CHM 1220-Dang Chapter 16 – Acid-Base Equilibria

17.5 Titration and pH curves

A procedure for determining the concentration of a solution by allowing a carefully measured volume to react with a solution of another substance (the standard solution) whose concentration is known.

buret

standard solution

(known concentration)

Erlenmeyer flask

unknown concentration solution

An indicator is added which changes color once the reaction is complete

Titrant: solution that is added from the buret

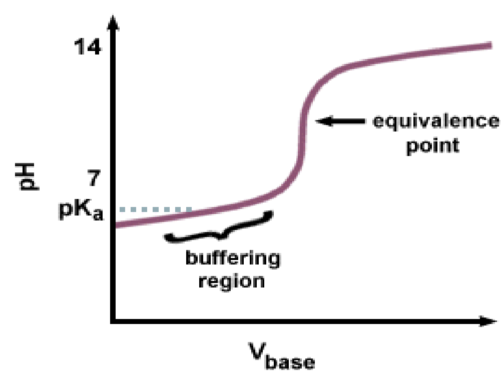
Equivalence Point: The point at which stoichiometrically equivalent quantities of acid and base have been mixed together.

Endpoint: is the point at which the titration is complete (usually by a sudden color change), as determined by an indicator

Acid-Base Titration Curves

Titrations are often plotted as an "acid-base titration curves" that displays the pH of the reaction (titration) mixture versus the volume of titrant (added base or acid). We will consider titrations curves for three types of titrations: strong acid-strong base, weak acid-weak base and strong acid-weak base titrations

- All three types of titration curves have two horizontal regions where the pH changes only slightly with additions of acid (or base). A solution that resists changes upon addition of acid or base is called a ___________________
- All three types of titration curves have a vertical region where the pH changes very rapidly with even small additions of titrant. For titrations involving a weak acid or base, this region is not as vertical as for the strong acid/strong base titrations.



Selecting Solutions for Acid-Base Titrations

If you are titrating an **acid**, make sure you use a **base** so that your titration reaction is a neutralization. It should have at least one STRONG reactant so it will go to completion.

For example, if you are titrating the acid CH_3COOH (WA), use a STRONG BASE like NaOH, KOH etc. You **could not** use another acid (like HCl etc.). Also, since CH_3COOH is a WEAK acid, you **cannot** use a weak base (like NH_3)

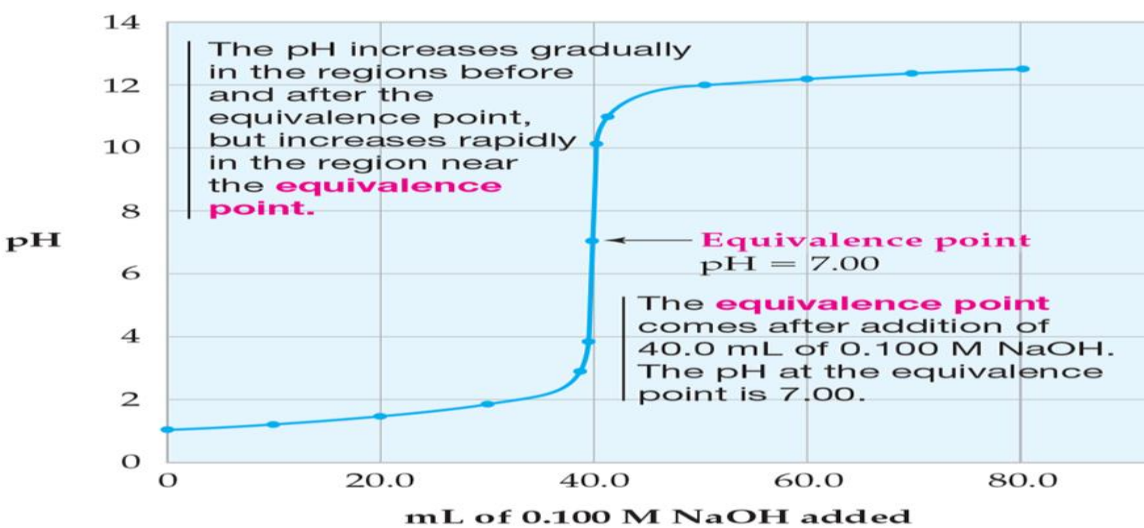
Also, the concentration of your standard should be relatively close to the concentration of the solution you are titrating so that the volumes used are comparable.

Example: In titrating 25.00 mL samples of NH_3 which is approximately 0.100 M, which of the following solutions should be used to determine the $[NH_3]$?

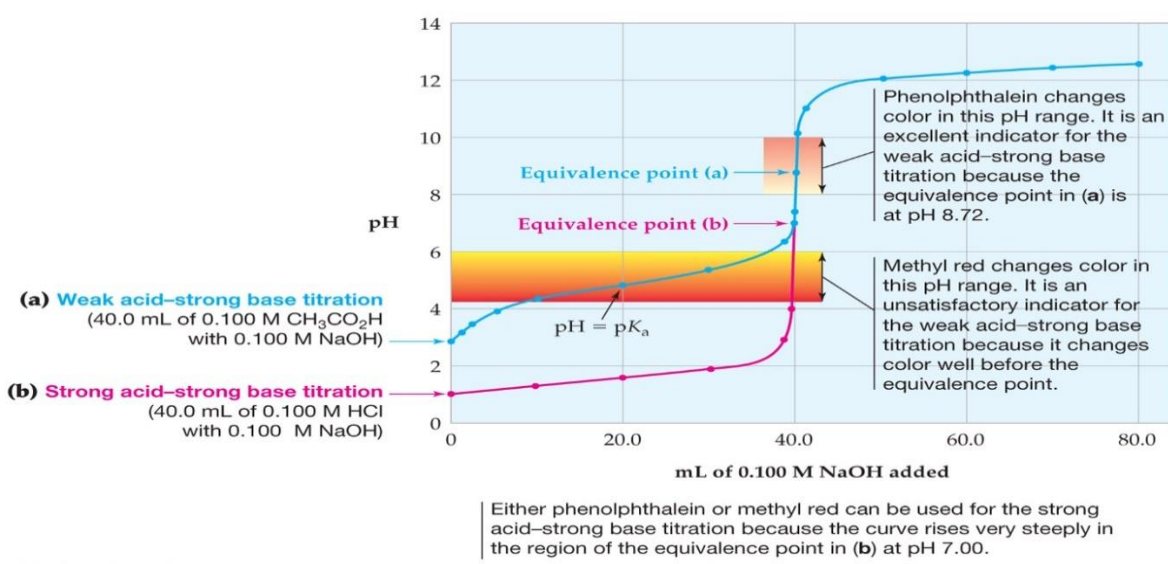
a) 0.00100M HCl   b) 0.125 M HCl   c) 6.00 M HCl   d) 0.100M NaOH

Three common types of titration curves

Strong Acid and Strong Base

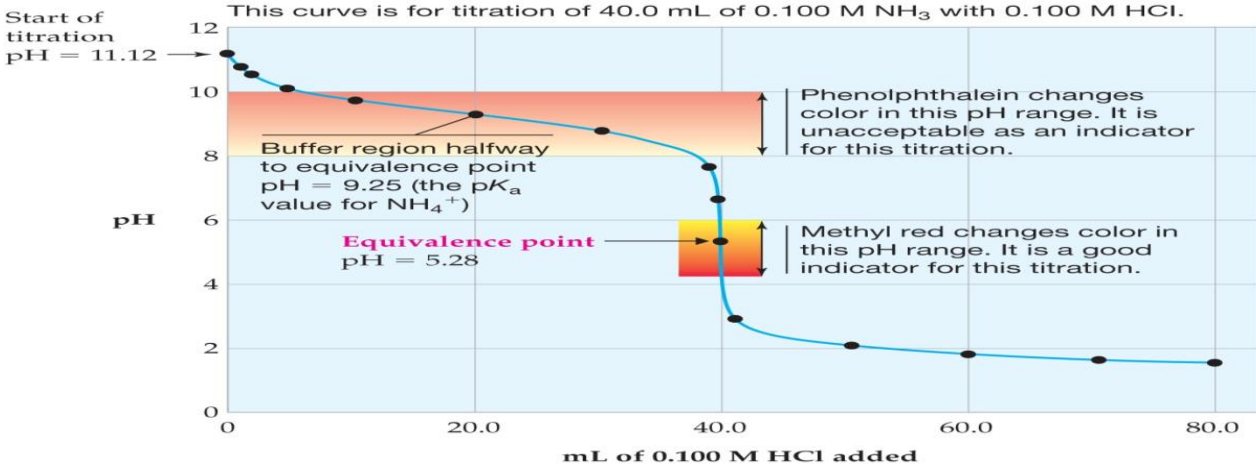


Weak acid and Strong Base



DANG2

Weak Base and Strong Acid



Calculating the pH of the Titration Solution

Because titrations typically use milliliter volumes, we'll express solution volumes in milliliters (mL) and amounts of solute in millimoles (mmol). Molar concentration can thus be expressed in mmol/mL, a unit that is equivalent to mol/L:

$$\textbf{Molarity} = \frac{\text{mmole of solute}}{\text{mL of solution}} = \frac{10^{-3}\text{ mole of solute}}{10^{-3}\text{ L of solution}} = \frac{\text{mole of solute}}{\text{L of solution}}$$

You must be able to calculate the pH at any point in the titration of all three titration types

- **Before any titrant has been added**
- **Before the equivalence point**
- **At the equivalence point**
- **After the equivalence point**

To be able to calculate the pH for the titration problem, you must be able to write the neutralization reaction between the acid and the base.

17.6 Strong acid-Strong base titrations

Example: A 30.0 mL of 0.150 M HNO_3 is titrated with 0.200 M NaOH at 25ºC.

a. What is the pH before any titrant has been added?

This is not really a titration problem. Remember, the "concentration" of the strong acid HNO_3 is actually the concentration of H_3O^+ (WHY?) which can be directly converted to pH.

b. Where is the "equivalence point" of the titration?

- *That is, what volume of titrant (NaOH) must be added to reach the equivalence point?*
- *Always calculated with* $\boldsymbol{M_a V_a = M_b V_b}$

c. What is the pH after 10.0 mL of titrant have been added?

Consider neutralization and dilution before calculating $[H_3O^+]$

d. What is the pH at the equivalence point?

At 25°C, the answer is **always pH = 7.00**. *At this point, the acid* (HNO_3) *has been completely "neutralized" by adding an "equivalent" amount of base (NaOH). At the equivalence point, a strong acid and a strong base are entirely converted to* H_2O *and "salt" (NaCl in this case). The salt produced will always be neutral (i.e., does not hydrolyze in water), the pH is just the result of the self-ionization of water at 25°C*

e. What is the pH after a total of 50.0 mL of titrant have been added?

Consider neutralization and dilution before calculating [H_3O^+]

17.7 Weak acid-Strong base titration

Hydrolysis Reactions of Weak Acids or Weak Bases

- Hydrolysis is the reaction of a weak acid or a weak base with water.
- Any weak acid or weak base that is produced through neutralization will hydrolyze, affecting the pH of the solution. Also, any unreacted weak acid or weak base will also hydrolyze, affecting the pH of the solution.

After neutralization, if only weak acid is present, write its hydrolysis reaction

After neutralization, if only weak base is present, write its hydrolysis reaction

After neutralization, if both weak acid and weak base are present, write either hydrolysis reaction

Example: 25.00 mL of 0.100 M acetic acid, $HC_2H_3O_2$, is titrated by 0.100 M NaOH. At 25°C, $K_a = 1.8 \times 10^{-5}$

a) **What is the pH before any titrant has been added?**

*This is not really a titration problem. It is a calculation of a pH of an acid solution.

b) **Where is the "equivalence point" of the titration?**

**Same calculation as for Strong acid/Strong base!!*

c) **What is the pH at the "midpoint" of titration?**

"midpoint": *half of the volume of titrant necessary to reach the equivalence point has been added*

The midpoint has a special meaning only for titration involving weak acid or weak base* **$pH = pK_a$

d) **What is the pH after 20.00 mL of titrant have been added?**

e) What is the pH at the equivalence point?

* **The answer is NOT 7.00**. The solution will always be basic at the equivalence point for this type of titration because all of the acid has been converted to the conjugate base ($C_2H_3O_2^-$). The conjugate base hydrolyzes in water to produce ^-OH, making the solution basic.

f) **What is the pH after a total of 35.00 mL of titrant have been added?**

17.8 Weak base-Strong acid titrations

Example: 15.00 mL of 0.100 M NH_3 ($K_b = 1.8 \times 10^{-5}$) is titrated with 0.100 M HCl.

a) **Where is the "equivalence point" of the titration?**

Same calculation as for Strong acid-Strong base

b) **What is the midpoint of the titration?**

The formula is still $\boldsymbol{pH = pK_a}$. *Be sure to convert from* K_b *to* K_a

c) What is the pH at the equivalence point?

The answer is not 7.00. The solution will always be acidic at the equivalence point for this type of titration because all of the base has been converted to the conjugate acid (NH_4^+). The conjugate base hydrolyzes in water to produce H_3O^+, making the solution acidic.

d) What is the pH after a total 25.00 mL of titrant have been added?

At any point past the equivalence point, the solution will contain both the weak conjugate acid (NH_4^+) and the excess strong acid, H_3O^+. The pH is assumed to be dependent only on the concentration of the strong acid that is present.