Water: the amazing substance
And Aqueous Geochemistry

The water molecule

The water molecule is asymmetric. This results in polarity (a positively charged end and a negatively charged end) and, hence, a high dielectric constant.

The dielectric constant

- The dielectric constant of a solvent is a relative measure of its polarity.
Hydrogen bonds

Hydrogen bonds occur when the positive end of the molecule (hydrogen side) is attracted to the negative end of adjacent molecules (oxygen side). This attraction is responsible for many of the important properties of water.

Properties of water

- Only substance on Earth to exist in all three states of matter at the same time
- High boiling point
- Excellent solvent
- High surface tension
- High viscosity
- High specific heat capacity
...there are many more

Density...water ice floats

In liquid water each molecule is hydrogen bonded to approximately 3.4 other water molecules.
In ice each molecule is hydrogen bonded to 4 other molecules.
The T, P phase diagram for water

The critical point is the temperature and pressure beyond which there is no physical distinction between the liquid and the gas phase. At supercritical T and P, water is considered a supercritical fluid.

Solubility Product

Most simple salts (simple ionic salts of a cation and anion) can be expressed as a solubility product (the equilibrium constant).

\[
\text{NaCl(s)} = \text{Na}^+(aq) + \text{Cl}^-(aq) \quad \text{K}_{\text{sp}} = [\text{Na}^+][\text{Cl}^-] \\
\text{CaSO}_4(s) = \text{Ca}^{2+} + \text{SO}_4^{2-} \quad \text{K}_{\text{sp}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]
\]

\[
\log K = 1.5855 \\
\log K = -4.3064
\]

The magnitude of the solubility product can give you an idea as to how soluble a mineral is.

Henry's Law

- The solubility of a gas is proportional to its partial pressure

\[
\text{CO}_2(g) = \text{CO}_2(aq) \\
K = \frac{[\text{CO}_2(aq)]}{[\text{CO}_2(g)]}
\]

\[
\text{CO}_2(aq) = K \cdot [\text{CO}_2(g)] \
\text{...K is often written as } K_H
\]
CO\(_2\)(g) = CO\(_2\)(aq) \quad \log K_c = -1.4689

O\(_2\)(g) = O\(_2\)(aq) \quad \log K_c = -2.8983

The data above was calculated at 25°C and 1 atmosphere total pressure.

Which gas is more soluble in water at these conditions?

Why didn’t I do the calculation using an equilibrium constant at 25°C and the partial pressure of the gas phase?

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**Units**

- Since we are now discussing the solubility of aqueous species, we must introduce the units that are used in solubility calculations.

  The three most commonly used units are:

  - **Parts per million (ppm)** = mg(solvent)/Kg(solution)...mg/kg
  - **Molality (m)** = mols(solvent)/Kg(water)...mol/kg
  - **Molarity (M)** = mols(solvent)/Liter(water)...mol/L

  Whenever we are doing a calculation using an equilibrium constant we should use molality.

  Why do we want to use mass units and not volume units?
Charge Balance:

All Earth materials tend to be electrically neutral. We saw this in mineral formulas and balanced chemical reactions.

The same holds true for aqueous solutions...

In the Na₂O-H₂O system, charge balance would be written as
\[ m\text{Na}^+ + m\text{H}^+ = m\text{OH}^- \]

In the CaO-H₂O system, charge balance would be written as
\[ 2*m\text{Ca}^{2+} + m\text{H}^+ = m\text{OH}^- \]

Why do we multiply \( m\text{Ca}^{2+} \) by 2?

Multiplying the concentration (mol/kg) of an ion by its charge results in equivalents (eq/kg).

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\( \text{pH} \)

- \( \text{pH} = -\log[H^+] \)
- As a matter of fact, \( -\log \) means \( -\log \) anything.
- Example: \( -\log \) anything

The water reaction can be written as \( \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \)

If the activity of water is 1 then the equilibrium constant for this reaction is essentially a solubility product

If we calculate deltaG at 25°C and 1 atmosphere the value of K is \( 10^{-14} \)

Or... the \( \text{pK}=14 \) so \( K=[\text{H}][\text{OH}] \) when \( \text{H}=\text{OH} \) we have neutrality and \( [\text{H}]^2(K)/2 \) or \( \text{pH}=\log(K)/2 \) neutral \( \text{pH}=7 \)

What if the temperature and pressure is not 25°C and 1 atmosphere?

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**pH of natural waters**

- The pH range of natural waters near or on the Earth’s surface ranges from about 6-8.

- Why?

- The answer is the carbonate system
When CO₂(g) dissolves in water, four species are produced:

- H₂CO₃ (carbonic acid)
- CO₂(aq) (dissolved CO₂)
  (taken together with H₂CO₃ we get H₂CO₃⁻)
- HCO₃⁻ (bicarbonate)
- CO₃²⁻ (carbonate)

Bjerrum plot for carbon dioxide

Carbonate Alkalinity

Alkalinity is the capacity of a water to accept protons. It is the sum of all bases in the water minus the protons…in most waters, the carbonate system dominates the alkalinity.

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

Alkalinity is also equal to the charge imbalance by subtracting the conservative anions (Cl, Br…) from the conservative cations (Na, Mg, K…)
\[ mNa + mK + mh + 2mCa = mCl + mHCO_3 + 2mCO_3 + mOH \]

If we rearrange we can get...

\[ (mNa + mK + 2mCa) = mCl + mHCO_3 + 2mCO_3 + mOH - mh \]

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**pH of rain in equilibrium with CO2(g)**

\[ \text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3 \quad (\text{K}_{\text{CO}_2}) \]

\[ \text{H}_2\text{CO}_3 = \text{HCO}_3^- + \text{H}^+ \quad (K_1) \]

\[ \text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+ \quad (K_2) \]

Charge balance in water for this system is...

\[ m\text{H}^+ = m\text{HCO}_3^- + 2^* m\text{CO}_3^{2-} + m\text{OH}^- \]

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- Water in equilibrium with atmospheric CO2(g) pressure (10^{-3.5}) at 25C fixes pH at \( \sim 6 \) (5.66)

- Water in equilibrium with calcite and atmospheric CO2(g) pressure at 25C fixes pH at \( \sim 8 \) (8.26)

- Hence the natural range of water pH (additional solutes in water and different T and P causes these pH values to vary a little bit)...

  The pH of seawater is \( \sim 7.5 \) - 8.5
Hydrolysis

- Reaction of a mineral with water.

\[
\text{Anorthite} + 4 \text{H}_2\text{O} = \text{Ca}^{++} + 2 \text{Al}^{+++} + 2 \text{SiO}_2(\text{aq}) + 8 \text{OH}^{-}
\]

\[
\text{H}_2\text{O} = \text{H}^{+} + \text{OH}^{-}
\]

\[
\text{Anorthite} + 8 \text{H}^{+} = 4 \text{H}_2\text{O} + \text{Ca}^{++} + 2 \text{Al}^{+++} + 2\text{SiO}_2(\text{aq})
\]

\[\Delta G = -15.44 \text{ kJ/mol}\]
Congruent vs Incongruent Dissolution

- Congruent-all components of the mineral dissolve (Ksp)
  Gypsum = Ca^{2+} + SO_{4}^{2-} + 2 \text{H}_2\text{O}

- Incongruent-there is an insoluble secondary phase
  (aluminum is so insoluble that a secondary aluminosilicate phase forms during hydrolysis of most silicate minerals)
  Anorthite + H_2O + 2 H^+ = Ca^{2+} + Kaolinite
  2 Orthoclase + H_2O + 2 H^+ = 2 K^+ + Kaolinite + 4 SiO_2(aq)

Saturation State

- If a mineral is in equilibrium with water, it is said to be saturated.

- A mineral will precipitate from water when the mineral is supersaturated and dissolve in water when undersaturated.

- The state of saturation is determined from the saturation index

Saturation Index

- The saturation index is defined as logQ/K
  K is the equilibrium constant for the reaction and Q is the reaction quotient.

  The reaction quotient is similar to K, but the actual measured chemistry is used to calculate a value for Q.

  When Q=K the mineral is in equilibrium and, therefore, saturated
logQ/K

- If Q=K then Q/K=1 and logQ/K = 0 saturated
- If Q>K then Q/K>1 and logQ/K = (+) supersaturated
- If Q<K then Q/K<1 and logQ/K = (-) undersaturated

Example

The average concentration of Na+ and Cl- in the oceans is 0.479 mol/kg and 0.558 mol/kg respectively...

Ksp for Halite...Ksp=[Na+][Cl-] where logKsp=1.593 at 25°C and 1 atmosphere (K=10^1.593 = 39.174)

Q = [Na+][Cl-] = [0.479][0.558]=0.267

logQ/K = -2.166

Q<K so Halite is undersaturated in seawater at 25°C and 1 atmosphere

Example #2

The average concentration of Ca++ and SO4-- in the oceans is 0.011 mol/kg and 0.029 mol/kg respectively...

Ksp for Gypsum...Ksp=[Ca++][SO4--] where logKsp = -4.443 at 25°C and 1 atmosphere (K=10^-4.443 = 3.6E-5)

Q = [Ca++][SO4--] = [0.011][0.029] = 3.19E-4

logQ/K = 0.947

Q>K so Gypsum is supersaturated in seawater at 25°C and 1 atmosphere (Did I do this wrong?)
Temperature (°C)

Saturation, other minerals (log Q/K)

- Anhydrite
- Aragonite Calcite
- Gypsum
- Halite