

Experiment 16

12/18/2018

HYDRONIUM ION CONCENTRATION

MATERIALS: 7 centrifuge tubes with 10 mL mark, six 25 x 150 mm large test tubes, 5 mL pipet, 50 mL beaker, 50 mL graduated cylinder, 1.0 M HCl, 1.0 M CH₃COOH, 1.0 M CH₃COONa, methyl violet and methyl orange indicator solutions, test tube rack, calibrated pH meter (instructor use only).

PURPOSE: The purpose of this experiment is to perform serial dilutions and use indicators to estimate the pH of various solutions. Analysis of the latter will illustrate the distinction between strong acids and weak acids.

LEARNING OBJECTIVES: By the end of this experiment, the students should be able to demonstrate the following proficiencies:

1. Prepare solutions by serial dilution.
2. Correlate the H₃O⁺ ion concentration of a solution with its pH value.
3. Use indicators to estimate the pH of solutions of various acid concentrations.
4. Explain the common ion effect.
5. Understand the difference between strong and weak acids and calculate percent dissociation of a weak acid.

PRE-LAB: Read over the experiment and complete the pre-lab questions on p.E16-7 or on OWL, as directed by your instructor, BEFORE lab.

DISCUSSION:

Because of the autoionization equilibrium of water, in any aqueous solution the product of the hydronium ion concentration and the hydroxide ion concentration is equal to a constant, known as K_w. The equilibrium, and the K_w at 25°C are:



In pure distilled water at 25°C, the concentrations of hydronium and hydroxide ions are the same:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \quad (25^\circ\text{C}) \quad (2)$$

If the [H₃O⁺] concentration is altered, the [OH⁻] concentration will also change, so that the product of the two terms remains 1.0 x 10⁻¹⁴, as in equation (1).

The concentrations of hydronium and hydroxide ions found in real samples vary over a wide range of values. To describe acidity in a simple way, the logarithmic pH scale was adopted:

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] \quad (3)$$

Thus, for pure, distilled water at 25°C:

$$\text{pH} = -\log_{10}(1.0 \times 10^{-7}) = 7.00 \quad (25^\circ\text{C}) \quad (4)$$

The practical range of pH in aqueous solutions at 25°C is from 0 to 14. For acidic solutions, the [H₃O⁺] is greater than that in distilled water and the pH is therefore < 7; for basic solutions the [H₃O⁺] is less than that in distilled water and the pH is > 7. Neutral solutions have [H₃O⁺] = [OH⁻] and therefore, the pH of such a solution is 7.00 at 25°C. You may have noticed the frequent references to the 25°C temperature in the discussion above. This was necessary because the autoionization equilibrium constant K_w is temperature-dependent, as with other equilibrium constants. The value of K_w increases with temperature, so the concentrations of hydronium and hydroxide ions will increase with temperature, even while remaining equal to each other in pure water. That means that the pH of neutral water (when [H₃O⁺] = [OH⁻]) will *decrease* as the temperature increases. For example, the pH of pure neutral water at 50°C is 6.63.

An acid-base indicator is a substance which changes color with changes of hydronium ion concentration.¹ This color change may occur near the neutral point, $\text{pH} = 7$ (at 25°C), or it may occur at some other value of pH depending on the indicator. A color change in an indicator does not necessarily indicate a transition from an acidic to a basic solution. For example, an indicator such as thymol blue may change color as the pH goes from 1 to 3. (Notice that both the initial and the final solutions in this case are acidic.) The specific color of the indicator can be a measure of the pH , and thus of the concentration of hydronium ions, through the small pH range where the color transition occurs. (Outside of that small color change region, the color remains the same for all values of higher or lower pH .) In this lab we will observe that behavior with two different indicators, both of which change in different ranges of acidic solutions. We will use that behavior to explore the differences between strong and weak acids of the same nominal concentration.

PROCEDURE:

Part A. Preparation of Standard HCl Solutions of pH 0 to 5

Thoroughly rinse all glassware to be used in this experiment with distilled water.

1. Rinse the 5 mL pipet with 1.0 M hydrochloric acid. Use the rinsed pipet to transfer 5.00 mL of the hydrochloric acid solution to a 50 mL graduated cylinder (previously rinsed with distilled water). Add sufficient distilled water to make the resulting solution 0.10 M HCl. Gently swirl the solution to mix.
2. Rinse a large test tube with a small portion of the 0.10 M HCl and discard the rinses. Transfer the remaining 0.10 M hydrochloric acid solution to the test tube and place it in the test tube rack in the position marked "1" (indicating a pH of 1.00).
3. Rinse the 50 mL graduated cylinder with distilled water. Rinse the 5 mL pipet with the 0.10 M HCl solution which you just prepared. Use the rinsed pipet to transfer 5.00 mL of the 0.10 M HCl solution to the 50 mL graduated cylinder. Add sufficient distilled water to make the resulting solution 0.010 M HCl. After mixing, transfer this 0.010 M HCl solution to a large test tube and place it in the rack in the position marked "2" (indicating a pH of 2.00). This process of generating a series of new solutions by successive dilution of previously prepared solutions is called "serial dilution."
4. By serial dilution, prepare solutions of hydrochloric acid in which the concentrations are 1.0×10^{-3} M, 1.0×10^{-4} M, and 1.0×10^{-5} M (pH of 3.00, 4.00 and 5.00 respectively). As before, transfer each of these to a clean large test tube and place in the rack.
5. Finally, label one test tube "0" and place the original (undiluted) 1.0 M hydrochloric acid solution in it. You should now have six large test tubes of hydrochloric acid solution varying in concentration from 1.0 M to 1.0×10^{-5} M. These solutions have pH values very close to 0.00, 1.00, 2.00, 3.00, 4.00, and 5.00, since hydrochloric acid is a strong acid that completely dissociates in water.
6. Rinse a centrifuge tube with the 1.0 M HCl solution. After rinsing, fill the centrifuge tube to the 10 mL mark with the 1.0 M HCl. Place this centrifuge tube in the position in the rack marked "0".
7. Repeat this process for all the remaining solutions, first rinsing each tube with the solution it is to contain. In the seventh tube, place an extra 10 mL sample of the pH 3.00 solution. Place each tube in that position in the rack corresponding in number to the pH of the solution.

Part B. Color Changes of Various Indicators in Standard HCl Solutions

1. Add one drop of methyl violet indicator solution to the *four* HCl solutions of pH 0.00, 1.00, 2.00, and 3.00 (which are in the centrifuge tubes).

¹For a discussion of pH and acid-base indicators, see *Chemistry and Chemical Reactivity 9E*, by Kotz, Treichel, Townsend and Treichel, Cengage Learning, Stamford CT, 2015, pp. 161-164, 589-592, 655-658.

2. Starting with the extra tube containing the HCl solution of pH 3.00, add one drop of methyl orange indicator solution to each of the three remaining solutions (pH 3.00, 4.00, and 5.00). Mix each solution thoroughly, using a small glass stirring rod. Be sure to rinse the stirring rod between uses to prevent cross contamination of the solutions.
3. Record the observed colors of the solutions in the Data Section. (You may see different shades of the same color; be as descriptive as possible.) The useful range for each indicator lies between the pH value for the first and the last tube for that indicator. The color outside the useful range will be the same as the last color in the useful range. *Save these solutions for use as color standards for Parts C and D. Have your instructor check these standards before proceeding.*

Part C. Color Changes of Various Indicators in Acetic Acid Solutions and Estimated pH Values

1. Empty only the two centrifuge tubes containing the color standards for pH 0.00 and 1.00, and all the large test tubes. Rinse all the tubes thoroughly with water. These tubes will be used for preparing and testing various solutions of acetic acid.
2. Serial dilution will again be used to prepare the acetic acid solutions. Starting with 5.00 mL of the 1.0 M solution of acetic acid, prepare 50 mL of 0.10 M acetic acid. Use 5.00 mL of this solution to prepare 50 mL of 0.010 M acetic acid. Then prepare 50 mL of a third solution of 0.0010 M acetic acid.
3. Fill two of the empty centrifuge tubes to the 10 mL mark with the 0.0010 M acetic acid solution. Add methyl violet to one centrifuge tube and methyl orange to the other.
4. Compare these tubes with the color standards of Part B by looking down through the tubes at a piece of white paper. (Indicator colors should always be compared directly with standards.) Record the colors in the Data Section. Also, based on your experimental observations, estimate the pH of the solution to the nearest half unit and record it in the appropriate space in the Data Section.
5. In similar fashion, test 10 mL samples of the 0.010 M, 0.10 M, and 1.0 M acetic acid solutions with each of the two indicators recording the colors and estimating the pH values. Calculate the corresponding approximate concentrations of hydronium ion, H_3O^+ , for both the HCl and acetic acid solutions based on the pH values.

Part D. The Common Ion Effect

1. Fill a centrifuge tube to the 10 mL mark with the 0.10 M acetic acid solution saved in part C and add one drop of methyl orange indicator to it. Mix thoroughly. Record the color and estimate the pH based on the color. Bring your solution to your instructor to be tested with a pH meter. How does your measured pH compare to your estimate?
2. In this solution dissolve as much solid sodium acetate, CH_3COONa , as can be held on the end of a spatula. Mix the solution until all of the solid dissolves. Note any change in color and estimate the pH of the solution by comparison with the standards from Part B.
3. Bring your solution to your instructor to be tested with a pH meter. How does your measured pH compare to your estimate?
4. After you clean up, start working on the calculations for this lab on page E16-5.

Clean up:

1. Dispose of all aqueous solutions down the drain.
2. Clean all glassware and return them to their original locations.

Name _____

Section _____

Partner _____

Date _____

DATA SECTION
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Part B. Observed Colors of Various Indicators in Standard HCl Solutions

| pH | 0.00 | 1.00 | 2.00 | 3.00 | 4.00 | 5.00 |
|---------------|---------------------------|------|------|------|---------------------------|------|
| Methyl Violet | | | | | ← Same color as pH 3.00 → | |
| Methyl Orange | ← Same color as pH 3.00 → | | | | | |

Instructor's Initials _____

Part C. Observed Colors of Various Indicators in Acetic Acid Solutions

| Acetic Acid | 1.0 M | 0.10 M | 0.010 M | 0.0010 M |
|---------------|-------|--------|---------|----------|
| Methyl Violet | | | | |
| Methyl Orange | | | | |

Instructor's Initials _____

Part C. Estimated pH Values of Hydrochloric Acid and Acetic Acid Solutions

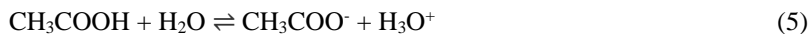
| Undissociated Acid Concentration | Hydrochloric Acid | | Acetic Acid | |
|----------------------------------|-------------------|-----------------------|--------------|-----------------------|
| | approximate pH | calculated $[H_3O^+]$ | estimated pH | calculated $[H_3O^+]$ |
| 1.0 M | 0.00 | | | |
| 0.10 M | 1.00 | | | |
| 0.010 M | 2.00 | | | |
| 0.0010 M | 3.00 | | | |

Part D. The Common Ion Effect

| Solution | observed color | estimated pH | measured pH |
|---|----------------|--------------|-------------|
| 0.10 M CH_3COOH | | | |
| 0.10 M CH_3COOH containing CH_3COONa | | | |

QUESTIONS
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1. In this experiment the concentration of H_3O^+ ion in the solution of acetic acid could only be roughly determined. More accurate values are given in the table below. *Using these values*, complete the table, calculating any missing values. Be sure to use the equilibrium expression derived from equation (5) to determine the K_a . Clearly show the calculations for the first row in the table. ($T = 25^\circ\text{C}$)



| Initial conc. of CH_3COOH | Equilibrium conc. of H_3O^+ | Equilibrium conc. of CH_3COO^- | Conc. of undissociated CH_3COOH | Percent dissociation | K_a |
|---|---|--|---|----------------------|-------|
| 1.00000 M | 0.00419 M | | | | |
| 0.50000 M | 0.00296 M | | | | |
| 0.20000 M | 0.00187 M | | | | |

Calculations for 1.00000 M initial conc. of CH_3COOH :

- equilibrium conc. CH_3COO^-

- conc. undissociated CH_3COOH

- percent dissociation

- K_a

2. As a solution of acetic acid is diluted, do the calculations in the previous question show that:
- the percent dissociation increases, decreases, or remains the same? Give a justification for your answer, using your data and calculations. Explain why this occurs.
 - the dissociation constant, K_a , increases, decreases, or remains the same? Give a justification for your answer, using your data and calculations.

3. Which of the two indicators cannot be used to estimate the pH of acetic acid solutions of different concentrations? Why not?
4. a. In Part D, how does the addition of sodium acetate shift the equilibrium? Write out the acetic acid dissociation equilibrium reaction and explain your answer in that context.
- b. What effect will the addition of sodium acetate have on the pH of the solution? Should pH increase, decrease, or remain the same? Explain in the context of the acetic acid dissociation equilibrium.
- c. Did the experimental results match your predicted change in pH? Explain any discrepancies.

