

ACID-BASE TITRATIONS

In this exercise you will use Excel to construct titration curves for a titration between a strong acid and strong base and between a weak acid and strong base. To set up a spreadsheet for the titration between a strong acid and strong base is quite straightforward, and you will use this as a way of getting practice for setting up the spreadsheet for the weak acid – strong base titration. At the end of the exercise you should hand in print outs of the plots you created and answers to the questions in each section.

A titration curve is a plot of solution pH in a flask vs. volume of titrant (solution in the buret). Figure 1 shows a titration curve for a strong acid – strong base, where the acid is in the flask and the base in the buret. As base is added to the acid solution, the pH of the solution in the flask increases – slowly at first, then very sharply and then again slowly. The point at which the pH changes dramatically for a very small addition of base is called the end point.

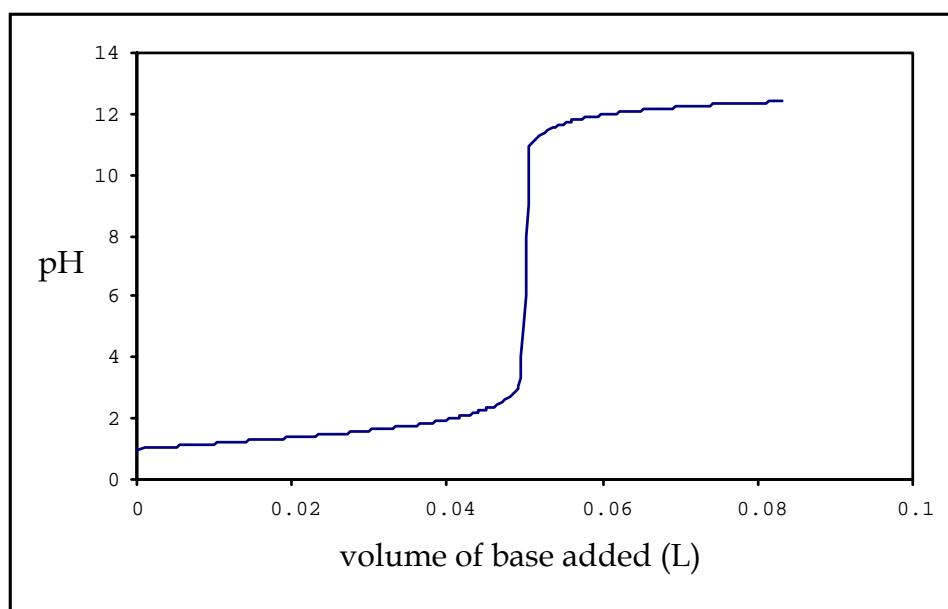


Figure 1

Titration of A Strong Acid with a Strong Base

Here you will create a spreadsheet which will simulate the titration of 0.050 L of 0.10 M HCl (in flask) vs. 0.10 M NaOH (in buret). The objective of this exercise is to plot a

titration curve (pH of solution in flask vs. volume of NaOH added to flask) similar to the one shown in figure 1. Looking at the titration curve in figure 1, you can see that before any NaOH is added the solution is highly acidic (since HCl is a strong acid). As NaOH is added, the acidity of the solution decreases (pH increases). At the end point the pH changes dramatically with very small changes in the volume of NaOH added. Beyond the end point the pH changes slowly with addition of NaOH.

Creating the spreadsheet for the titration curve

Equations: To calculate the pH of the solution in the flask as the base is added you have to look at what reaction occurs in each region of the titration curve. The titration curve is defined by four regions - (i) before any base is added to the acid solution in the flask, (ii) before the end point (once base is added to the solution in the flask), (iii) at the end point (iv) beyond the end point. Let's take each region separately.

i) Initial conditions (before base is added to the acid solution).

The flask contains 0.050 L of 0.10 M HCl. Since HCl is a strong acid it completely dissociates in solution:



And so the pH of the solution is determined by the concentration of the H^+ ions in solution.

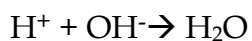
$$\text{pH} = -\log [\text{H}^+]$$

Since the concentration of the acid is 0.10 M the concentration of the H^+ ions in solution is also 0.10 M and so the pH of the solution is 1.0.

ii) Before the end point

Let's start the titration by adding 0.001 L of base to the acid solution in the flask.

The acid in the flask now reacts with the base added. The net ionic equation is:



Before any base has been added, the number of moles of acid in the flask is

$$0.1\text{M} \times 0.050 \text{ L} = 0.0050 \text{ moles}$$

Adding 0.0010 L of a 0.10 M solution of base corresponds to adding 0.00010 moles of base. Since the acid completely neutralizes the base this means that the 0.00010 moles of base reacts with 0.00010 moles of acid. Upon adding 0.001 L of the 0.10 M base to the acid, the number of moles of acid remaining in the flask is, thus, $0.0050 - 0.00010 = 0.0049$ moles. The pH of the solution is determined by the concentration of the unreacted H^+ ions.

However, to calculate the concentration of the unreacted H^+ , you not only need to know the moles of the unreacted H^+ ions but also the volume of the solution in the flask. This volume is now $0.050 \text{ L} + 0.001 \text{ L} = 0.051 \text{ L}$

So the concentration of the unreacted H^+ ions is

$$[\text{H}^+] = \frac{0.0049}{0.051} = 0.096 \text{ M}$$

$$\text{pH} = 1.02$$

For each increment of base, the pH of the solution can be calculated in a similar way.

iii) At the end point

The end point is reached when enough base has been added so that all the acid in the flask has been neutralized. This is when the number of moles of base added equals the number of moles of acid initially present. The number of moles of acid initially present is 0.0050 moles, and so, when 0.0050 moles of base have been added, the end point is reached. With 0.10 M base, 0.0050 moles of base will be added when the volume of the base added to the flask is 0.050 L. At this point, there is no unreacted acid or base in solution and hence the pH of the solution in the flask at the end point is the pH of neutral water i.e 7.00.

iv) Beyond the end point

If more base is added beyond the end point, since all the acid in the flask is reacted, the unreacted base determines the pH of the solution in the flask.



The end point is reached when 0.050 L of base is added. If another 0.0010 L (i.e. a total of 0.051 L of base) is added to the flask then it is the moles of base in this 0.0010 L that

determines the pH of the solution i.e. 0.00010 moles of base. The total volume of solution in the flask is 0.050 L of acid + 0.051 L of base = 0.101 L of solution. The concentration of the unreacted OH⁻ is

$$[\text{OH}^-] = \frac{0.00010}{0.101} = 0.00099 \text{ M}$$

$$\begin{aligned} \text{Hence the pH} &= \text{pK}_w + \log[\text{OH}^-] \\ &= 14 + \log[0.00099] = 10.9 \end{aligned}$$

Now with this information you can create a spreadsheet for the strong acid – strong base titration curve. However, you have to be careful to use the right equations to calculate the pH depending on which of the above four regions you are in, which in turn depends on how much base has been added to the acid solution. Below are the four equations you will use to create this spreadsheet. Given the information above, you will have to determine which equation should be used in creating the spreadsheet. Remember deciding which equation to use depends on the amount of base that has been added to the solution in the flask.

General equations

Define:

C_a - concentration of acid

C_b - concentration of base

V_a - initial volume of acid

V_i - total volume of base added at a given point along the titration

$V_a + V_i$ - Total volume at any point along the titration

1) Initial conditions - before any base added

$$\text{pH} = -\log [C_a]$$

2) Before equivalence

$$\text{pH} = -\log\left(\frac{C_a V_a - C_b V_i}{V_a + V_i}\right)$$

3) At the end point

$$\text{pH} = 7.00$$

4) Beyond the end point

$$\text{pH} = 14 + \log\left(\frac{C_b V_i - C_a V_a}{V_a + V_i}\right)$$

Open the Excel spreadsheet titled "stracid_strbase". You will find some entries made in this spreadsheet.

First note the concentrations of the acid, base and volume of acid have been entered. These values have been defined as constants in the spreadsheet.

Ca - concentration of acid (M)

Va - volume of acid (L)

Cb - concentration of base (M)

- (i) The concentration of the acid is 0.10 M and that of base is 0.10 M. The volume of acid in the flask (V_a) = 0.050 L.
- (ii) Column A - In this column you will enter the volume of base added for each step of the titration. This is denoted as V_i in the equations. In filling this column remember that away from the end point the volume increment of the base added can be large (say 0.001 L), but close to the end point (within 0.0010 L on either side of the end point) smaller increments of the base should be added (0.0005 L). Beyond the end point the volume increments of the base can be increased (0.001 L). Fill this column till the maximum volume of the base added is around 0.085 L.

3) Column B - In this column calculate the pH of the solution in the flask for each point.

The equation you will use to calculate the pH depends in which region of the titration curve the point lies. (See page 4)

- (i) Before any base is added - the pH is determined by the acid in solution
Enter an appropriate equation in cell B12
- (ii) Before the end point
Enter an appropriate equation in cell B13

Copy cell B13 and paste into cells B14 down to the cell before the end point

(iii) At the end point

In column B enter the appropriate pH into the cell for the end point

(iv) Beyond the end point

In the cell after the end point enter an appropriate equation

Copy this cell and paste into cells below.

Plot the titration curve

You should now have a completed spreadsheet for plotting the titration curve. Select all cells for which there are entries in columns A and B. From the menu select Insert->Chart. Choose an XY scatter plot using the sub-option in the middle left (scatter with data points connected by smooth lines). Finish the plot on the same sheet. You should see a titration curve as shown in figure 1. Look at the data points. Notice that close to the end point, points along the y axis (pH) are spaced far apart, even though they are closely spaced in x (volume of base added). This shows that near the end point the pH changes very dramatically with very small increments of added base. The end point can be very easily determined from the graph.

QUESTIONS

1) Let's say you were to repeat the above titration, but with the acid in the buret and the base in the flask. Describe how the pH of the solution in the flask would vary as more acid is added (i.e. describe the shape of the titration curve). What would be the pH of the solution at the end point?

Titration of a weak acid - strong base.

For the next exercise you will create a spreadsheet for a titration between a weak acid and a strong base and plot the titration curve. The steps to do this are essentially the same as that for the strong acid - strong base case but the equations for calculating the pH for the different regions of the titration curve are different. Let's first look at these equations and then go through the steps for creating the spreadsheet.

A titration curve for a weak acid – strong base has similar features to that for a strong acid – strong base titration, namely (i) a region in which the pH slowly increases with addition of base, (ii) a region where the pH dramatically increase with small changes in pH and (iii) beyond this a region where the pH slowly increases with addition of the base.

Figure 2 shows a titration curve of a weak acid versus a strong base.

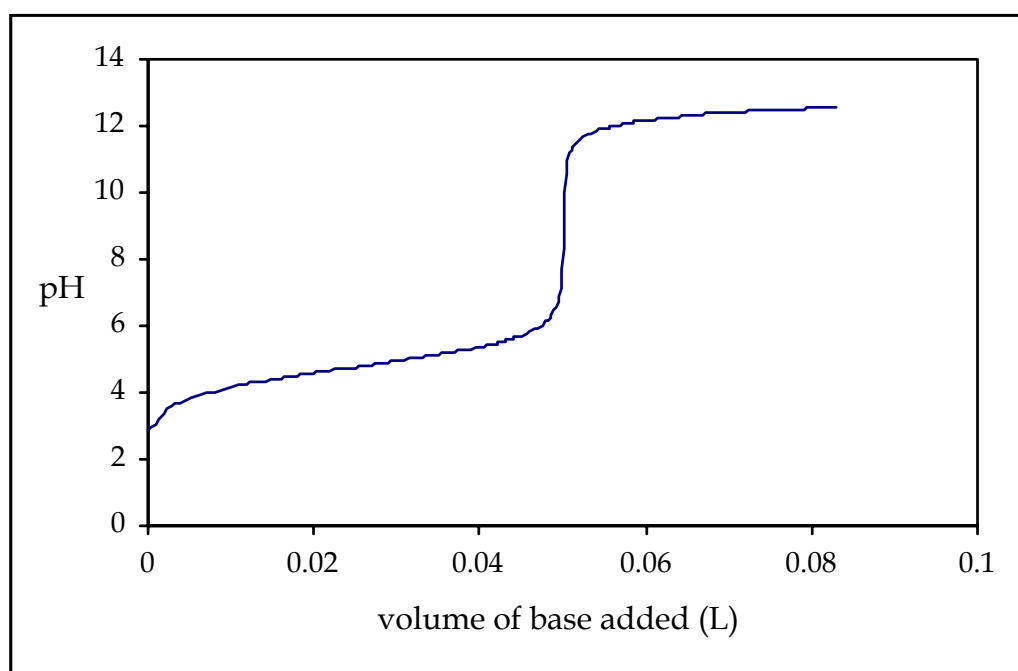
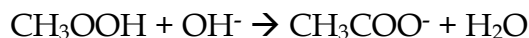


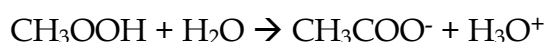
Figure 2

In this exercise you will titrate 0.050 L of 0.10 M CH₃COOH (in flask) versus 0.10 M NaOH (in buret). The net ionic equation for this reaction is :



Let's look at the equations for calculating the pH of the different regions of the titration curve.

i) Before any base is added – The pH is determined by the dissociation of the weak acid.



To calculate the pH for the solution of weak acid you have to account for the amount of CH₃COOH that dissociates. Unlike a strong acid, CH₃COOH does not dissociate completely in solution. The extent to which CH₃COOH has dissociated is characterized by its acid dissociation constant K_a.

The concentration of CH₃COOH in the flask is 0.10 M. Let x be the concentration of the H₃O⁺ and CH₃COO⁻ formed at equilibrium. Hence, at equilibrium the concentration of the undissociated CH₃COOH is (0.1 - x) in molar units.

The acid dissociation constant is defined as:

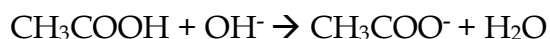
$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{0.1 - x}$$

Usually it is safe to assume that $x \ll 0.10$, so since $\text{pH} = -\log[\text{H}_3\text{O}^+]$, the pH of the solution, before any base has been added, is

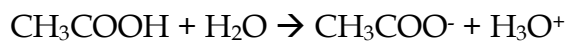
$$\text{pH} = -\log \sqrt{K_a C_a}$$

where C_a is the initial concentration of the acid (here 0.10 M).

ii) Before the end point – As base is added to the solution in the flask, the acid reacts with the base:



This creates a buffer solution where the pH of the solution can be determined by the dissociation of the unreacted acid:



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

Hence,

$$\text{pH} = -\log\left(\frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}\right)$$

So as OH^- is added, we need to calculate the concentration of the unreacted CH_3COOH and the concentration of CH_3COO^- formed.

The moles of CH_3COO^- formed = moles of OH^- added = $C_b V_i$

where C_b is the concentration of the base, V_i the volume of base added.

$$\text{So the concentration of } \text{CH}_3\text{COO}^- \text{ formed} = \frac{C_b V_i}{V_a + V_i}$$

where V_a is volume of acid in the flask.

$$\text{The concentration of } \text{CH}_3\text{COOH} \text{ unreacted} = \frac{C_a V_a - C_b V_i}{V_a + V_i}$$

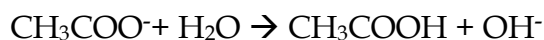
We can now calculate the solution pH at any point before the end point

$$\text{pH} = -\log\left(\frac{K_a (C_a V_a - C_b V_i)}{C_b V_i}\right)$$

$$\text{pH} = \text{p}K_a - \log\left(\frac{C_a V_a - C_b V_i}{C_b V_i}\right)$$

$$\text{pH} = \text{p}K_a + \log\left(\frac{C_b V_i}{C_a V_a - C_b V_i}\right)$$

iii) At the end point - when enough base has been added to react with all the acid. In this example, where a 0.050 L of a 0.10 M solution of acid is being titrated against a 0.10 M solution of base, the end point is reached when 0.050 L of base has been added. The pH at the end point is determined by the reaction :



Note that CH_3COO^- is the conjugate base of CH_3COOH . The concentration of the OH^- ions formed in the above reaction determines the pH. As you will see when you construct the spreadsheet, the pH of the solution at the end point will be greater than 7, i.e. basic. In fact, the weaker the acid (the smaller the value of K_a), the more basic the solution at the end point (since the weaker the acid, the stronger is its conjugate base, and the above reaction goes further to the right).

From the reaction of the conjugate base:

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

where K_b is the dissociation constant of the base, in this case the conjugate base CH_3COO^- .

Hence:

$$[\text{OH}^-] = \frac{K_b[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

We need to calculate the concentration of CH_3COOH and CH_3COO^- at the end point.

The number of moles of CH_3COO^- initially formed, before it reacts with H_2O to form CH_3COOH and OH^- , is equal to the number of moles of the base added up to the end point.

Since the volume of the solution in the flask = $V_a + V_i$ the initial concentration of CH_3COO^- formed at the end point is

$$[\text{CH}_3\text{COO}^-] = C_b \frac{V_i}{V_a + V_i}$$

Since the CH_3COO^- further reacts with water to form CH_3COOH and OH^- , the final concentration of CH_3COO^- is

$$[\text{CH}_3\text{COO}^-] = C_b \frac{V_i}{V_a + V_i} - [\text{CH}_3\text{COOH}]$$

However, since $[\text{CH}_3\text{COOH}] \ll [\text{CH}_3\text{COO}^-]$, we can approximately express the concentration of CH_3COO^- as

$$[\text{CH}_3\text{COO}^-] \approx C_b \frac{V_i}{V_a + V_i}$$

Also since, $[\text{CH}_3\text{COOH}] = [\text{OH}^-]$, the equation

$$[\text{OH}^-] = \frac{K_b[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

can be re-written as

$$[\text{OH}^-] = \sqrt{K_b[\text{CH}_3\text{COO}^-]} = \sqrt{K_b \frac{C_b V_i}{V_a + V_i}}$$

Since

$$K_w = [\text{H}^+][\text{OH}^-]$$

where K_w is the ion product of water ($= 1 \times 10^{-14}$ at 25°C)

Therefore,

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]}$$

$$-\log[\text{H}^+] = -\log\left(\frac{K_w}{[\text{OH}^-]}\right)$$

$$-\log[\text{H}^+] = -\log K_w - (-\log[\text{OH}^-]) = -\log K_w + \log[\text{OH}^-]$$

$$\text{pH} = \text{p}K_w + \log[\text{OH}^-]$$

Hence,

$$\text{pH} = 14 + \log \sqrt{K_b \frac{C_b V_i}{V_a + V_i}}$$

iv) Beyond the end point - the pH is determined by the excess OH^- added. The pH can be calculated using the equation:

$$\text{pH} = 14 + \log\left(\frac{C_b V_i - C_a V_a}{V_a + V_i}\right)$$

General equations

i) Before base added

$$\text{pH} = -\log\sqrt{K_a C_a}$$

ii) Before the end point

$$\text{pH} = \text{p}K_a + \log\left(\frac{C_b V_i}{C_a V_a - C_b V_i}\right)$$

iii) At the end point

$$\text{pH} = 14 + \log\sqrt{K_b \frac{C_b V_i}{V_a + V_i}}$$

iv) Beyond the end point

$$\text{pH} = 14 + \log\left(\frac{C_b V_i - C_a V_a}{V_a + V_i}\right)$$

Open the Excel spreadsheet titled “wkacid_strbase” and note the entries made in the spreadsheet.

Ca - concentration of acid (M)

Va - volume of acid in flask (L)

Vb - concentration of base (M)

Ka - dissociation constant of the acid

pKa - $-\log(K_a)$

Kb - dissociation constant of the base

Kw - ion product of water

1) Column A - enter the volume increments for the base in L. Start in cell A12 and fill down till you are past the end point. Fill this column till the maximum volume of the base added is around 0.085 L. Note that within 0.001 L on either side of the end point, the volume

should change by 0.0005 L. So first determine the amount of base that must be added to reach the end point (remember the strong acid- strong base titration) before entering the volume increments.

2) Column B - calculate the pH for each point along the curve (See page 11):

- (i) Before base is added - the pH is determined by the dissociation of the acid
In cell B12 enter an appropriate equation
- (ii) Before the end point - the pH is determined in this buffer region by the dissociation of the unreacted acid and the amount of conjugate base formed.
In cell B13 enter an appropriate equation
Copy cell B13 and paste into cells B14 to the cell before the end point
- (iii) At the end point
In the cell corresponding to the end point ,enter an appropriate equation
- (iv) Beyond the end point
In the cell after the end point enter an appropriate equation
Copy this cell and paste into cells below.

Plot the titration curve

You should now have a completed spreadsheet for plotting the titration curve. Select all cells for which there are entries in columns A and B. From the menu select Insert->Chart. Create a scatter plot showing the data points and a line joining the points (similar to the plot you created for the strong acid - strong base titration). Finish the plot on the same sheet. You should see a titration curve similar to the one shown in figure 2. Once again note that near the end point a very small change in the volume of base added affects the pH dramatically. So once again the end point is very well defined on the graph.

Affect of the dissociation constant of the acid (K_a) on the shape of the titration curve.

The value of K_a affects the shape of the titration curve for a weak acid - strong base titration. Increase and decrease the value of K_a and see how the shape changes. For example, change the value of K_a from 1.75×10^{-5} to 1.75×10^{-7} and then to 1.75×10^{-4} . Notice

that the height of the curve changes as K_a changes. Also note how the pH of the solution at the end point changes as K_a changes.

QUESTIONS

- 1) How does the pH of the solution at the end point vary with K_a and why does it vary with K_a ?
- 2) By varying the value of K_a you can see how the shape of the titration curve is affected by K_a . Explain what the problem might be in isolating the end point if K_a were very small (e.g. if $K_a = 1.75 \times 10^{-9}$).
- 3) If you were to carry out a titration with weak base in the flask and a strong acid in the buret, how would the pH of the solution in the flask vary as acid is added to the solution? Would the pH of the solution at the end point be acidic or basic?