺ (aq) and one mole of Cl⁻ (aq).

The solubility is defined as the moles of NaCl (s) that will dissolve into a given volume of solution at saturation, which equals [Na⁺] which equals [Cl⁻]

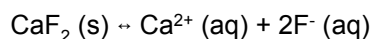
We have already defined $K_{sp} = [\text{Na}^+][\text{Cl}^-]$

So, setting $x = [\text{Na}^+] = [\text{Cl}^-] = \text{solubility}$, and using $K_{sp} = x^2$ we find that **Solubility = $x = K_{sp}^{1/2}$.**

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What about **cases** for ionic solids **that don't produce solutes on a one to one mole basis**?

For instance, fluorite (CaF₂) dissolves as follows



In this case, it is easier to define solubility in terms of Ca²⁺ (aq) since one mole of fluorite dissolves to make one mole of calcium ions.

$$\text{Solubility} = x = [\text{Ca}^{2+}]$$

We also see that solubility = $\frac{1}{2}$ [F⁻], since 2 moles of fluoride are produced for each mole of solid dissolved.

How is solubility (again as "x") related to K_{sp} ?

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$$

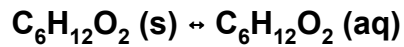
$$\text{since } [\text{F}^-] = 2[\text{Ca}^{2+}]$$

$$K_{sp} = x \cdot (2x)^2 = 4x^3$$

$$\text{Solubility} = x = (K_{sp}/4)^{1/3}$$

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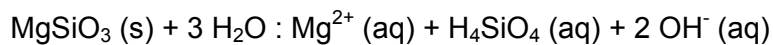
For **covalently bonded** solids:



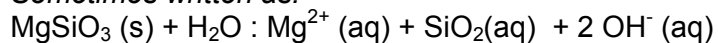
$$K = [\text{C}_6\text{H}_{12}\text{O}_6] \quad \text{and } x = k$$

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An important **congruent dissolution** reaction in nature is the dissolution of pyroxene minerals :



Sometimes written as:



In either event, 1 mole of enstatite, $\text{MgSiO}_3 (\text{s})$, dissolves to produce:

- ✎ 1 mole of $\text{Mg}^{2+} (\text{aq})$
- ✎ 1 mole of dissolved Si as either " $\text{SiO}_2(\text{aq})$ " or " $\text{H}_4\text{SiO}_4(\text{aq})$ "
- ✎ 2 moles of $\text{OH}^- (\text{aq})$.

$$\text{Solubility} = x = [\text{Mg}^{2+}] = [\text{SiO}_2(\text{aq})] = \frac{1}{2} [\text{OH}^- (\text{aq})]$$

$$K = [\text{Mg}^{2+}] [\text{SiO}_2 (\text{aq})] [\text{OH}^-]^2 \quad K = x \times (2x)^2 = 4x^4$$

and $X = (K/4)^{1/4}$

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The same logic applies to **incongruent dissolution reactions**

For a **solid that reacts with water upon dissolution to make a new solid**, we define solubility based upon a resulting solute that is easily related back to the original substance being dissolved (if possible).

We could also define the solubility based on the proportion of modified to unmodified substance in the undissolved state.

An important incongruent dissolution that occurs during chemical weathering and soil formation is:



solid K-feldspar & water reacting to produce solid Kaolinite, dissolved silica, & potassium ions

1 mole of K-feldspar dissolves to produce 1 mole of K^+ .

We define solubility using $[\text{K}^+]$ at saturation.

$$\text{solubility} = x = [\text{K}^+] = \frac{1}{2} [\text{SiO}_2(\text{aq})]$$

$$\text{solubility also} = -[\text{H}^+] \text{ (hydrogen ions consumed)}$$

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The common ion effect.

In complex solutions this tends to lower the expected solubility of a salt relative to that in pure water.

For example..

both NaCl and CaCl_2 produce Cl^- ions upon dissolution.

The solubility of NaCl can be written as $x = [\text{Cl}^-]$

The solubility of CaCl_2 can be written as $x = \frac{1}{2} [\text{Cl}^-]$.

The solubility of NaCl and CaCl_2 in a solution of both depends on each other, *due to the common Cl^- ion.*

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Organic Geochemistry of Natural Waters

- 1 Intro
- 2 Structure, Nomenclature and Functional Groups
- 3 Humic substances and other natural "OC"
- 4 Reactivity
- 5 DOC/POC distribution
- 6 Acidity

We will look at *natural* and *pollutive* organic molecules and summarize their behavior in the environment from the perspective of:

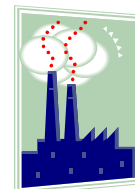
- functionality
- aqueous solubility
- environmental reactivity.

Aqueous solubility is an important feature you should be able to recognize/predict since it affects reactivity and dispersion rate of organic contaminants.

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1. Hydrospheric Organic Carbon

Organic Carbon occurs in the hydrosphere in:
natural and *contaminant* forms,
as well as in
dissolved and *suspended* forms:



DOC = Dissolved organic carbon, includes fulvic acids (and humic acids above pH=2).

POC = Particulate (suspended) organic carbon. Includes humin (and humic acids below pH=2).

DOC and **POC** concentration are variable in the hydrosphere but are generally higher in waters with high photosynthetic productivity:
e.g., watershed water in forested areas,
the outflow of high photosynthesis lakes or swamps
sewage outfalls

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*Examples of Common **natural** organic molecules in nature:*

- * simple organic molecules produced by organisms of synthesized naturally (i.e., methanol = $\text{CH}_3\text{-OH}$)
- * biomolecules (i.e., chlorophyll, amino acids, proteins)
- * fossilized biomolecules (i.e., petroleum components)

*Common **organic pollutants** in nature are:*

- * pesticides/insecticides/herbicides/fungicides of various types (which can migrate from the application area)
- * hydrocarbon components from leaky subsurface fuel storage or transfer vessels.
- * Biological waste products (untreated sewage, etc..).
- * Gaseous contaminants from various sources.

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2. Structure, Nomenclature and Functional Groups:

* Organic molecules consist of a C-H backbone, sometimes plus other entities called “functional groups”, which can be substituted for either C or H.

* The molecule takes its structural name from the number of carbon atoms it contains and how they are bonded.

Each carbon atom can have 4 attached bonds

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Nomenclature

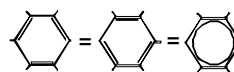
C, H - only molecules (aka hydrocarbons)

Alkane all C-C single bonds ("saturated" molecule)

Alkene at least one C=C double bond ("unsaturated" molecule, has few H atoms in structure). If more than one C=C double bond, they are said to be "conjugated" if they are arranged like this: C=C-C=C-C=C

Alkyne at least one C≡C triple bond (also "unsaturated" molecule, has few H atoms in structure)

Aryl special "unsaturated" molecule with "conjugated" C=C double bonds in a ring structure (like benzene = C₆H₆)



Benzene

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Nomenclature:

| | | |
|-----------|---|---|
| 1 carbon: | Methane | <i>note: when one of these molecules is attached to another molecule, it take the names "methyl", "ethyl" or "ethylene" group for methane-like, ethane-like, and ethene like functionalities, etc..</i> |
| 2 carbon: | Ethane (H ₃ C-CH ₃) Ethene (H ₂ C=CH ₂) Ethyne aka acetylene (H-C≡C-H) | |
| 3 carbon: | Propane (H ₃ C-CH ₂ -CH ₃) Propene (H ₂ C=CH-CH ₃) Propyne (HC≡C-CH ₃) | |

Carbon atoms in these molecules are numbered, starting at the highest order functionality (see below), if one exists.

Functional groups:

* These determine compound reactivity and water solubility.

In general, more functionality = more soluble molecule = more reactive molecule.

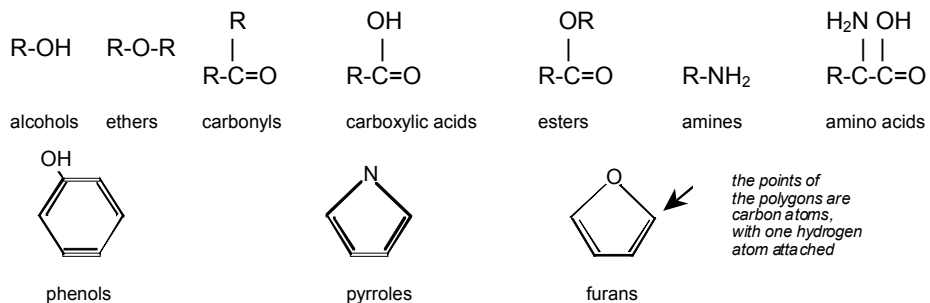
* **Functional groups typically set the name of the molecule:**

| name | formula | Alternate names: |
|------------------------------|---|------------------|
| a. Ethyl Alcohol (ethanol): | CH ₃ CH ₂ OH (= ethane + alcohol) | 1-hydroxy-ethane |
| b. Propyl Amine: | CH ₃ CH ₂ CH ₂ NH ₂ | 1-amino propane |
| c. <i>iso</i> -Propyl Amine: | CH ₃ CHNH ₂ CH ₃ | 2-amino propane |

the "iso" prefix denotes the location of substitution at the symmetrical center of the molecule.

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Common organic Functional groups:



Functional groups can be acidic or basic. Adding charge to an organic molecule generally makes it MORE water soluble and enhances Lewis acid/base interactions with metals in solution (i.e., chelation)

The more basic (electron donor) functional groups an organic molecule has, the more interaction it is likely to have with inorganic ions. These can also interact with solid surfaces (e.g., Suspended load components of a river, sediments, etc...).

One exception are halogen functional groups. "Halogenated" compounds do not act like Lewis bases because these functional groups are very electronegative.

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