

## The Use of Estimates in Solving Chemical Problems

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**Abstract:** The use of approximations in solving problems in sciences can be vital for students. Order of magnitude estimation also helps with physical understanding of the quantities involved in a calculation. For example, in the first exam in a first-year class in chemistry the student must find the mass in grams of an atom; a couple of students will multiply by Avogadro's number instead of dividing; for atomic weight around 100, this gives the order of magnitude of the mass of the moon; the moon is big, atoms are small. If the student considered the physical meaning of the mass, this would not be a possible mistake. Another example: calculate the total energy, and potential energy, of a system, and from these find the kinetic energy. If the kinetic energy comes out negative, something is wrong; the student should realize this. One place a student is taught an approximation in first year chemistry is finding the ionization of a weak acid; ionization is approximated by taking the square root of the dissociation constant times concentration, which only works if the concentration is large compared to the dissociation constant. If the student applies the approximation thoughtlessly, this produces an error. The adequacy of any approximation for accurate use is another concept that must be taught. Part of the use of approximations includes attaching error estimates to answers (sometimes expressed as significant figures). There is a second, related, matter that needs to be taught with the estimates; units must match. A book, "The Use of Estimates in Solving Chemistry Problems" (Green and Garland, 1991, Saunders) went through the quantitative parts of first year chemistry, showing how to estimate answers for all sections. A few examples from more advanced material are included too, as this kind of error persists past the first year.

**Keywords:** Estimates, Order of magnitude, Problem solving, Physical meaning of values

### Introduction

The introduction of calculators in place of slide rules has produced a number of great advantages, but one major disadvantage. When students used slide rules, the order of magnitude of the result had to be provided by the student, so totally ridiculous answers were relatively rare. Of course, they were not non-existent, but the fact that the order of magnitude was the responsibility of the user of the slide rule meant that doing a calculation required at least some consideration of what the numbers meant. There were still cases of occasional students who memorized a formula instead of understanding it, getting it wrong, and then putting down an answer that was incorrect; rarely was it totally ridiculous, however. The classic case is the student who, on the first exam in first

year chemistry, when asked to find the mass in grams of an atom with atomic mass 100, multiplies by Avogadro's number instead of dividing, getting something of the order of magnitude of the mass of the moon. The moon is big; atoms are small. If the student had any sense of the physical meaning of the number, he or she would immediately recognize that the answer is ridiculous, and would correct it. Even if calculators give the order of magnitude, a student who is not thinking may leave the answer, because it is what the calculator said; the student is not thinking about what the order of magnitude should be. While I do not regret the replacement of slide rules by calculators, slide rules did force consideration of what the order of magnitude had to be. Having a sense of what is reasonable is a skill that has been recognized by well-known physicists, at least. Enrico Fermi famously proposed problems with very little data, the most famous of which asked simply "How many piano tuners are there in Chicago?". No data was given, but if you think through the problem you can get the right order of magnitude. It is still the case that estimating orders of magnitude is part of the education of most physics students, and physicists routinely estimate orders of magnitude. This is less common in chemistry instruction, but would be just as useful. In order to find the answers to chemistry problems, it is a good idea to start with understanding what the system properties are. Unfortunately, it is all too common for chemistry to be taught with a lot of memorization, including equations. When a student relies on memorizing equations, it is usually the last chemistry course that student will pass. More advanced courses cannot be passed by memorizing equations. If the student is accustomed to thinking through the physical meaning of the numbers in the problems, then that student will understand the work, and will be able to move forward. The use of estimates in chemistry problems is offered in this spirit. The essential point has been recognized, sometimes in regard to particular cases, sometimes more generally, but limited or specific applications. For example, Penn has pointed out the general issue (Penn, 2018). Ryan and Wink gave a general example (candies in a jar), general in the sense that it introduces the idea of approximation without being tied to a particular chemical example (Ryan & Wink, 2012). Matsumoto et al gave examples suitable for a high school class (Matsumoto, Tong, Lee, & Kam, 2009). Specific examples include one topic that is found in most first year chemistry texts, but which students may find confusing, namely,  $pK_a$  calculations (Flynn & Amellal, 2016). By the time one gets to physical chemistry, approximations are even more necessary, and specific examples have been offered by a number of authors (Gasyna & Light, 2002; Lombardo, 2000; Nassiff & Boyko, 1978; Olivieri, 1990; Soares da Costa Junior, Marques da Silva, & Moita Neto, 1999; Viossat & Ben-Aim, 1993; Wallner & Brandt, 1999).

The overall approach can be illustrated by the one example in which an estimate is normally used in first year chemistry. The student is taught to make an approximation in calculation of the degree of ionization of a weak acid. The general form for this calculation is

$$K_d = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+][A^-]}{([HA]_0 - [A^-])} \quad (1)$$

where  $K_d$  is the dissociation constant,  $[A^-]$  ( $= [H^+]$ ) is the concentration of the corresponding ion,  $[HA]$  is the concentration of the undissociated acid, and  $[HA]_0$  the total concentration of the acid plus  $[A^-]$ , thus the known concentration that was added to make the solution. If  $[H^+] = [A^-] \ll [HA]_0$  one can approximate this by

discarding  $[A^-]$  in the denominator, making  $[H^+] \approx (K_d[HA]_o)^{1/2}$ , simpler than solving the quadratic that would be necessary without the approximation. The trouble is that the approximation is valid only for cases in which  $[HA]_o \gg K_d$ . This is rarely explained to the student, leading to inappropriate use when the latter condition is not fulfilled. Usually the dissociation of a weak acid is introduced in cases where the condition is fulfilled, and later, if a case arises in which the approximation is no longer valid, the student still uses the approximation, as he or she has not been taught to think about the meaning of the numbers. For that matter, the approximation may be good when it is only necessary to get the pH to  $\pm 0.3$ , but not, with the same  $[HA]_o$  and  $K_d$ , if it is necessary to calculate the pH to  $\pm 0.03$ . The connection between approximation and the accuracy of the estimated result also needs to be taught. Obviously, there are many more examples, and we will consider some more in the main discussion. The two main points are that numbers have physical meaning in chemistry and physics, and approximations are only accurate to a certain extent and it is possible to estimate the accuracy. Students often miss these points. They must be taught.

This is not trivial even in professional literature, where there are approximations, often, but not always, in connection with constructing models. Sometimes these approximations are used under conditions in which they are so far from correct, because the assumptions on which they are based are not nearly fulfilled, as to constitute physical errors. For example, calculating Debye lengths in systems that are too small to have enough ions to form an ionic cloud produces nonsense. Small systems, such as found in biology, for example in sub-cellular compartments, are subject to large fluctuations, a point which may reasonably be ignored in a first-year class, but which must not be ignored in professional literature. The same is true for some inorganic systems at surfaces, which, having one small dimension, sometimes act like a small system. This is not the main point of this paper; nevertheless, when this type of error appears in professional literature, it suggests that this should have been taught in the undergraduate curriculum, at least in simplified form, perhaps not in the first-year course, but certainly no later than physical chemistry. In the first year it may be possible to introduce fluctuations in an Honors section.

There are on-line tutoring sites, mostly intended for generic use with textbooks. The author is not aware of any first-year textbooks that systematically use estimates across the curriculum, and generally point to the physical significance of quantities in problems. There are exceptions in specific chapters of some texts, but it is generally correct that the use of approximations is not used as much as it should be, nor as systematically. The online sites are a good representation of standard treatments of introductory chemistry problems.

It is not the case that there will never be a gross error in a calculation, and this not limited to students; it is the case that such an error should be recognized and corrected. To do this, estimating the answer, at least as to order of magnitude, will allow these errors to be avoided, or else corrected. Green and Garland (Green & Garland, 1991) addressed this problem in a book by going through the quantitative parts of the first-year chemistry curriculum and showing, using examples, how to start on problems by estimating an answer, at least as to order of magnitude. The standard solution followed the estimate in each example in the book, often with some discussion

of what the physical meaning of the answer suggests. The usefulness of the estimate is somewhat variable, in that some answers allow simply an order of magnitude estimate rather than *a priori* physical reasoning, without use of any equations. However, even these order of magnitude uses of an equation can generally illustrate what is being calculated. The Table of Contents of the book shows the topics covered.

### *Table of Contents*

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Each chapter had about 10 worked out problems, some chapters more, some less, in the format 1) QUESTION 2) ESTIMATED ANSWER 3) ANSWER. The third section contained the conventional answer, as it would be done in most textbooks. The second section is the new element discussed here. Many of the examples had two or three parts, of increasing complexity (although in this paper, we will mostly avoid these), in addition to comments or notes, suggesting that the student think further about whether the numbers given in the problem are in fact plausible, or inviting the student to think further about possible extensions. In this paper, mostly examples from the simplest problems, in a fraction of the chapters, are discussed, which suffice to illustrate the general principles of the approach. However, one or two instances of more complex cases or more advanced topics, are also included here to suggest what is possible. Many problems ran to three or four pages, with the complete explanations and comments.

The discussion of the weak acid dissociation problem in the introduction to the book suggests what is involved. The introduction covers certain mathematical approximations. For example, to estimate square roots, a reasonably good approximation comes from expanding, for  $a > b$ ,  $(a^2 + b^2)^{1/2}$  as  $a + b^2/2a$ . The student does not need to know anything about expansions; it is enough to simply know the rule, and check that  $(a + b^2/2a)^2 = a^2 +$

$b^2 + b^4/4a^2$ . If  $a > b$ , the error is small; the worst case is  $a = b$ ; try  $2^{1/2} = (1 + 1)^{1/2} \approx 1 + 1/2 = 1.5$ , approximately a 6% error from the correct value of 1.41. By the time one gets to  $10^{1/2} = (9 + 1)^{1/2} \approx 3 + 1/6 = 3.167$ , the approximation is good to three figures ( $10^{1/2} = 3.162$ ). The student should test a few examples to know how valid the expansion is. While pushing buttons on a calculator could obviously give the correct answer in any numerical case, there are times when one has an expression that is the sum of two quantities, one clearly larger, and the approximation gives a general result that is much more useful than carrying the radical expression. What is more, it gets the student used to using approximations, even if the derivation will not come until later in the student's education. Other examples include logarithms ( $\ln(1+x) \approx x$  for  $x \ll 1$ ). Several other useful approximations are included in the introduction.

This approximation to the square root is useful, for example, in solving a quadratic equation, as might be expected. The quadratic equation formula,

$$X = -b/2a \pm (1/2a)(b^2 - 4ac)^{1/2} \quad (2)$$

because it involves a square root, is an obvious candidate for the use of this approximation. We can combine this with the weak acid approximation we discussed earlier. For that case, the solution, assuming  $[HA]_o \gg K_d$  is  $[H^+] = (K_o[HA]_o)^{1/2}$ . Without the assumption,

$$[H^+] = -K_d/2 \pm 1/2(K_d^2 + 4[HA]_oK_d)^{1/2} \quad (3)$$

which reduces to the approximate answer if  $4[HA]_o \gg K_d$ . What if  $4[HA]_o \leq K_d$ ? We can use the approximation for the square root to get  $[H^+] \approx -K_d/2 + 1/2(K_d + 4[HA]_oK_d/2K_d) = [HA]_o$ . Note that we must take the plus sign for the square root to get the concentration to be positive, and for that matter for the approximation for the high concentration case to appear from the exact answer. The final answer for the  $4[HA]_o \leq K_d$  case,  $[H^+] \approx [HA]_o$ , means the acid dissociates completely, so we could have reached the same solution by understanding fundamental chemistry—if the concentration is less than the dissociation constant, the acid acts like a strong acid, dissociating completely. However, it is most likely the student does not have enough experience with chemistry for this to be intuitive, so the use of approximations can make the point, which can in turn be reinforced by the teacher. This would help the student gain a start toward considering what the approximations mean, and the way in which it is possible to attach real chemical meaning to the results of calculations.

The chapter on dimensional analysis is not quantitative, but it is very necessary. One of the most common errors students make is to confuse units. There are normally unit conversion exercises in the first chapter of chemistry first-year texts, but rarely are the students put through the exercise of first determining reasonable values of the answer to a calculation. Each chapter in the Green and Garland book has a brief (some chapters, very brief) introduction going over the fundamentals of the topic of the chapter. However, these introductions are not intended to take the place of a textbook.

### An Example of a Worked-Out Estimate, Emphasizing Unit Conversions

This example is not the first in the chapter, so it is not the first the student should work through. QUESTION: On a certain day in New York, the concentration of CO (carbon monoxide) was measured as  $2.0 \times 10^{-5} \text{ g L}^{-1}$ . If the total volume of air over the city is  $1.5 \times 10^{12} \text{ ft}^3$ , how many English tons of CO were present? (An English ton weighs 2000 lbs, as compared to a metric ton which weighs 1000 kg, about 10% more.)

ESTIMATED ANSWER: To begin with, we ignore the difference between English and metric tons—it is 10% different, so not important in an estimate. Let's split the problem up. Again, we have to make two conversions, one on mass, one on volume. The mass conversion is easy,  $10^6 \text{ g}$  to 1 ton, so  $2 \times 10^{-5} \text{ g L}^{-1} = 2 \times 10^{-11} \text{ tons L}^{-1}$ . (Note that grams are smaller than tons, so there are more of them,  $10^{-5}$  instead of  $10^{-11}$ , in the same volume, 1 L, of air.) *[An obvious error that a beginning student can make is to do the conversion in the reverse direction—one would hope that seeing  $10 \text{ g L}^{-1}$  would immediately tell the student to go back; this is not always something the student thinks of—the note points out that the direction of conversion should give a smaller number, but does not, in this case, point out that the result of choosing the wrong direction is ridiculous—although it might be good to do so.]* However, we have lots of liters *[italic “lots” in the original]* A cubic foot is bigger than a liter. So we are looking for a number which is bigger than  $(1.5 \times 10^{12} \text{ ft}^3)(2 \times 10^{-11} \text{ ton L}^{-1}) = 30 \text{ ft}^3 \text{ ton L}^{-1}$ . Actually, one foot  $\approx 30 \text{ cm}$  so  $1 \text{ ft}^3 \approx 27,000 \text{ cm}^3 = 27 \text{ L}$ . Therefore, we want a number in the vicinity of  $30 \text{ ft}^3 \text{ ton L}^{-1} \times 27 \text{ L ft}^{-3} \approx 800 \text{ tons}$

This is the end of the estimate. We forget about the 10% correction to English tons, because we have only one significant figure or not even that, in the estimate. The problem is then worked out in the standard manner, getting 937 tons, rounded immediately to 900 tons (metric). The volume of air over New York cannot be so exact, so at most one significant figure is justified, and there is no real point in bothering to convert to English tons, but one would get 1000 English tons to one figure. This is one of the examples in which the student is invited to consider the plausibility of the conditions and of the given quantities in a problem. Obviously, this problem is only valuable as an exercise, but it is a useful exercise, requiring two conversions, and thinking about the direction of each conversion before carrying it out. When the complete problem is worked out, it checks as to order of magnitude (better, in this case). Before the student pushes buttons on the calculator, the answer is available as a check on whether it is reasonable. If, for example, the student had reversed the conversion from  $\text{ft}^3$  to L, and gotten around 1 ton, it should have been immediately obvious that something was wrong (should, because it is not so obvious in this case what the order of magnitude should be—it is more the order of conversions that should be checked). It may seem that this was a fairly oversimplified example, but students do get this type of question wrong often enough to make it worth going through it. By requiring an estimate first, the student must think through the steps, which is normally enough to avoid mistakes. The book gave two significant figures for the volume and the concentration. An astute student might note that the concentration can be measured and averaged over the city, but that the volume depends on some sort of definition of boundary, so that the second significant figure of the volume is somewhat arbitrary, and the concentration must depend on an

average, since pollutant concentration is unlikely to be as high in wealthy areas of the city as in poorer areas. However, all this goes beyond what would be expected in a first-year chemistry class.

### Summary of Other Problems

From this point forward, we will only summarize problems, showing the main point(s) that illustrate what is being emphasized to the students.

#### *Molecular and atomic mass*

- 1) The isotopes of Cl are given to five significant figures, together with the percentage composition. Of course, the student must realize by looking at the figures, without starting to use a calculator, that if the sample is roughly  $\frac{3}{4} \approx 35$  atomic mass,  $\frac{1}{4} \approx 37$  atomic mass, the result should be closer to 35, but  $>35$ , without doing any arithmetic at all. The simplest approximation is to round off the given molecular masses to 35 and 37 and average these using  $\frac{3}{4}$  and  $\frac{1}{4}$  as proportions, getting about 35.5. After that the complete calculation, using a calculator, should be trivial. If the answer is very different, the student should be able to see at once that the calculation must be redone.
- 2) In the same chapter, suppose we ask for the mass in grams of an atom of X, given that the molecular mass of  $AX_2$  is 120, and the atomic weight of A is 60. This looks totally trivial, but the student should note that mass in grams, not atomic mass units, is asked for, so the answer should be of the order of  $10^{-23}$ , not 10.
- 3) Find the molecular mass of  $YBa_2Cu_3O_7$ . Estimate: note that there are 6 metal atoms and 7 oxygen atoms. If we use 100 for a metal atom, and 100 for 7 O atoms, we get 700. This takes almost no time, and the student should be very suspicious of any result out of the 500 to 1000 range. There is no claim that 700 is actually correct to even one significant figure, although it happens that it is in this case; the answer is 668.9

#### *Gases*

Here the book first very briefly reviews the ideal gas laws, but really relies on standard textbooks; it is assumed that the student has access to a standard textbook. There are a couple of van der Waals equation problems also included, which also help the student understand the order of magnitude of the correction. Anywhere in the general vicinity of STP, and past room temperature, the estimates of the total quantities remain unchanged, as the correction is too small to see to one significant figure. However, the problems can be used in estimating the magnitude of the correction itself.

- 1) Interstellar space has about 1 atom of H per  $\text{cm}^3$ . The temperature is around 3 K. Find the pressure.  
*Estimate:* To begin with, this is a one significant figure problem, so there is no extensive calculation in

any case, but it is not so obvious how to get the order of magnitude. By now the student should know that the molar volume of an ideal gas at around 300 K, 1 bar pressure is roughly 25 L (22.4 L at standard temperature and pressure (STP)). If there is a mole in 25 L, the volume for one atom (averages: here we do not introduce fluctuations, so we omit the word averages) is  $25/6 \times 10^{23} \approx 2.5 \times 10^{-22}$  L, or, using the fact that there are 1000 cm<sup>3</sup> per L,  $2.5 \times 10^{-19}$  cm<sup>3</sup> per atom, if we were at 300 K. Pressure should be around 19 orders of magnitude below the 1 atm value at around STP since there is only 1 atom instead of  $10^{19}$ . However, the temperature is 3 K, so the pressure will be another factor of 100 times less; taken together, we should expect a pressure around 21 orders of magnitude below that near STP. Again, this is a one significant figure problem; the estimate of 1 atom per cm<sup>3</sup> is not good to more than this, and the assumption that the gas is at equilibrium with the cosmic background temperature is not locally accurate, except perhaps by accident, either. The estimate in effect is the answer in this case. Nevertheless, it is a very useful problem in getting students used to the idea of dealing in orders of magnitude, and obtaining reasonable results.

- 2) A syringe is filled with 25 mL of CO<sub>2</sub> gas at 30° C. The syringe is then immersed in an ice bath at 0° C, and the pressure remains in equilibrium with the new surroundings. What is the new volume of the gas? *Estimate:* here the number of molecules is unchanged, and the pressure is unchanged, so we only have a drop-in volume with lower temperature. To begin with, the student should note that one gets a drop, not an increase, in volume, as the temperature drops, while all else remains constant. Second, the student should convert to Kelvins, getting a drop from 303 K to 273 K, almost exactly a 10% drop, so the volume drops approximately 10%, and in this case, it makes sense to take the estimate to be pretty close to exact, making the final volume 22.5 mL. To three figures, this is the final answer as well. The difference with the standard approach to the problem, in which the Gay-Lussac Law is plugged into, is that the student should reason through the steps, observing that the volume must drop, and seeing at once that the drop is close to 10%. If this is done before plugging in to the Law, all possible incorrect answers are eliminated.

Standard variations on the same theme include changing the number of molecules and pressure as well as volume and temperature. As noted above, there are also a couple of van der Waals equation problems in the book, but these illustrate the point that when small corrections are involved, the estimate is useful instead for the magnitude of the correction; the overall quantities can be estimated by sticking to ideal gases, except under unusual conditions, such as near the critical point. However, it is at least useful to see at once the direction of the change. The  $(p+a/V^2)$  term means the pressure will be less, while the  $(V-b)$  term means the volume must be larger, compared to the ideal gas values. For the magnitude of the correction, given the magnitude of the  $a$  and  $b$  terms makes it possible to estimate the magnitude of the *difference* from the ideal gas case.

### *Stoichiometry*

- 1) Lavoisier heated tin, Sn, in air, and found that it gained weight. If he started with 10.00 g of tin, how



much weight would it gain? Given:  $\text{Sn} + \frac{1}{2} \text{O}_2 = \text{SnO}$

*Estimate:* first we have to know some basic chemistry: tin reacts with oxygen, but not nitrogen, and the compound formed is SnO. (We ignore the contribution of SnO<sub>2</sub>—this is given to the student as an SnO product, without the complication) Then, with one atom of oxygen to one atom of tin, it is only necessary to look at the atomic weights. Oxygen mass is about 1/8 that of tin, so the weight of oxygen added is about 1/8 that of the tin, or around 1.25 g. So far, there has been no calculation other than finding 1/8 of 10. The problem is then worked out formally, and the final answer is 1.35 g. Here, the problem can be talked through, so that the student knows, before resorting to the calculator, that the answer must be pretty close to 1.25 g. Checking that the weight of oxygen is a bit more than 1/8 that of tin tells us that the answer must be >1.25.

Part 2: Extending this problem, Lavoisier found that if he heated 10.00 g of Sn with air in a sealed 10.00 L vessel, the total weight did not change. The initial pressure in the vessel was 1.000 atmospheres. Find the final pressure if the system is brought back to the initial laboratory temperature of 17.0 °C.

*Estimate:* To begin with, gas is being subtracted from what was in the vessel initially, so an upper limit on the final answer is 1.00 atm. If all the oxygen reacted, given that O<sub>2</sub> is about 20% of air, 80% of the air must remain, so a lower limit must be 0.8 atm. Before we do anything, we know the answer must be 0.9 atm ±0.1 atm. We can refine the estimate as follows: We have about 0.08 moles of Sn (by this time, the student should know how to get from grams to moles); each mole of Sn uses 0.5 mole of O<sub>2</sub>, hence we use ≈ 0.04 moles of O<sub>2</sub>, or, anywhere in the general vicinity of STP, about 1 L volume of gas, meaning about 0.1 of the original volume, so the final pressure should be about 0.9 of the original pressure, or about 0.9 atm.

If the calculation is done to four significant figures, the answer is 0.8998 atm. In order to get the final answer, it is necessary to have the temperature. The student is informed that the fact that the estimate equaled the final answer to three significant figures is just luck, but again having a reasonable estimate allows confidence in the result of a calculation that takes several steps. The 17.0 °C allows four figures, when 273.1 is added. Actually, if we assign an error of one in the last place of volume and initial pressure, the answer should really be truncated to three figures. This was not discussed in the book, as error calculation that assumes the maximum and minimum values of the data are not covered, nor the use of root mean square error estimates. These topics are not usually appropriate for a first-year course.

*Chemical equilibrium:* There are several types of problems in this category. Essentially these are problems that involve equilibrium constants: K<sub>eq</sub>, including K<sub>a</sub> (acid dissociation), K<sub>sp</sub> (solubility products), K<sub>p</sub> for gas pressure equilibrium, and related problems. Although this chapter comes before thermochemistry, the introductory material includes the relation

$$\Delta G = -RT \ln K_{\text{eq}} \quad (4)$$

without much explanation of  $\Delta G$ , but enough to do some problems.

We start out by pointing out that if  $K_{eq}$  approaches zero, we have almost entirely reactant, if  $K_{eq} \gg 1$ , we have mostly product (all product if  $K_{eq}$  reaches infinity, but we do not discuss in this section the fact that exactly zero or infinity is impossible—that requires more of thermodynamics than we can use in this chapter—however, the student might surmise this from the fact that

$$K_{eq} = \frac{[P1][P2]}{[R1][R2]}, \text{ (P}_i \text{ = products, R}_i \text{ = reactants)} \quad (5)$$

or similar forms for other stoichiometries, together with the  $\Delta G$  relation. If  $K_{eq} \approx 1$ ,  $\Delta G$  must be fairly small, from the log relation. “Small” must be in relation to  $RT$ . If  $|\Delta G| \gg RT$ ,  $K_{eq} \approx 1$  cannot be correct.

This said, the main point of the chapter concerns the  $K_{eq}$  calculations. For gas calculations,  $K_p$  is given, as is the relation between the  $K_p$  and  $K_{eq}$ . Some examples:

- 1) This problem is taken from a 1913 paper (6) on the dissociation of  $PCl_{5(g)}$  near 500 K:



$\alpha$  is the fractional extent of dissociation, so that if we have  $n$  moles of  $PCl_5$  to start, we have  $n\alpha$  of  $PCl_3$  and of  $Cl_2$ , and  $1 - n\alpha$  of  $PCl_5$ . *The problem is to find  $\Delta G_p$  at 500K.* The data are given in Table 1:

Table 1. Temperature-Pressure relation for  $PCl_5$

| T (K) | p(mm)  | $\alpha$ |
|-------|--------|----------|
| 462   | 762.8  | 0.244    |
| 485   | 814.7  | 0.431    |
| 534   | 1214.5 | 0.745    |
| 556   | 1370.1 | 0.857    |
| 574   | 1358.6 | 0.916    |

$\Delta G_p$  is the value of  $\Delta G$  in terms of pressure, and is independent of total pressure. The relation between this and the  $\Delta G_c$  (in terms of concentration) is given earlier in the chapter. If the amount of dissociation is about half, the  $\Delta G$  value must be small in absolute value—there is not much difference between reactant and product equilibrium concentrations. From the looks of the data, at 500 K the  $\alpha$  is around 0.5. This suggests  $K_p \approx (.5)^2/(1 - .5) = 0.5$ , so  $\Delta G \approx -RT \ln (.5) \approx 3$  kJ. The actual answer, which requires a rather extensive calculation, is +2.6 kJ. Again, the approximation happens to be closer than it has any right to be. However, that the value should be small is apparent without even this much effort. If the value were much greater than 20 kJ, or much less than -20 kJ, the degree of dissociation would be nowhere near 0.5 (the student should by this time know that  $RT$  near 300

$K$  is  $\approx 2.5$  kJ, so should know that around 600 K,  $RT \approx 5$  kJ). Once we have this much of an estimate, we can proceed with some confidence that the answer must not be large in absolute value, probably  $\leq RT$ .

- 2) The idea of free energy of formation was explained in the introductory material for this chapter. Hence, the student should know that if we give the free energy of formation of CO, it is the free energy of reaction for



*Question:* Given total pressure = 10 atm, and  $\Delta G_p = -137$  kJ mol<sup>-1</sup> find the final pressure of O<sub>2</sub> and CO. *Estimate:* We are able to find the partial pressure of CO given the total pressure. In this case, the  $\Delta G_p$  is far greater than  $RT$ , -137 kJ mol<sup>-1</sup> and is negative (the free energy of formation of CO is given).

A large negative  $\Delta G_p$  implies that the product, CO, will completely dominate the mixture. We expect  $p_{\text{CO}} \approx 10$  atm. Since we only have three significant figures, and at 300K,  $137/RT > 60$ , so that we have something like  $e^{-60} \approx 10^{-24}$  for the pressure of O<sub>2</sub> (this is not exact - and is not the way to do the exact calculation, but for the estimate it is good enough). If there is so little O<sub>2</sub>, all the rest must be CO, so its pressure is equal to the total pressure to more than three significant figures, making  $p_{\text{CO}} = 10.0$  atm. Again, the calculation is fairly complex if it is done properly, which allows room for mistakes. If the estimate is done first, an erroneous result will be immediately apparent.

- 3) Mix 100.0 mL of 0.1000 M HAc with 100.0 mL of 0.0750 M NaOH. Find the final pH. The  $pK_a$  of HAc is 4.75

*Estimate:* To begin with, the student must recognize that this is a buffer problem; we assume that the student does realize this. NaOH is a strong base and HAc a weak acid [*presumably the student already knows this, and the fact that the  $pK_a$  is given for HAc should be enough of a reminder, if one is needed*]. There is more than half as much strong base as acid, so this will form more salt of the acid than there is acid remaining. This already tells us that the ratio of  $[\text{Ac}^-]/[\text{HAc}] > 1$ , so we must have  $\text{pH} > pK_a$ . Since the ratio is not close to an order of magnitude, the difference will not be huge. We expect a  $\text{pH} > 4.75$ , but not by a full pH unit, so around 5. In solving the problem, remember that the final volume is 200 mL, so the concentrations are half those in the two starting solutions.

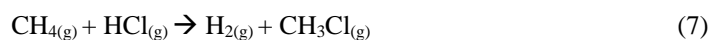
The final answer to the problem is  $\text{pH} = 5.23$ .

### Thermochemistry

This chapter has 8 pages of introductory material, since we were not satisfied with the presentation in some texts. There is a brief introduction to the most important thermodynamic quantities, to calorimetry, to the Laws,

and to definitions (reversible/irreversible, path independence, etc.). After this, it is possible to introduce problems knowing that the student has the basic concepts at least defined.

1) Part 1: For the reaction:



the free energies of formation,  $\Delta G_f^\circ$ , are:  $\text{CH}_4$ : -50.79 kJ;  $\text{HCl}$ : -95.27 kJ;  $\text{CH}_3\text{Cl}$  -58.5 kJ.

*Estimate:* We can just look at the values—as a rough approximation the  $\text{CH}_4$  and  $\text{CH}_3\text{Cl}$  values cancel, leaving a large negative value on the left, so the overall result must be around +95, but less because  $\Delta G_f^\circ$  of a product is more negative than that of the reactant we compared it to. The first thing the student should notice is that with a large negative value on the left, the overall result must be  $>0$ .

Actually, setting this up is almost trivial, and the answer is +87.6 kJ.

Part 2: Find the final partial pressure of  $\text{CH}_4$  and of  $\text{HCl}$  if their initial partial pressures are both 10.0 atm, and the initial partial pressures of the products are zero.  $T=298$  K. All reactants and products are gases, and can be assumed to be ideal. Then get the partial pressures of the products.

*Estimate:* With such a large positive  $\Delta G_f^\circ$  the reaction hardly gets started. Just looking at the exponential term  $\exp(-\Delta G^\circ/RT) \approx \exp(-35)$ , we see without doing any work the final partial pressure of the reactants is almost as large as the initial partial pressure, 10 atm. More than three significant figures would be needed to see a difference. We can use this to get the final partial pressures of the products easily, since the final partial pressure of the reactants is known. The one estimate we make is to note that the final partial pressure of products must be very small.

As there is no change in the number of moles,  $K_c = K_p = \exp(-87.6/(8.3*298)) = 4.49 \times 10^{-16}$ . Given the stoichiometry, let  $P$  = the final pressure of  $\text{H}_2$  = final pressure of  $\text{CH}_3\text{Cl}$ , so  $K_p = P^2/10^2$ , giving  $P = 2.12 \times 10^{-7}$  atm.

In this case, we skipped the estimate for the products, as there was only one step, and we only observe that  $P \ll 1$  is satisfied. We could have immediately realized that we needed  $< e^{-15}$  for the pressure from the  $e^{-35}$  we estimated for  $K_p$ . ( $e^{-15} = 3 \times 10^{-7}$ ). This could have been used as a check, or an estimate. At the least, the student should see that this is reasonable.

This problem, with its two parts, is interesting in that it requires the student to think through information in the problem and realize that much more can be obtained than the original, rather simple, thermochemistry problem.

We could add a third part, asking, given the number of moles that actually reacts, what the volume must be. Then this also becomes a very simple stoichiometry problem, and a somewhat more interesting gas law problem. In the latter part, the student is reminded of a short cut to estimate volumes in such problems, with  $V \approx 25 (n/p)$  L near room temperature, and use only one significant figure for  $n$  moles and  $p$  bar or atm (bar and atmosphere are equivalent for estimates).

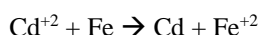
2: A solid melts to an “ordinary” liquid, which then boils. Given:  $\Delta H_m = 12.5 \text{ kJ mol}^{-1}$ ;  $\Delta S_m = 37.5 \text{ J mol}^{-1} \text{ K}^{-1}$ ;  $\Delta S_b = 85 \text{ J mol}^{-1} \text{ K}^{-1}$ ;  $MW = 120$ ;  $T_b = 393 \text{ K}$ . Find: a)  $T_m$  b)  $\Delta H_b$  per mole c)  $\Delta H_b$  per gram

- a) *Estimate:* For  $T_m$  we can use  $\Delta H_m = T_m \Delta S_m$ . Before we even start doing arithmetic, though, we should notice that we have an immediate upper limit, in that  $T_m$  will be less than  $T_b = 393 \text{ K}$ . If we get anything greater than  $393 \text{ K}$  for  $T_m$  when we do the arithmetic, we should look for a mistake. Also, “ordinary” liquids generally have a liquid range under  $100 \text{ K}$  at ordinary pressures (sometimes even less at  $1 \text{ atm}$ , like  $\text{CO}_2$ , which sublimates, and has no liquid range at  $1 \text{ atm}$ ). Salts and metals are also different, with much larger liquid ranges. Many simple salts have relatively high melting points (there are some complex salts that are ionic liquids at room temperature), and metals mostly have melting points above  $393 \text{ K}$  (exceptions include  $\text{Hg}$  and  $\text{Ga}$ , and, near the upper part of that range,  $\text{Na}$  and  $\text{K}$ ). Knowing some elementary chemical properties helps with the estimate in this problem. Now that we have thought of all this, let us return to our “ordinary” liquid, and find that  $T_m = 12500/37.5 = 333 \text{ K}$ , a reasonable value (remember that  $\Delta S$  is in  $\text{J}$ ,  $\Delta H$  in  $\text{kJ}$ , so don’t forget to adjust the decimal accordingly).
- b) *Estimate:*  $\Delta H_b = T_b \Delta S_b$ . This is almost trivial, but we must expect a value greater than  $\Delta H_m$ . In one sense, this is even more trivial than usual, as  $T_b > T_m$  and  $\Delta S_b > \Delta S_m$ .  $\Delta H_b = 33.4 \text{ kJ}$ . This is about  $3\Delta H_m$ , which is reasonable. The value of  $\Delta S_b = 85 \text{ J K}^{-1} \text{ mol}^{-1}$  is found, within a few  $\text{kJ}$ , for almost all “ordinary” liquids at around  $1 \text{ atm}$  pressure. The entropy of a gas is much greater than that of a liquid, usually, and therefore, the  $\Delta S_b = S_g - S_l$  is essentially that of the more or less ideal gas at the boiling point, where the liquid comes apart into gas molecules. The reason different substances, with different  $T_b$ , have about the same entropy of the gas phase at the boiling point, is more complicated, and not part of the first-year course. If the liquid is highly ordered, such as water, the  $\Delta S_b$  value is larger, as water still has more order which is destroyed at the boiling point, hence lower liquid entropy, than an ordinary liquid. The difference is not huge:  $\Delta S_b(\text{water}) = 109 \text{ J K}^{-1} \text{ mol}^{-1}$ . However, this is enough to remind us that water is more ordered than an ordinary liquid. The  $\Delta S_b \approx 85 \text{ J K}^{-1} \text{ mol}^{-1}$  value is known as Trouton’s Rule, and is fairly general for ordinary liquids. Metals and salts do not follow Trouton’s rule. The rule implies that  $\Delta H_b \propto 1/T_b$  over a range of liquids. This is not the same as the Clausius-Clapeyron equation, which relates boiling point of a single liquid to pressure.
- c) *Estimate:* Grams are smaller than molar mass, in this case  $120$  times smaller, so all the molar quantities must be divided by  $120$  to get the per gram values. It is only necessary to remember that grams are smaller than moles to get the relative order of magnitude correct,

*Electrochemistry:* This topic comes near the end of the course, and many of the concepts that had to be introduced earlier can now be assumed known by the students. By this time, thermodynamics, equilibrium, and kinetics have all been covered. The students know what a redox reaction is, and presumably should be able to handle quantities of charge, meaning numbers of electrons. There are 96,520 Coulombs (C) to a mole of electrons, and if one simply keeps a factor of  $10^5$  in mind, converting from charge to moles is quick. Since 1 ampere (A) means  $1 \text{ C s}^{-1}$ , it takes  $10^5$  seconds for 1 A to run a reaction long enough to produce a mole of product, if it is a 1 electron reaction. It is not difficult to correct if 2 or 3 electrons are involved, or, as is typically the case in laboratory experiments, the current is less than 1 A. Finding the order of magnitude for any problem involving a reaction driven by electric current is straightforward.

Redox potentials are a different set of problems. Here the energy is involved, and it is often necessary to translate from volts to kJ; the student must know that volts  $\times$  charge is energy; specifically,  $1 \text{ C} \times 1 \text{ V} = 1 \text{ J}$ . Again, there are a couple of conversion factors that enable the student to be sure of being in the right neighborhood. For a mole of electrons,  $\approx 10^5 \text{ C}$ , therefore a redox reaction that has a difference of half-cell potentials of 1 V will have  $\approx 100 \text{ kJ}$  difference in energy, and will go to completion (or, will not go at all, if written in the reverse direction). For a one electron reaction it takes approximately 60 mV to move the equilibrium one order of magnitude, for two electrons, 30 mV. This is reflected in pH meters, which are actually high input impedance voltmeters, and determine the pH from the potential produced by an electrode sensitive to  $[\text{H}^+]$ . One uses concentration without correcting for activity coefficients at first year chemistry level.

Problem 1. Consider the reaction



The half-cell potentials are



Find the ratio of concentrations  $[\text{Fe}^{+2}]/[\text{Cd}^{+2}]$  at the point that the reaction has no tendency to move in either direction (i.e., at equilibrium).

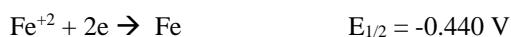
Estimate: The reduction potentials are not very different, so the ratio should not be orders of magnitude away from 1. On the other hand,  $|E_0| > 30 \text{ mV}$ , and it is a two-electron reaction, so the ratio to balance  $E_0$  must be  $>10$  (now check the sign and the ratio—or is it  $<0.1$ ?). To have the reaction have no driving force, that is for  $\Delta G = 0$ , we must have

$$= E_0 + RT/2F \ln [\text{Fe}^{+2}]/[\text{Cd}^{+2}] = 2.303 RT/2F \log_{10} [\text{Fe}^{+2}]/[\text{Cd}^{+2}]$$

where F is the Faraday, 96,520 C. At room temperature, we know  $2.3 RT/2F \approx 30 \text{ mV}$  at around 300K, so the ratio must be  $>10$  (careful of the sign--  $E_0$  is positive (reverse the Fe half reaction to get the reaction as written; one half reaction must be reversed to make the number of electrons cancel, a point that must be explained to the

student, especially for cases where a two electron half reaction and a one electron half reaction are involved), making  $\Delta G_o < 0$ , so the reaction goes to the right and there is more  $\text{Fe}^{+2}$  than  $\text{Cd}^{+2}$ , about one order of magnitude more. The actual answer is 17.8.

Problem 2. Given the following half reactions



Part 1: Find the largest voltage battery that can be made from two of the half reactions

Estimate: This part is pretty trivial, if you remember that the signs reverse when you reverse the direction of the half reaction from reduction, as shown, to oxidation. The battery voltage is the difference between the oxidation and reduction half reactions. We almost certainly want to use the Cs half reaction, with the largest half cell voltage. It becomes positive when we reverse it. Add this to the one positive voltage, the one half cell that “wants” to be reduced to the metal, and we get 3.722 V. This part is one case where it is only necessary to understand what the question is, and no numerical exercise is worth the effort.

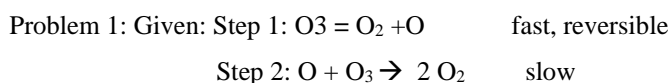
Part 2: What is the equilibrium constant for this reaction? Answer to the correct number of significant figures.

Estimate: This battery has a huge  $E_0$  so we expect the reaction to go “to completion”. In other words, the battery reaction will lead to essentially all  $\text{Ag}_{(s)} + \text{Cs}^+$ , and almost no  $\text{Ag}^+$  and  $\text{Cs}_{(s)}$ . The solids do not come into the equilibrium constant, so  $K_{\text{eq}} = [\text{Cs}^+]/[\text{Ag}^+]$ , and we know that it will be huge, around  $10^{(3.6/0.06)} \approx 10^{60}$  at equilibrium. We have already seen a couple of cases in which we had astronomical numbers like this. It means that there would be no  $\text{Ag}^+$  with a mole (actually many moles—even an amount large compared to the size of the earth) of  $\text{Cs}^+$ . It is however, possible to do the calculation, although we won’t bother here. One thing this does tell us is that if it were possible to carry through the calculation, we would get a nonsense answer, in real physical terms. However, why would we want to go to equilibrium? A battery that reaches equilibrium is, by definition, unable to do work, hence dead, until recharged. This system would work as a battery at a pair of concentrations that had a finite concentration ratio. We can calculate the voltage as a function of the ratio. As an exercise, write down an expression for the voltage as a function of the ratio  $[\text{Cs}^+]/[\text{Ag}^+]$ .

This concludes simple examples of problems from several chapters, which serve as a sample of the overall type of problems; they are pretty much the same as ordinary problems from texts. In some cases, we use extreme conditions, as in the 1 atom per  $\text{cm}^3$  gas law problem. These have the aim of causing students to consider what the numbers are actually telling them. In addition, there are a few more advanced problems, possibly useful in Honors sections; here is an example.

*A more advanced example:* If we consider a very small volume, fluctuations can be significant. Suppose we explain to the student that fluctuations in the number of molecules in a volume in contact with an external reservoir are of the order of the square root of the number of molecules. Consider a bacterium, with volume of roughly  $10^{-17} \text{ m}^3 = 10^{-14} \text{ L}$ . Suppose a molecule is present at a concentration of 0.4 M (something in the range of salt concentration, for example). Then we have  $0.4 \times 10^{-14} \times 6 \times 10^{23} = 2.4 \times 10^9$  molecules. The fluctuations are then roughly  $5 \times 10^4$  molecules, or about a fraction of  $2 \times 10^{-5}$  of the molecules in the bacterium, probably not enough for the bacterium to worry about, even if a much larger fraction than one would get in a macroscopic system. However, some substances are present in smaller quantities, but are still important. If you have a molecule that is present in 100 nanomolar quantities, replace 0.4 in the calculation above with  $10^{-7}$ . Then there are about 600 molecules; taking the square root (25 is close enough) and dividing by the total number, 600, we get fluctuations around 4%. This is not obviously trivial. It also means that carrying a calculation past 2 significant figures is not likely to produce a meaningful result. While this is an advanced topic in that it requires giving the student the concept of fluctuations in concentration, and pulling the square root relation out of the air—deriving it in a first-year class would definitely be going too far—it does reiterate in a new context that examining the meaning of a calculated number can be critical. One should also be careful to examine the conditions of a problem. A volume of  $10^{-14} \text{ L}$  is on the edge of the minimum size that makes sense for a bacterium. If the problem had stated the bacterial volume as, say,  $10^{-17} \text{ L}$ , it would be necessary to ask whether such a bacterium could exist. While this example might be restricted to the honors section of a first-year class, other cases in which ordinary systems are given impossible properties could be used to call the student's attention to the point that one must make sure that the physical conditions associated with the numbers in a problem are plausible. Once again, the actual calculations are not the point of the problem.

*Kinetics:* This can include discussion of reaction mechanisms.



Find the overall reaction mechanism.

*Estimate:* Unlike essentially all the previous examples, this is not a numerical example. The student must think through what the problem is asking. First, it is useful to have the overall reaction, which the student should get from adding the two steps:  $2 \text{O}_3 \rightarrow 3 \text{O}_2$ . The O atoms are not included in the product, as they are used up in the second step. Then, the student can observe that the second step is slow, so both  $\text{O}_3$  molecules must be in the rate step. If  $\text{O}_2$  increases, the first reaction must reverse, so we should expect that the rate is inversely proportional to  $\text{O}_2$ . This appears to give a rate law:

$$\text{rate} = k_r [\text{O}_3]^2 / [\text{O}_2]$$

At this point, we have a plausibility argument, but the student should understand that each of the two overall steps given may be complex, but this is not yet proof. Still, the putative rate law is at least plausible.



Answer: The student would have to find a steady state approximation for [O], and use this in the slow step. The answer turns out to be the estimated rate.

Problem 2: Given that the energy of activation for the reaction  $2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2$  is  $-185 \text{ kJ}$ , and the heat of formation of HI is  $-5.65 \text{ kJ}$ . Find the activation energy for formation of HI (i.e., the activation energy of the reverse reaction from  $\text{H}_2$  and  $\text{I}_2$ .)

Estimate: The forward and reverse reactions cannot be that different, because 185 is much greater than 6, which is the difference between the reactants and products. There are two HI molecules, so for one HI, the reaction should be  $\text{HI} \rightarrow \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{I}_2$ , which of course will have half the activation energy, or  $92.5 \text{ kJ}$ . Since the energy of formation of HI  $< 0$  it will add to the reverse reaction energy, meaning that it must subtract from the absolute value of the activation energy. The estimate is then a little **less** than  $92.5 \text{ kJ}$

Answer: We have practically done the entire problem. The answer is  $92.5 - 5.7 = 86.8 \text{ kJ}$ . We have three significant figures. However, it is worth drawing a diagram to show how the subtraction works.

## Discussion

This is a sampling of the type of problems that can be estimated; there are such problems in every topic. As can be seen from the Table of Contents, there are more chapters, therefore topics, than are illustrated in this summary of problems. In each chapter that is sampled, there are about five times as many problems as are given here. However, this much is sufficient to show the approach to finding estimates; in the book the conventional solution to each problem is also given in detail; here we only give the result of this calculation, as going through the standard solution of first year chemistry problems is routine. It is important for the student to compare the standard solution to the estimate. Thus, students should understand why one would first make an estimate, and how this helps in understanding how the estimate is useful. While there are qualitative chemistry problems, as in organic chemistry, where finding reaction mechanisms or synthetic paths does not require numerical calculations, much of chemistry, especially in the first year, is quantitative. Students who are able to understand that numbers have physical meaning in the context of chemistry problems, and understand that the orders of magnitude of the answers must be reasonable, can generally continue on to more advanced material. Usually, a student who tries to survive by memorizing equations will make unreasonable errors. In addition, because such students did not understand the material, they will be unable to advance to new material that builds on the material that they never understood in the first place.

Teaching students to pay attention to the orders of magnitude of the quantities being calculated, and to recheck their answer against the physical meaning of the answer, mainly requires calling their attention to the matter, and giving them some examples to work from. It is a matter of getting the student to think about what the numbers mean. The examples given here suggest how this can be done. However, any problem in which the

numbers have physical meaning would be a candidate for this approach.

Whether the best approach to bringing this to the student's attention is a separate book with such problems with estimates, or whether it is better to have the problems incorporated into the main text, is another question. In principle, incorporating formal estimates for most topics into standard texts seems to be uncommon; however, it would probably make more sense than having the estimates exiled to a supplementary text. The book on which this paper is based is out of print and no longer available, and would probably need revision in any case before any attempt at distribution were made. However, by taking examples from this book, one can see the possibility, and the means, of using these estimates to force the student to think about the physical meaning of the numbers. This appears to be different from any of the solutions to chemistry problems available on the internet, which we may take as a reasonable approximation to what is shown in most textbooks. None of these that this author has found takes an approach similar to what is proposed here. On the internet, there are many sample problems, carefully worked out, but not checked as to whether the answers are physically or chemically reasonable; they generally do not discuss the physical meaning of the numerical values. Such examples do not help with the problem of understanding the physical meaning of numbers.

## Conclusions

- 1) Students need to understand that numerical values in chemistry problems have physical meaning.
- 2) This can be accomplished in part by requiring the students to estimate at least the order of magnitude of an answer, to make sure that the answer is not ridiculous
- 3) Almost every topic in introductory chemistry has sufficient quantitative character for consideration of estimates to be applicable.

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