Chemical Equilibrium…Review?

Most chemical systems are governed by equilibria such that if:

$$aA + bB \rightleftharpoons cC + dD, \text{ then}$$

$$\frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b} = K$$

where K is the equilibrium constant, and a_X is the *activity* of X and described by the activity coefficient γ_X and [X]:

$$a_X = \gamma_X [X]$$

In dilute solutions, the activity coefficient approaches unity. Often, experimental conditions allow us to assume activity coefficients of one so that concentrations can be substituted for activities.
(This assumption isn't always good!)

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

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Chemical Equilibrium

So, knowledge of reaction stoichiometry and the equilibrium constant allows us to make some predictions about the system.

If K is very large, that the equilibrium lies far to the right (or towards products). If K is small, the reaction lies towards reactants.

For example, the KHP we are using in lab is a monoprotic acid that undergoes the following equilibrium:

$$HP^- + H_2O \rightleftharpoons H_3O^+ + P^{2-}$$

$$K = \frac{[H_3O^+][P^{2-}]}{[HP^-]} = 3.9 \times 10^{-6}$$

From the small magnitude of K, the equilibrium must lie to the left, which makes sense, since KHP is a *weak* acid.

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Manipulating Equilibria

It is possible to drive a reaction towards reactions or products by applying an appropriate stress to the system.

- **Le Chatlier's Principle**
- In the KHP titration, the *stress* is the loss of hydronium ion via neutralization with NaOH
  - What happens when we add NaOH?

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Quantitative Predictions

Assume we are at a point in the titration where $[HP^-] = 0.095M$, $[P^{2-}] = 0.00013M$, and $[H_3O^+] = 0.00029M$.

$$K = \frac{0.00029 \times 0.00013}{0.095} = 3.9 \times 10^{-6}$$

Now lets add enough NaOH to drop the $[H_3O^+]$ to =0.00014M, what does the reaction have to do to regain equilibrium?

Calculate a reaction quotient Q, (the equilibrium constant expression with non-equilibrium concentrations plugged in).

- If Q>K, the reaction must proceed to the left
- If Q<K, the reaction must proceed to the right
- If Q=K the reaction is at equilibrium

In our case,

$$Q = \frac{0.00014 \times 0.00013}{0.095} = 1.9 \times 10^{-7}$$

Q<K so the reaction must proceed to the right!

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Important items to remember regarding equilibrium constant expressions

1. Take care when assuming unit activity coefficients!
2. All solute concentrations should be in moles per liter
3. All gas concentrations should be in atmospheres
4. By convention, all K's are calculated relative to 1 M solutions or 1 atm gas, so the resulting constants are dimensionless
5. Concentrations of pure solids, pure liquids and solvents are omitted from the equilibrium constant expression.

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Equilibrium and Thermodynamics

ALWAYS REMEMBER: **Equilibrium constant expressions are *thermodynamic relations.***

So, they can provide information related to the _____

of a reaction to proceed, but say nothing about the _____.

Relating equilibrium constants and thermodynamic properties:

- Enthalpy
- Entropy
- Free Energy

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Thermodynamic Parameters

Enthalpy, ΔH:
"Heat" of reaction

If ΔH is positive, heat is absorbed (acts as a reactant), reaction is *endothermic*
If ΔH is negative, heat is released (acts as a product), reaction is *exothermic*

Entropy, ΔS:
"Disorder" of reaction

If ΔS is positive, products have greater entropy than reactants
If ΔS is negative, reactants have greater entropy than products

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Thermodynamic Parameters

The combination of entropy and enthalpy in a given reaction determine whether the reaction is spontaneous, or *thermodynamically favorable*.

This combination is the **Gibbs free energy** change in the system.

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

If ΔG is positive, the reaction is
If ΔG is negative, the reaction is

How do these situations occur?

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Free Energy and Equilibrium

$\Delta G° = -RT \ln(K)$, or

$$K = e^{-\Delta G^o / RT}$$

If K is large (>1), ln(K) is positive, and $\Delta G°$ is negative $\Rightarrow$ the reaction lies towards products.

If K<1 (small), ln(K) is negative, $\Delta G°$ is now positive, and the reaction lies to the left.

For KHP at 25°C,

$\Delta G° = -RT\ln(3.9 \times 10^{-6}) = - 8.3144 J/molK \times 298K \times -12.4545$

$\Delta G° = -(-30858.5 J/mol) = 30.9 kJ/mol$

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Solubility Equilibria

The *solubility product* describes the concentrations of species present when ions are in equilibrium with undissolved salt.

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$$[Ca^{2+}][CO_3^{2-}] = K_{sp} = 6.0 \times 10^{-9}$$

What is the concentration of calcium ion in a saturated solution of calcium carbonate?

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Solubility Equilibria

How does this concentration change if the solution originally contained 0.010 F Li_2CO_3?

This presence of carbonate results in a *common ion effect*.

- What does Le Chatlier's principle say should happen?
- How do we verify this quantitatively?

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Rules of Thumb Regarding Approximations

What does "<<" mean? Why make the approximation?

- It depends on the accuracy needed in the calculation.
- For example, if 1000x = y, then x is (1/1000)*100% = 0.1% of y, so if 99.9% accuracy is acceptable, x must be 1000 times less than y for "x << y"
- If 99% is acceptable, x<<y if x is 100 times less than y.
- Always document your approximations!
- Always check your approximations
  - Be sure x really is << y!

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Separation by Precipitation

- It is possible to quantitatively separate two or more species based on their solubility.
  - Ability to do so is related to the magnitudes of the K_{sp} for each ion.

Example: Is it *feasible* to perform a 99% complete separation of 0.010M Ca^{2+} from 0.010M Ce^{3+} by precipitation with oxalate ($C_2O_4^{2-}$)?

CaC_2O_4 $K_{sp} = 1.3 \times 10^{-8}$

$Ce_2(C_2O_4)_3$ $K_{sp} = 3.0 \times 10^{-29}$

Questions to ask:

1. What ion will precipitate first?

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Separation by Precipitation

2. What concentration of oxalate is needed to reduce the Ce^{3+} concentration to 1% of its initial value?

$$Ce_2(C_2O_4)_3 \rightleftharpoons 2Ce^{3+} + 3C_2O_4^{2-} \quad K_{sp} = 3.0 \times 10^{-29}$$

3. Will calcium precipitate at this oxalate concentration?

$$CaC_2O_4 \rightleftharpoons Ca^{2+} + C_2O_4^{2-} \qquad K_{sp} = 1.3 \times 10^{-8}$$

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Acids, Bases and Equilibria

Definitions (several):

1. Lewis - Electrons
2. Bronsted - Protons

Conjugate Acid-Base Pairs and Neutralization Reactions

Solvent Autoprotolysis or self-ionization

- Water is the most common:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

- Also occurs in all *protic* solvents.

$$2\ CH_3CH_2OH \rightleftharpoons CH_3CH_2OH_2^+ + CH_3CH_2O^-$$

pH

$$pH = -\log [H^+] \text{ (really activity of } H^+)$$

$$pH + pOH = pK_w = 14.00 \text{ at } 25^oC$$

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Acid and Base Strength

Based on percent dissociation in solution

- *Strong* acids/bases dissociate essentially completely in water
- *Weak* acids/bases only partially dissociate, results in equilibrium concentrations of both the acid and its conjugate base

Fraction of Dissociation:

Know the strong acids and bases in Table 6-2

TABLE 6-2 Common strong acids and bases

Formula	Name
Acids	
HCl	Hydrochloric acid (hydrogen chloride)
HBr	Hydrogen bromide
HI	Hydrogen iodide
H_2SO_4[a]	Sulfuric acid
HNO_3	Nitric acid
$HClO_4$	Perchloric acid
Bases	
LiOH	Lithium hydroxide
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
RbOH	Rubidium hydroxide
CsOH	Cesium hydroxide
R_4NOH[b]	Quaternary ammonium hydroxide

a. For H_2SO_4, only the first proton ionization is complete. Dissociation of the second proton has an equilibrium constant of 1.0×10^{-2}.

b. This is a general formula for any hydroxide salt of an ammonium cation containing four organic groups. An example is tetrabutylammonium hydroxide: $(CH_3CH_2CH_2CH_2)_4N^+OH^-$.

Harris, *Quantitative Chemical Analysis*, 8e
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Weak Acid/Base Equilibria

Weak Acid

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Examples:

Weak Base
(hydrolysis reaction)

$B + H_2O \rightleftharpoons BH^+ + OH^-$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Examples:

Relationship between K_a and K_b for conjugate acid/base pairs:

$$K_a \times K_b = K_W$$

Polyprotic acids/Polybasic bases (K_{a1}, K_{a2} …)

$H_3PO_4 = H^+ + H_2PO_4^-$ $K_{a1} = 7.11 \times 10^{-3}$
$H_2PO_4^- = H^+ + HPO_4^{2-}$ $K_{a2} = 6.32 \times 10^{-8}$
$HPO_4^{2-} = H^+ + PO_4^{3-}$ $K_{a3} = 7.1 \times 10^{-13}$

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Complexation Equilibria

Formation of coordinate bonds between Lewis Acids/Bases
Can be described by **step-wise** or **cumulative** formation constants

$M + X \rightleftharpoons MX$ $K_1 =$

$MX + X \rightleftharpoons MX_2$ $K_2 =$ $M + 2X = MX_2$ $\beta_2 =$

$MX_{n-1} + X \rightleftharpoons MX_n$ $K_n =$ $M + nX = MX_n$ $\beta_n =$

Influence on solubility:

Example: How many grams of Iron (II) Sulfide can be dissolved in 100.0 mL of 0.10 F KCl?

$Fe^{2+} + Cl^- \rightleftharpoons FeCl^+$ $K_f = 2.51$
$FeS \rightleftharpoons Fe^{2+} + S^{2-}$ $K_{sp} = 6.0 \times 10^{-18}$

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Tune-up Problems

What are the pH, pOH of a 0.015 F solution of benzoic acid?

What is the pH of a solution prepared by mixing 100 mL of 0.010 F acetic acid with 25 mL 0.010 F sodium hydroxide?

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