

ALE 15. Titration Curves

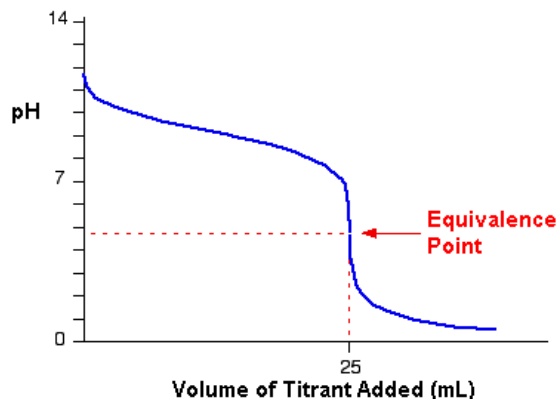
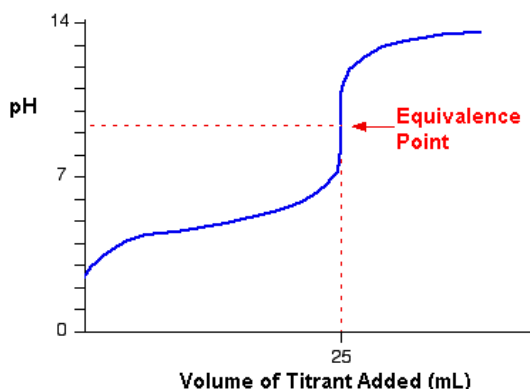
(Reference: 19.2 Silberberg 5th edition)

What is the pH at the equivalence point of an acid-base titration?

The Model

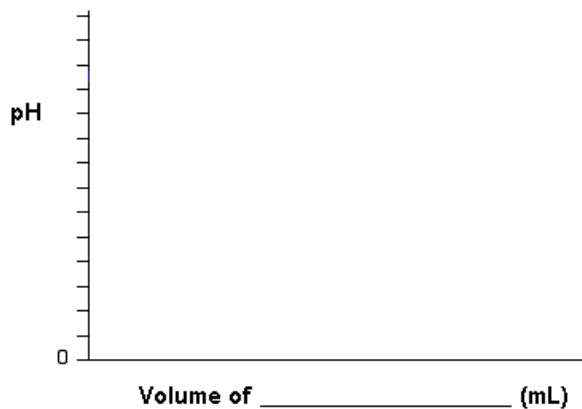
In a titration, either an acid is added to a base, or a base is added to an acid. As this is being done, it is possible to use a pH meter to monitor the pH of the solution. A titration curve is generated by plotting the solution's pH as a function of the volume of the added titrant. At the **equivalence point**, the number of "equivalents" (or moles, if the acid is monoprotic) of acid is exactly equal to the number of equivalents of base. Thus at the equivalence point the titrated solution is "neutralized" (stoichiometrically speaking – the pH need not be exactly 7). The **equivalence point** is identified as being the point on a titration curve at which the tangent line has the greatest slope (which may be either positive or negative).

Key Questions



1. One of the titration curves above describes the titration of a **weak acid with a strong base**. The other curve describes the titration of a **weak base with a strong acid**. Which is which? How can you tell?
2. Write the neutralization reaction that occurs between a...
 - a. monoprotic weak acid (the generic "HA") and a strong base ("OH").
 - b. weak base (the generic "B", which represents some amine) and a strong acid.

3. Why does the first of the titration curves in Question 1 have an equivalence point with a pH above 7 while the second curve has an equivalence point with $\text{pH} < 7$? (*Hint*: In each case, what species does Question 2 say remains dissolved in solution at the equivalence point? Is the species acidic or basic?)
- 4 a. What is the net ionic reaction that occurs in solution when any strong base is titrated with any strong acid?
- b. Sketch the titration curve that would be observed when a strong base (*e.g.*, NaOH) is titrated with a strong acid (*e.g.*, HCl)? You need not concern yourself with the scale of the *x*-axis, but *do* carefully label and scale the *y*-axis. Indicate where the equivalence point is on the titration curve.



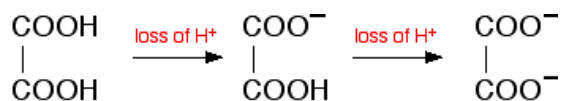
Exercises

5. Suppose 25.0 mL of 0.10 M CH_3NH_2 ($K_b = 4.4 \times 10^{-4}$) is titrated with 0.10 M HCl.
- a. Calculate the pH of the methylamine solution before the titration even begins. *Hints*: ① What reaction occurs between CH_3NH_2 and water? ② What is the K_b for this reversible reaction? ③ Set up an ICE table to write the equilibrium concentrations of the aqueous solutes in terms of an algebraic variable. ④ Set up the law of mass action. ⑤ Using the quadratic formula, solve for the variable and then solve for the pH.

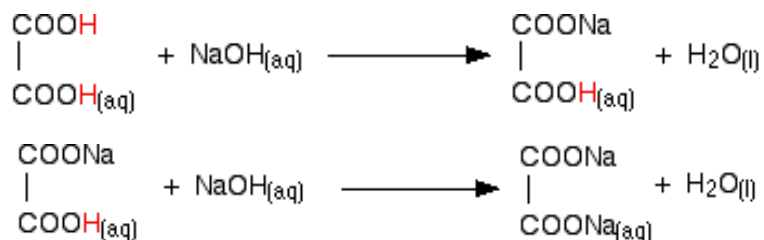
- b. How many milliliters of the 0.10 M HCl solution will it take to reach the equivalence point (i.e. to neutralize the 25.0 mL of 0.10 M CH₃NH₂)? What is the total volume of the resultant solution at the equivalence point (assuming that the volumes of the methylamine and hydrochloric acid solutions are additive)? Hint: First write the balanced equation between methylamine and HCl.
- c. Assume that the reaction between CH₃NH₂ and HCl is 100% complete. What is the product of the reaction? How many moles of this product are in solution? What is the molar concentration of the product?
- d. We had assumed that the reaction between CH₃NH₂ and HCl was 100% complete. Now we “allow” the reaction to become reversible. Write the reversible reaction that the product (*i.e.* the species you identified in part c, above) undergoes in aqueous solution.
- e. Calculate the pH of the solution at the equivalence point. Hints: ① What is the K_a for the reversible reaction you wrote in part d, above? ② Set up an ICE table to write the equilibrium concentrations of the aqueous solutes in terms of an algebraic variable. ③ Set up the law of mass action. This time make a simplification to make it easier to solve for the variable. ④ Solve for the variable and then solve for the pH.

Model: Titration Curves involving Polyprotic acids

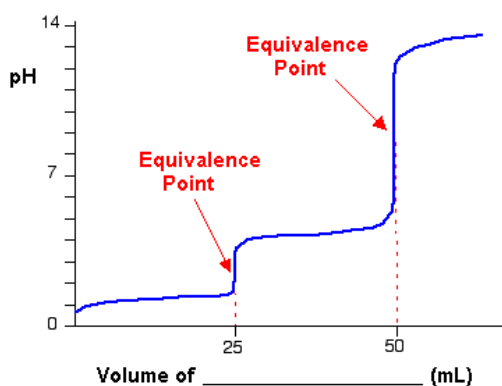
Oxalic acid is a **diprotic acid**, which means that it can give away 2 protons (hydrogen ions) to a base. An acid that can only give away one proton is known as a **monoprotic acid**—hydrochloric acid (HCl), nitric acid (HNO₃) and acetic acid CH₃COOH are examples of monoprotic acids.



The reaction with sodium hydroxide takes place in two stages because the first hydrogen ion is easier to remove than the second. The two successive reactions are:



Titration of aqueous oxalic acid and aqueous sodium hydroxide yields the following titration curve with two **inflection points**



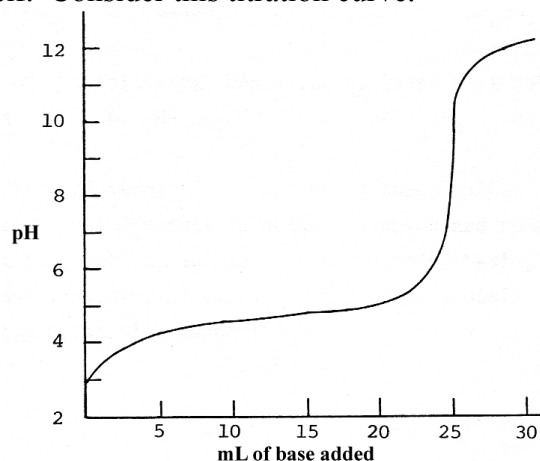
Key Questions

- Which solution was in the burette, oxalic acid or sodium hydroxide? (Circle your response.) How do you know?
- What is the approximate pH of the first equivalence point? _____ Explain why the pH of the first equivalence point is what it is (i.e. acidic, basic or neutral).
- What is the approximate pH of the second equivalence point? _____ Explain why the pH of the second equivalence point is what it is (i.e. acidic, basic or neutral).

Information from a Titration Curve

There are several things you can read from the titration curve itself. Consider this titration curve.

9. The titration curve to the right is a _____
(strong/weak) acid titrated with a strong base. The
acid is _____ (monoprotic/diprotic).
10. Place a dot (●) on the curve at the equivalence point.
The pH at the equivalence point is _____.
11. What volume of base was used to titrate the acid
solution to reach the equivalence point? _____ mL



12. Place a box (■) on the curve where the pH of the solution = the pK_a of the acid.
What is the pH at this point? _____ What is the pK_a of the acid? _____ What is the K_a of the
acid? _____
13. Sketch how the titration curve would look like if the other strength of acid were used.

