

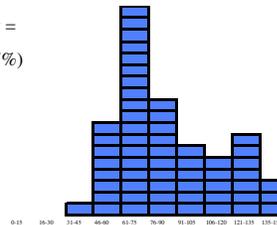
Lecture 5a

Last time:
Calculations for pH curve diprotic acids

Today:
Share-pair seating!
 K_{sp} equilibrium
Intro to Thermodynamics
Entropy

Midterm #1

Average \pm std dev =
 86 ± 27 (58% \pm 17%)
Highest = 136
Rough scale
A ≥ 120
B ≥ 100
C ≥ 65



Field trip to LA COUNTY SANITATION WATER DISTRICT

WHEN: July 27, 2009 - Monday

TIME: assemble 2:05pm;

2:15-3:30 pm-visit treatment plant

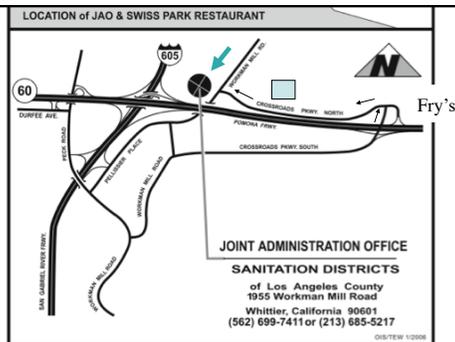
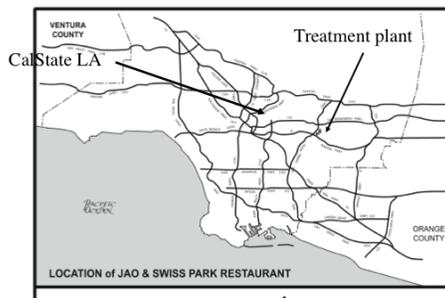
WHERE: 1965 So. Workman Mill Road, Whittier, CA
(closest exit: Crossroads at 60 Fwy, just east of 605 Fwy)

WHAT: Visit San Juan Creek Water Quality Laboratory.

EXTRA CREDIT? Yes. 15-25 points

Pls. sign up if you are interested.

Map to the place



Solubility and K_{sp}

K_{sp} equilibrium used for *sparingly soluble* ionic compounds.

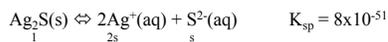
In the sequence: solid \rightleftharpoons aqueous ions

K_{sp} equilibrium constant is a *constant*. The smaller K_{sp} is, the less soluble (for the same stoichiometry of K_{sp})

Solubility (molar) is measure of moles of *formula units* of the compound dissolved per liter.

Example: K_{sp} equilibrium of Ag_2S

K_{sp} for Ag_2S is written:



In a saturated sol'n of Ag_2S in pure water, $[Ag^+] = ?$, etc

$$K_{sp} = [Ag^+]^2[S^{2-}] = 8 \times 10^{-51} = (2s)^2 (s) = 4s^3$$

$$s = \sqrt[3]{(8 \times 10^{-51} / 4)} = 1.3 \times 10^{-17} M \quad (\text{this is the "solubility"})$$

$$[S^{2-}] = 1.3 \times 10^{-17} M \quad \text{and}$$

$$[Ag^+] = 2s = 2(1.3 \times 10^{-17} M) = 2.6 \times 10^{-17} M \quad \text{n.b. } pAg^+ = -\log[Ag^+]$$

$$\text{What is } pAg^+? \quad pAg^+ = -\log[Ag^+] = 16.90$$

Q & K_{sp} determine if pptn occurs

Previous example: $[Ag^+] = 2.6 \times 10^{-17}$ and $[S^{2-}] = 1.3 \times 10^{-17} M$

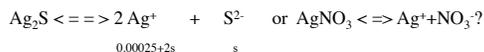
These are determined by K_{sp} and apply to *saturated* solutions

If $Q = [Ag^+]^2[S^{2-}] > K_{sp} \Rightarrow$ supersaturated, precipitn occurs

If $Q < K_{sp}$ precipitation does not occur.

Sample problem: common ion

Suppose we add Ag_2S crystals to a 0.00025M $AgNO_3$ solution, what is the solubility of Ag_2S ? Start with K_{sp} equilibrium!



$$K_{sp} = [Ag^+]^2[S^{2-}] = 8 \times 10^{-51} = (0.00025 + 2s)^2 (s) \approx (0.00025)^2 (s)$$

$$s = 1.3 \times 10^{-43} \quad (\text{compare to } 1.3 \times 10^{-17} M \text{ in pure water})$$

Here, $pAg^+ = 42.90$ (compare to 16.90 in pure water).

Common ion effect decreases solubility

Example: precipitation with 2 substances. $BaSO_3$ and $BaSO_4$.

If you can precipitate 2 different substances in a solution, the first to precipitate will be the less soluble one.

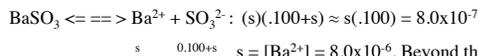
Sample Problem: A solution contains 0.100M Na_2SO_4 and 0.100M K_2SO_3 . Upon addition of Ba^{2+} ions to the solution, which will precipitate first? What percent of the ions will remain before the other ion starts to precipitate? (K_{sp} 's: $BaSO_4 = 1.1 \times 10^{-10}$ and $BaSO_3 = 8.0 \times 10^{-7}$)

Solution:

Solution to previous problem

Given: K_{sp} 's: $BaSO_4 = 1.1 \times 10^{-10}$ and $BaSO_3 = 8.0 \times 10^{-7}$.

$BaSO_4$ ppts first since $1.1 \times 10^{-10} < 8.0 \times 10^{-7}$. 2nd question: What % SO_4^{2-} is ppted before other ion ppts? When does $BaSO_3$ form?



$s = [Ba^{2+}] = 8.0 \times 10^{-6}$. Beyond that, $Q > K_{sp}$ and $BaSO_3$ ppts. So what's SO_4^{2-} ?

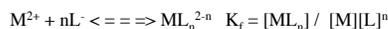
$$K_{sp} = 1.1 \times 10^{-10} = (8.0 \times 10^{-6}) [SO_4^{2-}]$$

$$\Rightarrow [SO_4^{2-}] = (1.1 \times 10^{-10}) / (8.0 \times 10^{-6}) = 1.4 \times 10^{-5};$$

$$\Rightarrow \% = (1.4 \times 10^{-5} M) / (0.100 M) \times 100 = 0.014\% \text{ free, } 99.986\% \text{ ppted.}$$

K_f = formation constant

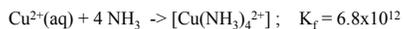
Formation of complex coordinate covalent compounds is described by K_f the formation constant. It is written as:



Carefully note which side contains the complex. K_f usually large.

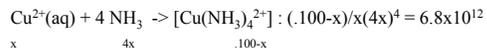
Example of K_f calculation

Consider the formation of copper tetraammine complex:



What is acting as a Lewis acid? Lewis base?

What is the free Cu^{2+} concentration in a solution containing 0.100 M $[\text{Cu}(\text{NH}_3)_4]^{2+}$? (use ICE):



$$256 x^5 \approx (0.100) / 6.8 \times 10^{12} = 1.5 \times 10^{-14}; \quad x^5 = 5.7 \times 10^{-17}$$

$$x = [\text{Cu}^{2+}]_{\text{free}} = 5.6 \times 10^{-4} \text{ M}; \quad \text{pCu}^{2+} = 3.25$$

Chapter 18: Thermochemistry

We already know:

Enthalpy

Kinetic energy

Conservation of energy

What is entropy? A measure of "disorder", the greater the disorder, the greater the entropy.

Reactions: Reactant- or product-favored?

Describe the following:

- 1) Melting of ice to water at 5°C: $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$
- 2) Freezing of water to ice at 5°C
- 3) Dissolution of AgCl in 1M AgCl, $K_{sp} = 1.8 \times 10^{-10}$
- 4) Burning of paper at room temp and 1 atm.
- 5) Dissolving of sugar in water at room temperature.
 $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) \rightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{aq})$

What determines direction of reaction?

- (a) whichever disperses energy more!
- (b) Whichever disperses matter more!
- (c) (information): whichever randomizes information more

Entropy

Measuring the dispersal of energy: S, entropy:

concept of **entropy**: state of *disorder*

- * dispersal of matter
- * dispersal of energy
- * dispersal of information

Reactions occur toward greater overall entropy

Comparing the entropy of substances

Which has greater entropy (assuming equal mass)

Solid vs Liquid vs Gas

Many small molecules vs one large molecule

Pure liquid + a crystal solute vs a solution of solute

Calculating Entropy change, ΔS

Calculation of ΔS :

$$\Delta S = S_f - S_i = Q_{rev}/T$$

Q_{rev} = heat transferred

if $\Delta S = 0$ for a rxn, it is reversible

if $\Delta S > 0$ it is irreversible (spontaneous, product favored)

For product favored reactions: $\Delta S > 0$

For a reaction to be spontaneous, to be product favored, $\Delta S_{universe} > 0$ (irreversible reaction, product-favored)

If $\Delta S_{univ} = 0$ (reversible)

If $\Delta S_{univ} < 0$ (nonspontaneous, reactant-favored)

Example: ice cube melting in a glass of cold (0°C) water in a 25°C room

$$\Delta S \text{ for the glass} = \Delta S_{\text{glass}} = Q_{\text{glass}} / 273 \text{ K}$$

$$\Delta S \text{ for the room} = \Delta S_{\text{room}} = -Q_{\text{room}} / 298 \text{ K}$$

$$\text{Net } \Delta S_{\text{net}} = \Delta S_{\text{glass}} + \Delta S_{\text{room}} = Q/273 - Q/298 > 0$$

Therefore the reaction is spontaneous.

Note: the glass is the **system** and the room + all the "rest" make up the **environment**. The sum total of the system and environment is the **universe**.

Calculate ΔS for the melting of ice at 273K ?

At $T=273$, ice and water coexist (it's the melting point)

Molar enthalpy of fusion, $\Delta H_{\text{fus}}^\circ$ of water is: 6020 J/mol

So per 1 mole of water: $Q = n\Delta H_f = (1\text{mol})(6020\text{J/mol})$

$$\Rightarrow \Delta S = \Delta H_{\text{fus}}^\circ / T$$

$$\Delta S = (1\text{mol})(6020\text{J})/273\text{K} = 22.0 \text{ J/K}$$

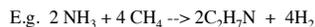
melting 1 mole of ice to 1 mole of water increases the entropy by 22.0 J/K (note unit of entropy)

Calculating reaction $\Delta S_{\text{rxn}}^\circ$ from absolute entropy S_f°

Every substance has an absolute entropy, S_f° that can be determined. Listed in tables (for standard conditions).

ΔS_{system} can be calculated for a reaction: We call it $\Delta S_{\text{rxn}}^\circ$

$$\Delta S_{\text{rxn}} = \sum n S_f^\circ(\text{prod}) - \sum m S_f^\circ(\text{rxt})$$



$$\Delta S_{\text{rxn}} = 4 S_f^\circ(\text{H}_2) + 2 S_f^\circ(\text{C}_2\text{H}_7\text{N}) - 2 S_f^\circ(\text{NH}_3) - 4 S_f^\circ(\text{CH}_4)$$

If there are more than 1 physical state, note that in the tables.

2nd Law of Thermodynamics

States: all processes lead to an increase in ΔS of the universe

Reversible processes: $\Delta S_{\text{univ}} = 0$; Irrev proc's: $\Delta S_{\text{univ}} > 0$

Consider the following derivation: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{env}} \geq 0$

But $\Delta S_{\text{env}} = -Q/T$ (Q = heat gained by system from env)

At const T and P , $Q = \Delta H$ (enthalpy)

So: $\Delta S_{\text{sys}} - \Delta H/T \geq 0$ or, $T\Delta S - \Delta H \geq 0$ or $\Delta H - T\Delta S \leq 0$

Define G such that: $\Delta G = \Delta H - T\Delta S \leq 0$ (G = Gibb's Free E).

Gibb's free energy