# Experiment # 9: The Henderson-Hasselbalch Equation

A buffer is commonly defined as a solution that resists changes in pH when a small amount of acid or base is added or when the solution is diluted with pure solvent. This property is extremely useful in maintaining the pH of a chemical system at an optimum value to appropriately influence the reaction kinetics or equilibrium processes. A buffer solution actually is a mixture of a weak acid and its conjugate base or a mixture of a weak base and its conjugate acid. The conjugate forms are commonly referred to as "salts".

For a typical weak acid, the dissociation equilibrium is represented as:

$$\text{Acid} \rightleftharpoons H^+ + \text{Base}; \quad K_a = \frac{[H^+]\,[\text{Base}]}{[\text{Acid}]}$$
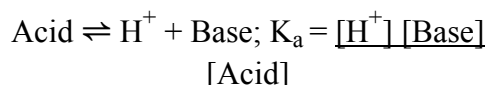
according to the Bronsted-Lowry concept. If a pure weak acid is dissolved in a pure solvent the concentrations of H^+ and conjugate Base will be equal, neglecting autoprotolysis of the solvent. Rearranging the dissociation constant equation and solving for $[H^+]$ gives: $[H^+]$ = $[K_a (\text{Acid})]^{1/2}$. If other factors governing conjugate base concentration are present in the system (either as added salt of the weak acid or as added base to partially neutralize the acid), the concentrations of H^+ and conjugate Base will no longer be the same. Under these conditions, the equation for $[H^+]$ becomes:

$$[H^+] = K_a\,[\text{Acid}]/[\text{Base}] = K\,[\text{Acid}]/[\text{Base}].$$

Taking negative logarithms of both sides of the above equation gives:

$$-\log([H^+]) = -\log(K_a) - \log([\text{Acid}]/[\text{Salt}])$$
$$\text{or } pH = pK_a - \log([\text{Acid}]/[\text{Salt}]).$$

Upon inversion of the argument the last log term becomes positive, as:

$$pH = pK_a + \log([\text{Salt}]/[\text{Acid}]).$$

This form of the ionization or dissociation constant expression is called the Henderson-Hasselbalch equation. This equation is very useful in calculating the pH of a solution containing a weak acid and its conjugate base (or salt). A comparable equation is obtained for a buffer solution consisting of a mixture of a weak base and its salt, namely:

$$pOH = pK_b + \log([\text{Salt}]/[\text{Base}]).$$

Solutions of a weak acid and its salt (conjugate base) may be obtained by mixing an excess of weak acid with some strong base to produce the salt by partial neutralization. A similar mixture can be obtained by mixing an excess of salt with a strong acid to produce the weak acid component. Most often, however, a weak acid-conjugate base buffer is prepared by a direct mixing of the weak acid with

its salt. This third method allows an accurate control of the concentrations of both the weak acid and conjugate base species.

The buffering mechanism of a mixture of a weak acid and its salt can be explained as follows. The buffer pH is governed by the logarithm of the ratio of the salt and acid concentrations, as: pH = constant + log ([Salt]/[Acid]), where the constant is the pK_a of the particular weak acid used in the buffer. If the buffer solution is diluted with pure solvent, the common volume of the salt and acid components is increased, but the amounts of each are unchanged. Consequently, the ratio remains constant, and the solution pH does not change. (In actuality, the pH increases slightly due to an increase in the activity coefficient of the salt resulting from the decrease in ionic strength. But for practical purposes, the pH does not change significantly)

If a small amount of a strong acid is added to the buffer, the strong acid will combine with an equivalent amount of the conjugate base, converting it to the weak acid form. Thus, [Salt] decreases and [Acid] increases, but the logarithm of the overall ratio does not change significantly. A comparable affect is seen if a small amount of strong base is added to the buffer; the [Salt] increases slightly as the [Acid] decreases accordingly, but the logarithm of the ratio changes only slightly.

The amount of acid or base that can be added without causing a large change in pH is governed by the buffering capacity of the solution. This property is determined by the relative concentrations of acid and salt. The higher their concentrations, the more acid or base the solution can accommodate before the relative acid/salt ratio is changed. The buffering capacity is also controlled by the ratio of acid to salt. The capacity is at a maximum when the ratio is unity, that is, when the pH = pK_a. In general, the buffering capacity is satisfactory over a pH range of $pK_a \pm 1$.

A buffer solution of a given pH can be prepared by choosing a weak acid (or a weak base) and its conjugate salt that has a pK_a value near the pH (or pOH) that is desired. There are a number of such weak acids and bases, and any pH region can be buffered by a proper choice of components. The salt does not react with water (or other solvent) to ionize as an acid or base due to the presence of the acid or base in the mixture. The presence of appreciable amounts of acid will suppress the ionization of the salt to the acid form (and similarly for a weak base/salt buffer system).

In this experiment, the dissociation constant, K_a, of a weak acid will be determined by a technique based on the Henderson-Hasselbalch relationship. Specifically, standard solutions (equimolar) of a weak acid and its conjugate base (or salt) will be mixed in a standard series. For this system, it may be considered that negligible reaction occurs, since transferring a proton between the species in a conjugate acid-base pair changes nothing, and the relative concentrations of the conjugate pair species in the mixture will be the same as that in the proportionate volumes of standard solutions.

Plots of measured mixture pH versus various functions of the conjugate pair concentrations will be made in order to demonstrate the usefulness of the Henderson-Hasselbalch equation in determining the acid strength (i.e., K_a) of the weak acid in the buffer. The functions of conjugate pair concentrations to be examined with respect to mixture pH include: volumes of acid (or salt), ratio of volumes of salt and acid, and logarithm of the ratio of volumes of salt and acid.

Interpretations of the resulting plots should show that the Henderson-Hasselbalch equation gives an accurate description of the variation of pH in mixtures of conjugate pairs or buffers. If such a plot of pH versus log ratio salt/acid results in a straight line, the intercept should measure the acid dissociation

constant, K_a. Being assured that the relationship is valid allows the preparation of a buffer of desired pH by a simple mixing of the acid and its salt in the ratio indicated by the equation for the desired pH.

Preparation of buffer mixtures

Students will work in groups of no more than three students. One or more buret stations will be set up. Each will consist of a buret stand and clamp supporting a pair of 50.00-mL burets. The number of such stands and the responsibility for setting them up will be determined by the lab instructor. Those responsible will clean the burets, and rinse each with one of the standard equimolar solutions of acid or salt provided on the storage table. The weak acid is a 0.100 M acetic acid solution; the salt or conjugate base is a 0.100 M sodium acetate solution. Fill each of the burets with the standard solution used as that burets final rinse, either acid or salt.

Collect a set of fourteen clean, labeled, dry test-tubes (15 x 125 mm), following the specified volumes of acid and salt listed in Table I, prepare a standard mixture series of buffers. Note that the total volume of each mixture is 10.0 mL. Be sure that all acid-salt mixtures are well mixed, and do not get the test tubes out of order. An easy check is to remember that the pH should increase steadily as the salt content is increased. If a mixture does not fit into the trend when the pH is measured, discard the buffer, and prepare a new mixture of the appropriate volumes of acid and salt solutions.

Measurement of buffer mixture pH's

Use standard buffers of pH = 7 and pH = 4 to calibrate a pH meter, as described in Experiment 8. In these measurements of pH, the combination electrode will be inserted into each of the test tubes, and the solution stirred to take a pH reading. Rinse the electrode with deionized water after the calibration (making sure to turn the pH meter control to "standby" whenever the electrode is removed from solution), and dry the outside/bottom with tissue paper before immersion into the test samples. Measure the pH of each of the twelve buffer mixtures and the two solutions of pure acid and salt. Record the experimentally determined pH of each mixture in Table I, reading the pH value to the second decimal place. Check to see that the pH values follow the expected trend of increasing with salt content. When the pH of each buffer mixture has been determined, discard the solutions, and clean the test tubes.

Data treatment and report

A three-page report will be required for this experiment. On the first page, make a complete, titled, copy of the data in Table I, including a heading and all pertinent information about the acid and salt solutions. The remaining two pages of the report will be graphs of measured pH versus functions of acid and salt concentrations.

The second page should include two half-page plots, one for pH versus volume of acid and the other for pH versus salt/acid ratio. Since the acid and salt standard solutions are equimolar (each is 0.100M), the resulting concentrations can be expressed in terms of the number of mL's of each solution in the mixture. For the two plots, the scales should be chosen such that one-half of the graph page is used for each plot. The ordinates should be appropriately scaled to present the graphs as large as feasible. The abscissa should be mL's of acid or ratio of salt/acid with a range of mL's 0 to 10.0 or ratio's 0 to 5. In each plot, connect the experimental data points in a smooth curve, and do not attempt to force a straight line unless the actual points call for one.

On the third page, make a single plot of pH (ordinate) versus log ratio salt/acid (abscissa), using appropriate large scales. Since the log of ratio values will range from negative to positive numbers, set the ordinate origin in the center of the long side of the papers and place negative log values on the left side and positive log terms on the right side. Select a pH scale such that the experimental data points cover the full graph page.

Table I

Sample #	mL acid	mL salt	Salt/acid ratio	Log ratio	pH
1	10.00	0.00			
2	8.00	2.00			
3	7.50	2.50			
4	7.00	3.00			
5	6.50	3.50			
6	6.00	4.00			
7	5.50	4.50			
8	4.50	5.50			
9	4.00	6.00			
10	3.50	6.50			
11	3.00	7.00			
12	2.50	7.50			
13	2.00	8.00			
14	0.00	10.00			

Draw the best straight line through the data points, assuming that the Henderson-Hasselbalch equation is valid: $pH = pK_a + \log ([salt]/[acid])$. Determine the value of the pH at the intersection of the data point line through the ordinate axis; this value of pH equals the pK_a of the weak acid. Write the value on the graph beside the point of intersection, and label it as pK_a .

Look up the literature value for the pK_a of acetic acid, and record this as the "literature" value on the first page of the report, citing the source. Record the experimental value of pK_a for acetic acid, labeling it "Henderson-Hasselbalch" value.