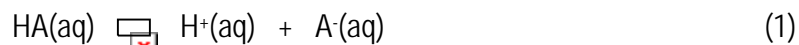


# pK<sub>a</sub> of a Weak Acid

INTRODUCTION: A weak acid, symbolized HA, is one which is only slightly ionized in water, i.e., exists in equilibrium with its ions (equation 1).



The equilibrium constant for this reaction is given by the law of mass action:

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

where the square brackets signify that the concentrations are those existing at equilibrium. A convenient form of this equation may be derived if one first takes the common logarithm of both sides:

$$\log K_a = \log[\text{H}^{\text{+}}] + \log([\text{A}^{-}]/[\text{HA}]) \quad (3)$$

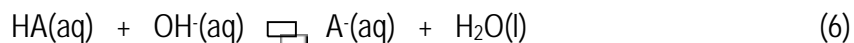
Definition:  $\text{p}X = -\log_{10}X$ , where  $X$  may be a variable or a constant. The pH of a solution is thus defined to be equal to  $-\log_{10}[\text{H}^{\text{+}}]$ . Substituting into equation 3 now yields

$$-\text{p}K_a = -\text{pH} + \log([\text{A}^{-}]/[\text{HA}]) \quad (4)$$

Rearrangement of equation 4 gives the **Henderson-Hasselbalch equation**:

$$\text{pH} = \text{p}K_a + \log([\text{A}^{-}]/[\text{HA}]) \quad (5)$$

This equation serves as the basis for the determination of the ionization constant,  $K_a$ . Inspection of equation 5 reveals that it has the form of the equation of a straight line, where the pH depends upon the value of  $\log([\text{A}^{-}]/[\text{HA}])$ . We will prepare solutions with five different values of the ratio  $[\text{A}^{-}]/[\text{HA}]$ . The amounts of the conjugate base and unionized acid are adjusted by partial neutralization of the acid with standard base solution:



The pH values of the five solutions will be measured (read about the [use of a pH meter](#)), and graphical analysis using linear regression techniques will then be applied to provide a statistically more valid value of  $\text{p}K_a$  than a single determination would provide. By having five measurements instead of only one and using a best-fit line, the individual random errors will average out.

## PRE-LAB QUESTIONS:

1. Briefly describe the electrode and the quantity that is actually measured by the pH meter.
2. What buffer solution is used in addition to the pH 7 buffer for calibration of the meter when acidic solutions are to be measured?
3. What are the practical limits for temperature of solutions when using a pH meter?
4. State two reasons why it would be inappropriate to use the pH meter to measure the pH of a 12 M NaOH solution.

EQUIPMENT: 25-mL pipet, 50-mL burette, 10- and 100-mL graduated cylinders, five 150- or 250-mL beakers, wash bottle, pH meter.

EXPERIMENTAL: **Caution:** KOH is a caustic substance, and the weak acids are also corrosive. If any of these substances is spilled on the skin, immediately rinse thoroughly with large amounts of water. Be sure to wear your goggles.

Record the **identification code** of your unknown acid and the **concentrations** of all reagents. Make up the five solutions using the amounts listed in Table I. Measure carefully, using a pipet to measure the acid, a burette for the base, and graduated cylinders for the sodium perchlorate. This last reagent is used to provide a constant ionic strength, necessary for the pH measurements. Mix all of the solutions thoroughly.

The pH measurements may be made in the original beakers. Do not move any controls on the pH meter except as directed. With the meter on standby (some models of pH meters do not have a standby mode), rinse the electrode with deionized water, gently shake off the excess water, and immerse the electrode in the sample solution. Switch the meter to the pH mode, allow the reading to stabilize, and record the pH. Switch the meter back to the standby mode, rinse the electrode again, and leave the electrode immersed in deionized water. Repeat this procedure for all five solutions.

Table I. Amounts of Reagents for Weak Acid Solutions

Solution	mL HA	mL KOH	mL NaClO <sub>4</sub>
1	25.00	5.00	25.0
2	25.00	10.00	20.0
3	25.00	15.00	15.0
4	25.00	20.00	10.0
5	25.00	25.00	5.0

CALCULATIONS: Carry out all calculations in terms of milliliters and millimoles; note that 1 mol/L = 1 mmol/mL. Set up a table showing initial mmols HA, initial mmols KOH, final mmols HA, final mmols A<sup>-</sup>, [A<sup>-</sup>]/[HA], and log([A<sup>-</sup>]/[HA]) for each solution. Use equation 6 to determine the respective values of these quantities. Explain in detail the calculations for solution 1 in your report, including your reasoning as well as the actual numerical calculations. The remainder of the calculations may be done using the spreadsheet software.

Carry out a spreadsheet regression analysis using Excel to determine the value of pK<sub>a</sub>. Report this value **and its uncertainty** and calculate the value of K<sub>a</sub>. Use the spreadsheet program to draw a graph of pH vs. log([A<sup>-</sup>]/[HA]). Plot the experimental points and the best-fit line. Be sure to scale the graph such that the data points fill the page as much as possible.

Obtain the identity of your unknown acid from the instructor. Look up the literature value of K<sub>a</sub> (reference it) and determine the percent error in your determination of the K<sub>a</sub> and pK<sub>a</sub>. Is the true pK<sub>a</sub> within the limits of uncertainty of your experimental value? Include a discussion of possible sources of systematic error and the effects (high or low) of each with explanations.

REPORT: Write a formal report for today's experiment.