We judge ourselves by what we feel capable of doing, while others judge us by what we have already done. --Longfellow

The Common Ion Effect and Buffer Solutions

From our discussion in class you are already aware that acids and bases can be divided into two large groups: *weak* and *strong*. One characteristic which distinguishes, for example, HCl from CH_3COOH is the extent to which each molecular substance dissociates into ions in solution. We make this distinction on paper when we write the expressions:

$$HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

$$CH_3COOH(aq) + H_2O(\ell) \leftrightarrows H_3O^+(aq) + CH_3COO^-(aq)$$

The first equation is a system which goes to completion while the second one represents an equilibrium system. So we are not surprised to find that a 1 Molar solution of HCl will have more $H_3O^+(aq)$ present than a 1 Molar solution of CH_3COOH.

Since the weak acid system is subject to the same factors which affect other systems at equilibrium, we might also expect some kind of reaction to occur when excess acetate ion (CH_3COO^-), the conjugate base of acetic acid, is added. In contrast, the HCl should not be affected by the addition of excess Cl^-.

Mixed solutions involving weak acids or bases and their conjugates demonstrate an interesting application of the common ion effect: maintaining the pH within a narrow range. Such mixtures are called buffer solutions. Their behavior is based on establishing excesses of both the original acid or base, and the conjugate (generally obtained by adding a salt). For the hypothetical pair HA (a weak acid) and NaA (a salt containing the ion A^-, the conjugate base of HA) this system of reactions is relevant in aqueous solution:

$$HA(aq) + H_2O(\ell) \leftrightarrows H_3O^+(aq) + A^-(aq)$$
$$NaA(s) \rightarrow Na^+(aq) + A^-(aq)$$

The presence of excess A^- (the "common ion") causes a shift in the equilibrium of the first reaction and sets up the required condition for buffering behavior.

In this experiment you will have a chance to investigate these and other behaviors by using a *universal indicator*.

Acid-base indicators are generally weak acids (hence we typically add them in small amounts) which are distinguished by the fact that the molecular form of the acid is a different color than the conjugate base. For the hypothetical indicator HIn we might write:

$$\underset{\text{color 1}}{HIn} + H_2O \leftrightarrows H_3O^+ + \underset{\text{color 2}}{In^-}$$

Changing the concentration of H_3O^+ (or the pH) will thus change the color of the indicator. An indicator like that represented above will probably have three colors since at the 50% distribution point (when [HIn] = [In^-]) colors 1 and 2 will blend to yield a transition color. This is true of indicators like bromthymol blue which is yellow in acidic solutions, blue in basic solutions, but green in neutral mixtures. Phenolphthalein is somewhat unusual in that the molecular form is colorless. Thus there is only the transition from colorless to pink as a solution becomes basic.

The universal indicator you will use in this experiment contains both of these indicators and others. Each indicator in the recipe is chosen so that the pH range from 1 to 14 is covered either by individual color changes or by overlapping colors of several indicators. The effect is like "liquid pH paper". Incidentally, the technique of choosing the proper indicator for a situation is not difficult. A table of indicator K_a values is all that is required. An indicator is chosen so that its pK_a ($-\log K_a$) is the same as the pH of interest.

Preparing to experiment

You will be provided with the following materials:

1. 0.10 M HCl solution
2. solid NaCl
3. 0.10 M CH_3COOH solution
4. solid $NaCH_3COO$
5. a mixed solution that is 1.0 M in *both* CH_3COOH and $NaCH_3COO$
6. a mixed solution that is 0.10 M in *both* CH_3COOH and $NaCH_3COO$
7. 0.20 M NaOH
8. pH buffer solutions (1-6)
9. universal indicator solution (use 2 drops each time)
10. a 24/96-well combination micro-plate
11. a disposable beral pipet
12. a plastic stirrer

Design an experiment in which you:

--determine the pH of each acid-containing solution provided (in each case you only need to use enough solution to cover the bottom of the well--about 2 drops).

--determine the effect on pH of adding a small amount of solid with a common ion to the HCl and CH_3COOH

--determine the effect on pH of adding 2 drops of HCl to the 0.10 M CH_3COOH and the 0.10 and 1.0 M mixed acetic acid solutions

--titrate each acid-containing solution with NaOH to pH 6 (in each case start with about 10 drops of the acidic solution and use 4 drops of indicator; estimate pH to 0.5 after each drop)

Pre-lab take-home quiz

These questions should be answered on a separate sheet of paper to be turned in on the same day you begin this experiment.

1. Using "HBb" as the chemical formula for the indicator Bromthymol blue, write the equilibrium dissociation for this substance in water and identify which form is yellow and which is blue.

2. Write the K_a expression for "HBb" ($K_a = 1 \times 10^{-7}$) and *explain* why the indicator is green in neutral solution. Alternatively, explain why an indicator is selected so that its pK_a (that is, $-\log K_a$) value is equal to the pH of interest in an experiment.

3. Write the equilibrium reaction for the dissociation of the weak acid HA in water and describe what you would expect to happen to the pH of such a solution if NaA (containing the common ion A^-) is added and WHY. (*hint:* LeChâtelier's principle)

4. When equal volumes of 0.10 M CH_3COOH and 0.10 M $NaCH_3COO$ are mixed, what is the relationship between $[CH_3COOH]$ and $[CH_3COO^-]$ in the solution? What is the relationship between K_a and $[H^+]$ in the solution? (*hint:* write out the K_a expression and plug in the concentrations to see what happens!)

Analysis

1. Since they have the same Molarity, account for the difference in pH of the HCl and CH_3COOH solutions.

2. The two mixed acetic acid/sodium acetate solutions have different Molarities. Account for the pH values you recorded. [*hint*: look back at your answer to PLTHQ #4]

3. Explain the pH results of adding the solids containing the common ions to the two acid solutions [*hint*: LeChâtelier's Principle]

4. Solutions containing weak acids and their conjugate bases (or weak bases and their conjugate acids) are called "buffer solutions" because they resist changes in pH. Compare the effect of adding HCl to 0.10 M acetic acid and to the 0.10 M and 1.0 M mixed acid/salt solution (which are buffer solutions). Write the equilibrium dissociation reaction of acetic acid in water. Write the 100% dissolution of sodium acetate in water. In the mixture these two reactions occur in the same system. Can you suggest a reason why the mixed solutions are able to maintain a fairly constant pH when acid is added?

5. "Buffering capacity" is a term used to describe how much acid or base a buffer can absorb for a certain small change in pH. Based on your titration results, which buffer mixture (1.0 M or 0.10 M) had the greater capacity? Why?

6. Compare the changes in pH for the titrations of the 0.10 M HCl, 0.10 M CH_3COOH and the 0.10 M buffer solution. As the acetic acid is being titrated it forms a buffer solution (until it is completely neutralized). Why does this happen and what evidence of this behavior is there in the titration data?