CH302 Exam 3 Review

SOLUBILITY EQ, KINETICS, NUCLEAR

pH = -log[H+]

14 = pH + pOH

Exam Three Breakdown

20 Q's → Dr. McCord

30% Ksp

45% Kinetics

25% nuclear

11 calc, 9 concept

Dr. B

30% Ksp

45% Kinetics

25% inorganic

9 calc, 11 concept

Don't Study: TTH Keq w/ mechanisms

Dr. B → Q17 HW09 (don't study gchem)

McCord → nuclear applications

DO KNOW → basics of nuclear power plant & bomb

Chill wave: Astral throb, asthenic, odysseus

Lofi: Chilled Cow, Chilldhop Music, Mellowbeat Seeker

Nuclear

***MWF AND MCCORD STUDENTS ONLY

Rate ↓ over time

Nuclear Reaction Types

1. **Fission: a large atom splits into medium nuclei**
   - Fission reactions are exothermic with atoms larger than iron
   - Common with large, unstable nuclei such as uranium

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{137}_{56}Ba + ^{97}_{36}Kr + \underline{\underline{2\,^{1}_{0}n}}$$

Rate ↑ over time

2. **Fusion: small nuclei join to form larger nuclei**
   - Fusion reactions are exothermic with atoms smaller than iron
   - Common with hydrogen, deuterium, helium in extreme conditions (such as in stars)

$$^{2}_{1}H + ^{3}_{1}H \rightarrow ^{4}_{2}He + ^{1}_{0}n$$

3. **Nuclear Decay:** an unstable nucleus reaches a lower energy state by spontaneously releasing ionizing radiation (beta decay, positron decay, alpha decay, electron capture)

$$^{210}_{84}Po \rightarrow ^{206}_{82}Pb + ^{4}_{2}He$$

$$^{14}_{6}C \rightarrow ^{14}_{7}N + ^{0}_{-1}\beta$$

Nuclear Fundamentals of Decay

$${}^{210}_{84}Po \rightarrow {}^{4}_{2}He + {}^{206}_{82}Pb$$

${}^{4}_{2}He$ α decay: emission of an α-particle

- The result is a new atomic species (z-2, m-4) and a new mass

${}^{0}_{-1}\beta$ β decay: emission of an electron

- The result is a new atomic species (z+1) with the same mass
- Neutron becomes a proton

${}^{0}_{1}\beta$ β^+ decay: emission of a positron

- The result is a new atomic species (z-1) with the same mass
- Proton becomes a neutron

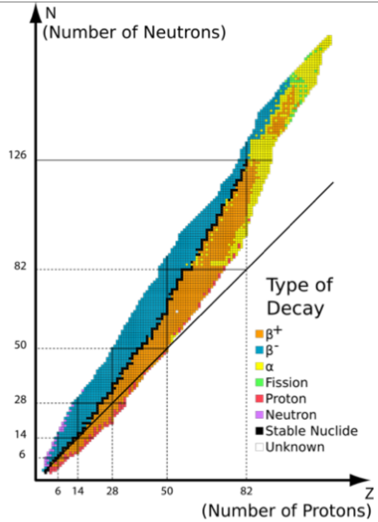
} Products

${}^{0}_{-1}e^-$ Electron capture: the **addition** of an electron } Reactant

- The result is a new atomic species (z-1) with the same mass
- Proton becomes a neutron (same effect as positron decay)

Note: z = atomic number ; m = atomic mass

The Band of Stability



- The band of stability tells us the stable ratio of protons : neutrons for each element.
  - Additional isotopes exist outside of the band of stability
  - Where you are in relationship to the stable isotope dictates the type of decay necessary to get to the lowest energy state
- Above the line: too many neutrons (beta decay)
- Below the line: too many protons (positron decay)
- *Notice how the band of stability ends at lead – everything after lead is radioactive*

Nuclear Rate of Decay: Half-Life

- The rate at which an unstable isotope decays is measured by its half-life.

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

- Radioactive decay follows first order kinetics. This means the rate of decay is dependent on the amount of the decaying material.

✓ $$\ln\frac{[A]_0}{[A]} = kt$$

$$\frac{\ln\frac{[A]_0}{[A]}}{k} = t$$

1. Easy: How long will it take for 256 grams of Pu-241 to decay into 64 grams? The half-life of Pu-241 is 14.4 years.

   $256 \rightarrow 128 \rightarrow 64$

   $2 \times 14.4 = 28.8$ y

2. Involved: How long will it take for 43,453 grams of Pu-241 to decay into 6,378 grams? The half-life of Pu-241 is 14.4 years.

Solubility Equilibria

FYI, you will need:
pH = -log[H$^+$]
14 = pH + pOH

K_{sp} Experimental Scenarios

There are four main scenarios of solubility equilibria:

1. You add a chunk of a sparingly soluble salt to deionized water and calculate the molar solubility from the K_{sp} and stoichiometry (or vice versa).
2. You add a chunk of a sparingly soluble salt to a a solution with a common ion already in solution
3. You mix two aqueous solutions to perform a double displacement precipitation reaction and evaluate if a precipitate forms
4. You mix two aqueous solutions to perform a double displacement precipitation reaction and quantify the mass of the precipitate formed

$$\begin{tikzcd} K_{sp} \arrow[r] & x\left(\frac{Mol}{L}\right) \arrow[dl, leftrightarrow] \arrow[dr, leftrightarrow] & \\ \frac{Kg}{L} & & \frac{g}{mL} \end{tikzcd}$$

Solubility Equilibrium Overview

ALL SALT RATIOS

1:1 $K_{sp} = x^2$

1:2 $K_{sp} = 4x^3$

1:3 $K_{sp} = 27x^4$

2:3 $K_{sp} = 108x^5$

Evaluating Solubility using *x*

Ranking solubility depends on molar solubilty, x, and **not K_{sp} directly**

$AlPO_4$ $K_{sp} = 9.8 \times 10^{-21}$ $= x^2$ $x = \sqrt{Ksp} = \underline{9.9 \times 10^{-11}\ M}$

$Ba(IO_3)_2$ $K_{sp} = 4.0 \times 10^{-9}$ $= 4x^3$ $x = \sqrt[3]{\frac{Ksp}{4}} = \underline{1 \times 10^{-3}\ M}$

$BaSO_4$ $K_{sp} = 1.1 \times 10^{-10}$ $= x^2$ $x = \sqrt{Ksp} = \underline{1.05 \times 10^{-5}\ M}$

Scenario 1: K_{sp} to Molar Solubility

What is the molar solubility of Li_3PO_4? The K_{sp} of Li_3PO_4 is 3.2×10^{-9}.

$[Li^+] = 3x$

$$K_{sp} = [Li^+]^3[PO_4^{3-}]$$

$$K_{sp} = (3x)^3 x = \underline{\underline{27x^4}}$$

$$\sqrt[4]{\frac{K_{sp}}{27}} = x$$

$$x = 3.3 \cdot 10^{-3} M$$

K_{sp} is the "Solubility Product," which is a constant unique to a particular compound that represents the product of ion concentrations that are present at equilibrium

x represents the "Molar Solubility," which is a direct measurement of solubility. Molar solubility is the concentration of a solute that dissolves in molarity (M) for a reaction.

Common ion present, $x \downarrow\downarrow\downarrow$

Scenario 2: Common Ion Effect

$$K_{sp} = [Li^+]^3[PO_4^{3-}]$$

$$K_{sp} = (3x)^3 x = 27x^4$$

$$\sqrt[4]{\frac{K_{sp}}{27}} = x \qquad x = 3.3 \cdot 10^{-3} M \Bigg\} \text{Previous}$$

Now, what is the molar solubility of Li_3PO_4 in a solution of 0.5 M $LiNO_3$? The K_{sp} of Li_3PO_4 is 3.2×10^{-9}.

$$K_{sp} = (0.5M \cancel{+3x})^3 x = 3.2 \times 10^{-9} = .125x$$

$$x \approx 2.6 \times 10^{-8} M$$

1A metal ions (Na^+, Li^+, K^+), nitrates (NO_3^-)

Scenario 3: Does a precipitate form?

- K_{sp} represents the ion product of a saturated solution.
- Q_{sp} represents the starting point when you put in real/experimental concentrations

1. $Q_{sp} < K_{sp}$ (unsaturated) ; more solid can dissolve if added to the solution ✓
2. $Q_{sp} = K_{sp}$ (saturated) ; your reaction is at equilibrium ✓
3. $Q_{sp} > K_{sp}$ (over saturated) ; precipitation occurs until $Q_{sp} = K_{sp}$ ✓

0.5 M 250 mL $LiNO_3$ are mixed with 0.5 M 250 mL Na_3PO_4. → Final solution
0.25 M Li^+
0.25 M PO_4^{3-}

What is the resulting precipitate (if any)? The K_{sp} of Li_3PO_4 is 3.2×10^{-9}

$$Q_{sp} = [Li^+]^3[PO_4^{3-}]$$

$$(.25)^3(.25) = 3.9 \times 10^{-3}$$

$Q > K$, Li_3PO_4 forms

K_{sp} Scenario 4: Quantifying Precipitate

What is the mass of a precipitate formed when 0.5 M 250 mL NaCl are mixed with 0.05 M 250 mL $CuNO_3$?

K_{sp} of CuCl = 1.7×10^{-7}

$$.0125 \text{ mol} \times \frac{99\text{g}}{\text{mol}} = 1.24\text{g}$$

1. Write your reaction
2. Prove that a precipitation forms
3. Solve for the mass of the precipitate (limiting reagent stoichiometry) ← Major hint: to make this problem straightforward, assume it is a 100% reactant (yes, you can get away with this based on the small size of K)

in moles

R	$NaCl_{(aq)}$ +	$CuNO_{3(aq)}$ →	$CuCl_{(s)}$ +	$NaNO_{3(aq)}$
I	.125	.0125	0	0
C	−.0125	−.0125	+.0125	+.0125
E	.1125	0	$\boxed{.0125}$	.0125

Kinetics

* Stoich is important

Kinetics Question Scenarios

1. **Relative rates of a reaction (stoichiometric rates):** If you can measure the rate of formation for a product, you can use stoichiometry to determine the rates for all other products and reactants *
2. **Rate Laws**: The rate law is a fundamental equation used to calculate the rate of a reaction from the rate constant, *k*, and the concentrations of the reactants raised to the power of their "order". The overall reaction order is the sum of the orders of the reactants.
3. Method of Initial Rates: Because the order of reactants are not necessarily based on stoichiometry, you must run an experiment to measure this value based on the initial rate of reaction at different starting concentrations
4. Integrated Rate Law: Knowing the order of a reaction, you can determine the rate or concentrations of a reactant at any given point in time (calculus is necessary here because if the rate is dependent on concentration, the rate is changes as the reaction proceeds)
5. Mechanisms: Use the known steps of a reaction to determine the overall rate law and reaction coordinate diagram *
6. Arrhenius Theory and Catalysis: quantify the rate if we decrease the activation energy (catalyst) or temperature

} initial rates

} time has passed

Four Factors That Affect Rates

1. **Nature of reactants/ Availability of the molecules**
   - Larger surface area = faster rate
2. **Concentration (and pressure)**
   - Higher concentration, higher rate **if your rate depends on the concentration**
   - Increases the rate based on the fact that the rate law is concentration dependent

increase rate without affecting rate constant

3. **Temperature**
   - Higher temperature, higher rate **always** (in this class)
   - Increases the rate based on the fact that the **rate constant** in temperature dependent
4. **Catalysts**
   - Catalysts decrease the **activation energy**, which increases the rate based on the Arrhenius Equation
   - The activation energy is decreased by modifying the substrate orientation
   - Increases the rate based on the fact that the rate constant is proportional to the **negative activation energy**

increase rate by increasing rate constant

Stoichiometric Rates

Relative Rates of a Reaction

The fundamental rate of a reaction can be described by the rate of change of any reactant or product of the reaction.

1. **Coefficients play an important role**
   - A coefficient in front of a species means it is going that number times the overall reaction rate
   - Nitrogen dioxide (NO_2) is going 4x the overall rate
2. **The rate of change for reactants and products are always opposite in sign**
   - The overall rate of N_2O_5 is negative, NO_2 and O_2 are positive

If N_2O_5 is changing at an initial rate equal to -18.6 M/s, what is the overall rate of the reaction? What is the rate of change of NO_2?

$$\overbrace{2N_2O_5 \rightarrow 4NO_2 + O_2}^{\text{1 mol rxn}}$$

$$\text{Rate} = \frac{-\Delta[N_2O_5]}{2\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

$$\text{Rate of Rxn} = -\frac{1}{2}\,\text{Rate } N_2O_5$$

$$\underline{9.3}\ M/s = -\frac{1}{2}(18.6\ M/s)$$

$$18.6\ M/s\ N_2O_5 \times \frac{4\,NO_2}{2\,N_2O_5} = 37.2\ M/s$$

coefficients

Overall Reaction Order, Rate Constant

Order can be applied to the total reaction:

- The order of the reaction is the sum of the exponents in the rate law.
- Our units of *k* are dependent on the order of the total reaction
  - 0th order: $k = Ms^{-1}$
  - 1st order: $k = s^{-1}$
  - 2nd order: $k = M^{-1}s^{-1}$
  - 3rd order: $k = M^{-2}\,s^{-1}$
  - nth order: $k = M^{-(n-1)}s^{-1}$

$$K = \frac{1}{M^{\text{order}-1}\,s}$$ ✓

These are all based on the fact that the rate must be in M/s, and you are cancelling out the concentration terms on the rate law

A few ways we can give the reaction order:

(these are all first-order, think about how they would be different for other orders)

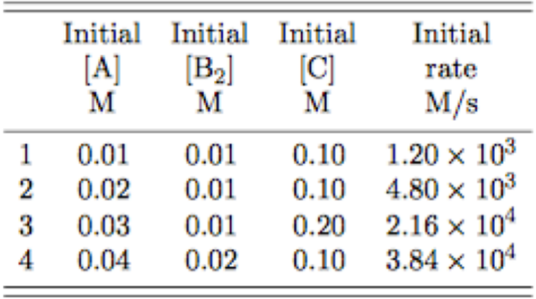
- "A reaction is first order…"
- The slope of ln[A] vs t gives a straight line with a slope equal to -0.05
- The rate constant for a reaction is 0.05 s^{-1}
- "For the radioactive decay of…" (McCord and MWF ONLY)
- "The substrate A has a half-life that is independent of concentration…"
- The concentration of [A] is 1.5 mM and the concentration of [B] is 200mM

(harder than the...) Exam Question (do on your own)

For the reaction:

$A + B_2 + 2C \rightarrow D$

You run an experiment to determine the initial rates of the reaction under 4 different starting conditions. Write the complete rate law for the reaction. What is the value of k?



	Initial [A] M	Initial [B$_2$] M	Initial [C] M	Initial rate M/s
1	0.01	0.01	0.10	1.20×10^3
2	0.02	0.01	0.10	4.80×10^3
3	0.03	0.01	0.20	2.16×10^4
4	0.04	0.02	0.10	3.84×10^4

$$\frac{Rate_2}{Rate_1} = \frac{k[A]_2^x[B_2]_2^y[C]_2^z}{k[A]_1^x[B_2]_1^y[C]_1^z}$$

(harder than the...) Exam Question - Answer

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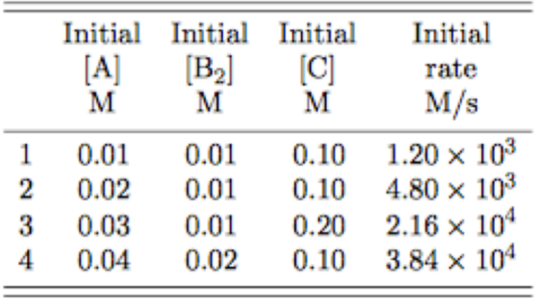

	Initial [A] M	Initial [B_2] M	Initial [C] M	Initial rate M/s
1	0.01	0.01	0.10	1.20×10^3
2	0.02	0.01	0.10	4.80×10^3
3	0.03	0.01	0.20	2.16×10^4
4	0.04	0.02	0.10	3.84×10^4

Rate = $1.2 \times 10^{10}\ M^{-3}s^{-1}[A]^2[B_2][C]$

$$\frac{Rate_2}{Rate_1} = \frac{k[A]_2^x[B_2]_2^y[C]_2^z}{k[A]_1^x[B_2]_1^y[C]_1^z}$$

Integrated Rate Law Equations

	0 Order	**1^{st} Order**	**2^{nd} Order**
Integrated Rate Law	$\underline{[A] = [A]_o - kt}$	$\underline{\ln[A] = \ln\ [A]_o - kt}$ $\ln\frac{[A]_o}{[A]} = kt$ ✓	$\underline{\frac{1}{[A]} = \frac{1}{[A]_o} + kt}$
Straight Line Slope	$[A] = -kt + [A]_o$ slope = $-k$	$\ln[A] = -kt + \ln\ [A]_o$ slope = $-k$	$\frac{1}{[A]} = kt + \frac{1}{[A]_o}$ slope = K
Half Life	$\underline{t_{1/2} = \frac{[A]_o}{2k}}$	$\underline{t_{1/2} = \frac{\ln 2}{k}}$	$\underline{t_{1/2} = \frac{1}{k[A]_o}}$

$$[A] = [A]_0 - kt$$

$[A]$ ↓ 1.25 (3 half-lives)

$[A]_0$ ↓ 10

kt ↓ from $t_{1/2}$ or provided in question

Half-Lives of Integrated Rate Laws

- First Order Half-Life: Independent of concentration

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

Half life 1 = Half life 2 . . . . .

- 0th Order Half-Life: Directly related to concentration

$$\frac{[A]_0}{2k} = t_{1/2}$$

$10\,M = [A]_0$, 3 ½ lives

$t_{1/2\,(1)} = \frac{10}{2k}$, $t_{1/2\,(2)} = \frac{5}{2k}$, $t_{1/2\,(3)} = \frac{2.5}{2k}$

$[A]$↓ $t_{1/2}$ ↓

- 2nd Order Half-Life: Inversely related to concentration

$$\frac{1}{k[A]_0} = t_{1/2}$$

$[A]$↓ $t_{1/2}$ ↑

Kinetics: Temperature and Catalysts

Ea ↓
k ↑

T ↑ k ↑ Ea same

How does temperature affect the rate of reaction? Altering equilibrium

- By increasing the temperature, you are increasing the number of particles that have enough energy to collide successfully. In other words, **you are increasing the number of particles with the ability to overcome the activation energy.**
- **Based on the Arrhenius Equation, you will get a higher rate constant that will give you a faster rate of reaction.**

little k

Know
$$\ln\left(\frac{k_2}{k_1}\right) = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
✓

Kelvin not °C

How does adding a catalyst affect the rate of reaction? Altering the mechanism

- Catalysts lower the activation energy **by stabilizing the transition state.**
- Like temperature, **this mathematically results in a higher rate constant**
- Unlike temperature, changing the activation energy will have no effect on the equilibrium properties of the products and the reactants.

$$k = Ae^{\frac{-Ea}{RT}}$$

understand conceptually

This is the other example where stoichiometry DOES matter

1) Slow step = rate law
2) No intermediates

Fundamentals of Mechanisms

We can propose a mechanism that dictates the kinetics of the reaction. The mechanism explains what is actually going on and helps us define the following terms:

1. **Rate-limiting step:** the slow step of a mechanism; dictates the rate of the reaction and activation energy
2. **Molecularity:** the number of species involved in the rate-limiting step
   - Unimolecular: the rate-limiting step involves a single species changing (breaking apart, dissolving, decomposing, etc.) into products; the rate law for this step is first order
   - Bimolecular: the rate-limiting step involves the collision of 2 species ; the rate law for this step is second order
   - Note: we do not often propose elementary steps that are termolecular and beyond. This is because it is very improbable for 3 species to collide with the correct energy / orientation
3. **The Overall Rate Law:** the rate law properly expressed in terms of only reactants
   - If the rate-limiting step involves an intermediate, you will need to substitute to in to express your rate in terms of only the reactants of the overall reaction

Reaction Mechanisms: Reaction Coordinate

Consider the following reaction mechanism for the formation of hydrochloric acid.

Overall : $H_2 + Cl_2 \rightarrow 2HCl$

$Cl_2 \rightleftharpoons 2Cl$ $\quad k_1$ (fast, eq.)

$Cl + H_2 \rightleftharpoons H_2Cl$ $\quad k_2$ (fast, eq.)

$H_2Cl + Cl \longrightarrow 2HCl$ $\quad k_3$ (slow)

Provide the rate law and reaction coordinate diagram for this mechanism, knowing this reaction is exothermic.

Reaction Mechanisms: Rate Law

Replace all Cl with F, Br, I

Consider the following reaction mechanism for the formation of hydrochloric acid.

Overall : $H_2 + Cl_2 \rightarrow 2HCl$

1 $Cl_2 \rightleftharpoons 2Cl$ k_1 (fast, eq.)

2 $Cl + H_2 \rightleftharpoons H_2Cl$ k_2 (fast, eq.)

3 $H_2Cl + Cl \longrightarrow 2HCl$ k_3 (slow)

Provide the rate law and reaction coordinate diagram for this mechanism, knowing this reaction is exothermic.

$$\cancel{\frac{k_3 k_2 k_1}{k_{-2} k_{-1}}} [H_2][Cl_2]$$

$$k'[H_2][Cl_2] \checkmark$$

$$\text{rate} = k_3 [H_2Cl][Cl]$$

$$k_2 [Cl][H_2] = k_{-2}[H_2Cl]$$

isolate

$$\frac{k_2}{k_{-2}}[Cl][H_2] = [H_2Cl]$$

$$\text{new Rate} = \frac{k_3 k_2}{k_{-2}}[H_2][Cl]^2$$

$$k_1[Cl_2] = k_{-1}[Cl]^2$$

isolate

$$\frac{k_1}{k_{-1}}[Cl_2] = [Cl]^2$$