

## 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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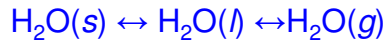
## Chemical Reactions

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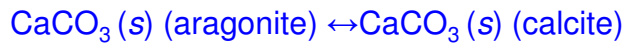
## Chemical reactions

Let's review 6 geochemically pertinent chemical reaction types. *l*, *v*, *s* and *aq* refer to "liquid", "vapor or gas", "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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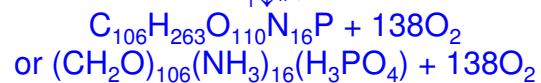
## Chemical reactions

### b. Bond Reorganization

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



↑↓↑↓



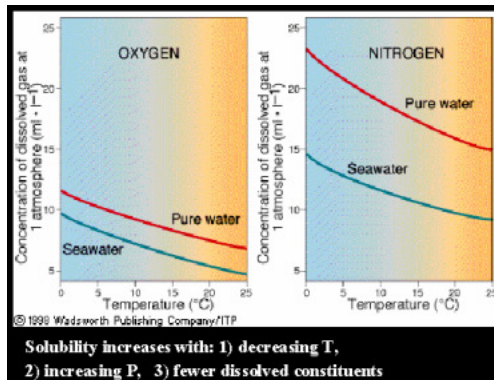
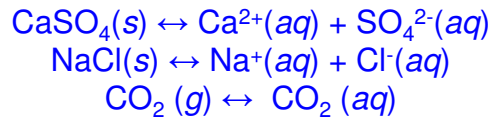
the "Urey" rxn is important for understanding rock weathering and global controls on atmospheric  $\text{CO}_2$ :



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## Chemical reactions

### c. Dissolution/precipitation & Dissolution/gas release



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## Chemical reactions

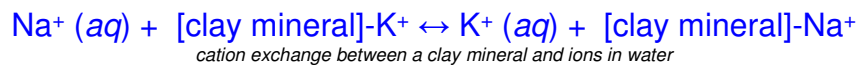
### d. Oxidation/Reduction - "Redox": electron transfer



*An important reaction all over the hydrosphere/geosphere*

*Photosynthesis/Respiration is in this category too*

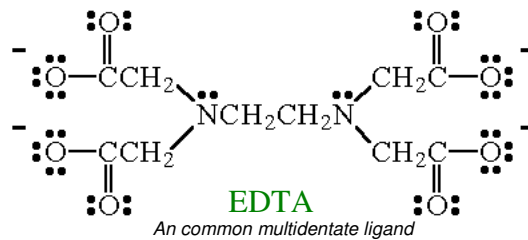
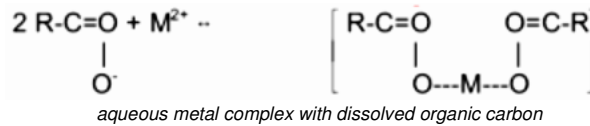
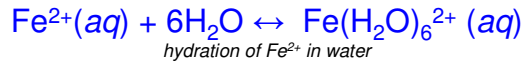
e. **ion substitution** - many different sub classes of this process will be important this semester.



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## Chemical reactions

### f. Complexation/Chelation

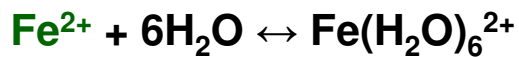


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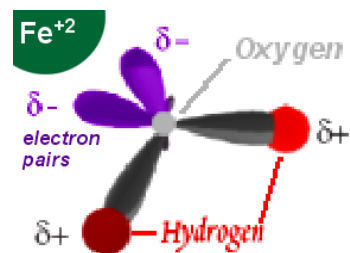
## complexation/chelation

Complexes involve *ligands* and *host* ions.

*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  $\text{Fe}^{2+}$  ion in solution. The hydrate itself involves 5 other water molecules.



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### ligands:

Other common natural ligands are  $\text{Cl}^-$  (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  $\text{Fe}^{+3}$  solution with both  $\text{Cl}^-$  and  $:\text{NH}_3$ , many complexes are possible involving these two ligands and  $\text{H}_2\text{O}$ .

The charge on the complex remains unchanged relative to  $\text{Fe}^{+3}$  with  $\text{H}_2\text{O}$  and  $\text{NH}_3$  ligands, but each  $\text{Cl}^-$  ligand brings one negative charge.

All of the following complexes are possible in this solution:



As you might expect, the relative proportions of these complexes will vary with pH since  $\text{NH}_3 + \text{H}^+ \leftrightarrow \text{NH}_4^+$  (*ammonium is not a good ligand*)

At low pH  $[\text{FeCl}_6]^{-3}$  would be favored

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### ligands:

*Chelation* is a type of complexation that involves *multidentate* ligands.

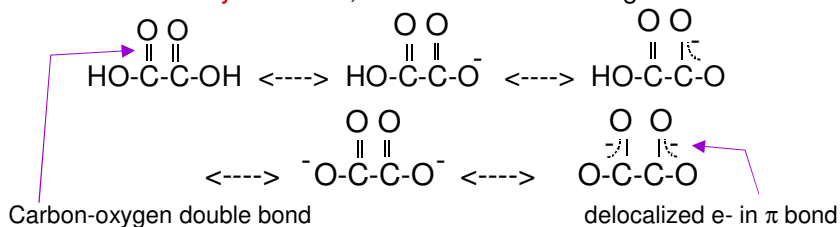
A *chelate* is a complex involving such a ligand.

A *multidentate ligand* is one that has more than one electron pair to donate to a cation. The simplest type is a bidentate ligand.

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

e.g., ethylene diamine,  **$:\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-H}_2\text{N}:$**

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

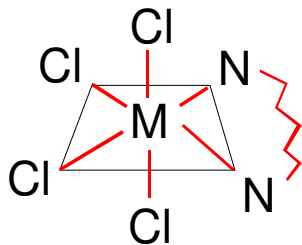


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## ligands:

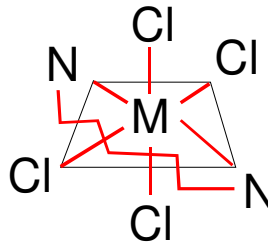
Bidentate ligands can bind in two ways:

"stick figure" notation for a 5 carbon-hydrogen (CH<sub>2</sub>) 5 linear chain. This ligand molecule is -- NH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub> (diamino pentane)



*cis*

next to



*trans*

across

Here, M is a metal or other cation and N is where the donor electron pairs are in the ligand (squiggly line indicates linked carbon atoms).

a "small" bidentate ligand such as ethylene diamine (NH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>) can usually only bind *cis* for geometric reasons.

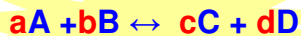
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## *Mathematically describing chemical reactions*

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 so 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 how much 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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$A^a B^b$

$$K = \frac{C^c D^d}{A^a B^b}$$

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 H<sub>2</sub>O(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. At non-equilibrium conditions, the **reaction coefficient Q** is defined as

$$Q = \frac{C^c D^d}{A^a B^b}$$

**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 some during the semester).

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## Using equilibrium constants

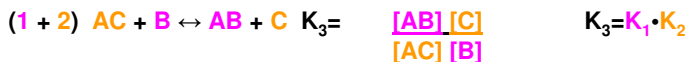
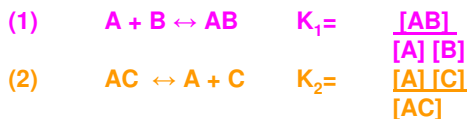
### What do the absolute values of K mean?

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**.

**Chemical equations and Equilibrium constants can be combined algebraically.**



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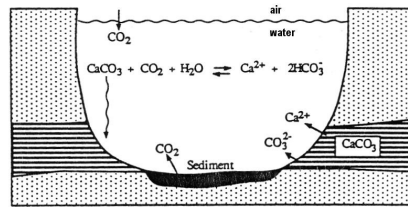


### Example: Combining Equilibria in the aqueous CO<sub>2</sub> system

Let's combine the system of inorganic reactions governing the amount of dissolved CO<sub>2</sub> in natural waters (which bears directly on the amount of CO<sub>2</sub> in our atmosphere, geosphere and biosphere)

CO<sub>2</sub> 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                      CO<sub>2</sub>(aq)
- b. carbonic acid    H<sub>2</sub>CO<sub>3</sub>(aq)
- c. bicarbonate anion    HCO<sub>3</sub><sup>-</sup>(aq)
- d. carbonate anion    CO<sub>3</sub><sup>2-</sup>(aq)

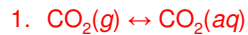


Carbon dioxide-calcium carbonate equilibria.

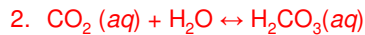
Note that CaCO<sub>3</sub> formation (by inorganic precipitation or biogenic precipitation) is the primary upper limit control on dissolved carbon dioxide concentration

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The 4 forms of CO<sub>2</sub> 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<sub>H</sub>)



This is a bond reorganization reaction. It is also a type of hydration (reaction with water). K = K<sub>eq</sub> (no "special" nomenclature)



An acid dissociation reaction. Commonly given equilibrium constant notations of K<sub>a</sub> if it is a *monoprotic* acid, or K<sub>a1</sub> for the first acid dissociation of a *polyprotic* acid



Another acid dissociation reaction. This is the second dissociation of *diprotic carbonic acid*, so we call it or K<sub>a2</sub>.

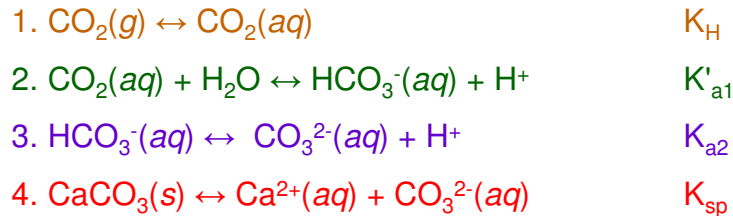


This is a solubility/dissolution reaction. K is K<sub>sp</sub>.

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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  $\text{H}_2\text{CO}_3(\text{aq})$  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  $\text{CaCO}_3$  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  $\text{Ca}^{2+}$ ,  $\text{H}^+$  or  $\Sigma \text{CO}_2(\text{aq})$  (carbon dioxide in all of its aqueous forms).

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Working backward from reaction 4:  
we can rearrange to:

$$K_{\text{sp}} = [\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}]$$

$$[\text{Ca}^{2+}] = K_{\text{sp}} / [\text{CO}_3^{2-}] \quad \text{A.}$$

from reaction 3:  
we can rearrange to:

$$K_{\text{a2}} = [\text{H}^+] \cdot [\text{CO}_3^{2-}] / [\text{HCO}_3^-]$$

$$[\text{CO}_3^{2-}] = K_{\text{a2}} [\text{HCO}_3^-] / [\text{H}^+]$$

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:

$$K_{\text{H}} = [\text{CO}_2(\text{aq})] / P_{\text{CO}_2}$$

$$P_{\text{CO}_2} = K_{\text{H}} \cdot [\text{CO}_2(\text{aq})] \quad \text{D.}$$

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  $\text{CO}_2$  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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