Experiment 24: Systems in Equilibrium

(This experiment was adapted from Santa Monica College, Chemistry 12, Properties of Systems in Equilibrium – Le Chatelier's Principle)

Purpose: The purpose of this experiment is to study systems at equilibrium and equilibriums that have been disrupted.

Background: The concentrations of reactants and products at equilibrium are constant as a function of time. Thus, for a homogeneous aqueous system of the form

$$aA\ (aq) + bB\ (aq) \quad \rightarrow \quad cC\ (aq) + dD\ (aq) \qquad (1)$$

we can express the equilibrium-constant expression for this reaction as,

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (2)$$

It has been observed that when a reaction at equilibrium is disturbed by applying a stress, the reaction will respond by shifting its equilibrium position so as to counteract the effect of the stress. In other words, the concentrations of the reactants and products will shift so that the relationship described by Equation (2) is again satisfied. This idea was first proposed by Henri-Louis Le Châtelier and has since been referred to as, “Le Châtelier’s Principle”.
Note that when a reaction makes more products as a response to the disturbance, we call it a right-shift. When a reaction makes more reactants in response to the disturbance, we call it a left-shift.

For chemical reactions at equilibrium in aqueous solution, the most common types of disturbances (stresses) include changing the concentration of one of the aqueous solutes, changing the concentrations of all aqueous solutes by changing the total solution volume, or changing the temperature. The general responses of an aqueous system to these particular disturbances (perturbations) are tabulated below.

Perturbation	**Effect on Equilibrium Position**	**Effect on K_c**
Increase in concentration of a single reactant, or, decrease in concentration of a single product.	Shift to the right	None
Decrease in concentration of a single reactant, or, increase in concentration of a single product.	Shift to the left	None
Decrease in all aqueous concentrations due to an increase in solution volume resulting from the addition of solvent	Shift towards side with more solute particles	None
Increase in all aqueous concentrations due to a decrease in solution volume resulting from the removal of solvent (evaporation)	Shift towards side with less solute particles	None
Increase temperature of an exothermic reaction	Shift to the left	Decrease
Decrease temperature of an exothermic reaction	Shift to the right	Increase
Increase temperature of an endothermic reaction	Shift to the right	Increase
Decrease temperature of an endothermic reaction	Shift to the left	Decrease
Addition of an inert substance, catalyst, pure liquid, or pure solid	None	None

In this experiment you will disturb reactions that have attained equilibrium. You will then observe how each reaction responds to that disturbance in order to restore equilibrium. In your notebook, describe these changes in terms of Le Châtelier’s Principle.

Part A – Acid-Base Equilibrium

Here you will use **coupled equilibria** to change the equilibrium position of an acid-base reaction. In order to understand how coupled equilibria work, consider the reactions described by the chemical equations below (both reactions are in the same beaker):

$$A\ (aq) \rightarrow B\ (aq) \qquad \text{eqn. (1)}$$

$$B\ (aq) + C\ (aq) \rightarrow D\ (aq) \qquad \text{eqn. (2)}$$

Notice that the species B (*aq*) is common to both reactions. The presence of this common species couples these two reactions.

We can disturb the equilibrium position of equation (2) by the addition of some C (*aq*). The addition of C (*aq*) will cause the equilibrium position of equation (2) to shift right. This right shift in the equilibrium position of equation (2) will also result a corresponding decrease in the concentration of B (*aq*). Because B (*aq*) is also present in equation (1), the decrease in the concentration of B (*aq*) will in turn result in a right shift in the equilibrium position of equation (1). Thus, the addition of C (*aq*) to equation (2) actually results in a right shift in the equilibrium position of equation (1) because the equilibria are coupled.

In Part A we will observe the effect of various solutes on an acid-base indicator (a weak acid) at equilibrium. The equilibrium system can be written in the general form

$$HA\ (aq) \rightarrow H+\ (aq) + A–\ (aq) \qquad \text{eqn. (3)}$$

The equilibrium-constant expression for this reaction is

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \text{eqn. (4)}$$

In this experiment, HA and $A^–$, are the acidic and basic forms of the indicator bromothymol blue. Since the two forms are different colors, you will be able to determine which form is predominant in the equilibrium mixture. In other words, you will be able to determine whether the equilibrium position lies to the left or to the right.

Your goal will be to find a reagent that will shift the position of this equilibrium to the opposite side, and then another reagent that will shift it back towards its original position. Instead of directly adding HA or A^- to the system, you will affect these shifts by adding H^+ or OH^-. Note that in order to determine the effect of OH^- we must consider a second chemical reaction that shares a common species with the Reaction (3). The second reaction is the autoionization of water, which can be described by the equation

$$H_2O_{(l)} \rightarrow H^+_{(aq)} + OH^–_{(aq)} \qquad (5)$$

Because Reactions (3) and (5) share a common chemical species (H+), you can use the concept of coupled equilibria to shift the equilibrium position of Reaction (3) by increasing or decreasing the concentration of $OH^–$ (*aq*).

Part B – Solubility Equilibrium
Here you will test the effects of changing temperature on the solubility of a salt.
This type of equilibrium is often called a **solubility equilibrium** because it is written in the direction of the dissolution of the solid, as shown in the following example:

$$AxBy\ (s) \rightarrow xA+\ (aq) + yB-\ (aq) \qquad \text{eqn. (6)}$$

You will use an ionic compound, KNO_3, that is soluble at one temperature, but insoluble at another temperature.

Part C – Complex Ion Equilibrium
Certain metal ions, most often transition metals, exist in solution as complex ions in combination with other ions or molecules, called ligands. Common ligands include H_2O, NH_3, Cl^- and OH^-. Many of these complex ions exhibit vibrant colors in solution.
You will use the $Cu^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}{}_{(aq)}$ reaction in this part eqn. (7)

Part D – Dissolving Insoluble Solids
In Part D you will use coupled equilibria to affect the solubility equilibrium of $Zn(OH)_{2(s)}$.
The solubility equilibrium can be described by the equation

$$Zn(OH)_{2\ (s)} \rightleftharpoons Zn^{2+}\ _{(aq)} + 2\ OH^-\ _{(aq)} \qquad \text{eqn. (8)}$$

Now consider the reactions described by the following chemical equations, each of which shares a common species with the reaction (8):

$H_2O\ _{(l)} \rightleftharpoons H^+\ _{(aq)} + OH^-\ _{(aq)}$ $K_w = 1 \times 10^{-14}$ eqn. (9)
$Zn^{2+}\ _{(aq)} + 4\ OH^-\ _{(aq)} \rightleftharpoons Zn(OH)_4^{2-}\ _{(aq)}$ $K_f = 3 \times 10^{15}$ eqn. (10)
$Zn^{2+}\ _{(aq)} + 4\ NH_3\ _{(aq)} \rightleftharpoons Zn(NH_3)_4^{2+}\ _{(aq)}$ $K_f = 1 \times 10^{9}$ eqn. (11)

Because equations (9), (10), and (11) each share a common species with equation (8) they can be coupled together. In Part D of this experiment you will observe the effect of coupling each of these equilibria on the solubility of $Zn(OH)_{2\ (s)}$. *(Notice that the products in equations 9, 10, and 11 are all aqueous.)*

Chemicals

Bromothymol blue	6 M HCl	6 M NaOH
KNO_3, solid	0.1 M $CuSO_4$	6 M NH_3
0.1 M $Mg(NO_3)_2$	0.1 M $Zn(NO_3)_2$	

Equipment

6 large test tubes	Test tube rack	Stirring rod
Plastic droppers	10-mL graduated cylinder	Ice
Beakers	Hot plate	

Safety and Waste Disposal
6 M HCl, 6 M NaOH, and 6 M NH_3 are extremely caustic and great care must be taken to avoid contact with eyes or skin. The bottle should be kept in a plastic tray and not removed from the fume hood.

Procedure

Part A: Acid-Base Equilibrium
Here you will find a reagent that will shift the acid-base equilibrium given by equation (3) in one direction and then a second reagent that will cause the equilibrium position to shift back in the opposite direction.
Reagents needed for this part are: deionized water, bromothymol blue solution, a 6 M HCl and a 6 M NaOH.

1. Add approximately 5 mL of deionized water to each of two large test tubes. Add 4 drops of the bromothymol blue indicator solution to each test tube. Report the color of your solution on your data sheet. Keep one of these test tubes as the original reference point.

2. Your solution from Step 1 currently contains one form of bromothymol blue (see background). Now predict which of the two 6 M reagents, the strong acid or the strong base, will cause a color change in your solution by making the bromothymol blue indicator shift to its other form. Add the 6 M reagent of your choice drop-by-drop and if your solution changes color, write the color of the solution and formula of the reagent in your notebook. If the addition of your reagent does not result in a color change, try other reagents until you are successful.

3. Since equilibrium systems are reversible, it is possible to shift a reaction left or right repeatedly by changing the conditions. Now use the other 6 M reagent that will cause your solution from Step 2 to revert back to its original color (but diluted in intensity). Add the 6 M reagent drop-by-drop and record your observation in your notebook.

Part B: Solubility Equilibrium
You will test the effects of temperature change on the solubility of potassium nitrate. The solubility of KNO_3 increases as the temperature of the water is increased.
Reagents needed: solid KNO_3 and deionized water

1. Set up a hot-water bath (50-60°C) using a 400 mL beaker with approximately 200 mL of tap water on a hotplate set on medium-low heat. You will need this for steps 3 and 5. Set up an ice bath using a 250 mL beaker, tap water and ice. You will need this for step 4.

2. Put 5.0 mL of room temperature deionized water into a large test tube. Measure 1.600 g of KNO_3 on tared weighing paper at the balance, and add this to the DI water in the large test tube. Cover with Parafilm and mix well. Record your observations.

3. Place this test tube in the hot-water bath (50-60°C). Make your observations as the contents of the test tube get warmed. Mix well and be patient.

4. Transfer this test tube to the ice-water bath. Make your observations as the contents of the test tube reach the temperature of the ice water. Mix well and be patient.

5. Transfer this test tube back to the hot-water bath. Make your observations as the contents of the test tube reach the temperature of the hot water. Mix well and be patient.

6. Dispose of the potassium nitrate solution in the waste bottle. Rinse and reuse the large test tube as needed.

Save the hot-water bath and the ice bath for use in Part C.

Part C: Complex Ion Equilibrium

Here you will test the effects of changing the volume and temperature on the complex ion equilibrium between Cu^{2+} and NH_3 as in equation (7).
Reagents needed for this part are: 0.1 M Cu^{2+}, 6 M NH_3, 6 M HCl (*aq*), and deionized water.

1. Use the hot-water bath **in the fume hood** for this part. The hot-water bath will be used in Step 4.

2. Put 5 mL of 0.1 M Cu^{2+} solution into a large test tube. Record the color of this original solution. Working in the fume hood, carefully add 3 drops of 6 M $NH_{3(aq)}$ Record the color of this solution. Add enough NH_3 to make the original solution change from clear light blue to dark blue with a precipitate. Add a few more drops of NH_3 to make the precipitate dissolve. Record all of your observations and number of drops used.

3. Using a 10-mL graduated cylinder, add deionized water to the solution in your test tube in approximately 2 mL increments, stirring after each addition, until no further color change occurs. (Approximately 8 mL of DI water.) Record your observations.

4. Prepare another test tube by repeating Step 2. Place the test tube into the hot-water bath and record any color change.

5. Cool the solution down in the ice bath and record any color change.

6. Put the test tube back in the hot-water bath and record any color change.

Part D: Dissolving Insoluble Solids

Here you will further examine how one reaction can affect the behavior of another reaction when the reactions share one or more common chemical species.
Reagents needed are: 0.1 M $Zn(NO_3)_{2\,(aq)}$, 0.1 M $Mg(NO_3)_{2\,(aq)}$, 6 M NaOH (*aq*), 6 M HCl (*aq*), and 6 M $NH_{3\,(aq)}$.

1. Label three large test tubes A, B, and C. Add about 2 mL of 0.1 M $Zn(NO_3)_2$ solution to each test tube. Add one drop of 6 M NaOH solution to each test tube. Mix each solution and record your observations.

2. Into test tube A, add 20 drops of 6 M HCl (*aq*) drop-by-drop while mixing. Record all observations.

3. Into test tube B, add 20 drops of 6 M NaOH (*aq*) drop-by-drop while mixing. Record all observations.

4. Into test tube C, add 20 drops of 6 M NH_3 (*aq*) drop-by-drop while mixing. Record all observations.

5. Label three additional large test tubes D, E, and F. Add about 2 mL of 0.1 M $Mg(NO_3)_2$ solution to each test tube. Add one drop of 6 M NaOH solution to each test tube. Mix each solution and record your observations.

6. Into test tube D, add 20 drops of 6 M $HCl_{(aq)}$ drop-by-drop while mixing. Record all observations.

7. Into test tube E, add 20 drops of 6 M $NaOH_{(aq)}$ drop-by-drop while mixing. Record all observations.

8. Into test tube F, add 20 drops of 6 M $NH_{3(aq)}$ drop-by-drop while mixing. Record all observations.

For the Data section of your notebook: Record all of your observations made in each part of this experiment. Neatly organize your observations, and provide a brief statement with each observation so someone reading your notebook can tell what was done experimentally that caused that observation.

For the Results section of your notebook: Explain each observation by referring to Le Châtelier's Principle, shifts to the right, shifts to the left, temperature effects, dilution effects, and coupled reactions. *<u>Include the chemical equations</u>*.

For the Conclusion section of your notebook: Comment on whether the results matched up with what you expected based on Le Châtelier's Principle. Try to explain any discrepancies.