

Lecture 3

More General Chemistry Review

Pease read chapter 1 and 2 of McSween et al. for this week

- Classes of chemical reactions
- Mathematically describing chemical reactions

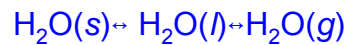
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Chemical reactions

Let's review 6 geochemically pertinent chemical reaction types.

The tems in parentheses (*l*, *g*, *s* and *aq*) refer to "liquid", " gas, aka vapor ", "solid" and "dissolved aqueous" phases, respectively.

a. **Phase change**



These two reactions drive the hydrologic cycle.



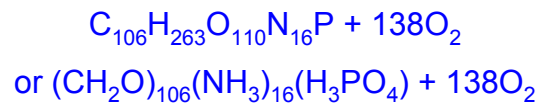
(important for formation/preservation of carbonate sediments globally)

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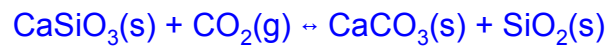
Chemical reactions

b. Bond Reorganization

The Redfield equation of Photosynthesis/Respiration (most plant matter is made and destroyed by organisms using something very close to this):



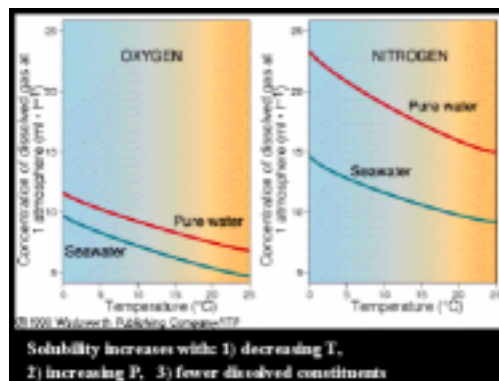
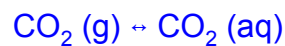
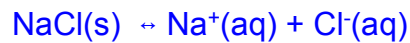
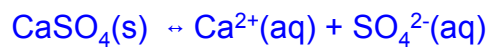
the "Urey" rxn is important for understanding rock weathering and global controls on atmospheric CO_2 :



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Chemical reactions

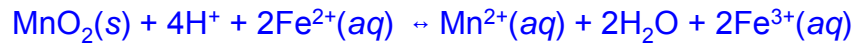
c. Dissolution/precipitation & Dissolution/gas release



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Chemical reactions

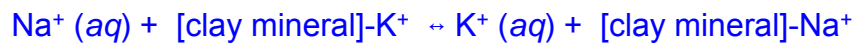
d. Oxidation/Reduction - "Redox": electron transfer



An important reaction all over the hydrosphere/geosphere

Photosynthesis/Respiration is in this category too

e. ion substitution - many different sub classes of this process will be important this semester.



cation exchange between a clay mineral and ions in water

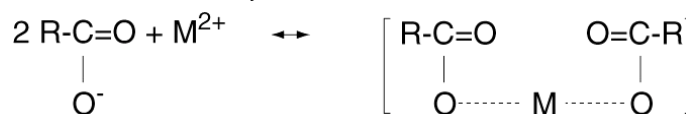
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Chemical reactions

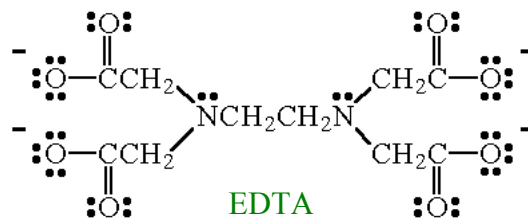
f. Complexation/Chelation



hydration of Fe²⁺ in water



aqueous metal complex with dissolved organic carbon



EDTA

a common multidentate ligand

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Mathematically describing chemical reactions

how do we quantify reactions using chemical equations?

All reactions can be described by algebraic equations of reactants and products. They must be material and charge "balanced" to be used quantitatively.

For a generic chemical reaction involving reactants A and B and products C and D, their reaction is mathematically balanced using **stoichiometric coefficients** a, b, c, d such that the values of these coefficients equalize the matter and electrical charge on both sides of the equation.



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Equilibrium

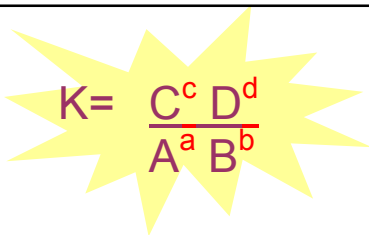
Chemical reactions involve reorganization of atoms and molecules to form new materials. It is useful to have a numeric description of reactions that will help us predict if and to what extent it will occur under various circumstances.

For almost any environmental condition there is a **unique mix of reactants and products in an assemblage of molecules that doesn't change with time** because an energetically favorable balance is achieved.

This condition is **chemical equilibrium**, wherein the relative proportions of reactants and products are expressed with an

equilibrium constant (K):
$$K = \frac{C^c D^d}{A^a B^b}$$

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The quantities A, B, C and D are element **activities**, which are approximately equal to molar concentration (in liquids) or pressure (in the gas phase). We will discuss situations this semester where activity \neq concentration.

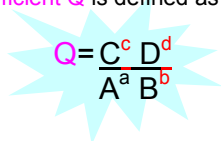
By standard practice activities of **solids** and **pure H₂O(l)** in chemical equations always **equal 1** in the formulation of K.

There is only one unique value of K for a given reaction at a certain value of pressure, P, and temperature, T.

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Non-Equilibrium

If we find a system that has concentrations of reactants or products that differ from those predicted by K, it is not in equilibrium. Under non-equilibrium conditions, the **reaction coefficient Q** is defined as



Q < K: deficit of products.

reaction proceeds in the direction written to correct this.

Q > K: excess of products.

reaction will proceed in the reverse direction.

Unfortunately, the value of Q says almost nothing about the **rate** at which the system will return to equilibrium. This is the domain of another field of chemistry known as **Kinetics** (which we will discuss somewhat during the semester).

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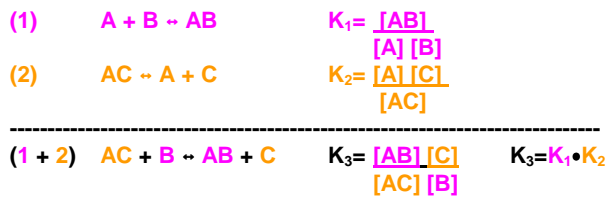
Using equilibrium constants**What do the absolute values of K mean?**

Consider two solubility reactions (solid \leftrightarrow dissolved (aq) solute). For this type of reaction K is denoted with the subscript "sp" = K_{sp} .

$\text{NaCl}(s) \leftrightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$ has a **large K_{sp}** - **Products are favored**, therefore **halite is very soluble in water**.

$\text{BaSO}_4(s) \leftrightarrow \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)$ has a **small K_{sp}** - **Reactants are favored**, so **barite is sparingly soluble in water**.

Chemical equations and Equilibrium constants can be combined algebraically.



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Let's now see how equilibrium constants can be combined.

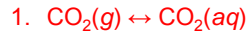
We'll use the system of inorganic reactions that govern the amount of dissolved CO_2 in natural waters. These reactions bear directly on the amount of CO_2 in our atmosphere, geosphere and biosphere.

CO_2 has four forms in water:

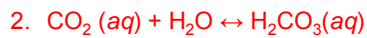
- | | |
|-------------------------------------|-----------------------------|
| a. dissolved gaseous carbon dioxide | $\text{CO}_2(aq)$ |
| b. carbonic acid | $\text{H}_2\text{CO}_3(aq)$ |
| c. bicarbonate anion | $\text{HCO}_3^-(aq)$ |
| d. carbonate anion | $\text{CO}_3^{2-}(aq)$ |

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The 4 forms of CO_2 in water are related by 5 chemical reactions: (disregarding for now photosynthesis and respiration)



This is a gas solubility reaction (sometimes called a Henry's law reaction. K is given the subscript "H": K_H



This is a bond reorganization reaction. It is also a type of hydration (reaction with water). $K = K_{\text{eq}}$ (no "special" nomenclature)



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



Another acid dissociation reaction. This is the second dissociation of *dioprotic carbonic* acid, so we call it or K_{a2} .

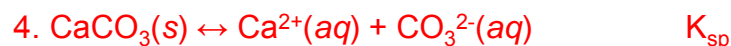


This is a solubility/dissolution reaction. K is K_{sp} .

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Many texts use the simplifying assumption that reactions "2" and "3" (on the prior slide) can be combined. This is because so little $\text{H}_2\text{CO}_3(aq)$ 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 $[\text{Ca}^{2+}(aq)]$).

The water is open to gas exchange with the atmosphere and we assume there are no other reactions affecting Ca^{2+} , H^+ or $\Sigma \text{CO}_2(aq)$ (carbon dioxide in all of its aqueous forms).

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Working backward from reaction 4:
we can rearrange to:

$$K_{sp} = [Ca^{2+}] \cdot [CO_3^{2-}]$$

$$[Ca^{2+}] = K_{sp} / [CO_3^{2-}] \quad \text{A.}$$

from reaction 3:
we can rearrange to:

$$K_{a2} = [H^+] \cdot [CO_3^{2-}] / [HCO_3^-]$$

$$[CO_3^{2-}] = K_{a2} [HCO_3^-] / [H^+]$$

substituting into A. gives: $[Ca^{2+}] = K_{sp} \cdot [H^+] / K_{a2} \cdot [HCO_3^-]$ B.

the same type of rearrangement of equation 2 in terms of $[HCO_3^-]$ yields:

$$[HCO_3^-] = K'_{a1} \cdot [CO_2(aq)] / [H^+]$$

substituting into B. gives: $[Ca^{2+}] = K_{sp} \cdot [H^+] \cdot [H^+] / K_{a2} \cdot K'_{a1} \cdot [CO_2(aq)]$ C.

Finally rearrangement of equation 1
gives:

$$K_H = [CO_2(aq)] / P_{CO_2}$$

$$P_{CO_2} = K_H \cdot [CO_2(aq)] \quad \text{D.}$$

substituting into C. gives:

$$[Ca^{2+}(aq)] = \frac{K_{sp} \cdot [H^+]^2}{K_H \cdot K'_{a1} \cdot K_{a2} \cdot P_{CO_2}}$$

What does this equation tell us? $[Ca^{2+}(aq)]$ will depend on the amount of CO_2 present in the atmosphere and the pH ($= -\log[H^+]$) 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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Energy and Chemical Equilibrium

Recall from your prior chemistry classes that the total system energy available for chemical work is known as *Gibbs Free Energy*, ΔG .

• $\Delta G_{\text{reaction}} = 0$ at chemical equilibrium, (the total system energy is no longer changing.)

$\Delta G^\circ_{\text{reaction}}$ is directly related to the equilibrium constant for a chemical reaction:

$$\Delta G^\circ = -RT \ln K \quad (\text{the superscript } \circ \text{ indicates conditions of STP})$$

For $aA + bB \rightleftharpoons cC + dD$, $K = \frac{C^c D^d}{A^a B^b}$...so $\Delta G^\circ = -RT \ln \frac{C^c D^d}{A^a B^b}$

R is the *Universal Gas Constant* (8.314 J = 0.08206 L-atm = 82.06 cm³-atm = 1.987 calories all per mol °K)

large K (products favored) = negative ΔG°

Small K (reactants favored) = positive ΔG°

• What if we are not at chemical equilibrium?

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{remember, AT EQUILIBRIUM (Q=K) and } \Delta G = 0$$

We will discuss more about what energy terms go into ΔG next week.

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