

# Experiment Chemical Equilibria

In principle, all chemical reactions are reversible. It is frequently found that the conversion of reactants to products is incomplete because the product formed decomposes, once again producing reactant molecules. When the rates of product formation and product decomposition are the same, the system has reached a state of **dynamic equilibrium** in which there is no net change in the concentration of any of the materials (reactants or products) involved in the reaction.

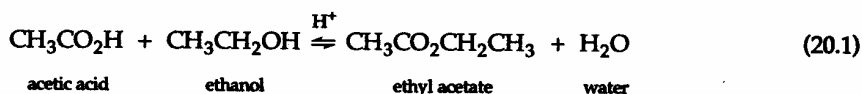
In this experiment, the esterification reaction between acetic acid and ethanol to produce ethyl acetate and water is studied. The reverse of this reaction—the hydrolysis of ethyl acetate—is also studied, to illustrate the point that equilibrium may be approached from either side.



## PRINCIPLES

Alcohols react with carboxylic acids to produce esters. Esters often have very pleasant odors and tastes and are found in many flowers and fruits. The reaction of ethanol (ethyl alcohol) with acetic acid produces ethyl acetate, which occurs naturally in bananas.

The process of esterification is acid-catalyzed. In addition to the ester, water is a product of the reaction of the alcohol and carboxylic acid. In the reverse reaction, called **hydrolysis**, the elements of water are added to the ester, resulting in the regeneration of the acid and the alcohol. Like esterification, hydrolysis is acid-catalyzed. The reversible reaction of ethanol with acetic acid is shown in Equation 20.1.



The equilibrium constant for this reaction is given in Equation 20.2. The square brackets indicate that concentrations are in units of moles/Liter.

$$K = \frac{[\text{ethyl acetate}][\text{water}]}{[\text{acetic acid}][\text{ethanol}]} \quad (20.2)$$

The concentrations of acetic acid in the esterification mixture and in the hydrolysis mixture are easily determined via titration with standardized sodium hydroxide. Concentrations of the other reactants and products may be determined from initial conditions and the stoichiometry of the reaction. Information given in Table 20.1 may prove useful in obtaining the necessary concentrations.

**Table 20.1** Molar Masses and Densities of Reagents.

Reagent	Molar Mass	Density
Acetic acid	60.0	1.05 g/mL
Ethyl Acetate	88.1	0.90 g/mL
Water	18.0	1.00 g/mL
Ethanol	46.0	0.80 g/mL



## PROCEDURE



### Procedure in a Nutshell

Prepare solutions in which either esterification or hydrolysis will take place. Titrate samples of the mixtures to determine the initial molarity of acetic acid and/or sulfuric acid catalyst in each mixture. Allow the mixtures to equilibrate. Titrate samples to determine the equilibrium concentration of acetic acid in each mixture.

### B. Initial Conditions of Esterification Reaction

Place 10.0 mL of ethanol and 10.0 mL of deionized water in a 50-mL Erlenmeyer flask. Place the flask on an analytical balance and use the "tare" function to set the balance reading to zero. Add (**CAUTIOUSLY!**) 1.4–1.6 g of glacial acetic acid to the tared flask. Stopper the flask and invert it several times to ensure a homogeneous mixture. Use a 2-mL pipet to transfer a sample of the mixture to a clean flask. Add 10 mL of distilled water and 3 drops of phenolphthalein to the 2.00 mL sample in the second flask. Then, titrate to the phenolphthalein end point with the 0.1 M sodium hydroxide solution that you have standardized. Record the titration data on the Summary Report Sheet.

**CAREFULLY** add 5 drops of 6 M  $\text{H}_2\text{SO}_4$  (sulfuric acid) to the 50-mL flask containing the esterification mixture. Mix thoroughly once again. Then use the 2-mL pipet to transfer another sample of the esterification mixture to a new clean flask. As before, add 10 mL of distilled water and 3 drops of phenolphthalein indicator to the sample in the new flask. Titrate this second sample with the standardized base and record the titration data on the Summary Report Sheet.

Obviously, the titration of the 2.00 mL sample containing the sulfuric acid catalyst will require more base than the titration of the 2.00 mL sample of the esterification mixture before the catalyst was added. The portion of the acidity contributed by the sulfuric acid catalyst will remain constant throughout the course of the reaction because a catalyst is not consumed as the reaction proceeds.

Label and stopper the 50-mL flask containing the esterification mixture and place it in your drawer until your next laboratory class.

### C. Initial Conditions of Hydrolysis Reaction

Place 10.0 mL of ethanol and 10.0 mL of deionized water in a 50-mL Erlenmeyer flask. Place the flask on an analytical balance and use the "tare" function to set the balance reading to zero. Add 2.1–2.3 g of ethyl acetate to the tared flask. Next, add 5 drops of concentrated  $\text{H}_2\text{SO}_4$ , stopper the flask, and mix its contents by inverting the tube several times. Pipet a 2-mL sample into a clean flask, add 10 mL of water, 3 drops of phenolphthalein, and titrate, as before, with standardized NaOH to determine the concentration of protons provided by the sulfuric acid. Record the titration data on the Summary Report Sheet.

Label and stopper the 50-mL flask containing the hydrolysis mixture and allow it to remain in your drawer until your next laboratory class.

### D. Titrations to monitor Reaction Progress (Q)

At your next laboratory class, repeat the standardization of the sodium hydroxide solution. Record the standardization data on the Summary Report Sheet.

Pipet a 2-mL sample from each of your stored 50-mL flasks into a separate clean flask. Add 10 mL of distilled water and 3 drops of phenolphthalein to each of the new flasks. Titrate the contents of each new flask with your standardized NaOH to find the concentration of acetic acid in each. Remember that you must allow for the acidity that arises from the presence of the sulfuric acid catalyst. Calculate Q.

Repeat weekly until equilibrium is reached.

### Disposal of Reagents

All reagents used and all mixtures produced in this experiment may be diluted and flushed down the drain.

## Data Tables and Analysis

### *ESTERIFICATION*

Volume of ethanol:

Volume of water:

Mass of acetic acid:

Concentration of NaOH solution:

Titration data

	<i>Initial:</i> Week 1	H <sub>2</sub> SO <sub>4</sub> correction	Week 2	Week 3	Week 4
Final Burette Reading (mL)					
Initial Burette Reading (mL)					
Volume NaOH (mL)					
Mole NaOH (mol)					
	Moles of acetic acid	Moles of H <sup>+</sup> present from catalyst:	Moles of acetic acid (corrected for catalyst)	Moles of acetic acid (corrected for catalyst)	Moles of acetic acid (corrected for catalyst)

I-C-Q table



Initial	Calculate from <i>initial</i> titration	Convert 1.0 mL → mol	-	Convert 1.0 mL → mol
Change	- X (determined from change)	- X	+ X	+ X
Current reaction conditions	Calculate from the titration of the current week (with correction for H <sub>2</sub> SO <sub>4</sub> )	Calculate	Calculate	Calculate

## HYDROLYSIS

Volume of ethanol:

Volume of water:

Mass of ethyl acetate:

Concentration of NaOH solution:

Titration data

	H <sub>2</sub> SO <sub>4</sub> correction	Week 2	Week 3	Week 4
Final Burette Reading (mL)				
Initial Burette Reading (mL)				
Volume NaOH (mL)				
Mole NaOH (mol)				
	Moles of H <sup>+</sup> present from catalyst:	Moles of acetic acid (corrected for catalyst)	Moles of acetic acid (corrected for catalyst)	Moles of acetic acid (corrected for catalyst)

I-C-Q table



Initial	–	Convert 1.0 mL → mol	<sup>1</sup> / <sub>10</sub> of mole in overall reaction mixture	Convert 1.0 mL → mol
Change	+ X (determined from change)	+ X	– X	– X
Current reaction conditions	Calculate from the titration of the current week (with correction for H <sub>2</sub> SO <sub>4</sub> )	Calculate	Calculate	Calculate