

Determination of the K_a of an Unknown Acid

Objective: To identify a weak acid by determination of its acid ionization constant, K_a

Concept to be Tested: The value of K_a for a weak acid can be determined from the concentrations of the species present at equilibrium. K_a is a physical property that can be used to identify an unknown acid.

Textbook References: McMurray and Fay: Chapter 14.7-14.15, and 15.1-15.9

Laboratory Techniques References: Review *Titration* and *Pipetting*

Introduction

Acids and bases are often described as being “weak” or “strong.” While this classification seems somewhat arbitrary, other more quantitative descriptors exist. The acids and bases that we will be dealing with are in water solution. As a result, K_a values are commonly used to represent the degree of ionization of a particular acid in water and thereby represent its relative acidic strength. The ionization of an acid can be represented as follows:



You may notice that water is left out of this ionization. Realize that the ionization would not take place without water. The equilibrium constant for this is:

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

Since water is being left out of the equation, this constant is described as K_a rather than K_c . The larger the value of K_a the greater the ionization of the acid is in water and the “stronger” the acid. This value is highly characteristic of the acid and can be used to identify an unknown acid. A similar value K_b exists for bases.

pH

Critical to this experiment will be the measurement of pH. First, it is necessary to look at pH. The concept of pH was introduced in 1909 by the Danish chemist Søren Sørensen as a convenient way to express acidity. The reasons for introducing this concept include the relatively slow color change of indicators, and the need of electrical methods to determine the relative acidity or basicity of a concentration. This coupled with the convenience of comparing concentrations (*e.g.*, “the pH changes from 1 to 12” rather than $[\text{H}_3\text{O}^+]$ goes from 0.1 *M* to 0.000000000001 *M*). There is another subtly lurking here; the comparisons of pH are limited to the same set of conditions, especially temperature. The pH scale is based upon the Brønsted-Lowry model and is minimized to 0 to 14 because it assumes an excess of water. The IUPAC endorsed a pH scale based

upon comparison with a standard buffer of known pH using electrochemical measurements.

Sørensen used the letters PH for “pondus hydrogenii” literally meaning ‘potential hydrogen’ meaning hydrogen power as acidity caused by the predominance of H^+ . The actual term pH was introduced by W.M. Clark (inventor of the Clark oxygen electrode). Clark used pH for typographical convenience and used the “p” to stand for “power” (from the German word *potenz*) so pH is an abbreviation of “power of hydrogen.”

In most cases pH has been defined as $pH = -\log aH^+$ where aH^+ is the hydrogen ion **activity**. In solutions that contain other ions and under varied conditions, activity and concentration **are not** the same. The activity indicates the hydrogen ions that are active, rather than the true concentration. This accounts for the fact that other ions and conditions surrounding the hydrogen ions might shield them and affect their ability to participate in chemical reactions. In relatively dilute aqueous solutions this activity equals 1 and its affect can be ignored. Because of this, the IUPAC has restricted the pH range to dilute aqueous solutions of less than 0.1 M (or a pH range of 2 to 12). In reality, using a Brønstead-Lowry model, the pH range is probably **limited to values between 0 and 14**. Outside this range **in water** a negative pH does not meaningfully measure relative acidity.

Be aware that when dealing with pH, you **must consider the system**. pH values depend upon the conditions and the nature of the solvent. In water at 25 °C, a pH of 7.0 is considered to be neutral. For ethanol, the neutral concentration of H^+ is 1.58×10^{-10} which translates to a pH of 9.8. In ethanol, a pH of 8 would be acidic while this same pH in water would be basic. The conditions of the system also must be considered. When dealing with drugs or human systems, pH is determined and reported at 37 °C. Generally speaking pHs that are reported outside the 0 to 14 range are dealing with **nonaqueous** systems.

Determination of K_a

Two methods will be used to determine the K_a of the unknown acid. Both will require the use of a pH meter. In the first method, a sample of the acid is titrated with base. The pH values are plotted versus the volume of the base added. The equivalence point is determined from the graph and the pH at this volume is noted. Next the volume of base halfway to the equivalence point is found and the pH at this volume is noted. The pH at this point **is equal** to the pK_a of the unknown acid. At this point $[HA] = [A^-] = [H^+]$ so $[HA]$ and $[A^-]$ cancel out of the equation and $[H^+] = K_a$.

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

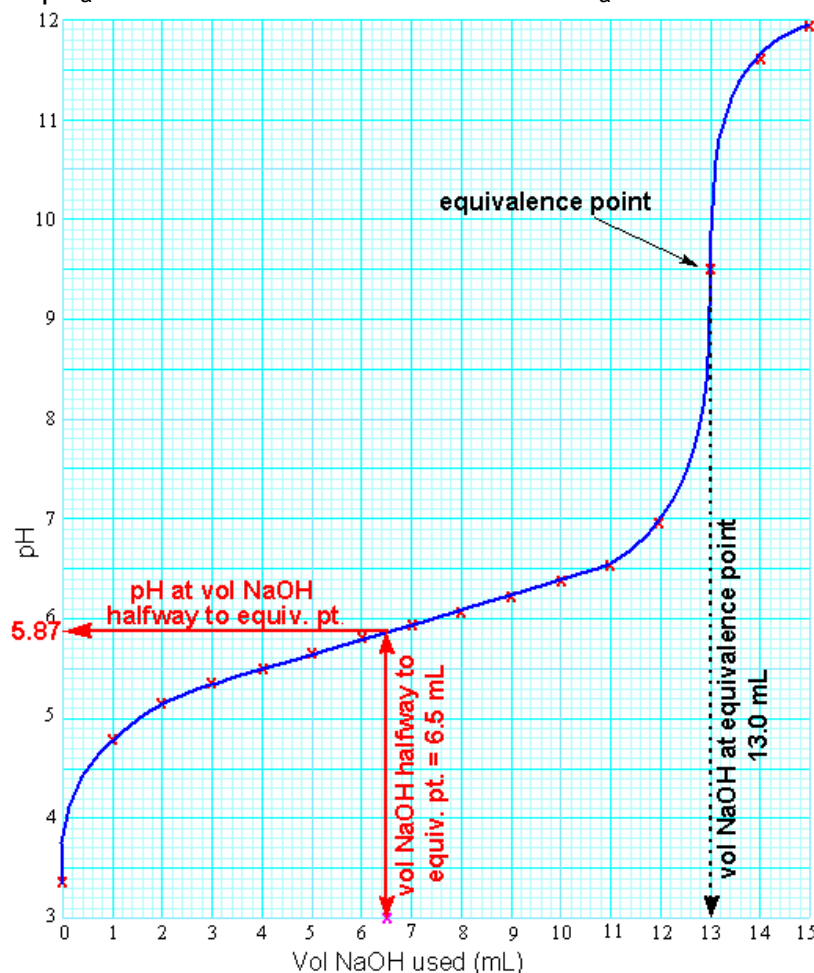
To determine the K_a it will only be necessary to convert the pK_a .

$$K_a = 10^{-pK_a}$$

This is probably best seen in an example.

Example.

You are given a sample of an unknown acid of approximately 0.1 M concentration. You place 10.0 mL of this acid in a clean beaker, determine its pH using a pH meter and then begin adding 1.0 mL portions of 0.10 M NaOH. You determine the 'new' pH of the solution following each addition. You stop the titration after the pH reaches approximately pH 12. You then plot the data and determine the pK_a of the unknown acid and also the K_a .



The equivalence point is seen where the sharp rise in pH occurs. The volume at the equivalence point is 13.0 mL. The volume of NaOH "halfway" to the equivalence point is 6.5 mL. Using the curve you have generated, the pH at 6.5 mL is 5.87. This is your pK_a .

$$pH_{\text{at half way point}} = pK_a = 5.87$$

$$K_a = 10^{-pK_a} = 10^{-5.87} = 1.35 \times 10^{-6}$$

Only one equivalence point is seen (only one sharp rise) so this is a monoprotic acid (HA). Although it was not asked, knowing that you started with 10 mL of unknown acid and titrated with 0.10 M NaOH, you also know that the initial concentration of your unknown acid was 0.13 M.

The second method for determining the K_a values involves a “half volume” method. A solution of the acid is prepared and divided in half as accurately as possible. One portion is titrated to its endpoint with phenolphthalein. The two portions are then recombined, and the pH of the resulting solution is measured. Since half of the acid has been titrated $[HA] = [A^-] = [H^+]$. Again $[HA]$ and $[A^-]$ cancel out of the equation and $[H^+] = K_a$. The pH of the solution at this point is equal to pK_a . The K_a is again determined by taking the antilog of the $-pK_a$.

Notice in both cases that the initial concentration of the acid is not important. What is sometimes overlooked is that the base must be fairly concentrated. The concentration of the base needs to be at least within the range of concentration of the acid. A sharp endpoint (equivalence point) is needed. This reduces the error at the estimation of the halfway point to neutralization. This is also important for the “half volume” method of determination of K_a . You do not want to drastically alter the concentration of the acid. Realize also that the neutralization of the acid with the base is exothermic and this change in temperature will shift the pH of the reaction slightly.

Since pH is a logarithmic scale, a change of up to 5% in the hydrogen ion concentration will not change the pH by more than a few hundredths of a pH unit. Typically, pH values are reported to the nearest tenth of a pH unit. If you were to cut the concentration of the acid in half, you would change the pH value less than 0.3 units. With the concentrations being used in this experiment, changes in concentration should produce very little effect on the pH or pK_a you determine.

The K_a is a physical property of the weak acid that may be used as a method for the identification of the weak acid. You will use the K_a you determine for you unknown acid to identify the acid present in your sample.

Dissociation Constants of Some Common Weak Acids at 25 °C

Weak Acid		pK_a	K_a
Acetic acid		4.75	1.76×10^{-5}
Benzoic acid		4.19	6.46×10^{-5}
Citric acid	K_{a1}	3.14	7.10×10^{-4}
	K_{a2}	4.77	1.68×10^{-5}
	K_{a3}	6.39	8.4×10^{-6}
Chloroacetic acid		2.82	1.51×10^{-3}
Dichloroacetic acid		1.25	5.62×10^{-2}
Formic acid		3.75	1.77×10^{-4}
Lactic acid		3.08	8.4×10^{-4}
Oxalic acid	K_{a1}	1.23	5.90×10^{-2}
	K_{a2}	4.19	6.40×10^{-5}
Tartaric acid	K_{a1}	3.22	6.0×10^{-2}
	K_{a2}	4.82	1.53×10^{-5}
Trichloroacetic acid		0.70	2.0×10^{-1}

Values taken from CRC Handbook of Chemistry and Physics 56th Edition (1975)

Your unknown acid will be taken from this list.

Notice that several of the acids that may be used as unknowns are diprotic and one is triprotic. You will have to determine the additional pK_a (and K_a) by plotting the data and observing the changes in the curve you are plotting. You **will not** be able to determine multiple pK_a values with a single “half volume” experiment.

Titration of a weak base with a strong acid produces a buffer situation. The equivalence point of the titration **will not** be at pH 7. For this reason phenolphthalein has been chosen as an indicator. Phenolphthalein will change color between pH 8 and pH10. Since the pH of the solution will change rapidly once all of the weak acid has been neutralized (the buffer capacity is lost), this indicator should be quite sufficient for showing the end point near the equivalence point of the reaction.

Phenolphthalein is a powerful laxative that is associated with significant abdominal cramping. Be certain to wash your hands before you leave the laboratory.

You will use phenolphthalein in all of the beakers containing the weak acid. This will be needed for the “half volume” experiment; the phenolphthalein is a safety net for the first procedure. You will be using phenolphthalein to detect potential contamination of the beakers you will be using. For the experiments most commonly run in the laboratory, it is common to encounter a bit of residual base in a flask or beaker. Depending upon the level of contamination, this could mask the fact that you may have chosen a di- or triprotic acid as your unknown. The use of the phenolphthalein will detect any contamination by a strong base so that you can take steps to eliminate this potential error before beginning your experiment.

Experimental Procedure

Calibration of pH Meter

Obtain a pH meter, two small beakers, a 250 mL beaker (to catch rinses), and a wash bottle. Your pH meter has been recently calibrated but it will be necessary to check the calibration. Place ~ 1 inch of pH 7 buffer in the small beaker to be used as one calibration standard, place ~ 1 inch of pH 4 buffer in the other beaker. ***It may be possible to have a single beaker of pH 7.0 buffer and a single beaker of pH 4.0 buffer used for the entire class.*** Remove the tip from the pH meter and thoroughly rinse the tip with distilled water. Gently blot the tip of the pH meter with a paper towel. Place the pH meter into the buffer (fully submerge the tip) and allow the reading to stabilize. The pH meter should read between 6.9 and 7.0. (If the reading is outside this range, inform your instructor. The pH meter may be recalibrated or you may be instructed to use a different pH meter.) Regardless, rinse the tip of the electrode thoroughly with distilled water, carefully blot the tip and then place the electrode into the pH 4.0 buffer. The pH meter should read between 3.8 and 4.1. (Your instructor may need to adjust the pH meter.) Thoroughly rinse the electrode with distilled water, carefully blot it dry and replace the tip. The pH meter is ready for use.

Neutralization of the Weak Acid with Base

Obtain two (2) 100 to 150 mL beakers and rinse each with water. Add 2 drops of phenolphthalein indicator to each. If the indicator turns “pink” discard the contents and rinse the beaker several more times before testing with phenolphthalein again. You expect to see a white cloudiness from the phenolphthalein this is normal, any indication of pink means that the beaker contains significant quantities of base so you need to remove this contamination before you perform the experiment.

Obtain a ring stand, buret clamp, buret, 150- to 200-mL beaker, a (*small*) stirring bar, and stir motor. Rinse the stirring bar thoroughly with water before placing it into your beaker. Place 80 to 90 mL of base into the beaker and take it to your workstation. Choose one of the unknown acids (record the letter identifying this acid into your lab notebook) and using a graduated cylinder place 10 mL of the unknown acid into each of your two pre-cleaned beakers. Use a small amount of the base to rinse the buret and then fill the buret with the base.

Generally titrations are performed in Erlenmeyer flasks. However since you will be monitoring the pH by use of the pH meter, it is best to use a beaker for this experiment.

Place the stirring bar into one of the beakers, place the beaker on the stir motor and adjust the stirring rate until you get a smooth stirring. Remove the tip from the pH meter and rinse the electrode thoroughly with distilled water. Carefully blot the electrode dry and then place it into the beaker.

IF the liquid does not completely submerge the tip of the electrode **add** a small quantity of *distilled* water to the beaker to raise the level of liquid in the beaker. Neither the amount of liquid nor the volume of acid is important in this experiment, hence the use of a graduated cylinder to measure the volume of acid used.
Manually hold the pH meter or clamp it in place to prevent it from tipping over the beaker – DO NOT allow the stir bar to strike the pH electrode.

Allow the reading on pH meter to stabilize and record the initial pH reading. Now begin adding the NaOH solution in 0.5 mL portions. Record the pH reading after each 0.5 mL of base added. Continue the addition until you reach the phenolphthalein endpoint (pH>9). Record the final reading, retrieve the stir bar, and discard the contents of the beaker down the drain.

Thoroughly rinse the stirring bar with distilled water and place it into the second beaker. Place the beaker on the stirring motor and again adjust the stirring until smooth stirring is obtained. Thoroughly rinse the pH electrode with distilled water, blot it dry and place it into the second beaker. Again make certain that the pH meter is secured (manually or

with a clamp to prevent tipping the beaker) and that the stirring bar will not come in contact with the electrode. Adjust the volume of liquid in the beaker if necessary and allow the reading on the pH meter to stabilize. Record the initial pH of the solution and then begin adding NaOH in 0.5 mL portions. Record the pH after each addition. Continue the addition of NaOH (and recording of the reading on the pH meter) until the phenolphthalein endpoint is reached (pH>9). Record the final reading, retrieve the stir bar, and discard the contents of the beaker down the drain. Thoroughly rinse the electrode, blot it dry and replace the tip.

Plotting the volume of NaOH used against the pH will allow you to visually determine the equivalence point(s) of your unknown acid. The pH reading that corresponds to half of this volume of NaOH is equal to the pK_a of your unknown.

A polyprotic acid will have two or more equivalence points. You will use this same procedure to determine each of the pK_a values. The only difference is that for the second or third pK_a value, you will determine the volume of NaOH that corresponds to a point half way between the two equivalence points being considered.

Determination of the pK_a by the Half Volume Method

Obtain three (3) 100 mL beakers and rinse each with water. Add 2 drops of phenolphthalein indicator to each. If the indicator turns “pink” discard the contents and rinse the beaker several more times before testing with phenolphthalein again. You expect to see a white cloudiness from the phenolphthalein this is normal, any indication of pink means that the beaker contains significant quantities of base so you need to remove this contamination before you perform the experiment.

Use the same set-up as you used for the first portion of the experiment. Use a **10.00 mL volumetric pipet** to transfer 10 mL of your unknown acid into each of the beakers. Refill the buret with the NaOH solution, add a stir bar to one of the beakers, and begin to titrate the first beaker. This is a **trial run** to establish the volume of NaOH needed to titrate 10.00 mL of your unknown acid. Stop the titration when the solution **just** turns pink (and remains pink for 30 seconds). Note the volume of NaOH solution required. You will use the volume of NaOH used to titrate this **trial** beaker to help you ‘fine tune’ your titration of the second beaker. Retrieve the stir bar and discard the contents of the beaker down the drain.

Thoroughly rinse the stir bar with water and place it into the second beaker. Note the total volume of NaOH used to titrate the first beaker of acid. You may rapidly add the NaOH solution until you get within 1 to 2 mL of the volume required in the trial run. At this point stop the addition and begin **slowly** adding the NaOH solution **dropwise**. Stop the addition when the solution just turns pink (and remains pink for 30 seconds). Now **add** the contents of the remaining beaker containing 10.00 mL of ‘untitrated’ acid to **this** titrated solution.

Remove the tip from the pH meter, thoroughly rinse the electrode on the pH meter, blot it dry, and place it into this mixture. Wait for the reading on the pH meter to stabilize and record the pH of the solution. Remove the pH meter, thoroughly rinse the electrode with distilled water, blot the electrode with a paper towel and replace the tip. Remember to turn off the pH meter.

The volumetric pipet allowed you to precisely transfer the same quantity of acid into each of the beakers. When you neutralized (titrated) one beaker of the acid, you produced the salt of that acid. By adding the contents of the last beaker to this titrated solution, you have a mixture that contains exactly equal quantities of the free acid and its salt. The pH should equal the pK_a of the unknown acid. If this was a polyprotic acid, the pK_a that you determine is for the completely neutralized acid (pK_{a2} for a diprotic acid or pK_{a3} for a triprotic acid).

Cleanup

All of the solutions used in this experiment may safely be disposed of by pouring down the drain followed by rinsing with water. Wash and dry all of the beakers and replace them in the appropriate storage cabinet. Return the stirring bar, stirring motor, ring stand and clamps to their appropriate storage areas. Rinse the buret thoroughly with water making certain that the stopcock assembly has been thoroughly flushed with water. Allow the buret to dry and return it to its storage location.

Safety

You must wear departmentally approved eye protection while in the laboratory. Sodium hydroxide, even as a dilute solution, is a corrosive irritant and is particularly hazardous to eyes. The dilute acid solutions should all be considered to be corrosive irritants. Phenolphthalein is a powerful (causes abdominal cramping) purgative laxative. All solutions may safely be discarded by pouring down the sink followed by rinsing with water. Make certain to wash your hands before leaving the laboratory.