Chem 321 Lecture 13 - Acid-Base Titrations

10/10/13

Student Learning Objectives

Indicators

A common end point for acid-base titrations is the color change associated with an **acid-base indicator**. An acid-base indicator is usually an organic weak acid or base that has a different color in solution than its conjugate form. These substances strongly absorb light so that even a very small concentration in solution produces an obvious color. If the weak acid form of the indicator is taken as HIn, the acid dissociation process for this indicator is represented by:

$$HIn + H_2O \overset{K_a}{\rightleftharpoons} H_3O^+ + In^-$$

At equilibrium,

$$K_a \simeq \frac{[H_3O^+][In^-]}{[HIn]}$$

and

$$\frac{[In^-]}{[HIn]} \simeq \frac{K_a}{[H_3O^+]}$$

This means that as $[H_3O^+]$ changes, so do the relative amounts of the different colored conjugate species in solution. Thus, the indicator in solution will take on a specific color depending upon the solution pH.

As an example, consider the acid-base indicator methyl orange indicator. The weak acid form is red in solution while the conjugate base form is yellow (that is, HIn = red and In^- = yellow). In order to anticipate the pH range in which this indicator changes from yellow to red, or vice versa, assume that a 10-fold excess of one colored form over the other is needed to establish the color of one of the conjugate pairs. Thus, to see predominately yellow in solution,

$$\frac{[yellow]}{[red]} \simeq \frac{10}{1} \simeq \frac{K_a}{[H_3O^+]} \quad and \quad pH \simeq pK_a + 1$$

In a similar way it can be shown that the red color dominates when the solution pH is about equal to pK_a - 1. Therefore, an indicator color change is expected in a pH range equal to $pK_a \pm 1$. The pK_a for methyl orange is 3.46, so it should change from red to yellow as the pH increases from about 2.5 to 4.5. This is in substantial agreement with the pH transition range for methyl orange in the table below.

Table of Common Acid-Base Indicators

Indicator	Transition range (pH)	Acid color	Base color
Methyl violet	0.0 - 1.6	Yellow	Violet
Cresol red	0.2 - 1.8	Red	Yellow
Thymol blue	1.2 - 2.8	Red	Yellow
Cresol purple	1.2 - 2.8	Red	Yellow
Erthrosine disodium	2.2 - 3.6	Orange	Red
Methyl orange	3.1 - 4.4	Red	Yellow
Congo red	3.0 - 5.0	Violet	Red
Ethyl orange	3.4 - 4.8	Red	Yellow
Bromocresol green	3.8 - 5.4	Yellow	Blue
Methyl red	4.8 - 6.0	Red	Yellow
Chlorophenol red	4.8 - 6.4	Yellow	Red
Bromocresol purple	5.2 - 6.8	Yellow	Purple
p-Nitrophenol	5.6 - 7.6	Colorless	Yellow
Litmus	5.0 - 8.0	Red	Blue
Bromothymol blue	6.0 - 7.6	Yellow	Blue
Phenol red	6.4 - 8.0	Yellow	Red
Neutral red	6.8 - 8.0	Red	Yellow
Cresol red	7.2 - 8.8	Yellow	Red
α-Naphtholphthalein	7.3 - 8.7	Pink	Green
Cresol purple	7.6 - 9.2	Yellow	Purple
Thymol blue	8.0 - 9.6	Yellow	Blue
Phenolphthalein	8.0 - 9.6	Colorless	Red
Thymolphthalein	8.3 - 10.5	Colorless	Blue
Alizarin yellow	10.1 - 12.0	Yellow	Orange-red
Nitramine	10.8 - 13.0	Colorless	Orange-brown
Tropaeolin O	11.1 - 12.7	Yellow	Orange

Consequently, knowledge of the pH at the equivalence point allows one to select an indicator that will undergo a color change in a pH range that brackets the equivalence point pH.

Check for Understanding 9.3 **Solutions**

1. Which indicator would be suitable for the titration of:

   a) $HC_2H_3O_2$ with NaOH?

   b) NH_3 with HCl?

   See Example 9.1 and Check for Understanding 9.1 for estimates of the equivalence point pH for these titrations.

Polyprotic Acid and Base Titrations

The titration of a polyprotic acid or base is very similar to that for a monoprotic weak acid or base except that more than one equivalence point is observed. The maleic acid experiment in lab involves such a titration. The titration curve for the titration of 50.0 mL of 0.100 M Na_2CO_3 with 0.100 M HCl is shown in Figure 9.5. Since the analyte and titrant concentrations are the same, the first equivalence point occurs at 50 mL and the second one occurs at 100 mL.

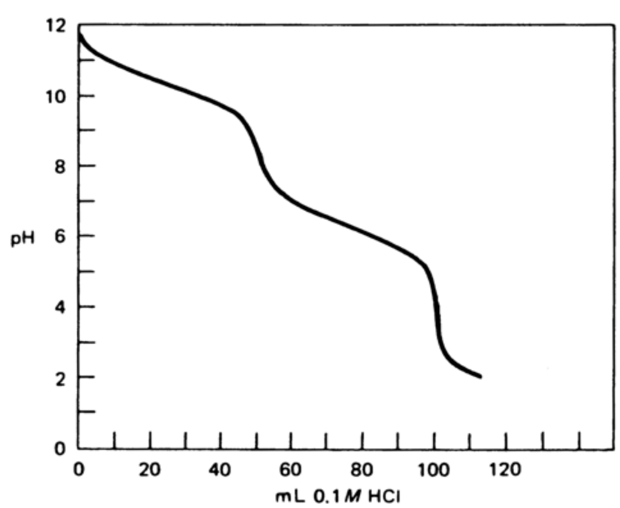

Figure 9.5 Curve for the titration of Na_2CO_3 with a HCl(aq)

The titration reaction to the first equivalence point involves neutralization of the weak base carbonate.

$$CO_3^{2-} + H_3O^+ \rightarrow HCO_3^- + H_2O$$

As this process occurs, a CO_3^{2-}/HCO_3^- buffer is formed. The region before the first equivalence point where the pH is changing slowly with added titrant corresponds to this first buffer region. Throughout this portion of the titration pH ~ pK_a and at the halfway point (25 mL), pH = pK_a = 10.33. Note that the K_a is that for the weak acid in the buffer, that is, HCO_3^-, which corresponds to K_{a2} for H_2CO_3.

At the first equivalence point, all the CO_3^{2-} has been converted to HCO_3^- and additional titrant starts neutralizing the bicarbonate.

$$HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O$$

As this process occurs, a HCO_3^-/H_2CO_3 buffer is formed. The region between the first and second equivalence points where the pH is changing slowly with added titrant corresponds to this second buffer region. Throughout this portion of the titration pH ~ pK_a and halfway between the first and second equivalence points (75 mL), pH = pK_a = 6.35. Here K_a is that for the weak acid H_2CO_3 and is thus K_{a1} for carbonic acid.

An estimate of each equivalence point pH can be made as before by taking the average of the pH plateau values before and after the equivalence point. For the first equivalence point pH ~ (10.33 + 6.35)/2 = 8.3.

Check for Understanding 9.4 **Solutions**

1. Estimate the pH at the second equivalence point in the carbonate titration.

2. Which indicators are suitable for use at the first and second equivalence points in the carbonate titration?

Because the pH jump at either equivalence point in the carbonate titration is not very large, an indicator color change is not a very sharp end point. An indicator color match can be used instead as the end point. For this to be a valid end point, the indicator must have the same color in the comparison solution as it has in the titration solution at the second equivalence point. This is true only if the pH of the comparison solution is the same as the pH at the second equivalence point. Previously you have calculated, using activities, the pH of a CO_3^{2-}/HCO_3^- buffer solution that is suitable for use as a comparison solution for the carbonate titration, and above you have estimated the pH at the second equivalence point. To make a more careful comparison of pH, make the following calculation of the second equivalence point pH.

Check for Understanding 9.5 **Solution**

1. What is the pH at the second equivalence point in the titration of Na_2CO_3 with 0.100 M HCl? Use activities and assume a 0.200-g sample of Na_2CO_3 is dissolved in 60.0 mL of deionized water and titrated.

Gran Plots

For the maleic acid experiment, you will use a graphical method known as a Gran plot to determine the second equivalence point in your titration. In this approach, the pH of your maleic acid solution is recorded as a function of the volume of added base (V_b) and a graph of $V_b \cdot 10^{-pH}$ versus V_b is made using data just before the equivalence point. Assuming that the ionic strength of the solution is constant, the *x*-intercept of this linear plot is the equivalence point volume (V_e). An example of a Gran plot is shown below.

Derivation of relationship used for Gran plot

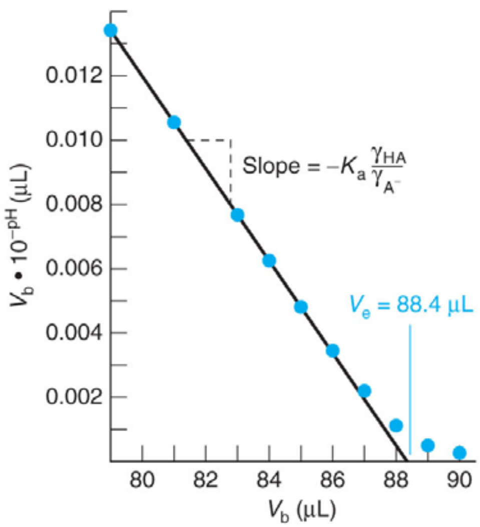

Figure 9.6 Gran plot for a weak acid-strong base titration

The ionic strength of the maleic acid solution is fixed by adding a large amount of KCl to the titration solution. The key advantage of using a Gran plot is that the equivalence point can be determined by using only data before the equivalence point (typically the data between $0.9V_e$ and V_e). The slope of the Gran plot also allows one to determine the K_a of the weak acid (for a weak acid-strong base titration, slope = $-K_a\gamma_{HA}/\gamma_{A^-}$).

Exercises for Acid-Base Titrations