CH302 Unit 3 Day 1

KSP, PRECIPITATION REACTIONS, INTRO TO KINETICS

$PbI_2(s) \rightleftharpoons Pb^{2+}_{(aq)} + 2I^-_{(aq)}$

K_{sp}, Q_{sp}, and Saturation - Definitions

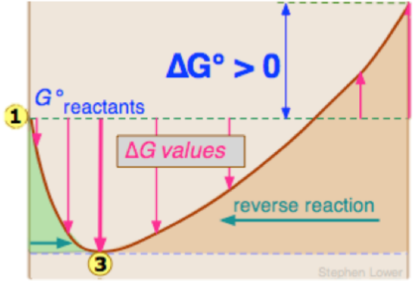
- **Solubility Product (K_{sp}):** K_{sp} is a constant that represents the mass action expression at equilibrium specific to a given salt. **This is the K of the salt dissolution reaction.**
- **Molar Solubility:** Solved from K_{sp}, molar solubility represents the maximum amount of solute that can dissolve for a reaction in terms of molarity (M). This term is represented by the "x" in K_{sp} calculations. **This is your best measurement of the solubility of a salt.**
- **Common Ion Effect:** When an ion is already present in solution, the molar solubility of a salt containing that ion significantly decreases.
- **Reaction Quotient Solubility Product (Q_{sp}):** Q_{sp} is a variable that is calculated by the product of all ion concentrations typically **at a point away from equilibrium**. Solved in the same way as K_{sp}, Q_{sp} uses experimental values rather than equilibrium values.
- **Saturation:** when the maximum amount of ions are present in solution ($K_{sp} = Q_{sp}$)
  - Saturation is an equilibrium position where Q = K.
  - Dissolution: when $Q_{sp} < K_{sp}$ and your reaction moves forward (solid becomes ions)
  - Precipitation: when $Q_{sp} > K_{sp}$ and your reaction moves backward (ions become solid)

NOT equilibrium

Saturation and Comparing Q_{sp} vs. K_{sp}

- K_{sp} represents the ion product of a saturated solution in terms of molar solubility (x). You can think of it as a measurement of the maximum saturation capacity of a solution.
- Q_{sp} represents the ion product of the actual concentrations of ions at any given time. You can control these concentrations experimentally. **You can think of Q_{sp} like a starting point**
- **Remember:** K_{sp} is a fixed value ; Q_{sp} is defined by the your actual concentrations in your experiment. **Therefore, your value of Q_{sp} in relationship to K_{sp} will describe what happens:**

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 $Q_{sp} = K_{sp}$



Solubility Equilibrium Overview

ALL SALT RATIOS

1:1 $K_{sp} = x \cdot x = \boxed{x^2}$ $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

1:2 $K_{sp} = x \cdot (2x)^2 = \boxed{4x^3}$ $CaF_{2\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)}$

1:3 $K_{sp} = x \cdot (3x)^3 = \boxed{27x^4}$ $Li_3PO_{4\,(s)} \rightleftharpoons 3Li^+_{(aq)} + PO_4^{3-}{}_{(aq)}$

2:3 $K_{sp} = (2x)^2(3x)^3 = \boxed{108x^5}$ $Nd_2(CO_3)_{3\,(s)} \rightleftharpoons 2Nd^{3+}_{(aq)} + 3CO_3^{2-}{}_{(aq)}$

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}.

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

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

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

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

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.

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

K_{sp}: ~~$AlPO_4 < Ba(IO_3)_2 < CuCl$~~

Question

Rank the following molecules according to their molar solubility (lowest molar solubility to highest molar solubility) Solve for $\underline{\underline{x}}$

$AlPO_4$, $K_{sp} = 9.8 \times 10^{-21}$ $= x^2$ $x = \sqrt{9.8\times10^{-21}} = \underline{9.9\times10^{-11}}$

$Ba(IO_3)_2$, $K_{sp} = 4.0 \times 10^{-9}$ $= 4x^3$ $x = \sqrt[3]{\frac{4.0\times10^{-9}}{4}} = \underline{1\times10^{-3}}$

$CuCl$, $K_{sp} = 1.7 \times 10^{-7}$ $= x^2$ $x = \sqrt{1.7\times10^{-7}} = \underline{4.1\times10^{-4}}$

✓ $AlPO_4 < CuCl < Ba(IO_3)_2$

K_{sp} Question Types

There are three 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).
   - $K_{sp} = [Pb^{2+}][I^-]^2 = (x)(2x)^2 = 4x^3$
   - x is your molar solubility
2. You add a chunk of a sparingly soluble salt to a a solution with a common ion already in solution
   - $K_{sp} = [Pb^{2+}][I^-]^2 = (x)(0.05M - 2x)^2 = 4x^3$
   - x is still your molar solubility, but much lower than in the previous example
3. You mix two aqueous solutions to perform a double displacement precipitation reaction and evaluate if a precipitate forms
   - $Q_{sp} = [Pb^{2+}][I^-]^2$
   - If Q > K, a precipitate forms

K_{sp} Scenario One

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).

What is the molar solubility of PbI_2?
The K_{sp} of $PbI_2 = 9.8 \times 10^{-9}$.

$$K_{sp} \rightarrow PbI_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2I^-_{(aq)}$$

$$\begin{array}{ccc} \text{a lot} & 0 & 0 \\ -x & +x & +2x \\ \hline & x & 2x \end{array}$$

$$K_{sp} = (x)(2x)^2 = 4x^3$$

$$9.8 \times 10^{-9} = 4x^3$$

$$\sqrt[3]{\frac{9.8 \times 10^{-9}}{4}} \rightarrow \boxed{x = 1.3 \times 10^{-3} M}$$

K_{sp} Scenario Two: Common Ion Effect

2. You add a chunk of a sparingly soluble salt to a a solution with a common ion already in solution.

Consider adding PbI_2 to a 0.05 M solution of NaI. What is the molar solubility of PbI_2?

The K_{sp} of PbI_2 = 9.8×10^{-9}.

$$\begin{array}{ccccc} PbI_2 & \rightleftharpoons & Pb^{2+} & + & 2I^- \\ \text{a lot} & & 0 & & .05 \\ -x & & +x & & +2x \\ \hline & & x & & 0.05+2x \end{array}$$

$$K_{sp} = (x)(0.05 \cancel{+2x})^2$$

$$\frac{9.8\times10^{-9} = .0025\,x}{.0025} \rightarrow x = 3.9\times10^{-6}\ M$$

$$Pb(NO_3)_2\,(aq) + 2NaI\,(aq) \rightleftharpoons PbI_2\,(s) + 2NaNO_3\,(aq)$$

K_{sp} Scenario Three: Precipitation Reaction

3. You mix two aqueous solutions to perform a double displacement precipitation reaction and evaluate if a precipitate forms.

Consider adding 100 mL 0.03 M $Pb(NO_3)_2$ to 100 mL 0.05 $\overset{M}{}$ NaI.

K_{sp} PbI_2 = 9.8×10^{-9}

What is the value of Q_{sp}? What precipitate, if any, forms? $\rightarrow$ Q>K

$$Q_{sp} = [Pb^{2+}][I^-]^2 = (0.015)(0.025)^2 = 9.38 \times 10^{-6}$$

$$Pb^{2+} \rightarrow .100\,L \cdot .03\,M = \frac{.003\,\text{moles}}{0.200\,L} = 0.015\,M$$

$$I^- \rightarrow .100\,L \cdot .05\,M = \frac{0.005\,\text{mol}}{.200\,L} = 0.025\,M$$

Q>K

PbI_2

ppt forms

→ 45%

My Favorite Exam Question

Which of the following is true regarding 15 g $Ba(NO_3)_2$ solid dissolved in 500 mL water?

[✓ 1.] $2[Ba^{2+}] = [NO_3^-]$

2. $[Ba^{2+}] = [NO_3^-]$

3. $[Ba^{2+}] = 2[NO_3^-]$

4. $[Ba^{2+}] = [NO_3^-]^2$

5. $[Ba^{2+}]^2 = [NO_3^-]$

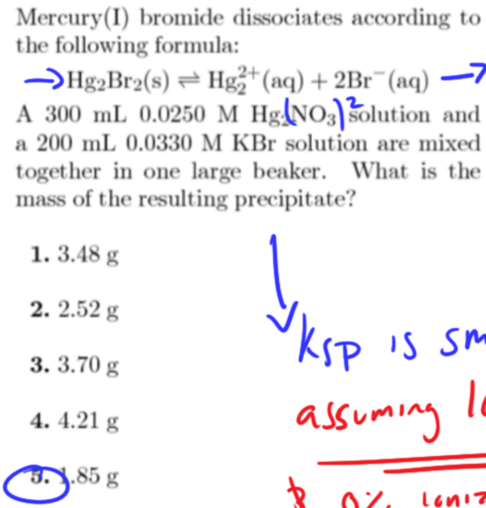
6. $2[Ba^{2+}]^2 = [NO_3^-]$

$$\begin{tikzcd}
 & Ba(NO_3)_2 \arrow[dl] \arrow[dr] & \\
Ba^{2+} & & 2NO_3^-
\end{tikzcd}$$

$$2(x) = 2x$$

$$2[Ba^{2+}] = [NO_3^-]$$

Exam Question



Mercury(I) bromide dissociates according to the following formula:

$$Hg_2Br_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Br^-(aq)$$ → Ksp

A 300 mL 0.0250 M $Hg_2(NO_3)^2$ solution and a 200 mL 0.0330 M KBr solution are mixed together in one large beaker. What is the mass of the resulting precipitate?

1. 3.48 g
2. 2.52 g
3. 3.70 g
4. 4.21 g
5. [✓ 1.85 g]

Ksp is small

assuming 100% reaction

& 0% ionization of Hg_2Br_2

In moles!

1 : 2 : 1 : 2

R	$Hg_2(NO_3)_2(aq)$ +	2KBr(aq) ⇌	$Hg_2Br_2(s)$ +	$2KNO_3$
I	.0075	.0066	0	0
C	-.0033	-.0066	+.0033	+.0066
E	.0042	0	$\boxed{.0033}$	.0066

.0033 × MM = ___ g

.0033 × 560.99 = 1.85g

Intro to Kinetics

RELATIVE RATES AND INTRO TO METHOD OF INITIAL RATES

Introduction to Kinetics

There are four types of kinetics questions types that we have discussed in this class:

1. Relative rates of a reaction (think stoichiometry): 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. Empirical Rate Law: 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)

These work well for initial rates

Takes into account the fact that the rate can change over time

The Four Factors that Affect Rates

1. **Nature of reactants/ Availability of the molecules**
    - Larger surface area = faster rate
    - Ex: this is the reason why we chew our food (mechanical digestion)
2. **Concentration (and pressure)**
    - Higher concentration, higher rate **if your reaction is first order or higher**
    - Increases the rate based on the fact that the rate law is concentration dependent

Increase the rate without changing the 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 the rate by increasing the rate constant

This is one example where stoichiometry DOES matter

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. A few important notes:

1. Coefficients play an important role: if *b* = 3, the rate of consumption for B is 3 times the overall reaction rate; if *d* = 4, the rate of formation for D is 4 times the overall reaction rate
2. The rate of change for different species can be interconverted: based on the information above, we can say that the rate of formation for D is 4/3 the rate of consumption of B
3. The rate of change for reactants and products are always opposite in sign

$$\underbrace{\overset{1}{\cancel{a}}A + \overset{3}{\cancel{b}}B}_{\text{consumed }(-)} \rightarrow \underbrace{\overset{2}{\cancel{c}}C + \overset{4}{\cancel{d}}D}_{\text{produced }(+)}$$

$$rate = \frac{-\Delta[A]}{\overset{1}{\cancel{a}}\Delta t} = \frac{-\Delta[B]}{\overset{3}{\cancel{b}}\Delta t} = \frac{+\Delta[C]}{\overset{2}{\cancel{c}}\Delta t} = \frac{+\Delta[D]}{\overset{4}{\cancel{d}}\Delta t}$$

$$\overbrace{\frac{-\overset{4}{\cancel{d}}\Delta[B]}{\overset{3}{\cancel{b}}\Delta t} = \frac{\Delta[D]}{\Delta t}}$$

Overall Rate of a Reaction - Example

$$1N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

→ 1 mol rxn

1. Write an expression that represents the overall rate of the reaction in terms of each of the reactants and products
2. Write the rate of formation of ammonia (NH_3) in terms of hydrogen (H_2).
3. Suppose the initial rate of formation of ammonia is 0.6 M/s. Write the overall initial rate of the reaction.

$$\text{Overall rate} = \frac{-\Delta[N_2]}{1\Delta t} = \underbrace{\frac{-\Delta[H_2]}{3\Delta t} = \frac{+\Delta[NH_3]}{2\Delta t}}$$

$$\frac{-2\Delta[H_2]}{3\Delta t} = \frac{\Delta[NH_3]}{2\Delta t}$$

$$\frac{-2\Delta[H_2]}{3\Delta t} = \frac{\Delta[NH_3]}{\Delta t}$$

2 × rate of rxn = rate NH_3

0.3 M/s = rate of rxn = $\frac{1}{2}$ rate NH_3 = 0.5 · 0.6

Introduction to Rate Laws

$$aA + bB \rightarrow cC + dD$$

$$rate = k[A]^x[B]^y$$

Rate of reaction in the units of M/s

Rate constant (measured value). Units depend on the order of reaction; must cancel units of $[A]^x$ and $[B]^y$ to get rate = M/s

x = order of A
y = order of B
$x + y$ = overall order of the reaction
Order is usually positive integers, but can be fractional or negative in rare cases

Introduction to Rate Laws

$$aA + bB \rightarrow cC + dD$$

$$rate = k[A]^x[B]^y$$

0th Order:

First Order:

,

Second Order:

Empirical Rate Laws

Consider the bromination of pentene:

$$C_5H_{10} + Br_2 \rightarrow C_5H_{10}Br_2$$

Start with the rate law:

$$rate = k\,[C_5H_{10}]^x[Br_2]^y$$

Then use the data to solve for x, y, and k.

Trial #	$[C_5H_{10}]$	$[Br_2]$	Rate
1	2 M	2 M	10 M/s
2	4 M	2 M	20 M/s
3	4 M	4 M	40 M/s

Empirical Rate Laws: solution

Trial #	**[C_5H_{10}]**	**[Br_2]**	**Rate**
1	2 M	2 M	10 M/s
2	4 M	2 M	20 M/s
3	4 M	4 M	40 M/s

Between trials 1, 2: we doubled the concentration of pentene and the rate doubled. No change was made to bromine.

Between trials 2, 3: we doubled the concentration of bromine and the rate doubled. No change was made in pentene. This is indicative of a reaction that is first order in bromine.

Now that we know the order of the reaction, we can set up our equation: rate = $k[C_5H_{10}]^1[Br_2]^1$. The reaction is second order overall.

We can use any trial to solve for k. For example: 10 M/s = k(2 M)(2 M), k = (10 M/s)/ $(2\ M)^2$, **$k = 2.5\ M^{-1}S^{-1}$**

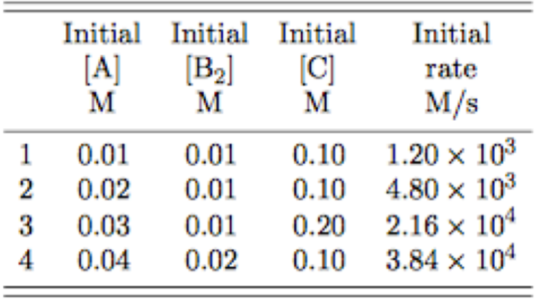
Important: trials 1, 3 don't make for a great comparison at the beginning because both reagents have different concentrations. It's difficult to determine which reagent is causing the rate to change

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

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

Exam Question

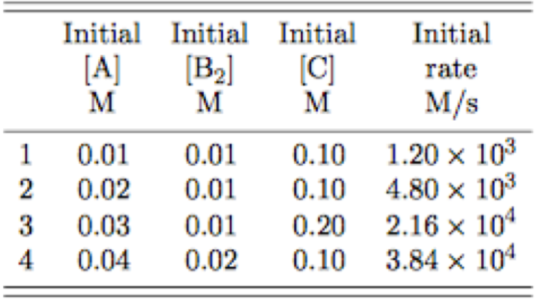
For the reaction:

$A + B_2 + 2C \rightarrow D$,

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?

Rate = $1.2 \times 10^{10}[A]^2[B_2][C]$

(units of *k* omitted)



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