Purpose

To explore the concept of chemical equilibrium and apply Le Châtelier's principle to explain the response of chemical systems to stresses.

Learning Objectives

- Recognize that not all reactions go to completion and that often after a reaction, both products and reactants are present at equilibrium.
- Recognize and interpret the effects caused by a disturbance to a system at equilibrium, as explained by Le Châtelier's principle.
- Identify the formulas of precipitates formed in double displacement ionic reactions.

Introduction

The stoichiometry of chemical equations shows the mole ratios of reactants needed relative to products formed. The stoichiometry does not show how fast the reaction occurs or if all of the reactants will be used up to form products. Some reactions proceed to completion, such as titrations of strong acids with bases, and combustion reactions. In many reactions, however, all of the reactants are not consumed to form product. These reactions reach an equilibrium with a mixture of both reactants and products present. At equilibrium, products are reacting to reform reactants and the reactants continue to react to form products, and the rate of this forward and reverse reaction are the same, so that the concentrations of all species in the container are not changing. This chemical equilibrium will be reached whether the *reactants*, *products*, or a *combination of the two* are added to a reaction vessel initially.

Consider a case where only reactants are initially present in a reaction vessel. The forward reaction rate will initially be high as the concentrations of the reactants are high; whereas, the reverse reaction rate will be zero since the concentrations of the products are zero. As the reaction progresses, the forward reaction rate will decrease as the reactants are consumed and the reverse reaction rate will increase as the concentrations of products increases until a point is reached where both the forward and reverse reaction rates are the same. At this point the reaction has reached chemical equilibrium. It is important to note that the reaction in both the forward and reverse direction have not stopped. At equilibrium the forward reaction is simply creating products as quickly as the reverse reaction is producing reactants. Examine the generic reversible reaction, Reaction LCP.1:

$$\mathrm{aA + bB \rightleftharpoons cC + dD} \qquad \text{(Reaction LCP.1)}$$

At equilibrium, some of each of the reactants and products will be present in the reaction vessel. When the reaction reaches equilibrium under conditions of constant temperature and pressure, the ratio of the concentrations of the products to reactants, with each species raised to the exponent of its coefficient in the balanced equation, K_{eq}, shown mathematically in Equation LCP.1, is constant.

$$K_{\mathrm{eq}} = \frac{[\mathrm{C}]_{\mathrm{eq}}^{c}\,[\mathrm{D}]_{\mathrm{eq}}^{d}}{[\mathrm{A}]_{\mathrm{eq}}^{a}\,[\mathrm{B}]_{\mathrm{eq}}^{b}} \qquad \text{(Equation LCP.1)}$$

> The square brackets, [ ], represent molar concentrations.

Le Châtelier's principle states that a system at equilibrium, when subjected to an action which stresses the equilibrium, will respond in a way that lessens the stress and restores the equilibrium. As applied to a chemical reaction, this response means that the rate of the forward reaction or the reverse reaction will increase or decrease until a new position of equilibrium is restored. In other words, the reaction mixture will either *shift in concentration toward products* or *shift in concentration toward reactants* in order to regain a chemical equilibrium. Mathematically, when a system is not at equilibrium, the ratio of products over reactants as expressed in Equation LCP.1 no longer is equal to K_{eq}, and the reaction will proceed so that when the reaction is again at equilibrium, that ratio will again equal K_{eq}.

Possible perturbations to equilibrium include changing the concentrations of one or more of the chemicals in the vessel, changing the volume or pressure in a container in which gases are among the reactants or products, and changing temperature. Temperature changes can cause a shift in equilibrium because temperature changes either add or remove heat from a reaction. Look at the exothermic reaction for the formation of gaseous hydrogen chloride in Reaction LCP.2:

$$\mathrm{H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)} \qquad \Delta H = -184\,\mathrm{kJ} \qquad \text{(Reaction LCP.2)}$$

In exothermic reactions, heat is released during the process and another way to write the reaction is given in

Reaction LCP.3 where heat is explicitly shown as a product of the reaction.

$$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g) + 184\,kJ \qquad \text{(Reaction LCP.3)}$$

If heat is added to the reaction shown in Reaction LCP.2 or Reaction LCP.3, the reaction will shift to the left to relieve the stress of the added "product" of the reaction and if the reaction is cooled in some manner, the reaction will shift to the right to produce more heat and restore the equilibrium. A thorough explanation of the effect of heat would include thermodynamic properties, which may be covered in the associated lecture course but is not necessary for the understanding of these experiments.

Examples of Chemical Equilibria

Dinitrogen tetroxide/nitrogen dioxide

A frequent example in general chemistry textbooks of an application of LeChâtelier's principle in gaseous systems is the equilibrium of dinitrogen tetroxide with nitrogen dioxide, a temperature dependent equilibrium (Reaction LCP.4). Of the two gases in Reaction LCP.4, one gas is brown and the other is colorless. This reaction is reversible and, at equilibrium, *some of each gas* is present. Depending on whether more of the brown gas is present or more of the colorless gas is present, the intensity of the color of the mixture will change in the reaction chamber. This reaction will be observed in this experiment.

$$N_2O_4(g) + 57.2\,kJ \rightleftharpoons 2\,NO_2(g) \qquad \text{(Reaction LCP.4)}$$

Iron(III) thiocyanate complex

Examine the net ionic equation of a reaction that will be thoroughly investigated during this experiment (Reaction LCP.5):

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq) \qquad \text{(Reaction LCP.5)}$$

Stressing the equilibrium of this reaction by adding more iron(III) ions will cause the reaction to shift toward products (the right), because a shift towards the products will cause a reduction in the iron(III) ions lessening the stress, restoring equilibrium. Removing some iron(III) will cause the reaction to shift toward reactants (the left) in order to produce more iron(III) and restore equilibrium. In today's experiment, look for examples that demonstrate this behavior. Be aware that species can be removed from a reaction by adding something else that causes a side reaction.

An example of this would be to add something that forms a precipitate with a reactant. For example, if carbonate ion ($CO_3{}^{2-}$) were added to the reaction vessel containing iron(III), the carbonate could react with Fe^{3+} to form the insoluble salt $Fe_2(CO_3)_3$ and the Fe^{3+} now bound up in the solid would no longer be available in aqueous solution to react with SCN^- to form the complex, $FeSCN^{2+}$. If this happened, in which direction (forward or reverse) would the reaction in Reaction LCP.5 have to proceed in order to reestablish equilibrium?

Methy red indicator

Good visual reactions of Le Châtelier's principle involve organic dyes used as indicators, of which methyl red is an example. Figure LCP.1 shows the reaction methyl red undergoes with the addition of acid. Observe the large size of methyl red with the six-membered carbon ring systems. These types of structures will be discussed thoroughly in organic chemistry, but it is useful to understand that the conjugated rings, indicated by the circles inside the six-membered ring structures, along with double bonds, allow for more movement of electrons between atoms in the molecule. In dyes such as these and in other chemical systems, it is the ability of electrons to move that causes color to be observed.

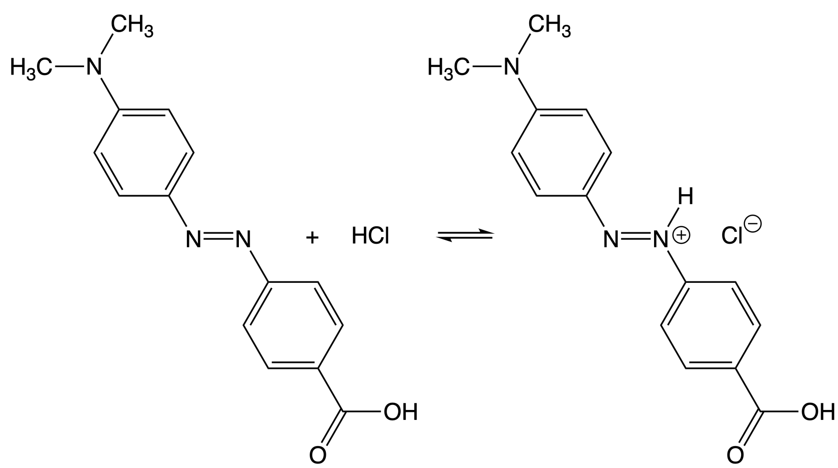

Figure LCP.1: Equilibrium reaction of methyl red and hydrochloric acid.

$$C_{15}H_{15}N_3O_2(aq) + HCl(aq) \rightleftharpoons C_{15}H_{16}N_3O_2Cl$$

The reaction of methyl red with the addition of acid or base is a reversible reaction and by adding or consuming the proton (H^+) on one of the double-bonded nitrogen atoms between the rings, the ability of electrons to move in the molecule is altered, and a color change may be observed.

Copper(II) complexes

This experiment provides an opportunity to observe color changes among complexes. A complex usually consists of a metal ion covalently bonded to neutral molecules or anions. Examples are the products in Reaction LCP.6 and Reaction LCP.7. Aqueous solutions of metal ions complexes are examples of equilibria. When a copper(II) salt is dissolved in water, the copper(II) ion forms covalent bonds with four water molecules and this assists in its dissolution. By Le Châtelier's principle, the more water present, the more the reaction is pushed to the right (Reaction LCP.6).

$$Cu^{2+}(aq) + 4\,H_2O(l) \rightleftharpoons [Cu(H_2O)_4]^{2+}(aq) \qquad \text{(Reaction LCP.6)}$$

When ammonia (NH_3) is added to an aqueous solution of the copper(II) salt, the ammonia molecules displace the water molecules in the complex and a new complex is formed, for which a color change is observed (Reaction LCP.7).

$$4\,NH_3(aq) + [Cu(H_2O)_4]^{2+}(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 4\,H_2O(l) \qquad \text{(Reaction LCP.7)}$$

Bismuth chloride/bismuth oxychloride

A final interesting reaction to observe is the reaction to form bismuth oxychloride when adding bismuth trichloride to water. Bismuth trichloride is soluble in water but the oxychloride is not (Reaction LCP.8). Expected shifts in the equilibrium can be predicted when considering relative amounts of reactants or products added.

$$BiCl_3(aq) + H_2O(l) \rightleftharpoons BiOCl(s) + 2\,HCl(aq) \qquad \text{(Reaction LCP.8)}$$

Procedure

Dinitrogen tetroxide/nitrogen dioxide

At some point during the lab time, make observations about the equilibrium reaction between dinitrogen tetroxide and nitrogen dioxide, which will be set up as a demonstration in the laboratory. One flask containing this reaction mixture will be immersed in a beaker of water at room temperature and the other will be in a heated beaker of water. Record the temperature of the water in the beakers in which these flasks are held and record observations. Relating Reaction LCP.4 and observations to Le Châtelier's principle, determine and record the color of each gas. Explain observations.

Iron(III) thiocyanate complex

Obtain dropper bottles containing iron(III) nitrate and potassium thiocyanate and record the color of each solution. Mix 1 mL each of 0.1 M iron(III) nitrate, $Fe(NO_3)_3$, and 0.1 M potassium thiocyanate, KSCN, solutions in a 150-mL or a 250-mL beaker and record the color of the resulting solution. Dilute this solution with 50 mL water, mix well, and pour 5 mL of this solution into each of 3 clean test tubes in a test tube rack. Label one test tube "control," to which no changes will be made. Add 10 drops of 0.1 M $AgNO_3$ to one of the remaining test tubes, and 10 drops of 6 M NaOH to the other. Mix very well and allow two or three minutes for any reaction to occur before recording observations, comparing them to the control. Explain the results in terms of the original reaction (Reaction LCP.5), any additional side reactions, and Le Châtelier's principle.

Dilute the solution remaining in the beaker with an additional 50 mL of water. Mix well and pour 5 mL of this solution into five separate clean test tubes in a test tube rack. Label one tube "control," to which no changes will be made. It is the reference solution for this part of the experiment. Immerse one of the test tubes in a beaker of ice water for 7 minutes and another in a beaker of hot water (50–70 °C) for 7 minutes. Record observations about the effect of temperature on the equilibrium after the 7 minutes have passed. If no change is observed, consult the instructor.

For the two remaining test tubes containing the $FeSCN^{2+}$ solution, add 10 drops of 0.1 M $Fe(NO_3)_3$ to one and 10 drops of 0.1 M KSCN to the other; mix all. Record detailed observations for any changes to these four test tubes, comparing them to the control. Explain the results in terms of the original reaction (Reaction LCP.5), and Le Châtelier's principle.

Methyl red indicator

For this experiment, it is important to rinse the test tubes 5 times with deionized water to make sure all soap is removed. Soap will alter the observations. Into 3 test tubes, put 1 mL of deionized water and 6 drops of methyl red indicator solution. Record the color. One test tube will serve as the control for comparison. Add *dilute* HCl dropwise with mixing to one of the other two test tubes until a color change is observed. Record observations. To the remaining test tube, add dilute NaOH dropwise until a color change is seen. It is possible for more than one color change to be observed, so after an initial color change, add a few more drops, looking for additional changes. Record observations. Describe the reactions in acid and base in terms of Le Châtelier's Principle, referencing Figure LCP.1.

Copper(II) complexes

Add 1 mL of 0.5M copper(II) nitrate solution to a test tube and dilute to 5 mL with deionized water. Record the color of the solution. The observed color is the color of the complex of the metal ion with four water molecules. In solution, the nitrate ions are spectator ions. Add 2 mL of 6 M aqueous ammonia *dropwise* to the copper (II) nitrate solution. Mix well by shaking after each drop. Record all observations and changes during the addition until 2 mL have been added. An intermediate product should form before the final product described in Reaction LCP.7 is formed. Thinking about the ions available in solution, identify the intermediate base formed. Then record the formula of the final product containing the copper(II) ion. Explain the reaction with ammonia in terms of Le Châtelier's principle.

To the same test tube add 6 M HNO_3 dropwise with mixing to the solution until the original color reappears and remains. Record observations and explain them in terms of Le Châtelier's principle the connection between Reaction LCP.9 (see Report Sheet), a reaction occurring with ammonia when acid is added, and Reaction LCP.7.

Bismuth chloride/bismuth oxychloride

Add 5 drops of 0.10 M bismuth trichloride solution and 4 mL of deionized H_2O to a test tube and record observations. Add 6 M hydrochloric acid dropwise, mixing after each drop, looking for any changes to the solution. Avoid adding a large excess of the acid. Record observations. Pour the solution from the previous test tube into a small beaker, add 25-mL of deionized water, and record observations.

> Allow time for any reaction to occur, up to several minutes.

Finally, add a few drops of 0.1 M bismuth trichloride solution to a beaker containing 150-mL of deionized water and record observations.

> Allow time for any reaction to occur, up to several minutes.

Explain the results in terms of in terms of Le Châtelier's principle and Reaction LCP.8.

Dispose of all waste properly and clean all test tubes and any other glassware with soap using a brush, rinsing well with water.

It is helpful to recognize that simplifying net ionic equations have been given in the Introduction, which can be used to interpret results of the experiment. It should also be recognized that there will be spectator ions resulting from the compounds used in the reactions and the spectator ions do not need to be part of the discussions about results. Knowing solubility rules, such as, all common compounds containing nitrates are always soluble and all compounds containing Group I metal cations are always soluble, will help determine which ions are available in solution.

(Except where otherwise noted, 2 pts for each answer)

Dinitrogen tetroxide/nitrogen dioxide

$$N_2O_4(g) + 57.2\,kJ \rightleftharpoons 2\,NO_2(g)$$

Room temperature bath

Temperature______________

Observations:

Hot water bath

Temperature______________

Observations:

Color: NO_2 ______________ N_2O_4 ______________

Explain the evidence that led to the color determinations: (4 pts)

Iron(III) thiocyanate complex

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

Color:

$Fe(NO_3)_3$ solution ______________

KSCN solution ______________

$FeSCN^{2+}$ solution ______________

Observations after cooling:

Observations after heating:

Is the reaction endothermic or exothermic? Explain the evidence that led to this conclusion. (4 pts)

Observations after adding $Fe(NO_3)_3$:

Explain in terms of the equation, $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$, and Le Châtelier's principle:(4 pts)

Observations after adding KSCN:

Explain in terms of the equation, $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$, and Le Châtelier's principle:(4 pts)

Observations after adding $AgNO_3$:

Using the ions present in the solution, write a net ionic equation that would explain the precipitate observed.

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Use the net ionic equation above and $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$ to explain the observations in terms of Le Châtelier's principle. (3 pts.)

Observations after adding NaOH:

Using the ions present in the solution, write a net ionic equation that would explain the precipitate observed.

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Use the net ionic equation above and $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$ to explain the observations in terms of Le Châtelier's principle. (3 pts.)

Methyl red indicator

$$C_{15}H_{15}N_3O_2(aq) + HCl(aq) \rightleftharpoons C_{15}H_{16}N_3O_2Cl$$

Color of solution of water with methyl red ______________

Observations when acid (HCl) was added to the solution:

Observations when base (NaOH) was added to solution:

Referencing Figure LCP.1, explain observations in terms of Le Châtelier's principle. (4 pts.)

Copper(II) complexes

$$4\,NH_3(aq) + [Cu(H_2O)_4]^{2+}(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 4\,H_2O(l)$$

Color of dilute solution of copper(II) nitrate ________________

All observations after adding NH_3:

Formula of insoluble base formed after a small amount of ammonia was added?

____

Color of final solution after addition of excess NH_3: ________________

Formula of the complex ion that causes the solution color after addition of ammonia. ________________

In terms of Le Châtelier's principle and using Reaction LCP.7, explain the observations resulting in the final product after the addition of NH_3. (4 pts.)

All observations after adding the strong acid, HNO_3:

When an acid is added to a solution of ammonia, an equilibrium reaction will occur (Reaction LCP.9):

$$NH_3(aq) + H^+(aq) \rightleftharpoons NH_4{}^+(aq) \qquad \text{(Reaction LCP.9)}$$

It should be expected that this reaction will affect the equilibrium expressed in Reaction LCP.7. In terms of Le Châtelier's principle, explain the observations and the resulting final color of the solution after the nitric acid addition. (4 pts.)

Bismuth chloride/bismuth oxychloride

$$BiCl_3(aq) + H_2O(l) \rightleftharpoons BiOCl(s) + 2\,HCl(aq)$$

Observation when water was added to an aqueous solution of $BiCl_3$:

Observation when 6 M HCl was added to the solution.

Explain the results after the addition of acid in terms of Le Châtelier's principle.

Observation when the acidic solution was diluted with more water.

Explain the results after dilution with water in terms of Le Châtelier's principle.

Observation when a few drops of $BiCl_3$ solution were added to a large volume of water.

Explain the results of added $BiCl_3$ in terms of Le Châtelier's principle.