The Hong Kong Polytechnic University
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Laboratory Worksheet C17: **pH, Buffer, and Titration**.

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Objective:    To review the concept of acid-base equlibria and to obtain the basic understandings of the acid-base titration. Be capable to calculate the buffer capacity of a known or unknown acid solution through titration experiments.

Reminder:    Care must be taken when handling the acids and bases. Wear gloves and safety goggles before working on the chemicals.

**Introduction**

Titration is commonly used by environmental researchers to quantify the ion strength of an unknown acid or base in water environments. In this experiment, three acid solutions (i.e. one strong acid and two weak acids) will be titrated by a strong base (0.1M NaOH). You will plot the titration curves of the solutions and use them to evaluate the ionization constant ($K_A$) and calculate the buffer indexes of the acids. The titration curve of a weak acid (HA) can be described by the ionization function, such as:

$$HA \leftrightarrow H^+ + A^- \qquad (1)$$

where HA is the dissolved weak acid before dissociation; $A^-$ is dissociated acid ion; $H^+$ is the dissociated hydrogen ion. This reaction is always under equilibrium, and the relationship among the dissolved ions under equilibrium can be described by the ionization constant $K_A$ as follows:

$$K_A = \frac{[H^+][A^-]}{[HA]} \qquad (2)$$

where the square brackets [ ] represents the molar concentrations (M) of the acid and the ions.

Henderson-Hasselbach equation was derived based upon Equation (2), which can be used to calculate the pH of the solution during the titration.

$$pH = pK_A + \log\frac{[A^-]}{[HA]} \qquad (3)$$

where pH and $pK_A$ are the negative logarithms of the molar concentrations of the hydrogen ion and $K_A$ (i.e. $pH = -\log[H^+]$; $pK_A = -\log K_A$). $K_A$ can be calculated mathematically by incorporating the titration data and the Henderson-Hasselbach equation with charge and mass balances. We will cover more details about this technique in the lecture.

Another way to define $K_A$ is to direct estimate the constant from the titration curve. A titration curve of a weak acid was shown in Figure 1. In the figure the pH and $\triangle$pH were plotted against the volume of titrant. The titration process can be classified into different phases, such as the initial phases, titration midpoint, and equivalence point. The equivalence point is achieved when a significant change in pH and $\triangle$pH occurs, and the midpoint is defined when 1/2 volume of the titrant was added (comparing to the volume used at the equivalence point). At the titration midpoint approximately a half of HA is dissociated hence the concentrations of HA and $A^-$ are approximately equal (i.e. [HA]=[A$^-$]). If we plug this relationship in Equation (3), the second term of the equation (i.e. log [A$^-$]/[HA]) becomes zero. The pH is equal to $pK_A$ at the titration midpoint. $pK_A$ can be defined by reading from the curve.
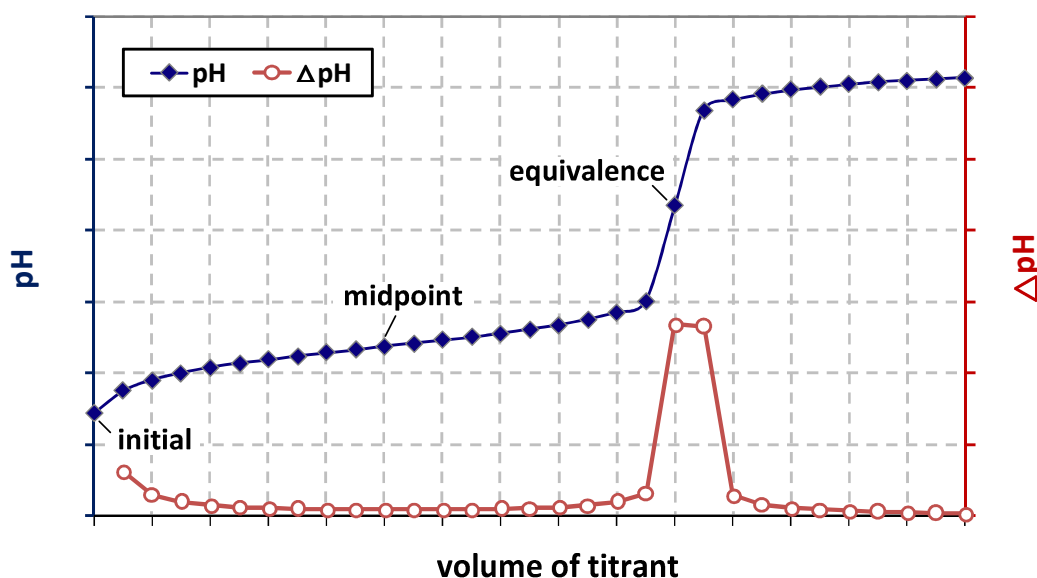


Figure 1. Example of a weak acid titration curve using strong base as the titrant.

Buffer index ($\beta$) is developed to quantitatively indicate the capacity of the buffer. The buffer index is defined as the slope of a titration curve of pH versus moles of strong base added ($C_B$), and can be calculated by the following equation:

$$\beta = \frac{-dC_B}{dpH} = 2.303 \left[ \frac{K_W}{[H^+]} + [H^+] + \frac{C_T K_A [H^+]}{(K_A + [H^+]^2)} \right] \quad (4)$$

where 2.303 is the unit converter; $K_W$ is the ionic product (i.e. a constant = $10^{-14}$); $C_T$ is the total concentration of the acid. Buffer index can be calculated when $K_A$ and the molar concentration of the weak acid is available.

**Apparatus and Materials**

- pH probe
- Buret
- 250 mL beaker
- 0.1M NaOH
- Solution A – 0.1M HCl
- Solution B – 0.1M CH$_3$COOH
- Solution C – 0.1M unknown acid

**Procedures**

1. Calibrate the pH probe by using two standard buffers (i.e. pH7 and a pH10 or pH4 buffers).
2. Rinse the pH probe with distilled (DI) water and blot dry gently.
3. Place exactly 100 mL of DI water in the 250 mL beaker. Add 8.0 mL of the untested solution in the beaker.
4. Rinse the burette by the standard base solution (0.1M NaOH) and then fill the burette with the standard base.
5. Assemble the titration equipment as shown in Figure 2. Place the pH probe in the solution (Note: be careful to leave sufficient space between the head of the pH probe and the magnitude stirring bar) and stir until the reading is steady. Record the pH in the attached sheet.

6. Slowly add the standard base into the beaker and record the volume of base added. Keep stirring and record the pH after the reading is stabilized. At least one reading of the volume and pH should be recorded per 0.2-pH change.

7. Continue to titrate until pH reach 10.

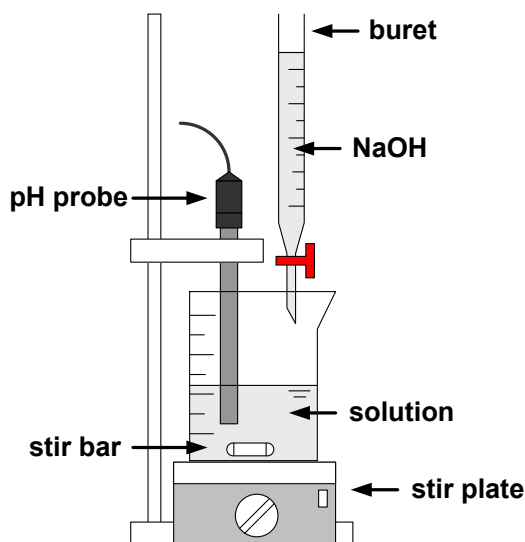8. Repeat step 3 to step 7 for the other two acids.



Figure 1 setup of the titration tests

## Results and Discussion

1. Plot the following curves for the three titrated acids: (1) the titration curves (pH versus volume of titrant), and (2) the curves of the pH derivatives ($\triangle$ pH versus the volume of titrant). You may plot the curves by hand or in an excel spreadsheet.

2. Estimate the $K_A$ of the weak acids and compare the results with reference values (Appendix B). Suggest a type of unknown acid been tested for solution C.

3. Calculate the buffer index of the strong and weak acids before titration.

4. Discuss the meanings of the titration experiments and the importance of the findings.

## Useful Links

Titration Simulation Software – http://www2.iq.usp.br/docente/gutz/Curtipot_.html#Download

Online Laboratory (Virtual Lab Applet) – http://www.sciencegeek.net/VirtualLabs/VLab.html

# Appendix A – Data Record Sheet

| Solution A | | | Solution B | | | Solution C | | |
|---|---|---|---|---|---|---|---|---|
| Volume (mL) | pH | $\triangle$pH | Volume (mL) | pH | $\triangle$pH | Volume (mL) | pH | $\triangle$pH |
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# Appendix B – Ionization Constants of Common Acids

## Table / 3.5

### Common Acids and Bases and Their Equilibrium Constants When Added to Water at 25°C

| Acids | | | | Bases | | |
|---|---|---|---|---|---|---|
| | Name | $pK_a = -\log K_a$ | | | Name | $pK_b = -\log K_b$ |
| $HCl$ | Hydrochloric | $-3$ | | $Cl^-$ | Chloride ion | 17 |
| $H_2SO_4$ | Sulfuric | $-3$ | | $HSO_4^-$ | Bisulfate ion | 17 |
| $HNO_3$ | Nitric | $-1$ | | $NO_3^-$ | Nitrate ion | 15 |
| $HSO_4^-$ | Bisulfate | 1.9 | | $SO_4^{2-}$ | Sulfate ion | 12.1 |
| $H_3PO_4$ | Phosphoric | 2.1 | | $H_2PO_4^-$ | Dihydrogen phosphate | 11.9 |
| $CH_3COOH$ | Acetic | 4.7 | | $CH_3COO^-$ | Acetate ion | 9.3 |
| $H_2CO_3^*$ | Carbon dioxide and carbonic acid | 6.3 | | $HCO_3^-$ | Bicarbonate | 7.7 |
| $H_2S$ | Hydrogen sulfide | 7.1 | | $HS^-$ | Bisulfide | 6.9 |
| $H_2PO_4^-$ | Dihydrogen phosphate | 7.2 | | $HPO_4^{2-}$ | Monohydrogen phosphate | 6.8 |
| $HCN$ | Hydrocyanic | 9.2 | | $CN^-$ | Cyanide ion | 4.8 |
| $NH_4^+$ | Ammonium ion | 9.3 | | $NH_3$ | Ammonia | 4.7 |
| $HCO_3^-$ | Bicarbonate | 10.3 | | $CO_3^{2-}$ | Carbonate | 3.7 |
| $HPO_4^{2-}$ | Monohydrogen phosphate | 12.3 | | $PO_4^{3-}$ | Phosphate | 1.7 |
| $NH_3$ | Ammonia | 23 | | $NH_2^-$ | Amide | $-9$ |

SOURCE: From Mihelcic (1999), reprinted with permission of John Wiley & Sons, Inc.