Science, Las Cruces Academy, grades 4-7, 15-26 October 2018

A series of fourteen 35-minute classes, focused on a classic chemical reaction, in which students learned elements of:

- Chemical reactions, particularly their kinetics
- Math, using arithmetic, ratios, estimation, exponential notation of numbers, and an introduction to some functions
- Electronics, as Ohm's law, photocurrents, and the neat use of operational amplifiers
- Construction – hands-on wiring of circuits
- Instrumental methods in chemistry – making or using a spectrophotometer
- Chemical techniques – measuring, mixing, some cleaning, calibration
- Beautiful colors of dyes – yes, see the beauty
- Data analysis – seeing if our results fit a proposed model
- Naturally, the deductive method, testing a hypothesis
- A bit of statistics – a brief look at significance of results
- Experimental design – from an idea through all the steps of how we might test it
- Recovery from failures – how to move on
- Light – colors from selective absorption, propagation of light through an absorbing medium

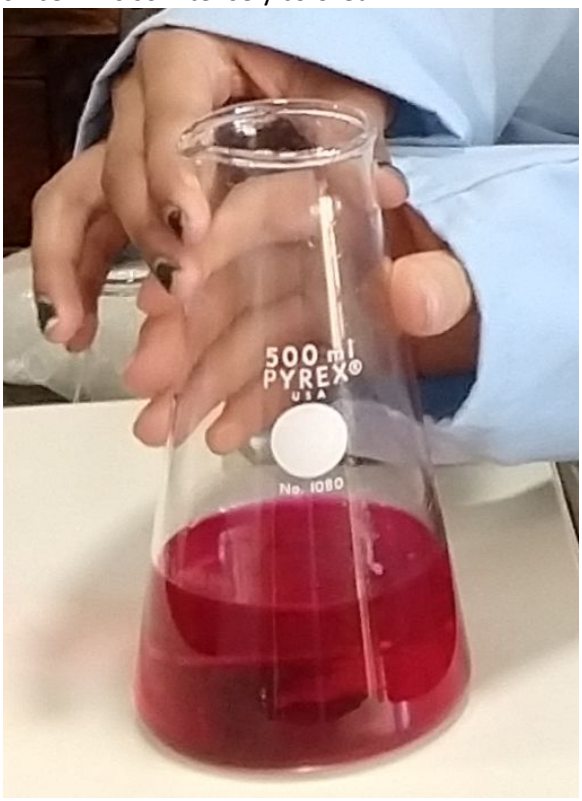
Measuring the rate of a chemical reaction – the rate of decolorization of the beautiful pink/red dye, phenolphthalein (fen-all-thay-leen) – by hydroxyl ions, using light absorption to track the concentration of the dye (call it *Ph*) as it declines over time.

There are various possibilities for how fast the chemical reaction goes, particularly for its dependence on the concentration of the reactants. We have a hypothesis, that the rate of the reaction is directly proportional to the concentration of *Ph*:

$$\frac{\text{loss of concentration}}{\text{time interval}} = (\text{a constant})^*(\text{the current conc. of Ph})$$

We'll focus first on how to measure the concentration. We'll make a calibration curve, to relate the fraction of light absorbed to the concentration. We have to prepare known concentrations of Ph, which we'll express in molarity, which is moles of the molecule per liter of solution (a mole is Avogadro's number of molecules, set as a mass of the substance equal to its molecular mass in grams; for Ph, that's

318 g). It will be quite dilute, only some tens of millionths of a mole per liter, or tens of *micromolar*, since Ph is so intensely colored:



What is the chemical reaction? We'll see that at the end of part 2, below.

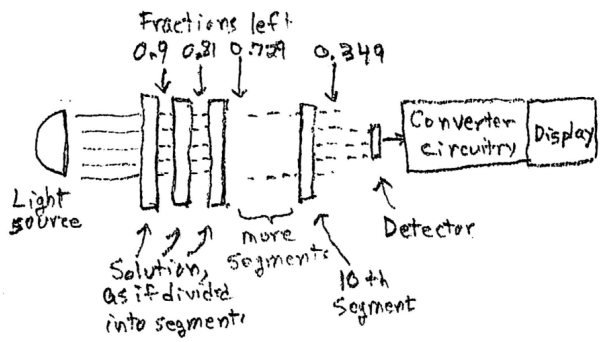
1. How light absorption lets us measure the concentration

We'll be performing spectrophotometry – "metry" meaning measurement, "photo" meaning that we're using light for the measurement, and "spectro" meaning that we carefully choose a specific part to the spectrum of light – a narrow range of color or equivalent wavelength.

We discussed in class how the fraction of light absorbed in passing through a given path length of solution is related to the path length, the concentration of the light absorber, and the intrinsic nature of the absorber.

It's clear that, the greater the path length through a colored solution, the more intense is the color. That is, the more light of other colors that is absorbed. Just how does the transmitted fraction of light of a given color vary with the length of the path?

A key concept is that the fractions transmitted through segments of the optical path *multiply*, not subtract. Consider a path of total length L broken up into a succession of thin segments – say, N segments, each of a length dL; clearly, L = N*dL. Here's a sketch. Note that I've separated the segments from each other, for clarity; a separation doesn't matter, as long as the light doesn't spread out, rather keeping a straight path (plane waves).



The first segment absorbs a fraction, say, 10%, leaving a fraction 90% or 0.9 to continue. That light passes the second segment, which leaves 90% of the light reaching it. Thus, it passes 0.9*0.9 = 0.81 or 81% of the *original* intensity of light. Suppose we have 10 segments. The fraction transmitted is 0.9*0.9*0.9....*0.9, 10 times. That's 0.349, or 34.9%.

We need a general way to account for the fraction transmitted – how it's related to the path length as well as the intensity of absorption by the solution (or a solid – it works for that, too). The intensity of absorption per unit of path length depends upon the molecule – its molecular absorptivity, *a*, at the chosen color or wavelength of light – and its concentration, *c*. We could make a calibration curve for a given path length and use it in a "backward" or inverse sense – plot transmission against concentration and then turn the graph on its side when we get T and want *c*. That's clumsy. We can use a mathematical function, the exponential,

$$T = \exp(-a'cL)$$

If you want to learn about the exponential, I have a write-up on my website (science-technology-society.com; go to Fun, then Math). Commonly, people doing spectrophotometry use the base 10 instead of the base *e*:

$$T = 10^{-a\,c\,L}$$

(no need to do the math, but a=2.303 a'). We need the inverse function, called the logarithm. It's the power to which 10 must be raised to get our result, say, the numerical value of T.

How does this help? When we do our calibration curve, we get T as a function of *c*. It's more conveniently expressed using the logarithm,

$$-\log_{10}(T) = acL$$

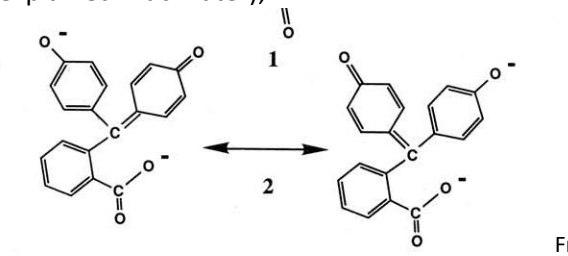
You don't need to know how to compute a logarithm – an Excel spreadsheet can do it for you. Ta da. Now, every time we see a value of T – say, as we make a measurement of a new, unknown concentration, we compute $-\log_{10}(T)$ (with T as a fraction, not a percent); we know the path length we used, and we know the molecule we used, so we know *a* → we know the concentration, *c.*

2. Choosing our molecule, phenolphthalein

Reasons:

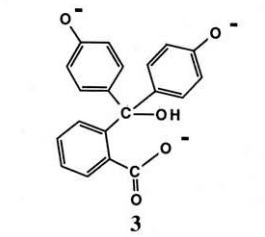
- It's pretty – a beautiful rose red, and easily tracked by eye to locate the right solution!
- It's readily available in chem labs. It's used as an indicator in titrating an acid with a base. You can look up titration. In any event, in a titration one keeps adding measured amounts of a base,

such as sodium hydroxide (lye) to a solution of an acid – say, hydrochloric acid – until the quantities of the acid and the base are the same. Add a little extra base, with phenolphthalein present in a tiny amount, and the solution turns a beautiful pink. You stop adding and use the final amount you added as your result.

- It absorbs light very strongly. That's good in a titration, because you don't want its reaction with the base to be a distraction. You need a very tiny amount.
- It reacts with the hydroxyl ion, OH^-, such as is provided by a reasonable concentration of sodium hydroxide, to lose its color. Essentially, a hydroxyl group gets inserted into the somewhat complicated molecule. Here is the starting configuration, with two "resonance" forms (to be explained much later);
- 

From Robert Reeves, Marlborough School, Los Angeles

After the reaction, a hydroxyl (OH) group has been inserted, in the middle:

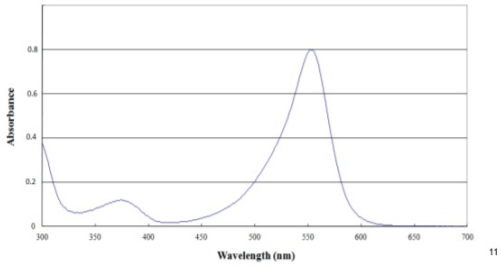


3. Setting up a system to measure the fractional light transmission through a solution of Ph

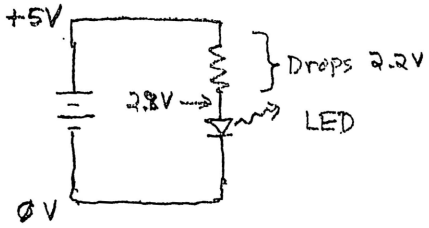
In essence, we just need a source of light, a container to hold the solution in the path of the light, and a detector to measure the amount of light getting through. Let's add some qualifiers:

- We want the light to go through in a rather straight path; angled paths add complications in the analysis.
- We want to use a narrow section of the spectrum of light – as small a range of colors or wavelengths as is practical. That's because the absorption of light by Ph, or most things, depends strongly on color or wavelength. If two or more colors of light are being transmitted, we have a mixed transmission that's harder to interpret (or worse).
    - For phenolphthalein, yellow is good. A red color of the transmitted light means that Ph absorbs light of colors from blue through green and yellow, leaving red. A more quantitative way to look at it is to view the measured molecular absorptivity as a function of wavelength:

UV spectrum of phenolphthalein

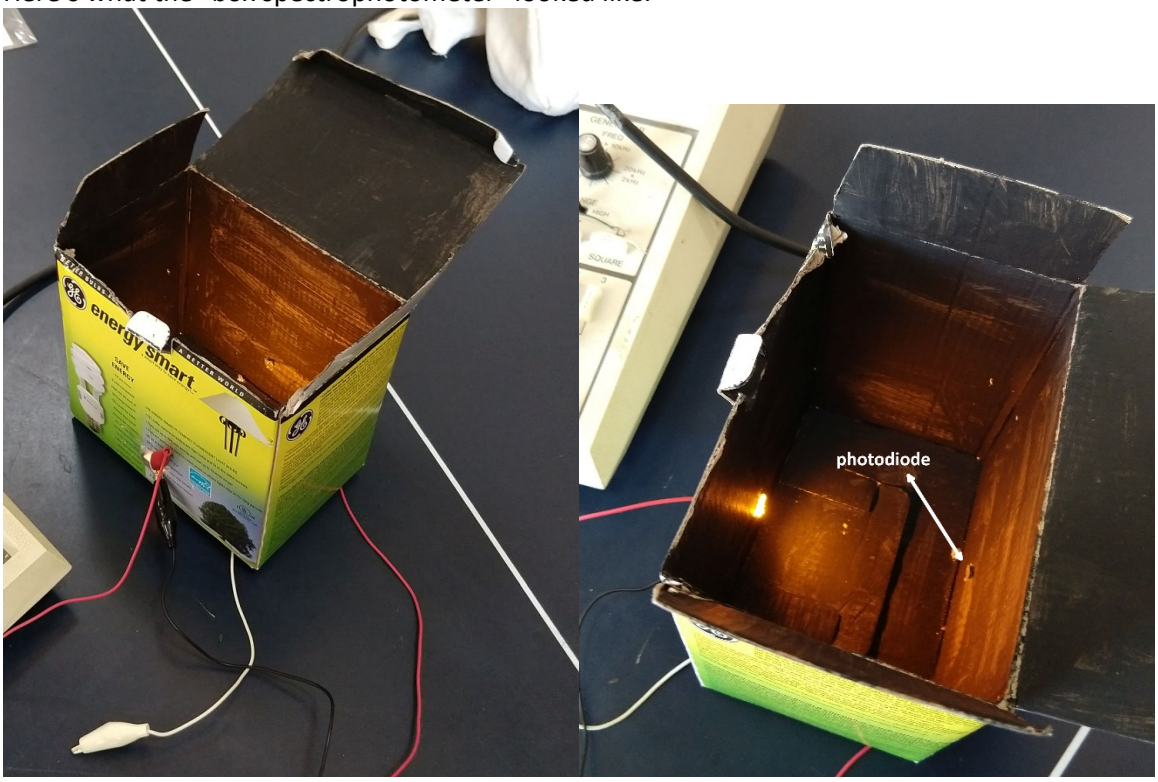


- We chose a handy light source for our first setup, a light-emitting diode or LED, with intense yellow light output centered at 592 nm (nanometers, the wavelength of light, which is, of course, very small). That's considerably off the peak absorbance, but still high enough. We could have picked a better wavelength (but we were trying to use the LED). A wavelength with a high absorption:
    - Makes it possible to measure very small concentrations, and
    - Minimizes any problem of the wavelength drifting a bit, say, if the LED warms up. The relative change in absorptivity will be small and our measurements using a fixed value for the absorptivity will be very accurate in spite of a change.
    - The current input to the LED has to be kept constant and below damaging levels. Our LED can take up to 350 mA (350 milliamperes, or 0.35 ampere). We use a current-limiting resistor and chose a current of 300 mA.



    -
    - The supply voltage is 5V. The LED must drop about 2.8V, the energy per electron needed to create photons of yellow light; we talked about this in an earlier class. Then, the remaining 2.2V has to drop through the resistor. Since that drop is current x resistance, $V=iR$, it's straightforward to compute R= 2.2V/0.3A = about 7.3 ohms. I found a resistor with a measured resistance of 7.1Ω.
    - It has to be a physically larger resistor than the common ones in use today, in order to safely dissipate the heat generated in it, which is a power $P=iV=i^2R$. That comes to about 0.66 W (watts), above the 1/8-watt rating of smaller resistors. Yes, it is a fatter one.
- It's best to have the solution in a container with flat sides; curved sides cause light to traverse a range of path lengths, again causing some complications. (In my first trial of making a spectrophotometer, several years earlier, I did use a curved bottle, and it worked accpetably.)
- We have to keep out any other light that might reach the detector.

Here's what the "box spectrophotometer" looked like:



Constructing it involved finding an appropriate box (with a handy size and handy closable lid), painting it black inside to absorb stray light, poking (cutting, really) two holes on opposite sides, putting the LED to shine through one hole and a photodetector to face it on the other side. The container with the solution goes inbetween.

I chose the LED from an electronic catalog, one that emitted strong yellow light while being affordable ($5 or so). You can learn how to read specifications of electronic devices, though we need not get into that here.

The detector has to be:

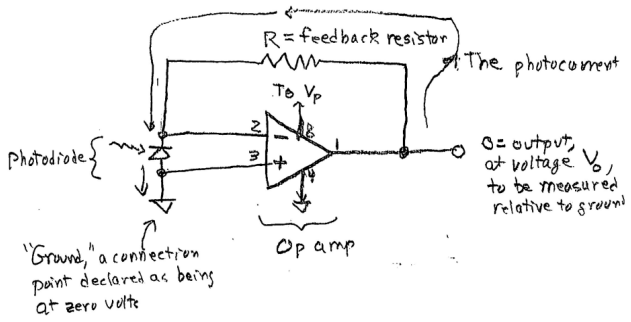
- Sensitive, giving a usable electrical signal at what are pretty low light levels, and
- Linear, preferrably – having its signal in direct proportion to the intensity of light (flux density) hitting it.

I chose a classic photodiode, a Hamamatsu PH208, in part because I have a bunch of these, used in a device that three other workers at Los Alamos National Lab and I ended up patenting (to no real purpose – researchers measuring light on freely moving leaves of plant use it all the time, as fair use in research, not paying fees, and that's great). This semiconductor (related in structure to transistors) generates a tiny electrical current in direct proportion to the light "intensity," in fact, measured as photons per unit area per unit time. (Our class had talked earlier about light being a flow of photons, discrete particle of electromagnetic energy.)

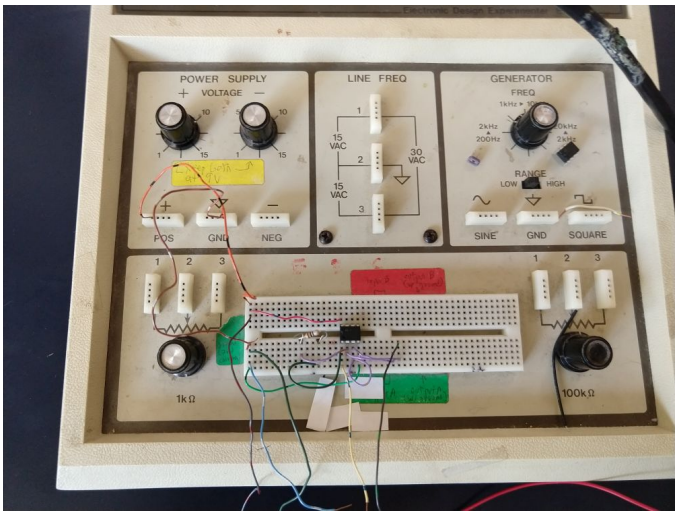
By the way, a sophisticated laboratory spectrophotometer uses these same principles, with the added feature that one can dial in whatever wavelength one wishes to use, within a broad range. That's important for being able to measure a great variety of colored compounds.

4. The electronics – turning a tiny photocurrent into a measurable signal

In our box spectrophotometer, the photodiode puts out a current that's only about one-millionth of an ampere. That's too small for our handy lab multimeter to measure. So, we feed that current into an electronic circuit called a current-to-voltage converter. It takes a bit of exposure to diagrams of electronic circuits to get used to what they mean, but let's draw one, to get to the chase:



The solid lines indicate wires, or conductors. The zigzag form indicates a resistor, providing a know numerical value of electrical resistance to the flow of current. The small device with a wiggly arrow pointing to it is the photodiode. The triangular item in the center is the operational amplifier, or op amp. On it I have labeled the connections to its "pins" – "1" denotes the output, "2"denotes the inverting input (we'll see what that means, shortly), "3" denotes the non-inverting input, "8" denotes the connection to the power supply, on the positive side, and "4" denotes the negative side of the power supply (here used as "ground" also, or zero volts). Note that the sizes of the elements in the diagram have no relation to the physical sizes of the elements – they are only drawn at sizes convenient to show connections.



Here's how it works: first, an op amp is a sophisticated combination of transistors and other electronic elements, with the property that it has a huge gain or amplification factor, perhaps even a million. In the ideal case, the gain is infinite, so that the output voltage is only stable if the voltages at the inverting and the non-inverting inputs are exactly equal; any time the "-" input is a tiny bit higher, the output goes to its lowest possible value, and if the "+" input is higher, the output goes to its maximal value.

The photocurrent is fed back to the inverting input through a resistor. A current flowing through a resistor generates a voltage, V, measured in volts, equal to the product of the current, measured in

amperes, and the value of the resistance, measured in ohms. Suppose our photocurrent is 500 nA, or nanoamperes, billionths of an ampere, or, 0.5 μA, half a microampere. Suppose that the resistor has a value of 2 million ohms, or 2 megohms (2 MΩ). The product is then 0.5 millionths times 2 million, or 1V, one volt. It's easy to measure a volt very accurately with a simple multimeter, so we have our way of measuring light.

A few details:

- Op amps are not perfect. For one, there is a tiny offset of the + and – inputs naturally. Choosing an op amp with a very tiny offset makes life easier.
- Also, an ideal op amp requires no input current at all at its inputs. A real op amp takes a tiny input current. I chose an op amp with a very low input current, a very high input impedance.
- Finally, only some op amps can put out output voltages over the full range, from zero (or the negative supply voltage) to the positive supply voltage. These are called rail-to-rail op amps; they can be found easily in an electronics catalog.

We have to figure out exactly what resistance will give us output voltages in a reasonable range. Since the op amp is happy to run at a supply voltage of 5V, we want the maximal output to be a bit less than that, perhaps 4V. It takes some playing around. With our bright LED mounted about 10 cm from the photodiode, a value of about 4.7 MΩ seems to work, giving a 4V output when there is only clear pure water in the container positioned between the LED and the photodiode. (Note: it can be useful and fun to estimate the photocurrent and the needed resistance from "first principles," knowing the quantum flux density from the LED, the frontal area of the photodiode, and its "quantum efficiency" = how many electrons are generated per photon absorbed by the photodiode, a number a bit less than one.)

5. Learning from adversity – problems with the circuit in the box spectrophotometer; switching to a lab spectrophotometer

In brief, the output voltage was unstable, despite a lot of troubleshooting and modification of the circuit (e.g., changing the resistance value). I am still diagnosing why this happened. I used a different op amp, and that may be the problem. Perhaps the new one has insufficient input impedance.

But!.... I have a lab spectrophotometer, a Sequoia Turner.

It's not adjusted yet (in case you noticed the transmission greater than 100%).

How do we use it?

- Plug it in, turn it on, and let it warm up. The reason for warm-up is that it uses an incandescent lamp as a light source, and, I believe, vacuum tubes – but it is a very nice instrument.
- Set the wavelength of light to use, with its dial. The spectrophotometer lets the lamp light impinge on what is called a diffraction grating – a surface with extremely finely spaced lines that scatter light and cause the light waves to interfere constructively only at one angle for a given wavelength. The dial makes that angled light hit the place where we put the solution. You can get the diffraction effect with a CD or DVD, held at an angle from a narrow light source. The spectrum from deep blue to red is spread out. The "grating" in this case is the set of recording tracks, basically tiny dimples in a long spiral, with tracks very close to each other going outward from the center of the disk.
- Be sure that a proper stray light filter is inserted. These are aluminum items with a small colored area and a label indicating the range of light wavelengths for which they are good. In our case, we use the one marked 290-850 nm.
- Prepare a solution with zero concentration (in our case, pure water), to be measured. We''' adjust the "spec" (spectrophotometer) to indicate that this solution has 100% transmission, zero absorbance. Fill the cuvette ("little cave" with this solution and carefully lower it into the hole on top. The cuvettes are precision devices, and expensive, so be careful. They are made of fused quartz, which transmits light very well even into the ultraviolet. The faces are of very uniform thickness and are very flat.
- Zero the spectrophotometer. There's always a bit of stray light and/or some drift in the electronics. We can offset the electronics so that zero light through the cuvette gives zero voltage output (we don't see the voltage output – we just want the spec to report the fractional light transmission). There is a raised button to push and hold in. One sets the mode selector to "Trans," for transmission. While holding the button in, one adjusts the dials labeled "Zero," until the display reads 00.0 (as a percent). It's a very fine adjustment and one is happy to get it within 00.1%, using both coarse and fine controls.
- Set transmission at 100%, using the dial "Trans." Now we're ready.
- Assuming that we have made up our solution with a concentration we want to measure, pour it into the cuvette, after dumping out the water or other reference solvent. Rinse the cuvette with the solution a few times, if one is going to reuse the cuvette (not necessary, in fact – one can use a second cuvette, because the dimensions of the cuvettes are identical, to high precision).
- Switch the mode button to "Abs," for absorbance. Read and record the value – you're done!

6. Being able to calculate the actual concentration – making a calibration curve

We need to calculate a highest concentration we'll use, and we'll run measurements on a series of lower concentrations leading up to it. The highest concentration should have an absorbance near 1.0 (10% transmission). We could make the highest concentration, measure it, then dilute it repeatedly. It gets complicated for several reasons. It's advantageous to make a stock solution of high strength, a *concentrate*, and then add the right amount to create each desired concentration. Another reason to make the concentrate is that phenolphthalein is poorly soluble in water. We dissolve it in alcohol (ethanol, as the chemical term – we used denatured alcohol from a hardware store), at a concentration 200 times the final value. So, what is the final concentration we want? Recall that the absorbance of light is

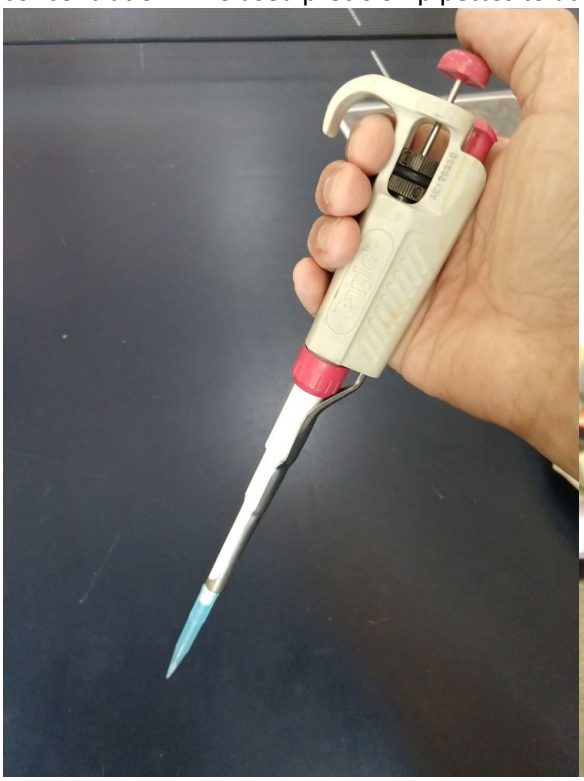
$$A = acL$$

The graph given earlier gives us the value of *a* at our chosen wavelength. We can also just note that we had planned to use a longer pathlength than is used in the lab spectrophotometer, 3.5 cm across the plastic bottle instead of 1 cm. For the lab measurement reported in the figure, A is about 0.1 at a wavelength of 592 nm when the path is 1 cm and the concentration is the remarkably low value of about $5x10^{-5}$ molar, 50 micromolar! We want A=1 at L=3.5 cm. That requires only 1/3.5 times the concentration from the greater path length, but 10 times more for the lower absorbance of only 1.0. So, we need about 2.8x the concentration used in the figure's study, or about 140 µM.

The molecular mass of Ph is 318 g. That means we want a final concentration of 318 g/mol * 0.00014 mol/L, or near 0.05 g/L. Our concentrate will be 200x that, or 10g/L. We're only making a small volume of concentrate, 10 ml, or 0.01L, so we want about 0.1g. We made up that solution.

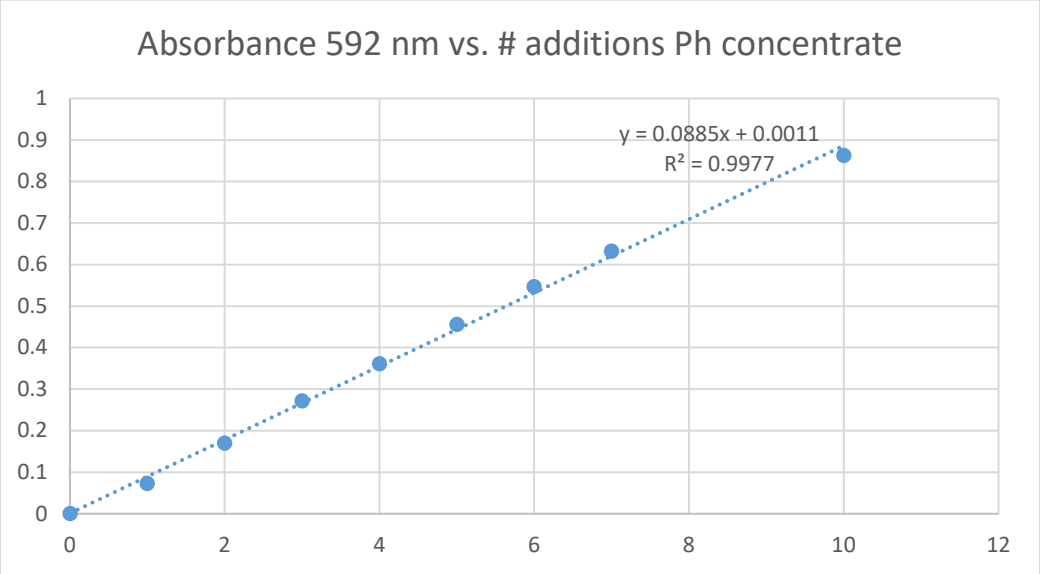
We had planned on using the bottle with a solution capacity of 200 ml (a bit of an overestimate). We kept using that volume, as we made up solutions in a flask before putting them in the device. That makes the calculation of dilutions easy: 1 ml of concentrate in the 200 ml flask.

We decided on a calibration curve using fractions 0.2, 0.4, 0.6, 0.8, and 1.0 of the top concentration. That makes the actual additions (aliquots) 0.2 ml each. We take 200 ml of pure water, add 0.2 ml of the Ph concentrate (and 1 ml of an NaOH concentrate – we'll discuss this shortly), and measure the absorbance. Then we add another 0.2 ml of Ph concentrate and read the absorbance, and so on. We actually went to 2x the top concentration, given that *A* was only about 0.4 at our computed top concentration. We used precision pipettes to add the concentrate:



The initial look of the solution shows a cloudy mass, as the Ph fails to dissolve in full at first, dissolving in full as we swirl the flask. (The red on the bottom is a reflection.)

The results for absorbance were quite "clean," showing a nearly perfect proportionality (linear curve) of absorbance to concentration:



We had some minor errors in measuring the aliquots, which accounts for a bit of "jitter" in the plot, but it's fine.

Here was a bit of statistics for the students. I asked Excel to run a line through the points, the best fit (by the method of least squares, which doesn't need elaboration at this time). I pointed out the report of an R^2 value of 0.9977, and its interpretation that choosing a straight line to fit the jumble of data points explains nearly 99% of the variation among the points. A great fit.

Back to the need for a concentrate of sodium hydroxide, NaOH: phenolphthalein only takes on its full color in a rather basic (alkaline) solution, with a pH value of 10. We didn't go into the theory of acids and bases and the pH scale at this time, but I noted to the students that this requires a concentration of hydroxyl ions of 10^{-4} moles per liter. (This is below the concentration that causes the rapid reaction we're going to follow.) NaOH ionizes in water completely, to Na^+ and OH^- iona, so we need 10^{-4} moles of NaOH in a liter. Again, we're making a 200x concentrate, in a quantity of 100 ml, so we need to calculate the mass of NaOH to use. The molecular mass of NaOH is 40 g, so 10^{-4} M solutions have 0.0001*40 g= 0.004 g or 40 mg of NaOH per liter. We're making a 200x concentrate, which then requires 8000 mg (8g), but only 0.1 L, so that indicates we should use 0.8 g. We put 3 pellets of reagent-grade NaOH, with a mass of 0.76 g into 100 ml, certainly close enough.

Students learned a fair bit of best lab practices – not putting implements into a reagent container, since they might contaminate it (tap out solids or pour out liquids), measure liquids carefully with graduated cylinders or pipettes, weigh out solids onto clean weighing paper and then tap the solids into the mixing vessel, etc.

7. The reaction!

A diversion: I ran into some problems using just hydroxyl ions to drive the reaction, so I first tried using hydrogen peroxide, H_2O_2, along with a high hydroxide concentration. That reaction went too fast, or, at

lower concentrations of H_2O_2, not fast enough. We went back to the "classic" reaction, using just hydroxyl ions as the other reactant with phenolphthalein.

After some tests just seeing how fast the reaction seems to go with various concentrations of hydroxyl ions, we settled using a 25x concentrate with 0.5 g of NaOH in 10 ml of water. After dilution, this made a concentration [OH^-] of

$$\frac{0.5g}{40\,g/mol} / 0.01L = 1.25M$$

in the concentrate, or 1/25 of that, 0.05M, in the final dilution.

Now we're using the 200 ml of final Ph mixture, putting a 25 ml aliquot into a flask, and adding 1 ml of the sodium hydroxide concentration. The reaction was still a bit slow, so we ended up using 3 ml of the NaOH concentrate. That also diluted the Ph to 25/28 of the original concentration...but that's no matter – we're going to measure the progress of the concentration from any convenient starting value.

The solution was mixed and we poured about 3 ml into the fused quartz cuvette, inserting that into the lab spectrophotometer. We started a stopwatch going. At appropriate intervals on the stopwatch readout we recorded the absorbance of the solution.

After the students finished one class, I asked one student, Janaki, for her notebook and entered the data into Excel. The next period, I asked another student, Erika, to do the manipulations in the spreadsheet to get our plot of concentration vs. time. I had calculated the concentration of Ph from the absorbance, so I started a data column with the concentration next to the column with the absorbances. For later use, I also started a column with the natural logarithm of the concentration; we'll see why, shortly.

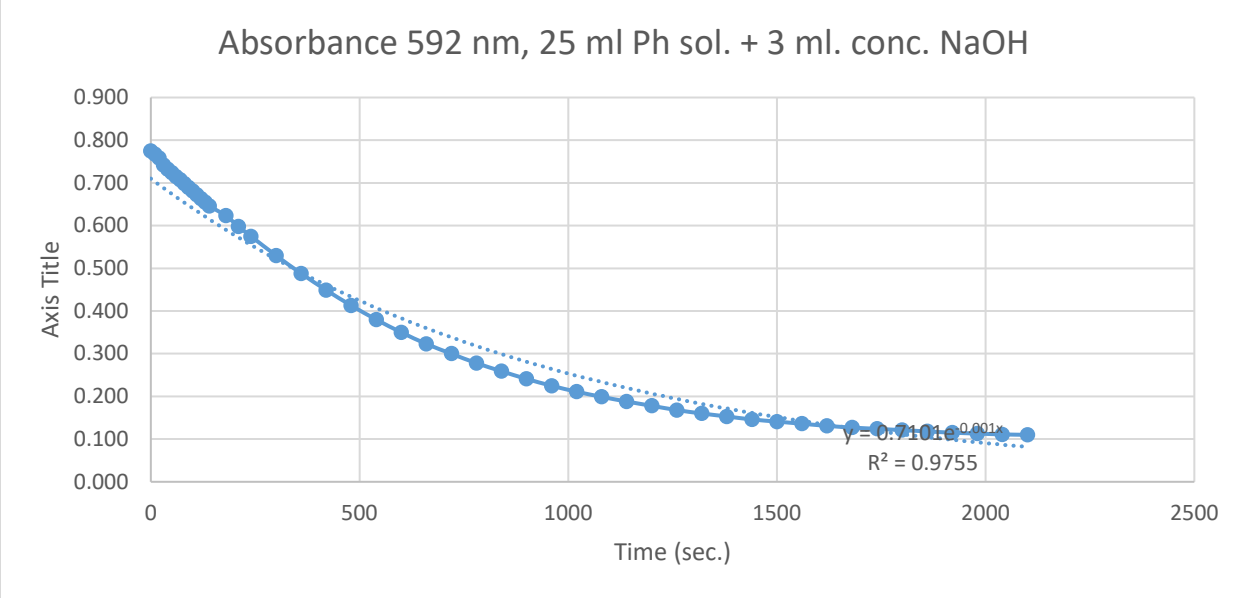
8. The data and the analysis – did we support our hypothesis of a first-order reaction?

Here's the first part of the data:

Time (s)	Abs.	Conc. (molar)	ln(Conc.)
0	0.775	0.00001085	-11.4313
10	0.767	0.000010738	-11.4417
20	0.758	0.000010612	-11.4535
30	0.742	0.000010388	-11.4749
40	0.732	0.000010248	-11.4884
50	0.724	0.000010136	-11.4994
60	0.715	0.00001001	-11.5119
70	0.707	0.000009898	-11.5232
80	0.698	0.000009772	-11.536
90	0.689	0.000009646	-11.549
100	0.681	0.000009534	-11.5606
110	0.672	0.000009408	-11.574
120	0.663	0.000009282	-11.5874
130	0.655	0.00000917	-11.5996
140	0.646	0.000009044	-11.6134

180	0.623	0.000008722	-11.6497
210	0.598	0.000008372	-11.6906
240	0.575	0.00000805	-11.7298
300	0.530	0.00000742	-11.8113
360	0.488	0.000006832	-11.8939
420	0.449	0.000006286	-11.9772
480	0.413	0.000005782	-12.0608
540	0.380	0.00000532	-12.144

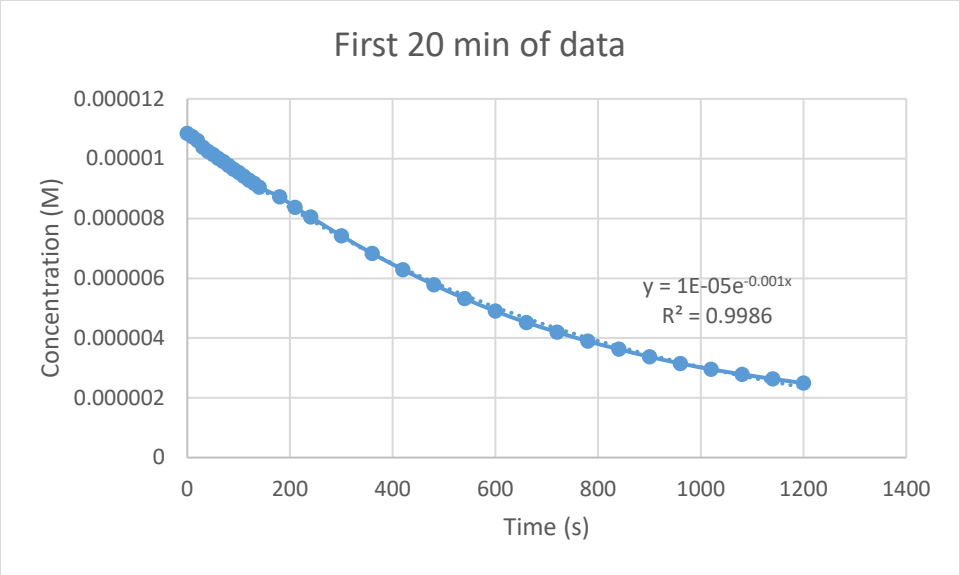
Now to the plot of how concentration declines over time:



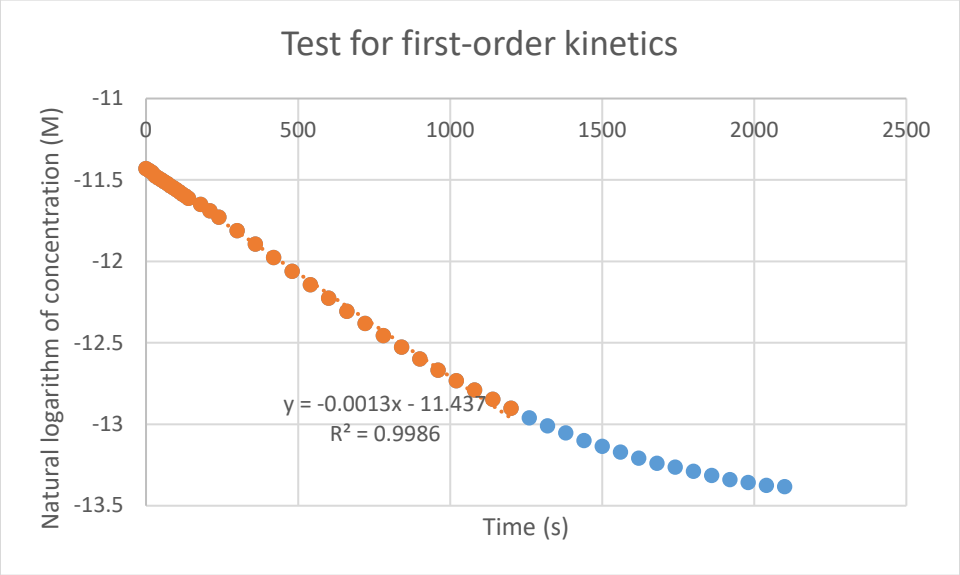
That's a beautiful, smooth curve... and it has the right shape if we assume that our hypothesis is correct, that the reaction is first order. A qualitative argument for this is that the rate of decline, the slope of the curve at any point, looks to be proportional to the concentration itself.

We can do a very quantitative assessment of how well the data fit a first-order reaction. There is a mathematical form, the negative exponential, that represents the solution of what we call the differential equation of the reaction. I didn't go into detail, since the math is well beyond the grades here. In any case, I asked the student to instruct Excel to fit an exponential curve to the data. Voila! That's the dotted line.

Well, the fit is fairly good, but I think the data are better than that, certainly at the beginning of the reaction. I then asked the student to redo the graph using only the first 20 min of data. Now the fit is extremely good, with an R^2 o 0.9986 – explaining 99.9% of the variation!



The curve seems to fit very well. Perhaps a clearer test is to fit the logarithm of the concentration vs. the time:



A straight line is what's expected and the fit is extremely good. (The R^2 value is again 0.9986 –it's the same data set, even after a mathematical transformation).

It also gives us a convenient measure of the reaction's rate constant, which Excel reports as 0.0013 per second. That means 0.13% of the current concentration of Ph disappears each second. Taking the inverse of the rate (times the natural log of 2) gives us the half-life of the reaction. Using the rate in the graph (alas, only two significant figures), we get a half-life of 0.692/0.0013 = 533 seconds. That looks right on – at 540 s, our closest data point, the absorbance (proportional to the concentration) is 0.380, which is a fraction 0.380/0.775 = 0.49 of the starting value, nearly exactly one-half. At 1080 s, the absorbance is 0.199 or 25.6% of the starting value, very near the expected ¼.

Question: the reaction seemed to slow down after 20 min. Why? One proposal I made is that the reaction is inhibited by the product, the decolorized Ph. That happens in many biochemical reactions that involve a catalyst, but it's not common in direct reactions. We don't know the reason, alas.

9. Going further – the order of the reaction for hydroxyl

We used just one concentration of hydroxyl ions. What if we change that concentration? Might the rate be proportional to [OH^-] also? That is, is the reaction also first order in the hydroxyl reactant?

To find out, we varied that concentration. I figured that we might use half the concentration. That's not using exactly ½ ml, since there is less of a dilution effect with a smaller amount. I calculated that we should use 1.41 ml of the NaOH concentrate (this uses a bit of algebra, below, if you're interested – actually, it used the algebra even without a third party's interest, neat thing about science).

Here's another boo-boo. Instead of squirting 1.41 ml of the NaOH concentrate into 25 ml of the Ph solution, I squirted it into the full 200 ml. That made it 1/8 as strong as projected. In turn, that makes it 1/16 as much as in the first reaction.

The reaction carried on, rather slowly, but we could measure it very well in the spectrophotometer. The simplest comparison with the original rate of reaction is to take the initial slopes, as fractions of the initial concentrations. In the original reaction, we lost a fraction of about 0.0011 of the phenolphthalein per second (a bit less than the 0.0013 for the whole time course). In this second reaction, we lost a fraction of 0.00008 per second, about 1/14 as much. The calculations follow the data here:

Time (s)	Absorbance
0	0.947
60	0.943
120	0.938
180	0.934
240	0.929
300	0.922
360	0.917
420	0.911
480	0.907
540	0.904

This shows an average fractional loss of (0.947-0.904)/0.947 = 0.0454 in 540 s. That's 0.0454/540 = 0.000084 per second.

We expected 1/16 as much, so we're very close. We have evidence that the reaction *is* first order also in hydroxyl ion concentration! We can propose a rate:

$$\frac{\Delta conc.}{\Delta time} = k'[Ph][OH^-]$$

Again, [ ] means concentration.

We learned a lot! We weren't totally distracted, even, by the beautiful color.

We appreciate your reading this account. We're proud of our students and of our curriculum.

Anish, Samantha, Erika, Janaki, Isaac at the finish line. Mohammed was in Chinese class this final period.