MODULE 2
pH, Titrations, and Buffers

Module learning outcomes:
- Perform accurate titrations, with attention to endpoint pH
- Quantify the level of random error in any measurement or laboratory result (level 2)
- Prepare and utilize buffer solutions at target concentration and pH values
- Automate repetitive calculations

Shopping / borrowing list:
In order to do this lab, you will need
- the equipment pack (scale, beakers, droppers, grad. cylinders)
- a few small bottles or containers for storing solutions
- a way to label these containers.

In addition, you will need to gather small amounts of the following items:
- purple cabbage
- blueberries (fresh or frozen)
- several small storage containers
- baking soda
- toilet cleaner (w/ HCl)
- oven cleaner (w/ NaOH)
- white vinegar
- vitamin C tablet

INTRODUCTION
Brief review of acid/base concepts:
- According to the Bronsted-Lowry definition, acids are proton donors and bases are proton acceptors. Acid/base behavior typically occurs in aqueous solution, where acids generate hydronium ions, H_3O^+, and bases generate hydroxide ions (OH^-).
- Water is *amphoteric* since it can function as either an acid or a base. It is also *amphiprotic* because it can both accept and donate a proton or H^+. It can therefore react with itself to autodissociate into H_3O^+ and OH^- ions.
$$2\ H_2O\ (l) \leftrightarrow H_3O^+\ (aq) + OH^-\ (aq)$$
The extent of autodissociation of water is very small. The equilibrium constant for the above reaction (the "ion product" of water) is only 1×10^{-14} at 25 ^oC.
$$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14} \qquad \text{eq (1)}$$
The brackets denote the concentration of the indicated ionic species in moles/liter of solution.
- The equilibrium equation (eq 1) must be satisfied for all aqueous solutions. In pure distilled water that is not in contact with air, the concentration of the H_3O^+ and OH^- ions are equal
$$[H_3O^+] = [OH^-] = 1 \times 10^{-7}$$
- In acidic solutions, H_3O^+ ions are more numerous than OH^- ions; in basic solutions, OH^- ions predominate, $[H_3O^+] < [OH^-]$.
- Acidic strength is frequently expressed as pH, defined as
$$pH = -\log [H_3O^+]$$
In neutral solutions, pH = 7.0; in acidic solutions pH < 7; and in basic solutions pH> 7.

The lower the pH, the more acidic the solution.

In order to calculate the pH of a solution, you must first sort its ingredients into the following categories:

- **Strong acids**, such as HCl, and **strong bases** such as NaOH are completely dissociated into their constituent ions in aqueous solution. There are a fairly small number of these.
- **Weak acids** are only partially dissociated or ionized. This means that an equilibrium is established between the dissociated and undissociated forms:

  $HA\ (aq) + H_2O\ (l) \Leftrightarrow H_3O^+\ (aq) + A^-(aq)$ $\quad K_a = \frac{[H_3O^+][A^-]}{[HA]}$ eq (2)

  Here HA is the weak acid and A^- is its conjugate weak base. The equilibrium constant for the dissociation of a weak acid in water is referred to as K_a. Note that pK_a is defined in a way comparable to *pH*, i.e. $pK_a = -log\ K_a$. To find the pH you must solve the equilibrium for $[H_3O^+]$. Once you have done so, you can also calculate the % dissociation of the weak acid using

  % dissociation = 100 * $[A^-]$ / [Total weak acid conc.] eq (3)

- **Weak bases** react with water to achieve equilibrium in which there is an excess of OH^- ions. They typically contain reduced nitrogen (N attached to H or C).

  $B\ (aq) + H_2O\ (l) \Leftrightarrow OH^-\ (aq) + BH^+\ (aq)$ $\quad K_b = \frac{[B^+][OH^-]}{[B]}$ eq (4)

  Here B is the weak base and BH^+ is its conjugate weak acid. The equilibrium constant for the dissociation of a B in water is referred to as K_b. This value can be derived from the K_a value of the conjugate acid (which may be easier to find) using

  $K_b = K_w / K_a = 1 \times 10^{-14} / K_a$ eq (5)

  For weak bases,

  % dissociation = 100 * $[BH^+]$ / [Total weak base conc.] eq (6)

- **Amphiprotic substances** are often ions that have lost some but not all of their acidic protons. Since they have characteristics of both an acid and a base, they will be involved in two equilibria simultaneously: a weak acid equilibrium eq (2), and a weak base equilibrium eq (4). The *pH* of a solution containing only an amphiprotic substance and water can be estimated using both equilibrium coefficients. See page 218 Harris 9th edition (page 224 Harris 10th edition) for a simplified version of this *pH* calculation.

- A **buffer** is a solution of a weak acid and its conjugate weak base. The equilibrium conditions given by equations (2) and (4) both hold in these solutions, though it is generally more convenient to use eq (2) in calculations. Buffers are able to hold their *pH* relatively constant upon the addition of H_3O^+ or OH^-. This is because the weak base, A^- , will react with added H_3O^+ and the weak acid, HA, will react with added OH^-, allowing eq (2) to stay in control of the *pH*. The Henderson-Hasselbalch equation shown below is an *approximated* form of eq (2) that is typically used for buffer calculations. If the weak base / weak acid ratio on the right stays between 0.1 and 10, it is reasonably accurate. Outside of this range, the H-H equation's built-in approximation fails, so you're better off using eq (2) and an ICE table.

$$pH = pK_a + log\left(\frac{[A^-]}{[HA]}\right) \quad (3)$$

To summarize, the *pH* of a weak acid buffer solution is dependent on the *pKa* of the acid and the ratio of conjugate base to acid in a solution.

- In many titrations, the pH changes very markedly near the equivalence point (when moles of acid = moles of base). When this sudden pH change occurs, using an indicator that changes color at a pH near the equivalence point can clearly signal a titration endpoint. However, not every indicator will work. In the example below (Figure 1), phenolphthalein has a color change at a pH that is too high above the equivalence point, and so it would indicate a false endpoint well before the equivalence point is reached.

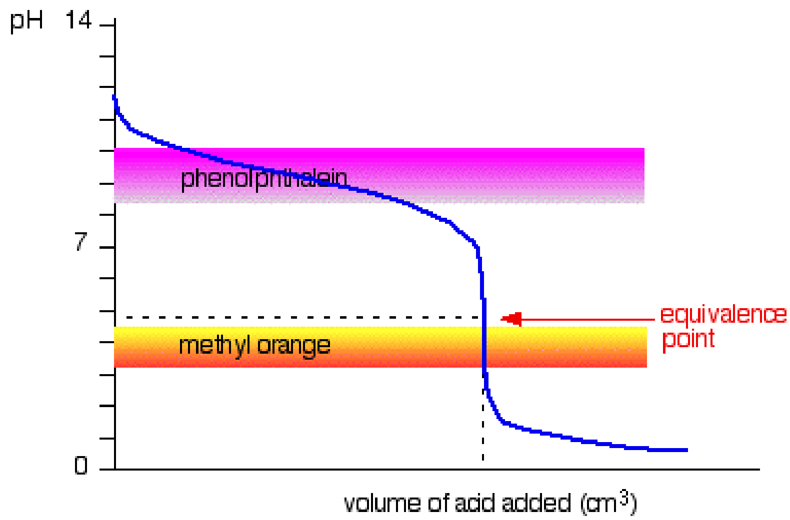

Figure 1: Generic Titration Curve of a weak base

Buffer solutions, acid / base calculations, and titrations are described in detail in Harris (Ch. 9.1-9.5 and 10.1-10.4). **Be sure to review these sections if any of this is unfamiliar or unclear!**

Overview of Experiment
In this lab, you'll work as a group to design a series of experiments to determine the concentrations of acids and bases in five common household chemicals: baking soda, toilet cleaner, oven cleaner, white vinegar, and vitamin C tablets. Along the way, you will investigate how best to determine titration endpoints. Once the household chemicals have been characterized, you will use them to generate and test buffers.

PRE-LAB ASSIGNMENT (DUE IN ELN BEFORE YOUR LAB DAY AT 11:59 PM)

1. Set up a table like the one below in the ELN pre-lab. In this table,

- List the ingredients contained in each of your five household products, taken from the product label or from the manufacturers' websites.

- Categorize each ingredient as either strong acid (sa), weak acid (wa), strong base (sb), weak base (wb), amphiprotic (ap), or pH-inactive (n).

- Based on the info you've added to the "Category" column, predict the overall pH of an aqueous solution of each product, given its ingredient list. Choose from highly acidic (pH < 3), slightly acidic (3 to 6), neutral (~7), slightly basic (8-11), or highly basic (pH > 11). Leave the last column blank – you'll get that data in lab.

Product Name	Ingredient List	Category	Predicted pH of product solution	Measured pH
a. Drano Liquid	NaOH (caustic, removes grease)	sb	Highly basic, pH > 11	
	NaOCl (bleach)	wb		
	Polymethylsiloxane (antifoaming agent)	n		
	Sodium silicate (corrosion inhibitor)	wb		
b.				

2. Do end-of-chapter problems 9-7 and 9-8 in Harris 9th edition (9-7 and 9-9 in 10th edition).

3. For the following 3 acid-base reactions, determine what compounds are present at the equivalence point (when moles of acid and base added are equal, for a complete reaction). Then, calculate the pH of a solution that contains those compounds at 0.15 M concentration. (This would be the equivalence point pH for each reaction.)
   (a) HCl + NaOH →
   (b) NaOH + CH_3COOH (acetic acid) →
   (c) NaOH + ascorbic acid →

4. Make the purple cabbage juice and the blueberry juice in advance before lab. You'll be using these juices in Module 2 *and* 3. Instructions: Place a small amount of chopped material in a pan or microwave-safe container. Add just enough water to cover – the less water, the better! Heat in microwave or on stove just long enough for the water to begin

to boil. Remove from heat and allow to cool. Remove chopped cabbage or blueberry solids and refrigerate the resulting colored liquids in labeled containers.
Untested alternative method: You can try using a juicer if you have one – it should work!
Upload a photo of your two juice samples to the ELN.

5. Add a goal and safety info to your Pre-lab section, with headings for each. Safety info should be based on the product labels. Then, prepare your Data & Observations section by summarizing the Task 1 procedure in 2-column format, then adding your ideas for the remaining procedure. (The full procedure will be refined and developed by your group during lab, so be sure to record this process in the ELN as it unfolds.)

EXPERIMENTAL (work in a collaborative group of 3 – 4 students)

Task 1: Making household chemical solutions and measuring their pH

Titrations will work best if the household chemicals are slightly diluted. Here are my recommendations for how to do this. For each measurement of volume or mass, include an estimate of the precision of the measurement, like you did in Module 1 ("9.96 +/- 0.02 mL").

- Toilet cleaner. Dilute a sample by a factor of 10. (Example: measure out 10 mL of toilet cleaner, transfer to 100 mL grad cylinder, add water to 90 mL, mix, and fill to 100 mL mark.)
- Oven cleaner. This product comes out of the spray can as a foamy mess, so we'll dilute it by mass instead of volume: spray several grams into a preweighed beaker, and calculate the mass difference. Then add seven times more water (by mass) and mix.
- White vinegar. Dilute a sample by a factor of 3. (Example: take 15 mL and dilute it with water to 45 mL.)
- Vitamin C. If you have a 1000 mg tablet, crush it and place it in 25 mL water. If you have 500 mg tablets, use two. (The mass refers to the amount of vitamin C in the tablet, not the total mass of the tablet, which is significantly more.)
- Baking soda. This is a pure, single-ingredient powder. Make 50 mL of a 0.3 M solution.

After making the five household chemical solutions described above, use pH strips to measure their pH to the nearest 0.5 pH unit. In the ELN, note whether these measurements match your predictions in the pre-lab. Try to explain any non-matching observations using the ingredient lists from the pre-lab.

Add several drops of indicators to small samples of each solution. Record your color observations for each indicator in a table. Do the observed colors and pHs match the table below? Are there any solutions (or pH's) that cause the two indicators to turn different colors? For example, you might observe that "solution X, which has a pH of Y, turns blueberry juice gray but turns red cabbage juice red-violet."

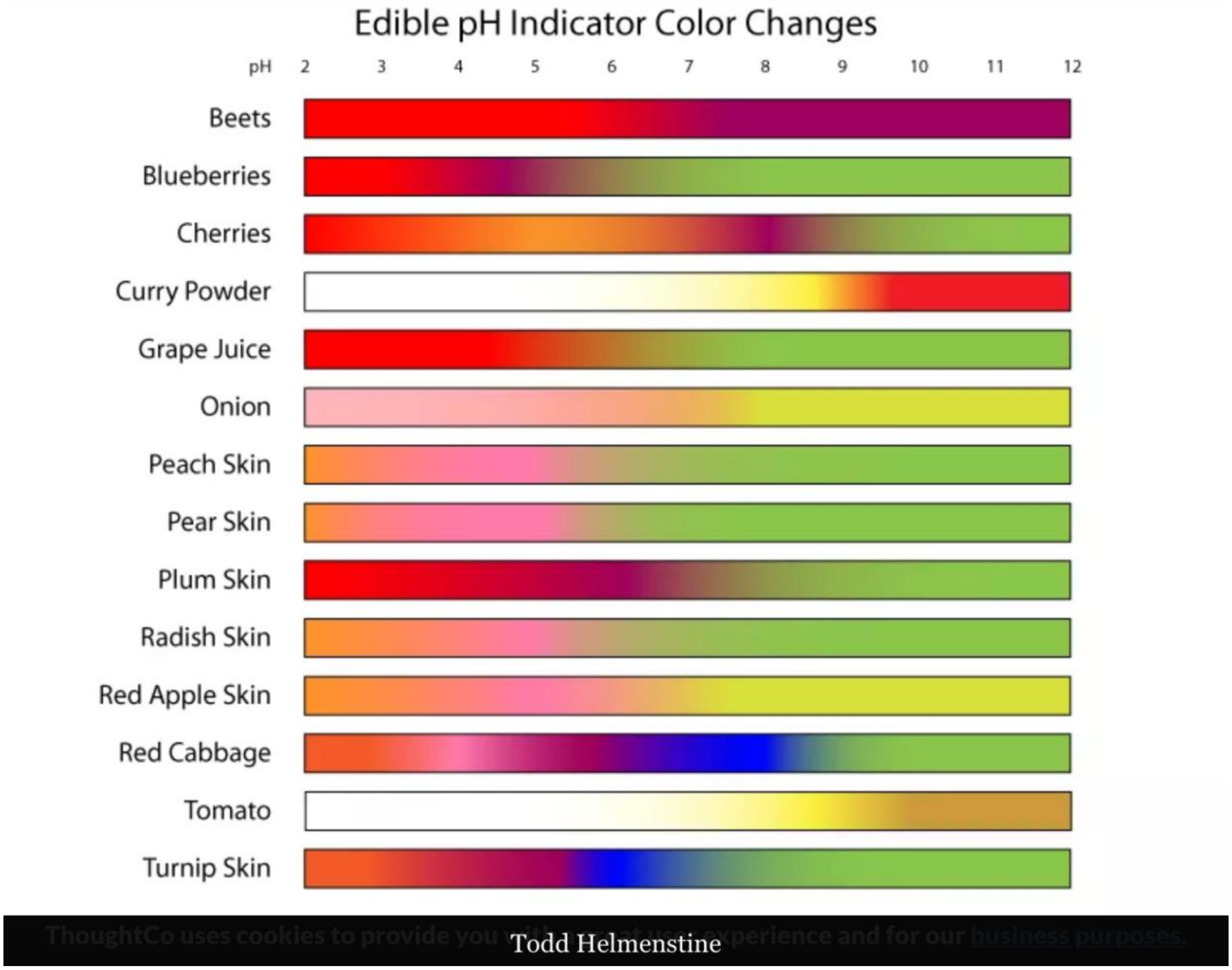

Figure 2: pH color changes of liquids extracted from common foods, courtesy of Todd Helmenstine.

<u>Task 2: Mapping out a titration strategy</u>

1. Your group must now work together to develop a **titration strategy**. The objective of the lab work today is to determine as accurately as possible the molar concentrations of acid or base in each household product by titrating them with each other. However, not every pair of products can be titrated successfully against each other! Your group should address questions such as:
    - What will be your **primary standard**? A primary standard is a solution where you know its concentration with high accuracy from the start, and that you use to determine the concentrations of at least some of the other solutions.
    - What solutions can be successfully titrated with (or into) a sample of the primary standard? A successful acid/base titration:
        - must involves two solutions with a fairly large initial pH difference
        - has a large and abrupt pH swing at the equivalence point (see Ch 7 in textbook for visual examples of this), and
        - contains an indicator solution that makes a distinct color change across this pH range, so that you can recognize the endpoint.

- Some helpful pH data from 5 household chemical titrations is shown below. Don't pay attention to the volumes – just look at the shape of the curves. The endpoint is the place on each graph where the slope gets the steepest. (We've included every combination Dr. D could do with an autotitrator!) Use this data to help determine which solution combinations look promising for titrations, given your indicator solutions, according to the criteria listed above.

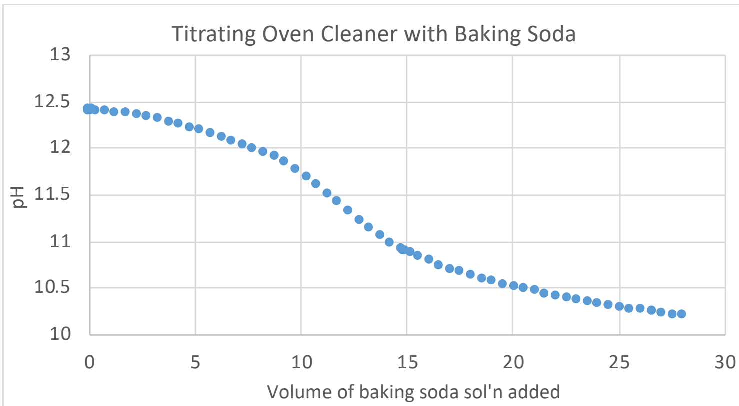

Figure 3: Titration curve for oven cleaner + baking soda solution.

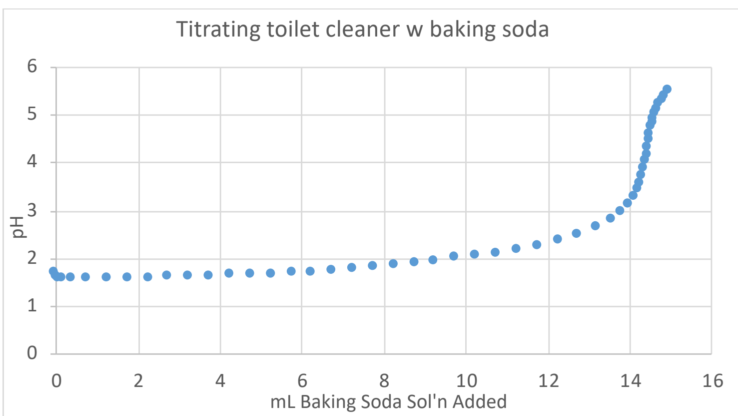

Figure 4: Titration curve for toilet cleaner + baking soda solution.

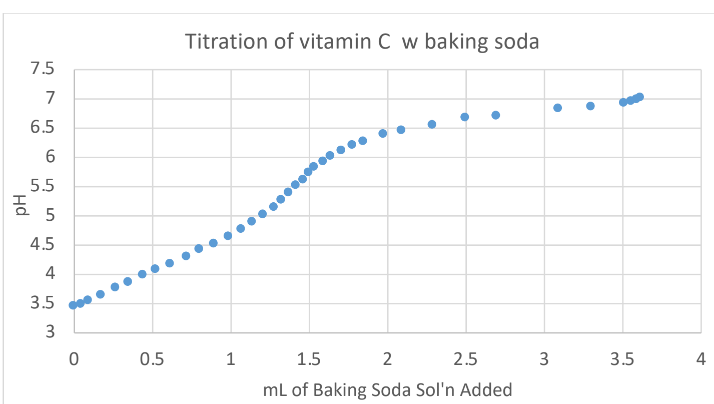

Figure 5: Titration curve for vitamin C + baking soda solution.

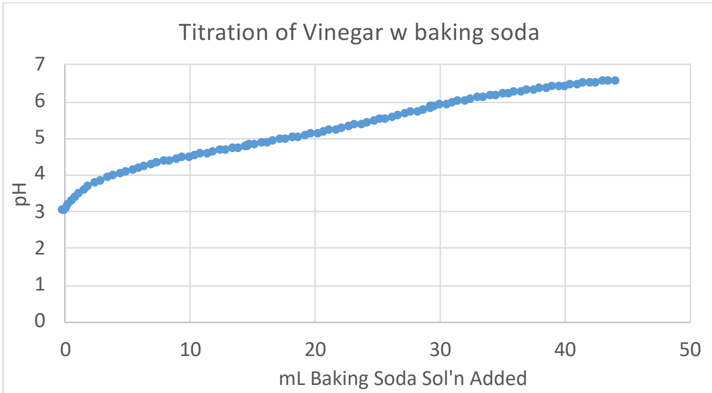

Figure 6: Titration curve for vinegar + baking soda solution

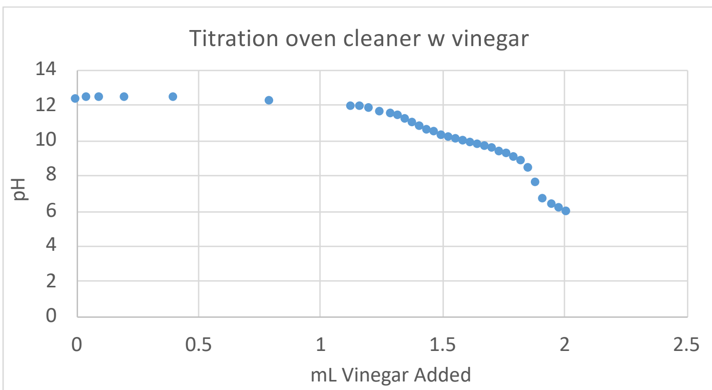

Figure 7: Titration curve for oven cleaner + vinegar.

2. Draw a diagram of your titration strategy on paper (or in Powerpoint or other drawing program), showing the pathways your group will attempt to use to determine concentrations of all 5 solutions. It might look something like Figure 7, shown below:

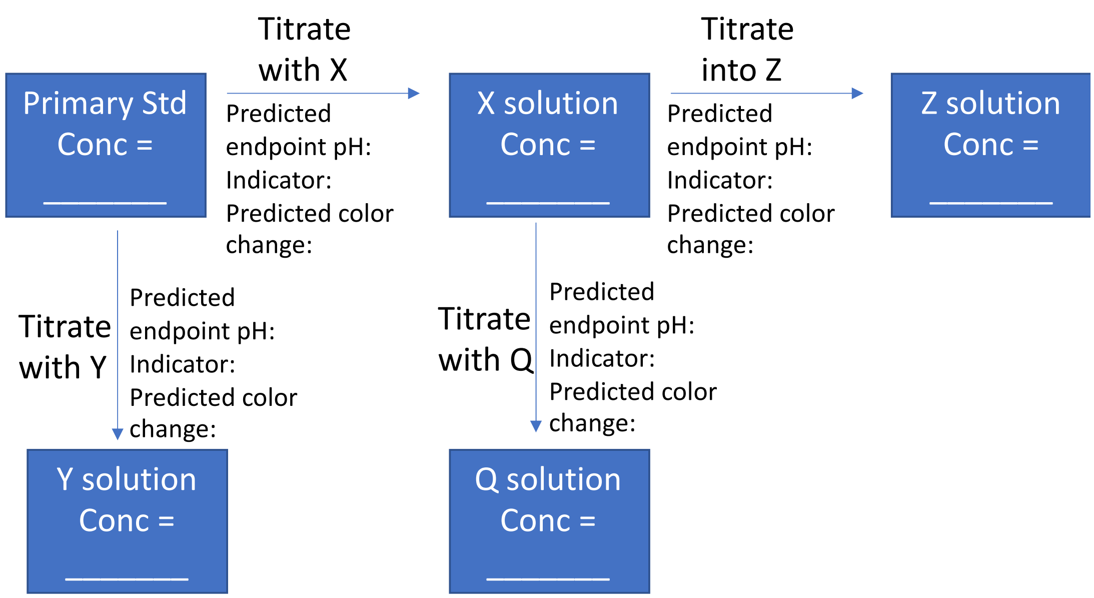

Figure 8: A sample titration strategy. "Titrate with X" means add X dropwise. "Titrate into Z" means place a sample of Z in a beaker and titrate dropwise with the solution of known concentration.

3. Next, have your group plan out a detailed procedure for carrying out an individual titration. Will you count drops, or use some other method to measure the volume of solution added? If you use the drop counting method, you will need to do a calibration for drop size. (Warning: the different solutions have very different drop sizes due to surfactant ingredients! If you count drops, the volume precision for a titration will be +/- the volume of a single drop.)

Task 3: Testing the strategy

4. Once your group has agreed on the overall titration strategy and the detailed titration procedure, it is time to try it out! Have different members of your group try out the different titrations in your strategy to see if each one works well, with an obvious endpoint. Record all data, color observations, as usual.

Task 4: Refining the strategy

5. Which titrations worked and which did not? For the ones that did not work (no obvious endpoint), what alternatives do you have? Would the other indicator work better? Is there a different titration you could do with the solution whose concentration is unknown?

6. Once your group has worked on refining its titration strategy, consult with Dr. D. and convince him your plan is sound. Repeat Task 3 and 4 activities until you have a fully functioning set of 4 titration reactions that will allow you to determine the concentrations of all 5 household chemical solutions.

Task 4: Final runs of the optimized titration strategy

Since each person in your group may have purchased different brands of household chemicals, and may have made the 5 solutions in slightly differing ways, you'll need to work individually now to execute the optimized titration strategy on your 5 particular solutions.

Once you finish Task 4, clean your plasticware (including pipets), store the remaining amounts of indicator solutions in a refrigerator, and store the 5 household chemical solutions in a convenient location. Next week, we'll use them all again!

If you have time in lab, work on calculating the concentration of your solutions based on the titrations that you performed. This will save you time on the pre-lab next week.

<u>PRE-LAB ASSIGNMENT, Module 2 Week 2</u> <u>(DUE IN ELN BEFORE YOUR LAB DAY AT 11:59 PM)</u>

1. Complete and summarize your calculations of the concentrations of acid (or base) in each household chemical solution in a table like that shown below. Show your calculations (photos in a single Word doc OK).

Product Name	Acidic (or Basic)?	Concentration of acid (or base) in my solution (M)	Based on titration with what other solution?	Concentration of undiluted product	Expectation from product label (if any)
a. Drano Liquid	Basic	0.458 M	Toilet cleaner	4.58 M since I diluted it 10-fold.	Concentration not given on label.

2. Do problem 9-36 and 10-14 in Harris 9th edition (9-33, 10-14 in 10th edition).

3. Prepare your Data & Observations section by adding your ideas for procedural steps. (The full procedure will be refined and developed by your group during lab, so be sure to record this process in the ELN as it unfolds.)

<u>EXPERIMENTAL, Week 2</u> (work in the same collaborative group of 3 – 4 students)

Today your lab group has the objective of preparing 3 buffer solutions using your collection of household chemicals and the solutions you made from them. Once made, you will test their pH and their buffer activity with pH strips and the indicator solutions, and make a quick video demonstration.

<u>Task 5: Preparing Buffers at Target Concentrations and pH</u>

1. Your group's goal is to make 25 mL of each of the following 3 buffers. Each group member should make at least one. The listed concentration is the total amount of conjugate base + conjugate acid present.
   a. pH 5.4, 0.05 M
   b. pH 4.3, 0.20 M

c. pH 9.8, 0.10 M

2. As a group, come up with a recipe for each buffer. What conjugate acid/base pair will you use to achieve a given pH? What weak acid or base solution will you use to get one of that pair in solution? What strong acid or base solution will you use to convert some of the weak acid or base to its conjugate? What volume of each solution will you need to add to hit the target concentration? target pH?
3. Once you've shown Dr. D your recipes, go ahead and make the buffers.

Task 6: Testing and Demonstrating the Buffers in Action

1. Test the pH of each buffer with pH strips and indicator solution. Are the pH's on target?
2. Create a short video(s) demonstrating each buffer in action. Show how it resists change in pH when strong acid (or strong base) is added, using a non-buffer for comparison. Also show how the buffer has a finite capacity to resist pH change – demonstrate how eventually it will be overwhelmed if too much added strong acid (or base) is added.

Once you finish Task 6, save your indicator solutions in a refrigerator. You'll need these for Module 3 labs. Since they are food based and should not be contaminated in any way, this is OK, but be sure to place "do not eat" labels on them – especially the blueberry juice!

Analysis and Results (ELN)

Summarize all results in a narrative section with tables (w/ titles), figures (w/ captions), and videos. What are the main features of your data that the reader should notice? Complete and upload the Jupyter notebook activity for this module. Finally, answer the following discussion questions, then finish by writing a conclusion.

1. How did buffer capacities correlate with their concentrations?
2. Give 3 examples of some other buffer pH's that you could have achieved by mixing various combinations of your 5 household chemical solutions. In addition, give an example of a buffer pHthat could *not* be made from these starting materials.
3. Make a table showing the % uncertainty in your measurements of
   a) The volume of the titrated solution in the beaker in each titration
   b) The volume of the titrant added to reach the endpoint in each titration
   c) The dilution volumes (or masses) to make each of the 5 household chemical solutions.
4. For the household chemicals that had information about concentrations on the containers, how did these concentrations compare to what you determined using titrations from a primary standard? Account for the sizes of the discrepancies.
5. Based on your Python calculations, which of the 3 explanations for NaCl causing a pH change in an HCl solution was at work in last semester's class data?
   1. Base action by Cl- ions
   2. Sodium impersonating H+ ions at the pH sensor surface
   3. Ion halos around H+ changing H+ activity at the pH sensor surface