

## Chem 116 POGIL Worksheet - Week 11

### Titration

#### Why?

Titration is the addition of a standard solution of precisely known concentration (the *titrant*) to a precisely measured volume of a solution with unknown concentration (the *analyte*) to react according to a known stoichiometry. It is an important technique in analytical chemistry. In an acid-base titration, the reaction is neutralization, and the acid or base can be either the titrant or the analyte. For example, if we are trying to determine the concentration of some acid (the analyte), we would carefully measure a sample volume of the acid with a pipet and then carefully add a solution of a strong base (e.g., NaOH) of precisely known concentration (the titrant) from a buret until all of the acid in the sample is neutralized. The volume of titrant (here, NaOH(aq) solution) needed to achieve complete neutralization is the *equivalence point*. By knowing the volume to reach the equivalence point and the concentration of the titrant, we can calculate the number of millimoles of titrant that was added ( $V_{\text{mL}} \times M = \text{millimoles}$ ) to achieve complete neutralization. Then, using the stoichiometry of the neutralization reaction, we can calculate the number of millimoles of analyte in the sample and with its known original sample volume we can calculate the original concentration of the sample solution. The equivalence point might be detected experimentally with an indicator that has a pronounced color change near the pH at the point of exact neutralization. The volume at which this color change occurs is called the *end point*. Ideally, if the indicator has been correctly chosen, the end point and the equivalence point are nearly the same, but in all real cases there is some difference that introduces a certain amount of experimental error.

From the standpoint of learning acid-base chemistry, titrations offer an opportunity to review all the kinds of calculations we have seen. Therefore, learning how to calculate the pH throughout the course of a titration is a useful way of bringing all of the material we have studied together in a meaningful way.

#### Learning Objectives

- Understand the principles of strong acid - strong base titration
- Understand the principles of weak acid - strong base and weak base-strong acid titrations

#### Success Criteria

- Be able to predict the equivalence point for a titration
- Know that  $\text{pH} = 7$  at the equivalence point *only* in a strong acid - strong base titration
- Know that  $\text{pH} > 7$  at the equivalence point in a weak acid - strong base titration
- Know that  $\text{pH} < 7$  at the equivalence point in a weak base - strong acid titration
- Be able to calculate the pH through the course of a strong acid - strong base titration
- Be able to calculate the pH through the course of a weak acid - strong base titration

#### Prerequisite

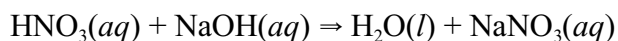
Have read Section 17.3

## Information (Stoichiometry of Acid-Base Titrations)

Titration are usually carried out in milliliter volume quantities, so it is most convenient to think of the amounts of analyte and titrant in terms of millimoles, rather than moles, where

$$V_{\text{mL}} \times M = \text{millimoles}$$

When considering a titration calculation, the first thing to know is the volume of titrant that is needed to reach the equivalence point. This calculation requires an understanding of the stoichiometric relationship between the analyte and titrant, the two reactants in the neutralization. If the stoichiometry between the two is 1:1, then it will take as many millimoles of titrant as there were millimoles of analyte in the sample to achieve neutralization. For example, consider the titration of a 25.0-mL sample of 0.100 M  $\text{HNO}_3(aq)$  (the analyte) with 0.0500 M  $\text{NaOH}(aq)$  (the titrant). The reaction equation has 1:1 stoichiometry:



Therefore, we can see that at the equivalence point

$$\text{millimol NaOH added} = \text{millimol HNO}_3 \text{ initially present}$$

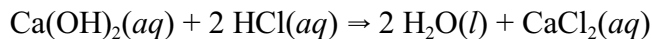
and

$$M_t V_t = M_a V_a$$

The volume of titrant needed to reach the equivalence point is

$$V_t = \frac{M_a V_a}{M_t} = \frac{(0.100\text{M})(25.0\text{mL})}{0.0500\text{M}} = 50.0\text{mL}$$

But suppose we are titrating a 15.0-mL sample of  $1.00 \times 10^{-3}$  M  $\text{Ca}(\text{OH})_2(aq)$  (the analyte) with  $1.00 \times 10^{-3}$  M  $\text{HCl}(aq)$  (the titrant). Now the stoichiometry between analyte and titrant is 1:2:



In this case at the equivalence point we have

$$\text{millimol HCl added} = 2 \times \text{millimol Ca}(\text{OH})_2 \text{ initially present}$$

and

$$M_t V_t = 2M_a V_a$$

The volume needed to reach the equivalence point is

$$V_t = \frac{(2)(M_a V_a)}{M_t} = \frac{(2)(1.00 \times 10^{-3} \text{ M})(15.0 \text{ mL})}{1.00 \times 10^{-3} \text{ M}} = 30.0 \text{ mL}$$

### Key Questions

1. A 25.0-mL sample of 0.100 M  $\text{HCl}(aq)$  is titrated with 0.125 M  $\text{NaOH}(aq)$ . How many milliliters of the titrant will be need to reach the equivalence point?
2. A 25.0-mL sample of 0.100 M  $\text{Ba}(\text{OH})_2(aq)$  is titrated with 0.125 M  $\text{HCl}(aq)$ . How many milliliters of the titrant will be need to reach the equivalence point?

### Information (pH at the Equivalence Point)

In a strong acid - strong base titration, neutralization produces water and an aqueous solution of a salt, whose cation and anion come from the base and acid, respectively. Neither ion is acidic or basic, so the pH at the equivalence point is that of neutral water; i.e., 7.00. But when a weak acid, HA, is titrated with a strong base, at the equivalence point all the HA has been converted to the conjugate base,  $\text{A}^-$ . This is now a solution of a pure weak base,  $\text{A}^-$ , in water, so the solution will be basic ( $\text{pH} > 7$ ). Likewise, when a weak base, B, is titrated with a strong acid, at the equivalence point all the B has been converted to the conjugate acid,  $\text{HB}^+$ . This is now a solution of a pure weak acid in water, so the solution will be acidic ( $\text{pH} < 7$ ). **In the titration of a weak acid with a strong base or a weak base with a strong acid, the pH is never 7 at the equivalence point. The pH is 7 at the equivalence point only in the case of a strong acid - strong base titration.**

### Key Questions

3. Determine if the pH at the equivalence point is 7,  $<7$ , or  $>7$  for the following titrations.
  - a.  $\text{NH}_3(aq)$  titrated with  $\text{HCl}(aq)$
  - b.  $\text{Ba}(\text{OH})_2(aq)$  titrated with  $\text{HCl}(aq)$
  - c.  $\text{HF}(aq)$  titrated with  $\text{NaOH}(aq)$

### Information (Calculating pH Through the Course of a Strong Acid - Strong Base Titration)

Calculating the pH at any point in the course of a strong acid - strong base titration is a matter of determining how many millimoles of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  are present after successive additions of titrant. Consider the titration of a certain volume of some strong acid  $\text{HA}(aq)$  of known concentration with  $\text{NaOH}(aq)$  titrant of given concentration. There are four regions to consider:

- I. Initial: Before any titrant has been added, the analytical concentration of acid,  $C_{\text{HA}}$ , is the same as the actual concentration of hydronium ion,  $[\text{H}_3\text{O}^+]$ , from which the pH can be calculated.

- II. Before the Equivalence Point: The number of millimoles of  $\text{H}_3\text{O}^+$  initially present ( $M_a V_a$ ) has been reduced by the number of millimoles of  $\text{OH}^-$  added ( $M_t V_t$ ). The concentration of  $\text{H}_3\text{O}^+$  is the number of millimoles left ( $M_a V_a - M_t V_t$ ) divided by the new volume (initial volume + volume of titrant added). Calculate pH from this concentration.
- III. At the Equivalence Point: The pH is 7.00. (Remember: This is true only for a strong acid - strong base titration!)
- IV. After the Equivalence Point: Calculate the total number of millimoles of base added ( $M_t V_t$ ) and subtract the amount consumed in neutralizing the acid (millimol excess  $\text{OH}^- = M_t V_t - M_a V_a$ ). Divide the number of millimoles of excess  $\text{OH}^-$  by the total volume of the solution (initial volume + volume of titrant added). Calculate pOH from this concentration, and get pH from  $\text{pH} = 14.000 - \text{pOH}$ .

To illustrate this general approach, consider the titration of 10.0 mL of 0.0300 M  $\text{HBr}(aq)$  (the analyte) with 0.0100 M  $\text{NaOH}(aq)$  solution (the titrant). Calculate the pH at each of the following points in the titration:

- (i) the initial point, before any titrant has been added;
- (ii) after adding 15.0 mL of 0.0100 M  $\text{NaOH}(aq)$ ;
- (iii) after adding 30.0 mL of 0.0100 M  $\text{NaOH}(aq)$ ;
- (iv) after adding 45.0 mL of 0.0100 M  $\text{NaOH}(aq)$ .

Before carrying out any other calculations, determine (a) the number of millimoles of analyte initially present, and (b) the volume of titrant that must be added to reach the equivalence point. It will be useful to keep these numbers in mind as we proceed to calculate the pH values throughout the course of the titration.

The number of millimoles of  $\text{HBr}$  initially present is  

$$\text{mmol HBr} = (0.0300 \text{ M})(10.0 \text{ mL}) = 0.300 \text{ mmol}$$

The neutralization reaction for this titration is  

$$\text{HBr}(aq) + \text{NaOH}(aq) \rightleftharpoons \text{H}_2\text{O}(l) + \text{NaBr}(aq)$$

At the equivalence point

mmol  $\text{HBr}$  initially present = mmol  $\text{NaOH}$  added

Therefore, the volume of  $\text{NaOH}(aq)$  solution needed to reach the equivalence point is

$$V_{\text{NaOH}} = \frac{M_{\text{HBr}} V_{\text{HBr}}}{M_{\text{NaOH}}} = \frac{(0.0300 \text{ M})(10.0 \text{ mL})}{0.0100 \text{ M}} = 30.0 \text{ mL}$$

Now, we are ready to carry out the calculations of the pH at the indicated points in the titration.

- (i) The initial point, before any titrant has been added

Here we simply have a solution of 0.0300 M HBr. Being a strong acid, we can assume complete dissociation and  $C_{\text{HBr}} = 0.0300 \text{ M} = [\text{H}_3\text{O}^+]$ .

$$\text{pH} = -\log(0.0300) = \mathbf{1.523}$$

(ii) After adding 15.0 mL of 0.0100 M NaOH(aq)

The number of millimoles of added NaOH is

$$\text{mmol NaOH} = (0.0100 \text{ M})(15.0 \text{ mL}) = 0.150 \text{ mmol}$$

The total volume of the solution at this point is

$$V_t = V_{\text{HBr}} + V_{\text{NaOH}} = 10.0 \text{ mL} + 15.0 \text{ mL} = 25.0 \text{ mL}$$

We can summarize the numbers of millimoles of analyte and titrant before and after the addition by the following table:

	$\text{HBr(aq)} + \text{NaOH(aq)} \rightleftharpoons \text{H}_2\text{O(l)} + \text{NaBr(aq)}$		
Initial	0.300 mmol	0.150 mmol	0
After rxn	0.150 mmol	0	0.150 mmol

Therefore,  $[\text{H}_3\text{O}^+] = C_{\text{HBr}} = 0.150 \text{ mmol}/25.0 \text{ mL} = 6.00 \times 10^{-3} \text{ M}$

$$\text{pH} = -\log(6.00 \times 10^{-3}) = \mathbf{2.222}$$

(iii) After adding 30.0 mL of 0.0100 M NaOH(aq)

The number of millimoles of added NaOH is

$$\text{mmol NaOH added} = (0.0100 \text{ M})(30.0 \text{ mL}) = 0.300 \text{ mmol}$$

This is the equivalence point (see preliminary calculation above), because we have added as many millimoles of NaOH titrant as there were millimoles of HBr analyte in the sample:

$$\text{mmol NaOH added} = 0.300 \text{ mmol} = \text{mmol HBr initially present}$$

Our table of millimols of analyte and titrant before and after the addition now has the following values:

	$\text{HBr(aq)} + \text{NaOH(aq)} \rightleftharpoons \text{H}_2\text{O(l)} + \text{NaBr(aq)}$		
Initial	0.300 mmol	0.300 mmol	0
After rxn	0	0	0.300 mmol

The only source of  $\text{H}_3\text{O}^+$  in the solution at this point is water's autoprotolysis. ( $\text{Br}^-$  from the dissociated Na Br has no acid-base character. Therefore,

$$\text{pH} = 7.000$$

(iv) After adding 45.0 mL of 0.0100 M  $\text{NaOH}(aq)$

This is 15.0 mL beyond the equivalence point. The number of millimoles of added NaOH is

$$\text{mmol NaOH added} = (0.0100 \text{ M})(45.0 \text{ mL}) = 0.450 \text{ mmol}$$

At this point our table of millimols of analyte and titrant before and after the addition now has the following values:

	$\text{HBr}(aq) + \text{NaOH}(aq) \rightleftharpoons \text{H}_2\text{O}(l) + \text{NaBr}(aq)$		
Initial	0.300 mmol	0.450 mmol	0
After rxn	0	0.150 mmol	0.450 mmol

The solution contains 0.150 mmol of NaOH beyond what was needed to neutralize the 0.300 mmol of HBr initially present. This excess  $\text{OH}^-$  ion is dissolved in the total volume of the solution at this point, which is the sum of the initial sample volume plus all the titrant volume we have added. The total volume of the solution at this point is thus

$$V_t = V_{\text{HBr}} + V_{\text{NaOH}} = 10.0 \text{ mL} + 45.0 \text{ mL} = 55.0 \text{ mL}$$

$$\text{Therefore, } [\text{OH}^-] = C_{\text{NaOH}} = 0.150 \text{ mmol}/55.0 \text{ mL} = 2.727 \times 10^{-3} \text{ M}$$

$$\text{pOH} = 2.564$$

$$\text{pH} = 11.436$$

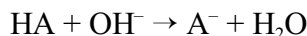
### Key Questions

4. Consider the titration of 25.0 mL of 0.100 M  $\text{HCl}(aq)$  (the analyte) with 0.0500 M  $\text{NaOH}(aq)$  (the titrant).
  - a. How many milliliters of  $\text{NaOH}(aq)$  are needed to reach the equivalence point?
  - b. How many millimoles of  $\text{H}_3\text{O}^+$  are present in the original sample?
  - c. What is the initial pH, before adding any titrant?
  - d. What is the pH after adding 25.0 mL of titrant?

- e. What is the pH after adding 50.0 mL of titrant?
- f. What is the pH after adding 75.0 mL of titrant?

### Information (Calculating the pH Through the Course of a Weak Acid - Strong Base Titration)

Now consider the titration of a weak acid, HA, with NaOH titrant. The neutralization reaction is



There are four distinct regions in the course of such a titration with four different approaches to calculating the pH in each region.

- I. Initial (no added titrant): This is just pure HA in water. Therefore, use  $K_a$  and  $C_{\text{HA}}$  to find  $[\text{H}_3\text{O}^+]$  and pH by the usual methods.
- II. Before the Equivalence Point (buffer region): Once we start adding titrant, we are creating significant amounts of  $\text{A}^-$  while still retaining significant amounts of not-yet neutralized HA. Because the solution now has significant amounts of both HA and  $\text{A}^-$ , it is a buffer solution. Recall that when we carried out calculations on buffer solutions, we only need to be concerned with the ratio between the number of millimoles of HA and the number of millimoles of  $\text{A}^-$  present in the solution, and not the actual solution volume. The same is true here, which is why this region after the initial point and before the equivalence point is called the buffer region. As we add titrant throughout this region, we are essentially making a series of various buffers. In each case,

$$\text{millimol HA remaining} = M_a V_a - M_t V_t$$

$$\text{millimol } \text{A}^- \text{ created} = M_t V_t$$

Once these amounts have been determined, use  $K_a$  or the Henderson-Hasselbalch equation to find  $[\text{H}_3\text{O}^+]$  and pH, just like a buffer solution.

- III. Equivalence Point: Once all the HA has been neutralized by adding the equivalent amount of titrant base, all HA has been converted to  $\text{A}^-$ . The solution is now just pure conjugate base in the volume at the equivalence point. The concentration of conjugate base is  $M_t V_t$  divided by the total volume at the equivalence point (initial volume + volume of titrant added to reach the equivalence point). Calculate  $K_b$  for  $\text{A}^-$  as  $K_w/K_a^{\text{HA}}$ . Use  $K_b$  to find  $[\text{OH}^-]$  and pOH as for a solution of pure  $\text{A}^-$  in water, then  $\text{pH} = 14.00 - \text{pOH}$ .
- IV. After the Equivalence Point: Here, the solution is essentially excess  $\text{OH}^-$  in water, with the conjugate base making negligible contribution to the total  $[\text{OH}^-]$ . Calculate  $[\text{OH}^-]$  and pOH, then pH, as in the strong acid - strong base case.

To illustrate this general approach, consider the titration of 10.0 mL of 0.0300 M benzoic acid (the analyte) with 0.0100 M NaOH(aq) solution (the titrant). Benzoic acid has the formula  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ , but for simplicity we will abbreviate it as HBz. For HBz,  $K_a = 6.46 \times 10^{-5}$ .

Calculate the pH at each of the following points in the titration:

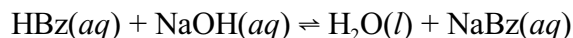
- (i) the initial point, before any titrant has been added;
- (ii) after adding 10.0 mL of 0.0100 M NaOH(aq);
- (iii) after adding 15.0 mL of 0.0100 M NaOH(aq);
- (iv) after adding 30.0 mL of 0.0100 M NaOH(aq);
- (v) after adding 45.0 mL of 0.0100 M NaOH(aq).

Once again, before carrying out any other calculations, determine (a) the number of millimoles of analyte initially present, and (b) the volume of titrant that must be added to reach the equivalence point. It will be useful to keep these numbers in mind as we proceed to calculate the pH values throughout the course of the titration.

The number of millimoles of HBz initially present is

$$\text{mmol HBz} = (0.0300 \text{ M})(10.0 \text{ mL}) = 0.300 \text{ mmol}$$

For our example titration the neutralization reaction is



At the equivalence point

$$\text{mmol HBz initially present} = \text{mmol NaOH added}$$

Therefore, the volume of NaOH(aq) solution needed to reach the equivalence point is

$$V_{\text{NaOH}} = \frac{M_{\text{HBz}} V_{\text{HBz}}}{M_{\text{NaOH}}} = \frac{(0.0300 \text{ M})(10.0 \text{ mL})}{0.0100 \text{ M}} = 30.0 \text{ mL}$$

Note that these are the same values we obtained in the example HBr/NaOH titration above, and we will be calculating the pH at the some of the same points throughout the course of the titration. You will want to compare the procedures and results in this weak acid - strong base example to those of the previous strong acid - strong base example.

- (i) The initial point, before any titrant has been added

Here we simply have a solution of 0.0300 M HBz. We must use  $K_a = 6.46 \times 10^{-5}$  to calculate  $[\text{H}_3\text{O}^+]$  and pH. But in this case,  $C_{\text{HBz}} \gg K_a$ , so we can ignore hydrolysis of molecular HBz and use the approximate method to calculate  $[\text{H}_3\text{O}^+]$ , without needing to solve the quadratic equation.

$$[\text{H}_3\text{O}^+] = \sqrt{C_{\text{HBz}} K_a} = \sqrt{(0.0300)(6.46 \times 10^{-5})} = 1.39 \times 10^{-3} \text{ M}$$

$$\text{pH} = 2.856$$



(ii) After adding 10.0 mL of 0.0100 M NaOH(aq)

The number of millimoles of added NaOH is

$$\text{mmol NaOH} = (0.0100 \text{ M})(10.0 \text{ mL}) = 0.100 \text{ mmol}$$

We can summarize the numbers of millimoles of analyte and titrant before and after the addition by the following table:

	HBz(aq) + NaOH(aq) $\rightleftharpoons$ H <sub>2</sub> O(l) + NaBz(aq)	
Initial	0.300 mmol	0.100 mmol
After rxn	0.200 mmol	0

This is a buffer solution, so we really do not need to be concerned with the total volume of the solution at this point, because a buffer's pH is independent of volume. All we need to do is substitute the numbers of millimoles of HBz and Bz<sup>-</sup> into the  $K_a$  expression and solve for [H<sub>3</sub>O<sup>+</sup>].

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Bz}^-]}{[\text{HBz}]} = \frac{[\text{H}_3\text{O}^+](0.100 \text{ mmol})}{0.200 \text{ mmol}} = 6.46 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = 1.292 \times 10^{-4} \text{ M}$$

$$\text{pH} = \mathbf{3.889}$$

(iii) After adding 15.0 mL of 0.0100 M NaOH(aq)

The number of millimoles of added NaOH is

$$\text{mmol NaOH} = (0.0100 \text{ M})(15.0 \text{ mL}) = 0.150 \text{ mmol}$$

We can summarize the numbers of millimoles of analyte and titrant before and after the addition by the following table:

	HBz(aq) + NaOH(aq) $\rightleftharpoons$ H <sub>2</sub> O(l) + NaBz(aq)	
Initial	0.300 mmol	0.150 mmol
After rxn	0.150 mmol	0

Note that we have added half the volume of NaOH(aq) solution needed to reach the equivalence point. This is called the **half-titration point**. As the table above shows, at the half-titration point, the solution contains equal numbers of millimoles of acid and conjugate base, making it an equimolar buffer solution. If we substitute into the  $K_a$  expression we obtain

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Bz}^-]}{[\text{HBz}]} = \frac{[\text{H}_3\text{O}^+](0.150 \text{ mmol})}{0.150 \text{ mmol}} = 6.46 \times 10^{-5} = [\text{H}_3\text{O}^+]$$

From which it follows

$$\text{pH} = \text{p}K_a = -\log(6.46 \times 10^{-5}) = \mathbf{4.190}$$

This is a general result worth knowing:

**At the half-titration point in any weak acid strong base titration,  $\text{pH} = \text{p}K_a$**

(iv) After adding 30.0 mL of 0.0100 M NaOH(aq)

The number of millimoles of added NaOH is

$$\text{mmol NaOH added} = (0.0100 \text{ M})(30.0 \text{ mL}) = 0.300 \text{ mmol}$$

This is the equivalence point (see preliminary calculation above), because we have added as many millimoles of NaOH titrant as there were millimoles of HBz analyte in the sample. At this point all of the HBz has been converted to Bz<sup>-</sup>, the conjugate base

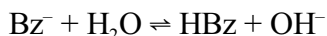
	$\text{HBz(aq)} + \text{NaOH(aq)} \rightleftharpoons \text{H}_2\text{O(l)} + \text{NaBz(aq)}$		
Initial	0.300 mmol	0.300 mmol	0
After rxn	0	0	0.300 mmol

We now have a solution of 0.300 mmol pure weak base Bz<sup>-</sup> in a volume that is the sum of the initial volume plus the volume of added titrant; i.e.,

$$V_t = V_{\text{HBz}} + V_{\text{NaOH}} = 10.0 \text{ mL} + 30.0 \text{ mL} = 40.0 \text{ mL}$$

and 
$$C_{\text{Bz}} = 0.300 \text{ mmol}/40.0 \text{ mL} = 7.50 \times 10^{-3} \text{ M}$$

The pH of the solution will be determined by the hydroxide ion produced by the hydrolysis of the weak base Bz<sup>-</sup>.



(Note that this is the back reaction to the neutralization reaction.) To calculate [OH<sup>-</sup>], we need the  $K_b$  of Bz<sup>-</sup>, which can be obtained from the relationship

$$K_b^{\text{Bz}^-} = \frac{K_w}{K_a^{\text{HBz}}} = \frac{1.00 \times 10^{-14}}{6.46 \times 10^{-5}} = 1.548 \times 10^{-10}$$

As this value indicates, Bz<sup>-</sup> is a very weak base, so we can ignore loss of the analytical concentration from hydrolysis and solve for [OH<sup>-</sup>] without using the quadratic equation.

$$[\text{OH}^-] = \sqrt{C_{\text{Bz}^-} K_b} = \sqrt{(7.50 \times 10^{-3})(1.548 \times 10^{-10})} = 1.077_5 \times 10^{-6} \text{ M}$$

$$\text{pOH} = 5.968$$

$$\text{pH} = \mathbf{8.032}$$

Note that the pH is greater than 7, as expected for a weak acid - strong base titration.

(iv) After adding 45.0 mL of 0.0100 M NaOH(aq)

This is 15.0 mL beyond the equivalence point. The number of millimoles of added NaOH is

$$\text{mmol NaOH added} = (0.0100 \text{ M})(45.0 \text{ mL}) = 0.450 \text{ mmol}$$

At this point our table of millimoles of analyte and titrant before and after the addition now has the following values:

	$\text{HBz(aq)} + \text{NaOH(aq)} \rightleftharpoons \text{H}_2\text{O(l)} + \text{NaBz(aq)}$		
Initial	0.300 mmol	0.450 mmol	0
After rxn	0	0.150 mmol	0.450 mmol

The solution contains 0.150 mmol of NaOH beyond what was needed to neutralize the 0.300 mmol of HBz initially present. This amount of excess  $\text{OH}^-$  is vastly greater than any amount supplied by the weak base  $\text{Bz}^-$ , and it alone governs the pOH and pH of the solution. In other words, the calculation in this region is identical to the previous strong acid - strong base case. As before, the total volume of the solution at this point is

$$V_t = V_{\text{HBr}} + V_{\text{NaOH}} = 10.0 \text{ mL} + 45.0 \text{ mL} = 55.0 \text{ mL}$$

Therefore,  $[\text{OH}^-] = C_{\text{NaOH}} = 0.150 \text{ mmol}/55.0 \text{ mL} = 2.727 \times 10^{-3} \text{ M}$

$$\text{pOH} = 2.564$$

$$\text{pH} = \mathbf{11.436}$$

### Key Questions

5. Consider 25.0 mL of 0.100 M HA, for which  $K_a = 1.00 \times 10^{-5}$ , titrated with 0.0500 M NaOH solution.
- How many milliliters of NaOH(aq) are needed to reach the equivalence point?
  - How many millimoles of HA are initially present in the sample?
  - What is the initial pH, before adding any titrant?
  - What is the pH after adding 10.0 mL of titrant?
  - What is the pH after adding 25.0 mL of titrant?
  - What is the pH after adding 50.0 mL of titrant?
  - What is the pH after adding 75.0 mL of titrant?