

Illinois Central College

CHEMISTRY 132

Laboratory Section: _____

Name: _____

Determination of K_a for a Weak Acid

Equipment

1-ring stand	stir plate and stir bar
1-25.00 mL burette	1-50 mL and 1-250 mL beaker
pH 7.00 buffer	0.100 N NaOH
pH Probe	phenolphthalein

Objectives.

The objective of this experiment is to illustrate the use of titration curves in the determination of acid ionization constants.

Background

A plot of the pH of a solution against the volume of "titrant" added is called a titration curve. The pH of the solution can be measured directly with a pH probe and the LabWorks interface while titrant is added through a burette.

For the acids in this experiment, the titrant will always be a 0.100 N solution of the strong base, NaOH. From the form of the titration curve, it can be determined whether the solution consists of a strong or weak acid. Furthermore, if it is a weak acid, the equilibrium constant for its dissociation can be calculated.

Strong acids

Last week we saw the titration curve of a strong acid titrated with a strong base. For a strong acid, HA, the equilibrium constant, K_a for the process



is so large that it is completely dissociated into H_3O^{+1} and A^{-1} at usual concentrations, and hence, *the H_3O^{+1} concentration simply equals the acid concentration which remains untitrated by the NaOH.* This is true until the titration has reduced the concentration of HA to less than 10^{-6} M.

At this point, the dissociation of water according to the equation



$$K_w = [\text{H}_3\text{O}^{+1}][\text{OH}^{-1}] = 10^{-14} \quad (3)$$

begins to govern the H_3O^{+1} concentration. At the exact equivalence point (where the moles of base added equals the initial moles of acid present), the H_3O^{+1} concentration comes entirely from this source and is therefore equal to 10^{-7} and the pH is 7.

Weak Acids

For a weak acid, the equilibrium constant for reaction (1) is small (between 10^{-2} and 10^{-7}), so that the concentration of $[\text{H}_3\text{O}^{+1}]$ and hence the pH is governed by the K_a .

$$K_a = \frac{[\text{H}_3\text{O}^{+1}][\text{A}^{-1}]}{[\text{HA}]} \quad (4)$$

The titration curve you obtain should be considerably different from that obtained last week when a strong acid was titrated. Obviously the $[\text{H}_3\text{O}^{+1}]$ concentration will be lower (and therefore the pH will be higher) throughout the titration, because not all of the acid is dissociated. You should also find the shape of the curve is somewhat different. The reason for this becomes clear if the following three points along the titration curve are considered in some detail.

a) Zero titrant added.

Since the dominant source of $[\text{H}_3\text{O}^{+1}]$ is the acid dissociation described by equation (1), $[\text{H}_3\text{O}^{+1}] = [\text{A}^{-1}]$ from the stoichiometry of the equation. Therefore, equation (4) reduces to:

$$K_a[\text{HA}] = [\text{H}_3\text{O}^{+1}]^2 \quad (5)$$

If we further assume that the degree of dissociation is so small that $[\text{HA}]_{\text{eq}} \approx [\text{HA}]_{\text{initial}}$, then the pH can be calculated if the K_a is known or vice versa.

The K_a , however, is most conveniently obtained from the next point on the titration curve that will be discussed.

b) Half-way to the equivalence point.

At this point, half of the acid has been titrated and hence half of the acid, HA, has had its H^{+1} removed and is now A^{-1} . Therefore $[\text{HA}] = [\text{A}^{-1}]$. So, now equation (4) reduces to the simple expression

$$K_a = [\text{H}_3\text{O}^{+1}] \quad \text{or} \quad \text{p}K_a = \text{pH} \quad (6)$$

This is a rather remarkable point on titration curves since the pH is determined solely by the value of the $\text{p}K_a$ ($-\log K_a$) and *is independent of the initial acid concentration or any subsequent dilution.*

To determine the $\text{p}K_a$ of a weak acid, *we need only to locate this half-equivalence point accurately*, and this can be done by first finding the following point on the titration curve.

c) the equivalence point.

When the monoprotic acid, HA, has been completely titrated by the addition of an equal number of moles of base, we have reached the equivalence point. On the titration curve, this will appear as the point of maximum slope.

If the data are obtained by adding equal amounts of titrant throughout, the equivalence point would probably be poorly defined because there would be a sudden jump between two points. *We will, therefore, attempt to add small amounts of titrant in the vicinity of the equivalence point and thus, accurately determine the point of inflection.* Once this has been determined, the half-way point can be calculated and the pK_a determined as discussed in part (b).

Let us now consider the calculation of the K_a , given the exact pH at the equivalence point.

Since all the HA has been converted (neutralized) to A^{-1} at the equivalence point, it is the hydrolysis, that is, the reaction with water, of A^{-1} to produce OH^{-1} that gives rise to a basic pH at the equivalence point. Consider the following equilibrium in which A^{-1} is said to be "hydrolyzed".



It is not difficult to show that the "hydrolysis constant", K_h , for reaction (7) is related to K_w and the K_a for HA.

$$K_h = \frac{[HA][OH^{-1}]}{[A^{-1}]} = \frac{K_w}{K_a} \quad (8)$$

where $K_w = 1.0 \times 10^{-14}$

From the stoichiometry of equation (7), $[HA] = [OH^{-1}]$ and equation (8) can be written

$$K_h = \frac{[OH^{-1}]^2}{[A^{-1}]} = \frac{K_w}{K_a} \quad (9)$$

So, knowing the pH at the equivalence point allows us to find the pOH which in turn leads us to $[OH^{-1}]$ at the equivalence point. This information, along with K_w , allows the calculation of the K_a using the titration data at equivalence.

To get consistent results, it is best to use method (b) at the half-way point of the titration, since the calculations are independent of the initial acid concentration or any subsequent dilution.

Safety Precautions

Safety goggles must be worn in the lab at all times. Any skin contacted by chemicals should be washed immediately.

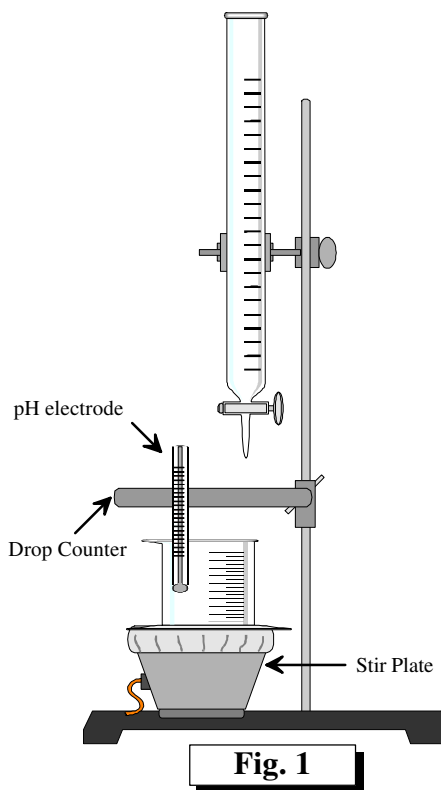
Procedure

Calibration of the pH probe

1. The pH probe used in this experiment **must not be allowed to dry out**, so when not in use, it should soak in distilled water or a pH 7 buffer.
2. Connect your pH probe to the **pH1** terminal of the interface. Obtain approximately 30 mL of a *pH 7 buffer* and place it in a 50 mL beaker with a magnetic stir bar. Place the beaker on a stir plate and set the speed so that the solution is very gently mixed.
3. Using a ring stand and a clamp, lower the pH probe into the solution so that the glass sphere at the end of the probe is completely submerged. ***Be careful that the stir bar does not strike the tip of the pH probe as the glass is very fragile.***
4. From the opening window of LabWorks, select the **Calibrate** button. In the next window select **pH1**. The new dialogue box will indicate the voltage reading (in millivolts) from the pH probe and prompt you to enter the pH of your calibration solution. Once the voltage reading has settled down, enter **7** for the calibration pH. That's it...your probe is calibrated.

Titration

1. Fill a 25.00 mL burette with 0.100 M NaOH, *making certain that the tip of the burette is filled with solution and free of air bubbles*. Clamp the burette to a ring stand and set it aside for the moment.
2. Obtain a 10.00 mL sample of one of the unknown acids (A, B, C, or D) in a 250 mL beaker. Add approximately 40 mL of distilled water. Place the magnetic stir bar in the beaker, and place it on the stir plate (stirring gently).
3. Position the ring stand holding the pH probe such that the probe tip is submerged in your acid solution toward one side of the beaker. Position the other ring stand holding the burette and the Drop Counter such that the NaOH can be dispensed through the Drop Counter into the acid solution. Plug the Drop Counter cable into "counter" on the LabWorks Interface .(see Fig.1)
4. From the LabWorks window, click the **Design** button on the toolbar and choose the **EZ Program** option button.
5. Drop the menu choices for the **"Read"** window in line (3.). Select **Counter** as you input and **"drops of base added"** as your label.



- Drop the menu choices for the "**Read**" window in line (4), select **pH1** as your input choice and set the **delay** to 1 second. The computer will automatically label this input as pH1.
- Select the **Acquire** button on the toolbar, and begin adding drops of base at a rate slightly greater than 1 drop/second. Simultaneously click on the **Start** button to begin the program and observe the titration curve that will be displayed on the monitor.
- Allow the titration to continue until the upper plateau is well established. (**NOTE:** You may have to adjust the stopcock on your burette during the titration to maintain a flow rate greater than 1 drop/second.) When the upper plateau has been well established, hit **Stop**.
- Click the **Save Data** button and assign a file name to your data, such as, Trial 1.
- Carefully place your pH probe back into the pH 7 buffer*, discard your first sample and obtain another 10.00 mL sample of the same unknown acid. As before, place it on the stir plate with the stir bar, pH probe, Drop Counter, and your re-filled burette.
- Click on the **Start** button to clear your Trial 1 data and repeat the entire titration process.
- Save your data as 'Trial 2' and repeat for a third trial.

Data Analysis

- After you have saved your data for trial 3, click the **Analyze** button and load the data from Trial 1 into the spreadsheet.
- Columns A and B should contain the "drops of base added" and the corresponding pH's. Highlight **Column C** and choose **Column Setup** from the **Menu Bar**. Enter "First Derivative" for the label of Column C and enter the formula **Deriv(b,a)**. Be sure to set the column to 3 decimal places. (This formula will take the first derivative of the pH values with respect to mL of base added. In essence, this will represent the values of the slope of our titration curve at any given point.)
- Choose **Graph Setup** from the **Menu Bar**, plotting Column A on the x-axis, Column B on the y1 axis and Column C on the y2 axis.
- The "spike" in the first derivative plot indicates the drops of base added at the endpoint (where the slope of the titration curve is at its maximum). Record the value on your Report Sheet.*
- From the value obtained in step 4, calculate the **number of drops of base** that was required exactly *half-way to the equivalence point*. Record this value on the Report Sheet
- From your Spreadsheet, estimate the **pH** at the halfway point and **record this value on your Report Sheet**.

7. Using equation (6), **calculate the K_a of the unknown acid** determined in this trial. Record this value on your Report Sheet.
8. Repeat steps 1-7 for your data from Trial 2 and Trial 3.
9. Calculate the **average K_a** from the three trials and enter this on the Report Sheet.
10. **Print the Graph and Data Table** for only one of the three trials and attach it to your Report Sheet. Exit the program.

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REPORT SHEET

Determination of K_a for a Weak Acid

	Trial 1	Trial 2	Trial 3
drops NaOH at equivalence point			
drops of NaOH half-way to equivalence point			
pH at half-way			
K_a of unknown acid			
Average K_a			

Show all calculations:

Trial 1:

Trial 2:

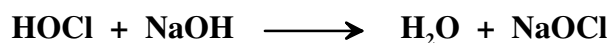
Trial 3:

Questions

1. Define "equivalence point".

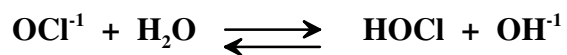
2. Define "buffer solution".

3. Consider the following equation



a) If 20.0 mL of 0.100 M HOCl is neutralized with 20.0 mL of 0.100 M NaOH, what is the approximate concentration of sodium hypochlorite, NaOCl?

b) Hypochlorite is a weak base and hydrolyzes as follows:



Write the equilibrium expression and find the K_b value for OCl^{-1} given that the K_a value for hypochlorous acid is 3.2×10^{-8} .

c) Find the pH of the above solution.

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SHOW YOUR WORK

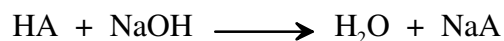
PRELAB: Exp. 4 Determination of K_a for a Weak Acid

1. A 0.100 M solution of an unknown weak acid has a pH value of 2.25.

a) Find the H^{+1} concentration.

b) Find the value for the K_a .

2. If 20.0 mL of 0.100 M weak monoprotic acid is **half** neutralized with 10.0 mL of 0.100 M NaOH according to the following equation;



a) calculate the amount of acid and base present (in millimoles) before they are added together. (Note: millimoles = Molarity x Volume (mL))

b) Upon half neutralization, the pH of the solution above is measured at 2.80. Find the K_a of the acid.

$$K_a = [H^{+1}] \times \frac{[A^{-1}]}{[HA]}$$

