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Experiment 4
Equilibrium and Le Châtelier's Principle

Chemistry 132
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Background

We have learned that at equilibrium the concentrations of products and reactants are quantitatively determined by the value of the equilibrium constant, *K*. For an arbitrary reaction, we can write the an expression for the equilibrium constant in terms of the concentrations of products and reactants, each raised to their respective coefficients in the balanced reaction as follows:

$$a\,\mathrm{A}(aq) + b\,\mathrm{B}(aq) \rightleftharpoons c\,\mathrm{C}(aq) + d\,\mathrm{D}(aq) \qquad K = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

For example, when a soluble ionic compound is added to water, it completely dissolves and forms dissociated ions in solution. However, if an insoluble (or slightly soluble) ionic compound, such as AgCl, is mixed with water, not all the solid will dissolve. In this case, the remaining solid is in equilibrium with the dissociated ions, resulting in a saturated solution:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$$

The equilibrium constant for this dissolution process has a special name: **the solubility product constant**, or $\boldsymbol{K_{sp}}$. The solubility product constant is no different than any other equilibrium constant — it just describes a dissolution reaction. Therefore, K_{sp} equals the product of the equilibrium concentrations of the ions formed, each raised to a power equal to the number that ion in the compound's formula. (*Remember: as with all equilibrium expressions, solids are excluded*). For example, for AgCl, we can write:

$$K_{\mathrm{sp}} = [\mathrm{Ag^+}]\,[\mathrm{Cl^-}] = 1.8 \times 10^{-10}$$

Note that for a compound such as $PbCl_2$, the expression for K_{sp} would instead be

$$K_{\mathrm{sp}} = [\mathrm{Pb^+}]\,[\mathrm{Cl^-}]^2$$

where the concentration of Cl^- is now squared because there are two Cl^- ions for every Pb^{2+} ion in $PbCl_2$.

If we prepare a saturated solution by adding pure AgCl to pure water, the concentration of dissolved silver ions *__must__* exactly equally the chloride ion concentration. (This is because there is no other source of those ions, and every dissolved AgCl unit produces equal numbers of Ag^+ and Cl^-). Using this fact, we can pretty easily solve for the concentration of dissolved silver ions and chloride ions in a saturated solution by setting $[Ag^+] = [Cl^-]$, and solving using the value of K_{sp}:

$$[Ag^+] = [Cl^-] = x \quad \Rightarrow \quad x^2 = K_{sp} \quad \Rightarrow \quad x = \sqrt{K_{sp}} = 1.3 \times 10^{-5}\ M$$

Furthermore, ***Le Châtelier's principle*** allows us to predict how these concentrations would change if we alter the conditions of the equilibrium, for example by adding additional chloride ion or by changing the temperature. Le Châtelier's principle states "If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so to counteract the effect of the disturbance." In this lab, we will explore the concept of equilibrium in general and how Le Châtelier's Principle works in four "modules."

Part A. Effect of Temperature and Concentration I: Precipitate Formation

For this part, we will explore the following precipitation reaction:

$$Pb^{2+}(aq) + 2Cl^-(aq) \rightleftharpoons PbCl_2(s)$$

Notice that this reaction is *exactly* the same as the reaction described by K_{sp} for $PbCl_2$, except the reaction is written ***backwards***! (The equilibrium constant for this reaction is in fact K_{sp}^{-1}).

To study this reaction, you will mix aqueous solutions of lead nitrate, sodium chloride, and water in varying proportions to test the effect of the chloride ion concentration on the equilibrium position. The effect of temperature on the reaction will also be studied by subjecting your solutions to different temperatures and monitoring the reaction.

Part B. Effect of Acidity: [H+]

In this portion, we will explore the equilibrium between chromate and dichromate ions:

$$2\ CrO_4^{2-}(aq) + 2\ H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

If the $[H^+]$ is increased by adding acid, Le Châtelier's Principle says that the equilibrium will shift to consume some of the excess $H^+(aq)$. If a base is added, the $[H^+]$ will be decreased because the neutralization reaction $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ removes the H^+ ions from the solution. *Note: CrO_4^{2-} is yellow and $Cr_2O_7^{2-}$ is orange.*

Part C. Effect of Temperature and Concentration II: Complex Ion Formation

When cobalt ions are dissolved in water, the cobalt ions can form a cobalt-water complex, where six water molecules form what is called a coordination complex. In the presence of chloride ions, the water molecules are displaced with four chlorides:

$$Co(H_2O)_6^{2+}(aq) + 4\ Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6\ H_2O(l)$$

By increasing the concentration of chloride ion, the equilibrium position will shift. Also, by monitoring the effect of the temperature, the role of heat in this reaction on the equilibrium position can be determined. *Note: $Co(H_2O)_6^{2+}$ is pink and $CoCl_4^{2-}$ is blue.*

Part D. Common Ion Effect

The amount of solid that can be dissolved can be substantially decreased if one of its constituent ions is present in the solution. This is known as the "common ion effect." Consider a saturated solution of sodium chloride:

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$

In a saturated solution, the ions in solution are in equilibrium with the solid phase. If additional chloride ions (the "common ion") are added, then Le Châtelier's principle tells us that the equilibrium position will adjust to counteract these added ions.

Procedure

Part A. Effect of Temperature and Concentration I: Precipitate Formation

Dispose of all waste from this part in the aqueous waste container. Change gloves and/or wash your hands when finished.

1. **Label** three small test tubes that have been thoroughly cleaned and dried.
2. Using the volumes in the table below, add NaCl, H_2O, and $Pb(NO_3)_2$ to each test tube. Use a graduated cylinder to measure volume, but be sure not to cross-contaminate your solutions!

Test Tube	**Volume 0.50 M NaCl**	**Volume DI H_2O**	**Volume 0.20 M $Pb(NO_3)_2$**
1	1.0 mL	6.0 mL	1.0 mL
2	3.0 mL	4.0 mL	1.0 mL
3	5.0 mL	2.0 mL	1.0 mL

3. After the solutions are combined, cover each tube with a piece of parafilm. Placing your thumb over the top, mix thoroughly by quickly inverting the test tube a few times. Allow the tubes to sit for 5 minutes. Record your observations of the appearance of the test tubes. Measure and record the temperature of the solutions (which is just air temperature).
4. Place the three test tubes in an ice bath. Remove and shake gently several times during cooling. Record the temperature of the ice bath. After 5–10 minutes, record your observations of the test tubes. Now try 5–10 seconds in the *really* cold dry ice bath!
5. Place the three test tubes (with the parafilm removed) in a hot water bath. Heat carefully, occasionally removing the tubes to shake gently. Record the temperature of the hot water bath. After ~5 minutes, record your observations of the test tubes.

Part B. Effect of Acidity: [H^+]

Dispose of all waste from this part in the aqueous waste container. Change gloves and/or wash your hands when finished.

Label a multiwell plate, number wells 1 to 4, and add the following:

Chromate:	**1**	3 drops K_2CrO_4	plus	3 drops 1.0 M HCl
	2	3 drops K_2CrO_4	plus	3 drops 1.0 M NaOH
Dichromate:	**3**	3 drops $K_2Cr_2O_7$	plus	3 drops 1.0 M HCl
	4	3 drops $K_2Cr_2O_7$	plus	3 drops 1.0 M NaOH

Record the color of the initial solution and any changes that occur as a result the addition. Using your wash bottle, <u>carefully</u> rinse off the multiwell plate into a large beaker, and then dispose of in the aqueous waste container.

Part C. Effect of Temperature and Concentration II: Complex Ion Formation

Dispose of all waste from this part in the aqueous waste container. Change gloves and/or wash your hands when finished.

1. **Label** three test tubes 1 through 3. Place ~2 mL of acidified cobalt chloride solution in each.
2. In tube #1, *carefully* add <u>concentrated</u> HCl drop by drop until a clear color change is observed. Gently shake the test tube between additions. Record your observations. ***NOTE: Concentration hydrochloric acid is extremely caustic and <u>will eat through both clothes and skin</u>.***
3. In tube #2, add 0.2 M $Pb(NO_3)_2$ drop by drop until a distinct color change is observed. Gently shake the test tube between additions. Record your observations.
3. Place all three test tubes in an ice bath and chill thoroughly (5–10 min). Remove and shake gently a few times during cooling. Record your observations. Now dip them in the dry ice bath for a few seconds!
4. Now place all three test tubes in a hot water bath. Remove and shake gently a few times during heating. Record your observations.

Part D. Common Ion Effect

1. Clean and dry thoroughly a large test tube, your funnel, and a small dry beaker. (If there is **any** water anywhere, this will **not** work).
2. Set up a gravity filtration setup by folding a piece of dry filter paper in quarters. Place the folded filter paper in a funnel and open one fold of the filter paper. Pour approximately 5

mL of the saturated NaCl solution over the filter paper in the funnel, which should be placed over a test tube. Collect the filtrate in the test tube, and remove the funnel.

4. *Carefully* add a few drops of <u>concentrated</u> HCl drop by drop to the test tube. Observe and record the results. ***NOTE: Concentration hydrochloric acid is extremely caustic and <u>will eat through both clothes and skin</u>.***
5. Now take a new test tube. Pour approx. 5 mL of <u>un</u>saturated NaCl solution into a test tube. Repeat Step 4 with the <u>un</u>saturated solution of NaCl. Observe and record the results.

Part E. Indicators (bonus)

Experiment! Be creative! See what happens when you mix the available reagents. Can you cause a change? Can you reverse that change? Can you figure out what is going on?