

1. Chemical Equilibrium

Objective

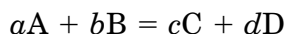
Many chemical reactions, especially those of organic substances, do *not* go to *completion*. Rather, they come to a point of **chemical equilibrium** before the reactants are fully converted to products. At the point of equilibrium, the concentrations of all reactants remain *constant* with time. The *position* of this equilibrium is described by a function called the **equilibrium constant**, K_{eq} , which is a *ratio* of the amount of product present to the amount of reactant remaining once the point of equilibrium has been reached. In Choice I of this experiment, you will determine the equilibrium constant for an esterification reaction. In Choice II, you will investigate how outside forces acting on a system at equilibrium provoke changes within the system (Le Châtelier's principle).

Introduction

Early in the study of chemical reactions, it was noted that many chemical reactions do not produce as much product as might be expected, based on the amounts of reactants taken originally. These reactions appeared to have *stopped* before the reaction was complete. Closer examination of these systems (after the reaction had seemed to stop) indicated that there were still significant amounts of all the original *reactants* present. Quite naturally, chemists wondered *why* the reaction had seemed to stop, when all the necessary ingredients for *further* reaction were still present.

Some reactions appear to stop because the products produced by the original reaction *themselves begin to react*, in the reverse direction to the original process. As the concentration of products begins to build up, product molecules will react more and more frequently. Eventually, as the speed of the forward reaction decreases while the speed of the reverse reaction increases, the forward and reverse processes will be going on at exactly the *same* rate. Once the forward and reverse rates of reaction are identical, there can be no further net change in the concentrations of any of the species in the system. At this point, a dynamic state of *equilibrium* has been reached. The original reaction is still taking place but is opposed by the reverse of the original reaction also taking place.

The point of chemical equilibrium for a reaction is most commonly described numerically by the **equilibrium constant**, K_{eq} . The equilibrium constant represents a *ratio* of the concentrations of all product substances present at the point of equilibrium to the concentrations of all original reactant substances (all concentrations are raised to the power indicated by the coefficient of each substance in the balanced chemical equation for the reaction). For example, for the general reaction



the equilibrium constant would have the form

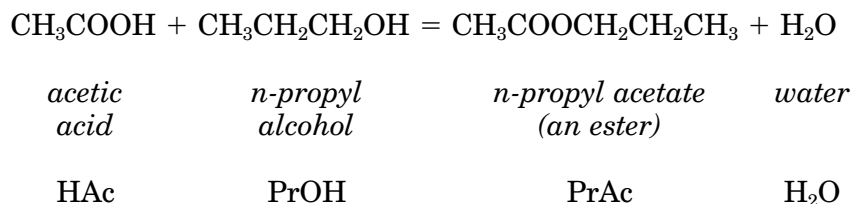
$$K_{\text{eq}} = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

A ratio is used to describe the point of equilibrium for a particular chemical reaction scheme because such a ratio will be independent of specific amounts of substance that might have been used initially in a particular experiment. The equilibrium constant K_{eq} is a constant for a given reaction at a given temperature.

Choice I. Determination of an Equilibrium Constant

Introduction

In Choice I of this experiment, you will determine the equilibrium constant for the esterification reaction between *n*-propyl alcohol and acetic acid.



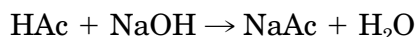
Using the abbreviations indicated for each of the substances in this system, the form of the equilibrium constant would be

$$K_{\text{eq}} = \frac{[\text{PrAc}][\text{H}_2\text{O}]}{[\text{HAc}][\text{PrOH}]}$$

You will set up the reaction in such a way that the *initial* concentrations of HAc and PrOH are *known*. The reaction will then be allowed to stand for one week to come to equilibrium. As HAc reacts with PrOH, the acidity of the mixture will *decrease*, reaching a minimum once the system reaches equilibrium. The quantity of acid present in the system will be determined by titration with standard sodium hydroxide solution. Esterification reactions are typically catalyzed by the addition of a strong mineral acid. In this experiment a small amount of sulfuric acid will be added as a catalyst. The amount of catalyst added will have to be determined, since this amount of catalyst will also be present in the equilibrium mixture and will contribute to the total acid content of the equilibrium mixture.

By analysis of the amounts of each reagent used this week in setting up the reaction and by determining the amount of acetic acid (HAc) that will be present next week once the system has reached equilibrium, you will be able to calculate the concentration of all species present in the equilibrium mixture. From this, the value of the equilibrium constant can be determined.

The concentration of acetic acid in the mixture is determined by the technique of *titration*. Acetic acid reacts with sodium hydroxide (NaOH) on a 1:1 stoichiometric basis



A precise volume of the reaction mixture is removed with a pipet, and a standard NaOH solution is added slowly from a buret until the acetic acid has been completely neutralized (this is signaled by an indicator, which changes color). From the volume and concentration of the NaOH used and the volume of reaction mixture taken, the concentration of acetic acid in the reaction mixture may be calculated.

SAFETY PRECAUTIONS

- **Wear safety glasses at all times while in the laboratory.**
- **Glacial (pure) acetic acid and sulfuric acid burn skin badly if spilled. Wash immediately if either acid is spilled, and inform the instructor at once.**
- **Acetic acid, *n*-propyl alcohol, and *n*-propyl acetate are all highly flammable and their vapors may be toxic or irritating if inhaled. Absolutely no flames are permitted in the laboratory.**
- **The NaOH solution used in this experiment is very dilute but will concentrate by evaporation on the skin if spilled. Wash after use.**
- **When pipeting solutions, use a rubber safety bulb. Do *not* pipet by mouth.**

Apparatus/Reagents Required

50-mL buret, plastic wrap, standard 0.10 *M* NaOH solution, phenolphthalein indicator solution, 1-mL pipet and rubber safety bulb, *n*-propyl alcohol (1-propanol), glacial acetic acid, 6 *M* sulfuric acid

Procedure

Record all data and observations directly in your notebook in ink.

A. First Week: Setup of the Initial Reaction Mixture

Clean a buret with soap and water until water does not bead up on the inside of the buret. Clean a 1-mL volumetric transfer pipet. Rinse the buret and pipet with tap water several times to remove all soap. Follow by rinsing with small portions of distilled water.

Obtain approximately 100 mL of standard 0.10 M NaOH solution in a clean dry beaker. Rinse the buret several times with small portions of NaOH solution (discard the rinsings); then fill the buret with NaOH solution. Keep the remainder of the NaOH solution in the beaker covered until it is needed.

Clean two 250-mL Erlenmeyer flasks for use as titration vessels. Label the flasks as 1 and 2. Rinse the flasks with tap water; follow with small portions of distilled water. Place approximately 25 mL of distilled water in each flask, and set aside until needed.

Since glacial acetic acid and *n*-propyl alcohol are both liquids, it is more convenient to measure them out by *volume* than by mass.

Clean and dry a 125-mL Erlenmeyer flask. Label the flask as *reaction mixture*. Cover a rubber stopper that securely fits the flask with plastic wrap (this prevents the stopper from being attacked by the vapors of the reaction mixture).

Clean and dry a small graduated cylinder. Using the graduate, obtain 14 ± 0.2 mL of glacial acetic acid (0.25 mol) and transfer the acetic acid to the clean, dry reaction mixture Erlenmeyer flask.

Rinse the graduated cylinder with water and redry. Obtain 19 ± 0.2 mL of *n*-propyl alcohol (0.25 mol) and add to the acetic acid in the reaction mixture Erlenmeyer flask. Stopper the flask and swirl the flask for several minutes to mix the reagents.

Using the 1-mL volumetric pipet and safety bulb, transfer 1.00 mL of the reaction mixture to each of the two 250-mL Erlenmeyer flasks (1 and 2). Restopper the flask containing the *n*-propyl alcohol/acetic acid reaction mixture to prevent evaporation.

Add 3–4 drops of phenolphthalein indicator to each of the two samples to be titrated.

Record the initial level of the NaOH solution in the buret. Place Erlenmeyer flask 1 under the tip of the buret, and slowly begin adding NaOH solution to the sample. Swirl the flask during the addition of NaOH. As NaOH is added, red streaks will begin to appear in the sample due to the phenolphthalein, but the red streaks will disappear as the flask is swirled. The endpoint of the titration is when a single additional drop of NaOH causes a faint, permanent pink color to appear. Record the level of NaOH in the buret.

Repeat the titration using Erlenmeyer flask 2, recording initial and final levels of NaOH.

Discard the samples in flasks 1 and 2.

From the average volume of NaOH used to titrate 1.00 mL of the reaction mixture and the concentration of the NaOH, calculate the concentration (in mol/L) of acetic acid in the reaction mixture:

moles of NaOH used = (concentration of NaOH, M) \times (volume used to titrate, L)

moles of HAc = moles of NaOH at the color change of the indicator

$$\text{molarity of HAc} = \frac{\text{moles of HAc}}{\text{liters of reaction mixture taken with pipet}}$$

Since the reaction was begun using equal molar amounts of acetic acid and n -propyl alcohol (i.e., 0.25 mol of each), the concentration of acetic acid calculated also represents the concentration of n -propyl alcohol in the original mixture.

B. First Week: Determination of Sulfuric Acid Catalyst

The reaction between n -propyl alcohol and acetic acid is slow unless the reaction is catalyzed. Mineral acids speed up the reaction considerably, but the presence of the mineral acid catalyst must be considered in determining the remaining concentration of acetic acid in the system once equilibrium has been reached. Next week, you will again titrate 1.00-mL samples of the reaction mixture with NaOH, to determine what concentration of acetic acid remains in the mixture at equilibrium. However, since NaOH reacts with both the acetic acid of the reaction and also with the mineral acid catalyst, some method must be found to determine the concentration of the mineral acid in the reaction mixture. Sulfuric acid will be used as the catalyst.

Refill the buret (if needed) with standard NaOH and record the initial level. Clean out Erlenmeyer flasks 1 and 2, rinse, and fill with approximately 25 mL of distilled water. Clean out and have handy the 1-mL pipet and rubber safety bulb.

Add, with swirling, 10 drops of 6 M sulfuric acid catalyst to the acetic acid/ n -propyl alcohol reaction mixture. *Immediately* pipet a 1.00-mL sample of the catalyzed reaction mixture into both flasks. Do not delay pipeting, or the concentration of acetic acid will begin to change as the reaction occurs.

Recording initial and final NaOH levels in the buret, titrate the catalyzed reaction mixture in flasks 1 and 2, using 3–4 drops of phenolphthalein indicator to signal the endpoint.

Since the samples of catalyzed reaction mixture contain the same quantity of acetic acid as the samples of uncatalyzed mixture, the increase in volume of NaOH required to titrate the second set of 1-mL samples represents a measure of the amount of sulfuric acid present.

By subtracting the average volume of standard NaOH used in Part A (acetic acid only) from the average volume of NaOH used in Part B (acetic acid + sulfuric acid), calculate how many mL of the standard NaOH solution are required to titrate the sulfuric acid catalyst present in 1 mL of the reaction mixture. This volume represents a correction that can be applied to the volume of NaOH that will be required to titrate the samples next week, after equilibrium has been reached.

Stopper the 125-mL flask containing the acetic acid/ n -propyl alcohol mixture. Place the reaction mixture in your locker in a safe place until next week.

C. Second Week: Determination of the Equilibrium Mixture

After standing for a week, the reaction system of *n*-propyl alcohol and acetic acid will have come to equilibrium.

Clean a buret and 1-mL pipet. Rinse and fill the buret with the standard 0.10 M NaOH solution.

Clean and rinse two 250-mL Erlenmeyer flasks (samples 1 and 2). Place approximately 25 mL of distilled water in each of the Erlenmeyer flasks.

Uncover the acetic acid/*n*-propyl alcohol reaction mixture. Using the rubber safety bulb, pipet 1.00-mL samples into each of the two Erlenmeyer flasks. You may notice that the *odor* of the reaction mixture has changed markedly from the sharp vinegar odor of acetic acid that was present last week.

Add 3–4 drops of phenolphthalein to each sample, and titrate the samples to the pale pink endpoint with the standard NaOH solution; record the initial and final levels of NaOH in the buret.

Calculate the mean volume of standard NaOH required to titrate 1.00-mL of the equilibrium mixture. Using the volume of NaOH required to titrate the sulfuric acid catalyst present in the mixture (from Part B), calculate the volume of NaOH that was used in titrating the acetic acid component remaining in the equilibrium mixture.

From the volume and concentration of NaOH used to titrate the acetic acid in 1.00-mL of the equilibrium mixture, calculate the concentration of acetic acid in the equilibrium mixture in moles per liter. Since the reaction was begun with equal molar amounts of acetic acid and *n*-propyl alcohol (0.25 mol of each), the concentration of *n*-propyl alcohol in the equilibrium mixture is the same as that calculated for acetic acid.

Calculate the *change* in the concentration of acetic acid between the initial and the equilibrium mixtures. From the change in the concentration of acetic acid, calculate the concentrations of the two products of the reaction (*n*-propyl acetate, water) present in the equilibrium mixture.

From the concentrations of each of the four components of the system at equilibrium, calculate the equilibrium constant for the reaction.

Choice II. Stresses Applied to Equilibrium Systems

Introduction

Many reactions come to equilibrium. The reaction in Choice I seemed to have stopped before the full amount of product expected had been formed. When equilibrium had been reached in this system, there were significant amounts of both products as well as original reactants still present. In this choice, you will study changes made in a system *already in equilibrium*.

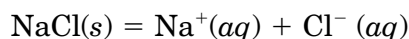
Le Châtelier's principle states that, if we *disturb* a system that is already in equilibrium, then the system will *react* so as to minimize the effect of the disturbance. This is most easily demonstrated in cases where additional reagent is added to a system in equilibrium, or when one of the reagents is removed from the system in equilibrium.

Solubility Equilibria

Suppose we have a solution that has been saturated with a solute: This means that the solution has already dissolved as much solute as possible. If we try to dissolve additional solute, no more will dissolve, because the saturated solution is in equilibrium with the solute:



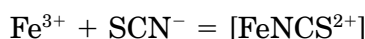
Le Châtelier's principle is most easily seen when an ionic solute is used: Suppose we have a saturated solution of sodium chloride, NaCl. Then



will describe the equilibrium that exists. Suppose we then try adding an *additional amount* of one of the ions involved in the equilibrium. For example, suppose we added several drops of HCl solution (which contains the chloride ion). According to Le Châtelier's principle, the equilibrium would shift so as to consume some of the added chloride ion. This would result in a net decrease in the amount of NaCl that could dissolve. If we watched the saturated NaCl solution as the HCl was added, we should see some of the NaCl precipitate as a solid.

Complex Ion Equilibria

Oftentimes, dissolved metal ions will react with certain substances to produce brightly colored species called **complex ions**. For example, iron(III) reacts with the thiocyanate ion (SCN^-) to produce a bright red complex ion:

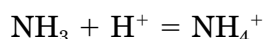


This is an equilibrium process that is easy to study, because we can monitor the bright red color of $[\text{FeNCS}^{2+}]$ as an indication of the position of the equilibrium: If the solution is very red, there is a lot of $[\text{FeNCS}^{2+}]$ present; if the solution is not very red, then there must be very little $[\text{FeNCS}^{2+}]$ present.

Using this equilibrium, we can try adding additional Fe^{3+} or additional SCN^- to see what effect this has on the red color according to Le Châtelier's principle. We will also add a reagent (silver ion) that removes SCN^- from the system to see what effect this has on the red color.

Acid/Base Equilibria

Many acids and bases exist in solution in equilibrium sorts of conditions: This is particularly true for the weak acids and bases. For example, the weak base ammonia is involved in an equilibrium in aqueous solution



Once again, we can use Le Châtelier's principle to play around with this equilibrium: we will try adding more ammonium ion or hydrogen ion to see what happens. Since none of the components of this system is itself colored, we will be adding an acid/base indicator that changes color with pH, to have an index of the position of the ammonia equilibrium. The indicator we will use is the same used in Choice I, phenolphthalein, which is pink in basic solution and colorless in acidic solution.

SAFETY PRECAUTIONS

- **Wear safety glasses at all times while in the laboratory.**
- **Concentrated ammonia is a strong respiratory and cardiac stimulant; use concentrated ammonia *only in the exhaust hood*.**
- **Concentrated hydrochloric acid is *severely damaging to skin* and its *vapor is highly toxic*; use concentrated HCl in the *exhaust hood*; wear disposable gloves while handling the acid to protect your hands; if HCl is spilled on the skin, wash immediately and inform the instructor.**
- **Iron(III) chloride and potassium thiocyanate are toxic; wash hands after use.**

Apparatus/Reagents Required

Saturated sodium chloride solution, 12 M HCl, 1 M HCl, 0.1 M FeCl₃, 0.1 M KSCN, concentrated ammonia solution, ammonium chloride, 0.1 M AgNO₃, phenolphthalein indicator

Procedure

Record all data and observations directly in your notebook in ink.

A. Solubility Equilibria

Obtain 5 mL of saturated sodium chloride solution in each of two test tubes. This solution was prepared by adding solid NaCl to water until no more would dissolve. Then the clear solution was filtered from any undissolved solid NaCl.

Add 10 drops of 12 M HCl (*Caution!*) to one test tube of saturated NaCl solution. A small amount of solid NaCl should form and precipitate out of the solution. The crystals may form slowly, and may be very small. Examine the test tube carefully.

Add 10 drops of 1 M HCl to the other test tube of saturated NaCl solution. Why does no precipitate form in this instance?

On the lab report sheet, describe what happens in terms of Le Châtelier's principle.

B. Complex Ion Equilibria

Prepare a stock sample of the bright red complex ion $[\text{FeNCS}^{2+}]$ by mixing 2 mL of 0.1 M iron(III) chloride and 2 mL of 0.1 M KSCN solutions. The color of this mixture is too intense to use as it is, so dilute this mixture with 100 mL of water.

Pour about 5 mL of the diluted red stock solution into each of four test tubes. Label the test tubes as 1, 2, 3, and 4.

Test tube 1 will have *no change* made in it, so that you can use it to compare color with what will be happening in the other test tubes.

To test tube 2, add about 1 mL of 0.1 M FeCl_3 solution. Watch very carefully as the FeCl_3 solution is poured into the red solution.

To test tube 3, add about 1 mL of 0.1 M KSCN solution. Watch very carefully as the KSCN solution is poured into the red solution.

To test tube 4, add 0.1 M AgNO_3 solution dropwise until a change becomes evident. Ag^+ ion removes SCN^- ion from solution as a solid (silver thiocyanate, AgSCN).

Describe the intensification or fading of the red color in each test tube in terms of Le Châtelier's principle.

C. Acid/Base Equilibria

In the exhaust hood, prepare a dilute ammonia solution by adding 4 drops of concentrated ammonia to 100 mL of water.

Add 3 drops of phenolphthalein to the dilute ammonia solution, which will turn pink (ammonia is a base, and phenolphthalein is pink in basic solution).

Place about 5 mL of the pink dilute ammonia solution into each of three test tubes.

To one of the test tubes, add several small crystals of ammonium chloride (which contains the ammonium ion, NH_4^+).

To a second test tube, add a few drops of 12 M HCl (*Caution!*).

To the third test tube, add 1 drop of concentrated ammonia (*Caution!*).

Describe what happens to the pink color in terms of how Le Châtelier's principle is affecting the ammonia equilibrium.

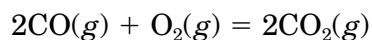
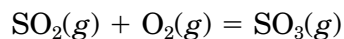
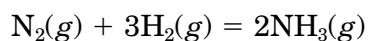
Chemical Equilibrium

Date: Student name:
Course: Team members:
Section:
Instructor:

Prelaboratory Questions

Choice I. Determination of an Equilibrium Constant

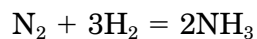
1. Write the expression for the equilibrium constants for the following reactions:



2. A 1.00-mL pipet sample of dilute acetic acid required 23.4 mL of 0.10 *M* NaOH to titrate the sample to a phenolphthalein endpoint. Calculate the concentration of acetic acid in the sample. How many significant figures are justified in your answer? Why?

Choice II. Stresses Applied to Equilibrium Systems

1. Given the gas-phase reaction



Suppose that the reaction has already taken place, and the system has come to equilibrium. If the following changes are made to the system in equilibrium, tell what effect these changes will have on the system (whether the equilibrium is shifted to the left, the right, or is not shifted).

- a. Additional N_2 is added to the system.
- b. Ammonia is removed from the system as soon as it forms.
- c. The pressure of the system is increased (all components are gases).
- d. A very efficient catalyst is used for the reaction.

Chemical Equilibrium

Date: Student name:
Course: Team members:
Section:
Instructor:

Results/Observations

Choice I. Determination of an Equilibrium Constant

Concentration of standard NaOH solution

	Sample 1	Sample 2
Volume of NaOH to titrate 1 mL initial uncatalyzed mixture (<i>first week</i>)
	Mean volume
Concentration of acetic acid, M , in original mixture
Volume of NaOH to titrate 1 mL catalyzed reaction mixture (<i>first week</i>)
	Mean volume
Volume correction for sulfuric acid (<i>to be applied next week</i>)
Volume of NaOH to titrate 1 mL of equilibrium mixture (<i>second week</i>)
	Mean volume
Volume (<i>corrected</i>) of NaOH to titrate acetic acid in equilibrium mixture
Concentration of acetic acid, M , in equilibrium mixture
Change in concentration of acetic acid in reaching equilibrium

Complete the following table:

	Concentrations, M	
	Initial mixture	Equilibrium mixture
Acetic acid
<i>n</i> -Propyl alcohol
<i>n</i> -Propyl acetate
Water

Calculate the equilibrium constant for the reaction:

Questions

1. Sulfuric acid was used as a catalyst in this reaction. Would the presence of a catalyst affect the position of the equilibrium (i.e., the relative amounts of substances present once equilibrium was reached)? Why?
2. Could some other acid have been used as the catalyst? Why?
3. A common misconception among beginning students is that “you leave liquids and solids out of equilibrium constants.” *All* the species involved in this reaction were liquids, and *all* of their concentrations were included in the calculation of the equilibrium constant. Explain.

Chemical Equilibrium

Date: Student name:
Course: Team members:
Section:
Instructor:

Results/Observations

Choice II. Stresses Applied to Equilibrium Systems

A. Solubility Equilibria

Effect of adding HCl to saturated NaCl observation

Explanation

B. Complex Ion Equilibria

Effect of adding Fe^{3+} to $[\text{FeNCS}^{2+}]$ observation

Explanation

Effect of adding SCN^- to $[\text{FeNCS}^{2+}]$ observation

Explanation

Effect of adding Ag^+ to $[\text{FeNCS}^{2+}]$ observation

Explanation

C. Acid/Base Equilibria

Effect of adding NH_4^+ observation

Explanation

Effect of adding HCl observation

Explanation

