

Acid-Base Equilibrium Constants, K_a & K_b

Objective

In this experiment, you will:

- Gain more experience preparing solutions of specified concentration.
- Experimentally determine the dissociation constant, K_a , of an acid.
- Investigate the effect of initial solution concentration on percent ionization of an acid.
- Experimentally estimate the ionization constants for weak acids and hydrolysis constants for weak bases.

Weak Acid Ionization, K_a

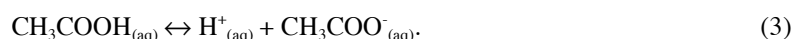
Weak acids IONIZE a few percent (or less) in water. As a result equilibrium is established between the molecular and ionized forms. For a general weak acid such as $HA(aq)$ we write the acid IONIZATION equilibrium as:



The equilibrium constant expression for the ionization is called K_a and is written as

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]} \quad (2)$$

One acid to be used in this experiment is acetic acid:



The acetate ion produced, CH_3COO^- , is the CONJUGATE BASE of acetic acid. The K_a for the ionization is written as

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \quad (4)$$

The experimental K_a for acetic acid¹ is 1.75×10^{-5} at $25^\circ C$.

For weak acids, the larger the value of K_a , the greater the % ionization and consequently more products are produced at equilibrium. The greater the value of K_a the “stronger” is the weak acid. Weak acids can also be ranked by strength using pK_a values:

$$pK_a = -\log K_a \quad (5)$$

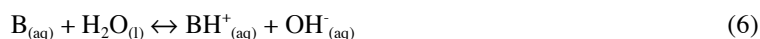
The pK_a of acetic acid is 4.756. The “stronger” the weak acid the smaller the pK_a value. Table I gives the K_a and pK_a of some common weak acids. They are ranked according to strength.

Table I. Some Common Weak Acids in Water at $25^\circ C$

Acid	Molecular Formula	Conjugate Base	K_a	pK_a
Hydrofluoric	HF	F ⁻	6.8×10^{-4}	3.17
Nitrous	HNO ₂	NO ₂ ⁻	4.5×10^{-4}	3.35
Benzoic	C ₆ H ₅ COOH	C ₆ H ₅ COO ⁻	6.5×10^{-5}	4.19
Acetic	CH ₃ COOH	CH ₃ COO ⁻	1.75×10^{-5}	4.756
Hypochlorous	HClO	ClO ⁻	3.0×10^{-8}	7.52
Hydrocyanic	HCN	CN ⁻	4.9×10^{-10}	9.31

Weak Base Hydrolysis, K_b

Weak bases HYDROLYZE a few percent (or less) in water. As a result equilibrium is established between the molecular and HYDROLYZED forms. For a general weak base such as $B(aq)$ we write the base HYDROLYSIS equilibrium as:

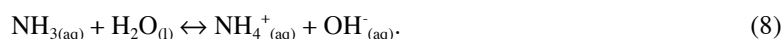


¹ Lange's Handbook of Chemistry, 14th ed. 1992.

In hydrolysis, one of the O-H bonds in water is broken and the hydrogen ion is transferred to the weak base producing its CONJUGATE ACID while leaving behind a hydroxide ion. The equilibrium constant expression for the hydrolysis is called K_b and is written as

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \quad (7)$$

One weak base to be used in this experiment is ammonia, NH_3 :



The ammonium ion, NH_4^+ , is the conjugate acid of ammonia. The K_b for the hydrolysis is written as

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \quad (9)$$

The experimental K_b for ammonia is 1.8×10^{-5} at 25°C .

Analogous to weak acids, for weak bases the larger the value of K_b the greater the % hydrolysis and consequently more products are produced at equilibrium. The greater the value of K_b the “stronger” is the weak base. Weak bases can also be ranked by strength using $\text{p}K_b$ values:

$$\text{p}K_b = -\log K_b \quad (10)$$

The $\text{p}K_b$ of ammonia is 4.74. The “stronger” the weak base the smaller the $\text{p}K_b$ value.

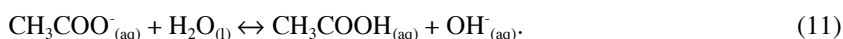
Acidic and Basic Salts

Salts can also be classified according to their acid-base behavior. The acid-base behavior of salts comes from the possible interaction of the cations and anions with the water solvent. Many ions are able to react with water to generate H^+ or OH^- ions. A salt that contains a basic anion will be basic. A salt that contains an acidic cation will be acidic. A salt that contains neither a basic anion nor an acidic cation will be neutral. Examples salts are:

1. Sodium acetate, NaCH_3COO . The Na^+ ion is neutral. The CH_3COO^- ion is basic since it is the conjugate base of a weak acid. Sodium acetate is a basic salt and when dissolved in water will produce a basic solution.
2. Ammonium chloride, NH_4Cl . The NH_4^+ ion is acidic since it is the conjugate acid of a weak base. The Cl^- ion is neutral. Ammonium chloride is an acidic salt and when dissolved in water will produce an acidic solution.
3. Sodium chloride. Both ions are neutral. Sodium chloride is a neutral salt.

Basic Anions in Salts

Anions, A^- , of a salt **that are the conjugate base of a weak acid** react with water (hydrolysis) to form OH^- ions and are thus **basic** anions. For example the acetate ion is basic:



An equilibrium is established in water between the anion and the conjugate acid of the anion, acetic acid. As a result of this hydrolysis reaction, a solution of sodium acetate will be basic ($\text{pH} > 7$).

An equilibrium constant expression can be written for the anion hydrolysis reaction and is given the symbol K_b since the reaction produces a basic solution:

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = 5.71 \times 10^{-10} \quad (12)$$

As always, K_b is calculated from equilibrium concentrations. K_b for the acetate ion is found to be 5.71×10^{-10} .

In contrast, anions that are the conjugate base of a strong acid, such as NO_3^- from HNO_3 , are not basic since no hydrolysis reaction takes place. The nitrate ion is much too weak a base to take a proton from water.



Acidic Cations in Salts

All cations except the group I and the heavier alkaline earth metals (Ca^{2+} , Sr^{2+} , and Ba^{2+}) act as weak acids in solution. It may surprise you that metal ions, such as Al^{3+} , and the transition metal ions form weakly acidic solutions. However, for this experiment we will be concerned with the ammonium ion, NH_4^+ . Ammonium reacts with water to produce hydronium ions:



An equilibrium is established in water between the cation and the conjugate base of the cation, ammonia. As a result of this ionization a solution of ammonium chloride will be acidic ($\text{pH} < 7$). An equilibrium constant expression can be written for the cation ionization and is given the symbol K_a since the reaction produces an acidic solution:

$$K_a = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = 5.6 \times 10^{-10}. \quad (15)$$

As always, equilibrium concentrations are used to calculate K_a . The accepted K_a for the ammonium ion is 5.6×10^{-10} .

The Relationship Between K_a and K_b for CONJUGATE Acid-base Pairs.

Since a weak acid is related to its conjugate base through the equilibrium constant expression K_a , and a base is related to its conjugate acid through the equilibrium constant expression K_b , it seems natural that the equilibrium constants for an acid-base conjugate pair are also related. One can show that the product of K_a for the acid and K_b for the conjugate base equals K_w :

$$K_a \times K_b = K_w \quad \text{or} \quad \text{p}K_a + \text{p}K_b = \text{p}K_w = 14.00 \quad (16)$$

For example, the K_a of acetic acid is 1.75×10^{-5} . The conjugate base of acetic acid is the acetate ion, CH_3COO^- . Therefore K_b for the acetate ion must be

$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}. \quad (17)$$

Thus, measurements of K_a will give you K_b for the conjugate base and vice versa.

Procedure

Determining K_a and K_b for Acidic or Basic Salts.

The K_a for an acid salt or K_b for a basic salt will be determined from a single pH measurement for a known concentration of the salt. Since a pH measurement gives $[H^+]_e$, the equilibrium concentration of hydrogen (hydronium) or OH^- ions can be found. Using a reaction table the equilibrium concentrations of the remaining species can be determined. The value of K_b or K_a is then calculated.

MATERIALS

LabPro System	0.50 M CH_3COOH (acetic acid)
TI Graphing Calculator	Distilled water
Vernier pH Electrode	100-mL volumetric flask
4 250-mL beakers	10-mL volumetric pipet
50-mL beaker	pipet bulb
8 large test tubes	600-mL beaker
Salt Solutions:	
0.10 M sodium acetate	0.10 M ammonium acetate
0.10 M ammonium chloride	0.10 M sodium carbonate
0.10 M sodium bicarbonate	0.10 M sodium phosphate
0.10 M sodium hydrogen phosphate	0.10 M sodium dihydrogen phosphate

1. Obtain and wear safety goggles.
2. Obtain about 5 to 10 mL of pH 4 and pH 10 buffer solutions in large, clean, dry test tubes.
3. **Calibrate the pH sensor with pH 4 and 10 Buffers. See the LabPro Quick Start Guide for details.**
4. Obtain about 40-mL of the 0.50 M acetic acid solution in a clean, dry 50-mL beaker. Prepare 100 mL of a 1/10 dilution of the stock acetic acid solution using volumetric glassware.
 - a) Rinse the electrode thoroughly with deionized water and pat the outside of the electrode dry with a paper towel.
 - b) To determine the pH of your two acetic acid solutions:
 - c) Rinse the electrode by pouring a small portion of the acetic acid solution being measured over the bulb portion of the pH electrode. Catch the rinse in a 600-mL beaker.
 - d) Use the remaining portion of the acetic acid solution to determine the pH. Immerse the pH electrode into the solution and swirl the solution (**not electrode!**) continually. (Note: Readings may drift without proper swirling!) Record the pH reading displayed on your calculator (**round to the nearest 0.01 pH unit**).
 - e) Repeat the previous step for the second acetic acid solution. Rinse the pH electrode before measuring the pH.
 - f) When done, place the pH electrode in distilled water.
5. Discard the acetic acid solutions into your rinse beaker.
6. Pour about 5 to 10 mL of the 0.10 M salt solutions into clean and dry large test tubes. Label the tubes!
7. Determine the pH of the 0.10 M salt solutions as follows:
 - a) Rinse the electrode with a squirt bottle filled with deionized water. Make sure the glass bulb on the bottom of the electrode is thoroughly rinsed. Catch the rinse in a 600-mL beaker. Pat the outside of the electrode dry with a paper towel.
 - b) Immerse the pH electrode into the solution and slowly move the pH electrode up and down in the tube (Note: Readings may drift without proper movement of the electrode) Record the pH displayed on your calculator (**round to the nearest 0.01 pH unit**).
 - c) Repeat the above procedure for the remaining salt solutions.
8. Discard the salt solutions into your rinse beaker and stir the waste solution.
9. When you are finished, rinse the pH electrode and return it to the storage solution.
10. Discard your waste in the appropriate waste container.

PROCESSING THE DATA

K_a and % Ionization of Acetic Acid

Complete the table on the report sheet for the two acetic acid solutions. Percent ionization is defined as $\frac{[H^+]_e}{[HA]_o} \times 100\%$ for an acid.

Acid-base Properties of Salts

Complete a table on the report sheet. To complete the table, write the corresponding ions that comprise each salt. Identify each ion as acidic, basic or neutral. **For the salts that have an acid and neutral ion determine K_a for the acidic ion. For salts that have a basic and a neutral ion calculate K_b for the basic ion.** For salts that contain both an acidic and basic ion, K_a or K_b cannot be determined.

Report Sheet: Acid-base Equilibrium

Name: _____

Lab section: MW or TTh Locker # _____

Partner: _____

K_a and % Ionization of Acetic AcidCalculate $[H^+]$, K_a , pK_a and the % ionization for the two solutions of acetic acid based on your pH measurement.

$[CH_3COOH]_0$	pH	$[H^+]$	K_a	pK_a	% ionization

1) What is the trend in % ionization as the initial concentration of acetic acid decreases?

a) Do you think this trend would be the same for any weak acid? _____

2) Based on the literature K_a for acetic acid, estimate the pH and percent ionization of a 0.0050 M solution. You may want to solve a quadratic for this!

Report Sheet: Acid-base Equilibrium

Name: _____

Lab section: MW or TTh Locker # _____

Partner: _____

Table 1: pH of Salt Solutions

Complete this table based on your measured pH in lab for each solution. **Show your work for the K_a (K_b) calculations on the last page of the lab report.**

0.10 M Salt Solution	pH	Acidic or Basic Salt?	Acidic Ion	Basic Ion	Neutral Ion	$[H^+]$	$[OH^-]$	Calculated K_a or K_b
<i>sodium acetate</i>			None	CH_3COO^-	Na^+			
<i>ammonium acetate</i>		Neutral						Undetermined
<i>ammonium chloride</i>								
<i>sodium bicarbonate</i>								
<i>sodium carbonate</i>								
<i>sodium phosphate</i>								
<i>sodium hydrogen phosphate</i>								
<i>sodium dihydrogen phosphate</i>								

- 1. Rank the ions** (not the salts) from the above salts in order of acidity. Most acidic ion to most basic ion. Don't forget Na^+ and Cl^- .
- 2. For the acidic ions** in table 1, write the corresponding K_a **chemical reaction**.
- 3. For the basic ions** in table 1, write the corresponding K_b **chemical reaction**.

Follow-up questions.

1. A 0.20-M solution of sodium nitrite, NaNO_2 , has a pH of 8.57.
 - a) Write a chemical equation showing why this salt has the given pH. (Hint you should write a K_a or K_b chemical equation, how do you know which one?)

 - b) Calculate K_b for the anion and K_a for the corresponding conjugate acid given the measured pH.

2. If one of the hydrogens bonded to the carbon atom in acetic acid is replaced by a chlorine atom, monochloroacetic acid is formed, CH_2ClCOOH .
 - a) Draw the Lewis structure for monochloroacetic acid.

 - b) The $\text{p}K_a$ of monochloroacetic acid is 2.865 at 25° C. Compare this $\text{p}K_a$ to that of acetic acid and suggest a explanation for the large difference in $\text{p}K_a$ values. Hint: see your textbook on strengths of acids and molecular structure.

 - c) Estimate the pH of a 0.10M monochloroacetic acid solution. What is the approximate percent ionization for this acid?

Report Sheet: Acid-base Equilibrium

Name: _____

Lab section: MW or TTh Locker # _____

Partner: _____

Page to show work when calculating K_a or K_b for table 1.

sodium acetate

ammonium chloride

sodium bicarbonate

sodium carbonate

sodium phosphate

sodium hydrogen phosphate

sodium dihydrogen phosphate