

Name: _____ Date: _____

Lab Partners: _____

Acid-Base Titrations

By Thomas Cahill, Arizona State University, New College of Interdisciplinary Arts and Sciences.

Background:

One of the most common reactions in chemistry is the reaction of an acid with a base. This type of reaction is also called neutralization. The mechanism of this process is the combination of hydroxide ions and hydronium to create water:



It is important to note that the hydronium ion (H_3O^+) is often simply represented as H^+ . The hydronium ion representation is technically a more accurate representation of association between a hydrogen ion and a water molecule, but either representation is acceptable and interchangeable in this class.

The acid-base reaction is a second order reaction, thus the rate of the reaction is dependent on the concentrations of both of the reactants. The concentration of hydronium ion is most commonly expressed as the pH of the solution. The equation to calculate pH is:

$$\text{pH} = -\text{Log}[\text{H}^+] \quad (2)$$

where $[\text{H}^+]$ is the concentration of the hydronium ion.

The pH of a solution is a measure of the hydronium ion concentration in a solution. The pH scale ranges from 0 to 14. Any pH value lower than 7 indicates an acidic solution, a pH value above 7 denotes a basic solution, and a pH value of 7 indicates a neutral solution. The pH for several familiar substances can help give an idea of what the capricious pH values represent. Gastric juice has a pH of 1 while wine has a pH of around three. Conversely, household bleach has a pH of 12 and baking soda has a pH of eight. Human blood and tears are very close to the neutral pH of seven.

One important thing to note about the pH scale is that it is based on the logarithmic scale. This means that for every single unit of change in pH there is actually a tenfold difference in the hydronium ion concentration. For example, if the pH of a solution drops from 6 to 5, the hydronium ion concentration has increased by a factor of 10, from 10^{-6} M to 10^{-5} M.

The most accurate method of measuring the pH of a solution is utilizing a device called a pH meter. A specialized electrode, which measures the concentration of hydronium ions, is simply placed into the solution. A few seconds after the probe is submerged, the pH of the solution will be displayed on the pH meter's screen. Colored pH paper and indicator dyes can also be used to roughly estimate the pH of the solution.

Another important concept in acid-base chemistry is that of acid-dissociation constants. An acid dissociation constant, denoted by K_a , is an equilibrium constant for the dissociation of a weak acid.



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

HA representing an acid and A⁻ representing the conjugate base of the acid. The acid dissociation constant is log-transformed to get it on the same scale as pH. This is defined as pK_a, which is calculated as:

$$\text{p}K_a = -\log K_a = -\log \left(\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \right) \quad (5)$$

The magnitude of K_a indicates the tendency of an acid to ionize in water. The larger the K_a value of an acid the stronger the acid. Conversely, the smaller the pK_a value the stronger the acid.

Equations #5 and #2 are combined and manipulated to the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right) \quad (6)$$

This is a very useful equation since it relates pH to pK_a and the fraction of the acid that is ionized. People who often work with buffers use this equation to calculate the pH of buffers.

Example:

What is the pH of a buffer that is 0.20 M in lactic acid (HC₃H₅O₃) and 0.05 M in sodium lactate? Lactic acid has a K_a of 1.4×10⁻⁴.

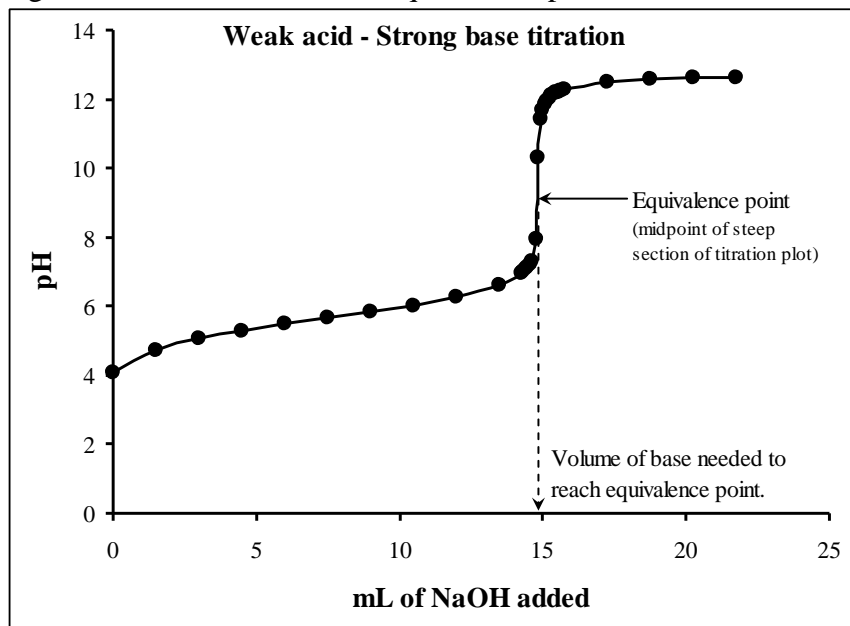
$$\begin{aligned} \text{pH} &= \text{p}K_a + \text{Log} ([\text{base}]/[\text{acid}]) = 3.85 + \text{Log}(.05/.20) \\ &= 3.85 + (-0.602) = 3.25 \end{aligned}$$

Titration Curves

Titration is the technique used to accurately measure the characteristics of an acid. Typically, the acid is dissolved in a solution and then a buret with a strong base is placed over the beaker containing the acidic solution. The pH of the solution is monitored as the strong base is added to the solution. The plot of solution pH (y-axis) as a function of the volume of base added (x-axis) as shown in Figure 1 below.

From this curve, the equivalence point can be determined and the stoichiometry of the reaction calculated. The equivalence point is the point at which equimolar amounts of acid and base have reacted, and is indicated by a sharp change in pH and an almost vertical rise in the titration curve. Figure 1 shows a graphical method for locating the equivalence point on a titration curve. This figure indicates that the equivalence point for the titration of a strong base with a weak acid occurs at pH 8.3.

Figure 1. Identification of the equivalence point of titration

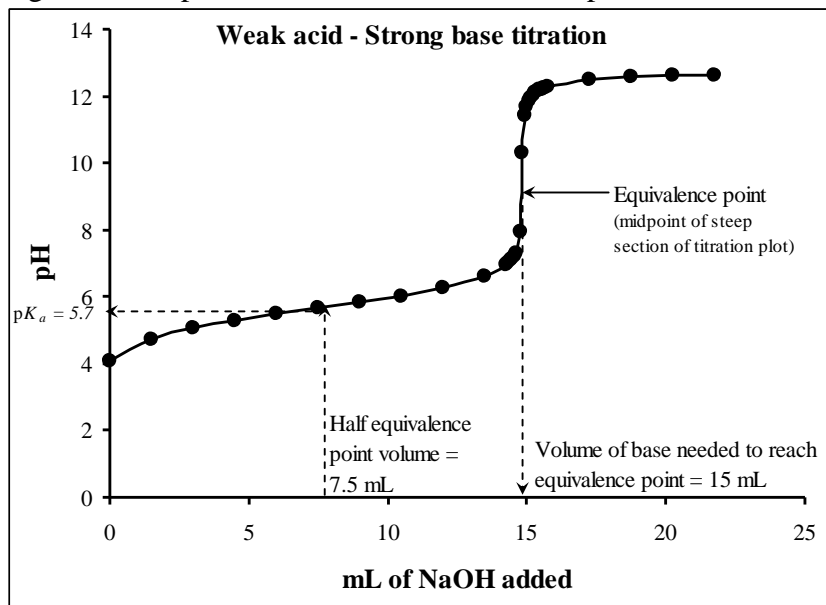


Determining the pK_a of a weak acid

If a weak acid is titrated with a base, there will be a point in the titration at which the number of moles of base added is half the number of moles of acid initially present. This is the point at which 50% of the acid has been titrated to produce A^- and 50% remains as HA. At this point $[A^-] = [HA]$ and the ratio $[A^-]/[HA] = 1$. From the Henderson-Hasselbalch equation, the log of 1 = 0 and $pH = pK_a$. The acid dissociation constant can then be determined from the relationship, $pK_a = -\log K_a$.

Figure 2 shows a graphical method for determining the pK_a from a titration curve of a strong base and a weak acid.

Figure 2. Graphical method to determine the pK_a of a weak acid



From the titration curve, the point denoted as half the equivalence point, where $[HA] = [A^-]$, has a $pH = 5.7$, and the ionization constant is calculated as:

$$pH = pK_a = 5.7$$

$$pK_a = -\log K_a = 5.7$$

$$K_a = 2.0 \times 10^{-6}$$

Determining the Molar Mass of an Unknown Salt

The titration method can also be used in order to determine the molar mass of an unknown salt. A salt is composed of a positively charged cation and a negatively charged anion. For example, NaF is composed of Na^+ and F^- . Anions are simply deprotonated acids and they can accept H^+ to again become acids. $F^- + H^+ \rightarrow HF$

With the exception of the conjugate anions of strong acids (NO_3^- , Cl^- , Br^- , I^- , ClO_3^- , ClO_4^- and HSO_4^-), the anions of acids are weak bases. Therefore, you can titrate the weak anionic base with a strong acid and plot a titration curve of pH versus volume of acid added. The resulting equivalence point is the point at which equal moles of acid and base have been added together, thus the moles of acid will equal the moles of the anion.

With the moles of anion calculated, you then divide the mass of the unknown sample by the moles of unknown that have been titrated and it will give you an estimate of the molar mass of the unknown substance. NOTE: this is the complete molar mass of unknown substance including the cation and any hydration complexes.

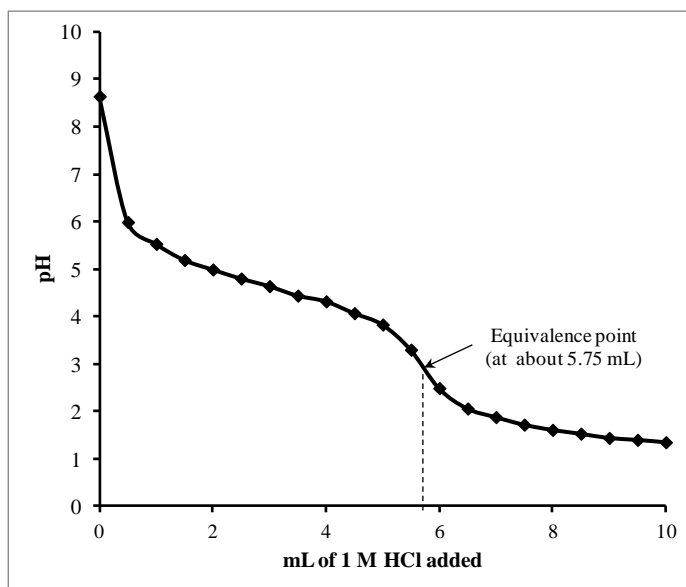
For example:

An aqueous solution of an unknown salt that was prepared by adding 1.02 g of unknown to 100 mL DI water. The unknown salt solution is then titrated with 1.0M HCl. The volume of HCl added at the titration equivalence point was determined to be 5.75 mL. Calculate the molar mass of the unknown salt. Assume the salt cation:anion ratio is 1:1.

1) Moles HCl at equivalence point = $(1.0\text{M}) \times (0.00575\text{ L}) = 0.00575\text{ moles} = \text{moles anion solution}$

2) Molar mass (g/mol) = $1.02\text{ g} / 0.00575\text{ mol} = \underline{\underline{177.4\text{ g/mol}}}$

Figure 3. Graphical method to determine the equivalence point of titration and the molar mass of an unknown salt



In this experiment you will be creating titration curves using Excel. For Part A you will consider three types of reactions: (1) strong acid - strong base titrations, (2) weak acid - strong base titrations, and (3) polyprotic acid - strong base titrations. In Part B of the lab you will use the titration method to determine the molar mass of an unknown salt.

Materials

- 50ml burette (2)
- Stir bar
- waste beaker
- 60 mL of 1.0 M sodium hydroxide
- 100 mL of 0.1 M glacial acetic acid
- 15 mL 1.0 M hydrochloric acid
- 250 mL beaker
- pH meter
- Burette clamp stand
- 100 mL of 0.1 M hydrochloric acid
- 100 mL of 0.066 M phosphoric acid
- Unknown salt

The information of the materials above are used in the excel calculations.

- Online computer simulation link:

http://introchem.chem.okstate.edu/DCICLA/acid_base.html

- Excel file “Calculate pH for Titration of Acetic acid vs. NaOH”
- Excel file “Calculate pH of H₃PO₄ from mL of NaOH added”
- Excel file “Calculate pH of Unknown Salt #1 from mL of HCl added”
- Excel file “Calculate pH of Unknown Salt #2 from mL of HCl added”
- Excel file “Calculate pH of Unknown Salt #3 from mL of HCl added”

Procedure - Part A

Strong Acid – Strong Base Titration

0. To get start, click or copy the URL into a web browser to open the online computer simulator, which needs adobe flash player unblocked.

http://introchem.chem.okstate.edu/DCICLA/acid_base.html

You will see the simulator as in the picture below:

The screenshot shows a web browser window with the URL http://introchem.chem.okstate.edu/DCICLA/acid_base.html. The simulator interface is titled "Determination of the Molarity of an Acid or Base Solution" and features several interactive elements:

- 1. Select Type of Reaction:** Radio buttons for "Strong Acid vs. Strong Base" and "Weak Acid vs. Strong Base".
- 2. Fill the Burette with:** Radio buttons for "Acid" and "Base", and a "Total Volume of" input field in ml.
- 3. Select the Acid and Base:** A vertical box containing this text.
- 4. Select the Indicator:** Radio buttons for "Methyl Orange" and "Phenolphthalein".
- 5. Push Slider Up to Add a Volume of:** A slider control with an input field in ml.
- 6. After Titration, Calculate and Enter Molarity of:** An input field in M and a red "OK" button.
- Molarity of Volume of:** Input fields for M and ml.
- Dropwise:** A red button with a drop icon.
- Reset:** A red button in the bottom left corner.

The central part of the simulator shows a burette with a scale from 0 to 50 ml, a titration flask containing a solution, and a stir bar.

1. In “**1. Select Type of Reaction**”, click on “Strong Acid vs. Strong Base”
2. In “**2. Fill the Burette with**”, click on “Base”
3. In “**3. Select the Acid and Base**”, click on “HCl” for acid, “KOH” for base.
On a scratch paper, record the volume and molarity of the acid shown near the bottom of the screen and to the left of the Erlenmeyer flask.
4. In “**4. Select the Indicator**”, click on “Phenolphthalein”
5. If the liquid in the burette is not at the 50 mL mark, the “Concordant Values” button will shown to the left of the Erlenmeyer flask, and “Click on “Concordant Values” button to re-fill the liquid. If no “Concordant Values” button shown yet, then go to next step.
6. The “**Slider**” above the “**Dropwise**” button can be used to do a quick titration to find the approximate equivalent volume of the base needed. To do that, simply drag the slider upward and release it to see the color change of the solution in the Erlenmeyer flask.
To do an accurate titration, click on “**Concordant Values**” button to the left of the Erlenmeyer flask to re-fill the liquid in the burette. DO NOT click on the reset button. The reset button will reset everything. For an accurate titration, when the added solution is near the equivalent point:
 - a. Add the base dropwise and pay close attention to the color change of the liquid mixture in the Erlenmeyer flask. It will change from clear to pink.
 - b. After the color change of the liquid in the Erlenmeyer flask, record the volume of the base used. It is the number in the box to the left of the burette. The number of mL to the right of the burette is the volume added with the “Slider”. It may not be the actual volume used.
7. Write the balanced chemical reaction equation between the chosen acid and base on a scratch paper. .
8. Use the volume and molarity of acid from step-3 and the volume of the base used in step-6b, and the coefficients ratio between the acid and the base from the balanced equation in step-7, to calculate the molarity of the base.
9. Enter the molarity of the base into the box underneath “**6. After Titration, Calculate and Enter Molarity of Base**”. Click on “OK”, you should see the confirmation “**Correct**” underneath the “OK” button. If the answer is “**Wrong**”, check your calculation or redo the titration. Make sure you use the correct coefficient ratio from the balanced equation in calculating the molarity of the base. Because of some problems in the computer simulator, if you cannot get the “Correct” answer as you expected, close the browser, re-do the titration.
- 10. Take a screen shut of the titration and included the picture from the screen shut in your lab report.**
11. Click on the “Graph” button, which is to the right of the Erlenmeyer flask. You should see a graph of pH vs. “Volume added (ml)”. The vertical axis of the graph does not shown clearly. It is the pH values.
- 12. Take a screen shut of the graph and included the picture from the screen shut in your lab report.**
13. Click on the “Return” button underneath the graph to return to the simulator for more experiments.
14. Click on the “Reset” button at the left-lower corner of the simulator.

2. For the titration of CH₃COOH acid with NaOH, answer the following question:

Plot a titration curve of pH vs. mL NaOH added using Excel and attach it to your lab report.

pH at equivalence point: _____

mL base to reach equivalence point _____

mL base to reach half equivalence point _____

pH at half the equivalence point: _____

Acid dissociation constant $K_a =$ _____
(show work for full credit)

_____ of 4.5 pts

Procedure - Part A (continued)

Polyprotic Acid – Strong Base Titration

1. Use the provided excel file – “Calculate pH of H₃PO₄ from mL of NaOH added” to find the pH and fill in the data Table below.

Enter the “mL of NaOH added” in the table below into the excel file to find the pH

DATA - PART A

Polyprotic Acid – Strong Base Titration 1 M NaOH and 0.066 M H ₃ PO ₄			
mL NaOH added	pH	mL NaOH added	pH
0		11	
1		12	
2		13	
3		14	
4		15	
5		16	
6		17	
7		18	
8		19	
9		20	
10			

2. For the titration of H_3PO_4 acid with NaOH , answer the following question:

Plot a titration curve of pH vs. mL NaOH added using Excel and attach it to your lab report. Be sure to label graph and both of the axes.

pH at 1st equivalence point: _____

pH at 2nd equivalence point: _____

Write the three acid dissociation reactions for this polyprotic acid in H_2O :

-
-
-

_____ of 4.5 pts

Procedure - Part B

Part B - Unknown Salt – Strong Acid titration

1. Decide one unknown salt from among known salt #1, salt #2, salt #3
2. If you chose unknown salt # 1, then use the provided excel file – “Calculate pH of Unknown Salt #1 from mL of HCl added” to find the pH and fill in the data Table below.

If you chose unknown salt # 2, then use the provided excel file – “Calculate pH of Unknown Salt #2 from mL of HCl added” to find the pH and fill in the data Table below.

If you chose unknown salt # 3, then use the provided excel file – “Calculate pH of Unknown Salt #3 from mL of HCl added” to find the pH and fill in the data Table below.

One student do only one unknown salt.

Once you open the excel file, enter mass of the unknown salt in the appropriate cell in the excel file.

- Unknown #1 is approximately 1.0 g
- Unknown #2 is approximately 0.5 g
- Unknown #3 is approximately 0.8 g

Use the mL of HCl added shown in the table below to find the pH in the excel file.

DATA - PART B

UNKNOWN SALT #			
MASS UNKNOWN SALT			
Volume 1M HCl (mL)	pH	Volume 1M HCl (mL)	pH
0.0		5.5	
0.5		6.0	
1.0		6.5	
1.5		7.0	
2.0		7.5	
2.5		8.0	
3.0		8.5	
3.5		9.0	
4.0		9.5	
4.5		10.0	
5.0			

3. Use the data from the table above, plot a titration curve of pH vs. mL HCl added using Excel and **attach it to your lab report.** Be sure to label graph and both of the axes.
4. Answer the following question:

pH at equivalence point: _____

Volume HCl added at equivalence point: _____

Moles HCl = Moles salt: _____
(Show calculation)

Molar Mass of Unknown Salt: _____
(Show calculation)

_____ of 3.5 pts

Graphing Titration Curves in Excel

1. Enter data into an Excel spreadsheet.
2. Select chart wizard
3. Select XY scatter plot – **with the data connection lines**
4. Select data (X axis - Volume acid or base added) (Y axis – pH)
5. Title the graph and label axes.
6. Adjust the axis scales and add minor & major gridlines to accurately determine the equivalence point.
7. Print the graph and staple it to your report.

Post Lab Questions

1. How much (mL) of a 2.0 M sodium hydroxide solution would it take to neutralize 50 mL of a 6.0 M solution of hydrochloric acid? (Show work for full credit)
2. How much of a 2.0 M sodium hydroxide solution would it take to neutralize 500 mL of a 0.1 M acetic acid solution? (Show work for full credit)
3. Equivalence points occur during an acid-base titration when equal amounts of an acid and a base have reacted together. A graph of pH vs. volume of base added makes the equivalent point occur in the middle of the near-vertical section of the graph. The equivalent point of a titration is not necessarily reached at pH 7. Looking at your titration curve graphs, what is the difference between the equivalence point of the strong acid- strong base titration and the weak acid- strong base titration? Explain this difference
4. You are a scientist at a reputable lab researching how different polyprotic acids affect the pH of a solution. How many equivalence points would be visible on the titration curve if you fully titrated a given a solution of 1.0 M sulfurous acid (H_2SO_3)?
5. A buffer is made by adding 0.600 mol $\text{HC}_2\text{H}_3\text{O}_2$ and 0.600 mol $\text{NaC}_2\text{H}_3\text{O}_2$ to enough water to make 4L of solution. The $\text{p}K_a$ of the buffer is 4.74. Calculate the pH of solution after 0.035 mol of NaOH is added. (assume the volume doesn't change)

_____ of 5 pts

Total _____ of 25 pts