

pH: Measurement and Uses

One of the most important properties of aqueous solutions is the concentration of hydrogen ion. The concentration of H^+ (or H_3O^+) affects the solubility of inorganic and organic species, the nature of complex metal cations and the rates of chemical reactions.

For convenience the concentration of H^+ is frequently expressed as the pH of the solution rather than hydrogen ion molarity. pH is defined by the equation:

$$pH = -\log[H^+] \quad (1)$$

where the logarithm is taken to the base 10. If $[H^+]$ is 1×10^{-4} moles per liter, the pH of the solution is 4. If $[H^+] = 5 \times 10^{-2}$ M, the pH is 1.3.

Basic solutions are also described in terms of pH. In water the following relation exists:

$$[H^+] \times [OH^-] = K_w = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C} \quad (2)$$

Since $[H^+]$ equals $[OH^-]$ in pure water, by Equation 2, $[H^+]$ must be 1×10^{-7} M. Therefore, the pH of distilled water is 7. Solutions in which $[H^+] > [OH^-]$ are acidic and will have a pH < 7. When $[H^+] < [OH^-]$, a solution is basic and pH > 7. A solution with a pH of 10 will have $[H^+] = 1 \times 10^{-10}$ M and a $[OH^-] = 1 \times 10^{-4}$ M.

pH Measurement

pH can be determined experimentally in two ways. One is to use an indicator, a soluble dye whose color is sensitive to pH. Indicator colors change over a relatively short (about 2-unit) pH range. When properly chosen, they give the approximate pH of solutions. Two common indicators are litmus, usually used on paper, and phenolphthalein, commonly used in acid-base titrations. Litmus changes from red to blue in the pH range 6 to 8. Phenolphthalein changes from colorless to red in the range 8 to 10. Any one indicator is useful for determining pH only in the region where it changes color. Indicators are available for measuring pH in any part of the scale. Universal indicator papers, which contain a mixture of several indicators and change color over a wide pH range, are also in common use.

An electronic pH meter is used for more precise measurements. A pH meter determines pH from the electrical potential between two electrodes in a solution. The potential varies with pH and activates an analog or digital meter calibrated to read pH directly to the nearest 0.01 or 0.001 unit. A pH meter is used when reliable knowledge or control of pH is necessary.

Weak Acids and Bases

Strong acids such as HCl and HNO₃, ionize completely in solution. [H⁺] in a 1M HCl solution is also 1M because there are no undissociated HCl *molecules* in the system. Similarly, strong bases

such as NaOH, ionize completely in solution; [OH⁻] is 0.5M in 0.5M NaOH; there are no NaOH molecules present. Weak acids, so called because they do not dissociate completely in solution, also produce acidic solutions. The general formula of a weak acid can be written as HA. In water, HA ionizes to a small extent according to the equation

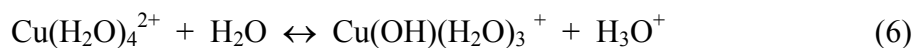


In 0.1 M CH₃COOH, [H⁺] equals about 0.001 M. [CH₃COO⁻] is also 0.001 M, [CH₃COOH] remains about 0.1 M and the pH of the solution is approximately 3 (see equation 5 below). In solutions of CH₃COOH, in contrast to those of HCl, there are many undissociated acid molecules. The species in solution will obey the law of chemical equilibrium, so that

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (4)$$

The conditions imposed by equation 4 are obeyed in any solution where some HA molecules are present. K_a, the equilibrium constant for the reaction, is the dissociation constant of HA, and has a constant value at a given temperature.

The species HA may be an organic acid, such as acetic acid, a hydrated metal cation, such as Cu(H₂O)₄²⁺, ammonium ion, NH₄⁺ or an inorganic molecule like H₂CO₃. Acid dissociation equations for these species are:

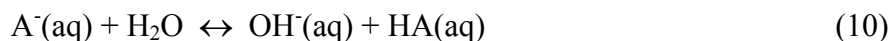


Hydrolysis

Other substances besides those identified as acids including many metal cations, form acidic solutions through hydrolysis. Metal cations, especially those having multiple positive charges and small radii, generate protons in solution from the dissociation of water molecules coordinated to the metal ion, as shown in equation (9).

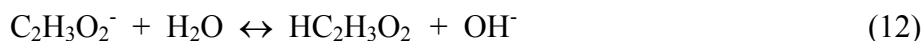


Many substances in addition to NaOH form basic solutions. These materials are related in a simple way to weak acids. Consider the properties of the A^- ion from the weak acid HA, in a solution of the salt NaA. Since HA is a weak acid, A^- ions in solution combine with H^+ to form HA molecules. In a solution of NaA, some anions undergo *hydrolysis*, that is, accept protons from the solvent water molecules, according to the equation:



Reaction 10 usually does not go very far, since K_a is typically very small. Even if the reaction proceeds to a small extent, excess OH^- ions are produced and the solution becomes basic. Because of Reaction 10, A^- ion is a weak base. As a general rule, the sodium or potassium salts of weak acids behave as weak bases.

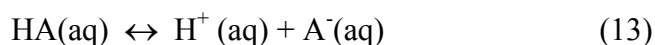
Ammonia, NH_3 is a common molecular weak base. NH_3 , in equation 11, plays the same role as $\text{C}_2\text{H}_3\text{O}_2^-$ in equation 12. Both are analogous to the A^- ion and both behave as weak bases. The reaction similar to (11) in which NH_3 participates is



In 0.1 M NH_3 about 1 per cent of NH_3 molecules react according to Equation 11. In that solution, $[\text{OH}^-]$ is about 0.001 M. $[\text{NH}_4^+]$ is also 0.001 M. $[\text{NH}_3]$ does not decrease significantly from 0.1 M.

Buffers

Solutions which undergo only a small change in pH when small quantities of acid or base are added to them are called buffers. For example, human blood is a complex buffered mixture with a normal pH range of 7.35-7.45. Three different buffer systems keep blood pH from varying more than ± 0.1 unit. A buffer solution consists of approximately equal amounts of a weak acid, HA, and its conjugate base, A^- , or of a weak base, B, and its conjugate acid, BH^+ . The $[H^+]$ depends primarily on K_a and to a lesser extent on the ratio of the concentration of undissociated acid to the acid anion is seen in equation 15:



$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (14)$$

$$[H^+] = K_a \left(\frac{[HA]}{[A^-]} \right) \quad (15)$$

Taking the log of both sides and rearranging the equation gives the Henderson-Hasselbalch equation that relates the pH of a buffer solution to the pK_a of the acid and the anion/acid concentration ratio.

$$pH = pK_a + \log \left(\frac{[A^-]}{[HA]} \right) \quad (16)$$

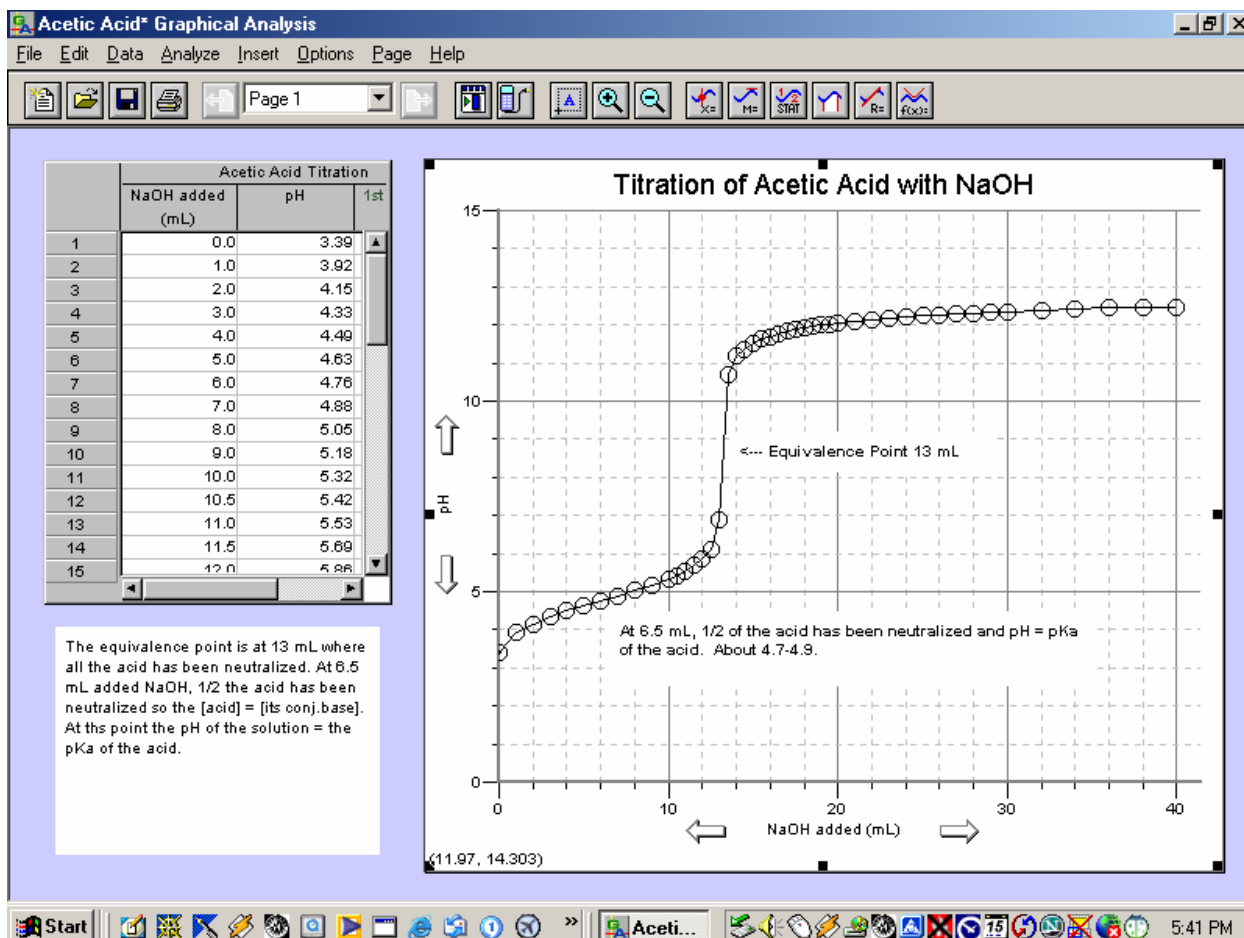
If a small quantity of base is added to a buffered acid solution, OH^- reacts with H^+ to form water. This reaction lowers $[H^+]$. However, the weak acid in the buffer solution then dissociates to produce additional H^+ , maintaining the equilibrium. $[HA]$ decreases slightly while $[A^-]$ increases. The ratio of $[HA]/[A^-]$, which controls pH, changes very little and the pH remains *almost* unchanged.

Solutions of weak bases and their salts behave in a similar manner to stabilize pH.

Molar Mass and pK_a of a Monoprotic Acid

The pK_a and molar mass of a weak acid can be obtained from its titration curve, a plot of pH versus volume of added base. The equivalence point is half way up the vertical part the titration curve. At the equivalence point, all the weak acid, HA, has reacted completely with an equivalent amount of base. The moles of base added equals the moles of acid originally present. From the mass of the acid weighed out, one can calculate the molar mass (g/mol) of the acid. The pK_a of an acid is the pH at which *half* of the acid has been neutralized. This is because when $[HA] = [A^-]$, their ratio is unity and the log term in the Henderson-Hasselbalch equation (16) becomes zero. pH then equals pK_a .

Your instructor will sketch the titration curve of a weak acid and a strong base, showing the equivalence point at pH above 7 and the pH at which half of the acid has been titrated. The following diagram shows the titration of acetic acid with NaOH. The equivalence point occurs at 13 mL. Going to $\frac{1}{2}$ the equivalence point, 6.5 mL of added NaOH, then going up to the titration curve and across to the pH axis we see the pH is around 4.7 to 4.9. The true K_a of acetic acid is 1.8×10^{-5} and its pK_a is 4.74.



Experimental

Your instructor will show you how to calibrate (**if not previously calibrated**) and operate the pH meter, taking care not to damage the delicate hydrogen ion electrode. For the best accuracy, the meter must be calibrated with a buffer solution of known pH in the range where you will be making your measurements.

A. The pH of a Buffer Solution

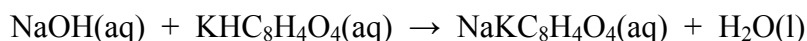
Prepare a buffer by adding 4.20 g of sodium acetate to 8.5 mL of 6.0 M acetic acid in a 250 mL beaker. Make the solution up to 100 mL with distilled water and mix. (As an exercise before you come to lab, verify that this solution contains equal concentrations of acetic acid and acetate ion.) Label four 50 mL beakers 1 through 4. Put 40 mL of this buffer solution into beakers 1 and 2. Put 40 mL of distilled water into beakers 3 and 4. Measure the pH of each solution. Pipet 1 mL of 6 M HCl into beakers 1 and 3. Pipet 1 mL of 6 M NaOH solution into beakers 2 and 4. Stir each solution and measure its pH.

B: Titration of a Monoprotic Acid

Preparation and Standardization of 0.10 M HCl

Prepare a 0.10 M NaOH solution by weighing 1.53 grams of concentrated NaOH (50% NaOH by mass) into a 250 mL Erlenmeyer flask and adding 200 mL of distilled water. **Be careful as concentrated NaOH is very corrosive. Mix the solution THOROUGHLY to insure a homogeneous mixture.**

Weigh 0.40 grams of potassium acid phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$, also labelled as KHP, 204.23 molar mass) into two separate 125 mL Erlenmeyer flasks, add 50 mL of distilled water, and 2-3 drops of phenolphthalein indicator to each. Fill a buret with the prepared 0.10 M NaOH solution and titrate each to a pink endpoint. Do a third titration if the first two do not agree and average the best two. Calculate the average molarity of the NaOH using the equation:



Titration of a Monoprotic Solid Acid

Obtain a vial of an unknown solid monoprotic acid and weigh the mass shown on the label into a 400 mL beaker. Add about 100 mL of distilled water and a magnetic stirring bar to the beaker. Place the beaker with the unknown acid on a magnetic stirrer plate and arrange the buret and pH electrode as shown by the instructor. Activate the magnetic stirrer, wait until the solid acid dissolves and record the initial pH of the solution.

Record the pH of the solution after each 1 mL addition of the 0.10M NaOH is added up to 10 mL of added base. Then record the pH for every 0.5 mL of added base until you have added a total of 20 mL. Then record the pH after every 1 mL of added base from 20 to 30 mL, and record the pH after every 2 mL added base until you have added a total of 40 mL of base.

Plot a graph of pH vs. volume of added base. Scale the x-axis from 0 to 40 mL and the y-axis from pH 0 to 15. Determine the K_a of the acid from the midpoint of the titration and the molar mass from the moles of base needed to titrate to the equivalence point.

Name: _____ Partner: _____

pH: Measurement and Uses: Data

A: pH of Buffer Solutions

Solution	Measured pH
Beaker 1, Buffer	
Beaker 2, Buffer	
Beaker 3, Distilled Water	
Beaker 4, Distilled Water	
Beaker 1, Buffer + HCl	
Beaker 2, Buffer + NaOH	
Beaker 3, Distilled Water + HCl	
Beaker 4, Distilled Water + NaOH	

B: Standardization of NaOH Solution

	Trial 1	Trial 2	Trial 3 (If necessary)
Mass $\text{KHC}_8\text{H}_4\text{O}_4$			
Moles $\text{KHC}_8\text{H}_4\text{O}_4$			
Moles NaOH used			
Final Buret Reading			
Initial Buret Reading			
Volume NaOH used			
NaOH Molarity			

Average NaOH Molarity _____

Name: _____ Partner: _____

pH Measurement and Uses: Data

B: Titration of Monoprotic Acid

mL Added NaOH	pH		mL Added NaOH	pH
0.00			16.50	
1.00			17.00	
2.00			17.50	
3.00			18.00	
4.00			18.50	
5.00			19.00	
6.00			19.50	
7.00			20.00	
8.00			21.00	
9.00			22.00	
10.00			23.00	
10.50			24.00	
11.00			25.00	
11.50			26.00	
12.00			27.00	
12.50			28.00	
13.00			29.00	
13.50			30.00	
14.00			32.00	
14.50			34.00	
15.00			36.00	
15.50			38.00	
16.00			40.00	

Plot a graph of pH vs. volume of added base. Scale the x-axis from 0 to 40 mL and the y-axis from pH 0 to 15. Determine the K_a of the acid from the midpoint of the titration and the molar mass from the moles of base needed to titrate to the equivalence point.

Name: _____ Partner: _____

pH Measurement and Uses: Calculations

Part A: pH of Buffer Solutions:

- a) What is the measured pH of the buffer solution you prepared?
- b) Using the Henderson-Hasselbalch equation, calculate the theoretical pH of the buffer solution you prepared. The K_a of acetic acid is 1.8×10^{-5} .

- c) What is the measured pH of the buffer solution to which you added hydrochloric acid?
- d) Calculate the pH of the buffer solution to which you added hydrochloric acid. (A mole of added HCl consumes one mole of acetate ion and creates one mole of acetic acid.)

- e) What is the measured pH of the buffer solution to which you added sodium hydroxide?
- f) Calculate the pH of the buffer solution to which you added sodium hydroxide. (A mole of added NaOH consumes one mole of acetic acid and creates one mole of acetate ion.)

Name: _____ Partner: _____

Unknown Acid Number _____

Part B: Calculation of the Molar Mass of the Monoprotic Acid

- a. Volume NaOH solution used to reach equivalence point: _____
- b. Molarity of the NaOH solution (page 6): _____
- c. Moles NaOH used in titration: _____
- d. Moles of unknown acid titrated: _____
- e. Mass of unknown acid titrated (on label of vial): _____
- f. Molar Mass of unknown acid: _____

Part B: K_a of the Monoprotic Acid

- a. pH at one half the equivalence point (see page 4): _____
- b. pK_a of the unknown acid: _____
- c. K_a of the unknown acid: _____

