

3—Determination of an Equilibrium Constant



Name: _____

Date: _____

Section: _____

Objectives

- Learn to Write an Equilibrium expressions for non-aqueous systems
- Learn to evaluate an equilibrium constant
- Explore the hydrolysis of an ester
- Review acid base titrations
- Review Stoichiometric calculations

Pre-Laboratory Requirements

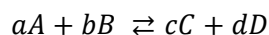
- Read Chapter in Silberberg sections 17.2, 17.5, and page 481
- Review CHEM 131 Lab 6
- Watch the instructional videos titled “Determination of an Equilibrium Constant”
- Pre-Lab Questions (if required by your instructor)
- Laboratory Notebook—prepared before lab (if required by your instructor)

Safety Notes

- Eye protection must be worn at all times

Discussion

A system is in a state of equilibrium when its macroscopic properties do not change with time. For chemical systems, this means that all chemical forces are in balance and that all the physical properties of the system (*such as color, density, and concentration*) remain constant. An important concept for determining the extent a reaction has proceeded to reach equilibrium is the *equilibrium constant* (K) for the reaction.



For this generalized reaction, the equilibrium constant expression is defined as:

$$K = \frac{c^c d^d}{A^a B^b} \quad [1]$$

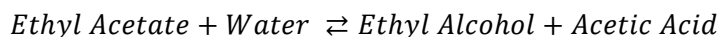
In this expression, $[A]$, $[B]$, $[C]$, and $[D]$ are the molar concentrations of the respective components *at equilibrium*. Each concentration term is raised to a power given by its stoichiometric coefficient. As you may have learned during the lecture portion of the class, the equilibrium constant (K) is only a function of

temperature. It should be constant if the temperature does not change. In this experiment, you will evaluate K for a specific reaction using three different initial concentrations to test the constancy of K at constant temperature. Theoretically, at a constant temperature, the value for K should be the same for each regardless of the initial conditions.

In order to determine the equilibrium constant, the stoichiometry of the chemical reaction must be known. In addition, you must have an analytical method for measuring the concentrations of reactants and products **at equilibrium**. Alternatively, it is possible to determine the value of the equilibrium constant by measuring **the equilibrium concentration of only one of the species** involved in the reaction, if the **initial concentrations of all species are known since the final concentrations can be determined using stoichiometry calculations**.

In this experiment, you will use this “alternative” method to determine the value of K . The concentration at equilibrium of one of the reaction products will be measured by titration. Once found, this value is used to calculate the equilibrium concentration of the remaining species. Once these concentrations are known, the equilibrium constant can be calculated.

In this experiment, you will be determining the equilibrium constant for the hydrolysis of ethyl acetate:



The reaction may be represented more simply by using abbreviated names:



The equilibrium constant K_c for equation [2] is defined by the following expression:

$$K_c = \frac{[\text{EtOH}][\text{HAc}]}{[\text{EtAc}][\text{H}_2\text{O}]} \quad [3]$$

If the initial concentrations of all reaction species are known, the determination of the equilibrium concentration of acetic acid will permit you to calculate the equilibrium constant for this reaction.

Note: Normally, as seen in lecture, the concentration of a pure liquid such as water or the solvent (usually water) does not appear in the equilibrium expression because its concentration does not vary significantly during the course of the reaction. However, there are no pure liquids in this experiment and water is not the solvent. It is a solute dissolved in the other non-aqueous components. Since all the reactants and products are in this solution and have similar concentrations, the concentration of each does change as the reaction progresses so each must be included in the equilibrium expression.

Procedure

Part I: Solution Preparation

1. Obtain three clean and dry test tubes (Marked A, B, and C).
2. To A add 5.00 mL 3 M HCl and 5.00 mL of ethyl acetate.
3. To B add 5.00 mL 3 M HCl, 4.00 mL of ethyl acetate and 1.00 mL of DI water.
4. To C add 5.00 mL 3 M HCl, 3.00 mL of ethyl acetate and 2.00 mL of DI water.
5. Carefully wrap a piece aluminum foil around a cork such that no cork is visible and stopper the test tube with this cork. Repeat for each test tube.
6. Use a small piece of Parafilm wax paper to further seal each test tube.
7. Place your tubes in the designated rack and allow the test tubes to stand at room temperature until the next lab period.

Note: *The HCl must be present to catalyze the reaction. Since this reaction is acid-catalyzed, the rate at which the reaction reaches equilibrium is greatly increased by the presence of this acid. Since the catalyst is neither a reactant nor a product, the concentration of the catalyst DOES NOT appear in the equilibrium expression.*

Part II: Determination of moles of HCl and H₂O in 3 M HCl solution

1. Review proper titration technique found in CHEM 131L, Experiment 6.
2. Add approximately 20 mL of DI water to an Erlenmeyer flask.
3. Add 5.00 mL of 3 M HCl to the flask.
4. **Add 1-2 drops of phenolphthalein indicator solution into the flask.**
5. Before you begin the titration, be sure to record the **initial** volume of NaOH in the buret (*You will be using 1.00 M NaOH solution*).
6. Begin the titration, stirring the solution in the Erlenmeyer flask as you add NaOH using a drop-wise approach (*Note: you will see your solution begin to turn pink, and then fade back to a colorless solution as stirred. A slowly fading color will indicate that it is time to slow down how quickly you are adding drops of NaOH into the flask*).
7. When the solution in the flask stays a light pink color for about 10 seconds, you have reached the endpoint of the titration. You should record the **final** volume of NaOH in the buret in the data table. (*Note: the lighter pink your solution, the closer you are to the equivalence point*).
8. Repeat this procedure two more times. You may refill the NaOH in the buret as needed.

Data

Table 1. Moles of HCl

	Trial 1	Trial 2	Trial 3
Concentration of standard NaOH (M)	_____	_____	_____
Initial buret reading (mL)	_____	_____	_____
Final buret reading (mL)	_____	_____	_____
Volume of NaOH used	_____	_____	_____
Moles of NaOH	_____	_____	_____
Moles of HCl in 5.00 ml of 3 M HCl solution	_____	_____	_____
Average moles of HCl		_____	

Part III: Determination of total moles of acid at equilibrium (week 2)

Each test tube should have had time to establish equilibrium by the time this part of the experiment is started:

1. Add approximately 20 mL of DI water to an Erlenmeyer flask
2. Add the solution in test tube A to the flask
3. **Add 1-2 drops of phenolphthalein indicator solution into the flask**
4. Begin the titration, using the 1.00 M NaOH solution
5. Repeat this procedure with test tubes B and C, recording all data in the data table.

Data

Table 2. Titration of Equilibrium Solutions

	Tube A	Tube B	Tube C
Concentration of standardized NaOH (M)	_____	_____	_____
Initial buret reading (mL)	_____	_____	_____
Final buret reading (mL)	_____	_____	_____
Volume of NaOH used	_____	_____	_____
Moles of NaOH = Total moles of acid	_____	_____	_____

Part IV: Equilibrium Constant Calculations

The equilibrium concentrations of all substances must be used to calculate the equilibrium constant. In this case, however, the number of moles of each substance at equilibrium may be used instead of concentration. The reason for this is because in the equilibrium expression [3] shown above, all volume terms that relate moles to molarity will algebraically cancel.

In order to determine the equilibrium constant, the initial number of moles of EtAc, H₂O, HAc, and EtOH must be calculated. Since only the reactants are present initially, the initial number of moles of the products (EtOH and HAc) is zero.

The initial number of moles of EtAc and water will be calculated using their measured volumes, molar masses, and densities. **Since the HCl catalyst was added as an aqueous solution, the amount of water present in this solution must be included in the calculation of the initial moles of water.**

The number of moles of HAc at equilibrium is calculated using the titration data for the moles of HCl present and total moles of acid present in the equilibrium solution. As you know, the equilibrium constant is calculated using the equilibrium moles of HAc, EtOH, EtAc, and water.

Here is an example calculation that you may follow when calculating your results:

1. Concentration of HCl:

Given:

Molarity of standard NaOH: 1.009 mol/L

Volume NaOH used: 15.00 mL

At equivalence point:

Moles NaOH = M * V

Moles NaOH = (1.009 mol/L)(0.01500 L) = 0.01514 mol NaOH

Since: Moles of OH⁻ = Moles of H⁺

Then: 0.01514 mol NaOH = 0.01514 mol HCl

M HCl = moles HCl / Volume HCl

M HCl = (0.01514 mol HCl) / (0.00500 L of HCl used)

M HCl = 3.03 mol/L

2. Mass of Water in HCl solution:

Given:

Density of 3 M HCl = 1.05 g/mL

Mass of 5.00 mL of 3 M HCl:

g HCl soln = density * Volume

g HCl soln = 1.05 g/mL * 5.00 mL

g HCl soln = 5.25 g

Mass of HCl in 3 M HCl soln:

Mass HCl = V HCl * M HCl * Molar Mass HCl

(0.00500 L * 3.03 mol HCl/L) * (36.46 g/mol) = 0.552 g of HCl in HCl soln

Mass of water in 5.00 mL of 3.0 M HCl:

Mass H₂O in solution = Mass Total – Mass HCl

(5.25 g HCl soln) – (0.552 g HCl) = **4.70 g of H₂O in HCl soln**

Moles of water in 5.00 mL of 3.0 M HCl:

Moles H₂O = Mass H₂O / Molar Mass H₂O

4.70 g H₂O x 1 mole H₂O / 18.0 g/H₂O = 0.261 moles H₂O

Note: The moles of water from the HCl solution must be added to the moles of water that was added into test tubes for B and C (This will give you the total initial moles of water, which gives different initial moles of water in each tube).

3. Initial moles of EtAc in each test tube:

Given:

Density of EtAc = 0.893 g/mL

For test tube B:

Mass = density * volume

g of EtAc = 0.893 g/mL * (4.00 mL of EtAc)

= 3.57 g EtAc

Moles = mass/ molar mass

(3.57 g EtAc) / (88.0 g/mol EtAc) = **0.0406 initial mol EtAc in test tube B**

4. Moles of HAc at equilibrium in each test tube:

Given:

Let's say (for test tube B) it took 40.00 mL of 1.009 M NaOH to reach the equivalence point

Calculate total moles of acid from the titration:

Moles NaOH = V NaOH * M NaOH

Moles NaOH = 1.009 M NaOH * 0.04000 L NaOH

= 0.04036 moles of NaOH = 0.04036 moles of acid

Remove moles of HCl from total moles of acid:

Moles HCl = V HCl * M HCl

Moles HCl = 3.03 M HCl * 0.00500 L HCl

= 0.0152 moles of HCl

Moles HAc = Total moles Acid – Moles HCl

Moles HAc = 0.04036 total moles of acid – 0.0152 moles of HCl = **0.0252 moles HAc**

5. Now, you may calculate the moles of EtAc, EtOH, and H₂O at equilibrium:

	EtAc	+	H ₂ O	⇌	EtOH	+	HAc
I	0.0406		0.3165		0.00		0.00
C	-0.0252		-0.0252		+0.0252		+0.0252
E	0.0154		0.2913		0.0252		0.0252

6. Calculate the value of the equilibrium constant:

$$K_c = \frac{[EtOH][HAc]}{[EtAc][H_2O]} = \frac{(0.0252)(0.0252)}{(0.0154)(0.2913)} = \mathbf{0.139}$$

Table 3. Equilibrium Constant Calculations

	Tube A	Tube B	Tube C
Initial moles of EtAc	_____	_____	_____
Initial moles of H ₂ O	_____	_____	_____
Final buret reading (mL)	_____	_____	_____
Total moles of acid (from Table 2)	_____	_____	_____
Average moles of HCl (from Table 1)	_____	_____	_____
Moles of HAc (at equilibrium)	_____	_____	_____
Moles of EtOH (at equilibrium)	_____	_____	_____
Moles of EtAc (at equilibrium)	_____	_____	_____
Moles of H ₂ O (at equilibrium)	_____	_____	_____
Equilibrium constant, (<i>K_c</i>)	_____	_____	_____