ADVANCED **AP** PLACEMENT

CHEMISTRY

Dissociation Constants of Weak Acids

Introduction

When an acid is dissolved in water it dissociates or breaks up into its component ions. Strong acids dissociate completely where as weak acids dissociate to a lesser extent. A proton from the acid associates with the water molecule in the following equilibrium equation:

$$HA + H_2O \Leftrightarrow H_3O^+ + A^-$$

where A is the anion of the weak acid. Since weak acids do not dissociate completely, an equilibrium constant (K_a) for the reaction indicates the degree to which the reaction occurs. The larger the K_a the greater the degree of dissociation and the stronger the acid. For the above reaction, the equilibrium constant is calculated as:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

where the brackets indicate the molar concentration of the moiety.

Acids which contain more than one ionizable hydrogen are called polyprotic acids and the dissociation occurs in steps with an equilibrium constant for each step:

Step #1 $$H_2A + H_2O \Leftrightarrow H_3O^+ + HA^-$$

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

Step # 2 $$HA^- + H_2O \Leftrightarrow H_3O^+ + A^{2-}$$

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

The second step in the dissociation of a diprotic acid is a less extensive reaction and therefore has a smaller K_a.

The following table gives information on several common acids of varying strength.

Acid	Formula	Ions	K_{a1}	K_{a2}	K_{a3}	pK_{a1}	pK_{a2}	pK_{a3}
Hydrochloric acid	HCl	H^+ Cl^-		-			-	
Phosphoric acid	H_3PO_4	H^+ $H_2PO_4^-$	$7.52 X 10^{-3}$			2.12		
		H^+ HPO_4^{2-}		$6.23 X 10^{-8}$			7.21	
		H^+ PO_4^{3-}			$2.2 X 10^{-13}$			12.67
Acetic acid	$HC_2H_3O_2$	H^+ $C_2H_3O_2^-$	$1.76 X 10^{-5}$			4.75		
Hydrocyanic acid	HCN	H^+ CN^-	$4.93 X 10^{-10}$			9.31		

(This information is found in the CRC Handbook of Chemistry and Physics as well as other reference books).
The values for K_a and pK_a can be determined empirically and therefore can be used to identify unknown acids.

Objective

The K_a and pK_a of three weak acids will be determined empirically. Using the literature values, the unknown acid can be identified. Using acetic acid as an example, the K_a can be determined as follows:

Acetic acid dissociates in water forming an equilibrium of acetic acid, hydronium ions and acetate ions.

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

The equilibrium constant is:

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

Acetic acid and the acetate ions are conjugate acid-base pairs. A conjugate acid has one more proton than its conjugate base. Since the solution contains equal concentrations of acid and base they cancel each other out and the $K_a = [H_3O^+] = 1.8 X 10^{-5}$ and the $pH = pK_a = 4.75$.

The solution of undissociated acid is titrated with base until the solution contains the conjugate base. Equal quantities of the acid and base are mixed. At this point the pH of the solution equals the pK_a and the K_a can be calculated.

Chemicals and Equipment

Materials included in this kit:

1 X 10g	Benzoic Acid
1 X 10g	Potassium Hydrogen Phthalate
1 X 10g	Sodium Hydrogen Sulfate
10X 250mL	Sodium Hydroxide, 0.1M
4 X 25mL	Phenolphthalein 1.0%

1 set of Student study and analysis masters
1 Teacher Guide

Materials needed but not supplied:

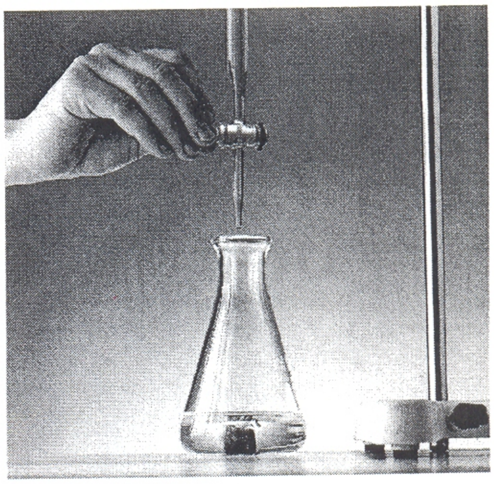
1 each	Analytical balance
15 each	250mL Erlenmeyer flasks
15 each	100mL Graduated cylinders
15 each	100mL beakers
1 each	pH meter

Safety equipment required:

Rubber gloves
Aprons
Safety goggles

Safety note: Acids and bases are hazardous to skin and eyes. Wash contaminated area immediately with water. Phenolphthalein solution contains alcohol and is flammable. Keep away from flames and other ignition sources.

Procedure



1.) Weigh out 0.5g of one of the unknown acids and dissolve in 50mL of de-ionized water. Stir until the acid is completely dissolved.

2.) Using a graduated cylinder, measure out 25mL of the acid solution and pour into an Erlenmeyer flask. Add 1-2 drops of phenolphthalein indicator and mix.

3.) Slowly titrate the acid solution with 0.1M NaOH while swirling the flask. Stop adding the NaOH when the first pink color appears and lasts for at least 5 seconds.

4.) Add the remaining acid solution to the flask and mix. Measure the pH of the solution with a pH meter and record your data.

5.) Repeat the experiment with each of the other two unknown acids and record your data. Calculate the K_a from the pK_a and look up the values in a reference to identify the unknown acids.

Chemical disposal: These dilute solutions can be safely flushed down the drain with copious amounts of water.

Discussion and Laboratory Report

1.) Write the chemical equations and equilibrium expressions for each dissociation experiment. Be sure to show the steps of any polyprotic acids.

2.) Explain the need for accuracy in the following steps of these experiments:

a.) weighing out the solid acid.
b.) diluting the acid in an exact amount of water
c.) knowing the exact molarity of the NaOH
d.) measuring out the amount of acid solution to be neutralized

3.) Show how the K_a can be calculated from the pH using the Henderson-Hasselbach equation.