food for thought

"Food for Thought" explores the relationship between food/drink and chemical engineering processes/concepts.

WINESICLE

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My husband and I were cooking up a nicer-than average roast chicken dinner when it independently occurred to each of us that:

a. it would be nice to have wine with dinner;
b. it ought to be white wine;
c. it ought to be chilled and;
d. that the chicken would be ready in 20 minutes, which wasn't enough time.

Thus, logically, the wine *had* to go into the freezer. We sat down to dinner, enjoyed the bird with a glass of white wine, and went on our merry way, all along failing to realize that as we *both* had had this idea, there was, in fact, another bottle of wine tucked into the recesses of the freezer, where it stayed for several days and had frozen quite solid before I discovered it and then realized this presented an excellent occasion for some food thermodynamics! Could I predict and then experimentally verify the melting point of wine? I recommend the following as either a fun in-class problem for anyone working on colligative properties (thermo, perhaps mass and energy balances), with or without the practical demonstration.

One benefit of bringing food-based examples into chemical engineering classrooms is that it's a really lovely way of making esoteric concepts real. Take mole fraction for example…I find that my students tend to be quite comfortable working in mole fraction in "school-world" calculations. Want to know the boiling point of a $x = 0.2$ octane mixture with hexane? No sweat, students will happily (okay, maybe not *happily)* assume ideal solution, whip out Raoult's law, construct a Txy diagram, and report on the result along with the composition of the vapor phase. Likewise, students firmly believe they *ought* to be able to do something similar to determine the freezing point of an ethanol and water mixture such as wine. But wait — wine is from the *real* world and as such, its composition is labeled in units much more convenient for the non-ChemEs among us, such as by mass (rare) or volume (common). In general, it can be quite a mind-blowing experience for students to work out the mole fractions of common foods and beverages.

For students used to thinking in "school-world," a mole fraction between 0.01 - 0.05 will tend to be thought of as small or perhaps even negligible. But ask students to calculate how much sugar is needed to make even a $x = 0.01$ mole fraction in water, and suddenly that previously *small* amount is understood to have a much bigger impact. The definition of mole fraction is:

$$x_i = \frac{n_i}{n_{total}} \tag{1}$$

For a binary mixture of sugar and water:

$$x_{sugar} = \frac{n_{sugar}}{n_{sugar} + n_{water}} \tag{2}$$

If n_{sugar} is the number of moles of sugar needed to bring 100 g of water to a mole fraction of 0.01 sugar, then:

$$0.01 = \frac{n_{sugar}}{n_{sugar} + 5.55} \tag{3}$$

Feeding this into what one of my professors called "the algebra machine," I find $n_{sugar} = 0.05611$ moles. Applying the formula mass of sucrose (342.3 g/mol), we need about 19.2 g of sugar plus 100g of water to make a solution that has a mole fraction of 0.01 sugar. That may sound somewhat

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unremarkable, but for comparison, 100 mL of Coca Cola® has a little over *half* that much sugar.[1] This calculation makes it clear that what the students might have previously considered very pure (“It’s 99% water — that’s almost all water!”) is quite perceptively *not* pure water if you were to taste it or use it for washing. Other things that are in the vicinity of 99% water by moles include sea water, most non-alcoholic beverages, and a great many edible fruits and vegetables such as strawberries!

Coming back to the wine in the freezer, we can do a similar calculation to find the mole fraction of water in the wine. In this case, we need an additional step because a typical wine label, according to the International Standard for the Labeling of Wines,[2] gives the alcohol percentage by volume fraction. If we assume this is a dry wine (that is, low- to no-dissolved sugar), we can make a reasonable approximation that the wine is a binary mixture of ethanol and water. To turn volume fractions into mole fractions, we need to pick a temperature for our comparison, which I encourage you to invite your class to brainstorm about, as well as do a search for applicable standards. I’m going to pick 20 ºC as my benchmark where water’s density is 0.998 g/mL and ethanol’s is 0.789 g/mL.[3] Assuming a basis of a typical bottle of wine (750 mL) and using the 15% alcohol v/v listed on the label, we can convert the volume to moles and the moles to mole fraction. I get a touch over $x_{ethanol} = 0.05$.

Now that we have the mole fraction of ethanol and of water in our solution, we can turn to everyone’s favorite approximation for freezing point depression, a variation on the integrated van’t Hoff equation (available in most thermodynamics textbooks[4]):

$$ln(x_w \gamma_w) = \frac{\Delta H_{fus,w}}{R}\left(\frac{1}{T} - \frac{1}{T_{m,w}}\right) \qquad (4)$$

To solve for T (the solution melting point), I need to plug in the enthalpy of fusion for water and the normal melting point of water (273.15 K). I’m going to assume an ideal solution and set the activity coefficient (gamma) to 1 for simplicity. You don’t *need* to assume ideal solution here. With a good activity model, you can calculate an activity coefficient for water and use it to correct the mole fraction for this calculation. (It can be an instructive calculation.) In this case, we are far enough from the water-ethanol azeotropic mixture that ideal behavior isn’t as bad an approximation as it might be at a greater mole fraction of ethanol.

Sticking with ideal solution for the moment, I find our new melting point for the solution is 267.6 K, or -5.5 ºC, aka 22 ºF. Which, much to my amazement, is exactly the temperature I observed when I stuck my cooking thermometer into the open bottle of wine-slush!* It was intensely gratifying to experimentally verify a calculation with reality in my own kitchen.** I was so excited, I immediately made a video about it.[5]

If you perform this as an in-class demonstration, please consider safety ahead of time — for my experiment, the fact that ice has a 9% greater volume than the same mass of liquid water did *not* result in perceptible damage to either the cork’s seal or the bottle itself, but if your container has less headspace, leakage may occur. This can be another interesting point to bring up in class — I did notice that the ice entirely filled the neck of the bottle when the wine was frozen solid, which is not normally the case. I recommend either doing this demonstration with students over the legal drinking age (because you’re going to have an open bottle of wine) OR picking a solution that everyone can enjoy when it melts (e.g., lemonade). BUT definitely try this at home ahead of time because the time it takes for a frozen-solid bottle to melt to solid-liquid equilibrium can be considerable. Perhaps, if you’re also teaching transport, you might have students estimate the time it would take to get to that point! In any case, make sure you take your bottle out of the freezer in time so that it will be at equilibrium by the right point in class. When you try it at home, be warned that other members of your household might, like the other members of *my* household, be deeply bewildered by your excitement at the synchrony between theory and experiment. Showing them a calculation involving mole fractions and natural logs may *not* increase their interest. But don’t worry, we — the ChemE education community — are here for you and cheering alongside!

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* You want to make your measurement at equilibrium, which I interpreted as a state where there is appreciable mass of liquid in the bottle, well mixed with the remaining solid. Yes, I did shake the bottle to make sure that was the case.

** Eagle-eyed thermodynamics fans (including one Reviewer) will notice that I’ve assumed the wine remains a solution of uniform concentration, which is likely not fully the case. The wine probably experiences differential freezing, where the first solid crystals that form are close to pure water, creating a liquid that has a *higher* fraction of ethanol and hence a lower freezing point. This would proceed as the bottle equilibrates with the temperature of the freezer and may mean there is always at least some liquid of very high ethanol concentration in the bottle, possibly trapped in a matrix of solid ice (and hence not readily observable). This is why my recommended temperature measurement point is when there is appreciable liquid in the bottle (with some solid) and not at the first instant that liquid is visible. The full stepwise calculation is left as an exercise to the interested reader.

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