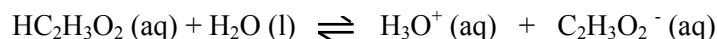


## CHEM 334L - Conductance of Solutions - Estimating $K_a$ for a Weak Acid

### **Introduction:**

When a strong electrolyte such as NaCl is placed in aqueous solution, it is said that it dissociates into its ions (essentially 100%). However, when a weak electrolyte is placed in aqueous solution, it is said that it dissociates only partially. In the case of acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , the dissociation is described by the following:



where the acid ionization constant,  $K_a$ , may be expressed as

$$K_a = c \frac{\alpha^2}{1-\alpha} \quad \text{Equation 1}$$

where  $c$  = the formal concentration of the acetic acid and  $\alpha$  = the fraction dissociated.

This experiment considers the electrical conduction of aqueous solution. Although “pure water” is a very poor conductor, ionic species present in aqueous solutions of acids, bases, and other electrolytes significantly improve its conduction. The conductivity of a solution is proportional to the concentration of ions present in solution. More specifically, the conduction of various ions depends on their charge and mobility in solution.

Aqueous solutions containing electrolytes obey Ohm's law in the same way that metallic conductors do:

$$V = I R \quad \text{Equation 2}$$

where  $V$  = Potential Difference (in volts),  $I$  = current (in amps), and  $R$  = resistance (in ohms  $\Omega$ ). Conductance is defined as the reciprocal of resistance, of a homogeneous body of uniform cross section is proportional to the cross-sectional area  $A$  and inversely proportional to the length  $L$ :

$$\frac{1}{R} = \frac{\kappa A}{L} \quad \text{Equation 3}$$

which can be rearranged to

$$\kappa = \frac{1}{R} \frac{L}{A} = \frac{k}{R} \quad \text{Equation 4}$$

where  $\kappa$  = the specific conductance ( $\Omega^{-1} \text{cm}^{-1}$ ).

The specific conductance is measured and the equivalent conductance ( $\Lambda$ ) is calculated using the following formula:

$$\Lambda = \frac{1000 \kappa}{c} \quad \text{Equation 5}$$

where  $c$  = the equivalents of electrolytes per liter (same as molarity for +1 ions).

For substance such as acetic acid that do not ionize completely the equivalent conductance will be lower than if it were completely ionized (i.e., at infinite dilution). The fraction of ionization ( $\alpha_c$ ) may be approximated by:

$$\alpha_c = \frac{\Lambda_c}{\Lambda_0} \quad \text{Equation 6}$$

where  $\Lambda_c$  is the equivalent conductance at concentration  $c$  and  $\Lambda_0$  is the equivalent conductance in dilute solution.

The equivalent conductance of a strong electrolyte in dilute solution can be estimated by using the equation:

$$\Lambda_c = \Lambda_0 - \Lambda_0 \beta (c)^{1/2} \quad \text{Equation 7}$$

Therefore for a plot of  $\Lambda$  versus the square root of the electrolyte concentration yields a straight line. The y-intercept (where  $c=0$ , i.e. infinite dilution) =  $\Lambda_0$ .

The equivalent conductance for a weak electrolyte can be estimated by using Kohlrausch's Law. For an acetic acid solution this would be:

$$\Lambda_{0, \text{acetic acid}} = \Lambda_{0, \text{HCl}} + \Lambda_{0, \text{NaC}_2\text{H}_3\text{O}_2} - \Lambda_{0, \text{NaCl}} \quad \text{Equation 8}$$

In this experiment, specific conductances ( $\kappa$ ) will be measured for four solutions ( $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{HCl}$ ,  $\text{NaC}_2\text{H}_3\text{O}_2$ , and  $\text{NaCl}$ ). Equivalent conductances ( $\Lambda_c$ ) will be calculated for each of these at various electrolyte concentrations. For the strong electrolytes, the equivalent conductance at infinite dilution ( $\Lambda_0$ ) will be calculated by fitting data to **Equation 7**. These values will then be placed into **Equation 8**, to determine the value for acetic acid ( $\Lambda_{0, \text{acetic acid}}$ ).

For each concentration of acetic acid, the value of  $\alpha_c$  will be calculated using **Equation 6**. These values will be used to calculate  $K_a$  using **Equation 1**.

Table 1 • Some Conductivity Units

Conductivity:	
1 mho	= 1 $\Omega^{-1}$ = 1 Siemen
1 micromho ( $\mu\text{mho}$ )	= 1 microSiemen ( $\mu\text{S}$ )
1 millimho (mmho)	= 1 milliSiemens (mS) = 1,000 $\mu\text{S}$
Equivalent conductance:	
$\Lambda$	= $\Omega^{-1} \text{cm}^2 \text{equivalent}^{-1}$

Table 2 • Some Conductivity Data for Common Aqueous Solutions

Conductivity ( $\mu\text{S}$ at 25°C)				
ppm (mg/L)	NaCl	NaOH	HCl	Acetic Acid
10	21.4	61.1	116	15.1
30	64	182	340	30.6
100	210	603	1140	63
300	617	1780	3390	114
1000	1990	5820	11100	209
3000	5690	16900	32200	368
10000	17600	53200	103000	640

**Procedure:****A. Stock Solution Preparation**

Prepare aqueous solutions of NaCl (aq), NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> (aq), HCl (aq), and HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>(aq) as described below:

1. Prepare 500 mL of 0.1XXX M NaCl (aq) in a volumetric flask. Carefully weigh solid NaCl into a weighing dish and determine its mass to the nearest 0.1 mg using an analytical balance. Transfer the sample quantitatively to your flask, dissolve with distilled water, and dilute to volume with the distilled water.
2. Repeat the procedure above to prepare 500mL 0.1XXX M NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> (aq).
3. Prepare a 250 mL of 0.2XXX M HCl (aq) by pipetting 25.00 mL of 2.00 M HCl (aq) into a 250 mL volumetric flask and then dilute to volume with distilled water.
4. Prepare 250 mL of 0.2XXXM HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> (aq) by pipetting 50.00 mL of 1.00 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> (aq) into a 250 mL volumetric flask and then dilute to volume with distilled water.

**B. Conductivity Meter Calibration and Use.**

You will be using one of the following instruments for measuring conductivity:

**Accumet Basic – AB30 Conductivity Meter**

**Thermo-Orion 150 A+ Conductivity Meter** (with data collection software)

**MicroLab 302 Sytem with Conductivity Sensor** (with data collection software)

To calibrate the conductivity meter , **follow the instructions in the manual** which is available on the CHEM 334L Website and in the lab. You will be using a Probe with a cell constant of 1.0 (optimal conductivity range = 0.01 to 2.0 mS/cm or 10 to 2000  $\mu$ S/cm). One standard is provided, 447  $\mu$ S. Since most of your measurements in dilute concentration will be around this range, that it is why it is recommended that you use it for calibration.

1. The probe requires 30 seconds to a minute to stabilize. Give it time and be patient.
2. Rinse probe with distilled water and gently blot dry between solutions. Be careful to watch for air bubble formation, this can give erratic readings.
3. The probe may have ATC (auto temperature compensation), however, record the temperature of your solutions for reporting purposes.

**C. Dilutions and Conductivity Measurements**

For each of the solutions prepared in Part A, prepare at least five solutions (by dilution) using 100 mL volumetric flasks and volumetric pipets of your choice. Solutions should range in concentration between 0.200 M and 0.001 M.

Using a calibrated probe, measure and record the conductivities of each of the solutions.

A reasonable procedure when making measurements is to start from dilute solution to concentrated. Also, record the conductivity of your distilled water.

Recheck any questionable data.

**Calculations and Graphs:**

(Subtract the conductance of the distilled water from that of each of your prepared solutions.)

You measured specific conductance:

$\kappa$  = specific conductance in Siemens (S)

The equivalent conductance ( $\Lambda_c$ ) is calculated using the following formula:

$$\Lambda_c = \frac{1000 \kappa}{c} \quad \text{Equation 2}$$

where  $c$  = the equivalents of electrolytes per liter (same as molarity for +1 ions) and  $\kappa$  has units of Siemens (S)! Watch your units!

**1. Plot three graphs, one for HCl, one for  $\text{NaC}_2\text{H}_3\text{O}_2$ , and one for NaCl. According to the following equation, the plots should be  $\Lambda_c$  vs the square root of molarity.**

$$\Lambda_c = \Lambda_0 - \Lambda_0\beta(c)^{1/2} \quad \text{Equation 3}$$

Take the intercepts from each graph ( $\Lambda_0$ ) and calculate

$$\Lambda_{0, \text{acetic acid}} = \Lambda_{0, \text{HCl}} + \Lambda_{0, \text{NaC}_2\text{H}_3\text{O}_2} - \Lambda_{0, \text{NaCl}} \quad \text{Equation 4}$$

**2. Then calculate ( $\Lambda_c$ ) for acetic acid. The fraction of ionization ( $\alpha_c$ ) may be approximated by:**

$$\alpha_c = \frac{\Lambda_c}{\Lambda_0} \quad \text{Equation 5}$$

where  $\Lambda_c$  is the equivalent conductance at concentration  $c$  and  $\Lambda_0$  is the equivalent conductance in dilute solution.

**3. Using  $c$  (Molarity of Acetic Acid),  $\alpha_c$  (the fraction of ionization) and Equation 1, calculate  $K_a$  for each of the Acetic Acid solutions.**

**4. Finally, report the average value of  $K_a$  and its 95% confidence limits. As a reference,  $K_a = 1.8 \times 10^{-5}$  at 25° C. Comment on error observed in your graphs.**

References:

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