A P CHEMISTRY

Lab 13-1 Determination of an Equilibrium Constant

Pre-Lab Questions - (Must be completed before lab work begins.)

1. Write the expression for the equilibrium constants for the following reactions:
   $N_2(g) + 3H_2(g) = 2NH_3(g)$
   $SO_2(g) + O_2(g) = SO_3(g)$
   $2CO(g) + O_2(g) = 2CO_2(g)$
2. A 1.00-mL pipette 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?

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 aA + bB = cC + dD, the equilibrium constant would have the form $K_{eq} = [C]^c[D]^d / [A]^a[B]^b$

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.

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

$CH_3COOH + CH_3CH_2CH_2OH = CH_3COOCH_2CH_2CH_3 + H_2O$

acetic acid	*n*-propyl alcohol	n-propyl acetate (an ester)	water
HA	PrOH	PrAc	H_2O

Using the abbreviations indicated for each of the substances in this system, the form of the equilibrium constant would be $K_{eq} = [PrAc][H_2O]/[HAc][PrOH]$.

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

$$HAc + NaOH \rightarrow NaAc + H_2O$$

A precise volume of the reaction mixture is removed with a pipette, and a standard NaOH solution is added slowly from a burette 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

- ⇒ 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* pipette by mouth.

Procedure

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

A. First Week: Set-up of the Initial Reaction Mixture

2. Clean a burette with soap and water until water does not bead up on the inside of the burette. Clean a 1-mL volumetric transfer pipette. Rinse the burette and pipette with tap water several times to remove all soap. Follow by rinsing with small portions of distilled water.
3. Obtain approximately 100 mL of standard 0.10 *M* NaOH solution in a clean dry beaker. Rinse the burette several times with small portions of NaOH solution (discard the rinsing); then fill the burette with NaOH solution. Keep the remainder of the NaOH solution in the beaker covered until it is needed.
4. 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.
5. Since glacial acetic acid and *n*-propyl alcohol are both liquids, it is more convenient to measure them out by volume than by mass.
6. 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).

7. 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.
8. 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.
9. Using the 1-mL volumetric pipette 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,
10. Add 3-4 drops of phenolphthalein indicator to each of the two samples to be titrated.
11. Record the initial level of the NaOH solution in the burette. Place Erlenmeyer flask 1 under the tip of the burette, 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 burette.
12. Repeat the titration using Erlenmeyer flask 2, recording initial and final levels of NaOH.
13. Discard the samples in flasks 1 and 2.
14. 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. M) x (Volume used, L)

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

    $$\text{molarity of HAc} = \frac{\text{moles of HAc}}{\text{liters of reaction mixture taken}}$$
15. 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.

Results / Observations

Concentration of Standard NaOH Solution		
	Sample 1	Sample 2
Volume of NaOH to titrate 1 mL of initial uncatalyzed mixture (first week)		
Mean (average) volume		

B. First Week: Determination of Sulfuric Acid Catalyst

16. 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.
17. Refill the burette (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.

18. Clean out and have handy the 1-mL pipette and rubber safety bulb.
19. Add, with swirling, 10 drops of 6 M sulfuric acid catalyst to the acetic acid/propyl alcohol reaction mixture. *Immediately* pipette a l.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.
20. Recording initial and final NaOH levels in the burette, titrate the catalyzed reaction mixture in flasks 1 and 2, using 3-4 drops of phenolphthalein indicator to signal the endpoint.
21. 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.
22. 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.
23. Stopper the 125-mL flask containing the acetic acid/*n*-propyl alcohol mixture. Place the reaction mixture in a safe place until next week.

Results / Observations

	Sample 1	Sample 2
Concentration of acetic acid, M, in original mixture		
Volume of NaOH to titrate 1 mL of initial catalyzed mixture (first week)		
Mean (average) volume		

Volume correction for sulfuric acid (to be applied next week) ____________________

C. Second Week: Determination of the Equilibrium Mixture

24. After standing for a week, the reaction system of *n*-propyl alcohol and acetic acid will have come to equilibrium.
25. Clean a burette and 1-mL pipette. Rinse and fill the burette with the standard 0.10 M NaOH solution.
26. 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.
27. Uncover the acetic acid/*n*-propyl alcohol reaction mixture. Using the rubber safety bulb, pipette 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.
28. 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 burette.
29. 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.
30. From the volume and concentration of NaOH used to titrate the acetic acid in 1.00-niL 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.

31. 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.
32. From the concentrations of each of the four components of the system at equilibrium, calculate the equilibrium constant for the reaction.

Results / Observations

	Sample 1	Sample 2
Volume (corrected) 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		

	Concentrations, M	
	Initial Mixture	Equilibrium Mixture
Acetic Acid		
n-propyl alcohol		
n-propyl acetate		
water		

Calculate the equilibrium concentration for the reaction: _______________. Show the calculation.

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. The 6 M sulfuric acid used as the catalyst for this reaction quite naturally contains some water, and water is one of the products of the esterification reaction. How will the presence of a small amount of water in the catalyst affect the position of the acetic acid/*n*-propyl alcohol equilibrium? How will this water affect the value determined for the equilibrium constant?
4. 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.
5. How would a change in *temperature* affect the equilibrium reaction studied? Would the *position* of equilibrium change? Would the *value of the equilibrium constant* change? Explain.