

Key Worksheet 15 Acids & Base Equilibria: Acid–Base Titrations

Objectives

To be able to calculate the pH, pOH, and concentrations of all species present at any point of an acid–base titration.

Vocabulary

Titrant: The substance whose concentration is known that is added in a titration. Usually the titrant is in the burette.

Analyte: The substance whose concentration is not known in a titration. Usually the analyte is in the flask or beaker beneath the burette.

Equivalence point – point in the titration where the number of moles of the titrant added is exactly enough to react with all of the moles of the analyte.

Strong Acid – Strong Base: Before the equivalence point the pH is determined by the quantity of the analyte that remains unreacted. The solution will have been diluted by the addition of the titrant. The solution will be neutral (pH 7) at the equivalence point. After the equivalence point the pH will be determined by the amount of excess titrant that remains unreacted.

Weak Acid – Strong Base: Before the equivalence point the pH is determined by the quantity of the analyte that remains unreacted. To calculate the pH before the equivalence point use the equilibrium expression (K_a). Use an I.C.E. table. The solution will have been diluted by the addition of the titrant.

At halfway to the equivalence point the solution will be a buffer solution. You can usually use the Henderson – Hasselbach equation to find the pH here, but check the 5% rule if you have any doubts. Since the analyte is a weak acid the pH will be greater than 7 at the equivalence point. The primary species affecting the pH present will be the conjugate base of the weak acid.

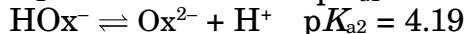
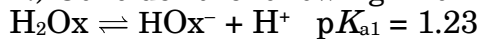
After the equivalence point the pH will be determined by the amount of excess titrant that remains unreacted. There will be some of the conjugate base of the weak acid present, but it's effect will be negligible compared to that of the strong base.

Weak Base – Strong Acid: Before the equivalence point the pH is determined by the quantity of the analyte that remains unreacted. To calculate the pH before the equivalence point use the equilibrium expression (K_b). Use an I.C.E. table. The solution will have been diluted by the addition of the titrant.

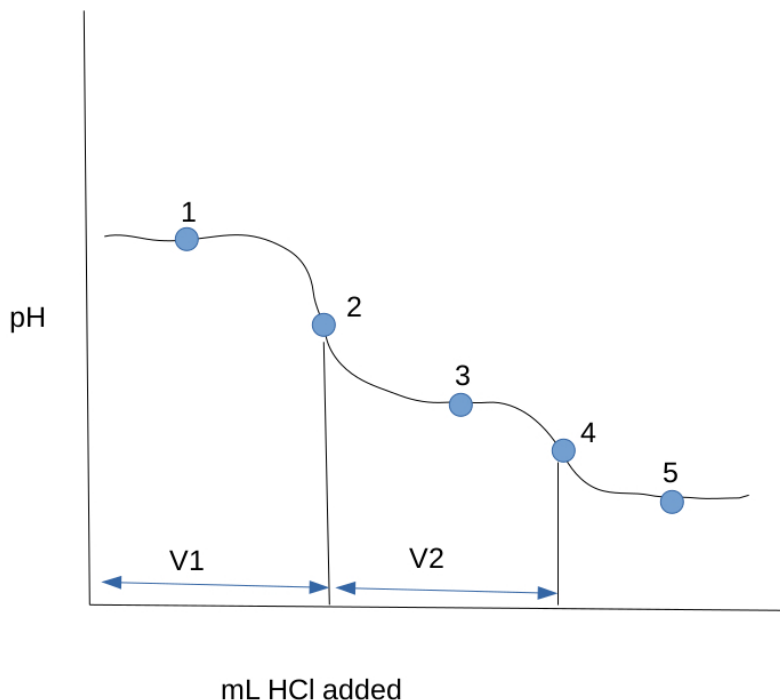
At halfway to the equivalence point the solution will be a buffer solution. You can usually use the Henderson – Hasselbach equation to find the pH here, but check the 5% rule if you have any doubts. Since the analyte is a weak base the pH will be less than 7 at the equivalence point. The primary species affecting the pH present will be the conjugate acid of the weak base.

After the equivalence point the pH will be determined by the amount of excess titrant that remains unreacted. There will be some of the conjugate acid of the weak base present, but it's effect will be negligible compared to that of the strong acid.

1.) Consider the following information about the diprotic acid, oxalic acid. (H_2Ox for short)



The titration curve for disodium oxalate, Na_2Ox , with standard HCl is shown below:



a.) What major species is (are) present at each of the points (1 – 5)?

Point 1: Ox^{2-} , HOx^- Point 2: HOx^- Point 3: HOx^- , H_2Ox Point 4: H_2Ox Point 5: H^+

b.) What is the pH at point 1 (halfway to the first equivalence point)?

$$pH = pK_a = 4.19$$

c.) What is the pH at point 3 (halfway between the 1st and 2nd equivalence points)?

$$pH = pK_a = 1.23$$

2.) Calculate the pH at the following points in the titration of 25.00 mL of 0.451 M HNO_3 with 0.255 M NaOH.

a.) Before any NaOH is added.

$$pH = -\log[H^+] = -\log(0.451) = 0.3458$$

$$pH = \underline{0.346}$$

b.) After 10.00 mL of NaOH is added.

$$10.00 \text{ mL} \times \frac{0.255 \text{ mmol NaOH}}{\text{mL}} = 2.55 \text{ mmol NaOH}$$

$$25.00 \text{ mL} \times \frac{0.451 \text{ mmol HNO}_3}{\text{mL}} = 11.27 \text{ mmol HNO}_3$$

$$11.27 \text{ mmol HNO}_3 - 2.55 \text{ mmol reacted} = 8.725 \text{ mmol HNO}_3 \text{ left}$$

$$\frac{8.7_{25} \text{ mmol HNO}_3}{35.00 \text{ mL}} = 0.24_9 \text{ M} \quad \text{pH} = -\log(0.24_9) = 0.60_3$$

$$\text{pH} = \underline{0.60}$$

c.) After 22.11 mL of NaOH is added.

$$22.11 \text{ mL NaOH} \times \frac{0.255 \text{ mmol}}{\text{mL}} = 5.63_8 \text{ mmol NaOH added}$$

$$11.2_7 \text{ mmol HNO}_3 - 5.63_8 \text{ mmol reacted} = 5.63_6 \text{ mmol HNO}_3 \text{ left}$$

$$\frac{5.63_6 \text{ mmol HNO}_3}{47.11 \text{ mL}} = 0.11_9 \text{ M} \quad \text{pH} = -\log(0.11_9) = 0.92_2$$

$$\text{pH} = \underline{0.92}$$

d.) After 44.22 mL of NaOH is added.

$$44.22 \text{ mL NaOH} \times \frac{0.255 \text{ mmol}}{\text{mL}} = 11.2_7 \text{ mmol NaOH added}$$

mmol NaOH added = mmol HNO₃, so the solution is neutral. pH = 7.00

$$\text{pH} = \underline{7.00}$$

e.) After 50.00 mL of NaOH is added.

$$50.00 \text{ mL NaOH} \times \frac{0.255 \text{ mmol}}{\text{mL}} = 12.7_5 \text{ mmol NaOH added}$$

$$12.7_5 \text{ mmol NaOH} - 11.2_7 \text{ mmol HNO}_3 = 1.47_5 \text{ mmol NaOH excess}$$

$$\frac{1.47_5 \text{ mmol OH}^-}{75.00 \text{ mL}} = 0.019_6 \text{ M OH}^- \quad \text{pOH} = -\log(0.019_6) = 1.70_6$$

$$\text{pH} = 14.00 - 1.70_6 = 12.29_3$$

$$\text{pH} = \underline{12.29}$$

3.) Calculate the pH at the following points in the titration of 35.00 mL of 0.308 M KCN with 0.269 M HCl. $\text{p}K_a$ of HCN = 9.210.

a.) Before any HCl is added.

$$\text{p}K_b = 14.00 - 9.210 = 4.79 \quad K_b = 10^{-4.79} = 1.6_2 \times 10^{-5}$$

$$K_b = \frac{x^2}{0.308 - x} \approx \frac{x^2}{0.308} \Rightarrow x = 0.0022_3 = [\text{OH}^-]$$

$$\text{pOH} = -\log(0.0022_3) = 2.65_0 \quad \text{pH} = 14.00 - 2.65_0 = 11.34_9$$

$$\text{pH} = \underline{11.35}$$

b.) After 10.00 mL of HCl is added.

$$10.00 \text{ mL} \times \frac{0.269 \text{ mmol H}^+}{\text{mL}} = 2.69 \text{ mmol H}^+$$

$$35.00 \text{ mL} \times \frac{0.308 \text{ mmol CN}^-}{\text{mL}} = 10.7_8 \text{ mmol CN}^-$$

$$10.7_8 \text{ mmol CN}^- - 2.69 \text{ mmol reacted} = 8.09_0 \text{ mmol CN}^- \text{ left}$$

We formed 2.69 mmol of HCN, we have 8.09₀ mmol CN⁻, which makes this a buffer solution. We can use the Henderson–Hasselbach equation to calculate the pH.

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{CN}^-]}{[\text{HCN}]}\right) = 9.210 + \log\left(\frac{8.09_0}{2.69}\right) = 9.688_1$$

$$\text{pH} = \underline{9.688}$$

c.) After 20.04 mL of HCl is added.

$$20.04 \text{ mL} \times \frac{0.269 \text{ mmol H}^+}{\text{mL}} = 5.39_0 \text{ mmol H}^+ \text{ added}$$

This is halfway to the equivalence point, which means $\text{pH} = \text{p}K_a = 9.210$

$$\text{pH} = \underline{9.210}$$

d.) After 40.07 mL of HCl is added.

$$40.07 \text{ mL} \times \frac{0.269 \text{ mmol H}^+}{\text{mL}} = 10.7_7 \text{ mmol H}^+ \text{ added}$$

This is the equivalence point. The only important species present that affects the pH is HCN.

$$[\text{HCN}] = \frac{10.7_7 \text{ mmol}}{75.07 \text{ mL}} = 0.143_5 \text{ M}$$

From our I.C.E. table we get

$$K_a = 10^{-9.210} = 6.16_5 \times 10^{-10} = \frac{x^2}{0.143_5 - x} \approx \frac{x^2}{0.143_5} \Rightarrow x = 9.40_6 \times 10^{-6} = [\text{H}^+]$$

$$\text{pH} = -\log(9.40_6 \times 10^{-6}) = 5.026_5$$

$$\text{pH} = \underline{5.027}$$

e.) After 50.00 mL of HCl is added.

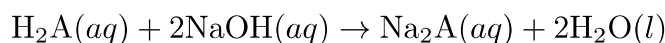
$$50.00 \text{ mL} \times \frac{0.269 \text{ mmol H}^+}{\text{mL}} = 13.4_5 \text{ mmol H}^+$$

$$13.4_5 \text{ mmol H}^+ - 10.7_8 \text{ mmol neutralized} = 2.6_7 \text{ mmol H}^+ \text{ excess}$$

$$[\text{H}^+] = \frac{2.6_7 \text{ mmol H}^+}{85.00 \text{ mL}} = 0.031_4 \text{ M} \Rightarrow \text{pH} = -\log(0.031_4) = 1.50_2$$

$$\text{pH} = \underline{1.50}$$

4.) You dissolve 0.314 grams of an unknown diprotic acid in H₂O. This solution is just neutralized by 7.34 mL of a 0.7872 M NaOH solution. What is the molar mass of the unknown acid?

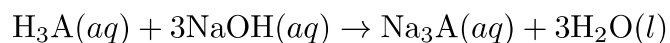


$$0.00734 \text{ L} \times \frac{0.7872 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol H}_2\text{A}}{2 \text{ mol NaOH}} = 0.00288_9 \text{ mol H}_2\text{A}$$

$$\frac{0.314 \text{ g H}_2\text{A}}{0.00288_9 \text{ mol}} = 108.6 \text{ g/mol}$$

$$\text{Molar Mass} = \underline{109 \text{ g/mol}}$$

5.) A 25.00 mL sample of citric acid is titrated to a phenolphthalein endpoint with 37.22 mL of 0.8859 M NaOH. Given that citric acid is triprotic, what is the molarity of the citric acid solution?



$$0.03722 \text{ L} \times \frac{0.8859 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol H}_3\text{A}}{3 \text{ mol NaOH}} = 0.01099_1 \text{ mol H}_3\text{A}$$

$$\frac{0.01099_1 \text{ mol H}_3\text{A}}{0.02500 \text{ L}} = 0.4396_4 \text{ M}$$

$$[\text{Citric Acid}] = \underline{0.4396 \text{ M}}$$