6

Shifts in Equilibrium: Le Châtelier's Principle

Introduction

Whenever a chemical reaction occurs, the reverse reaction can also occur. In such a case, as the original reactants (on left side of the equation) react to form products (on right side of the equation), and the products (on the right side of the equation) also react to re-form the reactants. Since forward rate decreases as reactant concentration decreases and reverse rate increases as product concentration increases, eventually rates of the forward and reverse reactions become equal. At this point, both reactants and products are used up as fast as they are formed, so their concentrations cease to change with time. The reaction system has reached equilibrium. The equilibrium state is always the most stable, lowest Gibbs free energy, state that the reaction system can reach. (We will learn about Gibbs free energy later in the course)

If a reaction system in an equilibrium state is subjected to a perturbation away from that equilibrium state (change in temperature, volume, pressure, or amount of a reactant or product) then the system will respond to reach a new equilibrium state, i.e. new equilibrium concentrations of reactants and products. In summary, a new equilibrium state may result if the temperature or pressure of the reaction system is altered, or if the concentration of any of the components of the reaction system is changed.

The new equilibrium position will always be the most stable state for the reaction system under the new conditions. **The direction in which the system will shift to reach a new equilibrium in response to a change in conditions can be predicted by Le Châtelier's principle.** This principle has been stated in many different ways, including the following:

- If a system at equilibrium is altered in any way, the system will shift so as to minimize the effect of the change.
- When a stress is applied to a system in equilibrium, the concentrations of the reactants will change in such a way that the stress is partially relieved.
- If a system at equilibrium has any change imposed on it, it will shift in the direction helped most by that change.

The principle can be applied to the specific cases of changes in concentration, pressure, and temperature.

Concentration:

Consider the reaction:

$$\underset{\text{(white solid)}}{NaCl\ (s)} \rightleftharpoons \underset{\text{(both are colorless in solution)}}{Na^{+}\ (aq)\ +\ Cl^{-}\ (aq)}$$

Suppose we start with a saturated solution of sodium chloride; that is, we have a solution of Na^{+} (*aq*) and Cl^{-} (*aq*) in equilibrium with excess solid NaCl. After letting the excess solid settle to the bottom of the container, we add a few drops of concentrated hydrochloric acid (HCl). We observe that the solution immediately becomes cloudy, and more solid settles out of solution.

These observations can be explained using Le Châtelier's principle. Adding concentrated HCl initially increases the concentration of Cl^{-} ions. The resulting cloudiness shows that the system responded by forming more solid NaCl (the equilibrium has shifted to the left), thereby using up some of the added Cl^{-} ions. The new equilibrium has more solid NaCl (and a lower concentration of Na^{+}) than the original equilibrium. If we increase the concentration of one component in any equilibrium system, the system will shift to minimize the change by using up some of that component.

Every shift in equilibrium position predicted by Le Châtelier's principle can be explained in terms of reaction kinetics. In the above example, increasing the concentration of Cl^{-} ions increases the rate of the reverse reaction (precipitation of NaCl). The rate of the forward reaction (dissolution of NaCl) is initially unaffected, because it depends only on the surface area of the solid NaCl. At this point, the system is no longer at equilibrium, because the two opposing rates are not equal. The opposing rates will become equal again after some Na^{+} and Cl^{-} ions are used up and their concentrations have decreased (thereby decreasing the reverse reaction rate), and more solid NaCl has formed and its concentration has increased (thereby increasing the forward reaction rate). Again, the new equilibrium position has more solid NaCl, and less dissolved Na^{+} ions.

Pressure:

For reactions involving gases, the total pressure of the system is an important factor. Consider the reaction:

$$\underset{\text{(brown smog)}}{2\ NO_2\ (g)} \rightleftharpoons \underset{\text{(colorless)}}{N_2O_4\ (g)}$$

Suppose we start with a piston filled with a brown mixture of NO_2 and N_2O_4 gases. We squeeze the piston to decrease the total volume of the reaction mixture. The brown color of the reaction mixture fades to colorless.

These observations can also be explained using Le Châtelier's principle. Decreasing the volume increases the total pressure of the system, which depends on the total number of gas-phase molecules. The resulting color change from brown to colorless shows that the system responded to the increased pressure by using up some NO_2 (the equilibrium has shifted to the right). Since two NO_2 molecules are used to make only one N_2O_4 molecule, this new equilibrium has fewer total gas-phase molecules, and thus a lower pressure. If we increase the total pressure of any equilibrium system involving gas phase molecules, the system will reduce its total pressure by shifting in the direction that produces fewer gas phase molecules.

The observations can also be explained in terms of reaction kinetics. Increasing the total pressure increases the rate of the forward reaction and the rate of the reverse reaction. The shift arises because the two opposing rates increase by different amounts. For simplicity, let's assume that the reaction occurs all in one step, so that the rate laws of the opposing reactions follow the reaction stoichiometry. Doubling the total pressure doubles the concentrations of both NO_2 and N_2O_4. Since the forward reaction is bimolecular, its rate is proportional to $[NO_2]^2$, and increases by a factor of four. The reverse reaction is unimolecular; its rate is proportional to $[N_2O_4]$ and increases only by a factor of two. At this point, the system is no longer at equilibrium, because the rate of the forward reaction is faster than the rate of the reverse reaction. The rates will become equal again after some NO_2 is used up and there is a decrease in the concentration of NO_2 (thereby decreasing the forward reaction rate), and more N_2O_4 is formed and there is an increase in the concentration of N_2O_4 (thereby increasing the reverse reaction rate). This reasoning also shows that the equilibrium shifts to the right, the side with fewer gas phase molecules, so that there is more N_2O_4 and less NO_2.

Temperature:

Consider again the reaction:

$$\underset{\text{(brown smog)}}{2\,NO_2\,(g)} \underset{\text{endothermic}}{\overset{\text{exothermic}}{\rightleftharpoons}} \underset{\text{(colorless)}}{N_2O_4\,(g)} + \text{“heat”} \qquad \Delta H = -55\text{ kJ}$$

Suppose we start with a flask filled with a brown mixture of NO_2 and N_2O_4 gases. We place the flask in a boiling water bath. The brown color of the reaction mixture intensifies.

If we think about increasing the temperature as "adding heat" to the reaction mixture, we can use Le Châtelier's principle to explain these observations. Placing the flask in the boiling water bath added heat to the reaction mixture. The resulting color change to a darker brown color shows that more NO_2 was formed (the equilibrium has shifted to the left), thereby using up some of the added heat. The new equilibrium has a higher concentration of NO_2 (and a lower concentration of N_2O_4) than the original equilibrium. If we increase the temperature of any equilibrium system, the system will try to use up the added heat by shifting in the endothermic direction.

In terms of reaction rates, increasing the temperature increases both the rate of the forward reaction and the rate of the reverse reaction. Again, the shift in equilibrium arises because the two opposing rates increase by different amounts. The activation energy in the endothermic direction is greater than the activation energy in the exothermic direction. (Why?) Therefore, the rate in the endothermic direction is more sensitive to changes in temperature, and increases more when the temperature is increased.

In all of these examples, making a change will have the opposite effect. Decreasing the concentration of one component shifts the equilibrium to form more of that component. Lowering the total pressure favors the side of reaction that has more molecules in the gas phase. Lowering the temperature favors the exothermic direction.

Four different reaction systems will be examined in this experiment. In each of these, equilibrium will be established then the reaction conditions will be changed. The direction in which the equilibrium shifts in response to this change will be established by observing a change in the concentration of one of the components of the reaction. If the concentration of this component increases, the equilibrium has shifted toward its side of the equation. If its concentration decreases, equilibrium has shifted towards the other side.

Experimental Procedure

SAFETY PRECAUTIONS: Wear your SAFETY GOGGLES. Wash your hands and clothing immediately with copious amounts of water, if you spill any of the solutions on them. Be particularly careful with the silver nitrate solution (Part II) and the concentrated hydrochloric acid (Part III). The silver nitrate ($AgNO_3$) produces permanent black stains on skin and clothing; these stains appear gradually after exposure to sunlight. The concentrated hydrochloric acid (12 M HCl) has irritating vapors and is highly corrosive. If you spill any of this acid on the lab bench, neutralize it with sodium bicarbonate before wiping it up.

WASTE DISPOSAL: Pour the solutions from Part I and Part IV down the drain, followed by plenty of running water. Pour the solutions from Part II and Part III into the INORGANIC WASTE containers in the fume hood.

Part I. Dissociation of Acetic Acid

$$\underset{\text{acetic acid}}{CH_3COOH\,(aq)} \rightleftharpoons \underset{\text{acetate ion}}{CH_3COO^-\,(aq)} + \underset{\text{hydrogen ion}}{H^+\,(aq)}$$

Acetic acid is typical weak acid. In water, it dissociates slightly to produce a low concentration of ions. Unlike ionic salts, it does not dissociate completely when added to water. This reaction reaches equilibrium with most of the acetic acid remaining undissociated (that is, equilibrium lies to the left). Acetic acid solutions are weakly acidic because some hydrogen ions are released into solution. The concentration of hydrogen ions can be monitored with an acid-base indicator.

To set up this reaction system, you will add acetic acid to water containing a few drops of bromophenol blue indicator, until the blue color just changes color from blue to green (on its way to yellow). The green color means that $[H^+]$ is about 10^{-4} M. The color of the indicator will tell you if $[H^+]$ changes. If the indicator turns yellow, $[H^+]$ has increased to more than 10^{-4} M. If the indicator turns blue, $[H^+]$ has decreased to less than 10^{-4} M.

You will make one change to this equilibrium system:

- Adding solid sodium acetate (CH_3COONa), which is a typical ionic salt.

Procedure

Fill a beaker about half full with water. Add a few drops of bromphenol blue solution. Then add acetic acid from a dropper to the beaker until the indicator changes color from blue to green.

Add a small amount of solid sodium acetate to the beaker and stir to dissolve it. Record your observations.

Part II. Formation of the $Fe(SCN)^{2+}$ Complex Ion

Fe^{3+} (*aq*)	+	SCN^- (*aq*)	$\rightleftharpoons$	$[FeSCN]^{2+}$ (*aq*)
ferric ion		thiocyanate ion		complex
(light yellow)		(colorless)		(deep red)

Ferric ion, Fe^{3+}, reacts with thiocyanate ion, SCN^- to form the deep red, complex ion, $FeSCN^{2+}$. The intensity of the red color will tell you if $[FeSCN^{2+}]$ changes.

You will make three changes to this equilibrium system:

- Adding solid potassium thiocyanate (KSCN),
- Adding silver nitrate ($AgNO_3$), which removes one of the ions from the equilibrium system by forming an insoluble silver salt, and
- Heating and cooling the system.

Procedure

Add approximately 50 mL of 0.001 M potassium thiocyanate (KSCN) solution to a beaker or flask. Add about 10 drops of 0.1 M ferric nitrate [$Fe(NO_3)_3$] solution, and stir. This should give a red color which is intense enough to see but not so intense that changes in the color cannot be noticed.

Pour approximately 1/4 of the solution into each of four test tubes.

Test 1: To one of the test tubes, add a few crystals of solid potassium thiocyanate (KSCN). Record your observations.

Test 2: To another tube, add several drops of 0.1 M silver nitrate solution ($AgNO_3$). Record your observations.

Test 3: Place one of the remaining test tubes in a beaker filled with ice and water. Place the other test tube in a beaker half filled with water, and then heat the water while supporting the beaker on a ring stand. Record your observations.

III. Formation of the $CoCl_4^{2-}$ Complex Ion

$Co^{2+}\,(aq)$	+	$4\ Cl^{-}\,(aq)$	$\rightleftharpoons$	$CoCl_4^{2-}\,(aq)$
cobalt II ion		chloride ion		complex
(pink)				(deep blue)

Solutions containing cobalt II ion, Co^{2+}, dissolved in water are ordinarily pink or red. This is the color of the cobalt ion when it is associated with water molecules. In the presence of chloride ion, however, Co^{2+} reacts to form the blue complex ion $CoCl_4^{2-}$.

To set up this reaction system, you will add chloride ions to a solution containing cobalt II ions until the pink color changes to purple (in between pink and blue). The purple color shows that both pink Co^{2+} ions and blue $CoCl_4^{2-}$ ions are present. Color changes from purple to pink or from purple to blue tell you if $[Co^{2+}]$ and $[CoCl_4^{2-}]$ change.

You will make two changes to this equilibrium system:

- Diluting the system with water, and
- Heating and cooling the system.

Procedure

Add about 5 to 6 mL of 0.3 M cobalt nitrate $[Co(NO_3)_2]$ solution to a test tube. Add concentrated HCl in very small portions until the color has changed to purple. BE CAREFUL!! Concentrated HCl (12 M hydrochloric acid) is highly corrosive!

Add about half of the solution to a second test tube to keep for comparison.

Test 1: To one of the tubes, very slowly add a little water. Add just enough water to observe a significant color change. Record your observations.

Test 2: Place the test tube to which the water has been added in a beaker partly filled with water. Heat the beaker while supporting it on a ring stand. Compare the color to that of the other test tube. If you like, try heating this test tube as well. Record your observations.

IV. Bicarbonate Ion-Carbon Dioxide Equilibrium

$CO_2\,(aq\ and\ g)$	+	$H_2O\,(l)$	$\rightleftharpoons$	$H^{+}\,(aq)$	+	$HCO_3^{-}\,(aq)$
carbon dioxide		water		hydrogen ion		bicarbonate ion

When carbon dioxide (CO_2) gas dissolves in water, a weakly acidic solution is created, with a small concentration of H^+ ions in solution. You will set up this equilibrium, starting from the other side of the reaction. By adding a small amount of a strong acid (HCl) to a solution of sodium bicarbonate ($NaHCO_3$), carbon dioxide will be produced. At equilibrium, carbon dioxide gas will be present both within the solution (aqueous phase) and in the vapor phase above the solution. As in Part I, shifts in the position of the equilibrium can be observed by following the H^+ ion concentration. The indicator bromothymol blue will be used.

You will add hydrochloric acid to a solution containing bicarbonate ions and a few drops of bromothymol blue, until the blue color just changes color from blue to green (on its way to yellow). The green color means that $[H^+]$ is about 10^{-7} M. The color of the indicator will tell you if $[H^+]$ changes. If the indicator turns yellow, $[H^+]$ has increased to more than 10^{-7} M. If the indicator turns blue, $[H^+]$ has decreased to less than 10^{-7} M.

You will make one change to this equilibrium system:

- Lowering the total pressure.

Procedure

Obtain a heavy walled Erlenmeyer flask with a side-arm, a rubber stopper that fits the flask, and a piece of thick-walled rubber tubing. Connect one end of the tubing to the side-arm of the flask. Clamp the flask in place on a ring stand near a water faucet with an aspirator.

Add 50-100 mL of 0.4 M sodium bicarbonate solution to the flask, and then add a few drops of bromothymol blue. Add 3 M HCl to the flask drop by drop, just until the indicator color has become light green. (Do not add so much HCl that the indicator becomes yellow.) As soon as enough HCl has been added, place the stopper securely on the flask.

Turn on the aspirator, attach the rubber tubing from the side-arm of the flask to the aspirator, and observe the effect of reducing pressure on the equilibrium position. Record your observations.

Analysis

In the data analysis section of your report, you should describe how the results of each test performed in this experiment are consistent with Le Châtelier's Principle, and you should also explain them using your knowledge of reaction kinetics. You may organize this discussion in any logical way you choose. Here are specific questions that you should answer as part of your discussion of each test:

- How were the concentrations of each reaction component <u>initially</u> affected after you made the specified change?
- You were able to <u>see</u> changes in the concentration of another component. As a result of this change, did its concentration increase or decrease? Your answer should be supported by the observations recorded in your lab notebook. Did the equilibrium shift to the left or to the right?
- Was the observed shift in equilibrium consistent with Le Châtelier's Principle? Explain.

Your discussion of the reactions in Part II and Part III may be a little bit different, as you may not have been able to predict the response to temperature changes in advance. For each of these reactions, you should be able to deduce from your observations **whether the forward reaction** is endothermic or exothermic.

Pre-Lab Questions

Use Le Châtelier's Principle to predict how the four equilibrium systems will respond to the changes you will make:

I. $CH_3COOH\ (aq) \rightleftharpoons CH_3COO^-\ (aq) + H^+\ (aq)$

How will adding sodium acetate (CH_3COONa) initially change [CH_3COOH], [CH_3COO^-], and [H^+]? How should the equilibrium system respond to this change?

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

1. How will adding potassium thiocyanate (KSCN) initially change [Fe^{3+}], [SCN^-], and [$FeSCN^{2+}$]? How should the equilibrium system respond to this change?
2. How will adding silver nitrate ($AgNO_3$) initially change [Fe^{3+}], [SCN^-], and [$FeSCN^{2+}$]? How should the equilibrium system respond to this change?

III. $Co^{2+}\ (aq) + 4\ Cl^-\ (aq) \rightleftharpoons CoCl_4^{2-}\ (aq)$

How will diluting with water initially change [Co^{2+}], [Cl^-], and [$CoCl_4^{2-}$]? How should the equilibrium system respond to this change?

IV. $CO_2\ (aq\ and\ g) + H_2O\ (l) \rightleftharpoons H^+\ (aq) + HCO_3^-\ (aq)$

How should the equilibrium system respond when the pressure is lowered?