Lecture 9 - Chemical Equilibrium and Solution Chemistry

Why do we need to study chemical equilibrium?
The material in this lecture comes from the field of chemical thermodynamics.
Those that need some refreshing on their inorganic chemistry should open a chemistry textbook.
For the purpose of this class there are only a few basic concepts you need to know in order to conduct equilibrium calculations. With these calculations we can predict chemical composition using chemical models. The main questions we ask are:
1. Is a geochemical system at chemical equilibrium?
2. 2. If not, what reaction(s) *are most likely* to occur?
3. 3. What are the relative amounts of energy and materials that *might* occur in a system?

Here are some examples of problems where equilibrium calculations are useful.
Examples:
- Diatoms exist in surface seawater. The solubility of diatom shell material (called opal) is written as: $SiO_2 \cdot 2H_2O$ (Opal) $\leftrightarrow H_4SiO_4$
  There are two chemical problems here:
  o The surface ocean is everywhere under saturated with respect to opal, yet diatoms form. Furthermore, they are preserved in sediments over long time periods (millions of years).
  o The favored form of solid SiO_2 (s) at earth surface conditions is quartz not opal! Why does opal form instead?

- We place a piece of $CaCO_3$ (calcite) in distilled water. After a short time, there will be a measurable amount of Ca^{+2} and CO_3^{-2} ions dissolved in the water. After a long time, the concentration of these ions becomes constant because the system reaches equilibrium. If we add some NaCl to the water, the concentrations of Ca^{+2} and CO_3^{-2} will increase because more solid $CaCO_3$ dissolved. Why?

- Zinc is known to be an essential nutrient for growth of plankton and is also toxic at high concentrations. We develop a phytoplankton culture in seawater and add Zn until the number of doublings per day decreases due to the zinc toxicity. When EDTA is added to the solution the plankton revive and begin growing rapidly again. Why?

Similar questions involving introduction of pollutants into sediments, reactions of trace metals such as Fe with natural organic ligands and more are considered using chemical equilibrium and solution chemistry considerations.

There are two main types of calculations that we do in chemical oceanography.
1. We can determine the potential for a given chemical reaction to occur. What reactions are likely to occur? For example, we can determine what solids will precipitate or dissolve in seawater or we can determine if a metal in seawater will react with specific organic compounds to form complexes.
2. We can calculate chemical distributions at equilibrium. For example, we can compare the actual composition of seawater with that calculated from equilibrium.

The main points of this lecture are: Define the equilibrium constant - K
Define the free energies: ΔG_f^0, ΔG_r^0 and ΔG_r
Show how to calculate K from ΔG_r
Explain the difference between Q and K and how they are
used to determine which direction a reaction will proceed.

The Equilibrium Constant (K)
Chemical reactions can be characterized by an **equilibrium constant,** K. This constant expresses
the ratio of the product of the reaction products to the product of the reactants.

$$K_{eq} = \frac{\text{product of reaction product activities}}{\text{product of reactant activities}}$$

bB + cC <==> dD + eE   b,c,d,e: stoichiometric coefficient (units of moles)
at equilibrium:

$$K_{eq} = \frac{aD^d\ aE^e}{aB^b\ aC^c} = \frac{(D)^d\ (E)^e}{(B)^b\ (C)^c}$$ a: activity, written as aD or (D)

Always check that a reaction is balanced (elements and charge), and keep track of the units

For example: $CaSO_4 \cdot 2H_2O$ <==> $Ca^{2+} + SO_4^{2-} + 2H_2O$ $K = 10^{-4.58}$

For this reaction the equilibrium constant can be defined as:
$$K = a_{Ca2+} \times a_{SO42-} \times a^2_{H2O} / a_{CaSO4 \cdot 2H2O}$$

This type of equilibrium constant for a reaction where a solid goes into solution as free ions, is
often called the solubility product (K_s) where the "a" values stand for activity.
Remember **activity is the effective concentration**. Note that activities are raised to the power of
their stoichiometric coefficient (e.g. $2H_2O = a^2_{H2O}$). If ions are dilute enough (this is called an
ideal solution) the activity "a" or "( )" and absolute concentration "C" or "[ ]" are essentially
equal (i.e. $a_{Ca2+} = C_{Ca2+}$). The thermodynamic convention is to set the activity of solvent (e.g.
H_2O) and pure solids (e.g. $CaSO_4 \cdot 2H_2O$) equal to 1 thus H_2O and $CaSO_4 \cdot 2H_2O$ do not appear is
this version of the expression. After these simplifications, the solubility constant, for this case,
which is in dilute solution can be written as:
$$K_s = (Ca^{2+})\ (SO_4^{2-}) = [Ca^{2+}][SO_4^{2-}]$$

Assuming ideal solutions we can imagine hypothetical situations where:
If $[Ca^{2+}] = [SO_4^{2-}] = 10^{-3}$ M, The product of $[Ca^{2+}] \times [SO_4^{2-}]$ is 10^{-6} which is less than the value
of $Ks = 10^{-4.58}$. The solution is under saturated (any solid will continue to dissolve).
If $[Ca^{2+}] = [SO_4^{2-}] = 10^{-2.29}$ M, The product of $[Ca^{2+}] \times [SO_4^{2-}]$ is $10^{-4.58}$ which is exactly equal to
the value of K_s. The solution is at saturation equilibrium (solid phase will precipitate and
dissolve at same rate). If $[Ca^{2+}] = [SO_4^{2-}] = 10^{-2}$ M, The product of $[Ca^{2+}] \times [SO_4^{2-}]$ is 10^{-4} which
is greater than the value of $K_s = 10^{-4.58}$. The solution is supersaturated (more solid will form).

How to Calculate Equilibrium Constants:
Values of K are calculated from a thermodynamic property known as Gibbs free energy (or G). See Appendix for a more detailed explanation of G and how it relates to enthalpy (H) and entropy (S).

ΔG units of kJ/mol (kilojoule/mol); old units are kcal/mol. This is the property that governs all thermodynamic chemical equilibrium. A reaction that has a negative free energy is favorable (e.g. energy is released). To determine whether a reaction involves a negative free energy, chemists have assigned an energy value to each chemical substance. It is the individual free energy content of chemicals that determines the value of an equilibrium constant. It isn't possible to know the absolute energy value; we only know the relative change in energy.

There are three different types of Free Energy.

1. $\Delta G°_f$ ---- Standard Free Energy of Formation is change in free energy when one mole of a substance is formed from its constituent elements at the standard state (activity = 1, 1 atm, 25°C).

Convention: free energy of formation of pure elements in most stable state = 0.
e.g. $\Delta G°_f = 0$ for   H as H_2 (g)
   O as O_2 (g)
                        C as graphite
Convention: for ions in water $\Delta G°_f = 0$ for H^+ and e^-

$\Delta G°_f$ values are relative to the defined zero values. Many useful values are found in Stumm and Morgan (1996) and the Handbook of Chemistry and Physics.

2. $\Delta G°r$ ---- Standard Free Energy of Reaction. To assess the possibility of a reaction, one sums the standard free energies of formation to derive the Standard Free Energy of Reaction. This is the free energy released or absorbed by a chemical reaction with all substances in their standard states (1 atm, 25°C, activity = 1, pure solids = 1, solvent = 1, ideal gas = 1, ions = 1M).

$$\Delta G°r = (\Sigma \Delta G°_f)_{products} - (\Sigma \Delta G°_f)_{reactants}$$

For the generalized reaction where B and C are reactant compounds with stoichiometric coefficients b and c and D and E are product compounds with coefficients d and e:

$$bB + cC \Longleftrightarrow dD + eE$$
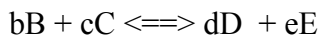
$$\Delta G°_r = (d\Delta G°_{f,D} + e\Delta G°_{f,E}) - (b\Delta G°_{f,B} + c\Delta G°_{f,C})$$

The **equilibrium constant (K)** is calculated from $\Delta G°r$ as follows:

$$\Delta G°r = - RT \ln K = -2.3\ RT \log K \quad \text{(note: } \ln K = 2.3 \log K\text{)}$$

Where R = gas constant = 8.314 J deg^{-1} mol^{-1} or 1.987 cal deg^{-1} mol^{-1}
T = absolute temperature = X° C + 273;   T= 298° for 25° C

At 25 °C, K can be simply calculated from:

$\Delta G°r = -5.708 \log K$ (for G in kJ) $= -1.364 \log K$ (for G in kcal)

The equilibrium constant K gives the ratio of the products to the reactants at equilibrium, with all species raised to the power that corresponds to their stoichiometry. For the generalized reaction given above, K would be written as:

$$K = a_D{}^d \times a_E{}^e / a_B{}^b \times a_C{}^c$$

Thus $\Delta G°_r$ and K tell you the equilibrium ratio of products to reactants.

3. ΔG_r ---- Free Energy of Reaction

There is a whole class of problems where we know the concentrations for a specific set of conditions and we want to ask the question a slightly different way. Is a specific reaction at equilibrium, and if not, which way will it spontaneously want to proceed for these conditions. The way we do this is to calculate the reaction quotient using the observed concentrations (converted to activities). We call this ratio Q to distinguish it from K, but they are in the same form (same units). Comparison of the magnitude of Q with K tells us the direction a reaction should proceed.

The free energy change for a given set of conditions is written as

$$\Delta G_r = \Delta G°_r + RT \ln K \quad \text{or} \quad \Delta G_r = \Delta G°_r + 2.3\ RT \log (a_D{}^d \times a_E{}^e / a_B{}^b \times a_C{}^c)_{\text{in situ}}$$

This is the same as:

$$\Delta G_r = \Delta G°_r + RT\ln\left\{\frac{(D)^d (E)^e}{(B)^b (C)^c}\right\}$$

$$\Delta G_r = \Delta G°_r + 2.3\ RT \log Q$$

Where $Q = a_D{}^d \times a_E{}^e / a_B{}^b \times a_C{}^c = $ Ion Activity Product (IAP) $= \dfrac{(D)^d (E)^e}{(B)^b (C)^c}$

We can replace $\Delta G°_r$ with its log K expression. Then:

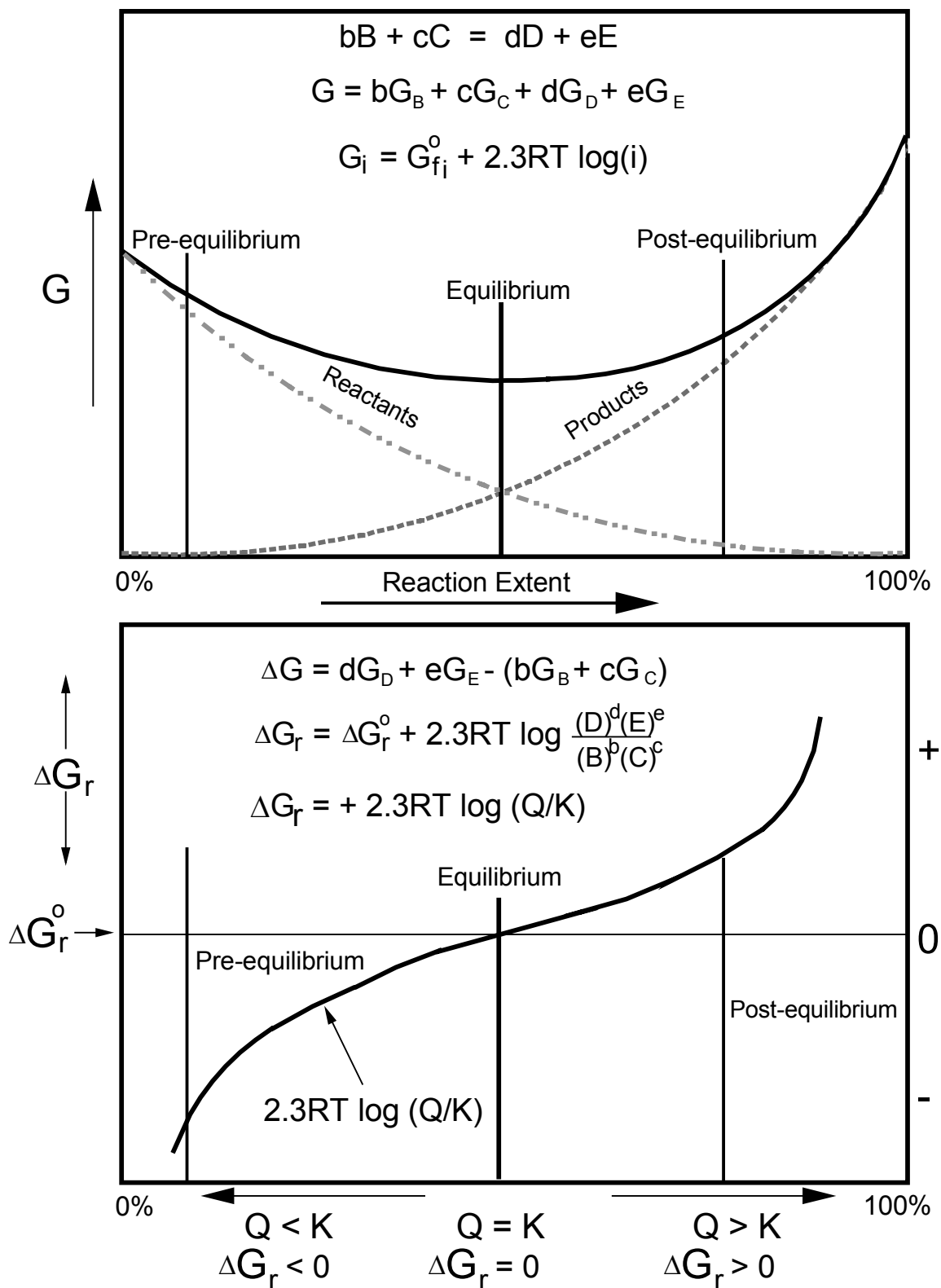$$\Delta G_r = -2.3\ RT \log K + 2.3\ RT \log Q$$

or

$$\Delta G_r = 2.3\ RT \log Q/K = 2.3\ RT \log \Omega \text{ where } \Omega = Q / K$$

for: $bB + cC \Longleftrightarrow dD + eE$

if $K = Q$ $\Delta G\ r = 0$ reaction is at equilibrium system's free energy is at a minimum
       $Q > K$ $\Delta G\ r > 0$ reaction goes to the left, system has too many products.
       $Q < K$ $\Delta G\ r < 0$ reaction goes to right, system has too many reactants.

This is a plot of total free energy (G) and change in free energy (ΔG) as a function of extent of reaction. 0% reaction extent means that only reactants are present and that zero products have formed. The equilibrium point corresponds to $Q = K$ and $\Delta Gr = 0$. Total G is calculated from:
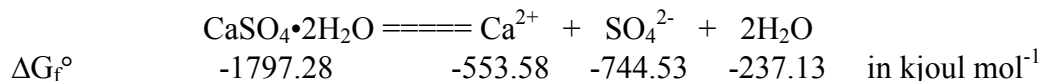
$$G_{tot} = \Sigma\, n_i\, G_i \quad \text{where } G°r = G_i + RT \ln a_i$$

$$bB + cC = dD + eE$$

$$G = bG_B + cG_C + dG_D + eG_E$$

$$G_i = G^o_{f_i} + 2.3RT \log(i)$$

Pre-equilibrium   Post-equilibrium

G

Equilibrium

Reactants

Products

0%   Reaction Extent   100%

$$\Delta G = dG_D + eG_E - (bG_B + cG_C)$$

$$\Delta G_r = \Delta G^o_r + 2.3RT \log \frac{(D)^d(E)^e}{(B)^b(C)^c}$$

$$\Delta G_r = + 2.3RT \log (Q/K)$$

ΔG_r

+

Equilibrium

$\Delta G^o_r \rightarrow$ 0

Pre-equilibrium

Post-equilibrium

2.3RT log (Q/K)

−

0%   100%

| Q < K | Q = K | Q > K |
| $\Delta G_r < 0$ | $\Delta G_r = 0$ | $\Delta G_r > 0$ |

Examples:

1. Calculation of gypsum solubility (K) at STP

Using the values of $\Delta G_f°$ and the relation $\Delta G°r = (\Sigma \Delta G°_f)_{products} - (\Sigma \Delta G°_f)_{reactants}$

$$CaSO_4 \bullet 2H_2O ===== Ca^{2+} + SO_4^{2-} + 2H_2O$$

$\Delta G_f°$ -1797.28   -553.58   -744.53   -237.13   in kjoul mol^{-1}

$\Delta G_r° = [(-553.58) + (-744.53) + 2(-237.13)] - [(-1797.28)] = +24.91$

$\Delta G°r = -5.708 \log K$ so $\log K = -\Delta G°r / 5.708 = -4.36$ so $K = 10^{-4.36}$

2. Acid-Base Reactions

$$CO_2(aq) + H_2O = HCO^{3-} + H^+$$

$\Delta G_f°$ -92.31   -56.69   -140.31   0   in kcal mol^{-1}
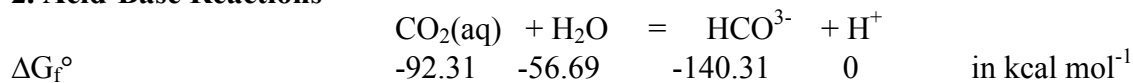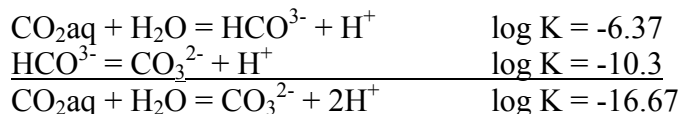
$\Delta G_r° = [(-140.31) + (0)] - [(-92.31) + (-56.69)] = +8.69$ kcal mol^{-1} = 36.3 kjoul mol^{-1}

$\log K = -\Delta G°r / 1.364 = -8.69$ kcal mol^{-1} / 1.364 = -6.37

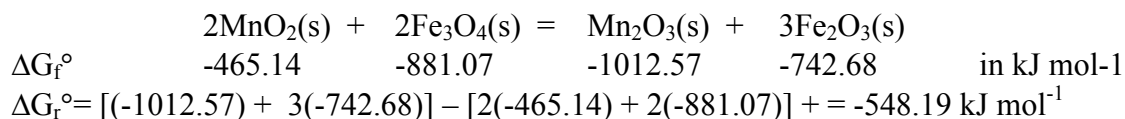so $K = (HCO^{3-})(H^+) / (CO_2aq)(H_2O) = 10^{-6.37}$

3. Adding reactions

Sometimes the exact form of the reaction you what is not given and you need to combine other reactions to get the K you need. When you add reactions you add the log Ks as follows.
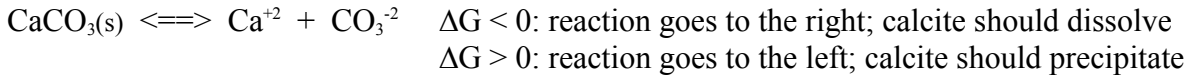
$CO_2aq + H_2O = HCO^{3-} + H^+$	$\log K = -6.37$
$HCO^{3-} = CO_3^{2-} + H^+$	$\log K = -10.3$
$CO_2aq + H_2O = CO_3^{2-} + 2H^+$	$\log K = -16.67$

4. Stability among oxides

Say we want to know which pair of manganese and iron oxides is most stable? We have the reaction where pyrolusite and magnetite react to form manganite and hematite.

$$2MnO_2(s) + 2Fe_3O_4(s) = Mn_2O_3(s) + 3Fe_2O_3(s)$$

$\Delta G_f°$ -465.14   -881.07   -1012.57   -742.68   in kJ mol-1

$\Delta G_r° = [(-1012.57) + 3(-742.68)] - [2(-465.14) + 2(-881.07)] + = -548.19$ kJ mol^{-1}

Since $\Delta G_f° < 0$; pyrolusite and magnetite are unstable relative to manganite plus hematite. There is no equilibrium constant because the reaction involves only pure solids whose activities are equal to 1.

5. Does CaCO₃(calcite) dissolve or precipitate in marine surface waters?

$$CaCO_{3(s)} \Longleftrightarrow Ca^{+2} + CO_3^{-2}$$ ΔG < 0: reaction goes to the right; calcite should dissolve
ΔG > 0: reaction goes to the left; calcite should precipitate

From thermodynamic tables we obtain values for $\Delta G°_f$ for the relevant chemical species and calculate $\Delta G°_r$ for the above reaction.

$$\Delta G°_r = \sum \Delta G°_f (products) - \sum \Delta G°_f (reactants)$$
$$= (\Delta G°_{f,Ca^{+2}} + \Delta G°_{f,CO_3^=}) - (\Delta G°_{f, CaCO_3})$$
$$= (-553.54) + (-527.9) - (-1128.8) \text{ kJ/mol} = 47.36 \text{ kJ/mol}$$

$\Delta G_r = \Delta G°_r + RT \ln Q$ calculate activities

$$= 47.36 + RT \ln \frac{(Ca^{+2})(CO_3^=)}{(CaCO_3)}$$ $(Ca^{+2}) = [Ca^{+2}] \gamma Ca = (10.4 \times 10^{-3})(0.25)$

$$= 2.6 \times 10^{-3} \text{ mol/kg}$$

$$= 47.36 + RT \ln \frac{(2.6 \cdot 10^{-3})(6.3 \cdot 10^{-6})}{(1)}$$

$(CO_3^{-2}) = [CO_3^{-2}] \gamma CO_3^{-2} = (350 \times 10^{-6})(0.018)$
$$= 6.3 \times 10^{-6} \text{ mol/kg}$$

$= 47.36 + 5.701 \log (1.64 \times 10^{-8}) = 2.97$ $(CaCO_3)s = 1.0$ [assume it's a pure solid]

Therefore.... ΔG > 0 or Q > K

Reaction will not go to the right; calcite will not dissolve in surface seawater.

Based on thermodynamic arguments, calcite is predicted to precipitate in surface seawater!

References:
Drever J.I. (1997) The Geochemistry of Natural Waters. Prentice Hall, Upper Saddle River, NJ, 436pp.
Klotz I.M. (1964) Chemical Thermodynamics. W.A. Benjamin, New York, 468pp.
Langmuir D. (1997) Aqueous Environmental Geochemistry. Prentice Hall, Upper Saddle River, NJ, 600pp.
Lewis G.N. and M. Randall (revised by K.S. Pitzer and L. Brewer)(1961) Thermodynamics. McGraw-Hill, New York, 723pp.
Morel F.M.M. and J.G.Hering (1993) Principles and applications of Aquatic Chemistry. John Wiley, New York, 588pp.
Stumm W. and J.J. Morgan (1996) Aquatic Chemistry. 3rd edition, John Wiley, New York, 1022 pp.