Acidity in beverages

The acid content of wines, beers, and other beverages is serious business. Check this out: https://wineserver.ucdavis.edu/sites/g/files/dgvnsk2676/files/research-summaries/220%20relationship%20between%20total%20acidity%2C%20TA%2C%20and%20pH%20.pdf

The wine chemists at UC Davis are talking about how to measure acidity, and they define quantities called **total acidity** and **titratable acidity**. Some protons on the acidic molecules never react with NaOH, so titratable $[H^+]$ is smaller than total $[H^+]$. Therefore, technically these two quantities are different, but for our purpose we will take them as synonyms. What's probably more important is to realize that the titratable protons in a solution are more than just the "free protons" responsible for pH. As the titration proceeds you pull more protons off the acidic molecules. So $[H^+]$ determined by the pH at the start of the titration is smaller than titratable $[H^+]$.

We will define total acidity as **equivalent g/L of acetic acid** in the beverage. We will titrate the solution with NaOH to a phenolphthalein endpoint, and use the information from the titration to compute the number of grams of acetic acid per liter of solution that would account for the results of the titration. Now here's the weird part: we will do this even if the acid in the beverage *isn't acetic acid*. Most beverages have a mixture of acidic components, and we usually don't know the identities of all of them, so to compute a mass of acid components we have to make an assumption. The simplest assumption is that there is only one acid present, and we use that acid's molecular weight to do the calculation. In the wine business the acid is usually assumed to be malic acid, a common acid in wine. Here we will us acetic acid, which seems pretty different, but actually gives similar values for total acidity. Let's check that!

Malic acid has a molecular weight of 134 g/mol, and it has two protons that will react with NaOH. Acetic acid has a molecular weight of 60.1 g/mol, and just one titratable proton.

Suppose we titrate 25.00 ml of wine and find that it reacts with 19.31 mL of 0.1034 M NaOH. The titratable $[H^+]$ in the wine is $V_{base}M_{base}/V_{acid}$ = 19.31*0.1034/25.00 = 0.07987 M. The molar concentration of malic acid would be half this value, since each malic acid has two titratable protons. So the mass concentration would be 0.07987 M/2*134 g/mol = 5.35 g/L. That would be a pretty tart (acidic) wine!

Let's do the calculation using acetic acid. The molar concentration of acetic acid would be 0.07987 M, since it has just one acidic proton. So the mass concentration would be 0.07987 M*60.1 g/mol = 4.80 g/L. Not much different, because the molecular weight per acidic proton is about the same.

Prelab question (ask for help if you have trouble!):
Suppose you hada solution that was 10 g/L of citric acid. Citric acid has three titratable protons and a molecular weight of 192 g/mol. What would the solution's acidity be in equivalent g of acetic acid/100 mL? Confirm that it would be 9.39 g/L. Do the calculation in the prelab section of your lab notebook.

Titrations of acetic acid:

Generally we do acid-base titrations with a NaOH solution in the burette, and the acid in a 250 mL Erlenmeyer flask or 400 mL beaker. You will use beakers so that you can use a pH probe and a magnetic stirrer.

Be sure to coat the inside of your burette with the standardized 0.10xx M NaOH solution and rinse before filling the burette. You'll need to clear bubbles from the burette tip; sometimes they're hiding where you can't see them. Once you've filled the burette with NaOH solution and cleared bubbles from the tip, you should not have to do this again; just refill the burette after each titration and don't let the burette get emptied. Don't bother trying to start at exactly the 0.00 mL mark on the burette. You should never use a titration that consumes more than 50 mL of titrant.

Use a 5.00 mL micropipette to get a 5.00 mL sample of the acetic acid solution. Add 2 drops of phenolphthalein to the beaker before you start. Do a quick and dirty titration of the 5.00 mL sample so that you have an idea where the end point will be; you're looking for the phenolphthalein color change. That way you can do the big titrations faster (by what factor will you multiply the needed volume?).

Get a 25.00 mL pipette. Coat the inside of the pipette with your acetic acid solution and rinse it out before you use it. If you have forgotten how to use a pipette bulb, practice on water first before you pipette acid solution into the clean beaker.

Add DI water to the beaker if the volume is too small for the pH probe. Make a rough estimate of how much water you add and record it in your notebook. Add phenolphthalein as above, if you'd like.

Set up the Vernier LabPro to record data during the big titrations. (Instructions for the LabPro are below.) Plan your titration! You want to record more points as you pass through the endpoint region so that you can make an accurate graphical estimate of the endpoint volume -- but you don't want to waste time recording lots of unneeded points. While passing through the endpoint, add just 0.20 ml of titrant at a time and read the pH after each addition of titrant. You will continue a bit past the end point, until the pH starts to flatten off again. Your instructor may tell you to repeat a titration if your curve doesn't make sense.

Write your results (mL NaOH needed to reach the endpoint) on the board. Compare the results among groups; if one group gets values for acetic acid that are rather different from everyone else's, then that group should check their calculations and repeat the titration. On the acetic acid bottle, the concentration is given in grams of acetic acid/liter of solution, so we will be able to check your numerical values.

Lemon juice and cola:

Use a different pipette for each sample! **Never pipette directly from the original bottle!** Pour out some of the juice into a beaker and then fill you pipette from the beaker. It's a good idea to do a quick and dirty titration before investing time in a big titration, but you may find some issues with doing this with one of your samples. Write your observations in your lab notebook. As you work with the juice and soda, you should share information with the other groups about how much to titrate--that way you can get down to work faster. Compute the concentration of acid in each solution as g/100 mL (% acidity, as it is called) as if the acid is always acetic acid (we will call this equivalent g acetic acid/100 mL).

Setting up LabPro:

Obtain a LabPro and supply it with power using the AC Adapter. Using the USB cable, connect one end to the LabPro and the other to one of the USB ports on the left side of a laptop. Connect the pH probe to the one of the channels in the side of the LabPro and then open up Logger Pro (located on the desktop). Once this program opens, it should display a table on the left-hand side and a graph on the right.

You will need to calibrate the pH probe using pH 4 and pH 7 buffers. If the pH probe is not calibrated, your value of the pK_a will be wrong. To calibrate, go to *Experiment* → *Calibrate*. Rinse the electrode with DI water, and then put it in the pH 4 buffer; allow a few moments for the voltage to stabilize and then enter the pH value and select keep. Repeat for the pH 7 buffer. Rinse the electrode again before putting it into your sample.

Open up the *Experiment* menu and select *Data Collection*. Under the Collection tab, select *Events with Entry* from the pull-down menu. This will allow you to label the column as volume of base added, or something to that effect. There is also a spot for the units - mL. A modified table on the left should have two columns, one for the volume and one for the pH.

To adjust the scale on the graphs, right-click on the graph and select *Autoscale* from the menu. You can also select a value on the axis and type over it with the value you want. Get the axes right so that the titration curve will be big and easy to read on the computer screen.

To start recording readings: Click the *Collect* button at the top right of the screen in Logger Pro. At this point the *Keep* button should also become active. The current readings for the pH probe should be shown right above the table and graphs. Once the readings have had a chance to stabilize, click the *Keep* button and enter "0" in the blank. Now add two or three mL of titrant at a time to the beaker, **allow the reading to stabilize**, and click *Keep* once again to enter the amount of titrant added. Around the endpoint, add titrant 0.2 mL at a time. Be sure to take seven or eight data points beyond the endpoint so that you see the shape of the entire curve. Once your last data point has been collected, click *Stop* to end data collection. You MUST click *Stop* before you can print and save the data to a drive.

You may then print out the table and graphs separately by opening up the *File* menu and selecting *Print Data Table* and P*rint Graph*, respectively. A menu will come up in which you can add a footer if you would like.

To save your data, open up the *File* menu and select *Export as Text*. This will allow you to save the data as a text file to open in Excel. Then, open up Excel and select the *Open* command. Change the file type in the pull-down menu to Text Files and find your file and open it. A window will appear which helps to import the data into Excel. Make sure the Delimited option is selected, then click Next twice, and then Finish. The data should appear exactly as it was in your table in Logger Pro. Alternatively, you can highlight the data in Logger Pro, select Copy, switch to Excel, and finally select Paste. However, do not forget to save your data from Logger Pro.