Review

The use of estimates in teaching chemistry and other sciences

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ABSTRACT

Students often try to memorize equations in chemistry and other science classes. Although memorization plays an important role, it is terrible to learn science without understanding what the quantities physically mean. Here, it is recommended that teachers teach students to estimate answers, which requires them to understand what the quantities in the equation mean. Memorization without understanding prevents students from proceeding to more advanced classes.

Key words: Students, memorization, estimate, answers, quantities, equation.

INTRODUCTION

Numbers, in physical or chemical problems, refer to actual amounts of substances, or of their properties. Too often, students try to memorize equations, without understanding this fundamental concept. As a consequence, for these students, there might as well be no physical world—at least no physical world that corresponds to their course work. I have observed this sort of problem often enough that I think it is worth responding to in teaching. This is not a research paper, but is based on over a half century of teaching experience.

The students have to understand that you cannot get to first base if you are not in the ballpark. The essential point is that there are students who lack any feel for the connection between the numbers they see in the putative solution to a problem and the physical universe. Without this, there is no point in solving the problem; it becomes an exercise in arithmetic.

There is one point in the first year chemistry course where the students are explicitly taught to approximate the answer to a problem. In calculating the hydrogen ion concentration from a weak acid, given a pK and a concentration, the equation is found from the equilibrium constant. It is worth going through what the first year student is given:

\[ HA = H^+ + A^- \]
\[ \text{So } [HA] = c_0 - [H^+], \text{ and } [H^+] = [A^-]; \]
\[ K_{eq} = 10^{pK} = [H^+][A^-]/(c_0 - [H^+]) = x^2/(c_0-x), \text{ where } x = [H^+]; \]
\[ \]

Here the student, who has gone through the three steps to get to the final equation, is faced with a quadratic equation. This can be simplified if the x in the denominator is dropped. Here is where many books, and courses, tell the students to drop the x, without really telling them whether the approximation is justified. At this point, the student should ask whether this is justified, and under what conditions; very rarely do they do so, and too often they are not given an explanation. It is easy to see that the approximation is good if, \( c_0 \gg K_{eq} \), pretty good if \( c_0 \approx K_{eq} \), and completely wrong if \( c_0 < K_{eq} \), in which case the acid ionizes essentially completely. In that case, \( x \approx c_0 \), and if the student works through the cases, then s/he is able to know that the extent of dissociation approaches 100% when there is not so much acid relative to the probability of dissociation in water. Obviously, in case dissociation approaches 100%, it is nonsense to approximate \( c_0 - x \approx c_0 \) instead, \( c_0 - x << c_0 \). This could lead

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1 For those not acquainted with baseball, or some American aphorisms, the two in this sentence mean: 1) “You can’t get to first base”. There is no hope of making a start on a problem. 2) “if you are not in the ballpark” if you have no idea at all about the sense of the solution—say an order of magnitude estimate of a quantitative problem.
to a discussion of the importance of having enough water to react with the acid, but even if this is not done (and it may be too soon in the curriculum to do this, as it requires relating to the free energy of the dissociation reaction, as well as the interaction of the ions with water, which has not yet been covered, usually) the student should have a sense of what it means to be a weak acid; this is something that students are not generally asked to think about.

I have gone through this in some detail, as it illustrates the main point that the curriculum all too often is set to teach a simple calculation, but not the chemistry behind it, or even the validity of the arithmetic itself. This is hardly the only place in the curriculum where this is the case. While the classic example is the first year student who, faced with calculating the mass of a hydrogen atom, and depending on memorization, cannot remember whether to divide or multiply by Avogadro’s number; he/she ends up multiplying, getting a mass approaching the mass of the moon. The moon is big; atoms are small. The student with no sense of the meaning of numbers leaves the ridiculous answer. Fortunately, this gross a mistake is rare, but it should be completely unheard of, because the student should have been taught to pay attention to the meaning of the number.

A general method to approach teaching this sense of the order of magnitude of numbers is to have students estimate solutions to problems before performing the entire calculation. This would make it possible to see an order of magnitude before beginning. Back in the day, before there were calculators, students had to use slide rules. Not only did these limit the calculations to three significant figures, but they did not give the decimal point! This made it absolutely up to the student to realize what s/he was doing. Calculators make it possible to do problems to more significant figures, but, if an incorrect value is given to the calculator, there is nothing that requires the student to think about the result. It is therefore no longer natural to expect students to pay attention to estimating the answer. Requiring the student to make such estimates can prepare him or her for more advanced topics where a physical sense of the system is required.

If there were no other chemical approximations that could be introduced into the curriculum, this would not be a serious question. However, there are approximations to the majority of the problems associated with most topics. Here are a couple of examples.

Example 1: Stoichiometry: There are a number of ways to make sure that a calculation of the mass of a product is not ridiculous. For one thing, the student can check that the mass of the product is not larger than the mass of starting material (sometimes students do make errors in which they overlook this). Second, if there is an equilibrium constant given, its order of magnitude tells whether to expect the mass of product to be near the total mass of starting material, or a small fraction of this mass, or somewhere in between. If $K_{eq} \gg 1$, then most—nearly all—the total mass in the system will be converted to product; if $K_{eq} \ll 1$, one should be left with mostly starting material, and for $K_{eq} \approx 1$, the amount of reactant and product in the final mixture will be comparable. While this may seem obvious, for many students, it isn’t. Having gotten this far, it is time to begin to work the problem. If the amount of each of two reagents is given, as in typical problems, finding the limiting reagent is the place to begin. By this point in the course, the student should be able to find the number of moles of a reagent from the grams—finding the molecular mass should be second nature, and dividing to find the number of moles is quick. It may be worth doing this to one significant figure, which is often enough to find which reagent is limiting. One value of doing this to one figure is that it avoids possible wrong entries into a calculator, and similar trivial errors. However, the more important point is that the student can see what is happening, including finding roughly the number of moles of products to expect. Once this is done, the problem can be worked out conventionally; if there is a gross error it should be immediately apparent (and most errors in these problems are large enough that they can be considered gross, as they are way off—if there is an error, it is not likely to be something the calculator did wrong). An error is likely to be in the first significant figure. Stoichiometry is a particularly useful tool in introductory chemistry, as a large fraction of the course deals with equilibrium constants and equilibrium calculations, and pH calculations, which have a lot in common with stoichiometry problems, since they deal with pK calculations. This is not the place to go through a book’s worth of these problems, but the approach is similar for many problems. The original example above, for example, the dissociation of a weak acid, leads to a pK calculation, and the justification for using an approximation, or ruling the approximation out in favor of approximately complete dissociation. The latter suggests that pointing out to the students that having a sense of what to expect in a chemical system is necessary to understand how to approach calculations on that system.

Example 2: For a rather different part of the course, in which the students are introduced to the elementary ideas of quantum mechanics, it is necessary for the student to have been introduced to the magnitudes of the fundamental constants that appear in practically all calculations. These include Planck’s constant and the speed of light. This presents a somewhat more difficult problem, because these numbers are so far from one. Of course, one could introduce dimensionless units, in which Planck’s constant is one; however, this is a more difficult mental exercise, so it is
normal to keep the standard units with the very large or small magnitudes. That said, if the students are prepared with a sense of orders of magnitude, they should be able to approximate the solution to problems, and, even more important in this case, determine whether their calculations are producing reasonable results. Preliminary examples can be used to prepare the students for the first problems they will have to solve.

a) Suppose the students have to find the wavelength of light that corresponds to an energy of 2.3 electron volts. To begin with, the students have to convert electron volts into Joules. Then, assuming they are able to keep track of the orders of magnitude, the calculation becomes trivial. Here is one case where it is worth having the students learn a couple of conversion factors, such as electron volts to Joules(1 e.V. = 1.60 × 10⁻¹⁹ J). For order of magnitude, it may be easier for the students to remember 10⁻⁵ J for a mole of charge. The student should know that the charge on one charge times 1 volt is an electron volt; one thing that cannot be approximated is a definition. Dividing 10⁵ by Avogadro’s number gives 10⁻¹⁹; this is the correct order of magnitude. Actually, in practical terms, the students, once they are told to learn the conversion factor, don’t need to go through this process. However, they should realize how to do the conversion. Unit conversions are often necessary in themselves. In this case, we can move past this step; again, the student may be aware that visible light is in the range 400 – 700 nm; most often the corresponding frequency range is less well known. However, knowing that wavelength x frequency = velocity of wave, here, light wave, so 3 x 10⁸ m s⁻¹; then 600 nm (6 x 10⁻⁷ m) gives 5 x 10¹⁴ s⁻¹. Thus any visible light frequency will be in the range 7.5 to 4.3 x 10¹⁴ s⁻¹. Then, knowing that the frequency of UV light is higher, up to twice that of the violet – ultraviolet boundary, it is obvious that the highest ultraviolet frequency is 1.5 x 10¹⁵ s⁻¹; conversely, IR frequencies are less than 4.3 x 10¹⁴ s⁻¹. Starting with these boundaries, this class of problems can already be estimated; in this case, it is actually worth the student’s time to memorize a few numbers, at least as to order of magnitude—not something that is generally a good idea, but useful in this topic. This goes a little beyond realizing that atoms are small and the moon is large, but it is a similar idea.

b) Another problem that may come up in even an introductory course, although much more likely in a physical chemistry course, is the de Broglie wavelength of a particle. Here the equation is extremely simple, $\lambda = h/p$, and for a non-relativistic particle (essentially anything we have to deal with in chemistry, except inner shell electrons of heavy atoms) this becomes $\lambda = h/mv$, where $p = $ momentum, $m = $ mass of the particle, and $v = $ velocity of the particle. If we are concerned with a proton as the particle, and we are using standard (SI) units, we know that the mass is 1/6 x 10⁻²³ (remember, SI units, so mass in kg, not g—again, students often have to be reminded of this). h = 6.6 x 10⁻³⁴ Js. So, $\lambda \approx 4 \times 10^{-7}/v$ meters. So far, no approximations, except to round to one figure. What about velocity? Of course, we could be given the velocity, in which case this is just a problem in arithmetic. Suppose, as could be the case in a physical chemistry class, we are told to use the velocity of a thermal proton, that is, one with energy about $k_BT$, where $k_B$ = Boltzmann’s constant and $T$ is the temperature in Kelvins. At this point the student has to equate the kinetic energy of the proton, $\frac{1}{2}mv^2$, to $k_BT$ = 1.38 x 10⁻²³ T J. For a temperature of 300 K, $k_BT$≈ 4 x 10⁻²¹ J, making $v \approx (10^{-20}/(1/10^{23}))^{1/2} \approx 10^8 m s^{-1}$(order of magnitude), or, considering that the effort to plug these numbers into a calculator is minimal) $v \approx 2 \times 10^8 m s^{-1}$, making the wavelength 1.0 x 10⁻¹⁰ m, to two significant figures. So far, almost no approximations. However, this opens a discussion. We have found two quantities, a velocity and a wavelength. The velocity is about one ten-thousandth the speed of light, so the non-relativistic assumption is consistent. On the other hand, is this reasonable? We may not have much of a feel for the velocities of molecules, but the idea that they move pretty fast seems reasonable. Remembering that the velocity decreases with the square root of mass, a molecule in the gas phase with a molecular mass of 100 would move an order of magnitude slower—still pretty fast, but not unreasonable. Would you expect a molecule with molecular mass of 1000 to be in the gas phase at 300 K? Probably the 1 to 100 range pretty much covers it. This problem itself can be used to allow the student to use some chemical intuition—very heavy molecules are unlikely to be in the gas phase at room temperature. If the velocities were, say, a couple of orders of magnitude slower, we might expect the molecules to interact more slowly, and molecular collisions to be more sticky. However, it is hard to have much intuition for gas molecule velocities until you have calculated some. While we are not very surprised at the velocities we calculated, that is really the most we can say.

What about the wavelength? We have the proton wavelength at almost 1 Å. Here, we really can have some feel for the order of magnitude of the answer. If the wavelength were larger than a chemical bond, there would be some question as to how to define the bond in, say, an acid—the proton might not be properly described as bonded. Of course, using thermal energy as the energy that defines the wavelength is itself an approximation, but it is
reasonable to assume that this is roughly what a molecule has in any degree of freedom, including vibrational as well as translational degrees of freedom. A proton approaching a molecule does not have so large an extent that it could interact with more than one part of the molecule.

However, having a molecule, even a heavier one, with energy in any degree of freedom tremendously different from thermal energy is not probable. The approximate wavelength of the proton does fit with what we would consider reasonable. Heavier molecules have shorter wavelengths, inversely proportional to the square root of mass, so a molecule of weight around 100, as a single entity, would have a wavelength an order of magnitude shorter, in the hundredths of an Angstrom range. We are not surprised that we do not have to worry about quantum effects for anything macroscopic. What about the wavelength of an electron? Having gotten this far, we observe that the mass of the electron is about 1/1800 that of the proton, so the square root of the mass ratio is around 40. Starting from the proton’s 1 Å, this means that a free electron wavelength can be larger than a molecule, at around 40 Å. Whether this in turn might lead to a discussion of tunneling, for example, depends on the time available and the curriculum. Sometimes it is worth pointing out that the mass dependence of tunneling is different than that of the de Broglie wavelength, so the rough equivalence of tunneling length for a reasonable barrier, and the wavelength, is not a general result.

In these cases we use the “exact” values and the result of an extremely simple calculation to consider the physical and chemical consequences of the result. The “problem” itself could be done by a junior high school student, as far as getting the value of velocity and wavelength is concerned. Understanding the meaning of the result, or at least the consequences, is a more sophisticated exercise, and requires comparing the result to other known quantities, like molecular dimensions.

Many errors can be avoided by working through units. Fortunately, this is done in many texts. A classic case is the ideal gas law. While it is almost impossible to not memorize $PV = nRT$, let us assume an attack of brain fog on the exam, and require you to derive the law using $PV = nRT$ to solve the following problem:

$$V(L) = \frac{R \times n \times T}{P} = \frac{0.082 \times 2.00 \times 200}{1.00} = 32.8 \text{ L}$$

Of course, now we should do our diligence: is this reasonable? Did we lose a decimal point? Now we could call upon memory (somehow restored), and remember 22.4 L for one mole at standard temperature and pressure, $T = 273 \text{ K}$, $P = 1 \text{ atm}$. A moment consideration will show that 32.8 L is reasonable.

There is no need to elaborate on this as it is a frequently discussed topic, but there are cases in which checking the units is the key to getting a problem solved.

**A more advanced topic:** There is a second class of questions that is worth considering in the same context. These are related in the sense that the consequences, or conditions, for the approximations used in deriving these equations may not be fulfilled. The equations may be used in cases where they are simply not applicable. An example of this is using macroscopic equations in confined spaces. This is something that has to be included in a later part of the curriculum, as it is too sophisticated for the elementary classes. The problem has to do with fluctuations, in situations in which these are too large to neglect. We know that there is essentially no reason to pay attention to fluctuations in a normal macroscopic chemical system; fluctuations are of the order of the square root of the number of particles in the system, so if you have as much as $10^{-4}$ moles, the fluctuations are of the order of $10^{-10}$ of the number of particles—neglecting such fluctuations is obviously justified for any calculation that does not require accuracy of $10^{-10}$—in other words, any chemical calculation. The experiments that have that level of accuracy are some very specialized physical experiments. These include distance measurement, for example, in gravitational wave detectors, and even there it is the small difference in length that is measured. There are a few other such experiments that actually involve such accuracy, but these are not chemical experiments. However, there are cases in which chemical experiments may need to take fluctuations into account. The classic case occurs in the application of macroscopic equations in small systems.

As an example, consider how accurately we can measure pH in a small system. To begin with, let us see whether we can define pH “accurately”. If you need to define the pH to ±0.001, you need to define the hydrogen ion concentration to $10^{-6.001}$, or about 0.2%—not so accurate in many contexts, but not necessarily trivial. 0.2% means roughly one part in five hundred, so one needs roughly five hundred squared, or about $2 \times 10^5$ ions. Suppose we are near pH 7, and have a volume of roughly the size of a small bacterium, about $10^{-18}$ m$^3$, or $10^{-15}$ L, so if the hydrogen concentration is around $10^{-7}$ M, there are around $10^{22}$ moles, or about 60 hydrogen ions. Now the fluctuations are probably around $\sqrt{60}$, or about 12% of the H$^+$, limiting the possible accuracy to something close to ±0.3 pH unit. In general, confined spaces are likely to have appreciable fluctuations, because there are so few molecules, or ions. Of course, the fluctuations
become relatively small quickly as the number of ions increases. With a somewhat larger cell, say ten times bigger in each dimension, so that there are $10^3$ times as many ions, there would be fluctuations, but only $1/30$ as large, relatively.

Other forms of errors in confined spaces include using equations that require a mean field in a situation in which there are not enough ions to define a mean field, as for example is needed for the Debye-Huckel theory. Of course, with the requirement for a low concentration to apply the Debye-Huckel in the first place, it is an error to even think of applying this in a very confined space. Other systems in which it may be necessary to use caution in applying the normal macroscopic equations include surfaces, and systems of nanoparticles, although if the surface is large enough, or there are enough nanoparticles to make a macroscopic system, these can be treated macroscopically. The question is how to present these considerations to students. First year students would almost certainly be merely confused by having these matters discussed, but for physical chemistry students, this could be a valuable addition to their chemical intuition. While the importance of having a sense of the meaning of the numbers in calculations is important from the very beginning of studying any science, error analysis, and the difficulties of defining quantities so that the errors are meaningful, is much more subtle. That is generally covered in physical chemistry lab courses, and before that in analytical chemistry, but generally with a view to the scatter of replicate measurements rather than the physical meaning of the applicability of equations or the interpretation of the results.

One thing that is usually covered in first year chemistry is significant figures, and this is a way to specify the accuracy of a calculation as well. For introductory students this may be adequate, but an error analysis with actual error limits is necessary once one gets beyond the elementary level. Still, significant figures do have uses, and students should know enough to not use, say, $\pi$, to six places when only three significant figures are known.

**Conclusions**

Often, students solve chemistry problems mechanically without thinking about and understanding the physical meaning of the numbers in the answer or the chemical implications of the values of quantities such as pH or reaction rates. This can be addressed to some extent by requiring the students to estimate the answers, and to check whether their explicit calculation gives a reasonable result. Estimates can show what is reasonable. As a result, students are prevented from just plugging into formulas that they have memorized, which is impossible after the most elementary level in chemistry. Estimates can be done for almost all chemistry problems; some have extremely simple formulas, but there is much that can be gained from working through what the results mean physically. Working through units also helps.