Determination of the Dissociation Constant of Weak Acids

When a weak acid is dissolved in water, it breaks apart or dissociates to a slight extent. A proton from the acid is donated to a water molecule. The equations for the equilibrium and the equilibrium constant expression are as follows:

$$HA + H_2O \rightleftarrows H_3O^+ + A^- \qquad K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

where A represents the anion of the weak acid and the square brackets indicate molar concentrations of the species. For most weak acids the percent of acid that dissociates is less than 5%. The value of the equilibrium constant, K_a, indicates to what extent the reaction occurs. The greater the value of K_a, the stronger the acid, and the greater the amount of dissociation.

Polyprotic acids contain more than one ionizable hydrogen. The dissociation process occurs stepwise and there is an equilibrium constant for each of the steps:

$$H_2A + H_2O \rightleftarrows H_3O^+ + HA^- \qquad K_{a1} = \frac{[H_3O^+]\,[HA^-]}{[H_2A]}$$

$$HA^- + H_2O \rightleftarrows H_3O^+ + A^{2-} \qquad K_{a2} = \frac{[H_3O^+]\,[A^{2-}]}{[HA^-]}$$

The second reaction always occurs to a much smaller extent than the first, so K_{a2} is always a smaller value than K_{a1}.

Some values for K_a and pK_a (p$K_a = -\log K_a$) which cover a wide range of acid strengths are listed below:

Acid	Formula	K_{a1}	K_{a2}	pK_{a1}	pK_{a2}
Iodic	HIO_3	1.7×10^{-1}		0.77	
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	1.77	7.19
Acetic	$HC_2H_3O_2$	1.8×10^{-5}		4.74	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	6.37	10.25
Hypochlorous	$HClO$	3.0×10^{-8}		7.52	
Hydrocyanic	HCN	4.9×10^{-10}		9.31	

This experiment is designed to determine the K_a and pK_a values of a number of weak acids. Acetic acid, $HC_2H_3O_2$, will be used as an example for the experimental procedure.

When acetic acid is in water solution, an equilibrium exists in which a mixture of acetic acid, hydronium ions, and acetate ions will all be present:

$$HC_2H_3O_2 + H_2O \rightleftarrows H_3O^+ + C_2H_3O_2^-$$

Acetic acid and acetate ions are conjugate acid–base pairs. A conjugate acid is a substance that has one more proton in its structure than its corresponding conjugate base. This combination also results from a mixture of a weak acid, acetic acid, and its salt, sodium acetate.

The equilibrium constant expression is:

$$K_a = \frac{[H_3O^+]\,[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

If a solution contains equal concentrations of $HC_2H_3O_2$ and $C_2H_3O_2^-$, these concentration terms cancel out in the above equation so that $K_a = [H_3O^+] = 1.8 \times 10^{-5}$, and pH = p$K_a$ = 4.74.

We will prepare solutions in which the concentrations of acid and its anion are equal. The value of the pH of the solution will then equal the pK_a for the acid. Some of the substances tested will be salts of diprotic acids that still contain an ionizable hydrogen. For example, $NaHSO_4$ ionizes in solution forming Na^+ and HSO_4^-. The HSO_4^- then reacts with water in the equilibrium:

$$HSO_4^- + H_2O \rightleftarrows H_3O^+ + SO_4^{2-}$$

The value of K_a which is found when equal concentrations of HSO_4^- and SO_4^{2-} are in solution is K_{a2} for sulfuric acid, H_2SO_4.

Chemicals

- Unknown acids
- Phenolphthalein solution, 1%
- Vinegar, $HC_2H_3O_2$
- NaOH solution, approximately 0.1 M
- Baking soda, $NaHCO_3$

Equipment

- Beaker
- Graduated cylinder
- Dropper
- Erlenmeyer flask
- pH indicator paper or pH meter

Procedure

Safety Alert

Acids and bases are harmful to skin and eyes. Wash spills off skin with lots of water. Neutralize acid spills on the table with baking soda; neutralize base spills with vinegar.

Phenolphthalein is dissolved in alcohol, so it is flammable. Keep the solution away from flames.

Wear Chemical Splash Goggles and a Chemical-Resistant Apron.

Measure out a small quantity of the acid to be tested, about 0.2 g. It is not necessary to know the exact amount.

Measure precisely 50.0 mL of distilled water into a beaker, add the acid, stir to dissolve and mix well. Pour 25.0 mL of the acid solution into an Erlenmeyer flask. Add 3 drops of phenolphthalein solution to the acid solution in the Erlenmeyer flask, and then add NaOH solution dropwise while swirling the flask. Stop adding the NaOH when the first pink color persists throughout the solution for at least 5 seconds.

At this point the beaker contains exactly one-half of the original acid, essentially all of which is in the undissociated form, HA. The flask contains an equal amount of the anion of the acid formed by neutralization:

$$OH^- + HA \rightleftarrows H_2O + A^-$$

Pour the contents of the flask into the beaker and mix the solution. Using pH indicator paper or a pH meter, measure the pH of this solution which contains equal concentrations of weak acid and conjugate base. The measured pH is the pK_a of the acid. Calculate the value of K_a of the acid.

Disposal

The solutions may be washed down the drain with a large excess of water.

Discussion

In your lab report include answers to the following questions:

1. Assume the acid dissociation constant for the acid salt $NaHSO_4$ is to be determined.
   (a) Write the chemical equation to show this salt ionizing in water.
   (b) Write the chemical equation showing the anion acting as an acid in water.
   (c) Write the equilibrium expression for the acid dissociation of the anion.
   (d) Explain the procedure for determining the acid dissociation constant using the expression from (c).
2. Why is it not necessary to know the exact mass of the acid whose K_a is to be determined?
3. Why is it not necessary to know the exact concentration of the NaOH solution used?
4. Why is it necessary to precisely measure the volume of distilled water used to dissolve the acid?
5. Write the Henderson–Hasselbalch equation and show how it can be solved to find the K_a of an acid when the concentrations of conjugate acid and base are equal.

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Preliminary Lab Assignment

Name________________________________ Date______________ Class______________

For phosphoric acid, H_3PO_4, the values for the acid dissociation constants are:

$$K_{a1} = 7.5 \times 10^{-3}$$
$$K_{a2} = 6.2 \times 10^{-8}$$
$$K_{a3} = 4.2 \times 10^{-13}$$

1. Write the equation for the first dissociation of phosphoric acid with water.

2. Write the K_a expression for the above reaction.

3. What would be the pH of a solution when $[H_3PO_4] = [H_2PO_4^-]$?

4. Phenolphthalein would not be an appropriate indicator to use to determine the K_{a1} of phosphoric acid by the method used in this experiment. Why? What indicator would be appropriate?

5. What would be the pH of a solution prepared by combining equal quantities of NaH_2PO_4 and Na_2HPO_4? Explain with an equation.

6. Sufficient strong acid is added to a solution containing Na_2HPO_4 to neutralize one-half of it. What will be the pH of this solution? Explain.