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CEE 370 Environmental Engineering Principles

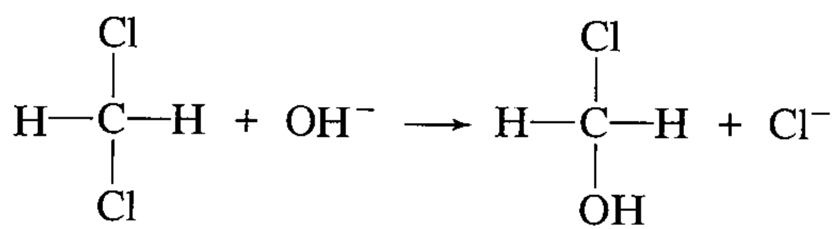
Lecture #6
Environmental Chemistry IV: Thermodynamics, Equilibria, Acids-bases I

Reading: Mihelcic & Zimmerman, Chapter 3

Davis & Masten, Chapter 2
Mihelcic, Chapt 3

Kinetics

- Base Hydrolysis of dichloromethane (DCM)
  - Forms chloromethanol (CM) and chloride



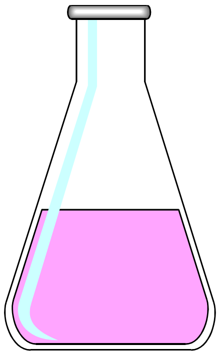
  - Classic second order reaction (molecularity of 2)

$$Rate = k[DCM][OH^-] = \frac{-d[DCM]}{dt} = \frac{-d[OH^-]}{dt} = \frac{d[CM]}{dt} = \frac{d[Cl^-]}{dt}$$

    - First order in each reactant, second order overall

Kinetic principles

- Law of Mass Action
  - For elementary reactions



$$aA + bB \xrightarrow{k} products$$

$$rate = kC_A^a C_B^b$$

where,

C_A = concentration of reactant species A, [moles/liter]

C_B = concentration of reactant species B, [moles/liter]

a = stoichiometric coefficient of species A

b = stoichiometric coefficient of species B

k = rate constant, [units are dependent on a and b]

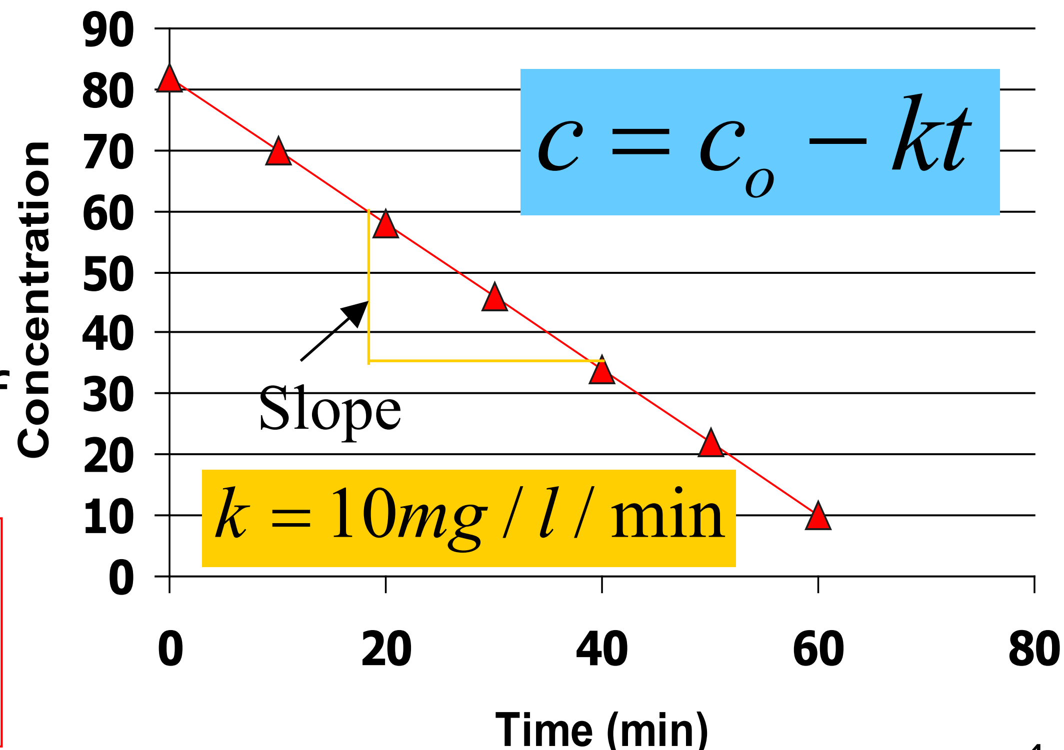
Kinetics: zero order

- Reactions of order "n" in reactant "c"

$$\frac{dc}{dt} = -kc^n$$

- When n=0, we have a simple zero-order reaction
  - Example: biodegradation of 2,4-D

$$\frac{dc}{dt} = -k$$

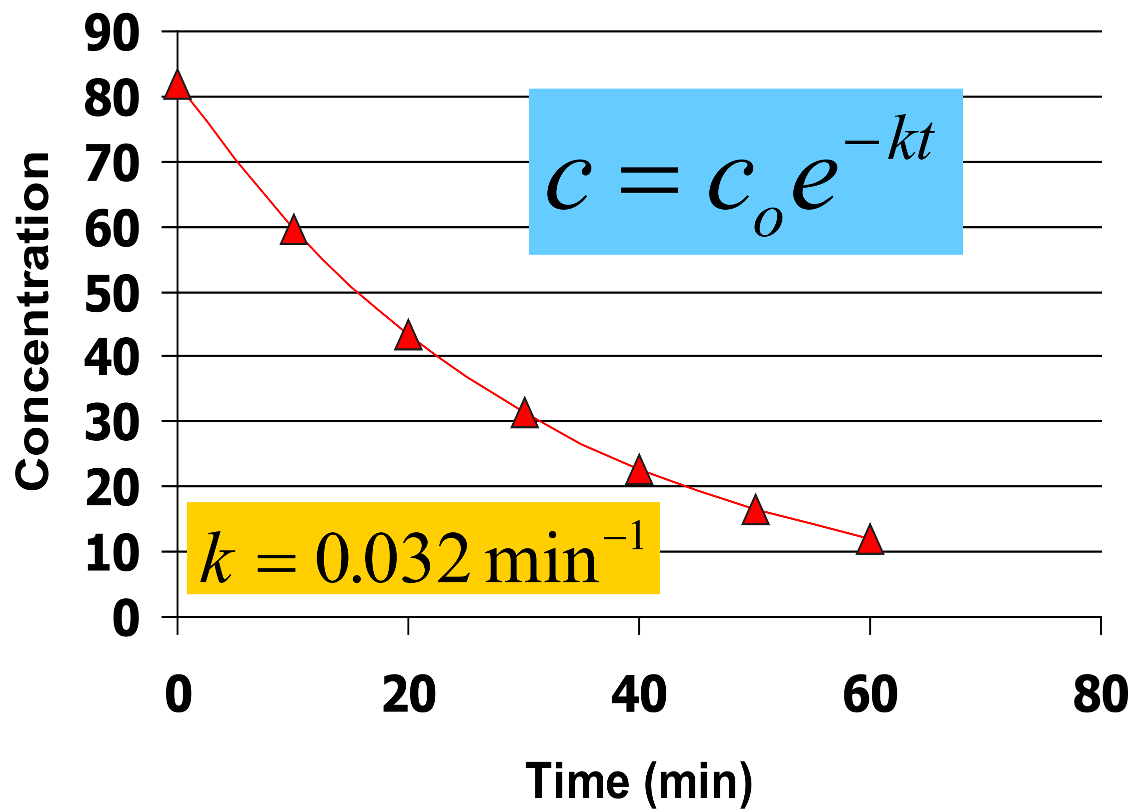


Kinetics: First Order

- When n=1, we have a simple first-order reaction
- This results in an "exponential decay"
  - Example: decay of ^{137}Cs from Chernobyl accident

$$\frac{dc}{dt} = -kc^{1}$$

A => products



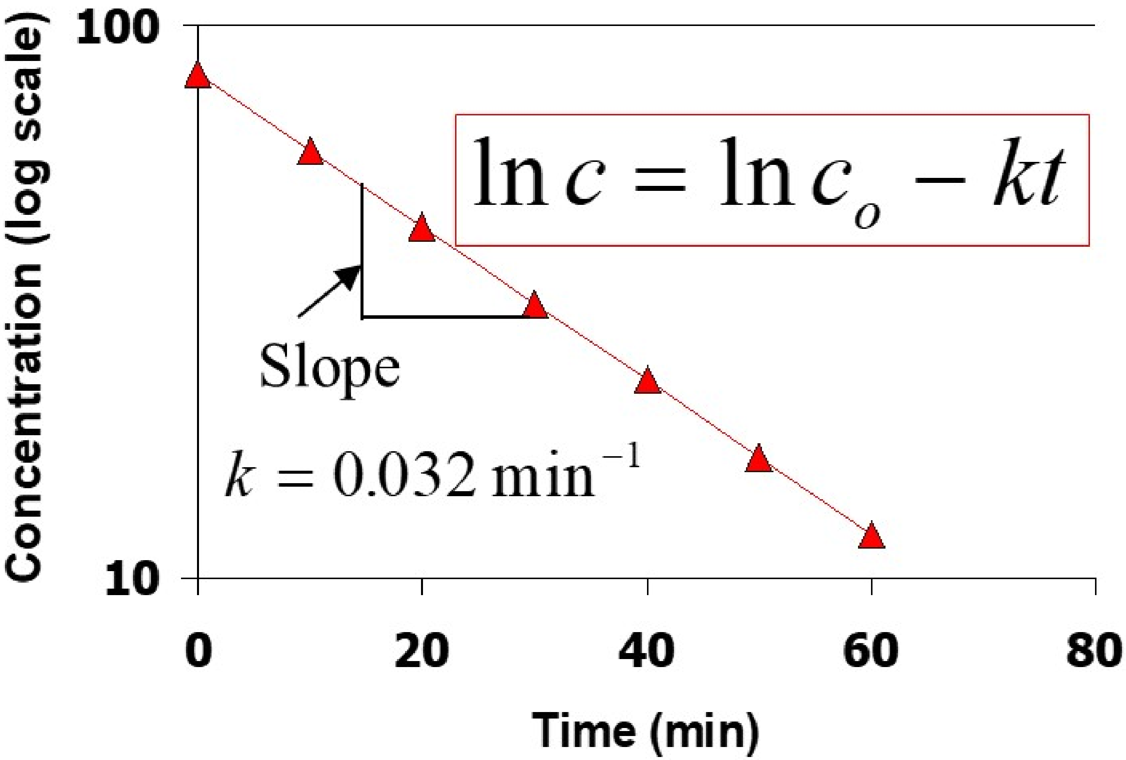
$$c = c_o e^{-kt}$$

$$k = 0.032\ \mathrm{min}^{-1}$$

Kinetics: First Order (cont.)

$$\frac{dc}{dt} = -kc^1$$

- This equation can be linearized
- good for assessment of "k" from data



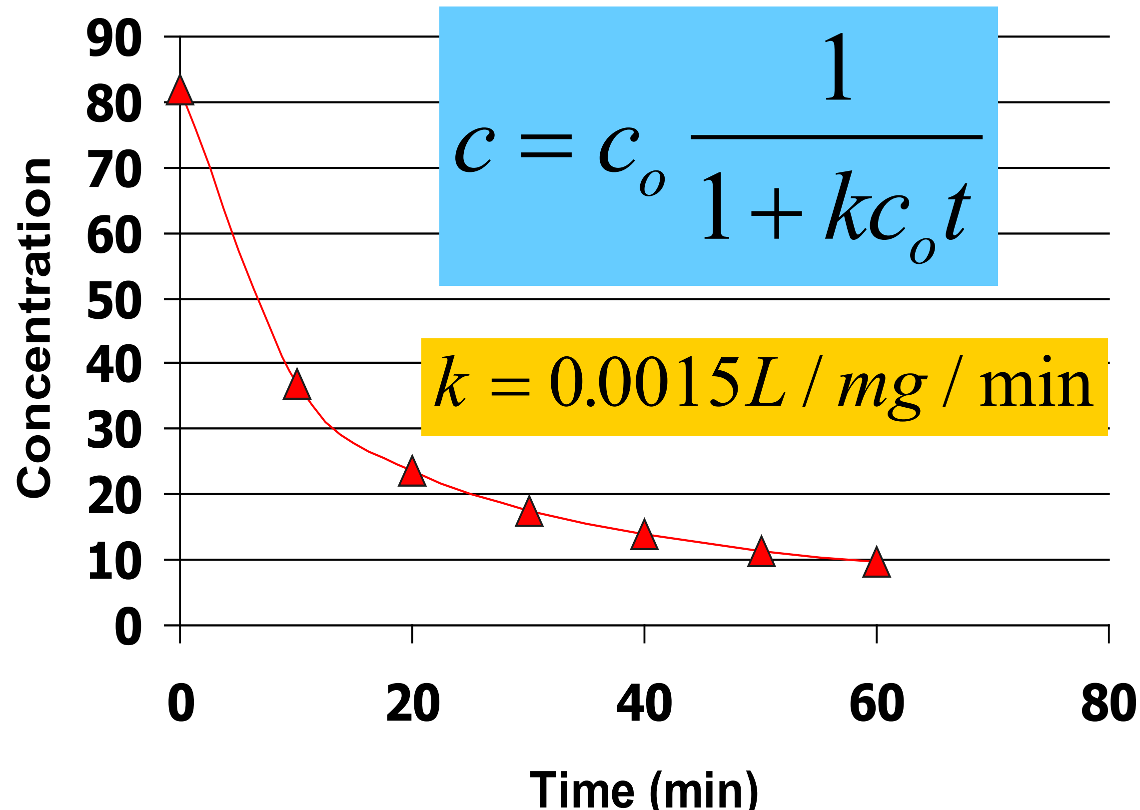
Kinetics: Second Order

$$\frac{dc}{dt} = -kc^2$$

- When n=2, we have a simple second-order reaction

A + A => products

- This is a reaction between two identical molecules
- More common to have different molecules reacting (see next slide)



$$c = c_o \frac{1}{1 + kc_o t}$$

$$k = 0.0015 L/mg/\min$$

Kinetics; Pseudo-1st Order

- When you have two different species reacting via 2nd order kinetics overall

A + B => products

$$\frac{dc_A}{dt} = \frac{dc_B}{dt} = -kc_A c_B$$

- If one reactant (c_B) is present in great excess versus the other, the concentration of that one can be treated as constant and folded into the rate constant to get a **pseudo-first order** reaction

$$\frac{dc_A}{dt} = -k_{obs} c_A$$

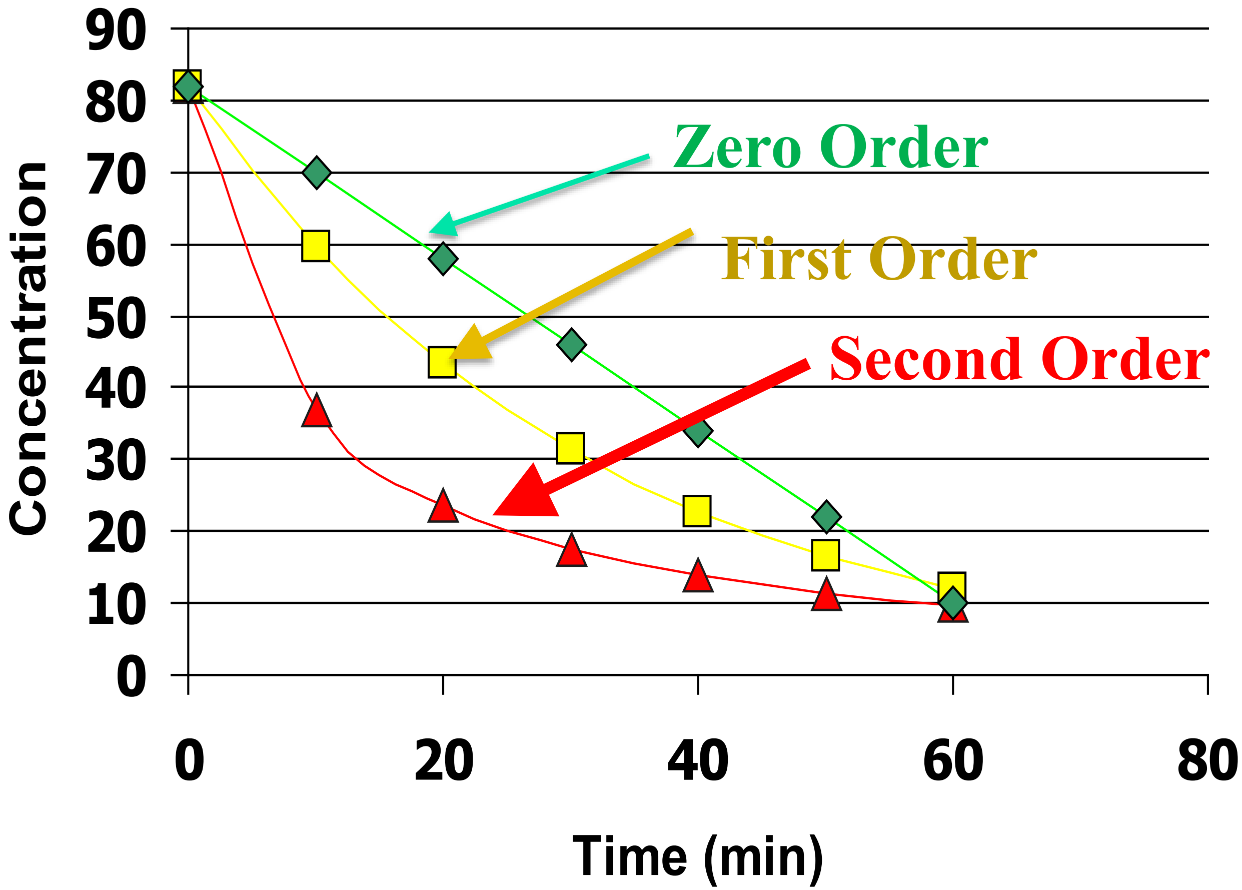
where

$$k_{obs} = kc_B$$

From here you can use the first order equations

Comparison of Reaction Orders

- Curvature: 2nd>1st>zero



Half-lives

- Time required for initial concentration to drop to half, ie., $c=0.5c_o$
  - For a zero order reaction:

$$c = c_o - kt$$

$$0.5c_o = c_o - kt_{1/2}$$

$$t_{1/2} = \frac{0.5c_o}{k}$$

  - For a first order reaction:

$$c = c_o e^{-kt}$$

$$0.5c_o = c_o e^{-kt_{1/2}}$$

$$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k}$$

Try example 3.5 & 3.6 in Mihelcic

Temperature Effects

Temperature Dependence

- Chemist's Approach: Arrhenius Equation

Activation energy

$$\frac{d(\ln k)}{dT_a} = \frac{E_a}{RT_a^2}$$

Pre-exponential Factor

$$k_{T_a} = Ae^{-E_a/RT_a}$$

$$k_{T_a} = k_{293^o K} e^{E_a (T_a - 293)/RT_a 293}$$

R = universal gas constant
= 1.987 cal/^{o}K/mole
T_a = absolute temp (^{o}K)

- Engineer's Approach:

$$k_T = k_{20^o C} \theta^{T-20^o C}$$

Or more generally where T_o is any "baseline" temperature

$$k_T = k_{T_o} \theta^{T-T_o}$$

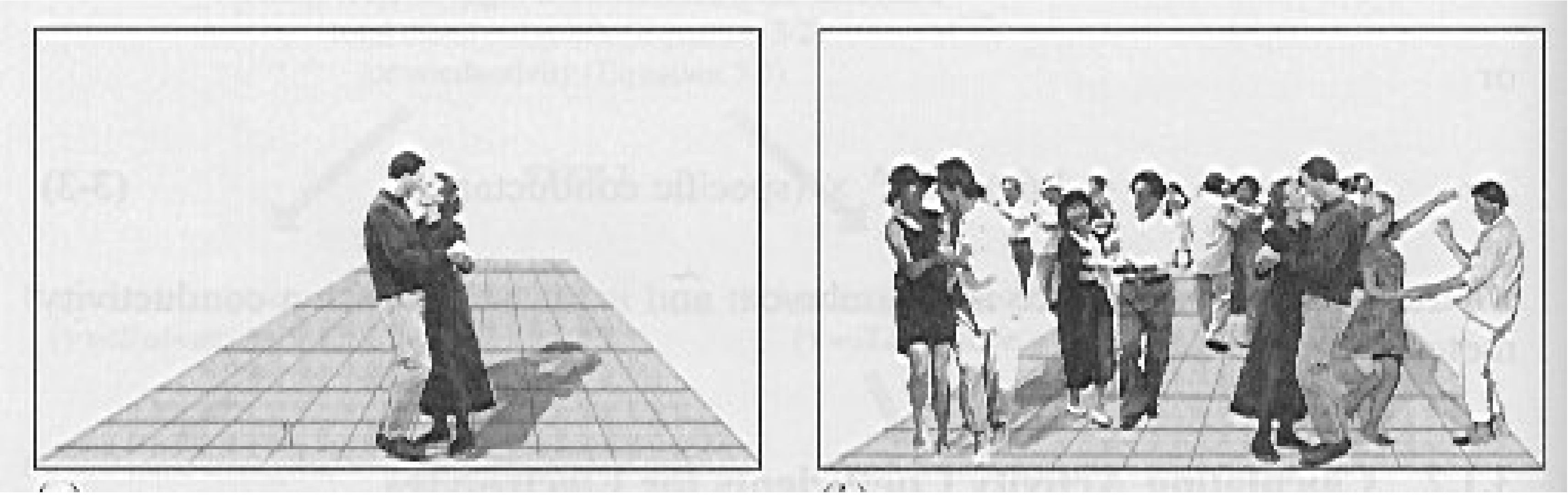
Typical values:
θ=1.02 to 1.15

Activity

- Activity is the "effective or apparent" concentration, which may be slightly different from the true "analytical" concentration
  - These two differ substantially in waters with high TDS, such as sea water.
- We identify these two as follows:
  - Curved brackets ({X}) indicate activity
  - Square brackets ([X]) indicate concentration
    - Usually this is molar concentration
    - This may also be used when we're not very concerned about the differences between activity and concentration

Why the difference?

- Mostly long-range interactions between uninterested bystanders (chemical species that are not involved in the reaction) and the two dancers of interest (those species that are reacting)



Activity & Ionic Strength

- Equilibrium quotients are really written for activities, not concentrations

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

- in most natural waters activities are nearly equal to the molar concentrations

$$\{A\} \approx [A]$$

- In saline waters, we must account for differences between the two
  - activity coefficients (f or γ) are used for this
  - Ionic Strength (I or μ) is used to determine the extent of correction

$$\{A\} = f_A [A]$$

$$\{A\} = \gamma_A [A]$$

$$I \text{ or } \mu = \tfrac{1}{2} \sum C_i z_i^2$$

μ Corrections

- From textbook
  - Mihelcic & Zimmerman

STEP 1

After deciding whether ionic strength effects are important in a particular situation, calculate ionic strength from

$\mu = \frac{1}{2}\Sigma_i C_i z_i^2$ (Equation 3-1)

or

estimate ionic strength after measuring the solution's total dissolved solids (Equation 3-2) or conductivity (Equation 3-3)

STEP 2

If species is an electrolyte (*γ will always be ≤ 1*)

for low ionic strengths, $\mu < 0.1$ M,

use the Güntelberg (or similar) approximation:

(Equation 3-5)

$$\log \gamma_i = \frac{-A z_i^2 \mu^{1/2}}{1+\mu^{1/2}}$$

for high ionic strengths, $\mu < 0.5$ M,

use the Davies (or similar) approximation:

(Equation 3-6)

$$\log \gamma_i = \frac{-A z_i^2 \mu^{1/2}}{[1+\mu^{1/2}] - 0.3\mu}$$

If species is a nonelectrolyte (*γ will always be ≥ 1*)

for all ionic strengths, use

$\log \gamma_i = ks\mu$

(Equation 3-7)

Correlations for ionic strength

- μ vs. specific conductance: Russell Approximation
  - $\mu = 1.6 \times 10^{-5} \times K$ (in μmho/cm) **Equ 3.3**
- μ vs. TDS: Langlier approximation
  - $\mu \sim 2.5 \times 10^{-5} \times TDS$ (in mg/L) **Equ 3.2**


Corrections to Ion Activity

Approximation	Equation	Applicable Range for I
Debye-Hückel	$\log f = -0.5z^2\sqrt{I}$	$<10^{-2.3}$
Extended Debye-Hückel	$\log f = -0.5z^2 \frac{\sqrt{I}}{1+0.33a\sqrt{I}}$	$<10^{-1}$
Güntelberg	$\log f = -0.5z^2 \frac{\sqrt{I}}{1+\sqrt{I}}$	$<10^{-1}$, solutions of multiple electrolytes
Davies	$\log f = -0.5z^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right)$	<0.5

From Stumm & Morgan, Table 3.3 (pg.103)

0.3, based on Mihelcic

Kinetic model for equilibrium

- Consider a reaction as follows:

$$A + B = C + D$$

- Since all reactions are reversible, we have two possibilities

$$A + B \xrightarrow{k_f} C + D$$
$$A + B \xleftarrow[k_b]{} C + D$$

- The rates are:

$$r_f = k_f\{A\}\{B\} \qquad r_b = k_b\{C\}\{D\}$$

- And at equilibrium the two are equal, $r_f = r_b$

$$k_f\{A\}\{B\} = k_b\{C\}\{D\}$$

- We then define an equilibrium constant (K_{eq})

$$K_{eq} \equiv \frac{k_f}{k_b} = \frac{\{C\}\{D\}}{\{A\}\{B\}}$$

Kinetic model with moles

- In terms of molar concentrations, the rates are:

$$r_f = k_f[A]\gamma_A[B]\gamma_B \qquad r_b = k_b[C]\gamma_C[D]\gamma_D$$

- And at equilibrium the two are equal, $r_f = r_b$

$$k_f[A]\gamma_A[B]\gamma_B = k_b[C]\gamma_C[D]\gamma_D$$

- And solving for the equilibrium constant (K_{eq})

$$K_{eq} \equiv \frac{k_f}{k_b} = \frac{[C]\gamma_C[D]\gamma_D}{[A]\gamma_A[B]\gamma_B} = \frac{[C][D]}{[A][B]}\left(\frac{\gamma_C\gamma_D}{\gamma_A\gamma_B}\right)$$

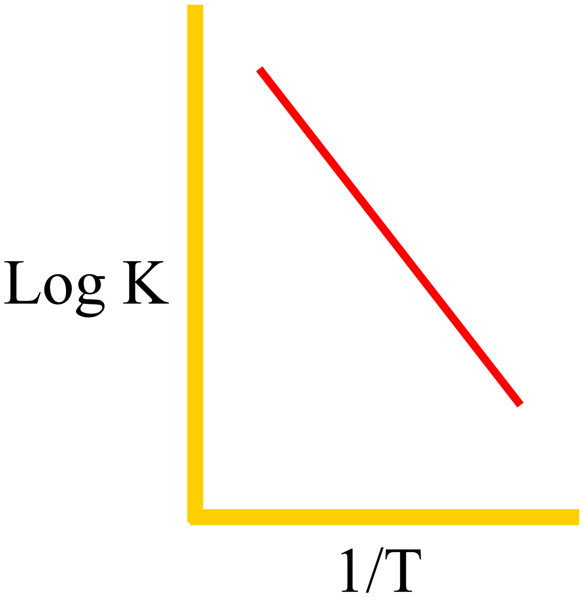
Equilibrium Chemistry

- Tells us what direction the reaction is headed in
- Doesn't tell us how fast the reaction is going (kinetics)
- Solving equilibrium problems
  - identify reactants and products
  - formulate equations
    - equilibrium equations
    - mass balance equations
    - electroneutrality equation
  - solve equations

Temperature Effects on K

- Need ΔH (enthalpy change)
  - $\Delta H < 0$, exothermic (heat evolved)
  - $\Delta H > 0$, endothermic (heat absorbed)
- The Van't Hoff Equation:

$$\log \frac{K_2}{K_1} = \frac{\Delta H^o (T_2 - T_1)}{2.303 R T_2 T_1}$$



  - recall that:

$$\Delta H^o = \sum \nu_i \Delta H_f^o$$

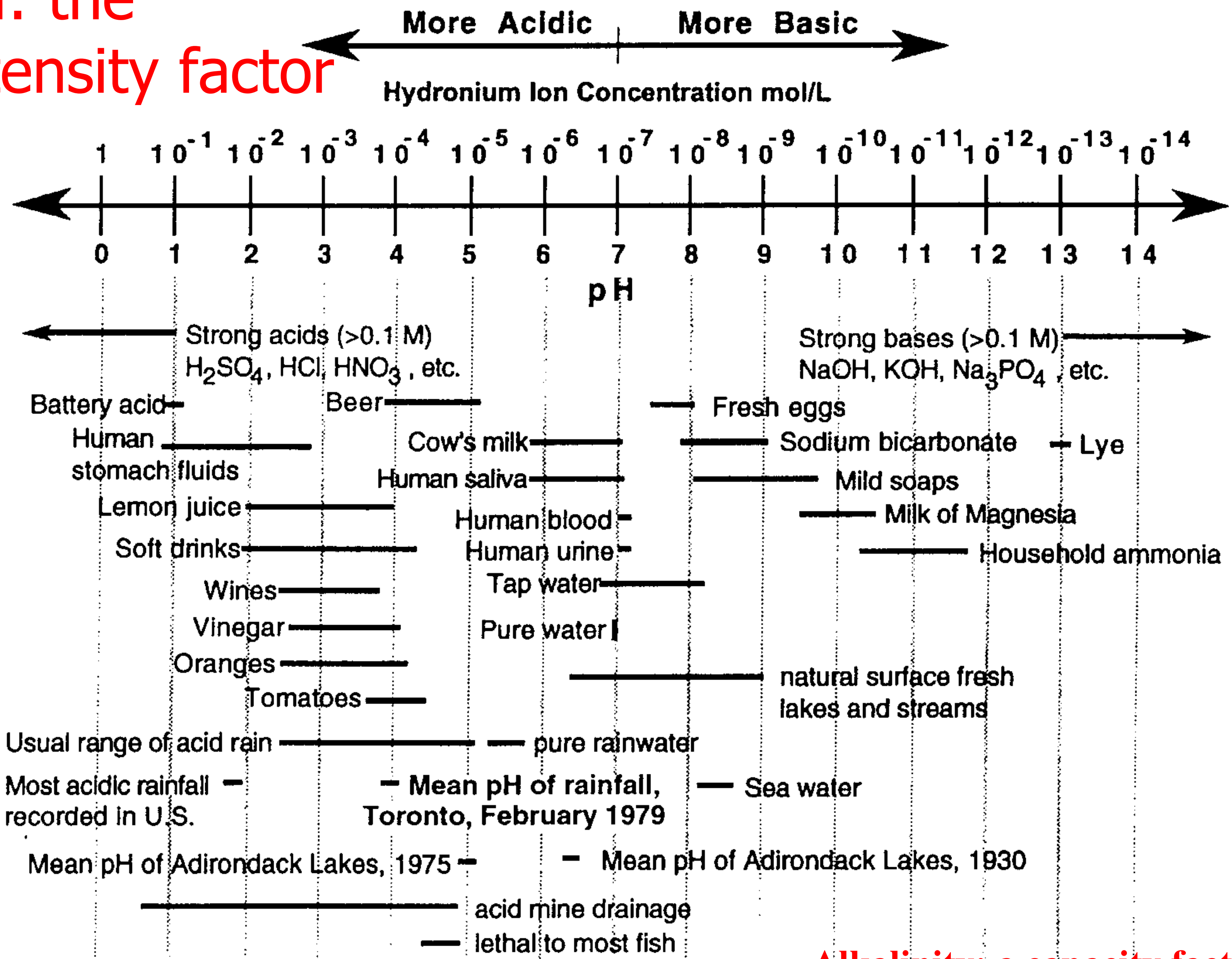
Acids & Bases

- pH of most mineral-bearing waters is 6 to 9. (fairly constant)
- pH and composition of natural waters is regulated by reactions of acids & bases
  - chemical reactions; mostly with minerals
    - carbonate rocks: react with CO_2 (an acid)
      - $CaCO_3 + CO_2 = Ca^{+2} + 2HCO_3^-$
    - other bases are also formed: NH_3, silicates, borate, phosphate
    - acids from volcanic activity: HCl, SO_2
  - Biological reactions: photosynthesis & resp.
  - Sillen: Ocean is result of global acid/base titration

Acids & Bases (cont.)

- Equilibrium is rapidly established
  - proton transfer is very fast
- we call $[H^+]$ the Master Variable
  - because Protons react with so many chemical species, affect equilibria and rates
- Strength of acids & bases
  - strong acids have a substantial tendency to donate a proton. This depends on the nature of the acid as well as the base accepting the proton (often water).

pH: the intensity factor



Alkalinity: a capacity factor

Mathematical Expression of Acid/Base Strength

- Equilibrium constant
  - acids: $HA = H^+ + A^-$
    - $HCl + H_2O = H_3O^+ + Cl^-$
    - $HCl = H^+ + Cl^-$

$$K_a = \frac{[H^+][Cl^-]}{[HCl]} \approx 10^3$$

  - Bases: $B + H_2O = BH^+ + OH^-$
    - $NH_3 + H_2O = NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 10^{-4.76}$$

Thermodynamics & Equilibrium

- Classical Thermodynamics
- Ideal Gas Law
- Equilibrium Chemistry
  - Working with equations
  - Phase Transfer
  - Acids/Bases
    - The Carbonate System
  - Precipitation/Dissolution
  - Adsorption

Review material on your own

Enthalpy or heat of reaction

For a generic reaction:

$$aA + bB \rightarrow pP + rR$$

$$\Delta H^\circ_{rxn} = (p\Delta H^\circ_P + r\Delta H^\circ_R) + (a\Delta H^\circ_A + b\Delta H^\circ_B)$$

where,

A,B	=	reactant species
P,R	=	product species
a,b	=	stoichiometric coefficients of the reactants
p,r	=	stoichiometric coefficients of the products
$\Delta H^\circ_{A,B}$	=	enthalpy of reactants A and B
$\Delta H^\circ_{P,Q}$	=	enthalpy of products P and Q

Enthalpy (cont.)

Or more generally:

$$\Delta H^\circ_{rxn} = \sum_{i=1}^{n} a_i \Delta H^\circ_{prod} - \sum_{j=1}^{m} a_j \Delta H^\circ_{rxtnts}$$

where,

a_i = stoichiometric coefficient of product species i

a_j = stoichiometric coefficient of reactant species j

ΔH°_i = enthalpy of product species i, [kcal/mol]

ΔH°_j = enthalpy of reactant species j, [kcal/mol]

Thermo-dynamic Constants

Species	ΔG°, kcal/mol	ΔH°, kcal/mol
Ca^{2+}(aq)	-132.18	-129.77
$CaCO_3$(s), calcite	-269.78	-288.45
$Ca(OH)_2$(s), lime	-214.7	-235.7
CO_2(g)	-94.26	-94.05
CO_2(aq)	-92.31	-98.69
CO^{-}(aq)	-126.2	-161.6
Cl^{-}(aq)	-31.3	-40.0
Cl_2(aq)	-19.1	-28.9
OCl^{-}(aq)	-8.8	-25.6
H^{+}(aq)	0	0
HNO_3(aq)	-26.6	-25.0
NO(aq)	-26.6	-49.5
HOCl(aq)	-19.1	-28.9
OH^{-}(aq)	-37.6	-55.0
O_2(aq)	3.9	-2.67
H_2O(l)	-56.7	-68.3
H_2(g)	0	0
O_2(g)	0	0

Table 4.2, pg. 57

Thermodynamic Constants for Species of Importance in Water Chemistry (Table 3-1 from Snoeyink & Jenkins) Part I

Species	$\Delta \overline{H}_f^o$ kcal/mole	$\Delta \overline{G}_f^o$ kcal/mole	Species	$\Delta \overline{H}_f^o$ kcal/mole	$\Delta \overline{G}_f^o$ kcal/mole
Ca^{+2}(aq)	-129.77	-132.18	CO_3^{-2} (aq)	-161.63	-126.22
$CaC0_3$(s), calcite	-288.45	-269.78	CH_3COO^-, acetate	-116.84	-89.0
CaO (s)	-151.9	-144.4	H^+ (aq)	0	0
C(s), graphite	0	0	H_2 (g)	0	0
CO_2(g)	-94.05	-94.26	Fe^{+2} (aq)	-21.0	-20.30
CO_2(aq)	-98.69	-92.31	Fe^{+3} (aq)	-11.4	-2.52
CH_4 (g)	-17.889	-12.140	$Fe(OH)_3$ (s)	-197.0	-166.0
H_2CO_3 (aq)	-167.0	-149.00	Mn^{+2} (aq)	-53.3	-54.4
HCO_3^- (aq)	-165.18	-140.31	MnO_2 (s)	-124.2	-111.1

Conversion: 1kcal = 4.184 kJ

Thermodynamic Constants for Species of Importance in Water Chemistry (Table 3-1 from Snoeyink & Jenkins) Part II

Species	$\Delta \overline{H}_f^o$ kcal/mole	$\Delta \overline{G}_f^o$ kcal/mole	Species	$\Delta \overline{H}_f^o$ kcal/mole	$\Delta \overline{G}_f^o$ kcal/mole
Mg^{+2} (aq)	-110.41	-108.99	O_2 (g)	0	0
$Mg(OH)_2$ (s)	-221.00	-199.27	OH^- (aq)	-54.957	-37.595
NO_3^- (aq)	-49.372	-26.43	H_2O (g)	-57.7979	-54.6357
NH_3 (g)	-11.04	-3.976	H_2O (l)	-68.3174	-56.690
NH_3 (aq)	-19.32	-6.37	SO_4^{-2}	-216.90	-177.34
NH_4^+ (aq)	-31.74	-19.00	HS (aq)	-4.22	3.01
HNO_3 (aq)	-49.372	-26.41	H_2S(g)	-4.815	-7.892
O_2 (aq)	-3.9	3.93	H_2S(aq)	-9.4	-6.54

Conversion: 1kcal = 4.184 kJ

Gibbs Free Energy

$$\Delta G = \Delta H - T\Delta S$$

where,

ΔG = Gibbs free energy, [kcal/mol]

ΔH = enthalpy, [kcal/mol]

ΔS = entropy, [kcal/K-mol]

T = temperature, [K]

Gibbs Free Energy

- Combines enthalpy and entropy
  - 1st and 2nd laws of thermodynamics
- Determines whether a reaction is favorable or spontaneous
- Practical form is based on an arbitrary datum
  - the pure and most stable form of each element at standard state

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Reactions under Standard State Conditions

$$aA + bB \rightarrow pP + rR$$

$$\Delta G^\circ_{rxn} = (p\Delta G^\circ_P + r\Delta G^\circ_R) - (a\Delta G^\circ_A + b\Delta G^\circ_B)$$

where,

A,B	=	reactant species
P,R	=	product species
a,b	=	stoichiometric coefficients of the reactants
p,r	=	stoichiometric coefficients of the reactants
$\Delta G^\circ_{A,B}$	=	Gibbs free energy of reactants A and B
$\Delta G^\circ_{P,Q}$	=	Gibbs free energy of reactants P and Q

General Equation

$$\Delta G^\circ_{rxn} = \left(\sum_{i=1}^{n} a_i \Delta G^\circ_i\right)_{prod} - \left(\sum_{j=1}^{m} a_j \Delta G^\circ_j\right)_{rxtnts}$$

where,

a_i = stoichiometric coefficient of product species i

a_j = stoichiometric coefficient of reactant species j

ΔG°_i = standard Gibbs free energy of product species i, [kcal/mol]

ΔG°_j = standard Gibbs free energy of reactant species j, [kcal/mol]

Non-standard state conditions

$$\Delta G = \Delta G^\circ + RT \ln \frac{P^p R^r}{A^a B^b}$$

And we define:

$$Q = \frac{P^p R^r}{A^a B^b}$$

At equilibrium, $\Delta G=0$, and $Q=K_{eq}$

$$\Delta G^\circ = -RT \ln K_{eq}$$

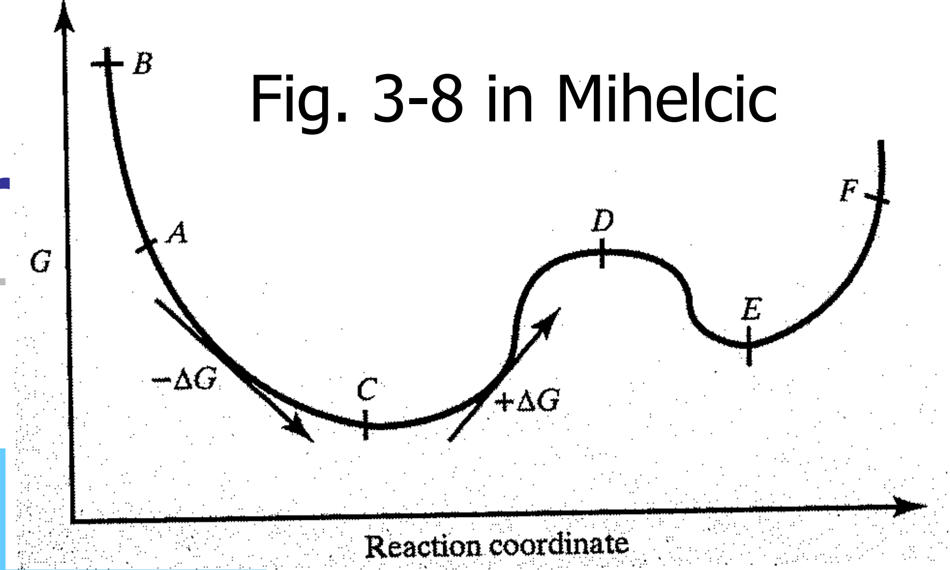
End

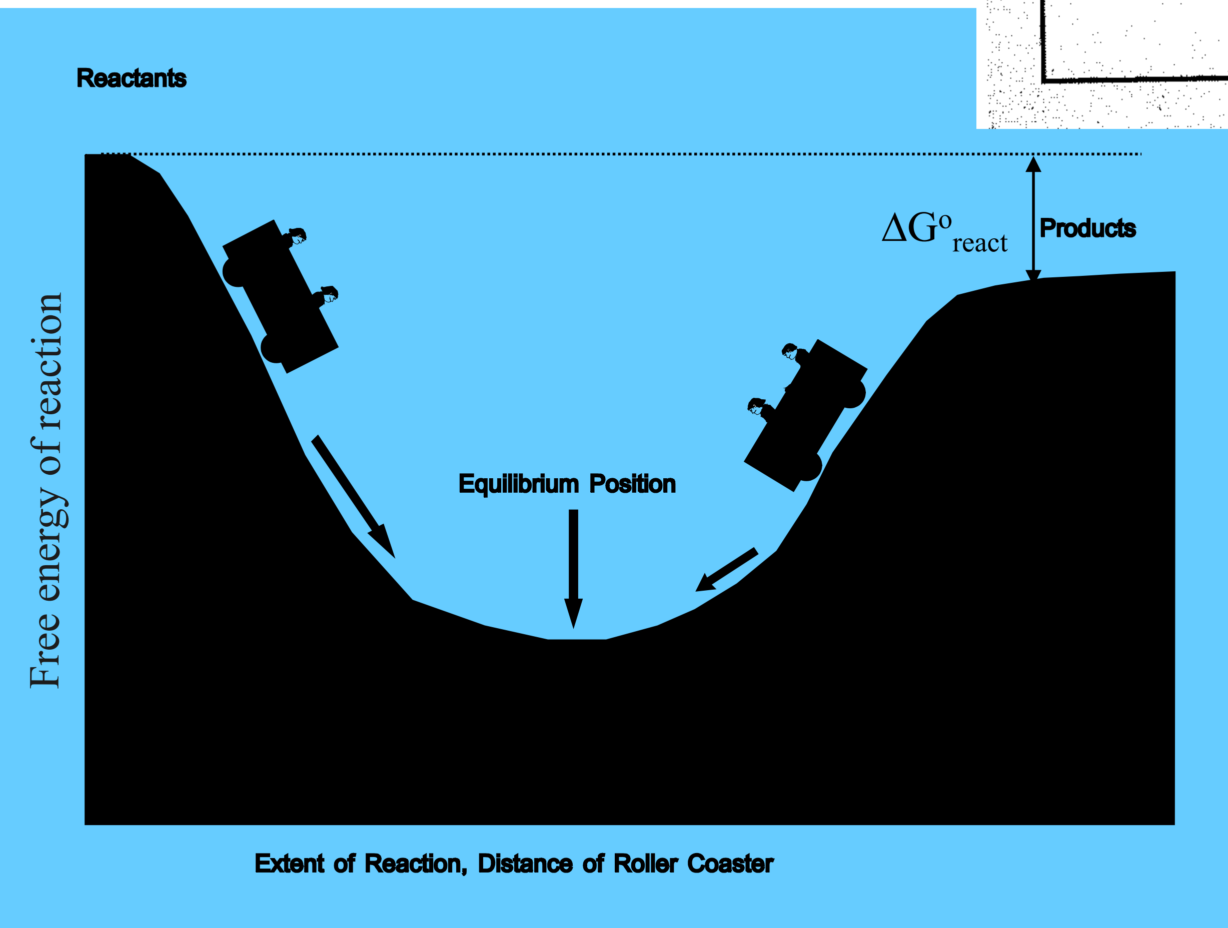
equilibria

What are standard state conditions?

Parameter	Standard State or Condition
Temperature	25°C
Gas	1 atm
Solid	Pure solid
Liquid	Pure liquid
Solution	1 M
Element*	0

Roller Coaster Analogy





A reaction with a negative ΔG will proceed from reactants to products. A reaction with a positive ΔG will proceed from products to reactants (backwards). A reaction in which ΔG is zero is at equilibrium

Temperature effects

- Increases in temperature cause:
  A. Increases in solubility of salts
  B. Decreases in solubility of salts
  C. Depends on the salt

Temperature effects

- Increases in temperature cause:
  A. Increases in solubility of dissolved gases
  B. Decreases in solubility of dissolved gases
  C. Depends on the gas

Lime Example

Lime, or calcium hydroxide, is commonly used to improve sedimentation processes or to precipitate toxic metals. A 500 L reaction vessel contains an excess amount of solid calcium hydroxide. The solution contains 10^{-8} M of Ca^{2+} and 10^{-8} M of OH^{-}. Is the lime still dissolving, is the solution at equilibrium, or is lime precipitating?

$$Ca(OH)_2(s) \rightarrow Ca^{2+} + 2OH^{-}$$

Example 4.6 from Ray

Solution to Lime example

First calculate the Gibbs Free Energy under standard state conditions

$$\Delta G^\circ_{rxn} = (\Delta G^\circ_{Ca^{2+}} + 2\Delta G^\circ_{OH^-}) - \Delta G^\circ_{Ca(OH)_2}$$

$$\Delta G^\circ_{rxn} = [(-132.3 \text{ kcal/mol}) + 2 \times (-37.6 \text{ kcal/mol}) - (-214.7 \text{ kcal/mol})]$$

$$\Delta G^\circ_{rxn} = +7.22 \text{ kcal/mol}$$

Solution (cont.)

Now we need to adapt to actual conditions:

$$\Delta G = \Delta G^\circ + RT \ln \frac{P^p R^r}{A^a B^b}$$

$$Ca(OH)_2(s) \rightarrow Ca^{2+} + 2OH^-$$

$$\Delta G_{rxn} = \Delta G^\circ + RT \ln [Ca^{2+}][OH^-]^2$$

$$\Delta G_{rxn} = (7.22 \frac{kcal}{K\text{-}mol}) + (1.987 \frac{cal}{K\text{-}mol}) \text{ x } (\frac{kcal}{1000\ cal}) \text{ x } (298\ K) \text{ x } \left(\ln (10^{-8})(10^{-8})^2\right)$$

$$\Delta G_{rxn} = -13.2 \text{ kcal/ mol}$$

Since ΔG is negative, the reaction will proceed as written

Kinetics & Equilibrium

- Kinetics
  - Rates of reactions
  - Dynamic, complex
  - Best approach for slow reactions
    - Oxidation reactions, biochemical transformations, photochemical reactions, radioactive decay
- Equilibrium: thermodynamics
  - Final stopping place
  - Static, simple
  - Best approach for fast reactions
    - Acid/base reaction, complexation, some phase transfer

DO Example

A polluted stream with a temperature of 25°C has a dissolved oxygen concentration of 4 mg/L. Use Gibbs free energy to determine if oxygen from the atmosphere is dissolving into the water, the oxygen is at equilibrium, or oxygen from the stream is going into the atmosphere.

$$O_2(aq) \rightarrow O_2(g)$$

Example 4.7 from Ray

Solution to DO example

$$\Delta G^\circ_{rxn} = \Delta G^\circ_{O_2(g)} - \Delta G^\circ_{O_2(aq)} = (0 \frac{kcal}{mol}) - (-3.9 \frac{kcal}{mol})$$

$$\Delta G^\circ_{rxn} = 3.9 \frac{kcal}{mol}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{p_{O_2}}{[O_2(aq)]}$$

$$[O_2(aq)] = 4 \frac{mg\ O_2}{L} \times \frac{g\ O_2}{1000\ mg\ O_2} \times \frac{mol\ O_2}{32\ g\ O_2} = 1.25 \times 10^{-4}\ M$$

Solution (cont.)

$$\Delta G = -3.9 \frac{kcal}{mol} \times \frac{1000\ cal}{kcal} + \left(1.987 \frac{cal}{K\text{-}mol}\right)(298\,K)\ \ln\left(\frac{0.209\ atm}{1.25 \times 10^{-4}\ M}\right)$$

$$\Delta G = 491 \frac{cal}{mol} > 0$$

Since ΔG is positive, the reaction will proceed in the reverse direction as written. From the atmosphere to the water.

- To next lecture