

self study

Most of this is probably background from a prior chemistry course;
some near the end is GG325 review

Aqueous Inorganic Geochemistry of Natural Waters

Three important topics:

1. Acids, bases and the aqueous CO₂ system
2. Behavior of ions in aqueous solution
3. Quantifying aqueous solubility and total dissolved solids (TDS)

Please read Manahan chapter 3 and review chapter 28 (6th Ed) for next week

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Acids and Bases

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1. Two Types of Acids and Bases:

a. **Brönstead acids** and **bases** contain H^+ and OH^-



water is acid and base simultaneously, $H_2O \leftrightarrow H^+ + OH^-$.

pure water and acid neutral aqueous solutions have equal amounts of H^+ and OH^- .

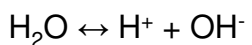
b. Lewis acids and bases

Brönstead acids can be thought of as **electron deficient ions** and **bases** as **electron excessive ions**, which provides a different perspective on acidity/basicity that we can extend to other (non protic and non hydroxyl) compounds. We call this the **Lewis acid/base** concept.

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Brönstead acidity:

K_w is the equilibrium constant for the dissociation of water.



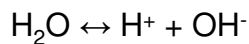
$$K_w = [H^+][OH^-] = 10^{-14} \text{ at } 25^\circ\text{C}$$

K_w has a slight temperature dependence:

Temp ($^\circ\text{C}$)	K_w	
0	$10^{-14.94}$	less dissociated
25	10^{-14}	
60	$10^{-13.02}$	more dissociated

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Brönstead acidity:



$$K_w = [\text{H}^+][\text{OH}^-]$$

An acid neutral solution always has $[\text{H}^+] = [\text{OH}^-]$.

Setting $[\text{H}^+] = x$, yields $x^2 = 10^{-14}$

$x = 10^{-7}$ = moles of H^+ in this solution.

$$\text{pH} = -\log a_{\text{H}^+} \sim -\log [\text{H}^+]$$

$\text{pH} = -\log [10^{-7}] = 7$ in an acid neutral at 25°C

A less common but sometimes useful variable is:

$$\text{pOH} = -\log a_{\text{OH}^-} \sim -\log [\text{OH}^-]$$

In an acid neutral solution $\text{pOH} = \text{pH} = 7$

In any water at 25°C , $\text{pH} + \text{pOH} = 14$

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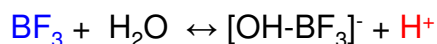
Lewis Acids and Bases

Lewis acid example:



BF_3 has an empty orbital on B and only 6 electrons involved in the 3 B-F bonds. It is electron deficient so it is known as a Lewis Acid (B needs $2e^-$ to achieve a Ne electronic configuration).

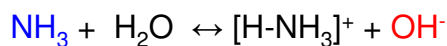
BF_3 will react with H_2O to get its needed electrons, creates new ions, and acidify the solution acid in a Brönstead sense.



Lewis base example:



In a similar fashion, NH_3 (Ammonia) can be shown to be a Lewis base, such that



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Aqueous acid-base relationships

Neutral pH = 7

"low" pH is <7 = acid solution = large H^+

"high" pH is >7 = base solution = small H^+

How much do natural waters deviate from acid neutrality?

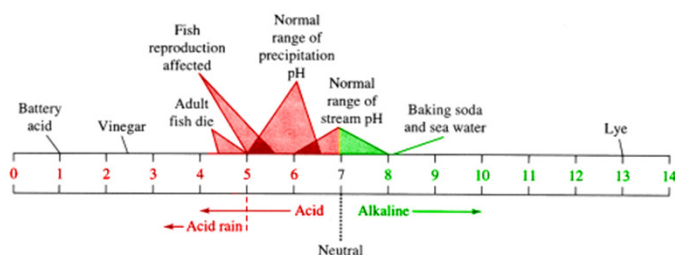


Figure 4-4 pH scale. The normal range of precipitation pH is from about 5.0 to 6.5. The pH of pure water in equilibrium with atmospheric carbon dioxide is 5.6. Normal rain is slightly acidic because of carbon dioxide (which forms the weak acid carbonic acid) and natural emissions of sulfur and nitrogen oxides and certain organic acids. Human activities produce more of these compounds and the result is "acid rain." The formation of strong acids such as sulfuric and nitric acids causes the pH of precipitation to be less than 5.0, producing acid rain. Occasional pH readings of well below 2.4, the acidity of vinegar, have been reported for rain and fog in large cities and highly industrialized areas.

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The aqueous CO_2 system

Equilibria involving carbon dioxide and its conjugate bases in water set the baseline pH of almost all natural waters at the Earth's surface

other constituents usually serve to alter this carbonate equilibrium pH.

Environmental chemists often speak of $\Sigma CO_2(aq)$ = aqueous carbon dioxide in all of its aqueous forms.

First, let's show that the amount of CO_2 present in the atmosphere and the pH ($= -\log[H^+]$) of water in equilibrium with it are linked,

.. as is the solubility of $CaCO_3$ as $[Ca^{2+}(aq)]$.

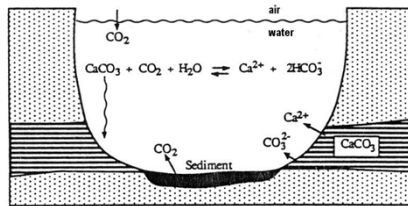
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Example: Combining Equilibria in the aqueous CO₂ system

Let's combine the system of inorganic reactions governing the amount of dissolved CO₂ in natural waters (which bears directly on the amount of CO₂ in our atmosphere, geosphere and biosphere)

CO₂ has 4 forms in water, which are related by a series of chemical reactions shown schematically in the figure below:

- a. dissolved gaseous carbon dioxide CO₂(aq)
- b. carbonic acid H₂CO₃(aq)
- c. bicarbonate anion HCO₃⁻(aq)
- d. carbonate anion CO₃²⁻(aq)



Carbon dioxide-calcium carbonate equilibria.

Note that CaCO₃ formation (by inorganic precipitation or biogenic precipitation) is the primary upper limit control on dissolved carbon dioxide concentration

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The 4 forms of CO₂ in water are related by 5 chemical reactions:

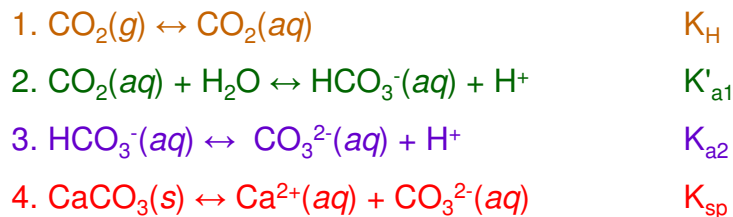
(disregarding for now photosynthesis/respiration)

1. $\text{CO}_2(g) \leftrightarrow \text{CO}_2(aq)$
This is a gas solubility reaction (sometimes called a Henry's law reaction. K is given the subscript "H": K_H)
2. $\text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3(aq)$
This is a bond reorganization reaction. It is also a type of hydration (reaction with water). K = K_{eq} (no "special" nomenclature)
3. $\text{H}_2\text{CO}_3(aq) \leftrightarrow \text{HCO}_3^-(aq) + \text{H}^+$
An acid dissociation reaction. Commonly given equilibrium constant notations of K_a if it is a *monoprotic* acid, or K_{a1} for the first acid dissociation of a *polyprotic* acid
4. $\text{HCO}_3^-(aq) \leftrightarrow \text{CO}_3^{2-}(aq) + \text{H}^+$
Another acid dissociation reaction. This is the second dissociation of *dioprotic carbonic* acid, so we call it or K_{a2}.
5. $\text{CaCO}_3(s) \leftrightarrow \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)$
This is a solubility/dissolution reaction. K is K_{sp}.

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Many texts use the simplifying assumption that reactions "2" and "3" can be combined since little free $\text{H}_2\text{CO}_3(\text{aq})$ is found in natural waters.

Because of this last point, the reaction sequence is shortened to



Let's mathematically combine them to determine an expression for the CaCO_3 solubility in a natural water (in terms of $[\text{Ca}^{2+}(\text{aq})]$). The water is open to gas exchange with the atmosphere and we assume there are no other reactions affecting Ca^{2+} , H^+ or $\Sigma \text{CO}_2(\text{aq})$ (carbon dioxide in all of its aqueous forms).

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It's all algebra...

Working backward from reaction 4: $K_{\text{sp}} = [\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}]$
 we can rearrange to: $[\text{Ca}^{2+}] = K_{\text{sp}} / [\text{CO}_3^{2-}]$ A.

from reaction 3: $K_{\text{a2}} = [\text{H}^+] \cdot [\text{CO}_3^{2-}] / [\text{HCO}_3^-]$
 we can rearrange to: $[\text{CO}_3^{2-}] = K_{\text{a2}} [\text{HCO}_3^-] / [\text{H}^+]$
 substituting into A. gives: $[\text{Ca}^{2+}] = K_{\text{sp}} \cdot [\text{H}^+] / K_{\text{a2}} \cdot [\text{HCO}_3^-]$ B.

the same type of rearrangement of equation 2 in terms of $[\text{HCO}_3^-]$ yields:
 $[\text{HCO}_3^-] = K'_{\text{a1}} \cdot [\text{CO}_2(\text{aq})] / [\text{H}^+]$
 substituting into B. gives: $[\text{Ca}^{2+}] = K_{\text{sp}} \cdot [\text{H}^+] \cdot [\text{H}^+] / K_{\text{a2}} \cdot K'_{\text{a1}} \cdot [\text{CO}_2(\text{aq})]$ C.

Finally rearrangement of equation 1 gives:
 $K_{\text{H}} = [\text{CO}_2(\text{aq})] / P_{\text{CO}_2}$
 $P_{\text{CO}_2} = K_{\text{H}} \cdot [\text{CO}_2(\text{aq})]$ D.

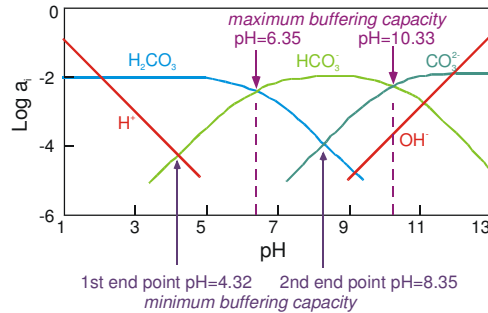
substituting into C. gives:

$$[\text{Ca}^{2+}(\text{aq})] = \frac{K_{\text{sp}} \cdot [\text{H}^+]^2}{K_{\text{H}} \cdot K'_{\text{a1}} \cdot K_{\text{a2}} \cdot P_{\text{CO}_2}}$$

What does this equation tell us? $[\text{Ca}^{2+}(\text{aq})]$ will depend on the amount of CO_2 present in the atmosphere and the pH ($= -\log[\text{H}^+]$) of the water. We will discuss the absolute values of these equilibrium constants and the predictions that can be made with the expressions on this page later in the semester.

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Let's now examine the pH relationships in a mixture of just water and CO₂ components, meaning we ignore for now the effects of CaCO₃ precipitation/dissolution. The Bjerrum plot shows dissolved CO₂, HCO₃⁻ and CO₃²⁻ as a function of pH. The curves are drawn using equations from last lecture.



Bjerrum plot, activities of different species in the aqueous carbonate system as a function of pH, for $\Sigma\text{CO}_2 = 10^{-2}$, $T = 25^\circ\text{C}$.

Note that one of these 3 chemical species essentially dominates the mixture in each of three domains, which are separated by vertical lines at values of pH = pKa1 and pH = pKa2. These vertical lines are the locus of maxima in **buffering capability** of the solution.

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What is "buffering capacity"?

It is the ability of a solution to withstand acid or base addition and remain at or near the same pH.

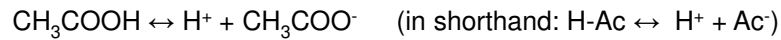
It occurs when the concentrations of acid and conjugate base are very similar.

Anti bufferingness?

Aqueous acid solutions *are least buffered* at the *endpoints* because the concentrations of acid and conjugate base are most different, so that their ratio is sensitive to slight changes in pH.

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This and the following slide look at a buffering capacity of an aqueous solution containing a weak monoprotic acid like acetic acid:



$$K_a = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{H-Ac}]}$$

a. take the -log of both sides of the K_a expression: $-\log K_a = -\log[\text{H}^+] - \log[\text{Ac}^-]/[\text{H-Ac}]$

b. rearrange

$$\text{pKa} - \text{pH} = -\log [\text{Ac}^-]/[\text{H-Ac}]$$

c. move sign

$$\text{pH} - \text{pKa} = \log [\text{Ac}^-]/[\text{H-Ac}]$$

Remember, pKa is a constant at a given P and T .

☛ To get pH knowing $[\text{Ac}^-]/[\text{H-Ac}]$ and pKa ,

rearrange c

$$\text{pH} = \text{pKa} + \log [\text{Ac}^-]/[\text{H-Ac}]$$

☛ To get $[\text{A}^-]/[\text{HA}]$ knowing pH and pKa ,

get rid of log in c

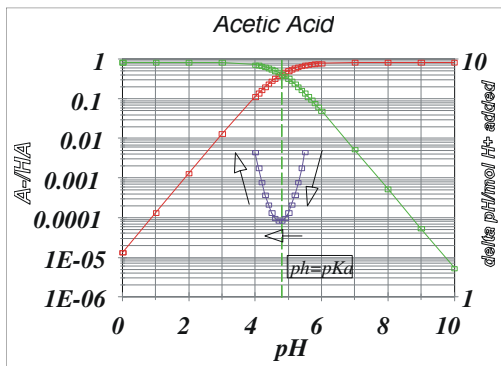
$$10^{\text{pH} - \text{pKa}} = [\text{Ac}^-]/[\text{H-Ac}]$$

To solve for $[\text{Ac}^-]$ and $[\text{H-Ac}]$, you need the total amount of acidic substance in the solution:

$$\Sigma[\text{H-Ac}] = [\text{Ac}^-] + [\text{H-Ac}]$$

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☛ In general when we add "x" mol/L acid (H^+) to a solution of H-Ac in water, the pH changes and $[\text{Ac}^-]/[\text{HAc}]$ changes to $[\text{Ac}^- - x]/[\text{HAc} + x]$.

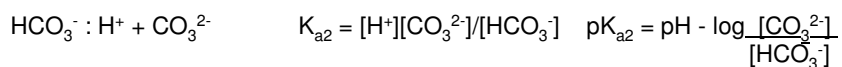
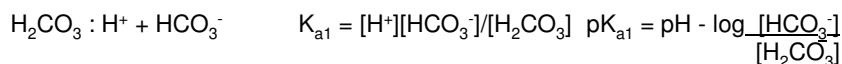


When $[\text{Ac}^-]/[\text{HAc}]$ is close to 1 (i.e. at $\text{pH} = \text{pKa}$), the solution is less sensitive to the added x so the solution is **buffered at $\text{pH} = \text{pKa}$** .

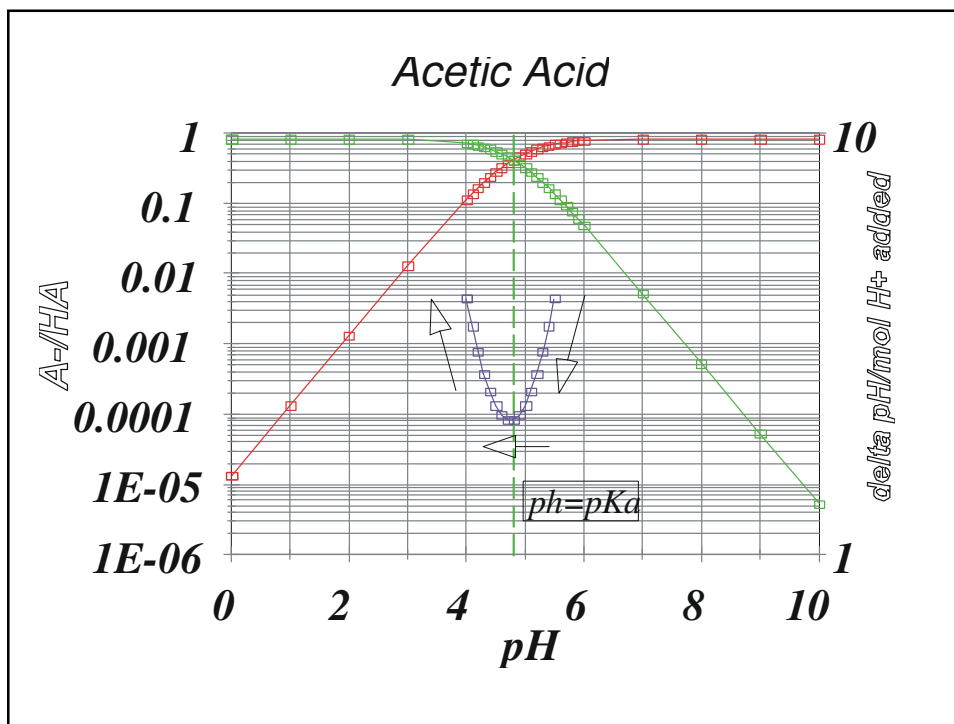
At $[\text{Ac}^-]/[\text{HAc}] < 1$ or > 1 , the solution is not buffered.

A plot of the pH sensitivity of an acetic acid solution as an external strong acid is added shows that near $\text{pH} = \text{pKa}$, $\Delta\text{pH}/\text{mol H}^+$ added is at a minimum

You can reason through the maximum and minimum buffering cases for CO_2 in water yourself using:



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Oxides of metals

Bond character and Lewis Acid/Base concepts help us understand how metal oxides will react in the hydrosphere.

Basic Oxides

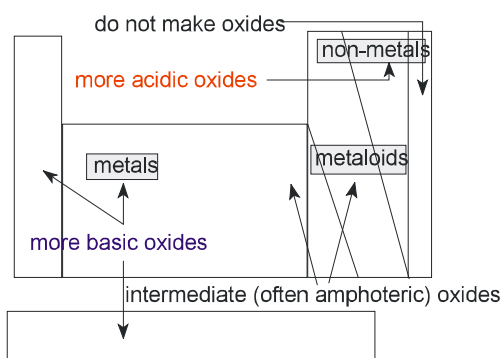
These are ionic oxides.

Example: Na_2O . In a compound where O has its e^- held tightly to itself in a highly electronegative bond with a metallic element (little sharing), O^{2-} ions are typically produced upon reaction with water; O^{2-} ions will react to take an H^+ from H_2O leaving two OH^- in its wake (and therefore a basic solution).

Acid Oxides

These are covalent oxides. **Example: (SiO_2)**

When O is in a more covalent bond the "metal" shares more of the e^- . To be stable in dissociated form in water, both elements in the bond try to get an electron by dissociating water and taking an OH^- ion out of circulation. This leaves an excess of H^+ (an acid solution).



pH Summary

- ☛ pH is a function of the ratio of conjugate base/acid.
- ☛ buffered: when acid and conjugate base are close to equal, $\log(\text{conjugate base/acid})$ goes to 0 and $\text{pH}=\text{pK}_a$.
- ☛ deviating from this point, each mole of H^+ added or subtracted goes into changing (conjugate base/acid).
- ☛ continue to change pH and approach an endpoint, this ratio changes more with each successive unit of pH change because almost all of the acid or conjugate base is consumed.
- ☛ oxides of elements can be thought of as Lewis acids and bases based on their bond character with O, and will make water acidic or basic accordingly

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Alkalinity

the acid-neutralizing capacity of an aqueous solution

- ☛ It is the sum of all the titratable bases in solution that can be neutralized with strong acid.
- ☛ **Alkalinity** is a significant environmental variable for natural waters and waste waters.
- ☛ The **alkalinity** of many natural waters is primarily a function of $\Sigma\text{CO}_2(\text{aq})$ and OH^- .

$$[\text{Alk}] \approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

- ☛ But the measured value can also include contributions from borates, phosphates, organic acid anions, silicates or other bases if present.

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Aqueous Solubility

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2. Behavior of ions in water:

Aqueous stability of ions is the primary determinant of the "distribution" of many elements between solids (minerals and organic matter) and water in surficial environments.

The **form** that the ion takes in aqueous solution is the **fundamental control** on element solubility.

Form is mostly a function of **how the ion interacts with water molecules** (as well as OH^- , H_3O^+ and dissolved oxygen, aka "DOx").

These interactions are essentially dictated by Ion-O bonding characteristics, particularly in very fresh waters.

During hydration (Lewis acid/base interaction with H_2O molecules),

Electronegativity

and

ion size

determine the bonding preference of a cation for DOx or water (and its conjugate bases: OH^- , O^{2-})

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Behavior of ions in water

Cation electronegativity determines how "ionic" or "covalent" the resulting O-cation "bonds" is:

electropositive elements make ionic "bonds" whereas electronegative elements make relatively covalent "bonds".

Un-hydrated **ion size** affects O-cation ligand "bond character" and the stability of the hydration complex, since the geometric "fit" of electrons in "bonds" worsens as cation size increases.

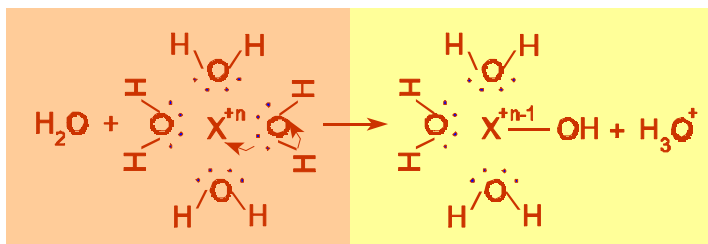
Cations that can form a stable covalent bond with O will do so in water. Those that don't will make ionic bonds.

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Behavior of ions in water

The relative solubility of the cation-oxygen compound depends on the relative stability in water of the resulting oxy- or hydroxy ion versus a solid composed of the original cation and oxygen.

For instance, the product would be favored in the reaction below for more covalent X-O bonds. Note that as H^+ is released the water becomes acidic.



Arrows depict the flow of electrons in breaking the H-O and forming the X-O bonds

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Behavior of ions in water

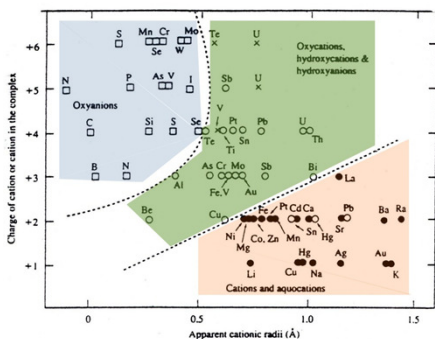


Figure 3.4 Charge of core cations in their aquocomplexes plotted against apparent crystal radii of the cations in solids (1 Å = 1 nm). The radii are mostly from Shannon and Pre-witt (1969). Dashed curves roughly divide species by their behavior. Radii of the cations were computed assuming the radius of the oxygen atom equals 1.4 Å and is constant. However, it is less than 1.4 Å in the oxyanions because of strong covalent bonding between oxygen and multivalent cations of N, C, S, and B, for example. Consequently, the apparent radii of these cations shown in the figure are only qualitatively meaningful. (●) cations and aquocations; (○) hydroxycations and hydroxyanions; (×) oxyanions; (□) oxyanions. Reprinted with permission from Techniques of estimating thermodynamic properties for some aqueous complexes of geochemical interest, D. Langmuir. In *Chemical modeling in aqueous systems*, ed. E. A. Jenne, Am. Chem. Soc. Symp. Ser. 93. Copyright 1979 American Chemical Society.

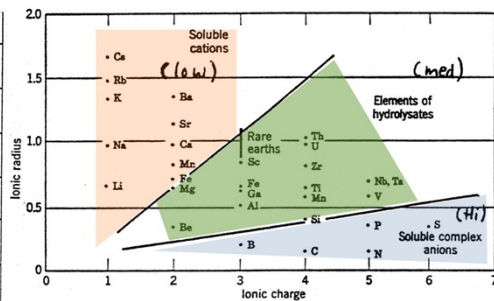


Figure 6.6 Geochemical separation of some important elements on the basis of their ionic potential.

Elements in green are largely insoluble

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Behavior of ions in water - Ionic Potential

(= charge divided by radius) is very useful for quantifying this behavior.

Table 6.3 Ionic Potentials = Z/r

Cs ⁺	0.60	Th ⁴⁺	3.9
Rb ⁺ Lo	0.68	Ce ⁴⁺ Med	4.3
K ⁺	0.75	Fe ³⁺	4.7
Na ⁺	1.0	Zr ⁴⁺	5.1
Li ⁺	1.5	Be ²⁺	5.7
Ba ²⁺	1.5	Al ³⁺	5.9
Sr ²⁺	1.8	Ti ⁴⁺	5.9
Ca ²⁺	2.0	Mn ⁴⁺	6.7
Mn ²⁺	2.5	Nb ⁵⁺	7.5
La ³⁺	2.6	Sr ²⁺	9.5
Fe ²⁺	2.7	Mo ⁶⁺	9.7
Co ²⁺	2.8	B ³⁺ Hi	13
Mg ²⁺	3.0	P ⁵⁺	14
Y ³⁺	3.3	S ⁶⁺	20
Lu ³⁺	3.5	C ⁴⁺	25
Sc ³⁺	3.7	N ⁵⁺	38

z = ionic charge r = radius

☀ **Intermediate IP** ions (~ 4 -10): generally the least water soluble.

☀ **Low IP** ions: take positive charges in solution (ionic interaction with O in water)

☀ **High IP** ions: take negative charges in solution (covalent interaction with O in water, such that the number of electrons donated by oxygen atoms exceeds the original +n charge of the raw cation, making an anion).

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Behavior of ions in water

The previous discussion notwithstanding, other aspects of aqueous solution chemistry can also affect an ion's solubility through similar Lewis acid-base type interactions.

X-Y interactions, where Y is something other than X-O, as well as ion-ion interactions ($X_1 - X_2$) can be rationalized using similar arguments, as we will see during this course.

Such effects become particularly pronounced in very saline waters and/or water enriched in dissolved organic substances.

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Solubility Summary



in pure water, elements on the extreme left and right sides of the Periodic Chart tend to be more soluble than those in the center.

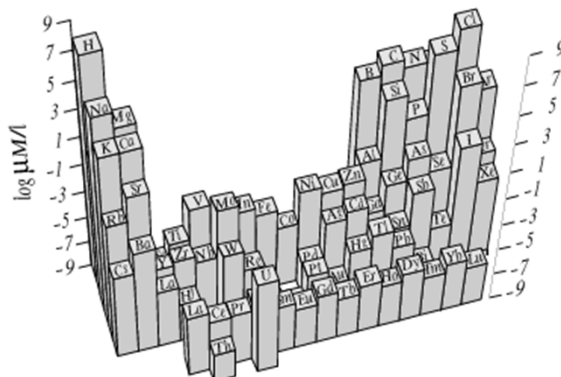


Figure 15.5. The composition of seawater. The most abundant elements are those on the sides of the periodic table. Elements in the interior tend to be less abundant. *from White, "Geochemistry"*

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Solubility Summary - 2



the solubility of **elements in the chart's center** is low in pure water, but **can be enhanced by other dissolved constituents** found in more complex aqueous solutions.

This is particularly true when the water contains dissolved organic carbon (DOC) compounds (which typically contain reactive O atoms).

The presence or absence of **dissolved organic matter** often determines whether or not many heavy metals are soluble (and thus mobile) in a particular environment.

An **additional complicating factor** in natural systems that we will discuss at length this semester is that **water often comes with various sorts of particles** (which also contain Lewis bases of O and/or other Y).

Thus, when X interacts with O or Y that are attached to a **solid**, X becomes part of the **suspended phase**

and when it interacts with O or Y on a **dissolved** material, X is part of the **dissolved phase**.

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complexation/chelation reactions in aqueous solution chemistry

Definition

A **complex** is an association of molecules in solution or at a particle surface where electrons 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.

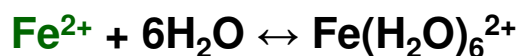
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complexation/chelation

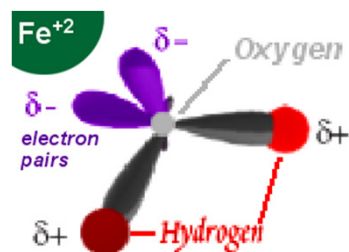
Complexes involve *ligands* and *host* ions.

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:

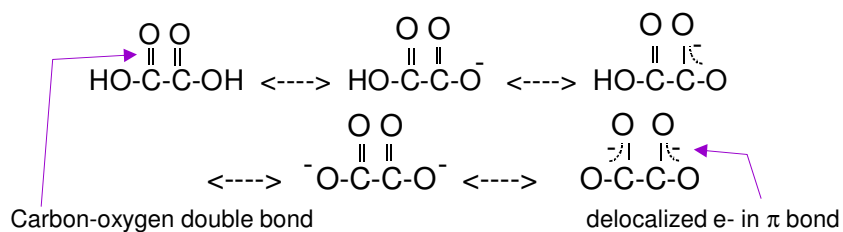
Chelation involves complexation by *multidentate* ligands.

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:**

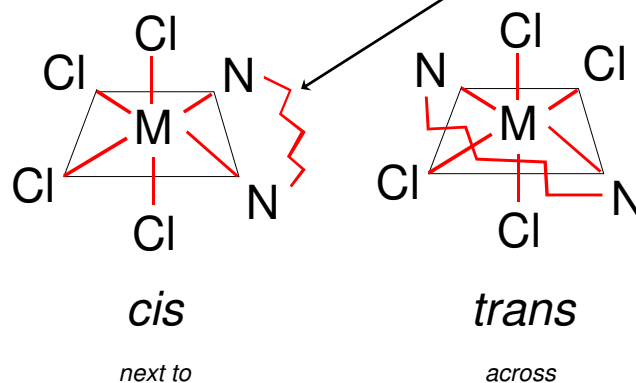
and **oxalic acid/oxylate anion**, which has the following forms in solution:



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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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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 later.

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

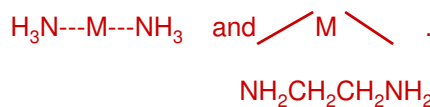
We can understand this phenomenon with thermodynamic reasoning (i.e., estimates of Gibbs free energy and K_{eq} should favor the chelate).

Recall that $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

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)

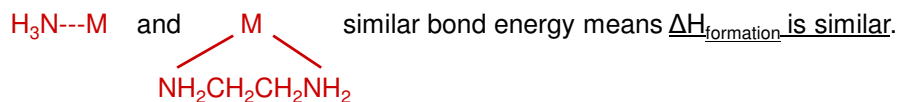
From a bond energy perspective, the M-N electron donor/acceptor relationship is very similar for



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, $K_{\text{eq}} > 1$ and products are favored as written.

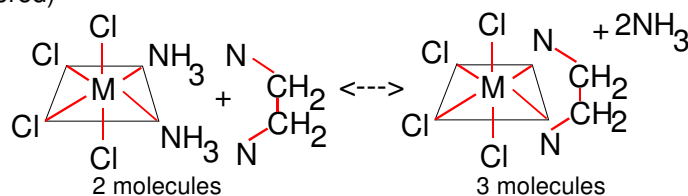
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Energetics of Chelates vs. Complexes

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)



ΔS is positive ----->

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

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Quantifying Aqueous Solubility

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3. Quantifying aqueous solubility

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 = $\mu\text{g/g}$)

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How stuff dissolves also matters:

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:

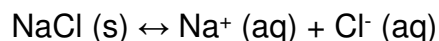
1. **Congruent** – all of a material goes into solution, leaving nothing behind when it is dissolved
2. **Incongruent** – parts of a material go into solution, leaving a new, modified material behind.

These terms refer to the undissolved solid left behind

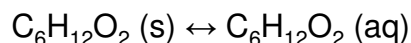
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There are also different type of solutes in solution:

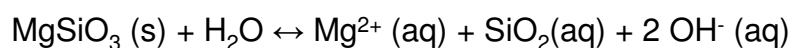
1. **ionically** bonded solids, which dissociate upon dissolution to form ions.



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

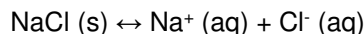


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We define **solubility** somewhat differently for each type of solute.

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 $K_{sp} = x^2$

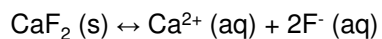
we find that

$$\text{Solubility} = x = K_{sp}^{1/2}$$

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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 = 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}?

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

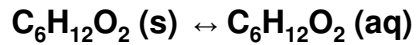
$$\text{since } [\text{F}^-] = 2[\text{Ca}^{2+}]$$

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

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

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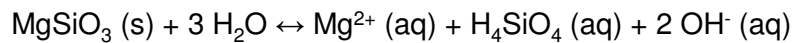
For **covalently bonded** solids:



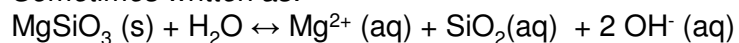
$$K = [\text{C}_6\text{H}_{12}\text{O}_6] \quad \text{and } x = k$$

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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 $\text{OH}^- (\text{aq})$.

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

$$K = [\text{Mg}^{2+}] [\text{SiO}_2 (\text{aq})] [\text{OH}^-]^2 \quad K = x \times (2x)^2 = 4x^3$$

and $X = (K/4)^{1/3}$

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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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