

Determination of the Equivalent Mass and pK_a of an Unknown Acid

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1 Purpose

The purpose of this experiment is to determine the equivalent mass of an unknown acid by the titration of a sample with a known base.

2 Procedure

First, the sodium hydroxide that will be used for titrating is standardized by using it to titrate a known quantity of potassium hydrogen phthalate (KHP). From the titration, the molarity of the NaOH solution is calculated.

Second, the equivalent mass of the unknown acid is determined by titrating a known amount of the acid with the standardized NaOH. Then the equivalent mass is calculated from the data.

Finally, the pK_a is determined by titrating a sample of the unknown acid while measuring the hydrogen ion concentration with a pH meter over constant intervals of included base. The data are then graphed to calculate the pK_a of the acid.

3 Data

The following data were collected. For part one,

Trial	KHP (g)	NaOH (mL)
#1	0.551	22.87
#2	0.464	20.60

For part two,

Trial	Unknown Acid (g)	NaOH (mL)
#1	0.434	26.56
#2	0.390	23.10

In part three, there were 0.820 g of the unknown acid.

4 Calculations

Since KHP is monoprotic, its equivalent mass (EM_a) is equal to its molar mass, which is $204.22 \frac{\text{g}}{\text{mol}}$. Because of

$$V_b \cdot M_b = \text{moles H}^+ \quad (1)$$

and

$$EM_a = \frac{\text{grams acid}}{\text{moles H}^+} \quad (2)$$

the following equation can be derived to calculate the molarity of the NaOH

$$M_b = \frac{\text{grams acid}}{V_b \cdot EM_a} \quad (3)$$

So, for each trial,

$$M_b = \frac{0.551}{\frac{22.87}{1000} \cdot 204.22} \text{ M} = 0.118 \text{ M}$$

$$M_b = \frac{0.464}{\frac{20.60}{1000} \cdot 204.22} \text{ M} = 0.111 \text{ M}$$

Then, the average molarity of the NaOH is $\frac{0.118+0.111}{2} \text{ M} = 0.115 \text{ M}$

From the graph, we can see there is an inflection point at 54.1 mL of NaOH, according to the second derivative. Then, the half neutralization point is at $\frac{54.1}{2} = 27.0$ mL. At this volume, the pH is 1.74. So, since the pH is equal to the $\text{p}K_a$ at this point, the $\text{p}K_a$ of the acid is 1.74. Because $K_a = 10^{-\text{p}K_a}$, $K_a = 10^{-1.74} = 1.82 \times 10^{-2}$

Using equation (3), we can determine the equivalent mass with

$$EM_a = \frac{\text{grams acid}}{V_b \cdot M_b} \quad (4)$$

Using the data in the second part and this equation,

$$EM_a = \frac{0.434}{\frac{26.56}{1000} \cdot 0.115} \frac{\text{g}}{\text{mol}} = 142 \frac{\text{g}}{\text{mol}}$$

$$EM_a = \frac{0.390}{\frac{23.10}{1000} \cdot 0.115} \frac{\text{g}}{\text{mol}} = 147 \frac{\text{g}}{\text{mol}}$$

Also, since the final trial took 54.1 mL of NaOH with 0.820 g of unknown acid,

$$EM_a = \frac{.820}{\frac{54.1}{1000} \cdot 0.115} \frac{\text{g}}{\text{mol}} = 132 \frac{\text{g}}{\text{mol}}$$

The average then for the EM_a is $\frac{142+147+132}{3} = 140 \frac{\text{g}}{\text{mol}}$

Letting this be the accepted value, the percent deviation is $\frac{\Sigma|EM_a-140|}{140 \cdot n} = \frac{2+7+8}{140 \cdot 3} = 4.05\%$

So, $pK_a = 1.74$ and $K_a = 1.82 \times 10^{-2}$ with $EM_a = 140 \frac{\text{g}}{\text{mol}}$ with a 4.05% deviation.

5 Discussion

1. The equivalent mass is the mass of an acid such that when dissociated will yield one mole of hydrogen ions. We determine equivalent mass and not molecular mass because some acids have more available hydrogen ions than others. It is useless in terms of calculations that depend on the amount of acid needed for a certain unit of hydrogen ions to use the molar mass which only guarantees a certain number of grams of the entire acid itself per mole of acid instead of grams of the entire acid per mole of hydrogen ions.
2. A standard solution is a solution in which there is a known molarity as found by experiment.
3. Titration is the method of determining concentrations by adding known volumes of a known concentration of a titrant, a standard solution, to another solution. An indicator or pH meter is often used to decide when to stop adding titrant.
4. The KHP and acid samples must be dried so that their measured masses are actually proportional to the number of moles of each acid sample. If they were not dried, they'd be heavier than they should with the excess water. This means that there are actually fewer moles of acid than there should and, likewise fewer hydrogen ions in solution. Then, less NaOH is required and it will appear to have fewer hydrogen ions per unit of mass, and therefore too high of an equivalent mass.
5. The pH is the logarithmic concentration of hydrogen ions. It is logarithmic to better account for the wide possible range of concentrations in a small band of easy to use numbers. When the pH changes by one unit, the hydrogen ion concentration changes by a factor of ten.
6. The equivalence point is not necessarily at a pH of 7 because it occurs just when there are equal concentrations of acid and base reacted in solution. Then, the final pH depends on the major species of ions present in solution after the reaction.

7. The K_a represents the equilibrium constant expression for a given acid. It is used to determine the concentrations of the ionic species of the acid that will dissociate when put into a solvent. From a graph relating titrant volume to pH, we find the equivalence point (which is the inflection point on the graph) and find the pH of the solution when the titrant volume is half that of that at the equivalence point. Since at half the equivalence point the concentrations of the acid and conjugate base are equal, pH is pK_a , so, using the pH, $K_a = 10^{-pH}$
8. The graph did not clearly give any indication of containing more than one ionizable hydrogen. There is a slight bend near the main inflection point, but this can be assumed to be pen-type pH meter instrument error since the slope there still seems too steep to allow for another deprotonation.
9. A buret can be read to within .01 mL and the balance can be read to within 0.001 g. It is better to titrate with a volume of base that fills most of the buret because any chance contamination will be minimized by the larger volume and the contaminants will have a lower concentration than otherwise. It is also easier to measure the base from the zero point, reducing error. Mainly, having a large volume allows titration without having to refill the buret, which is generally not a good thing to have to do.
10. The K_a value is 1.82×10^{-2} . At the equivalence point, there are equal amounts of acid and base. We know that $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$ and $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$. The NaOH will neutralize the acid at the equivalence point, $\text{OH}^- + \text{HA} \rightleftharpoons \text{H}_2\text{O} + \text{A}^-$ or $\text{H}_2\text{O} + \text{A}^- \rightleftharpoons \text{OH}^- + \text{HA}$

The K_b for this equation is $K_b = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]}$

The relationship between K_b and K_a is $K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{1.82 \times 10^{-2}} = 5.49 \times 10^{-13}$

H_2O	A^-	\rightleftharpoons	OH^-	HA
—	0		1	1
—	+x		-x	-x
—	x		1 - x	1 - x

$$5.49 \times 10^{-13} = \frac{(1-x)^2}{x}$$

Since the K_b is so small, we can just assume it is zero and $x = 1$. This means all of the HA and hydroxide have turned into A^-

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