Lectures 7 and 8

Aqueous Inorganic Geochemistry of Natural Waters

Pease read chapter White Ch6 (just 217 through page 249 – the second half of the chapter is for next week)

Lecture 7

1. pH, Brønsted-Lowry acidity, Lewis acids/bases
2. Behavior of ions in aqueous solution

Lecture 8

3. More about complexes and metal solubility
4. Quantifying aqueous solubility and total dissolved solids (TDS)

Acids and Bases

❶ **Two Types of Acids and Bases:**

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

b. **Lewis acids and bases**

Contain electron deficient ions (acids) and as electron excessive ions (bases)

❶ **Two Types of Acids and Bases:**

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

b. **Lewis acids and bases**

a different perspective on acidity/basicity involves the electron density around chemicals in aqueous solution.

Brønstead acids can be thought of as **electron deficient ions**

Brønstead bases can be thought of as **electron excessive ions**

This formalism alows the acid-base concept to be extended to non protic, non hydroxyl, and in fact non-aqueous compounds.

a. Strong **Brønsted acid** and **base** examples:

$HCl \leftrightarrow H^+ + \ + Cl^-$ (acid)

$NaOH \leftrightarrow \ Na^+ \ + OH^-$ (base).

water is **WEAK** acid and base simultaneously,

$H_2O \leftrightarrow \ \ H^+ + OH^-$.

an "acid" neutral solution has equal amounts of H^+ and OH^-, such H_2O without anything dissolved in it.

Brønstead acidity:

K_w is the equilibrium constant for the dissociation of water.

$H_2O \leftrightarrow H^+ + OH^-$

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

K_w has a slight temperature dependence:

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

Brønstead acidity:

$K_w = [H^+][OH^-]$

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

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

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

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

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

A less common but sometimes useful variable is:

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

In an acid neutral solution pOH = pH = 7
In any water at 25EC, pH + pOH = 14

Non-acid neutral aqueous solutions

"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?

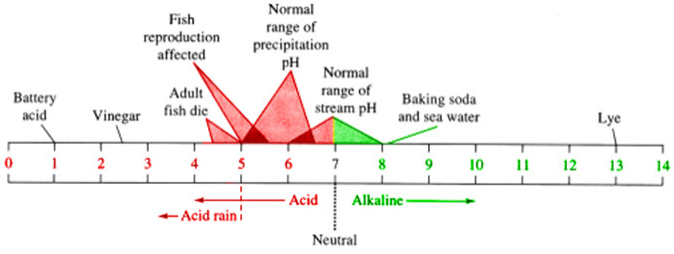


Figure 4-4 pH scale. The normal range of precipitation pH is from about 5.0 to 6.5. The pH of pure water in equilibrium with atmospheric carbon dioxide is 5.6. Normal rain is slightly acidic because of carbon dioxide (which forms the weak acid carbonic acid) and natural emissions of sulfur and nitrogen 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.

Lewis Acids and Bases

Lewis acid example: BF_3

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.

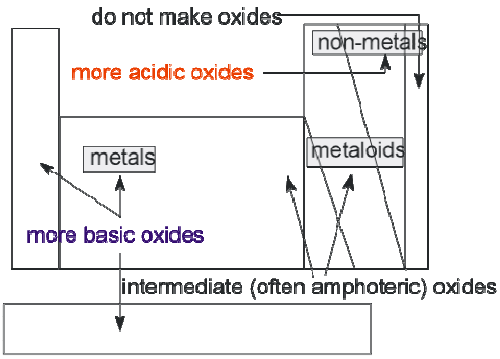
$BF_3 + H_2O \leftrightarrow [OH\text{-}BF_3]^- + H^+$

Lewis base example: NH_3

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

$NH_3 + H_2O \leftrightarrow [H\text{-}NH_3]^+ + OH^-$ ***note: NH_4^+ is an ammonium ion***

The acidity of metal oxides



Lewis Acid/Base and Bond character concepts help us understand why some elemental oxides form acids and some form bases 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 leave an excess of H^+ (an acid solution).

Acidity from the aqueous CO_2 system

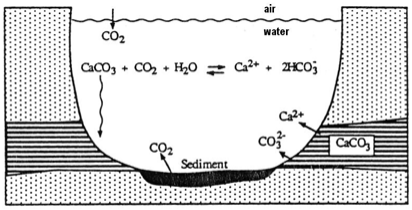
Equilibria involving carbon dioxide and its conjugate bases in water set the baseline pH of many waters at the Earth's surface

other chemical acids and bases usually serve to alter this carbonate equilibrium pH.

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

Recall from lecture 3 that these are:

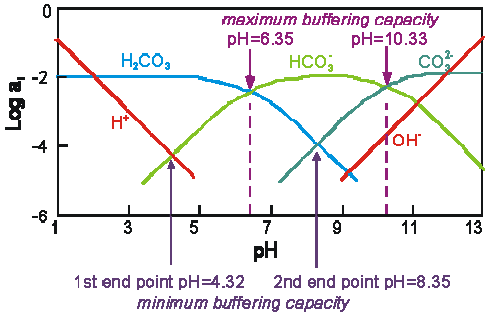
a. dissolved gaseous carbon dioxide	$CO_2(aq)$
b. carbonic acid	$H_2CO_3(aq)$
c. bicarbonate anion	$HCO_3^-(aq)$
d. carbonate anion	$CO_3^{2-}(aq)$



Carbon dioxide-calcium carbonate equilibria.

… and that Calcium Carbonate solubility also plays a role

First let's examine the pH relationships in a mixture of just water and CO_2 components, meaning we ignore for now the effects of $CaCO_3$ precipitation/dissolution. The Bjerrum plot shows dissolved CO_2, HCO_3^- and CO_3^{2-} 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 $\Sigma CO_2 = 10^{-2}$, T = 25°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.

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.

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

$CH_3COOH \leftrightarrow H^+ + CH_3COO^-$ (in shorthand: H-Ac $\leftrightarrow$ $H^+ + Ac^-$)

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

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

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

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

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

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

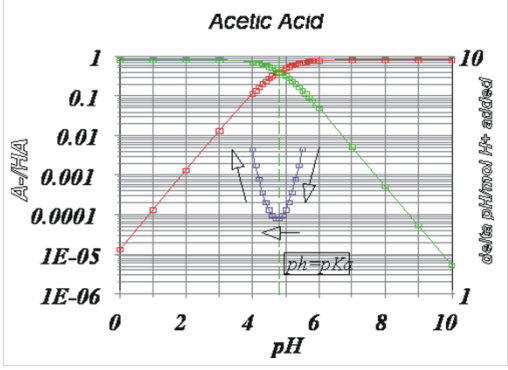
rearrange c $pH = pKa + \log [Ac^-]/[H\text{-}Ac]$

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

get rid of log in c $10^{pH-pKa} = [Ac^-]/[H\text{-}Ac]$

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

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



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

At $[Ac^-]/[HAc]$ <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 pHm = pKa, ΔpH/mol H+ added is at a minimum

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

$H_2CO_3 : H^+ + HCO_3^-$ $\quad K_{a1} = [H^+][HCO_3^-]/[H_2CO_3]$ $\quad pK_{a1} = pH - \log \frac{[HCO_3^-]}{[H_2CO_3]}$

$HCO_3^- : H^+ + CO_3^{2-}$ $\quad K_{a2} = [H^+][CO_3^{2-}]/[HCO_3^-]$ $\quad pK_{a2} = pH - \log \frac{[CO_3^{2-}]}{[HCO_3^-]}$

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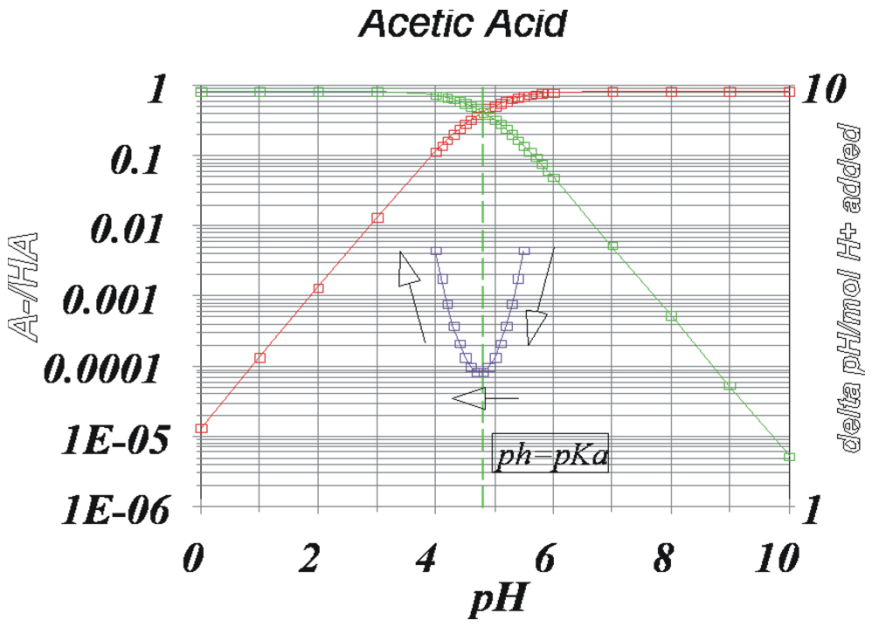


pH Summary

☛ pH is a function of the ratio of conjugate base/acid.

☛ buffered: when acid and conjugate base are close to equal, log(conjugate base/acid) goes to 0 and pH=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

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 $\sum CO_2(aq)$ and OH^-.

$$[Alk] \approx [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

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

Behavior of Ions in Water

❷ 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-})

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".

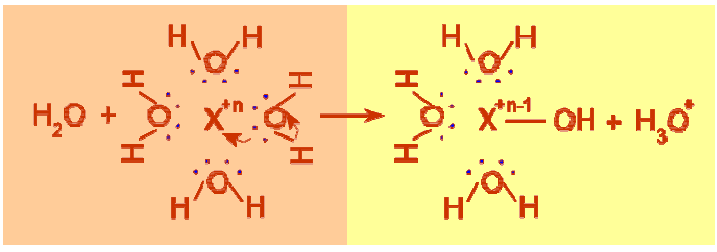
Un-hydrated ion size affects O-cation ligand "bond character" and the stability of the hydration complex, since the geometric "fit" of electrons in "bonds" worsens as cation size increases.

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

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

Behavior of ions in water

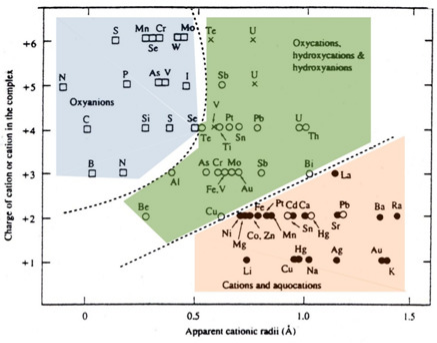


Figure 3.4 Charge of core cations in their aquocomplexes plotted against apparent crystal radii of the cations in solids (1 Å = 1 nm). The radii are mostly from Shannon and Prewitt (1969). Dashed curves roughly divide species by their behavior. Radii of the cations were computed assuming the radius of 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; (×) oxycations; (□) 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.

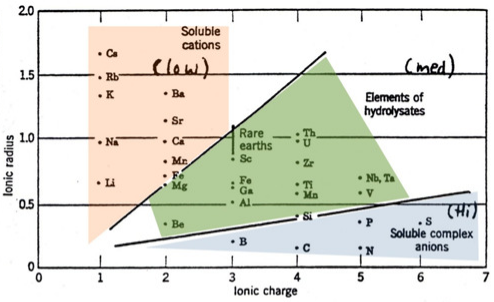


Figure 6.6 Geochemical separation of some important elements on the basis of their ionic potential.

Elements in green are largely insoluble

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	Si^{4+}		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).

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.

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.

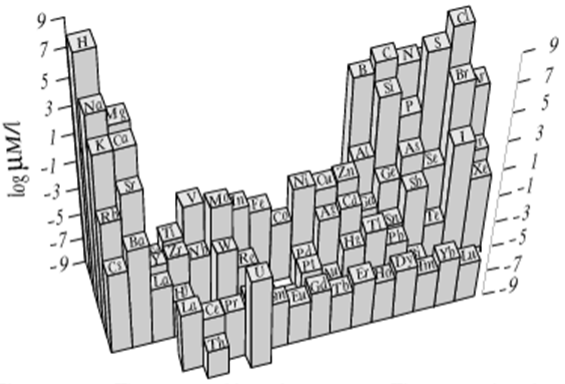


Figure 15.5. The composition of seawater. The most abundant elements are those on the sides of the periodic table. Elements in the interior tend to be less abundant. *from White, "Geochemistry"*

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 or **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**.

The role of complexation/chelation reactions on solution chemistry

Recall our discussion of complexes in week 1:

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.

Chelates are a type of complex involving multi-dentate ligands, which have more than one electron or electron pair to donate to a cation.

Chelates are an important control of ionic concentration in natuiral aqueous solution.

Many organic moluecule found in the environment serve as multidentate ligands to chelate metals.

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

Humic Substances are an important class of naturally occurring organic chelating agents that we will discuss next week.

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

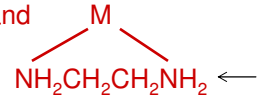
We can understand this phenomenon with thermodynamic reasoning (i.e., estimates of Gibbs free energy and K_{eq} should favor the chelate).

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

H_3N---M---NH_3 and



← ethylenediamine

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

Energetics of Chelates vs. Complexes

H_3N---M and M (with $NH_2CH_2CH_2NH_2$) similar bond energy means $\Delta H_{formation}$ is similar.

But $\Delta S_{formation}$ differs for both…

because it takes 2 NH_3 ligands and 1 metal ion to come together to make H_3N---M---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).

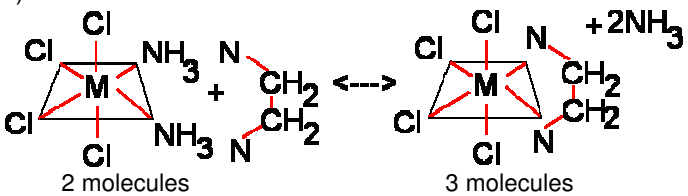
$\Delta S_{reaction}$ is positive for chelate formation relative to the ammonia.

$\Delta H° \sim 0$, so $\Delta G° = -T\Delta S°$, @ constant T, $\Delta G° = -\Delta S°$.
Since $\Delta G°$ is negative, $K_{eq} > 1$ and products are favored as written.

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 $\Delta G_{formation}$ of the chelate is more negative (and thus favored)



2 molecules 3 molecules

ΔS is positive ---------->

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

❸ 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 aquous 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.

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

TDS in values for different natural waters

Water "type"	TDS (mg/L)	Examples
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

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 = μg/g)

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

There are also different type of solutes in solution:

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

$$NaCl\ (s) \leftrightarrow Na^{+}\ (aq) + Cl^{-}\ (aq)$$

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

$$C_6H_{12}O_2\ (s) \leftrightarrow C_6H_{12}O_2\ (aq)$$

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

$$CO_2\ (g) \leftrightarrow CO_2\ (aq) \leftrightarrow HCO_3^{-}\ (aq) + H^{+}\ (aq)$$

$$MgSiO_3\ (s) + H_2O \leftrightarrow Mg^{2+}\ (aq) + SiO_2(aq) + 2\ OH^{-}\ (aq)$$

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

$NaCl\ (s) \leftrightarrow Na^+\ (aq) + Cl^-\ (aq)$

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 $K_{sp} = [Na^+][Cl^-]$

So, setting $x = [Na^+] = [Cl^-]$ =solubility, and using $K_{sp} = x^2$

we find that Solubility = $x = K_{sp}^{½}$.

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

For instance, fluorite (CaF_2) dissolves as follows

$CaF_2\ (s) \leftrightarrow Ca^{2+}\ (aq) + 2F^-\ (aq)$

In this case, it is easier to define solubility in terms of Ca^{2+} (aq) since one mole of fluorite dissolves to make one mole of calcium ions.

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

We also see that solubility = ½ $[F^-]$, since 2 moles of fluoride are produced for each mole of solid dissolved.

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

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

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

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

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

For covalently bonded solids:

$C_6H_{12}O_2$ (s) ↔ $C_6H_{12}O_2$ (aq)

K = $[C_6H_{12}O_6]$ and x = k

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

$MgSiO_3$ (s) + 3 H_2O ↔ Mg^{2+} (aq) + H_4SiO_4 (aq) + 2 OH^- (aq)

Sometimes written as:
$MgSiO_3$ (s) + H_2O ↔ Mg^{2+} (aq) + SiO_2(aq) + 2 OH^- (aq)

In either event, 1 mole of enstatite, $MgSiO_3$ (s), dissolves to produce:

- 1 mole of Mg^{2+} (aq)
- 1 mole of dissolved Si as either "SiO_2(aq)" or "H_4SiO_4(aq)"
- 2 moles of OH^- (aq).

Solubility = x = $[Mg^{2+}]$ = $[SiO_2(aq)]$ = ½ $[OH^-$ (aq)]

K = $[Mg^{2+}]$ $[SiO_2$ (aq)] $[OH^-]^2$ K = x x $(2x)^2$ = $4x^4$

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

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:

$2KAlSi_3O_8 + 2H^+ + H_2O \leftrightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 4SiO_2(aq)$

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 $[K^+]$ at saturation.

solubility = $x = [K^+] = ½ [SiO_2(aq)]$

solubility also = $- [H^+]$ (hydrogen ions consumed)

☛ *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.

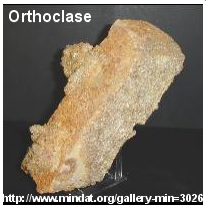
The solubility of NaCl can be written as $x = [Cl^-]$

The solubility of $CaCl_2$ can be written as $x = ½ [Cl^-]$.

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

Mineral Stability diagrams:

We can construct diagrams that relate primary equilibria together by finding common variables amongst the equilibria expressions, as we did we discussed E_H/pH diagrams. We will stick to the simplest diagrams involving minerals with only a few atomic constituents.

Take for example the reaction of incongruent dissolution of K-feldspar into water 

to produce Kaolinite:

$$2KAlSi_3O_8 + 2H^+ + 9H_2O \leftrightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 4H_4SiO_2(aq)$$

$$K_{eq} = [H_4SiO_2]^4 \cdot \frac{[K^+]^2}{[H^+]^2} \quad \text{-or-} \quad \log K_{eq} = 4\log[H_4SiO_2] + 2\log\frac{[K+]}{[H^+]}$$

This can be rearranged to form the equation of a line (y = mx + b), where:

$b = \frac{1}{2}\log K_{eq}$ $m = -2$ $x = \log[H_4SiO_2]$ $y = \log[K^+]/[H^+]$

Mineral Stability Diagrams:

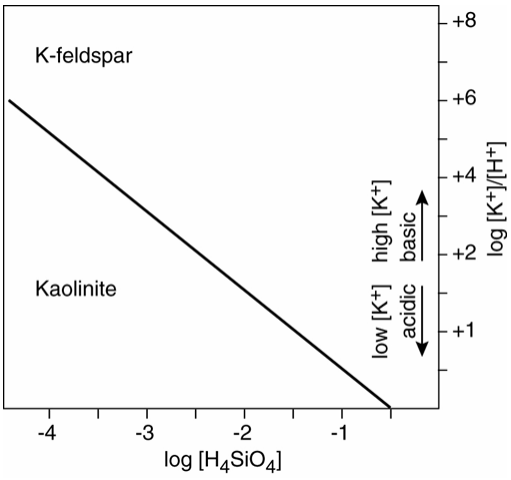
$$\log[K^+]/[H^+] = -2\log[H_4SiO_4] + \tfrac{1}{2}\log K_{eq}$$

$y = \log[K+]/[H+]$ and $b = \frac{1}{2}\log K_{eq}$ $m = -2$ $x = \log[H_4SiO_4]$

When plotted on a diagram of

$\log[K+]/[H+]$ vs. $\log[H_4SiO_4]$

this line provides information on the conditions of stability for both minerals. The line shown here is for 25°C and 1 atm.



Mineral Stability diagrams:

When we add a second line for the solubility of amorphous silica, the diagram can then also be used to predict solution chemistry if we know the solid(s) present and solution composition (at equilibrium). The resulting 2-equilibrium diagram is divided into 4 fields.

$SiO_2(s, amorph) + 2H_2O \rightleftarrows H_4SiO_4(aq)$ $K_{eq} = a_{H4SiO4} = 10^{-2.74}$ at 25°C

The dashed lines are meta-stable reactions (at equilibrium another reaction "takes over")

But depending on reaction kinetics, we can find "meta-stable" mineral assemblages based upon these dashed-line relationships that were "locked-in" before the system reached true equilibrium.

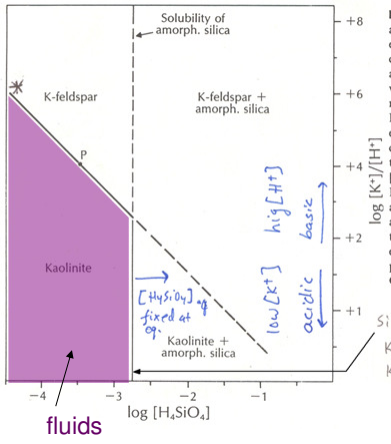


Figure 12.5 Partially completed activity diagram depicting the environmental conditions required to convert K-feldspar into kaolinite, and vice versa, in the presence of water at 25 °C. The line labeled 12.82 represents conditions at which K-feldspar and kaolinite coexist in equilibrium. Point *P* on the line was chosen arbitrarily to help determine the direction of reaction 12.78 when $[H_4SiO_4]$ is increased or decreased. Line 12.83 represents the solubility of amorphous silica, which limits the activity of $[H_4SiO_4]$ to values less than $10^{-2.74}$ mol/L, as shown in equation 11.89. (Line 12.82 was plotted from equation 10.16 of Garrels and Christ, 1965.)

fluids

Mineral Stability diagrams:

This extension of the diagram just discussed includes a few more mineral equilibria (K-mica, gibbsite and quartz).

Also plotted are fields for various actual water compositions. By comparing observations with predictions from the diagram we can get an idea if a particular system is at (or near) equilibrium control by one of these reactions, or if some other reactions are involved.

Some natural waters fall near defined equilibria boundaries but others do not. When they do not, it is mostly due to K^+ sorption onto other charged surfaces in those solutions.

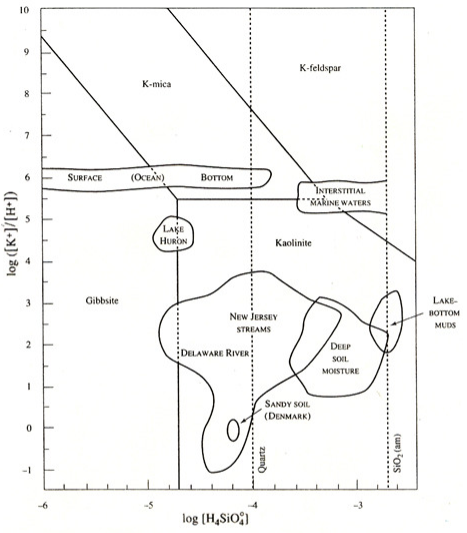


Figure 9.9 Log($[K^+]/[H^+]$) versus log$[H_4SiO_4^0]$ diagram at 25°C and 1 bar pressure, showing the stability fields of gibbsite, K-mica, K-feldspar, and kaolinite. The compositions of some natural waters have been plotted on the diagram.

We will next orient ourselves by calculating where certain water chemistries plot on a log($[K^+]/[H^+]$) versus log$[H_4SiO_4^0]$ diagram. Seawater, for example, has $K^+ = 10^{-2.00}$ mol/L (391 mg/L) and pH = 8.15. Accordingly, log($[K^+]/[H^+]$) = 6.15. Silica in seawater ranges from about 0.01 (surface) to 7 mg/L (bottom water) as SiO_2 (GFW = 60.085) or $10^{-6.8}$ to $10^{-3.9}$ mol/L as $H_4SiO_4^0$. These compositional ranges have been plotted in Fig. 9.9 along with the chemistry of interstitial waters in marine muds (cf. Lafon and Mackenzie 1974). Surface seawater is low in silica because of its scavenging from the water by planktonic (floating) organisms such as the diatoms, which use silica

Mineral Stability diagrams:

Mg-bearing minerals

was constructed in the same manner as we just discussed.

This diagram can also be used to predict what mineral will form from a solution if these parameters are increased.

Note that the activity of hydrated Al in solution is so low that it is ignored in Fig B. This is why none of the reactions involving hydrated Al are given (e.g., gibbsite + water ↔hydrated Al).

Each mineral in Fig. B will dissolve if $[Mg^+]/[H^+]$ or log $[H_4SiO_2]$ is lower their line. The "natural solutions" lie in a field below the lines for the least soluble minerals.

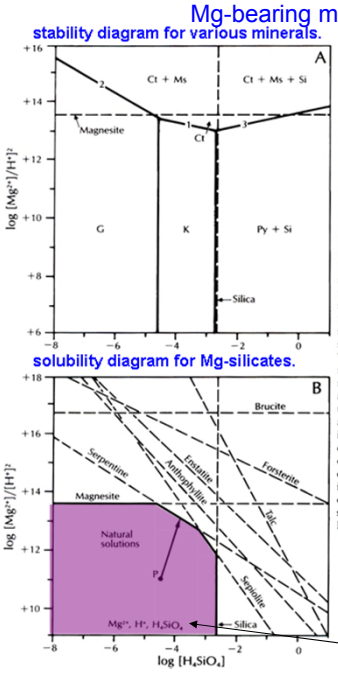


Figure 12.5 **A:** Stability diagram of Mg chlorite (Ct) (aluminosilicate) with respect to gibbsite (G), kaolinite (K), pyrophyllite (Py), amorphous silica (Si), and magnesite (Ms) at $[CO_2] = 3 \times 10^{-4}$ atm in the presence of acidified water at 25°C.

B: Solubility limits of pure Mg-silicates in acidified water at 25°C, based on equations in Table 12.3. Each of the minerals shown here dissolves in solutions whose $[Mg^{2+}]/[H^+]^2$ ratios and H_4SiO_4 activities are *less* than those of their respective solubility lines. Conversely, when these parameters increase in a solution in the lower left corner of the diagram, magnesite, serpentine, sepiolite, or amorphous silica precipitates, depending on which solubility line is reached by the solution. Consequently, these are the only stable minerals in contact with natural solutions on the surface of the Earth. The combination of solution and reprecipitation causes the replacement of forsterite, enstatite, talc, and anthophyllite by magnesite, serpentine, sepiolite, or amorphous silica. If amorphous silica precipitates first, and if one of the more soluble Mg silicates continues to dissolve, the $[Mg^{2+}]/[H^+]^2$ of the solution rises until sepiolite coprecipitates with silica. Similarly, the initial precipitation of magnesite may eventually result in the formation of serpentine, provided the activity of H_4SiO_4 increases sufficiently.

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fluids

Mineral Stability diagrams: Chemical reactions and data for the diagram on the previous page

Table 12.3 Stability Relations among Mg Silicates in the Presence of Acidified Water at 25°C and 1 atm pressure

A. Mg–Al Silicates

Kaolinite–chlorite

$$Al_2Si_2O_5(OH)_4 + 5\,Mg^{2+} + H_4SiO_4 + 5\,H_2O \rightleftharpoons Mg_5Al_2Si_3O_{10}(OH)_8 + 10\,H^+$$
$$\Delta G_R^\circ = +85.235 \text{ kcal} \quad K = 10^{-62.49}$$
$$\log \frac{[Mg^{2+}]}{[H^+]^2} = -0.2 \log [H_4SiO_4] + 12.50 \quad (1)$$

Gibbsite–chlorite

$$2\,Al(OH)_3 + 5\,Mg^{2+} + 3\,H_4SiO_4 \rightleftharpoons Mg_5Al_2Si_3O_{10}(OH)_8 + 10\,H^+$$
$$\Delta G_R^\circ = +72.48 \text{ kcal} \quad K = 10^{-53.14}$$
$$\log \frac{[Mg^{2+}]}{[H^+]^2} = -0.6 \log [H_4SiO_4] + 10.62 \quad (2)$$

Pyrophyllite–chlorite

$$Al_2Si_4O_{10}(OH)_2 + 5\,Mg^{2+} + 10\,H_2O \rightleftharpoons Mg_5Al_2Si_3O_{10}(OH)_8 + H_4SiO_4 + 10\,H^+$$
$$\Delta G_R^\circ = +92.51 \text{ kcal} \quad K = 10^{-67.82}$$
$$\log \frac{[Mg^{2+}]}{[H^+]^2} = +0.2 \log [H_4SiO_4] + 13.56 \quad (3)$$

Solubility limit of brucite

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2\,OH^-$$
$$\Delta G_R^\circ = +15.40 \text{ kcal} \quad K = 10^{-11.29}$$
$$\log \frac{[Mg^{2+}]}{[H^+]^2} = +16.71 \quad (4)$$

Solubility limit of periclase

$$MgO + 2\,H^+ \rightleftharpoons Mg^{2+} + H_2O$$
$$\Delta G_R^\circ = -29.45 \text{ kcal} \quad K = 10^{21.59}$$
$$\log \frac{[Mg^{2+}]}{[H^+]^2} = +21.59 \quad (5)$$

B. Solubility of Mg Silicates

Forsterite

$$Mg_2SiO_4 + 4\,H^+ \rightleftharpoons 2\,Mg^{2+} + H_4SiO_4$$
$$\Delta G_R^\circ = -38.76 \text{ kcal} \quad K = 10^{+28.42}$$
$$\log \frac{[Mg^{2+}]}{[H^+]^2} = -0.5 \log [H_4SiO_4] + 14.2 \quad (1)$$

Enstatite

$$MgSiO_3 + H_2O + 2\,H^+ \rightleftharpoons Mg^{2+} + H_4SiO_4$$
$$\Delta G_R^\circ = -15.31 \text{ kcal} \quad K = 10^{11.23}$$
$$\log \frac{[Mg^{2+}]}{[H^+]^2} = -\log [H_4SiO_4] + 11.23 \quad (2)$$

Serpentine

$$Mg_3Si_2O_5(OH)_4 + 6\,H^+ \rightleftharpoons 3\,Mg^{2+} + 2\,H_4SiO_4 + H_2O$$
$$\Delta G_R^\circ = -43.31 \text{ kcal} \quad K = 10^{31.75}$$
$$\log \frac{[Mg^{2+}]}{[H^+]^2} = -0.67 \log [H_4SiO_4] + 10.58 \quad (3)$$

Anthophyllite

$$Mg_7Si_8O_{22}(OH)_2 + 8\,H_2O + 14\,H^+ \rightleftharpoons 7\,Mg^{2+} + 8\,H_4SiO_4$$
$$\Delta G_R^\circ = -93.95 \text{ kcal} \quad K = 10^{68.88}$$
$$\log \frac{[Mg^{2+}]}{[H^+]^2} = -1.14 \log [H_4SiO_4] + 9.84 \quad (4)$$

Talc

$$Mg_3Si_4O_{10}(OH)_2 + 4\,H_2O + 6\,H^+ \rightleftharpoons 3\,Mg^{2+} + 4\,H_4SiO_4$$
$$\Delta G_R^\circ = -29.91 \text{ kcal} \quad K = 10^{21.93}$$
$$\log \frac{[Mg^{2+}]}{[H^+]^2} = -2 \log [H_4SiO_4] + 10.96 \quad (5)$$

Sepiolite

(a) $$Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O + H_2O + 8\,H^+ \rightleftharpoons 4\,Mg^{2+} + 6\,H_4SiO_4$$
$$\Delta G_R^\circ = -43.28 \text{ kcal} \quad K = 10^{31.73}$$
$$\log \frac{[Mg^{2+}]}{[H^+]^2} = -1.5 \log [H_4SiO_4] + 7.93 \quad (6)$$

(b) $$Mg_2Si_3O_8(OH)_4 + 2\,H_2O + 4\,H^+ \rightleftharpoons 2\,Mg^{2+} + 3\,H_4SiO_4$$
$$\Delta G_R^\circ = -21.26 \text{ kcal} \quad K = 10^{15.58}$$
$$\log \frac{[Mg^{2+}]}{[H^+]^2} = -1.5 \log [H_4SiO_4] + 7.79 \quad (7)$$

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