Determination of an Equilibrium Constant

Due at the start of class:
1. Last week's lab and calculations
2. This week's pre-lab (objective, procedure, & pre-lab questions)

Due at the end of class:
1. This week's data.

BACKGROUND INFORMATION

A system is considered to be in a state of equilibrium when its properties do not change as time passes. 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 the concentrations of all chemical species remain constant in magnitude. An important way of measuring the extent to which a reaction has proceeded once equilibrium is established is to measure the equilibrium constant for the reaction. For the most generalized reaction
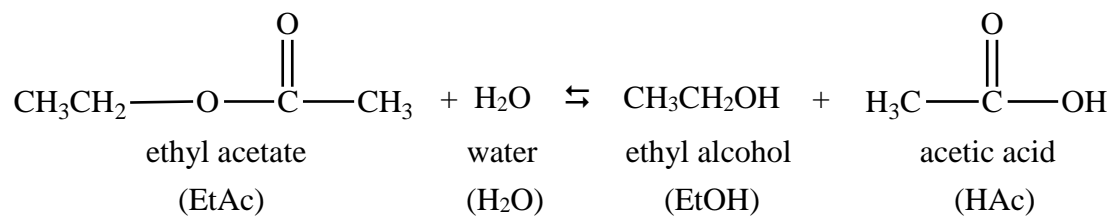
$$aA + bB \rightleftharpoons cC + dD \tag{1}$$

the equilibrium constant is defined as:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \tag{2}$$

where [A], [B], [C], and [D] are the molar concentrations of the respective components at equilibrium. The concentration terms in (2) are raised to powers (exponents) equal to their stoichiometric coefficients. K is constant under all conditions except for changes in temperature. In this experiment, we shall evaluate K for a specific reaction under different initial concentration conditions to test its constancy at constant temperature.
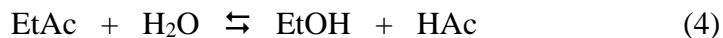
In order to determine the equilibrium constant, the stoichiometry of the chemical reaction must be known. In addition, we must have an analytical method for measuring the concentrations of reactants and products at equilibrium. Alternatively, it is possible to determine the value of the equilibrium constant by measuring the equilibrium concentration of only one of the species involved in the reaction, provided that the initial concentrations of all species are known. In this experiment the second method will be used. The concentration at equilibrium of one of the reaction products will be measured by titration and this value used to calculate the equilibrium concentrations of the remaining species. Once the equilibrium concentrations of all the reaction species are known the equilibrium constant will be calculated.

In this experiment we shall study the equilibrium system:

CH$_3$CH$_2$—O—C(=O)—CH$_3$ + H$_2$O $\rightleftharpoons$ CH$_3$CH$_2$OH + H$_3$C—C(=O)—OH
ethyl acetate   water   ethyl alcohol   acetic acid
(EtAc)   (H$_2$O)   (EtOH)   (HAc)

the reaction may be represented using abbreviated names

1

$$EtAc \ + \ H_2O \ \leftrightarrows \ EtOH \ + \ HAc \qquad\qquad (4)$$

From this equation, the equilibrium constant K_c is defined by the following expression.

$$K_c = \ \frac{[EtOH][HAc]}{[EtAc][H_20]} \qquad\qquad (5)$$

If the **initial** concentrations of all reaction species are known, the determination of the equilibrium concentration of acetic acid will permit one to calculate the equilibrium constant for this reaction. Note: Normally the concentration of a pure liquid such as water does not appear in the equilibrium expression because its concentration does not vary significantly during the course of the reaction. However, in this experiment water is present in a concentration that does change as the reaction progresses and therefore must be included in the equilibrium expression.

EXPERIMENTAL PROCEDURE

1. Preparation of Solutions:

   Obtain three clean and dry 125- or 250-mL Erlenmeyer flasks and label them A, B and C. Add the following materials to each flask using a burette or pipet. These three solutions will be used to make three independent determinations of the equilibrium constant.

   A. 5.00 mL 3 M HCl + 5.00 mL of ethyl acetate
   B. 5.00 mL 3 M HCl + 4.00 mL of ethyl acetate + 1.00 mL of distilled water
   C. 5.00 mL 3 M HCl + 3.00 mL of ethyl acetate + 2.00 mL of distilled water

   Notice that the volumes must be measured as precisely as possible. If you do not add exactly the specified volume of a reagent, write down in your laboratory notebook the exact volume that you do add and use this volume in your calculations. The HCl must be present even though it does not appear in the balanced chemical equation because this reaction is acid-catalyzed; the rate at which the reaction reaches equilibrium is greatly increased by the presence of acid. Stopper each flask tightly and swirl the contents vigorously. Allow the flasks to stand at room temperature until your next laboratory period. It will take about one day for equilibrium to be achieved.

2. Have your instructor demonstrate the technique of detecting the odor of a reaction. Only after you have seen that demonstration, and then only with the explicit permission of your instructor, very cautiously smell the reaction mixture just after you have prepared it and then, at least a day later, just before you titrate it. Can you tell that a reaction has occurred?

3. Determination of moles of HCl and H_2O in the 3 M HCl solution:

   Using a graduated cylinder, add approximately 20 mL of distilled water and three drops of phenolphthalein to 5.00 mL of the same 3 M HCl solution used as the catalyst in the preparation of the equilibrium solutions. Titrate the solution with 1.00 M sodium hydroxide solution. Use care in titrating; the acid and base are more concentrated than is typical of many titrations and this can cause the end point to arrive suddenly. Reminder: burettes are to be read to 2 decimal places.

4. Repeat the above titration a minimum of 2 more times until you obtain three titrations with a relative average deviation of 1% or less.

5. Determination of total moles of acid at equilibrium:

After equilibrium has been established in the reaction flasks, add approximately 20 mL of distilled water to increase the volume and titrate each solution (A, B and C) with 1.00 M NaOH; use phenolphthalein as the indicator. As your moles of acid will be different for each solution A, B, and C, your volume of NaOH needed will be different. Since you don't know how much NaOH you will need, you should refill your burette before beginning the titration. (Note: The 20 mL volume of water is not included in your calculations as there is not time enough for it to react.)

6. CALCULATIONS

Normally the concentrations of all substances at equilibrium must be used to calculate the equilibrium constant. However, in this experiment the number of moles of each substance at equilibrium may be used instead of concentration. This is because in the equilibrium expression shown in [5] all volume terms in molarity will cancel.

In order to determine the equilibrium constant the initial number of moles of EtAc, H_2O, HAc and EtOH must be calculated. Since only EtAc and water are present initially the initial number of moles of the products is zero. The initial number of moles of EtAc and water will be determined 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 (density of 3 M HCl = 1.05 g/ml). The number of moles of HAc at equilibrium is determined using the titration data for the moles of HCl present and total moles of acid present in the equilibrium solution. Once the initial moles of all species and the equilibrium moles of HAc have been determined, the equilibrium moles of EtAc, EtOH and water may be calculated using the stoichiometry of the chemical reaction. The equilibrium constant is calculated using the equilibrium moles of HAc, EtOH, EtAc and water in equation [5]. A sample of the type of calculation to be performed follows.

EXAMPLE CALCULATION:

A student prepared two flasks. Flask A contained 5.00 mL of 6 M HCl (density = 1.11 g/mL) ONLY (you're A and B flasks are NOT the same). Flask B contained 5.00 mL of 6 M HCl, 2.00 mL of ethyl acetate (density = 0.893 g/mL), and 3.00 mL of water. Flask A required 28.90 mL of 1.00 M NaOH for titration; flask B required 39.12 mL of 1.00 M NaOH. Compute K_c.

a. Calculate the moles of HCl in 5.00 mL of 6 M HCl solution.   This is necessary since the concentration of HCl was given to only one significant figure and must be known more percisely. Use the volume and molarity of NaOH to find the moles of NaOH used to titrate the HCl in flask A. This is equal to the number of moles of HCl present in both flask A and flask B.

$$0.02890 \text{ L} \times 1.00 \text{ M} = 0.0289 \text{ mol of NaOH} = 0.0289 \text{ mol of HCl}$$

b. Calculate the moles of water in 5.00 mL of HCl solution. The HCl solution is made up of the solute, HCl, and the solvent, H_2O. The total mass of the HCl solution is calculated using the volume and density of the solution.

$$5.00 \text{ mL} \times 1.11 \text{ g/mL} = 5.55 \text{ g of HCl solution}$$

The mass of pure HCl in the HCl solution is calculated using the moles of HCl in the solution and the molar mass.

$$0.0289 \text{ mol} \times 36.5 \text{ g/mol} = 1.069 \text{ g HCl in the HCl solution.}$$

The difference between the total mass of solution and the mass of solute (HCl) is the mass of water.

Determination of an Equilibrium Constant

$$5.55 \text{ g} - 1.069 \text{ g} = 4.49 \text{ g of water}$$

The number of moles of water is calculated using the molar mass of water.

$$4.49 \text{ g} / (18.0 \text{ g/mol}) = 0.249 \text{ mol of } H_2O$$

c. Calculate the initial moles of water in flask B. The number of moles of water in flask B is equal to the sum of moles water in the 5.00 mL of HCl solution and in the 3.00 mL of water added to flask B.

   3.00 mL x 1.00 g/mL = 3.00 g of water in 3 mL of water added
   3.00 g / (18.0 g/mol) = 0.167 mol of water in 3 mL of water added
   0.167 mol + 0.249 mol = 0.416 total mol of water in flask B

d. Calculate the initial moles of EtAc in flask B. Use the density and volume to find the mass of EtAc and then calculate the moles using molar mass.

   2.00 mL x 0.893 g/mL = 1.79 g of EtAc
   1.79 g / (88.0 g/mol) = 0.0203 initial mol of EtAc

e. Calculate the moles of HAc at equilibrium. First calculate the total moles of acid in flask B from the titration data. Then subtract the moles of acid due to the HCl solution.

   0.03912 L NaOH x 1.00M NaOH = 0.0391 mol NaOH = 0.0391 mol total acid
   0.0391 mol total acid - 0.0289 mol HCl = 0.0102 mol HAc

f. Calculate the moles of EtAc, EtOH and H_2O at equilibrium. For reactants the moles used during the reaction are subtracted from the initial moles. For products the moles formed in the reaction are added to the initial moles. The moles used or formed during the reaction are based on the moles of HAc and the stoichiometry of the reaction.   In this reaction the stoichiometry is a one to one relationship for all the species. These calculations are summarized below:
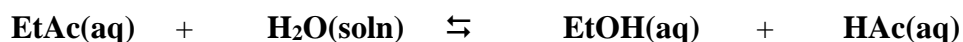
	EtAc(aq) +	**H_2O(soln)** ⇌	**EtOH(aq)** +	**HAc(aq)**
Initally	0.0203 mol	0.416 mol	0.00 mol	0.00 mol
Changes	-0.0102 mol	-0.0102 mol	+0.0102 mol	+0.0102 mol
At Equilibrium	0.0101 mol	0.406 mol	0.0102 mol	0.0102 mol

The value of the equilibrium constant is computed as follows:

$$Kc = \frac{[HAc][EtOH]}{[EtAc][H_2O]} = \frac{(0.0102)(0.0102)}{(0.0101)(0.406)} = 0.0254$$

Note that the student in the example used 6 M acid rather than 3 M acid and also performed the experiment at a different temperature so that his or her value of K_c will differ from yours. This example is not meant to be followed slavishly during the report write-up, but it does demonstrate the general method of performing the computations.

Disposal : Unused HCl and NaOH: There should be no reagents left over if burets are used to dispense them. However, if unused acid and base remain, mix them together in a beaker, add phenolphthalein and neutralize with 1 M HCl (the first disappearance of pink color) or 1 M NaOH (first appearance of permanent pink color). Flush the resulting salt solution down the sink with running water.

Titration solutions: These solutions already are neutral, and any unreacted ethyl acetate will hydrolyze to non-hazardous compounds. Therefore, they may be safely flushed down the sink with running water.

Determination of an Equilibrium Constant

The following tables may be used exactly as is in your report, but they **must be typed**. Alternatively, you may develop your own tables.

A. **Titration of HCl**

	Trial 1	Trial 2	Trial 3	Trial 4
Concentration of standard NaOH	_____	_____	_____	_____
Initial volume of NaOH	_____	_____	_____	_____
Final volume of NaOH	_____	_____	_____	_____
Volume of standard NaOH	_____	_____	_____	_____
Moles of NaOH	_____	_____	_____	_____
Moles of HCl in 3 M HCl solution	_____	_____	_____	_____

Average moles of HCl   _____

B. **Titration or Equilibrium Solutions**

	Flask A	Flask B	Flask C
Initial volume of NaOH	_____	_____	_____
Final volume of NaOH	_____	_____	_____
Volume of standard NaOH used	_____	_____	_____
Moles of NaOH = Total moles of acid	_____	_____	_____

Determination of an Equilibrium Constant

C. **Equilibrium Constant Calculations**

	Flask A	Flask B	Flask C
Initial moles of EtAc	_____	_____	_____
Initial moles of H_2O	_____	_____	_____
Total moles of acid (from B above)	_____	_____	_____
Moles of HCl (from A above)	_____	_____	_____
Moles of HAc (at equil)	_____	_____	_____
Moles of EtOH (at equil)	_____	_____	_____
Moles of EtAc (at equil)	_____	_____	_____
Moles of H_2O (at equil)	_____	_____	_____
Equilibrium constant	_____	_____	_____

The density of 3M HCl is 1.05 g/mL

Determination of an Equilibrium Constant

Pre-Lab QUESTIONS

1. How would this experiment be affected if the HCl was omitted unintentionally from one of the reaction mixtures? Please be specific.

2. Why can the moles of reactants and products, rather than their concentrations, be used in the equilibrium constant expression?

   Post-Lab QUESTIONS (To be included in your lab report – not just on the carbon copies)

3. Calculate the relative average deviation of the three equilibrium constants. What does this tell you about the precision of your K values?

4. Based on your values for the equilibrium constant, does equilibrium favor formation of products, reactants, or an approximately equal distribution of both?

5. If after the titration of an equilibrium solution in this experiment the solution is stoppered and allowed to reach equilibrium again, what will happen to the amount of ethyl alcohol present? (Hint: what is the ACID/BASE REACTION that took place **during the titration**, did the reaction add or remove product or reactant, how will equilibrium "shift"). What will be the relationship between the equilibrium constant associated with this new equilibrium and the equilibrium constant which you calculated?