

Experiment 9

pH METERS, HYDROLYSIS, AND BUFFER CAPACITY

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PURPOSE

Learn to use a pH meter. Measure the pH of a variety of solutions, including observing the effect of hydrolysis. Determine the pH and buffer capacity of an unknown buffer solution.

STRONG VERSUS WEAK ACIDS AND BASES

A strong acid is commonly defined as one whose ionizable hydrogens dissociate completely in water to produce H^+ (or H_3O^+ hydronium ions). By contrast, when a weak acid is dissolved in water, only a small fraction of the hydrogens dissociate. Parallel definitions in terms of hydroxide ion apply for strong and weak bases. The strengths of weak acids and bases range over a very broad continuum, from almost-strong to having negligible strength.

SØRENSEN'S pH SCALE

In 1909 the Danish chemist S. P. L. Sørensen proposed a useful way to quantify the total amount of free H_3O^+ as

$$pH = -\log[H_3O^+] \text{ or } [H_3O^+] = 10^{-pH} \quad (1)$$

where the p is from the words Potenz, puissance and power literally, "hydrogen power." $[H_3O^+]$ indicates molarity of free hydrogen ions. The minus sign before the log results in pH usually being positive, because $[H_3O^+]$ is usually less than 1, and logarithms of such numbers are negative.

Why is pH convenient? Given water's $K_w = 1.0 \times 10^{-14}$ (at 25°C), the range of hydrogen ion concentrations commonly encountered is from 1 to 10^{-14} M. The pH scale compresses this range of 14 orders of magnitude (involving negative exponents) into a simple, positive scale from 0 to 14. The pH of a neutral solution at 25°C falls in the middle of the scale, at pH 7.00. So, $pH < 7.00$ means acidic, and $pH > 7.00$ means basic.

Scientists have embraced Sørensen's "p operator", and now use it as a general shorthand notation for the negative logarithm of anything. For example, $pK = -\log K$ and $pOH = -\log [OH^-]$.

HOW CAN pH BE MEASURED?

Because of the great sensitivity of many chemical reactions to $[H_3O^+]$, a convenient method of measuring pH is essential. A pH meter is just a voltmeter that draws very little current (high input impedance). What does voltage have to do with pH?

The trick with this method is to take advantage of a special kind of glass which is permeable to H_3O^+ ions but not to other ions. H_3O^+ ions can diffuse from solution into this glass, but other ions can not follow. When a piece of this glass is used to separate two solutions of different $[H_3O^+]$, the

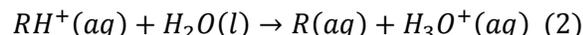
high $[H_3O^+]$ side of the glass develops a slight positive charge as more H_3O^+ ions diffuse into that side than the other. The result is a measurable voltage difference across the two sides of the glass. Only the fragile bulb on the end of the electrode is made from the special pH-sensitive glass.

Because the pH electrodes rely on electrical conduction through the test solution, the method doesn't work very well with nonaqueous solutions or even for aqueous solutions with very few ions in it (e.g., distilled water and rain water). The meter reading will either drift meaninglessly, or give a reading that is highly dependent on stirring rate and the pH of the previous solution in which it was used.

Like any instrument, a pH meter must be calibrated using known, or standard, samples. Theoretically, a change of 1 pH unit causes a change of 59.2 mV in the measured voltage. In practice, this number can vary, particularly as the electrode ages. Thus, the voltage is measured at two different pH values and the equation of a line can then be extrapolated which gives the relationship between pH and voltage. Typically, standard buffer solutions with pH's of 4, 7, or 10 are used. Buffer solutions are used since their pH's aren't significantly affected by slight contamination or dilution.

HYDROLYSIS — WHY SOME SALT SOLUTIONS AREN'T NEUTRAL

Many ions react with water to change its pH. Such a reaction is called hydrolysis meaning, "water splitting." For example, a cation RH^+ could react to make a solution acidic:



An anion A^- could react to make a solution basic:



You should study these reactions, and convince yourself that hydrolysis only happens if R is a weak base, or HA is a weak acid.

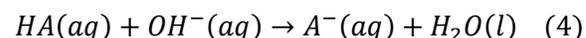
NaCl doesn't change the pH of water because NaOH is a strong base and HCl is a strong acid. However, a NaF solution would be basic, because F^- hydrolyzes water to form OH^- and the

weak acid HF. Similarly, a CH_3NH_3Cl solution would be acidic because the $CH_3NH_3^+$ ion hydrolyzes water to form H_3O^+ and the weak base CH_3NH_2 .

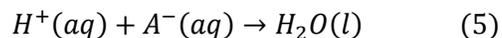
WHAT IS A BUFFER?

A solution is said to be buffered or to be a buffer if its pH doesn't change much when either a strong acid or base is added. Clearly, a buffer must contain chemicals capable of neutralizing either an acid or base. That must mean a buffer contains both a base and an acid. How is this possible? Why don't the acid and base neutralize each other?

The trick is to use a mixture of a weak acid (HA) and its conjugate weak base (A^-) which cannot neutralize each other. However, they will react nearly completely with any strong base or acid that is added. The weak acid will neutralize most of any strong base added, as follows:



and the conjugate base will neutralize most of any strong acid that is added, as follows:



Notice that although the above reactions produce the base A^- and the acid HA, they have effectively removed H^+ and OH^- from the solution, and thereby preserved the pH.

There are many important naturally occurring buffers. Our blood is buffered to hold around pH 7.4; if it weren't buffered, the increased acidity from lactic acid produced during exercise would be fatal. Unbuffered mountain lakes and streams are much more susceptible to acid rain than are the so-called limestone streams.

WHAT IS BUFFER CAPACITY AND HOW IS IT MEASURED?

Obviously if lots of acid or base were dumped into a buffer solution, the buffering ability could be overwhelmed. The ability of a buffer to resist pH change is referred to as its **buffer capacity**. Buffer capacity is defined as the moles of strong acid or base required to change the pH of 1 liter

of the buffer by 1 pH unit (either higher or lower). It has units of moles/L.

The procedure for determining buffer capacity is simple: Measure the volume of standard acid or base needed to change a known volume of the buffer by exactly 1 pH unit. Calculate the moles of standard acid or base used. Divide this by the number of liters of buffer used to obtain the buffer capacity in units of moles/L.

Sample Problem: Suppose you start with 10.0 mL of buffer to which 75 mL of water is added and the pH is read as 6.3. After the addition of 37.2 mL of 0.123M HCl from a buret, the pH has changed to 5.3. What is the buffer capacity?

Solution: First, how many moles of standard acid were added?

$$\left(\frac{37.2 \text{ mL of acid}}{1000 \text{ mL}}\right)\left(0.123 \frac{\text{mol}}{\text{L}}\right) = 0.00458 \text{ mol}$$

Next, divide by the liters of *buffer* used. In this example, only 10.0 mL of buffer were used. The 75 mL of water are irrelevant. This water was only added so that there would be sufficient solution present to immerse the pH electrode.

$$\frac{0.00458 \text{ mol}}{0.0100 \text{ L}} = 0.458 \text{ mol/L}$$

IN THIS EXPERIMENT

You will learn how to calibrate a pH electrode, and then try to read the pH of tap and distilled water. You will prepare a series of HCl dilutions and see the effect of concentration on pH. The pH of equal concentrations of a strong acid and a weak acid will be compared. You will prepare three salt solutions, and measure the pHs to test for hydrolysis. Finally, you will measure the buffer capacity of an unknown buffer solution.

WARNING. THE FOLLOWING SECTION IS RATED PG-21. Teachers should consider whether they wish to allow their students under the age of 21 to read this section without professorial guidance.

THE DARK SIDE OF THE FORCE

There is a dark side to pH which is normally kept hidden from general chemistry students.

The number reported by a pH meter does not exactly equal $-\log[\text{H}_3\text{O}^+]$. In fact, experimental pH values have no theoretically precise meaning. Some books will tell you that the problem is resolved by defining pH in terms of the H_3O^+ activity, or effective concentration. Thus, Equation (6) is sometimes offered as an improvement over Equation (1).

$$pH = -\log(\text{H}_3\text{O}^+ \text{ activity}) \quad (6)$$

According to the principles of thermodynamics, the activity of one kind of ion (e.g., H_3O^+) is unknowable. So, Equation 6 can't be legitimate, at least as far as experimental measurement is concerned. This is because thermodynamics deals with properties of matter on a bulk scale, rather than a microscopic or molecular scale, and it is impossible to prepare a bulk sample of just one kind of ion. The counterions will always be present, and any measured property, including pH, will represent some sort of ill-defined average of that property for all ions in the solution. Thus, although a pH meter reading is certainly related to H_3O^+ activity, it also depends in an indefinite way on the activities of everything else in the solution.

The U.S. National Bureau of Standards has assigned pH values to certain buffer solutions, which everyone (in the U.S.) uses to "calibrate" their pH meters. So, at least we can all measure the same thing, even if no one is sure exactly what it means. Other countries' bureaus of standards have assigned slightly different values to some of these very same solutions!

In practice, measured pH values correspond approximately to Equation (1), and we usually assume it is valid to the nearest 0.01 for ordinary solutions between about pH 3 and 10. The error increases at the extremes of the pH scale and at high salt concentrations. For example, a properly calibrated pH meter will record a pH of 1.10 for 0.10M HCl, rather than 1.00 as predicted by Equation (1). Similarly, 0.10M NaOH has a pH of 12.88, rather than the expected value of 13.00.

PRE-LABORATORY PREPARATION

1. Read the procedure and data analysis sections of the experiment.
 2. Complete the PRELAB assignment in Canvas. Refer to the procedure and data analysis sections of the experiment as needed. The prelab questions for this experiment replicate the questions in the data analysis section. Additionally, they aid in the preparation of several necessary solutions.
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EXPERIMENTAL SECTION

REAGENTS PROVIDED

HCl, Hydrochloric acid, 0.10 M.
HC₂H₃O₂, Acetic acid, 0.10 M.
NaOH, Sodium hydroxide, roughly 0.05 M.
NH₄Cl(s), Ammonium chloride, 53.49 g/mol.
NaC₂H₃O₂(s), Sodium acetate, 82.03 g/mol.
Na₂CO₃(s), Sodium carbonate, 105.99 g/mol.
Unknown buffer solution.

Hazardous Chemicals

Handle the acid and base solutions with care.

WASTE DISPOSAL

All of the chemicals used in this experiment may be safely disposed of by washing down the sink.

PROCEDURE

You will do this experiment with a partner. However, each student will do his/her own buffer capacity determination.

LEARNING TO MAKE pH MEASUREMENTS

Avoid leaving the pH electrode out of solution for long periods. It is best to keep the electrode in a beaker of distilled water between readings.

It is easy to get poor results when making pH measurements. This is almost always due to contaminated solutions.

TO AVOID CONTAMINATION: (1) BE SURE TO RINSE THE pH ELECTRODE THOROUGHLY BEFORE PLACING IT IN ANY SOLUTION! (2) WASH AND RINSE YOUR GLASSWARE BEFORE USING IT!

1. Setup and do a two-buffer calibration of your pH electrode following the directions in the Techniques section (located after the procedure section).

In this experiment we are primarily measuring the pH of acidic solutions, so we will use pH 4 and 7 buffers to calibrate the pH electrodes.

2. Read and record the pH of tap water.

After placing the electrode in a new solution, swirl it for a few seconds to homogenize the solution near the electrode.

Record all pH readings to the nearest 0.01 pH unit. If the reading fluctuates randomly, wait a few seconds and record the average reading. If the readings are drifting in one direction, wait a minute or two until the reading stabilizes.

A slow drift usually indicates that either (1) there are few ions present and the meter is having trouble getting an accurate reading; (2) gas is being adsorbed from the air (if the solution is sufficiently dilute); or (3) a contaminant is diffusing through the solution.

3. Try to read the pH of distilled water. Record your observations.

Do not spend all period staring at the pH meter while the reading slowly drifts. After a minute or two, take your reading and move on.

ACID pH MEASUREMENTS

4. Read and record the pH of the 0.10 M HCl solution provided.

5. Prepare 0.010 and 0.0010 M HCl solutions using the stock solution of 0.10 M HCl provided. Read and record the pH of each of these solutions.

Follow the plan described in your prelab for preparing these solutions. If you make 100 mL of each solution you will have plenty to prepare the next solution and measure the pH.

Rinse pipets thoroughly before using them in a new solution: (1) run some distilled water through them; (2) wipe the outside dry; (3) rinse/fill the pipet with the new solution and then drain it completely. After these three steps, it should be ready to use to measure the new solution.

6. Read and record the pH of 0.10 M acetic acid solution provided.

HYDROLYSIS STUDY

7. Prepare 100 mL of 0.10 M aqueous solutions of the salts ammonium chloride, sodium acetate, and sodium carbonate (see prelab calculations).

8. Read and record the pH of each solution.

BUFFER CAPACITY DETERMINATION

Each student should do this section individually.

9. Give the laboratory assistant a clean, dry 50 mL beaker for your unknown.

You will be given approximately 25 mL of unknown. Record the unknown number.

10. Measure out 10.0 mL of your unknown buffer solution into a 250 mL beaker and add about 100 mL of distilled water.

The 100 mL of water are added to ensure there is sufficient solution present to accurately read the pH. The water has no effect on the measured or calculated buffer capacity.

11. Read and record the pH of your buffer solution.

12. Fill a 50-mL buret with the 0.05 M NaOH(aq) provided. Record the initial buret reading (to the nearest 0.01 mL) and the actual NaOH concentration on your data sheet.

13. With the pH electrode immersed in the (diluted) buffer solution, add the NaOH from the buret until the pH has increased by 1.00 pH units.

The contents must be stirred during the addition. This can be done either by careful swirling of the beaker, or stirring with the pH electrode. Be careful not to hit the glass electrode on the sides of the beaker. The electrode should not be removed from the solution until the titration is complete.

14. Record the final pH and buret readings.

CLEAN UP

15. Rinse the pH electrode, wipe it with a Kimwipe and return it to its storage bottle. Dump leftover solutions down the drain. Rinse, dry, and store your glassware.

16. Shutdown the LabQuest2.

This can be done by first tapping **File**, then **Quit**. If asked, choose to **Discard** the data. Next, tap on the **System** folder and then **Shut Down** and, finally, **OK**.

RETURN EVERYTHING TO WHERE IT WAS AT THE START OF LAB. HAVE AN INSTRUCTOR CHECK YOUR STATION BEFORE LEAVING.

Once your station is clean, wash your hands.

TECHNIQUES

CALIBRATION AND USE OF A pH PROBE

1. Turn on the LabQuest2 by pressing the red power button on the top.

It takes a minute to warm up.

2. Once warmup is complete, connect the pH Probe amplifier box to CH 1 on the left end of the LabQuest2.

Most of the pH probes will immediately be recognized and a box will appear containing the pH reading.

If the meter box does not appear, you have an older probe with an analog-to-digital adapter and it needs to be set up manually, as follows:

- Tap **Sensors** from the top menu line.
- Tap **Sensor Setup...**
- Tap in the large box next to CH 1 that reads “No Sensor”.
- Scroll down and tap **pH/mV/ORP Amplifiers**.
- Tap on **pH**.
- Tap **OK**.
- Tap **OK** to return to the meter screen, where you should now see the pH reading.

3. Prepare the electrode for use.

Remove the electrode from its small plastic storage bottle by unscrewing the top until you can slide the electrode out of the bottle. Set the bottle aside where it will not get knocked over. Rinse it off thoroughly (see the RINSING A pH ELECTRODE section, below).

4. Calibrate the pH electrode.

- Tap on **Sensors** from the menu line at the top of the screen. Next choose **Calibrate** and then **CH1: pH**.
- Tap **Calibrate Now**.
- Immerse the electrode in a bottle containing a pH 4 or 7 buffer and swirl it for a few seconds to remove any air bubbles or dilute any water droplets clinging to the end of the

electrode. The bulb at the bottom of the electrode must be completely submerged in order to get an accurate reading.

- In the Value 1 box, enter the buffer pH (4 or 7).
- Wait until the line voltage reading stabilizes and then tap **Keep**. Frequently, the last digit will be fluctuating—this is normal.
- Remove the electrode from the solution and rinse it thoroughly.
- Place the electrode in the other buffer solution and swirl it briefly (a few seconds).
- In the Known Value 2 box, enter the buffer pH (4 or 7).
- Wait until the line voltage reading stabilizes and then tap **Keep**. The voltage should have changed by approximately 0.6 – 0.8 V.
- Tap **OK**.

If the calibration was done properly, the pH reading on the screen should be roughly equal to the pH of the last buffer solution (± 0.03).

You are now ready to measure the pH of solutions. Simply immerse the pH electrode in a solution, swirl briefly to equilibrate, and read the pH when it stabilizes.

RINSING A pH ELECTRODE

1. Thoroughly rinse the electrode by spraying it with distilled water from a wash bottle. Be sure to spray the bottom where the sensitive pH glass is located.

2. Wipe the outside with a Kimwipe, and then give it a couple of firm shakes to remove the water from the bulb. Do **NOT** dry the bulb of the electrode with a Kimwipe or a paper towel.

The glass bulb of the pH electrode is very fragile. Be careful not to drop the electrode or hit it against something (like the edge of the sink or your lab partner), electrodes are expensive (and lab partners are valuable)!

Name

Station Used

Instructor/Day/Time

Partner

Station Checked & Approved

PRELAB CALCULATIONS

It is essential that this section be completed before coming to lab in order to have time to complete the experiment. The instructor may check that you have done this before you are permitted to start work.

1. Describe exactly how you will prepare 100 mL each of 0.010 and 0.0010 M HCl solutions by dilution of the 0.10M HCl provided.

DATA SHEET & DATA ANALYSIS

Record all values to the proper number of significant figures and with appropriate units (when applicable).

pH of tap water _____

Comments:

pH of distilled water _____

Comments:

pH of HCl: 0.10M _____; **0.010M** _____; **0.0010M** _____

Comments:

pH of 0.10M acetic acid _____

Comments:

1. Typically, how much does the pH increase each time the [HCl] decreases by a factor of ten?

2. Based upon the measured pH of the 0.10 M HCl and acetic acid solutions, which is the stronger acid: HCl or acetic acid? How can you tell based upon your data?

Hydrolysis Study:

For each salt, a single hydrolysis reaction, involving only one of the ions in that salt, should occur. Do not include any spectator ions in your reaction.

pH of 0.10M ammonium chloride _____

Comments:

Write the hydrolysis reaction that should have occurred for one of the ions in this salt.

pH of 0.10M sodium acetate _____

Comments:

Write the hydrolysis reaction that should have occurred for one of the ions in this salt.

pH of 0.10M sodium carbonate _____

Comments:

Write the hydrolysis reaction that should have occurred for one of the ions in this salt.

DATA SHEET & DATA ANALYSIS (Continued)

Each individual should attach this sheet containing his/her own buffer capacity results.

Buffer Capacity Determination:

Name _____

Unknown Number _____

	pH reading	Buret reading
Initial		
Final		
Change in Volume		

Concentration of NaOH solution _____

Calculate the buffer capacity of the undiluted, unknown buffer. Show your calculation, as always.

buffer capacity _____