K_a for Unknown Acid

METHOD OF PARTIAL NEUTRALIZATION
DISCUSSION;

Look at the ionization equilibrium of a weak acid:

$$HA\ (aq) + H_2O \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq)$$

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

This may also be written as:

$$K_a = [H^+]\ .\ \frac{[A^-]}{[HA]} \qquad (1)$$

You do not need to know both [A-] and [HA], *only their ratio* to calculate K_a from the observed pH.
When you begin to titrate an acid, you start to convert that acid to salt:

$$\underset{\textbf{acid}}{HA} + NaOH \rightarrow H_2O + \underset{\textbf{salt}}{NaA}$$

If you stop before you reach the end point, you will have excess *ACID* still un-neutralized in the beaker along with the *SALT* that has been formed. At this point the acid is very little ionized because of the effect of the salt present. So you can consider the acid to be almost entirely in the form of HA molecules. The A^- ion comes almost entirely from the salt, for the same reason, effect of excess A^- on the acid's ionization. So the ratio we want in equation (1) above, $[A^-]/[HA]$, is simply the salt-to-acid ratio.

To know the salt to acid ratio, you need only to know how far toward the endpoint you have gone. For example, at one-fifth the way to the end point you have neutralized (formed salt from) one-fifth of your acid. The other four-fifth is still un-neutralized. So your mixture is 1/5 salt and 4/5 acid. The salt to acid ratio is 1/5 to 4/5.

$$\underset{\textbf{acid=4/5}}{HA} + NaOH \rightarrow H_2O + \underset{\textbf{salt=1/5}}{NaA}$$

In terms of net-ionic equation the above equation could be written as:

$$\underset{\textbf{acid}}{HA} + OH^- \rightarrow H_2O + \underset{\textbf{conjugate base}}{A^-}$$

Since $\frac{\text{salt}}{\text{acid}} = \frac{[1/5]}{[4/5]}$,then $\frac{[A^-]}{[HA]} = \frac{[1/5]}{[4/5]}$

Substituting into (1) above, we find:

$$K_a = [H^+] \cdot \frac{[1/5]}{[4/5]}$$

In today's experiment you will first determine K_a of an unknown acid by measuring the pH of the pure acid (no salt present). Next you will titrate the acid to find what volume of base is needed to neutralize it completely.

Then you will make several known mixtures, in which the acid is 1/4 neutralized, 1/2 neutralized, and 3/4 neutralized. From the salt-to-acid ratio and the measured pH for each solution, you will calculate K_a.

Averaging the four K_a values calculated (for the pure acid solution and for the three mixtures of salt-plus-acid) should give a more reliable value than you would obtain from a single determination.

PRECISION OF K_a MEASUREMENTS

pH cannot be determined with the same precision as titration measurements. But high precision is not necessary for equilibrium constants. Here it is the order of magnitude that is of primary interest, that is, the value of the exponent. The numerical part is usually recorded to only one or two significant figures, and may even be left off entirely. For example, K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5} \sim 10^{-5}$

LABORATORY TECHNIQUES:

A pipet is a tube designed to deliver a specific known volume of solution with a high degree of accuracy. You will use a 10.00 ml pipet which has only one calibration mark . You will use a pipet pump to draw liquid into the pipet.

PIPET OPERATING INSTRUCTIONS:

The pipet that you will check out from the stockroom is clean and dry. Do not rinse it with water.
Your instructor will demonstrate the operating procedure which may be summarized as:

1. Hold the pipet close to the upper end and insert the chuck of the pump with a slight pressure and twist. This assures a secure fit. WARNING: EXTREME CARE SHOULD BE TAKEN WHEN INSERTING THE PIPET BECAUSE OF THE POSSIBILITY OF SHATTERING. To loosen the pipet, hold it near the chuck, twist slightly and pull.

2. Submerge the end of the pipet into the solution and turn the operating wheel with the thumb. Fluid will be drawn up into the pipet. To expel fluid, turn the wheel in the opposite direction. For fast emptying, press down on the plunger top. Some liquid will remain in the tip. It is meant to stay there. Never blow out the last liquid from the pipet; if you do, you will get more than the intended volume of the sample.

3. To rinse the pipet between solutions, draw in a little of the next sample to be used. Rotate the pipet so that the liquid covers all surfaces below the calibration mark, then throw the –rinse liquid- away.

EXPERIMENT:

1. Use a slip to sign out a buret, a 10.00 ml pipet, a pipet pump, and a pH pen.

2. Take your lab report and a clean dry 125 ml Erlenmeyer flask to your instructor who will put an unknown acid solution in your flask.

3. Determine the pH of your unknown acid, using the pH pen. From your observed pH calculate [H^+].

4. Pipet 10.00 ml of unknown acid into a 125 ml Erlenmeyer flask and titrate with the standard base provided, using phenolphthalein indicator. (Use a minimum volume of standard base. Probably you will need less than 40 ml total for all parts of the experiment.) The NaOH solution will be approximately 0.1 M but be sure to record its exact molarity given on the bottle.

5. Calculate the molarity of your unknown acid solution, which will be a monoprotic acid.

6. Calculate the value of K_a from the molarity and from the value of $[H^+]$ obtained above.

7. a. Pipet another 10.00 ml of unknown acid into a clean 125 ml Erlenmeyer flask. Add from the buret exactly ***one-fourth*** of the volume needed above for complete neutralization. Mix well, then transfer the mixture to 50 ml beaker, measure and record the pH.

   b. Repeat using 10.00 ml of unknown plus ***one-half*** the volume NaOH needed to neutralize it completely. Measure the pH of this mixture after transferring it to a 50 ml beaker.

   c. Repeat again with the acid ***three-fourth*** neutralized. Measure pH.

8. Average all ***four*** values of K_a of your unknown acid. Then ask your instructor for the accepted value of your acid. Report the precision and the accuracy of our K_a determination.

Report Sheet

K_a FOR UNKNOWN ACID BY PARTIAL NEUTRALIZATION METHOD

Name________________
Last First

Instructor's Initial_______

1, pH of unknown acid pH= ____________

2. Calculate the $[H^+]$ from measured pH $[H^+]$= __________M

3. Volume of unknown acid used Acid used= **10.00 ml**

4.Titration:

initial buret reading	final buret reading	Volume of NaOH
		setup: **=__________ml**

5. Molarity of NaOH (written on the bottle) M_{NaOH}= _________M

6. Consider the equation for the titration reaction to calculate the molarity of the unknown acid:

$$HA + OH^- \rightarrow H_2O + A^-$$

acid ***conjugate base***

Setup:

Molarity of unknown acid___________M

7. K_a of unknown acid:

Equilibrium equation

$$HA\,(aq) + H_2O \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$$

Initial concentration	______	________	________
Change in concentration	______	________	________
Equilibrium concentration	______	________	________

Equilibrium expression:

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

Calculate K_a of unknown acid:

Setup:

K_a = ________

8. Partial Neutralization Mixtures:

Initial buret reading	Final buret reading	ml base	$[A^-]/[HA]$	$pH_{measured}$	$[H+]_{calculated}$
a.			$\frac{[1/4]}{[3/4]}$		
b.			$\frac{[1/2]}{[1/2]}$		
c.			$\frac{[3/4]}{[1/4]}$		

Calculation of K_a by partial neutralization mixtures.

a. Setup:

K_a = ________

b. Setup:

K_a = ________

c. Setup:

K_a = ________

9. Average of four experimental values for K_a:

Setup:

Average K_a= _________

10. Precision: (standard deviation)

Setup:

± ________

11. Accepted value of K_a for unknown (from instructor):

K_a = _________

12. Accuracy of K_a determined:

Setup:

____________ %

Exercise:

1. 44.70 ml of 0.100 M NaOH are required to completely neutralize 50.00 ml of a weak monoprotic acid, HA. When 34.43 ml of NaOH are added to another 50.00 ml of the acid, the pH reading was 4.80. Calculate K_a for the acid using the partial neutralization method.

Setup:

2. The pH of a weak monoprotic acid, HA, is 4.55. It took 39.22 ml of 0.2334 M NaOH to titrate 25.00 ml of the acid.

a. Write an equation for the above reaction.

b. Calculate the molarity of the weak acid.
Setup:

_________M

c. Write the equilibrium equation. Construct a table showing initial conc., change in conc., and equilibrium conc. Calculate the ionization constant, K_a , for the above acid.
Setup:

Answer _________

d. 23.55 ml of the NaOH were added to **partially** neutralize a new 25.00 ml sample of the acid. The pH of the mixture was measured as 5.33. Calculate K_a for the acid, HA, using the partial neutralization method.
Setup:

Answer__________