Titration of a Diamine: Identifying an Unknown Diamine by Determining Molar Mass and Estimating the Protonation Constants for the Compound

(Adapted from Donald C. Bowman and Elizabeth A. Pfister, *Chem. Educator* 2007, *12,* 384–386)

Introduction:

Titration of a diamine with a strong acid yields a titration curve with two equivalence points. As is true with most titration curves for diprotic acids, the titration curve of a diamine shows one equivalence point more clearly defined than the other equivalence point. The more clearly defined equivalence point can be used to experimentally determine the molar mass of an unknown diamine and the log of the protonation constants for the compound.

The equivalence point volume, along with the known molarity of the titrant, produces the number of moles of titrant used. Using the more clearly defined equivalence point the number of moles of diamine is determined. The molar mass of the diamine is then determined with known mass of the diamine used for the titration.

The protonation constants, K_i^H, of a diamine (A) are defined as the equilibrium constants for the reactions:

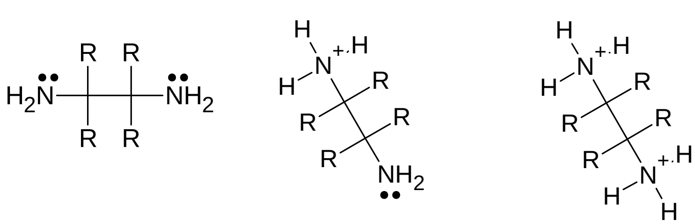
$$A(aq) + H^+(aq) = HA^+(aq) \qquad K_1^H$$
$$HA^+(aq) + H^+(aq) = H_2A^{+2}(aq) \qquad K_2^H$$

Using a half - titration method, both protonation constants can be determined from this experiment. The first half-titration point occurs when one half the amine molecules have been mono-protonated, so that $[HA^{+1}] = [A]$. From the equilibrium expression for the protonation equation, it can be shown:

$$K_1^H = \frac{[HA^+]}{[A][H^+]} = \frac{1}{[H^+]}; \quad \text{and @ first half neutrtalization point } pH = pK_1^H$$

$$K_2^H = \frac{[H_2A^{+2}]}{[HA^+][H^+]} = \frac{1}{[H^+]}; \quad \text{and @ second half neutrtalization point } pH = pK_2^H$$

Where A, HA^+ and H_2A^{+2} respectively are;



Reagents and Chemicals:
Diamine sample
Standardized HCl solution (Concentration clearly stated on the label)

Procedure:

1. Connect a pH sensor to the Logger *Pro* interface and then the interface to the computer. Prepare the computer for data collection by opening the file "25a Titration Dip Acid" from the *Chemistry with Computers* folder of Logger *Pro.* Highlight the graph portion of the screen, click on graph options, and rename the graph to reflect a titration of a diamine instead of a diprotic acid.

2. Pipette precisely 100 μL of the diamine sample into a 150 mL beaker containing ~60 mL of deionized water. Introduce a magnetic stir bar and quickly cover the beaker tightly with parafilm.

3. Fill a burette with a standard HCl solution; adjust the burette level to 0.00 mL. Note the concentration of the standard HCl solution.

4. Place the beaker on a magnetic stirring device. Puncture two holes in the parafilm; one hole just large enough to allow the tip of a burette to be lowered into the beaker and the other hole just large enough to allow the pH probe to be lowered into the solution. Lower the tip of the burette into the beaker far enough down to be seen clearly, but well above the liquid level.

5. Lower the pH sensor through the foil into the beaker and below the level of the solution. Adjust the stirring device to provide a slow and steady stirring action. Make sure that the stirring bar does not come in contact with the pH sensor.

6. Before adding HCl titrant, click “collect" and monitor the pH for 5-10 seconds. Once the pH has stabilized, click "keep". In the edit box, type "0" (for 0.00 mL of added acid), and press "enter" to store the first data pair. Add 1.0mL of HCl, and when the pH stabilizes, again click "keep". In the edit box, type the current burette reading to the nearest 0.01 mL. Press "enter". Continue adding HCl solutions in ~0.5mL increments (until pH ~9.5) enter the burette reading to the nearest 0.01 mL after each addition, always. Now change the volume increment to 2 drops until the pH ~8.

7. Return to additions of ~0.5 mL increments until the pH ~6.5. Then proceed by making 2 drop additions and until pH ~ 2.5 or until the equivalence point is passed. Take some more readings well past the equivalence point (1-2 mL more). Click "stop" and then save the file. Print both the graph and the data table.

8. Transfer the data into an Excel spreadsheet. Plot the second derivative plot in Excel. Determine the second equivalence point to the second decimal place.

9. Repeat the procedure twice more if time permits.

Processing the Data:

1. One of the equivalence points will be more clearly defined than the other. That point will be used for calculations. To find the precise volume of that equivalence point, find the second

derivative; i.e. "d^2" column on your printed data table. The equivalence point is the volume where the value of "d^2" switches algebraic sign from negative to positive.

2. Record that value in your data table. Estimate the molar mass of the unknown diamine by calculating the moles of diamine that were titrated by the standard acid (the acid to base mole ratio will be 1:1 if the 1st equivalence point is used, and the ratio will be 2:1 if the 2nd equivalence point is used.) From the following list of diamines, identify the unknown diamine:

Diamine	Formula	Molar mass (g/mol)
1,2-diaminoethane	$C_2H_8N_2$	60.1
1,2-propanediamine	$C_3H_{10}N_2$	74.1
1,2-butanediamine	$C_4H_{12}N_2$	88.2
1,2-pentanediamine	$C_5H_{14}N_2$	102.2
1,2-hexanediamine	$C_6H_{16}N_2$	116.2

Typical Notebook Entry: Data

Concentration of HCl, M			
Mass of diamine, g (density=0.8960g/mL)			
1st half-titration; Std HCl volume, mL			
2nd half-titration; Std HCl volume, mL			

Typical Notebook Entry: Calculations

(Show the calculations; hand calculations or computer outputs for the calculation of the following quantities) Calculate the Molar mass and the two pK values..

Use of a spreadsheet is recommended; regardless the notebook and spreadsheet entries must be well documented, always. Suggested steps of calculation are as follows.

Equivalence point HCl volume for calculation (indicate which one you used, 1st or 2nd), mL

Moles of HCl, mol

Moles of diamine, mol

Molar mass of diamine, g/mol

Identity and correct molar mass of diamine sample, g/mol

pK_1^H and K_1^H

pK_2^H and K_1^H