food for thought

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

EDIBLE THERMODYNAMICS

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Several years ago, I was reading the US Food and Drug Administration (FDA) technical guidance (as one does) and happened across the following: "*If the water activity (a_w) of food is controlled to 0.85 or less in the finished product, it is not subject to the regulations of 21 CFR Part 108.*"[1] I hope you will agree that this is a very exciting sentence. Why? The term "activity" is, like fugacity, one of the ways we describe the thermodynamic behavior of compounds in mixtures. Was the FDA really talking about the ratio of component-to-standard-state-fugacities in a document aimed at clarifying packaging of cheese spread? Surprise, yes! The thermodynamic concept of a_w is the bedrock "why?" of everything from the high salt and sugar content of processed food to chips going stale to the continually surprising fact that "creme-" filled baked goods are fine without refrigeration.

If you talk to the lucky folks who love thermodynamics, you'll find that some Chemical Engineering (ChE) thermo professors tend to describe the behavior of compounds in terms of chemical potential or Gibbs excess energy, while others prefer to think in terms of fugacity, and still others, activity. At the risk of offending some of my thermodynamically inclined colleagues, I'm going to assert that these concepts are somewhat interchangeable. No, they are not identical in equations or relations. But they are reasonably equivalent insofar as they communicate what we expect a compound to *do* in a given situation. Which approach we use in calculations is determined by a combination of convenience and culture (if you were to play Among Us as a ChE sneaking around a bunch of physical chemists, you'd reveal yourself the instant you said "fugacity"). So while it might be fun to talk about the fugacity of cheese, in food engineering, a_w of cheese is preferred because of two extremely useful properties: (1) a_w is relatively easy to measure, and (2) a_w is a convenient way to describe a dimensionless value generally falling between zero and one.

It's not obvious that the activity of anything ought to be easy to measure. Because we're interested in describing activity values under typical food storage conditions – temperatures between 0 ºC and 40 ºC, and pressures at or near atmospheric – we can assume that the vapor phase is ~ ideal. Here's the groovy thing: under these conditions, a_w is equal to the relative humidity, which takes its value from esoteric to a value inferred using standard laboratory equipment. Keen-eyed readers will have noticed that this only applies to gases, while foods tend to be *not* gaseous (I did once go to a restaurant that served a drink under a smoke-filled glass dome, but it's fair to say that 99.99% of foods *aren't* gases). The final piece of the puzzle is that at equilibrium, the activity of a given compound will be equal in all of the phases that are present. So if we want to know a_w for a piece of cheese, we seal the cheese in a box of initially dry air, wait until equilibrium is achieved, and then measure the relative humidity of the equilibrated air. Piece of cake! (Or cheese, as the case may be.)

Now that we've measured the a_w of our food, we can move on to think about what this value actually *tells* us. As we learned from the FDA, there's something special about $a_w = 0.85$. Water activity's influence on food is related to a_w's influence on osmotic pressure. At equilibrium, the activity

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of a given component will be equal on both sides of a phase boundary or semi-permeable membrane. When the activities are unequal, water will tend to move away from the region of high activity towards where it's lower. This is why your chips get soggy in August when the relative humidity is high – a chip ($a_w \sim 0.5$) will literally suck water right out of humid air ($a_w \sim 0.9$). Things get very interesting if there's a semi-permeable membrane present that allows movement of some species but not others. If there's pure water on one side of such a membrane and salt water on the other, and only water is allowed to pass through, the water will pass through the membrane and dilute the salt water until it runs out or is opposed by a sufficient force such as pressure. Just how much pressure is required can be estimated using the van't Hoff osmotic pressure equation:[2]

$$\Pi = -(RT/V_w)\ln[a_w] \tag{1}$$

Run a few numbers through and you quickly find that it doesn't take a whole lot of solute to generate dozens of atmospheres of osmotic pressure. This works against humanity's interest when we try to extract potable water from seawater with reverse osmosis, but very much *in* our interest for food preservation. That's because the bacteria and fungi that would spoil our food are essentially bags of water surrounded by a semi-permeable membrane. And while they have cell walls that allow them to withstand much more of a pressure difference than mammalian cells, this capacity isn't infinite. The upper limit of pressure that a cell can handle corresponds to its minimum a_w for growth – which for the worst of the worst food contaminants (such as salmonella and *E. coli*) is just above 0.85.

For example, sugar is yummy for bacteria, fungi, and chemical engineers. Ever wonder why it's perfectly fine to keep the granulated sugar in the cabinet, but if you leave sweetened coffee sitting on your desk over winter break, when you return in January, it'll be fuzzy? (An experiment I must admit to having conducted. Repeatedly.) The a_w of coffee with a teaspoon of sugar is somewhere around 0.99 – practically ideal conditions for all manner of microbes – while a_w of commercial sucrose crystals is around 0.01. Most fruits, vegetables, fresh dairy, and meat products start with a_w in the 0.99-0.97 range, which is why they don't last long before spoiling under ambient conditions.

If we want to keep food safe for human consumption, we can slow microbial growth (refrigeration), pause microbial growth (freezing), make the food a hostile environment for spoilage through fermentation/addition of antimicrobial compounds (see previous Food for Thought[3]), or make the food a hostile environment for spoilage through reducing a_w. It would seem like this should be a simple matter of drying out the food, but in practice it's difficult to get a_w below 0.85 by only removing water (blame thermodynamics and kinetics for this one; the less water there is, the more difficult it is to remove and the lower the driving force). Therefore, most foods preserved through a_w reduction use a combination of dehydration and addition of other tasty smallish molecules. Examples abound: in Nigeria there is kilishi (meat jerky with palm sugar, salt, spices, and peanuts); you can buy a bag of tabor niboshi to snack on in Japan (dried sardines); and a Roman cookbook first described jam (essentially reducing the water activity of fruit through evaporation and addition of sugar) almost 2000 years ago.

In fact, it's the hallmark of "processed" foods to be calorie dense and high in salt and/or sugar for precisely this reason. Calorie-dense, because as you remove water, the concentration of caloric elements increases. High in salt or sugar, because we have a limited menu of options to change a_w through adding components. If we imagine foods as ideal solutions, we can approximate a_w as the mole fraction of water (x_w) in a given food. Water has just about the lowest molecular mass of anything commonly found in food at 18g/mol. Reducing x_w therefore tends to require the addition of massive amounts of other solutes. Imagine – to bring 100g of water (5.55 moles) to an a_w of 0.85 through the addition of a solute requires 0.97 moles of that solute. That doesn't sound too bad until you multiply through by the molecular mass of sucrose and get 334g of sugar, which is a touch over a cup and a half! We do somewhat better with salt, because it dissociates into sodium and chloride ions. Therefore, about 28g of salt would do the job, but the resulting product tastes excessively salty. There aren't that many other molecules available that are relatively light, soluble in water, nonpoisonous, and good tasting. So if we want foods that can sit on a shelf for months at a time without spoiling, we end up with foods that are, well, processed. We can use this information to design foods that will be shelf stable. For example, the "creme" filling inside a commercial pastry often contains very little cream and instead contains a vegetable shortening ($a_w \sim 0$) sugar mixture, resulting in a palatable filling that preserves food safety to a much greater degree than possible with whipped cream ($a_w \sim 0.99$) – and that *is* a piece of cake!

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