EXPERIMENT 1

Determination of K_a, K_b, and % Ionization from pH

Background

Like many substances acids and bases were first defined phenomenologically. That is, chemists defined them according to their chemical behavior. For instance, acids were those substances that tasted sour, reacted with certain metals to produce hydrogen gas, and caused a color change in certain indicator solutions. Bases, were those substances that tasted bitter, turned certain indicator solutions a certain color, and felt slippery. As time has progressed chemists have devised more fundamental definitions of acids and bases.

There are a number of different definitions of acids and bases which are useful to chemists. One example is the **Arrhenius** defintion. In this definition acids are those substances that increase the concentration hydrogen ion in solution and bases are those substances that increase the concentration of hydroxide ion in solution.

A broader definition was developed by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definitions follow

Brønsted-Lowry Acid. A substance that can donate a proton

$$HA(aq) + H_2O \rightleftharpoons A^{-}(aq) + H_3O^{+}(aq) \qquad \textbf{(EQ 1.1)}$$

Brønsted-Lowry Base. A substance that can accept a proton

$$B(aq) + H_2O \rightleftharpoons BH^{+}(aq) + OH^{-}(aq) \qquad \textbf{(EQ 1.2)}$$

Acid and base molecules and ions that differ only by the addition or removal of a proton are called **conjugate pairs**. For example HA/A^- and B/BH^+ both represent conjugate acid-base pairs. It may be shown that the K_a of an acid times the K_b of its conjugate base are equal to K_w (*Make sure that you can derive this.*). Therefore for the acid HA, the K_b of its conjugate base, A^-, is K_w/K_a where $K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$.

Strong Acids and Bases

Acids and bases which are essentially 100 % dissociated in water are said to be strong. The common strong acids and bases are listed in Table 1.1

TABLE 1.1 **Strong Acids and Bases**

Strong Acids	Strong Bases
hydrochloric acid (HCl)	sodium hydroxide ($NaOH$)
hydrobromic acid (HBr)	potassium hydroxide (KOH)
hydroiodic acid (HI)	barium hydroxide ($Ba(OH)_2$)
nitric acid (HNO_3)	calcium hydroxide ($Ca(OH)_2$)
sulfuric acid (H_2SO_4)	
perchloric acid ($HClO_4$)	
chloric acid ($HClO_3$)	

Calculating K_a and K_b

The dissociation constants for the strong acids and bases are undefined because the concentration of the undissociated form is essentially zero, which would result in a value of infinity.

Numerical values of the dissociation constants for weak acids and bases may be determined by measuring the pH of the solution. For a weak acid, the hydronium ion concentration,$[H_3O^+]$, is approximately equal to the concentration of the conjugate base $[A^-]$ as shown below:

	HA	+	H_2O	$\rightleftharpoons$	A^-	+	H_3O^+
I	$0.10\ M$		$55\ M$		0		$10^{-7}\ M$
Δ	$-x$		$-x$		$+x$		$+x$
E	$0.10-x$		55		x		$10^{-7}+x$

If the pH is observed to be 3.20 then,

$$[H^+] = 10^{-3.20}M = 6.31\times10^{-4}M = x \tag{EQ 1.3}$$

Substituting the equilibrium values from above into the K_a expression yields a numerical value for K_a.

$$K_a = \frac{[x][x]}{(0.10-x)} = \frac{(6.31\times10^{-4})^2}{(0.10-6.31\times10^{-4})} = 4.0\times10^{-6} \tag{EQ 1.4}$$

We can also use the expression given above for the relationship of K_b to K_a.

$$K_b \text{ for } A^- = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{4.0\times10^{-6}} = 2.5\times10^{-9} \tag{EQ 1.5}$$

If the pH reading is greater than 7 the solution is basic and the $[OH^-]$ will be used to calculate K_b.

	B	+	H_2O	$\rightleftharpoons$	BH^+	+	OH^-
I	$0.10\ M$		$55\ M$		0		10^{-7}
Δ	$-x$		$-x$		$+x$		$+x$
E	$0.10 - x$		55		x		$10^{-7} + x$

If the pH is observed to be 11.45 then the $[OH^-] = 10^{-pOH} = 10^{-2.55}$ and,

$$K_b = \frac{(10^{-2.55})^2}{(0.10 - 0.003)} = 8.2 \times 10^{-5} \quad \textbf{(EQ 1.6)}$$

Within what pH range can you prudently neglect the molarities of the ions in deionized water when added to dissociation products?

A more precise way of measuring K_a for a weak acid is to prepare a solution containing *equal molarities* of the weak acid and a salt of its conjugate base. Under this maximum buffer capacity condition the $pH = pK_a$, or $[H^+] = K_a$. **Make certain that you know why this is so**.

Percent Dissociation

The percentage dissociation is a measure of the molarity of one conjugate species in the equilibrium mixture compared to the initial molarity of the other conjugate species. It is a measurement of the extent of ionization. The greater the % dissociation the more ionized the acid or base.

For a weak base the percent dissociation can be calculate in the following manner. The data are from the example above.

$$\%\ \text{dissociation} = \frac{[BH^+]}{[B]_{\text{initial}}} \times 100\% = \frac{[OH^-]}{[B]_{\text{initial}}} \times 100\% = \frac{10^{-2.55}}{0.10} \times 100\% = 2.82\% \quad \textbf{(EQ 1.7)}$$

Procedure

1. On Table 1.2 on page 9 you will find the pH of a number of acid, base, and salt solutions. Fill in the blanks on this sheet. Be sure to show representative calculation set-up as well. You can find the accepted values for K_a in the *CRC*.
2. Measure the pH of each of the following:
   - a. tap water
   - b. deionized water
   - c. "Outgassed" deionized water
   - d. The outgassed water after you have bubbled your breath through this water for 20-30 seconds.

> To outgas a sample of deionized water, gently boil it in an erlenmeyer flask for at least 10 minutes. Cool and stopper the flask to prevent contact with the lab's atmosphere.

Explain your observations for a-d.

3. Measure the pH of a sample of 6*M* acetic acid. Dilute exactly 5mL of the 6*M* solution to 25 mL in a graduated cylinder and measure its pH. Repeat the dilution by diluting 5 mL of the second solution to 25 mL and record the pH of the new solution. Repeat this procedure until $[HC_2H_3O_2] \approx 7\times10^{-5}$.
4. Calculate the % dissociation for each solution. Prepare a graph of %D vs $[HC_2H_3O_2]$ and compare it to the Figure 1.1 on page 8. Explain the trend observed. Generate a linear graph by choosing an appropriate function. Calculate K_a from the graph.

FIGURE 1.1

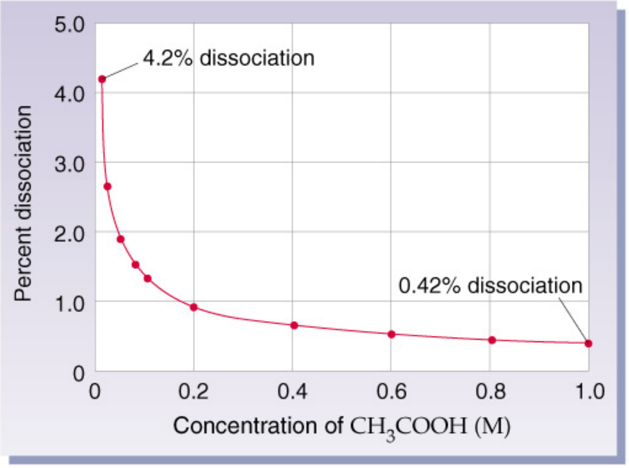

TABLE 1.2 K_a **Calculation Report Sheet**

0.25 *M* sol'n	Exp pH	Conjugate Acid	$[H^+]$	K_a	pK_a	Conjugate Base	pOH	$[OH^-]$	K_b	pK_b	% Diss.	Theo. pK_a	Theo. pK_b	% Err
CH_3NH_2	11.95	$CH_3NH_3^+$	1.1E–12	3.2E–11	10.50	OH^-	2.05	8.9E–3	3.2E–4	3.50	3.56	10.57	3.43	0.66
$HC_2H_3O_2$	2.65													
$NaC_2H_3O_2$	9.14													
NH_3	11.33													
NH_4^+	4.89													
$NaHSO_4$	1.36													
H_2SO_3	1.17													
Na_2CO_3	11.72													
$NaHCO_3$	9.82													
H_3PO_4	1.48													
KH_2PO_4	3.99													
K_3PO_4	12.86													
K_2HPO_4	10.25													
$C_{18}H_{21}NO_3$	10.91													
H_3BO_3	4.98													