Experiment 6
Determination of the Equilibrium Constant for Bromocresol Green

Reading assignment: Chang, Chemistry 10th edition, Chapter 15: Acids and Bases, sections 1-5.

Goals
To determine the acid dissociation constant (K_a) for bromocresol green (BCG), an acid-base indicator.

Discussion

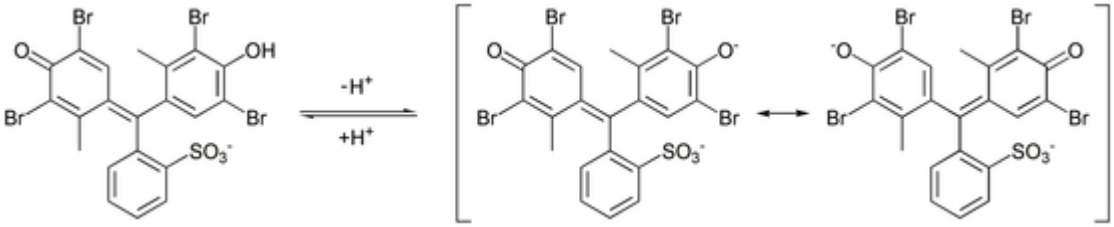
Acid-base indicators are often used to demonstrate the end-point of an acid-base reaction. Examples include phenolphthalein and the mixture of indicators used in universal indicator solution. Acid-base indicators are weak acids that dissociate into a hydronium ion (H_3O^+) and a conjugate base anion (In^-). This dissociation can be represented through the following equation and equilibrium expression:

$$\underset{\substack{\text{weak acid}\\\text{indicator}}}{HIn\,(aq)} + H_2O\,(l) \rightleftharpoons \underset{\substack{\text{hydronium}\\\text{ion}}}{H_3O^+(aq)} + \underset{\substack{\text{conjugate base}\\\text{indicator}}}{In^-(aq)} \qquad K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

In order for a compound to be a useful indicator, the acidic form (HIn) and the basic form (In^-) of the indicator should differ in color. Since equilibrium in acidic solution favors the formation of HIn, this species is called the acidic form of the indicator. Likewise, the In^- form is called the basic form since it is favored in basic solutions. An equilibrium mixture of the indicator will be colored according to the relative concentration of each form of the indicator. The position of the equilibrium and, therefore, the relative concentration of the two forms of the indicator will depend on the H_3O^+ concentration, $[H_3O^+]$ or in shorthand notation $[H^+]$.

The absorption curve of an indicator at different pH values can be studied to determine the equilibrium constant of the indicator. In this experiment, we will determine the equilibrium constant of bromocresol green (BCG). BCG is an indicator that is yellow in acidic solutions blue in basic solutions. When dissolved in water the conjugate pair (acidic and basic forms) display different absorption spectra since they possess different colors.

Structure of Bromocresol Green ($C_{21}H_{14}Br_4O_5S$, MM = 698 g/mol)



Acidic form
(yellow in solution)

Basic form- two resonance forms
(blue in solution)

For simplicity we'll use the following symbols to represent bromocresol green:

H_2B The protonated form of the indicator
HB^- The deprotonated form of the indicator
NaHB The sodium salt of the deprotonated form of the indicator
B^{2-} The fully deprotonated form of the indicator

The sodium salt of bromocresol green ionizes completely in water:
$NaHB\,(aq) \rightarrow Na^+(aq) + HB^-(aq)$

The HB^- form, which is a monoprotic acid, then partially dissociates to give B^{-2}:
$HB^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + B^{2-}(aq)$

Writing the dissociation without water (shorthand notation), we have

$$\underset{\text{acidic form (yellow)}}{HB^-(aq)} \rightleftharpoons H^+(aq) + \underset{\text{basic form (blue)}}{B^{2-}(aq)} \qquad K=\frac{[H^+][B^{2-}]}{[HB^-]}$$

HB^- is the acidic form and is yellow in solution. B^{2-} is the basic form and is blue in solution.

Taking logarithms of the above equation gives

$$\log K = \log [H^+] + \log \frac{[B^{2-}]}{[HB^-]}$$

$$\log \frac{[B^{2-}]}{[HB^-]} = pH + \log K$$

$$y = m\,x + b$$

where we have rearranged and noted that $pH = -\log [H^+]$.

This is a linear equation. A plot of $\log \frac{[B^{2-}]}{[HB^-]}$ versus pH should yield a straight line with a slope of 1 (m = 1) and an intercept equal to log K, where K is a concentration equilibrium constant. So our strategy will be to measure the ratio $\log \frac{[B^{2-}]}{[HB^-]}$ as a function of pH and use this data to determine the equilibrium constant for the dissociation of bromocresol green.

Absorbance and Spectrophotometry

Solutions that possess colors absorb visible light energy of specific wavelengths. Recall that a red solution appears red because it absorbs much of the blue-green part of the spectrum (complementary colors). Measurements of the amount of light absorbed by a substance at each wavelength (color) can be graphed giving an "absorption curve." The shape of this curve depends almost entirely on the electronic structure of the substance and is almost unique for each substance. Thus the curve serves as an aid to identification and, with the aid of modern theory, a clue to the structure of a substance.

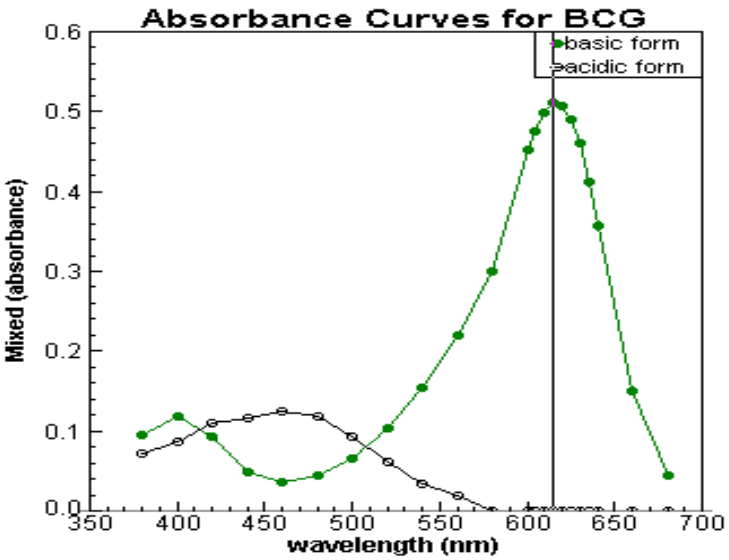
At a given wavelength the amount of light absorbed by a solute is proportional to its molar concentration, thus providing a widely used method of concentration analysis. The Beer-Lambert Law states that $A = \varepsilon lc$, where A = absorbance, ε = a constant characteristic of the absorbing molecule, l = path length, c = concentration. In our case, ε and l are each constant (known absorbing substance and a path length determined by the width of the cuvette). Thus the absorbance is proportional to the concentration in this experiment.

A spectrophotometer is an instrument used for measuring the amount of absorption at different wavelengths. Many such instruments are now commercially available. Some are designed to operate in the region of visible light, some in infra-red regions, some in ultra-violet and still others in several of these energy bands. You will use either a Spectronic 301 Spectrophotometer or a Genesys 20 Spectrophotometer to measured absorbance in this experiment. Both instruments are designed for use in the visible portion of the spectrum (400 to 700 nanometers, nm).

Determining the Equilibrium Constant

If the acidic form (HB^-) and basic form (B^{2-}) of an indicator both absorb light, then the ratio $\frac{[B^{2-}]}{[HB^-]}$ can be determined by measuring the absorption of light at the wavelength at which one of the forms absorbs a lot and the other form absorbs a little.

Plots of the absorption of light of various wavelengths (λ) versus wavelength for bromocresol green in its basic form and in its acidic form are shown in the chart to the right. Such graphs are called absorption spectra.



λ_{max}: Wavelength of maximum absorbance for base form

The graph shows that the basic form has maximum absorption (A_{II}) at λ_{max}. The absorbance of the acidic form (A_I) is small at λ_{max} (almost zero).

If we start with a solution of the pure basic form (B^{2-}) and add an acid to the solution (for example, acetic acid), then some of the basic form will be converted to the acid form (HB^-). Then the absorbance at λ_{max} will drop because the acidic form absorbs almost no light at λ_{max}. This change may be visible in that the solution will change from blue to yellow.

We will call an absorbance measurement with a mixture of the acidic and basic forms of the indicator A_x. In fact, all absorbance values along the vertical line drawn at λ_{max} in the graph are A_x values. These points all lie between A_{II} and A_I.

Referring back to the equation, $\log\frac{[B^{2-}]}{[HB^-]} = pH + \log K$, we see that in order to calculate the equilibrium constant, K, different ratios of $\frac{[B^{2-}]}{[HB^-]}$ must be found for different pH values. When these are plotted, a straight line with slope of one and y-intercept of log K is obtained. The relationship between the absorbance data at λ_{max} and the ratio $\frac{[B^{2-}]}{[HB^-]}$ is found from the following equation:

$\frac{[B^{2-}]}{[HB^-]} = \frac{A_x - A_I}{A_{II} - A_x}$ where

A_I = absorbance of the solution when all indicator is in the acidic form (pure HIn).

A_{II} = absorbance of the solution when all indicator is in the basic form (pure In^-).

A_x = absorbance of the solution when both some acidic and some basic form are present

Equipment: UV-vis spectrophotometer, two cuvettes, pipette pump, three 250-mL beakers, 100-mL graduated cylinder, 2-mL pipet, 10-mL graduated cylinder, Kimwipes, USB flash drive. Chemicals: 1.00 M acetic acid (HAc), 3.00 x 10^{-4} M bromocresol green (BCG), 0.200 M sodium acetate (NaAc), cuvette containing acidic form of BCG obtained from your instructor.

Use eye protection for this experiment.
Students will work in groups as assigned by the instructor.

Part 1: Absorbance Spectrum of Bromocresol Green in Basic and Acidic Solutions

1. We will need four solutions to perform this experiment. The instructions for making the first three are given in the text below. The fourth solution has already been prepared and will be distributed by your instructor in a cuvette. All solutions should be prepared in a graduated cylinder since volume markings on beakers are good to only 5%.

A. **Bromocresol green in sodium acetate solution**: Add 5.00 ml of 3 x 10^{-4} M bromocresol green solution and 5.00 mL of 0.200 M sodium acetate (NaAc) solution to a 100-mL graduated cylinder. Dilute to 100.0 mL with deionized water and pour quantitatively (this means all of the solution) into a clean, dry 250-mL beaker. This solution should be blue and will be referred to as the basic solution. The sodium acetate concentration in this solution is 0.0100 M.

B. **Acetic acid solution**: Rinse the graduated cylinder with distilled water, add 25.0 mL of the 1.00 M acetic acid (HAc) solution and dilute to 100.0 mL with deionized water. Pour this solution quantitatively into a clean, dry 250-mL beaker. The concentration of the acetic acid in this solution is 0.250 M.

C. **Blank Solution**: Add 5 mL of 1.00 M acetic acid and 5 mL of 0.200 M sodium acetate to a 100 mL graduated cylinder and dilute with deionize water to 100 mL.

D. **Bromocresol green solution in hydrochloric acid**: The instructor will supply a cuvette containing a BCG solution that has excess acid (HCl) added to it. This solution should be yellow.

A Note About Measuring Absorbance Using the Spectrophotometer and Use of the Blank Solution. Spectrophotometry measurements generally require that the absorbance of a blank solution be measured in order to counteract any absorbance or scattering of light from air, the container, solvents, and solutes. Once a "blank" has been performed, the instrument compares these signal losses from measurements of the signal coming from the sample. So a "blank" should always be performed prior to making a measurement at a particular wavelength. Likewise, when the wavelength setting of a spectrophotometer is changed (for example, from 400 nm to 420 nm) the amount of light reaching the detector can change. For that reason, it is necessary to perform a blank measurement again. If the wavelength setting isn't changed then a blank measurement isn't usually needed. However, optical and electronic properties of the spectrophotometer can "drift" over time. So if the instrument has been sitting for more than a few minutes, it's a good idea to re-perform a blank, even if the wavelength hasn't been changed. When in doubt, re-perform a blank measurement.

1. Measure the absorption spectrum of the solution containing BCG in sodium acetate (basic BCG solution) and the BCG solution containing HCl (acidic BCG solution) beginning at 380 nm and ending at 680 nm at 20 nm intervals. Record these measurements in the Data Sheet.

2. Review the absorbance data and locate the greatest value of the absorbance for the basic solution. Note what wavelength this absorbance corresponds to. Now measure the absorbance of the basic BCG solution and the acidic BCG solution at 5 nm intervals from 20 nm below to 20 nm above this wavelength. For example, if the wavelength of maximum absorbance occurs at 520 nm, make measurements at 5 nm intervals from 500 nm to 540 nm. However, don't duplicate readings—in this case don't take readings at 500 nm, 520 nm, and 540 nm.

3. Pour the BCG in sodium acetate solution in the cuvette back into the 250-mL beaker, taking care not to lose any of the solution.

4. Return the cuvette containing the acidic form of BCG to your instructor.

5. From the data taken for the basic and acidic forms, decide which wavelength is suitable for measuring A_x values and set the spectrophotometer at this wavelength. The suitable wavelength, $\lambda_{max,}$ is the wavelength in which the basic form has a maximum absorbance and the acidic form has a very small absorbance.

Part 2: Effect of pH on Absorbance of Bromocresol Green

1. Add precisely 2.00 mL of the 0.250 M acetic acid solution to the 250-mL beaker of BCG solution using a 2 mL pipet and a pipette pump. Mix the solution with a glass stirring rod and measure the absorbance at λ_{max}. Pour the solution in the cuvette back into the 250-mL beaker. Don't throw the solution in the cuvette out.

2. Add another 2.00 mL of the 0.250 M acetic acid solution, mix well, and measure the absorbance at λ_{max}. Again, pour the solution in the cuvette back into the beaker.

3. Repeat this procedure with a third and fourth 2.00 mL increment of the 0.250 M acetic acid solution. There should now be a total of 8.00 mL of 0.250 M acetic acid solution added to the BCG solution.

4. Rinse all solutions down the drain and clean any glassware used in the experiment before performing any calculations.

Data Sheet

Name_____ **Partner**_____

Partner_____

Absorbance Data at 20 nm Intervals		
wavelength (nm)	**Absorbance (basic form)**	**Absorbance (acidic form)**

Absorbance Data at 5 nm Intervals		
Wavelength (nm)	**Absorbance (basic form)**	**Absorbance (acidic form)**

Volume of Acetic Acid Solution Added (mL)	**Absorbance A_X**
2.00	
4.00	
6.00	
8.00	

λ_{max} = _____ nm. This is the wavelength having the largest absorbance of all the data you took for the basic form in the above tables.

Calculations

We will use graphical analysis to produce an absorbance spectrum of bromocresol green in basic and acidic solutions. Both spectra should be represented on the same chart. Vernier Graphical Analysis and Microsoft Excel are appropriate programs for this exercise. The instructions below are for Graphical Analysis.

1. Open Graphical Analysis on the computer.

2. Enter the combined absorbance data for the acidic form and base formic. Sort the data by wavelength. Label this data column (y-axis) "basic form"and enter "absorbance" for the units. Label the x-axis "wavelength" with units of "nm."

3. To graph the acidic form absorbance values in Graphical Analysis, you will need to add a second column to the Data Table Window. Do this by selecting New Column in the Data menu and choosing Manually Entered. Label the acidic data "acidic form" and enter "absorbance" for the units. Choose different point protectors for each of the two absorbance curves. Put a legend on the graph. This way you will be able to distinguish the curves.

4. You have now plotted two absorption spectra for bromocresol green—the blue basic form and the yellow acidic form. Also, in addition to A_I and A_{II}, you should have a precise measurement of the absorbance (A_x) of the bromocresol green solution at four different pH values. All these measurements have been taken at λ_{max}, the wavelength where the absorbance of the basic form of the indicator is at a maximum and the absorbance of the acidic form is very low. The next three pages can be used to perform the series of calculations required to find K_a for bromocresol green.

Name_____ **Partner**_____

Partner_____

1. Finding the number of moles of sodium acetate ($NaC_2H_3O_2$) in solution A

Molarity of sodium acetate solution on bottle _____

Volume of sodium acetate solution used in dilution in milliliters _____

Volume of sodium acetate solution used in dilution in liters (1000 mL = 1L) _____

Moles of sodium acetate solution used in dilution (n = MV) _____

2. Finding the molarity of acetic acid ($HC_2H_3O_2$) in solution B

Molarity of acetic acid solution on bottle _____

Volume of acetic acid solution used in dilution in milliliters _____

Volume of acetic acid solution used in dilution in liters _____

Moles of acetic acid solution used in dilution (n = MV) _____

Total volume of solution in dilution in milliliters _____

Total volume of solution in dilution in liters (1000 mL = 1 L) _____

Molarity of acetic acid in diluted solution (M = n/V) _____

1. Moles of Acetic Acid

Now we need to calculate the number of moles of acetic acid each time we added 2.00 mL of acetic acid solution to the bromocresol green solution in Part 2. The volume of acetic acid solution added was 2.00 mL through 8.00 mL. Convert these volumes to liters. The molarity of the acetic acid solution was calculated on the previous page and is the same for each addition. The moles of acetic acid added can be found from n = MV.

Volume of Acetic Acid Solution Added (mL)	**Volume of Acetic Acid Solution Added (L)**	**Molarity of Acetic Acid Solution (mol/L)* M = n/V**	**Moles of Acetic Acid Added (mol)**
2.00 mL			
4.00 mL			
6.00 mL			
8.00 mL			

*From the previous page. This amount should be the same for each addition.

2. Moles of Sodium Acetate (NaAc)

We also need to know the number of moles of sodium acetate used in the mixture for Part 2. This was calculated on the previous page.

3: Calculating the pH of the acetate solutions

The following table shows the progression of the calculations needed to find the pH of each solution in Part 2. We first use the moles of the acetic acid and the moles of sodium acetate (already calculated) to find the ratio of sodium acetate to acetic acid. We then take the log (base 10) of this ratio. The pH of a solution that contains a weak acid and its conjugate base is: $pH = pK_a + \log\left(\frac{\text{mol NaAc}}{\text{mol HAc}}\right)$. The pKa for acetic acid is 4.74. Find the pH of each solution.

Volume of Acetic Acid Solution Added (mL)	Moles of Acetic Acid* (mol)	Moles of Sodium Acetate* (mol)	$\frac{\text{moles sodium acetate}}{\text{moles acetic acid}}$	$\log\left(\frac{\text{mol NaAc}}{\text{mol HAc}}\right)$	pK_a of HAc	pH
2.00 mL					4.74	
4.00 mL					4.74	
6.00 mL					4.74	
8.00 mL					4.74	

***From 1.**

4: Equilibrium Constant K

To find the equilibrium constant (K_a) of bromocresol green we need to perform a plot of:

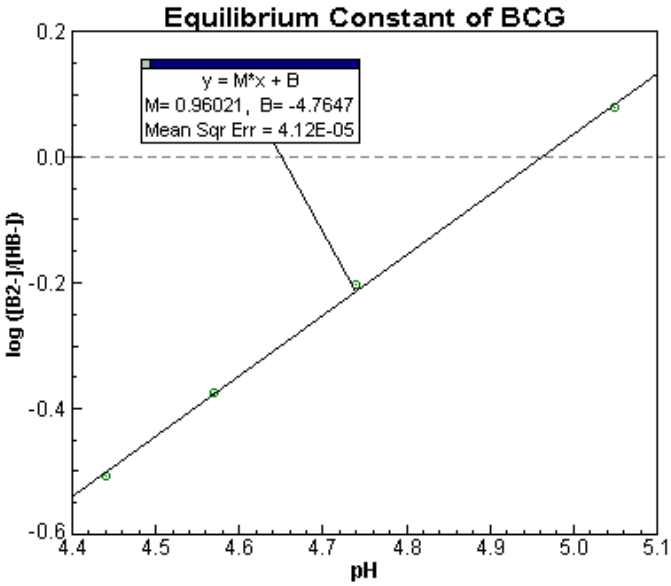
$\log \frac{[B^{2-}]}{[HB^-]}$ versus pH where pH is the x-axis. The following table shows the progression needed to find values needed for this graph. As a reminder (see page 3 for a more detailed discussion), A_{II} is the absorbance of the basic form of bromocresol green at the wavelength of maximum absorbance (λ_{max}). This absorbance was determined in Part 1 of the experiment and is a constant. A_I is the absorbance of the acidic form of bromocresol green at the wavelength of maximum absorbance (λ_{max}). This absorbance was also determined in Part 1 of the experiment and is also a constant. A_X is the absorbance of the bromocresol green solution after 2.00 mL additions of acetic acid solutions were made. With each addition of acetic acid solution, the bromocresol green became slightly more dilute, causing its absorbance to decrease. To compensate for this dilution use the following equation to correct for the dilution. Enter the values of these corrections in the column "Corrected A_X."

$\text{Corrected Absorbance} = A_X\left(\frac{100\,\text{mL} + V_{added}}{100\,\text{mL}}\right)$. Note that, unlike A_{II} and A_I, Corrected A_X varies. To complete the table, take the difference between Corrected A_X and A_I ($A_x - A_I$), the difference between A_{II} and A_X ($A_{II} - A_x$), and then take the ratio of these differences. The log of this ratio is equal to $\log \frac{[B^{2-}]}{[HB^-]}$. Re-enter the pH values from Step 3 in the calculations. Once you have completed the table you can construct the graph of $\log \frac{[B^{2-}]}{[HB^-]}$ versus pH and find K_a.

A_{II}	A_I	Corrected A_x	$\frac{A_x - A_I}{A_{II} - A_x}$	$\log \frac{A_x - A_I}{A_{II} - A_x} = \log \frac{[B^{2-}]}{[HB^-]}$	pH

Report

1. Hand in your original data tables, calculation tables, graphs, calculations and results.



2. Clearly indicate in your report the value of the equilibrium constant of BCG, K_a, and how you calculated it. K_a can be found from the y-intercept (B):

$B = \log (K_a)$
$K_a = 10^B$

3. When we calculate the pH of the solutions it's found by using the following equation:

$$pH = pK + \log \frac{(\text{moles sodium acetate})}{(\text{moles acetic acid})}$$

Bromocresol green is a weak acid, just like acetic acid. But our calculations assume that bromocresol green doesn't affect the overall acidity (pH) of the acetate solution. Why is this a good assumption? To prove this point, calculate the number of moles of bromocresol green (the indicator itself) in the sodium acetate solution and compare this number to the number of moles of sodium acetate and the number of moles of acetic acid used.

4. Type a discussion of your primary result. Compare your result to literature values. Discuss the accuracy of your result. Be sure to list the sources of your literature values.