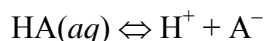


## Experiment 4 pH of Aqueous Solutions

**Introduction:** An *acid* is a substance which dissociates to produce hydrogen ions,  $H^+$ , when dissolved in aqueous solution. Once in solution, the  $H^+$  ion, which is simply a proton, immediately combines with water to form the *hydronium ion*,  $H_3O^+$ . **So when aqueous  $H^+$  appears in a chemical equation, it is understood that the actual species exists as  $H_3O^+$ .** An acid is classified as strong or weak depending on the extent to which the molecules of the acid dissociate into  $H^+$  and its anion,  $A^-$ . A *strong* acid dissociates completely in water (*e.g.*, HCl dissociates virtually 100% into  $H^+$  and its anion,  $Cl^-$ ), while a *weak* acid dissociates only partially and forms very little  $H^+$  (*e.g.*, only about 3% of the dissolved molecules of acetic acid,  $CH_3COOH$ , dissociate into  $H^+$  and the acetate anion,  $CH_3COO^-$ ). Weak acid dissociation can be represented as a generic reversible reaction:



where HA is the weak acid and  $A^-$  is the anion, or **conjugate base**, of HA. For this reversible reaction, an equilibrium constant can be defined:

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (1)$$

The equilibrium constant is called the ***acid dissociation constant*** or ***acid ionization constant***. If the undissociated acid (HA) is favored and the acid is weak,  $K_a$  is measurable and will be much less than one. For strong acids, the dissociated products, ( $H^+$  and  $A^-$ ) are so strongly favored, that [HA] approaches zero and  $K_a$  approaches infinity. Thus strong acids, of which there are very few, do not have values of  $K_a$  associated with them.

For convenience a log scale is often used to express very small quantities. For most aqueous solutions of interest, the concentration of  $H^+$  is small, ranging from approximately  $10^{-1}$  to  $10^{-12}$  M. Since it is also more convenient to deal with positive numbers, the negative value of the log ( $-\log$ , symbolized by “p”) of  $[H^+]$  is used to express the concentration of  $H^+$ . Thus the definition of pH is:

$$pH = -\log[H^+], \text{ and } [H^+] = 10^{-pH} \quad (2)$$

As noted earlier, it is always understood that  $H^+$  is in fact present in solution as the hydronium ion,  $H_3O^+$ . Notice that larger concentrations of  $H^+$  mean smaller values of pH.

Other  $-\log$  scales can be defined in a similar fashion. One such scale is pOH.

$$pOH = -\log[OH^-]$$

In aqueous solutions, the concentration of  $H^+$  and  $OH^-$  are always related by the *dissociation constant of water*,  $K_w$ , which arises from the reaction called the **autoionization of water**.



In this equilibrium, the molecular  $\text{H}_2\text{O}$  is heavily favored. In fact the concentrations of the ions in pure water are  $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}$  at  $25^\circ\text{C}$ . Thus the value of  $K_w$  is given by

$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ at } 25^\circ\text{C}.$$

In an aqueous solution that isn't acidic or basic, the concentration  $[\text{H}^+]$  is equal to that of  $[\text{OH}^-]$ , so the solution is neutral, the same as pure water. Since this occurs at a concentration of  $1 \times 10^{-7} \text{ M}$  for both ions. The values of pH and pOH are both 7 in a neutral solution.

$$\text{pH} = -\log[\text{H}^+] = -\log(1 \times 10^{-7}) = 7$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1 \times 10^{-7}) = 7$$

The following relationships regarding aqueous solutions should therefore be understood.

pH	$[\text{H}^+]$	Solution
less than $< 7$	$> 1.0 \times 10^{-7}$	Acidic
greater than $> 7$	$< 1.0 \times 10^{-7}$	Basic
equal to $= 7$	$= 1.0 \times 10^{-7}$	Neutral

Note also that if one takes  $-\log$  of both sides of the equation for  $K_w$ , the result is

$$\text{p}K_w = \text{pH} + \text{pOH} = 14$$

So in any aqueous solution, for which it is always true that  $K_w = 1 \times 10^{-14}$  at  $25^\circ\text{C}$ , the sum of pH and pOH of the solution must equal 14. Thus an acidic solution with  $\text{pH} = 4$  must have a pOH of 10.

**Part A - pH of Weak vs. Strong Acid:** When a solution of acid is prepared, its initial molarity (before any dissociation of the acid molecules occurs) is given by the moles of acid added divided by the liters of solution. For a strong acid, the concentration of  $[\text{H}^+]$  will be the same as the initial molarity of the acid because all the acid dissociates into  $\text{H}^+$  and the anion  $\text{A}^-$ . Because  $[\text{H}^+] = [\text{A}^-]$  in this case, thus the pH of a strong acid can be predicted from the molarity of the acid. You will measure the pH of a strong acid to verify this relationship.

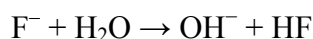
For a weak acid with much less than 100% dissociation,  $[\text{H}^+]$  is much less than the initial  $[\text{HA}]$ . You will measure the pH of a weak acid of known initial  $[\text{HA}]_{\text{initial}}$ . Then  $[\text{H}^+]$  can be calculated using equation (2). Since  $[\text{A}^-]$  is the same as the  $[\text{H}^+]$  just calculated, and  $[\text{HA}]$  at equilibrium can be calculated from  $[\text{HA}]_{\text{initial}} - [\text{H}^+]$ , the value of  $K_a$  for the acid can be calculated from these values using equation (1).

**Part B – Indicator Survey:** Many naturally occurring dyes in solution change color with the pH of the solution. You will add a number of these dyes (including a mixture of the dyes

which forms what is called a universal indicator) to buffer solutions of known pH, and observe how the dye color changes with pH.

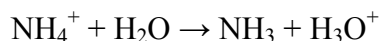
**Part C – pH of Common Household Products:** You will test the pH of a number of household products using the universal indicator you prepared. Then you will measure the pH of the products using the Vernier system and compare them to the pH values predicted by the universal indicator colors.

**Part D: - pH of Salt Solutions:** When a salt whose anion is the conjugate base of a weak acid, is dissolved in aqueous solution, the anion acts as a base, producing  $\text{OH}^-$  ions in solution. For example,  $\text{F}^-$  is the conjugate base of the weak acid HF. So in a solution of NaF, the  $\text{F}^-$  reacts with water in what's called a hydrolysis reaction to form  $\text{OH}^-$  in solution:



Thus, because the salt contains a conjugate base of a weak acid, it forms a basic solution. The  $\text{Na}^+$  ion is neither a conjugate acid or base and thus does not affect the pH of the solution.

On the other hand, a salt, such as  $\text{NH}_4\text{NO}_3$ , containing the conjugate acid,  $\text{NH}_4^+$  of a weak base,  $\text{NH}_3$ , will undergo hydrolysis to form an acidic solution:



The  $\text{NO}_3^-$  ion, the conjugate base of a strong acid, is a very weak base and thus does not affect the pH.

In this experiment you will use a Vernier pH sensor to measure the pH of weak and strong acids and determine  $K_a$  for  $\text{CH}_3\text{COOH}$ . You will also observe the colors of various indicators as a function of solution pH. Finally you will measure the pH of some common household products and salt solutions.

**Pre-Lab Notebook:** Provide a title, purpose, and a summary of the procedure.

**Equipment:**

Test tubes (12)  
24-well Microcell plates (4)  
100 or 150 mL Beakers (3)  
10.0 mL Graduated cylinder  
50.0 mL Graduated cylinder  
250 mL Beaker  
600 mL Beaker  
Vernier System with pH meter

**Stock Solutions:**

0.1 M HCl  
0.1 M  $\text{CH}_3\text{COOH}$

**In-Lab Experimental Procedure:** Work in groups of two.

**Calibrating the pH Electrode:**

1. Remove the storage bottle from the pH sensor by **FIRST UNSCREWING THE LID**, then removing the bottle and the lid from the shaft of the pH probe. Replace the lid to the bottle after the pH sensor has been taken out; place the bottle of electrode solution in a place where it will not spill over.
2. Following the first section of the Vernier tutorial, set up the Vernier system with the pH probe in channel 1. **YOU MUST** calibrate the pH meter before performing any experimentation. (**Do not assume that the pH meter is still in calibration from the previous user.**)
3. Enter the DATAMATE program after the pH sensor has been inserted into channel 1. Press “1” for SETUP from the main screen, then on the setup screen press “2” for CALIBRATION. On the CALIBRATION screen, there will be a reading for calibration slope and linear intercept (ignore these). Press “2” for CALIBRATE NOW to get to the CALIBRATE SENSOR screen.
4. Before proceeding, rinse the pH electrode thoroughly with DI water, and carefully blot it dry with a Kimwipe tissue. Place the pH electrode into a buffer 4 solution and the calculator will instruct you to monitor voltage, when the voltage is stable press ENTER. The next screen will prompt you to enter a value; you will enter “4” for the buffer 4 solution. Now you will have a value and voltage for POINT 1. Repeat the process (including rinse and blot) with a *buffer 7* solution for POINT 2; you will monitor the voltage, hit enter, and on the next screen enter “7” for the buffer 7 solution. After this is complete, the pH sensor is calibrated and you can return to the main screen by pressing OK twice, and begin experimentation.

**Part A – pH of Weak vs. Strong Acid:**

1. *Collecting data with the pH electrode:* (**When collecting pH readings from the pH sensor you can neglect which mode data collection is set at in the DATAMATE program**). To obtain the pH of a solution, place the pH electrode in the solution and wait for 15-30 seconds for the reading on the main screen to stabilize. Before placing the pH electrode in a new solution it must be rinsed thoroughly with DI water and blotted. Strong bases are hard to rinse off, take extra care in cleaning the electrode after measuring a basic solution ( $\text{pH} > 7$ ). It may be necessary to dab the pH electrode with a Kimwipe to clean a basic solution off. **Note: pH meters can be unpredictable. If you feel you are not getting reasonable readings, check with your instructor.**
2. Obtain about 400 mL of de-ionized water in a 600 mL beaker for use in the dilutions described below. Label with tape three 100 mL beakers: **(1) 0.1 M stock; (2) 1:10 dilution; and (3) 1:100 dilution.**
3. Obtain approximately 15 mL of the 0.1 M stock solution of HCl in the (1) labeled beaker, take it to your bench, and prepare a 1:10 dilution of this solution by placing 5.0 mL of it into a 50.0 mL graduated cylinder and diluting it with DI water to the 50.0 mL mark. Transfer the diluted solution to the (2) labeled 100 mL beaker.
4. Prepare a 1:100 dilution of the acid by taking the solution prepared in step 3 (the 1:10 dilution) and further diluting it by placing 5.0 mL of it into a 50.0 mL graduated cylinder

and diluting it to the 50.0 mL mark with DI water. Transfer this new solution to the (3) labeled beaker.

5. Measure and record the pH of all three solutions of HCl in your laboratory notebook in a table similar to the one shown below. Make sure to also record the exact molarity of the stock solution given on the bottle.

6. Rinse the three labeled beakers with tap water and then DI water and use them to **repeat steps 3-5 with acetic acid, 0.1 M CH<sub>3</sub>COOH, stock solution**, constructing a similar table.

HCl Solutions Data:

Solution:	(1) Stock	(2) 1:10 dilution	(3) 1:100 dilution
Molarity:			
pH			
H <sup>+</sup> Molarity, [H <sup>+</sup> ]			

### Part B: Indicator Survey:

1. Arrange three micro-cell plates to create an array of 11 columns by 7 rows.
2. Fill the first seven rows half-full with the pH 2 – 12 buffer solutions provided.
3. Place one drop of the six indicators (methyl orange, bromothymol blue, phenol red, phenolphthalein, thymolphthalein, and alizarin yellow) into each buffer and record the color (you can be creative here!) of the solution in a table in your laboratory notebook similar to the one shown below.
4. Prepare a universal buffer by mixing one drop each of methyl orange, bromothymol blue, phenolphthalein, and alizarin yellow into row seven of the micro-cell plate (Note: **NO** Phenol Red or Thymolphthalien are used in the universal indicator). Record the color of each of these solutions as well.
5. **Keep the micro-cell plates for comparison** with solution colors in Part C.

pH Buffer ⇒	2	3	4	5	6	7	8	9	10	11	12
Methyl orange											
Bromothymol Blue											
Phenol Red											
Phenolphthalein											
Thymolphthalein											
Alizarin Yellow											
Universal Indicator											

### Part C – pH of Common Household Products:

1. Place about 3 mL of the liquid household products into separate test tubes. For the solid products, place a spatula tip full into separate test tubes and add 3 mL of DI water.

2. Add the universal indicator, record the color, and estimate the pH of each in a table in your lab notebook as shown below.

3. Transfer the contents of each test tube to a clean section in the micro-cell plates and measure the pH with the Vernier pH probe. Record the value of pH for each household product in a table in your notebook as shown below.

Product name	pH (universal indicator)	pH (measured)

#### Part D: pH of Salt Solutions:

1. In separate test tubes, dissolve ~1 g each of  $\text{NaCH}_3\text{COO}$ ,  $\text{AlCl}_3$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{NaCl}$  in 5 mL of DI water.

2. Transfer each solution to a clean section of the microcell plate and measure the pH with the pH meter. Record in a table as shown below.

pH of Salt Solution Data Table:

Salt	$\text{NaCH}_3\text{COO}$	$\text{AlCl}_3$	$\text{Na}_3\text{PO}_4$	$\text{Na}_2\text{CO}_3$	$\text{NH}_4\text{Cl}$	$\text{NaCl}$
→						
pH →						

## Lab Report Outline for pH

### Graded Sections of Report Percent of Grade

Pre-Lab	10
In-Lab	
Part A Table – HCl	5
Part A Table – CH <sub>3</sub> COOH	5
Part B Table	10
Part C Table	5
Part D Table	5

Post-Lab (Put numerical answers in blocks  where they appear.)

#### Part A: pH of Weak vs. Strong Acid:

1. Show a sample calculation of the H<sup>+</sup> molarity from the pH values and complete the table in the In-Lab section of your notebook 5
2. Calculate K<sub>a</sub> for the CH<sub>3</sub>COOH using the [H<sup>+</sup>] and [CH<sub>3</sub>COOH]<sub>initial</sub> for each of the three solutions in the data table.     
15
3. Discuss how the data show that HCl is a strong acid and CH<sub>3</sub>COOH is a weak acid. 5
4. Explain how it is possible that a solution of a weak acid can have a lower pH than a solution of a strong acid. 5

#### Part C: Household Products:

1. How well did the measured pH values compare with the estimated values based on the universal indicator colors? Which product was most acidic? Most basic? 15

#### Part D: pH of Salt Solutions:

1. **First review Part D in the Introduction.** Using hydrolysis equations showing the reaction between water and the conjugate base or acid in each of the salts, explain why each salt solution would give the pH you measured. 15

