Le Châtelier's Principle

INTRODUCTION

Le Châtelier's Principle states that when stress is placed on a system in equilibrium, the system will react to relieve the stress.

Stress refers to changes in concentration, pressure, volume, and temperature. Consider the exothermic chemical reaction:

$$SO_2(g) + 0.5\ O_2(g) \rightleftharpoons SO_3(g)$$

Concentration: If the reaction has reached equilibrium, and we disturb this reaction at equilibrium by adding SO_2, the added SO_2 would be reduced in quantity by the reaction moving to the right, forming more of the SO_3.

Pressure: For this reaction, an increase in pressure on the system would also move the reaction to the right. There are 1.5 total moles of gas on the left of the arrows, and only one mole of gas on the right. As the reaction moves to the right, the number of moles present would reduce, and so the pressure would reduce.

Volume: For this reaction, if the volume of the container is increased, the reaction would move to the left, where there are more moles of gas than there are on the right. Increases of volume and decreases of pressure are complementary processes. They can be effected by a piston-cylinder reaction vessel.

Temperature: The reaction is exothermic. It gives off heat. If the temperature on the system were increased, the reaction would move to the left, thereby absorbing some of the heat added.

To easily apply Le Châtelier's principle, think of the arrows as a funnel for the reaction. The material on the left side can flow to the right, and the right side can flow to the left. If you "push" or "pull" on one side of the reaction by changing the concentration of a reactant, the quantities will "flow" through this funnel in a way to offset the change. If you increase the pressure (or decrease the volume) for the system, the reaction will flow in a direction to offset the increase, if possible. If you change the temperature, the system will flow in the direction that offsets the temperature change.

EXPERIMENT

Supplies

You will use test tubes from your drawer. You will estimate quantities of reactants, adding solutions from transfer pipets attached to the reagent bottles. These are marked to the proper volume. You will add other reactants by drop.

Except for Part 6, all of the reactions shown take place in water. The (aq) appendage, which shows that a substance is in water, is left off so that the equations would fit in the space allowed.

Part 1: Chromate/Dichromate Equilibrium.

$$\underset{\text{yellow}}{2CrO_4^{2-}} + 2H_3O^+ \rightleftharpoons \underset{\text{orange}}{Cr_2O_7^{2-}} + 3H_2O$$

Place about 1 milliliter of 1 M K_2CrO_4 in a test tube. Add several drops of 3 M H_2SO_4. Stir. Now add drops of 6 M NaOH with stirring until a change takes place. Add more H_2SO_4. Record your observations and explain what happened using Le Châtelier's principle. You need to know that H_2SO_4 produces H_3O^+ ions in solution, and NaOH produces OH^- ions which remove H_3O^+ ions.

Dispose of the solution in the waste container marked "Chromate Waste".

Part 2: Indicator Equilibria.

There is a class of dyes that changes color depending on the concentration of H_3O^+ ions in solution. These dyes are called acid-base indicators. The generic reaction

$$\underset{\text{one color}}{HIn} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{another color}}{In^-}$$

shows how the indicators work. They are usually carbon containing compounds with benzene rings. The concentration of H_3O^+ required to shift the equilibrium differs for different indicators. Methyl orange is red in the HIn state, yellow-orange in the In^- state. If the H_3O^+ is greater than 10^{-4} (pH of 4), methyl orange shifts to the HIn state. Phenolphthalein is colorless in the HIn state, pink in the In^- state. If the H_3O^+ is greater than 10^{-9} (pH of 9), phenolphthalein shifts to the HIn state.

Place about 1 milliliter of deionized water into each of two test tubes. Add a drop of methyl orange to one, a drop of phenolphthalein to the other. Add one drop of 6 M HCl to each test tube. Add two drops of 6 M NaOH to each test tube. Record your observations and explain what happened using Le Châtelier's principle. Here is the generic indicator equation rewritten for methyl orange:

$$\underset{\text{red}}{HMO} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{yellow-orange}}{MO^-}$$

HCl increases the H_3O^+, and NaOH decreases the H_3O^+. Rewrite the generic equation in a similar way for phenolphthalein in the explanation section on the next page.

Dispose of the solutions in the sink.

Part 3: Acetic Acid/Acetate Equilibrium.

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

Pour about 1 milliliter of 0.1 M $HC_2H_3O_2$ into each of two test tubes. Add a drop of methyl orange solution to each test tube. Add 1 M $NaC_2H_3O_2$ solution to one test tube a drop at a time until there is a difference in color between the two solutions. Record your observations and explain what happened using Le Châtelier's principle. When sodium acetate, $NaC_2H_3O_2$, dissolves in water, it breaks up into the Na^+ and the $C_2H_3O_2^-$ ions. The methyl orange changes color with changing H_3O^+ concentration, so refer to Part 2 of the experiment to help you interpret what the addition of acetate ions did to the equilibrium.

Dispose of the solutions in the sink.

Part 4: Ammonia/Ammonium Equilibrium.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The OH^- ion concentration controls the H_3O^+ ion concentration in water solutions. As the OH^- ion concentration gets larger, the H_3O^+ ion concentration gets smaller, and vice versa. The $[OH^-]$ in the original aqueous solution of ammonia, NH_3, is about 10^{-3}, which makes the $[H_3O^+]$ about 10^{-11}.

Pour about 1 milliliter of 0.1 M NH_3 into each of two test tubes. Add a drop of phenolphthalein solution to each test tube. Add 1 M ammonium chloride, NH_4Cl, solution to one test tube a drop at a time until there is a difference in color between the two solutions. Record your observations and explain what happened using Le Châtelier's principle. When NH_4Cl dissolves in water, it breaks up into the NH_4^+ and the Cl^- ions. As you were instructed in Part 3, use the information from Part 2 to help you interpret what the addition of ammonium ions did to the equilibrium.

Dispose of the solutions in the sink.

Part 5: Iron/Thiocyanate Equilibrium.

$$\underset{\text{pale yellow}}{Fe^{3+} + SCN^-} \rightleftharpoons \underset{\text{deep red}}{Fe(SCN)^{2+}}$$

Pour about 1 milliliter of deionized water to each of three test tubes. Add 1 drop of 0.1 M $Fe(NO_3)_3$ and 1 drop of 0.1 M KSCN to each test tube. Add two more drops of 0.1 M $Fe(NO_3)_3$ to one of the tubes, and two more drops of 0.1 M KSCN to another of the test tubes. Try to compare the colors of the solutions as quantitatively as possible. Record your observations and explain what happened using Le Châtelier's principle.

Dispose of the solutions in the sink.

Part 6: Temperature Effect.

$$\underset{\text{purple}}{CoCl_4^{2-}} + 6\,H_2O \rightleftharpoons \underset{\text{pink}}{Co(H_2O)_6^{2+}} + 4\,Cl^- + \text{energy}$$

Pour about 2 milliliters of 0.15 M $CoCl_2$ (in methanol) into a test tube. Add deionized water drop by drop with stirring until the blue color *just changes* to pink. Do not add excessive water. Place the test tube in a water bath in the fume hood. The temperature in the water bath should be 65 to 70 °C. When the color changes, remove the test tube from the hot water bath, and cool it by swirling it in tap water. (If you do not see a color change, you may have added too much water. Remake the solution. Take care to follow directions.) Record your observations and explain what happened using Le Châtelier's principle.

Dispose of the solution in the waste container marked "Cobalt Waste".

Part 7: Saturated Equilibrium.

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

Pour about 1 milliliter of saturated NaCl solution into a test tube. Add 12 M HCl drop by drop with stirring until you see a change taking place in the test tube. Continue to add 3 or 4 more drops, pausing after each drop. Record your observations and explain what happened using Le Châtelier's principle.

Dispose of the solution in the sink.

OBSERVATION TABLE

Rewrite the chemical equation for each part in the explanation.

Part 1 Observations   Explanation
Part 2 Observations   Explanation
Part 3 Observations   Explanation
Part 4 Observations   Explanation
Part 5 Observations   Explanation
Part 6 Observations   Explanation
Part 7 Observations   Explanation

Name____ Grade___________ Date ___________

QUESTIONS

1. What you did in Parts 3, 4, 5, and 7 are exam$\rightleftharpoons$les of the *common ion effect*. Why do you suppose it has that name? Give an explanation of the common ion effect based on what you did and what you observed.

2. Rewrite the chemical equation from Part 6 using ΔH notation for energy. Simply indicate if the ΔH is + or -.

3. Write the following equation in the manner the equation in Part 6 is written (note the energy term):
$2\ H_2O(l) + O_2(g) \quad 2\ H_2O_2(aq) \qquad \Delta H = 196.1\ kJ$

4. In Part 7, the $[Cl^-]$ in saturated NaCl is 5.4 M at room temperature. Assume that you had 1.00 ml of the saturated solution, and that you added 0.50 ml of 12 M HCl. What is the $[Cl^-]$ after you added the HCl. (When two solutions contain the same component, the numerator consists of the sum of the volume times the concentration for each solution. The denominator is the total volume.

5. Ammonia, NH_3, has a distinctive smell. In Part 4, how do you think the smell of the solution would be affected by the addition of NaOH? Explain.

6. Write out the K_{eq} expression for each reaction shown in the seven parts of the experiment. For reactions in water solutions, $[H_2O]$ is not shown in the expression because it is usually a large and relatively constant value.

1 **2** **3** **4**

5 **6** **7**