

CHE curriculum

STOICHIOMETRY WITHOUT TEARS

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Students who are about to take stoichiometry fear it, and many who are currently taking it hate it. The homework never ends, and you can spend hours on a single problem without getting anywhere. It's the weedout course—30%, or 50%, or 70% flunk it, depending on the institution, the class size, and who is teaching.

So what's in this killer stoichiometry course? "What goes in either comes out or stays in," that's what—and usually we never get to the part where it stays in, leaving us with $\text{Input} = \text{Output}$. Not exactly intellect-stretching stuff. Of course, there's more—gas laws ($PV = nRT$): given three variable values, solve for the fourth), simple vapor-liquid equilibrium relations [$y_A P = p_A^*(T)$: given a vapor pressure correlation and two of the variables y_A , P , and T , solve for the third variable], and energy balances ($Q = \Delta H$: given feed and outlet conditions, calculate ΔH by integrating heat capacities and adding latent heats, and then solve for Q). That's about it. The energy balances give the students their first brief immersion in the alphabet soup of thermodynamics, but only up to U and H —and most of those who go down in the course are lost well before they get there.

What defeats many of them, I believe, is the simplicity of the subject matter. The course starts off with deceptively easy material: units and dimensions, definitions of process variables, and material balance problems that can be solved with college freshman and even high school methods. We

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Educational psychologists tell us that you never ...teach anyone how to do anything by telling them how to do it. Rather, you teach them by showing them how, and then having them try it themselves and giving them corrective feedback.

I believe in this principle...

give sermons about carrying units, drawing and labeling flow charts, doing the problem bookkeeping or degree-of-freedom analysis before plunging into the math, but they don't believe us—and sure enough, they get the right answers doing it their way.

Then the game changes. The problems get longer, and we keep throwing more information into the pot. We give them multiple process units, recycle and purge, single and multiple reactions, volumetric flow rates instead of mass or molar flow rates, and relative saturations or dew points instead of mole fractions—and the problems that used to take them thirty minutes start taking an hour, then two hours. They write equation after equation, but never seem to have quite enough information to solve for the quantities they are trying to calculate. Some begin to believe that there may be a point, after all, in being systematic about setting up problem solutions, and save themselves; others resist to the bitter end and fail.

I don't recall ever failing a student in stoichiometry who really understood how to draw and label a flow chart and to use it systematically in the course of a problem solution. Consequently, since I began teaching the course twenty years ago I have directed more and more of my efforts toward motivating the students to do just that. It seems to work. Only about ten percent of the students who take the course from me these days fail it, and most of those give up early in the semester. Also, the attitudes of those who pass are neutral to positive; relatively few of my students drop out of chemical engineering as sophomores because they hated the stoichiometry course.

I don't claim that the approach to be described here is THE WAY to teach stoichiometry—there is

no such thing. I only say that it works for me and may also work for others.

COURSE STRUCTURE AND FORMAT

The course is taken in the first semester of the sophomore year. Enrollment has been as high as 180 students within the past decade, but prior to this year it has been fairly steady in the range of 60–70. There is only one lecture section, regardless of the enrollment.* Chapters 1–9 of the course text [1] are covered, which gets us through steady-state energy balances on reactive systems.

On the first day of class I hand out an assignment schedule identical or similar to the ones given in the instructor’s manual for the text. A number of problems are marked as “bonus problems.” They are typically more difficult and/or longer than the regularly assigned problems, or they require different thinking skills (*e.g.*, divergent thinking or problem-creation exercises), and many require computer solution. The bonus problems serve both to stretch the best students and to give me more flexibility in grading; they are optional unless the student wants to get an A in the course, in which case some of them are mandatory.

On the first day I also hand out and discuss a

written statement of policies and procedures (see Table 1). The policy statement serves to establish my ground rules, up front and in writing, thereby forestalling endless explanations, arguments, and bitter feelings at the end of the course. In my experience, students can deal with almost any rules, tough or lenient, as long as they know what the rules are and the instructor adheres strictly to them.

Let me make a few points about some of the policies mentioned in the handout. Students do a substantial part of their learning when they are doing homework: only then do they discover that they really didn’t get what looked completely straightforward in a lecture. Consequently, if I want them to get the material, I must do all I can to encourage them to do the homework. Counting homework performance toward the final course grade is one way to do this, and accepting late homework with a penalty is another.

Working together on homework in “study communities” has been shown to have dramatic positive effects on students’ course performance [2], and so I encourage cooperative efforts on homework in the stoichiometry course (and in every other course I teach). If I insist on individual efforts on all homework assignments, I deprive students of a powerful

TABLE 1
Policies and Procedures

- There will be three quizzes and a final examination. All tests will be open-book. The lowest quiz grade will be dropped. Required homework will be assigned every week, and there will also be a series of “bonus problems.”
- No excuses for missed exams will be accepted other than certified medical excuses. If your alarm fails to go off or your car doesn’t start on the day of a quiz, the zero you get will be the grade that is dropped. If it happens on the day of the final, see you next semester.
- Homework should be handed in at the beginning of the period in which it is due. Late homework will be accepted up to the Friday before the last week of class and will receive a maximum grade of 60%. However, if you abuse this privilege by routinely handing homework in late or coming in with 20 problem sets on the last day, the privilege will be withdrawn.
- A weighted average grade will be calculated as follows:

Midterms	2 units
Homework	1 unit
Final	2.5 units

Letter grades will be assigned on a curve. *However,*

- There will be a “gray area” between each two letter grades in

the final distribution, so that two people getting the same weighted average grade could get different letter grades. If you are in one of these gray areas, whether you get the higher or lower grade depends on two factors: (a) your performance on the bonus problems (how many attempted, grades achieved), and (b) whether your test and homework performance has been improving (you go up) or declining (you go down).

- To get an A in the course, you must attempt and do satisfactory work on at least eight bonus problems in addition to getting the necessary weighted average grade on homework and tests.
- You may work in groups on the required non-computer homework—in fact, you are encouraged to do so. Individual solutions must be handed in, however. You may *not* collaborate on the computer homework, except to get help with debugging; programs that are too nearly identical will be regarded with grave suspicion. You may do the bonus problems individually or in pairs; in the latter case, only one solution need be handed in.
- Homework solutions will not be posted. The burden is on you to make sure you find out how to solve the problems by getting help before they are due and/or asking about them in class after they have been handed in.

*I do not recommend this feature of the course.

learning tool. There is no good reason to do so. If they simply copy the work of others without understanding it, they will go down on the tests. On the other hand, if they are copying and learning enough to do well on the tests, then the homework has served its function—so why should I care?

I strongly recommend not posting homework solutions. When I post solutions, the students simply copy them without thinking about them, and thereafter I see my solutions coming back at me again and again in subsequent semesters.

Some of my colleagues are uncomfortable with the grading flexibility I grant myself by using such subjective (*i.e.*, non-numerical) criteria as “satisfactory” performance on bonus problems and rising or falling patterns in test grades. I understand their feeling. However, I am much more uncomfortable with the intrinsic unfairness of strictly objective grading, which is based on the illusion that there is a qualitative difference between a student who gets a 69 and one who gets a 70. Again, as long as I clearly state my criteria, objective or subjective though they may be, I do not get complaints from students about my unfairness in assigning grades.

CLASSROOM FORMAT

Educational psychologists tell us that you never (well, hardly ever) teach anyone how to do anything by telling them how to do it. Rather, you teach them by showing them how, and then having them try it themselves and giving them corrective feedback. I believe in this principle and so do very little formal lecturing in the stoichiometry course. Instead, I answer questions and outline (or get the students to outline) problem solutions, modeling for them the techniques I want them to learn. After repeatedly seeing me work problems in twenty minutes that took them two hours, they start to believe that my way works better than theirs.

I begin each period by asking if anyone has any questions about anything. Since I don't post solutions, there are almost always questions of the type “How do you do Problem 34?” My preferred procedure is to have the students form groups of three at their seats and work on the problems in these groups—one person writing, three talking. I first ask them to draw and label the process flow chart. I generally don't give them enough time to complete it, but stop them after two or three minutes and do it myself on the board, calling on specific groups to tell me what to write next. I then lead them through the solution in steps, giving them tasks, stopping them before most of them

can finish, and outlining the solutions on the board with their assistance. We don't do any algebra or arithmetic—that's their responsibility to do on their own time if they want the answers.

If I don't want to spend too much time on a given problem, I give the students less to do and go through most of the solution myself. I lecture sometimes when we get to concepts that they traditionally have trouble with (multicomponent vapor-liquid equilibrium calculations, for example, or the introductory material on the first law), but these lectures probably account for no more than twenty percent of the total class time.

In the next section I present a problem and then outline how I would go through the solution in class. The problem (a modified version of an example problem in the text) involves material balances on a process with recycle and a gas law calculation. The solution procedures to be shown are explicitly presented in the text, but like most formal problem-solving strategies in textbooks, they are universally ignored. Only through repeated illustration in class do they become part of the working tools of most of the students in the course.

AN ILLUSTRATIVE CLASS SESSION

*Crystalline potassium chromate (K_2CrO_4 , which we will abbreviate as **PC**) is to be recovered from an aqueous solution of this salt containing one-third **PC** by mass. Forty-five hundred kg/h of this solution is mixed with a recycle stream containing 36.4wt%**PC**, and the combined solution is fed to an evaporator, which operates at 75°C and –450 mm Hg. Two streams leave the evaporator: water vapor at the evaporator temperature and pressure, and an aqueous solution containing 49.4%**PC**. The latter stream is fed to a crystallizer in which it is cooled to 0°C, causing solid crystals of **PC** to precipitate out of solution, and the resulting slurry is then filtered at the crystallizer temperature. The filter cake consists of all the **PC** crystals and a solution containing 36.4 wt%**PC**. The crystals account for 95% of the total mass of the filter cake. The filtrate (the solution that passes through the filter), which also contains 36.4 wt%**PC**, is the recycle stream.*

Calculate the fraction of potassium chromate in the feed recovered as solid crystals, the ratio (kg recycle /kg fresh feed), the volumetric flow rate (m^3/h) of the vapor effluent from the evaporator, and the mass flow rates (kg/h) of the feed streams to the evaporator and crystallizer.

I outline below in excruciating detail how I might work through this problem in class. I hasten to say that I rarely do anything this elaborate for any individual problem. However, each question/response pair to be given illustrates an important aspect of the approach to process analysis that I am trying to teach, and so if a particular type of question does not come up in a given solution, it will come up in others. *I suggest that readers who are not specifically involved in teaching stoichiometry might skim the balance of this section to get an idea of what I am doing, and that readers who are teaching the course might pay a bit more attention to the details.*

My lines are in italics, and possible answers to my questions are in parentheses.

OK, get in groups of three, read the problem statement, and draw and completely label a flow chart of the process. You've got three minutes—go!

I am presuming that we've done group exercises in class before so I don't have to explain the procedure to them. The first time I do it, some students may be uncomfortable or think it's a game, but after two or three such exercises they start taking it seriously. As they get to work, the noise level increases and the classroom loses the usual wax museum atmosphere that characterizes typical lecture sessions.

(Three minutes later.) *Stop—everyone with me.*

Most groups will not have time to complete the task, which is fine. My objectives are to get them all to

think about the problem, to figure out how to get started, and to take the first few steps. Two or three minutes are more than enough time to achieve these goals.

I then draw the flowchart on the board and call on different groups to tell me how to label the streams. We end up with something like the illustration in Figure 1.

Next, I go through a series of questions designed to make sure the students understand the flowchart and the process it symbolizes and know what they are being asked to determine. I ask the groups to discuss some of the questions for a few seconds and decide on answers among themselves, and I call on the class as a whole for responses to other questions.

What's the basis of calculation here?

(4500 kg/h of fresh feed)

Is the filter cake stream labeled completely?

(Yes)

How do you know?

(Because you can express the flow rates of both stream components—PC and W—in terms of what's written on the chart.)

What's the flow rate of potassium chromate in that stream?

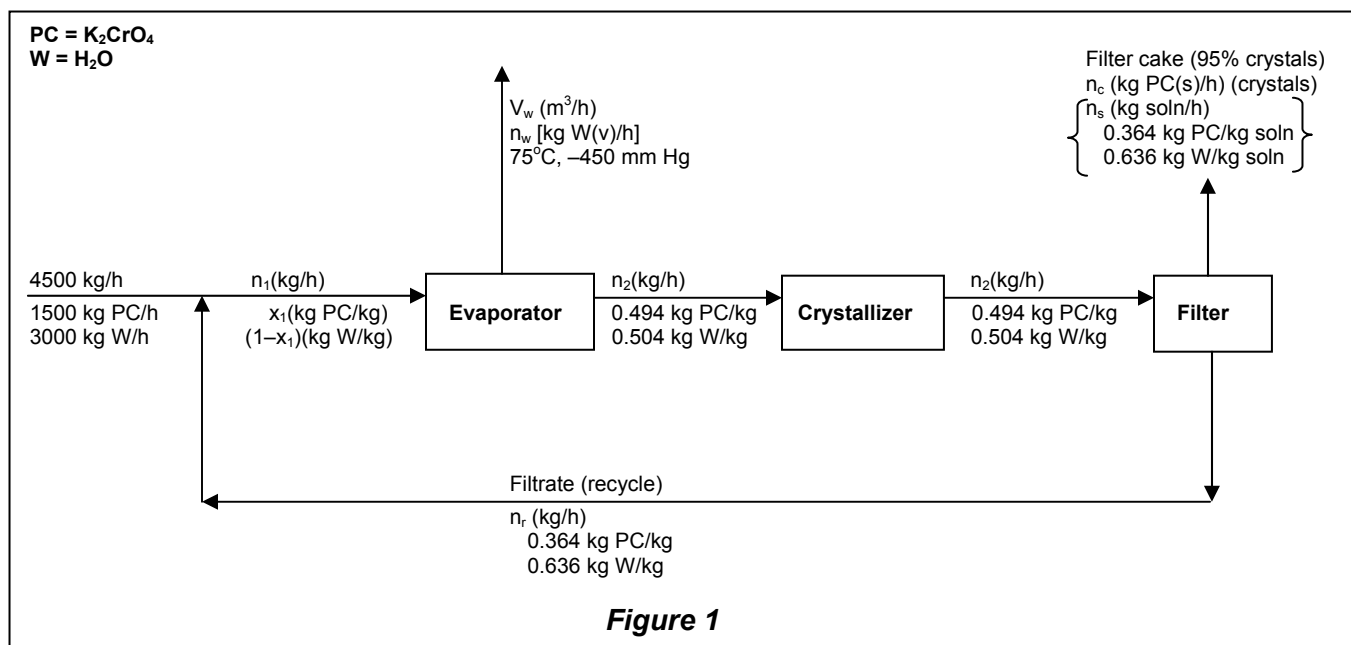
($n_c + 0.364 n_s$)

How about water?

($0.646 n_s$)

What if I asked you for the mass fraction of water in the total filter cake and not just the solution?

[$0.646 n_s / (n_c + n_s)$]



Is the whole chart labeled completely?

(Yes)

How do you know?

(Because every stream is labeled completely.)

In terms of the labeled variables on the chart, what does the problem call on us to calculate?

($n_c/1500$, $n_r/4500$, V_w , n_1 , and n_2)

Why is liquid in the filter cake, and why does that liquid have the same composition as the filtrate?

See if you can put it in terms of a filtration process many of us encounter every morning?

(It's like brewing coffee in a drip pot. You don't get dry powder left on the filter—it's a soggy mass containing solid grounds and coffee, the same liquid that goes through the filter.)

What might be the physical significance of the 36.4 wt%PC composition of the filtrate?

(It's the solubility or saturation concentration of PC in water at 0°C, the most potassium chromate that can be dissolved in water at that temperature.)

What do you think would happen if we cooled the solution in the crystallizer to a lower temperature than 0°C?

(PC would have a lower solubility and more crystals would precipitate.)

So why don't we do it?

(It might cost more for the additional cooling than the additional crystals are worth.)

What's the function of the evaporator?

(It concentrates the solution, so that when you cool it to the crystallizer temperature more solid precipitates.)

What if it weren't there?

(You would recover less salt for the same crystallizer temperature or you would have to cool to a much lower temperature to recover the same amount of salt.)

How could you recover pure solid potassium chromate, which is what you really want? In other words, where might the filter cake go next in the process?

(To a dryer, in which the residual water is vaporized. It's like letting the coffee filter stand in the sink for a few hours so the water in the wet grounds evaporates, leaving a dry powder.)

In practice, this process might not be truly continuous, so that the calculated flow rates would be averages over time. Can you think of which operation would probably not be continuous?

(Filtration—the filter would have to be taken out periodically, the filter cake dumped, and a clean filter put in.)

Can you invent a way to get around this, so that the process is truly continuous?

(Use a moving belt or screen as the filter, scraping the filter cake off at the end.)

OK, back to the problem. What next?

(Identify possible process subsystems and do the problem bookkeeping to find a starting point for the calculation.)

Which system would you try first?

(The overall process.)

Good—do it. Three minutes.

Possible subsystems include the overall process, the fresh feed/recycle mixing point, the three individual process units, and combinations of the units. Problem bookkeeping is an informal version of degree-of-freedom analysis; unknown variables associated with the streams entering and leaving the chosen system and sources of independent equations relating them are counted. If the number of variables equals the number of independent equations, the calculation can proceed. If there are more variables than equations, see if any information has been overlooked, and if none is found, try another system. The overall system is shown in Figure 2.

Bookkeeping! How many unknowns?

(Four)

What are they?

(V_w , n_w , n_c , and n_s .)

What equations can we come up with?

(Two material balances, the 95% figure for the filter cake, and the ideal gas law for the water vapor.)

Why two balances?

(Because there are two independent species and no reactions.)

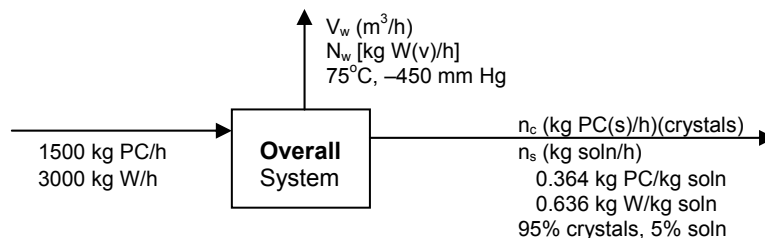


Figure 2

We have to play with the hand we are dealt: the next generation of engineers will come from this group of students... If the teaching method used for the past nine hundred years is ineffective, ... we need to find better methods.

What possible balances could I write?

(Total mass, potassium chromate, water, atomic potassium, atomic hydrogen,...)

So what's the significance of 2?

(That's the number that are independent—once you satisfy any two of the balances, the others are automatically satisfied.)

OK, so we can work out this system, at least in principle—four equations in four unknowns, including two that are asked for in the problem statement. What's our next decision?

(Which equation do we write first?)

What determines the answer?

(Which one involves the fewest unknowns.)

Fine—let's check the possibilities, balances first.

What form do all the balances take?

(Input = output)

Why?

(No generation and consumption because there are no reactions, no accumulation because we're at steady-state.)

Which unknowns are involved in an overall mass balance?

(n_w, n_c, n_s)

What is that balance?

($4500 = n_w + n_c + n_s$)

Which unknowns are involved in a chromate balance?

(n_c, n_s)

A water balance?

(n_w, n_s)

The gas law?

(n_w, V_w)

The filter cake composition relation?

(n_c, n_s)

How do you translate the statement "The crystals in the filter cake comprise 95% of the total mass of the filter cake" into an equation?

[$n_c = 0.95(n_c + n_s)$]

So the worst has happened—we can't come up with one equation in one unknown! What do we do now?

(Write the filter cake composition equation and the potassium chromate balance.)

Why those two?

(Because they involve the same two unknowns

and you can solve them simultaneously.)
Good, let's do it, circling the variables we're solving for.

(Write on board.)

Filter cake composition: $n_c = 0.95(n_c + n_s)$
Overall PC balance: $1500 = n_c + 0.363n_s$

What do I do once I've done the algebra and found n_c and n_s ?

(Write the values on the flow chart.)

Then what?

(Write the water balance or the total mass balance.)

Why not the gas law?

(Because the gas law still involves two unknowns, but the balances each involve only one.)

OK—we'll write the water balance.

Water balance: $(4500)(0.6667) = n_w + 0.6364n_s$

What now?

(Write the value of n_w on the chart.)

How can we find out if we've made an algebra error?

(Write the total mass balance and make sure it closes.)

OK, let's say it works. Now what?

(Now write the gas law.)

Sold!

$PV = nRT \Rightarrow (760 - 450)(V_w) = (n_w/18)R(75 + 273)$

What have we assumed here?

(Barometric pressure is 1 atmosphere and the ideal gas law works.)

How about the assumption of ideal gas behavior—think we might have a problem?

(Not likely—at temperatures above ambient and pressures less than one atmosphere the ideal gas law should work fine. To be on the safe side, we can always calculate the compressibility factor and correct V_w if Z is much different than 1.)

And now?

(Choose and analyze the next subsystem.)

Which one should we consider first?

(How about the recycle mixing point.)

The mixing point is where most students would start writing balance equations, since it looks like the simplest of the possible subsystems. If isolated, the system appears as shown in Figure 3.

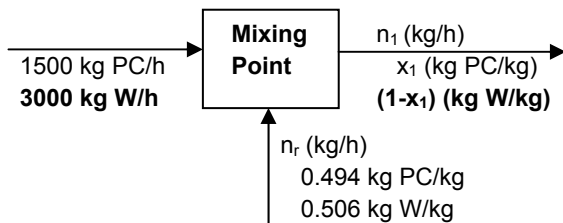


Figure 3

How many unknowns?

(Three— n_r , n_1 , and x_1 .)

How many equations?

(Two—two independent material balances.)

Any more information about these streams buried in the problem statement?

(No.)

So what do we do?

(Try a different system—this one won't work.)

We could, of course, just write equations for all the systems and sooner or later come up with a set that could be solved if the process is well-defined. However, most students will give up before they reach that point; moreover, if the process is not well-defined, the students will discover it in a few minutes this way rather than spending hours trying to solve an unsolvable problem.

We would go on to do the bookkeeping on the evaporator next (left to right seeming like a logical way to search) and would find that this system also would not work—it involves two equations in three unknowns (n_1 , x_1 , and n_2). We implicitly wrote balances on the crystallizer when we labeled the flow chart so there is nothing more we can do with that system. The filter is left as our last hope (see Figure 4).

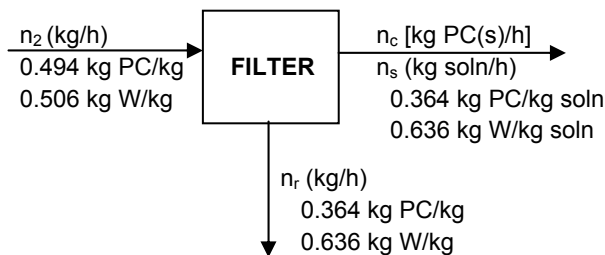


Figure 4

Bookkeeping. Unknowns?

(Two— n_2 and n_r .)

Equations?

(Two balances.)

Bingo! Which balance first?

(It doesn't matter. Balances on PC, W, and total mass each involve both unknowns. Write any two and solve simultaneously.)

OK—here we go.

$$\left. \begin{array}{l} \text{Mass balance on filter: } n_2 = n_c + n_s + n_r \\ \text{PC balance on filter: } 0.494n_2 = n_c + 0.3636n_s + 0.3636n_r \end{array} \right\}$$

Now what?

(Now we can attack either the mixing point or the evaporator—both involve two unknowns, n_1 and x_1 , and two equations.)

Fine. Let's do the mixing point. Which balance first?

(Total mass first—it only involves one unknown. Then either PC or W.)

Right. Here they are.

$$\begin{array}{l} \text{Mass balance on mixing point: } 4500 + n_r = n_1 \\ \text{PC balance: } 1500 + 0.364n_r = n_1 x_1 \end{array}$$

Now?

(Write them on the chart, and then calculate the remaining quantities the problem statement asked us to determine— $n_c/1500$ and $n_r/4500$.)

Good. Now before we leave this process, let's think about that recycle. What does it do for us?

(It lets us recover some of the potassium chromate that didn't precipitate the first time through.)

What if we didn't recycle?

(We'd lose a lot of PC in the filtrate.)

This is the kind of explanation that many students simply won't get, and many who think they got it really didn't. If I want my students to understand arguments like this, I must either show them the numbers or have them work them out themselves. In the case at hand, I might redraw the flow chart without recycle, quickly step through the solution, and observe that with recycle we recover 98% of the potassium chromate in the feed as solid crystals (and 100% of it if we include the subsequent drying step), while in an a cyclic process only 41% of the solute in the feed precipitates and 58% of it is lost with the filtrate. I could also get the class to speculate on why we might have chosen to use a complex evaporation-crystallization-filtration-drying sequence with recycle rather than simply running the feed solution through a single evaporator and driving off all the water in one operation.

One more question. What if we build this process, run it according to our design specifications, measure the yield of crystals, and find that it is less than our design value? What could be responsible?

(Errors in temperature, pressure, and flow rate measurements; not enough residence time in the crystallizer to achieve complete precipitation; more residual liquid in the filter cake than we figured on; the solubility of potassium chromate at 0°C is greater than we thought; the solute is not pure potassium chromate; operator errors; etc.)

DISCUSSION

And that's that. Does it take more time than simply laying out the solution myself in class and much more time than posting the solution outside my office? Yes, it does. Is there a more productive use I could make of the class time? I don't think so, and even if there is I know it isn't reciting the text material and doing algebra on the board. Besides, it isn't necessary to go through the whole elaborate dialogue for every problem; after I've done it a few times I can move through the solutions much more rapidly as the class becomes familiar with the drill.

I use this group-based Socratic approach because it feels comfortable to me, students respond well to it in terms of both their class performance and their attitude, and it is consistent with certain educational psychology principles and research findings [3,4]:

- Students do not learn anything nontrivial in one shot; for a skill to be learned and mastered, it must be taught and exercised repeatedly. If I want my students to develop a systematic approach to material and energy balance calculations, I have to model the approach for them and get them to follow it over and over again. Providing in-class exercises that step them through the procedure is an effective way to do that.
- People learn best either when they are acting (doing something, talking to someone) or reflecting (thinking about the information they are trying to understand or the problem they are trying to solve) [3]. They retain little of what they get when they are simply being passive—listening to a lecture, for example. This being the case, in a problem-solving course like stoichiometry I might as well use most class time for what instructs (solving problems) and spend little time on what does not (lecturing).
- Group problem-solving exercises in class are an effective way to teach material: they give active learners something to do and reflective learners a chance to think. They also involve all students—

it's easy to hide in a class of 30 or 60 or 150, letting your mind wander, but you can't readily hide in a group of three. Moreover, once students become involved they tend to stay that way, even after the exercise is over; as little as five minutes of this type of activity spread over the course of an hour can be enough to keep the whole class engaged for the entire period.

A final point concerns the technique of outlining a problem solution by writing down equations and circling the variables to be solved for but not doing the algebra and arithmetic. This technique does two things for me. First, it allows me to go through complex solutions in class in a reasonable period of time. Second, it allows me to put any problem I want to on a test.

A difficulty with the stoichiometry course is that problems involving combined material and energy balances and phase equilibrium calculations take a long time to solve, even when done efficiently. In particular, they simply do not fit on fifty-minute quizzes. Many instructors deal with this difficulty by giving fragmentary problems on quizzes (calculate a dew point, integrate a heat capacity formula) that do not test the student's ability to integrate the material. Alternatively, tests are given that are far too long to be completed in the allotted time, leading to terrible grades and student frustration and resentment.

What I do is announce to my class that some of their test problems will call on them to draw and label a flow chart, write the necessary equations, and circle the variables for which they would solve. If they follow this procedure, they will have enough time to show me that they know (or don't know) how to solve comprehensive problems. However, it is essential to illustrate the procedure in class several times before putting it on a test; if I didn't, many of the students would go back to the conventional method of grinding out all the calculations, probably running out of time with less than half of the test completed.

AFTERWORD

When large numbers of students fail the stoichiometry course, our unstated presumption is that none of them are qualified to be chemical engineers and we are serving society by weeding them out. I question this presumption. Since the course is conceptually not all that difficult, we should at least entertain the possibility that many are not learning the material because we are not teaching it well.

We can stoutly assert (as some will when they read this article) that by the time our students get to us they are "supposed to be adults," that we should not

have to “hold their hands” or “spoon-feed them”—and when their test averages are in the 40s and many of them fail and/or drop out, we can grumble about how they are unmotivated, apathetic, incompetent in mathematics, and so on.

All of that may or may not be true, but it misses the point. We have to play with the hand we are dealt: the next generation of engineers will have to come from this group of students, whether we like it (and them) or not. If the teaching method used at universities for the past nine hundred years (wherein professors speak and students sit at their feet and absorb wisdom) is ineffective, then we need to find better methods. This paper suggests an approach that has been found effective in the context of one chemical engineering course. It may not solve the problem, but it could be a start.

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