EXPERIMENT 10

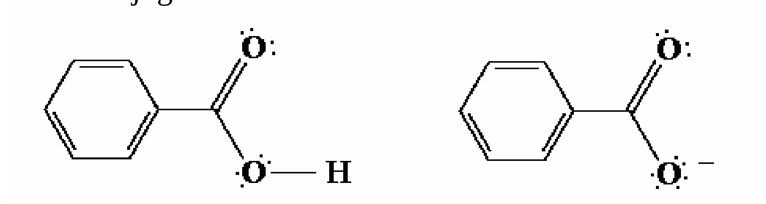
pKa OF A WEAK MONOPROTIC ACID

PURPOSE:

1. To determine experimentally the pKa of a weak monoprotic acid.
2. To obtain a percentage error of less than 5% for the experimental value.

PRINCIPLES:

Benzoic acid is a monoprotic acid, with one acidic hydrogen atom. It contains the acid group of carbon-containing molecules, -COOH and is called a carboxylic acid. The Lewis structure of benzoic acid and its conjugate base ion are shown below:



For convenience, we will write RCOOH to denote the acid formula. In water the benzoic acid establishes an equilibrium between the weak acid and the conjugate base.

$$RCOOH + H_2O \rightleftarrows H_3O^+ + RCOO^- \qquad \text{(Equation 1)}$$

The equilibrium constant, K_a, for this reaction is written:

For benzoic acid, the value of K_a equals 6.3 x 10^{-5}. The magnitudes of the K_a and pK_a values of different weak acids give us a comparison of their relative strength. A weaker acid has less dissociation to the conjugate base and the equilibrium favors the undissociated weak acid form (as in Equation. 1). This results in a smaller K_a value (in Eqn 2). A smaller K_a value corresponds to a larger pKa, since $pK_a = -\log K_a$. <u>The larger the pK_a value the weaker the acid.</u>

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]} \qquad \text{(Equation 2)}$$

When a weak acid is titrated, carefully measured volumes of strong base solution are added to it. Some titrations are done for the purpose of determining the concentration of a weak acid solution. In this case, base solution is added until the equivalence point is reached. At this point, enough base has been added to react with all the weak acid present in the sample. You will use a pH meter to determine the equivalence point of the titration. When the equivalence point is reached, the pH of the solution will change rapidly, because all the acid has reacted with the added base.

In addition to finding the concentration of benzoic acid, your titration will provide information about the behavior of this weak acid throughout the pH scale. You will measure the pH vs. volume base (mL) added to the benzoic acid solution, to determine the titration curve. A theoretical titration curve for benzoic acid is shown below.

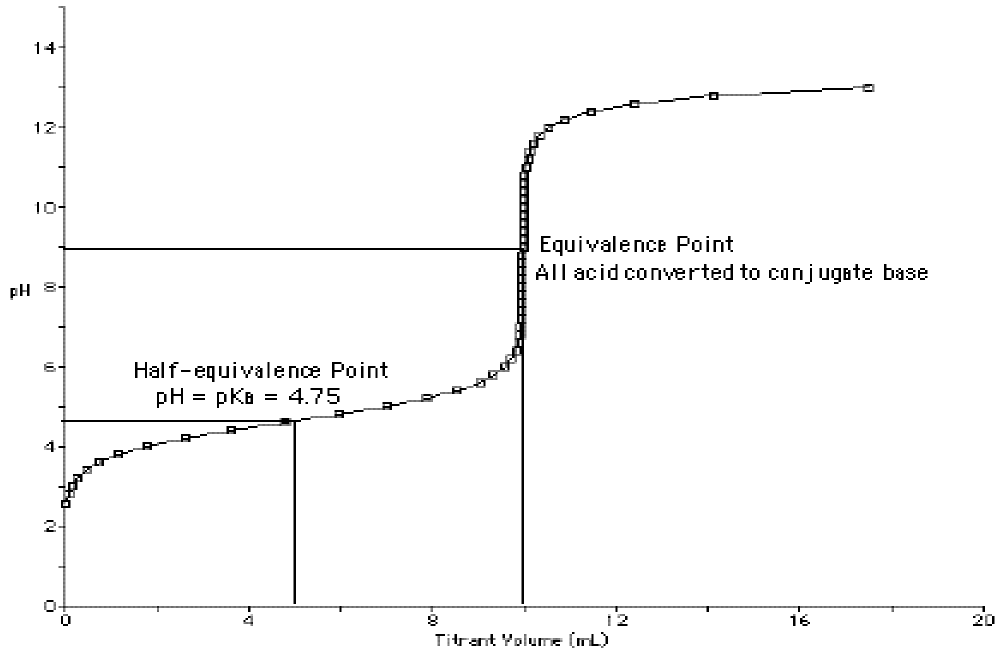


Figure 1

The flat portion of the titration curve before the equivalence point is called the buffer region. In this part of the pH scale, the acid and conjugate base are both present in significant concentrations and the solution resists changes in pH.

In the middle of the buffer region lies the half-equivalence point. Here the volume of base added is half that required to reach the equivalence point and half the benzoic acid has been converted to the conjugate base. This means that the concentrations of benzoic acid and conjugate base ion are equal. If we examine the equilibrium expression at the half-equivalence point, we find something interesting:

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]} \qquad \text{(Equation 2)}$$

At the <u>half-equivalence point</u>, $[RCOOH] = [RCOO^-]$, canceling these out of the equation equals:

$$Ka = [H3O+]$$

Taking the log and multiplying both sides by -1 yields pKa = pH

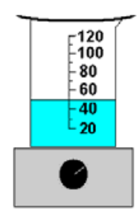
So at the half-equivalence point, half the benzoic acid has been converted to the conjugate base and the pH will be equal to the pKa of the acid. This gives us an experimental way to determine the pKa of a weak acid. This experiment will determine the pKa of benzoic acid and compare it to the literature value.

PROCEDURE:

You will titrate samples of benzoic acid whose mass is known with a solution of NaOH. The approximate concentration of that solution will be 0.1M. The NaOH solution will be delivered from a buret.

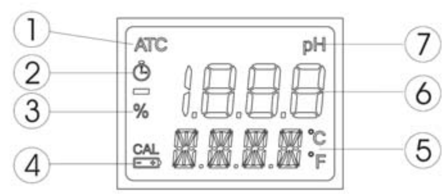
1. Accurately determine and record the mass of two samples, about 0.3 g each, of benzoic acid. The second sample is for a duplicate determination.

2. Carefully transfer the benzoic acid sample into a clean 150 mL beaker. Add about 50 mL of distilled water to the beaker.



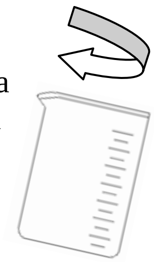
3. Cover the beaker with a clean watch glass and warm it to dissolve the acid. Allow the solution to cool to about 35 to 40 deg C. Change the temperature setting on the pH meter to the temperature of the solution.

4. Calibrate the pH meter.
   a. Rinse the electrode and wipe off the excess water with a Kimwipe.
   b. DO NOT TOUCH THE ELECTRODE WITH YOUR FINGERS



   c. From normal measuring mode, press and hold the /MODE button until OFF on the LCD, ⑤, is replaced by CAL. Release the button. The LCD enters the calibration mode displaying “pH 7.01 USE”. After 1 second the meter activates the automatic buffer recognition feature. If a valid buffer is detected then its value is shown on the LCD, ⑥, and REC appears on the LCD, ⑤. If no valid buffer is detected, the meter keeps the USE indication active for 12 seconds, and then it replaces it with WRNG, indicating the sample being measured is not a valid buffer.
   d. Place the electrode in pH 7.01 buffer.
   e. After the first calibration point has been accepted, the “pH 4.01 USE” message appears. (about 1 – 2 minutes)
   f. Place the electrode in pH 4.01 buffer.
   g. When the buffer is accepted, the LCD shows the accepted value with the “OK 2” message, and then the meter returns to the normal measuring mode. (about 1 – 2 minutes)

5. Immediately immerse the electrode into the benzoic acid solution.



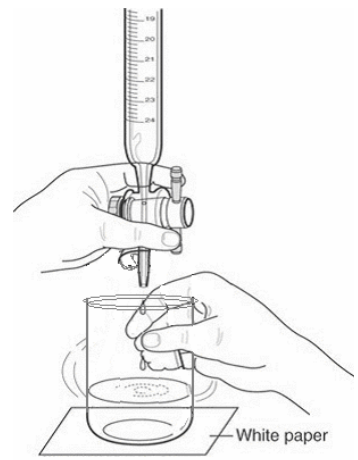
6. Stir the solution. Stirring is important because the pH will tend to drift until a completely homogeneous solution is achieved. Swirling the beaker back and forth a few times will be sufficient.

7. The buret should be clamped so that its tip is within the beaker but above the surface of the solution.

8. Record the initial buret reading.

9. Read and record the initial pH of the solution before any of the NaOH solution has been added.

10. Begin the titration by adding successive portions of 1 mL of the NaOH solution. Obtain and record the buret reading and the pH after each addition.



11. When the pH begins to increase by more than about 0.3 pH units after an addition, decrease the portions that you add to about 0.2 mL. Once the equivalence point has been passed, the pH change after each addition will decrease. When the change is again about 0.3 pH units, return to 1 mL portions. Continue the titration until the pH is about 11.5-12.0.

12. Repeat steps 2 through 11 with the second sample of benzoic acid.

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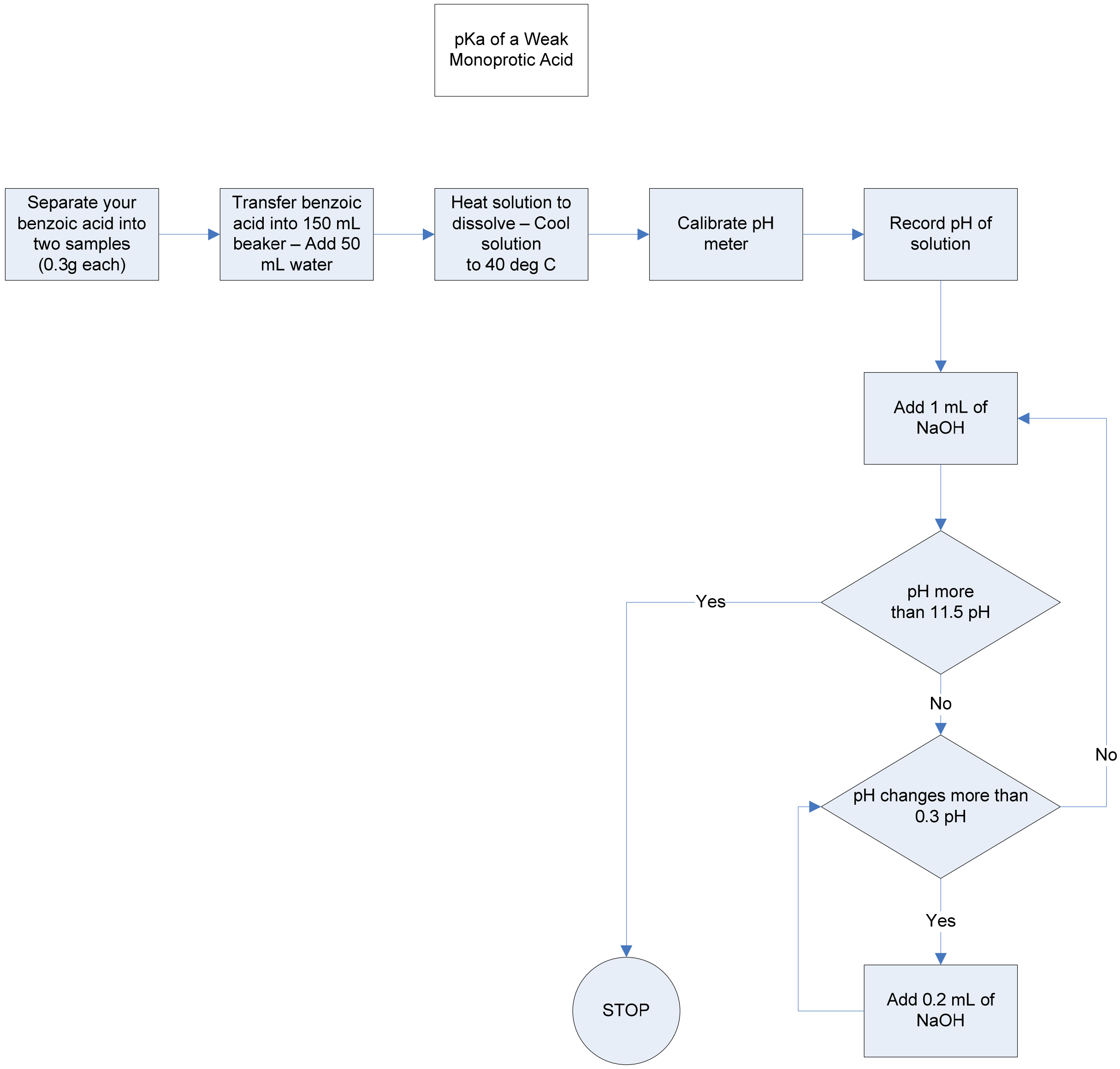

13. On your datasheet determine the mass of benzoic acid used for each of the two runs.

14. Record the temperature of the benzoic acid solution for each of the two runs.

15. Plot two separate graphs of the pH versus the volume of the NaOH added
    a. Clearly label each graph
    b. Determine the equivalence point for each titration from the graph
    c. Determine the volume of NaOH and the corresponding pH at the equivalency point.
    d. Determine the volume of NaOH and the corresponding pH at the half – equivalency point.

16. Calculate the following:
    a. The pKa of each sample
    b. The mean pKa
    c. The Ka of benzoic acid
    d. The percentage error of the Ka of benzoic acid.

17. Write a balanced molecular equation that illustrates the reaction between benzoic acid and sodium hydroxide including the state diagrams.

18. Write a net ionic equation that illustrates the reaction between benzoic acid and sodium hydroxide.

19. Calculate the molarity and mean molarity of the NaOH solutions.

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REPORT FORM

Name: ______________________________

Sample 1

Mass of vial + Benzoic acid: _______________ g
Mass of vial: _______________ g
Mass of Benzoic Acid: _______________ g
Initial pH: _______________ * (enter this value in the table)
Temperature of Solution: ^{0} C

Buret reading (mL)	Volume added (mL)	pH
	0.00	*

Buret reading (mL)	Volume added (mL)	pH

Buret reading (mL0	Volume added (mL)	pH

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Sample 2

Mass of vial + Benzoic acid: ________________ g
Mass of vial: ________________ g
Mass of Benzoic Acid: ________________ g
Initial pH: ________________* (enter this value in the table)
Temperature of solution: ^{0} C

Buret reading (mL)	Volume added (mL)	pH
	0.00	*

Buret reading (mL)	Volume added (mL)	pH

Buret reading (mL0	Volume added (mL)	pH

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1. Graphing the experimental data

Plot 2 separate graphs of pH versus volume of NaOH added.

a) Use 2 sheets of graph paper; one for each sample
b) Attach the graphs to your report. Please attach graph for Sample 1 behind page 1 and graph for Sample 2 behind page 2. Clearly label each graph.
c) From your graphs determine the equivalence point for each titration
d) Indicate on your graphs the volume of NaOH and the corresponding pH at the equivalence point.
e) Indicate on your graphs the volume of NaOH and the corresponding pH at the half - equivalence point.

2. Interpreting the experimental data

Complete the table below:

	Sample 1	Sample 2
Volume at equivalence point (mL)		
pH at equivalence point		
Volume at half-equivalence point (mL)		
pH at half-equivalence point		
pKa		
Mean pKa		
Ka of benzoic acid		

3. Percentage Error

The theoretical value for the Ka of benzoic acid is **6.3×10^{-5}** at 25^{0} C
Calculate the % error.

4. Expanding the Concepts
   Calculate the molarity of NaOH solution from each result and determine the mean molarity. The formula of benzoic acid is $HC_7H_5O_2$
   a) Write a balance molecular equation that illustrates the reaction between benzoic acid and sodium hydroxide. Include state designations.

   b) Write a net ionic equation that illustrates the reaction between benzoic acid and sodium hydroxide. Include state designations.

	Sample 1	Sample 2
Mass of sample (g)		
Molar Mass of BenzoicAcid (g/mol)		
Number of moles of Benzoic Acid added		
Number of moles of NaOH that have reacted with the Benzoic Acid		
Volume of NaOH added to react completely with the Benzoic acid (mL)		
Volume of NaOH added to react completely with the Benzoic acid (L)		
Molarity of NaOH (mol/L)		
Mean Molarity of NaOH (mol/L)		