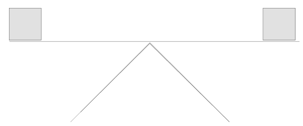
1.0 Introduction

Equilibrium in a chemical reaction is established when there is no *net* production of product or reactant molecules. Adding a substance to or removing a substance from an equilibrium mixture gives a new system that is *not* at equilibrium. This new system then reacts to restore (partially) the initial concentration of the added or removed substance. This is referred to as "shifting the equilibrium."

You can think of an equilibrium as a teeter-totter or seesaw. At equilibrium, a seesaw is level:



If you add a product, the right side of the seesaw is heavy:

Which way must the equilibrium shift to re-level the seesaw (go back to equilibrium)? This system would shift "to the left." After the shift, the system has reached (a new) equilibrium.

An important thing to remember is that when equilibrium is reached the chemical reactions have not stopped, the forward and reverse reaction rates are in balance so it appears that there is no net change in the relative amounts of reactants and products.

In this experiment we will observe such shifts and explain them in terms of effects on the concentrations of various participants and on heat effects.

General rules describing Le Chatelier's Principle are:

- Equilibria shift away from the side of increased concentration of one of the participants. A widespread example of this is "common ion effect."
- Equilibria shift towards the side of decreased concentration of one of the participants.
- Equilibria do not shift when "spectator" ions or molecules are added or removed.

Since we can view heat as a reactant (endothermic) or a product (exothermic) heat changes can shift the equilibrium. Heating a reaction at equilibrium causes a shift away from the side with the heat term; cooling a reaction at equilibrium causes a shift towards the side with the heat term. (Do you remember the signs of ΔH for endothermic and exothermic reactions?).

2.0 Procedure

In these experiments, use small 10 mm × 75 mm test tubes. The volumes are given in drops, assuming you are using a medicine dropper (20 drops/mL). The most common size of dropper bulb is 1 mL. If you squeeze one of these bulbs fully, then fill a medicine dropper, the total liquid in the dropper is about 1 mL.

Where instructed to use *x* mL of liquid, use the "full dropper" method to approximate the volumes.

2.1 The first equilibrium system to be studied is between chromate ion, CrO_4^{2-} (aq), and hydronium ion, H_3O^+ (aq), to form dichromate ion, $Cr_2O_7^{2-}$ (aq) and water:

$$2\ CrO_4^{2-}(aq) + 2\ H_3O^+(aq) \rightarrow \leftarrow \quad Cr_2O_7^{2-}(aq) + 3\ H_2O$$

Label four clean, dry test tubes 1–4. Put 4 drops of 0.1 M potassium chromate, K_2CrO_4 , solution in each test tube. Set test tube 4 aside for a reference. To test tubes 1, 2, and 3, add 1 drop 12 M HCl and mix thoroughly. Record the color change on your report sheet.

To test tube 1, add H_2O slowly, with mixing, until a color change occurs. Be careful not to confuse *dilution* of color with change of hue. Record the color change on the report sheet.

To test tube 2, add 6 M NaOH dropwise, with mixing, until a color change occurs. Record the color change on your report sheet.

To test tube 3, add about 0.2 g of crystalline sodium borate, Na_3BO_3 . Mix until dissolved. If there is no color change, add a bit more Na_3BO_3 . Record your observations on your report sheet.

If there is a waste container labeled "chromium waste," place your products in that container. Otherwise, place them in the holding beaker or the waste container for this experiment.

2.2 The second equilibrium system to be studied is between hexaaquocobalt(II) complex ion, $[Co(H_2O)_6]^{2+}$, and Cl^- (aq) to form the tetrachlorocobaltate(II) ion, $[CoCl_4]^{2-}$, and H_2O.

$$[Co(H_2O)_6]^{2+}(aq) + 4\ Cl^-(aq) \rightarrow \leftarrow \quad [CoCl_4]^{2-}(aq) + 6\ H_2O$$

Note: A bottle labeled "$[Co(H_2O)_6]^{2+}$ + $[CoCl_4]^{2-}$ " is provided for this procedure. This bottle contains these two cobalt complex ions, not necessarily in equal amounts. Each of these two ions has a distinct color. We will determine the color of each of these ions and whether the above reaction is exothermic or endothermic.

Put 6 drops of the solution labeled "$[Co(H_2O)_6]^{2+}$ + $[CoCl_4]^{2-}$ " in a test tube and add 12 M HCl dropwise, with mixing, until a color change is observed. Record the colors before and after adding 12 M HCl on your report sheet. Now add H_2O to the test tube until there is another color change. Record on the report sheet.

Put 6 drops of the solution labeled "$[Co(H_2O)_6]^{2+}$ + $[CoCl_4]^{2-}$ " in another test tube and heat in a water bath *gently*. Be careful not to splatter any of the solution on yourself or anyone else. Record the color change on the report sheet.

If there is a waste container labeled "cobalt waste," place your products in that container. Otherwise, place them in the holding beaker or the waste container for this experiment.

2.3 The third equilibrium system to be studied is the ionization of the weak monoprotic acid, acetic acid, $HC_2H_3O_2$, which ionizes as shown below to give the acetate ion, $C_2H_3O_2^-$:

$$HC_2H_3O_2\,(aq) + H_2O \rightleftarrows H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)$$

Acetic acid is often abbreviated HOAc, and acetate ion as OAc^-, so we could write the above equilibrium as:

$$HOAc\,(aq) + H_2O \rightleftarrows H_3O^+\,(aq) + OAc^-\,(aq)$$

Put 6 drops of 0.1 M HOAc in a test tube. Add 1 drop of methyl orange indicator. Record the color on the report sheet. Now add 8 drops of 1 M sodium acetate, NaOAc, solution, dropwise with mixing. (Hint: In a more acidic solution, methyl orange changes from yellow to red.) Record your observation on the report sheet.

3.0 Before You Leave

Clean your glassware and return to appropriate storage. Place your waste in an appropriate waste container and make sure to clean your work area of any spills including water.

4.0 Calculations

There are no calculations for this lab. Fill in the answer sheets and answer the questions on equilibrium at the end of the lab.

Report Sheet

2.1 $2\ CrO_4^{2-}(aq) + 2\ H_3O^+(aq) \rightleftarrows Cr_2O_7^{2-}(aq) + 3\ H_2O$

1.	Color of test tube 4	
2.	Color of test tubes 1, 2, 3 contents after HCl (aq) is added	

3. What causes the color change in test tubes 1-3? Explain on the basis of Le Chatelier's Principle.

4.	Color of test tube 1 after H_2O is added?	

5. What causes the color change in test tube 1? Explain on the basis of Le Chatelier's Principle.

6.	Color of test tube 2 contents after 6 M NaOH is added	

7. Explain the color change on the basis of Le Chatelier's Principle.

8.	Color of test tube 3 contents after Na_3BO_3 is added	

9. Explain this color change on the basis of Le Chatelier's Principle using the following information. The borate ion, BO_3^{3-}, is a Brønsted base that reacts with the H_3O^+ ion in test tube 3 to form H_3BO_3, boric acid.

2.2 $[Co(H_2O)_6]^{2+}(aq) + 4\ Cl^-(aq) \rightleftarrows [CoCl_4]^{2-}(aq) + 6\ H_2O$

10.	Color of test tube contents before 12 M HCl is added	
11.	Color of test tube contents after 12 M HCl is added	
12.	Color of test tube contents after H_2O is added	
13.	What is the color of $[Co(H_2O)_6]^{2+}$ (aq)?	
14.	What is the color of $[CoCl_4]^{2-}$ (aq)?	
15.	Which ion is present in greater concentration in the bottle?	

16. Explain the color changes you observed on the basis of Le Chatelier's Principle.

17.	Color of test tube contents after heating	
18.	Is the reaction between $[Co(H_2O)_6]^{2+}$(aq) and Cl^-(aq) exothermic or endothermic?	

19. Explain the color changes you observed on the basis of Le Chatelier's Principle.

2.3 $HOAc(aq) + H_2O \rightleftarrows H_3O^+(aq) + OAc^-(aq)$

20.	Color of solution after methyl orange is added	
21.	Color of the solution after 1 M NaOAc is added	

22. Explain the change you observed using Le Chatelier's Principle. Note that methyl orange is red in an acidic solution but yellow in a solution that is slightly acidic or slightly basic.

LeChatelier Questions:

1. Consider the reaction: $N_2(g) + 3\ H_2(g) \rightarrow \leftarrow 2\ NH_3(g)$ $\Delta H = -91$ kJ

   Once at equilibrium what would happen if:

   a) the pressure of the reaction was increased

   b) ammonia was removed from the reaction mixture

   c) the reaction was heated

   *all three of these changes are used in the manufacturing of ammonia

2. When a reaction is at equilibrium, what is the effect of adding a catalyst?

3. If the reaction: $H_2(g) + Cl_2(g) \rightarrow \leftarrow 2\ HCl(g)$ $\Delta H = -180$ kJ is at equilibrium what would be the effect of:

   a) pressurizing the reaction mixture

   b) adding more hydrogen chloride gas

   c) cooling the reaction