by J. Peter Clark

Thermodynamics and Food Processing

Few areas of science can be as intimidating as thermodynamics, even for engineers. In my case, I encountered the subject in courses in physics, physical chemistry, chemical engineering, and then two more courses in graduate school. I am still learning. Here, I want to explain some of the basic concepts and show how they actually are intuitive and how we encounter these concepts in food processing.

The Laws of Thermodynamics

There are said to be three laws of thermodynamics but many ways to express them. For example, Saravacos and Maroulis (2011) put the laws this way:

1) The total energy in various forms in a system remains constant.

2) The total entropy change of a system is positive.

3) The efficiency of an energy to work cycle cannot approach 100%.

Gleick (2011) has a more whimsical formulation:

1) The energy of the universe is constant.

2) The entropy of the universe always increases.

He said this was equivalent to the following:

1) You can't win

2) You can't break even either.

Of course, it might help if one understood entropy.

Thermodynamics helps in understanding the process of heat transfer. *This open flow heat exchanger,* FusionLine, *from Alfa Laval, is the latest addition to the company's extensive portfolio of heat exchangers.*

Photo courtesy of Alfa Laval

Entropy

Mathematically, entropy is defined as the change in heat energy divided by the absolute temperature of some process. (Absolute temperature is degrees Celsius plus 273 or degrees Fahrenheit plus 460.) Gleick describes it as a measure of information. He makes the point that perfect regularity conveys little information because everything is predictable, while perfect randomness (if it exists) requires every bit of information.

In physical terms, entropy measures the value of energy—heat at a high temperature is generally worth more than heat at lower temperatures, because, by the first law, it can be converted to more useful work. It also warns us that the universe is slowly heading to an equilibrium where no work can be done, because everything is at the same low temperature. One hopes this takes a long time.

Even without formal study, we know that most of the energy from gasoline in our cars or electricity in our homes goes to unuseful heat instead of propulsion or lighting.

Practical Applications of Thermodynamics in Foods

Thermodynamics helps us understand heat transfer, refrigeration, water activity, and mass transfer, among many other phenomena. The rates at which physical and biochemical processes occur are the realm of kinetics and hydrodynamics, but the limits and ultimate states are often determined by thermodynamics.

For example, in heat exchange, there must be a finite difference between the phases exchanging energy, whether the objective is heating or cooling. The rate is determined by the magnitude of the difference (among other factors), but nothing useful will occur if the gradient of temperature is not in the correct direction. One cannot cool a food to 35°F with a 40°F coolant.

Refrigeration

Refrigeration is one of the most important utilities in food processing. It is possible to understand because of thermodynamics. A working fluid, any one of many synthetic chemicals, ammonia, or carbon dioxide, is converted from gas to liquid and then back again by changing its pressure, which then changes the temperature at which it vaporizes or condenses. Most fluids boil or condense at higher temperatures when at higher pressure. Thus, a working fluid can be compressed to a pressure such that it will condense against ambient air, typically at 90°F. If the pressure is reduced, by passing through a valve, a mixture of liquid and vapor results at a much lower temperature.

The vapor can be returned to the compressor while the liquid is vaporized by the heat of the cooling load (evaporated). There are sophisticated modifications of this simple cycle, but air conditioners, coolers, and freezers all operate on the same fundamental principle.

The thermodynamic concepts involved include phase change, heats of vaporization and of condensation (usually the same), heat exchange, and theoretical efficiency. The efficiency of a refrigeration cycle is expressed as the coefficient of performance (COP) equal to the amount of cooling provided divided by the work required in equivalent units, such as British Thermal Units (BTU). One BTU is the energy required to heat one pound of water one degree Fahrenheit. Work is often expressed in kilowatt hours (kWh). 3412.14 BTU equal one kWh. COP is dimensionless and often has values around 4.0.

Another measure of refrigeration or cooling is the chiller ton, which is 12,000 BTU/hr, derived from the energy removal necessary to freeze one ton of ice in a day.

***There are said to be three laws of thermodynamics** but many ways to express them.*

Water Activity

Water activity is a specific case of a broader concept from thermodynamics, namely chemical potential. Chemical potential is an intensive property, as contrasted with an extensive property, of matter. An intensive property is independent of the quantity of material. Examples of other intensive properties are temperature, density, and pressure. Extensive properties depend on the amount of material, such as volume, mass, and energy. Equilibrium is defined as a condition in which there is no change in intensive properties and no exchange of material or energy with the environment of a system.

A system can consist of multiple phases, such as solid, liquids, and gases, but also can involve multiple solid states, such as crystal forms, or configurations of molecules. So long as there exist differences in intensive properties among phases in contact with one another, in a closed system, there will be a tendency toward equilibrium.

Examples, illustrating how intuitive this really is, are the following. A hot rock is dropped into a bucket of cool water. What happens? The rock cools and the water warms. We can measure the initial and final temperature of the water and determine, if we wish, the energy capacity of the rock at its starting temperature. We need also to know the weight of the rock. A version of this exercise is the basis for calorimetry and the determination of the caloric or energy value of food. In that case, combustion of the food provides the energy to warm water.

A large quantity of salt in contact with a finite amount of water will partially dissolve until the liquid solution is saturated (about 76% salt by weight). Beyond that point, nothing further will happen. Likewise, if a solution of salt in water is evaporated by boiling, removing some of the water, eventually the solution will be saturated and salt will crystallize and precipitate. This, of course, is one way we obtain salt for use from the sea and, by analogy, purify and recover other materials, such as sugar.

***To understand the principles of refrigeration, it is necessary to have an understanding of thermodynamics.** This LVS® Refrigerant Feed System from JBT Food Tech (Frigoscandia) provides liquid/vapor separation at the freezer to allow a dry suction vapor to return to the engine room, improving the compressor efficiency, reducing the system refrigerant charge, and eliminating the need for a circulation pump and surge drum.* Photo courtesy of JBT Corporation

In a closed system of salt and water at normal temperatures, there is a third phase, which is in equilibrium with the solution and the solid salt, namely the gas over the solution. The gas phase contains water vapor and air. Salt has no substantial

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vapor pressure, so is not present in the gas. The other components of the gas, nitrogen and oxygen (simplifying somewhat), are not substantially present in the solution or solid. Water is present in both solution and gas, but at equilibrium, we say its chemical potential in each phase is equal. So, what is this chemical potential, and how might it be useful?

The chemical potential of a material in an ideal solution is exactly equal to its mole fraction. Mole fraction is the ratio of the moles of a substance to the total moles of the phase, and is an intensive property. (Many unit or ratio properties are intensive—density, for instance is the ratio of mass to a unit volume, while mass is an extensive property.) Moles are the amount of a mass that contains Avogadro's number of atoms or molecules. That number is defined as the number of atoms in 12 g of carbon 12 and is about 6.022×10^{23}, the same for all molecules or atoms. For instance, the moles of water present in 100 g of water is 100/18 = 5.55.

Gases at normal temperatures and pressures are essentially ideal, and so the mole fraction or chemical potential of the components of a gas are equal to the partial pressures of each divided by the total pressure. The partial pressure of water in the gas over pure water is equal to the pure component vapor pressure of water at that temperature. Since the liquid phase is pure water, its chemical potential is 1.0 and so is the chemical potential of water in the gas phase. By convention, we call the partial pressure of water vapor above pure water at a given temperature relative humidity and express it as 100%. The partial pressure of water in gas above a solution of water and some other substance will be less than if the solution were pure water, because the mole fraction of water is less than one, and so its chemical potential at equilibrium is less than one.

We call the actual value of the chemical potential of water in a solution water activity and measure it conveniently by measuring the relative humidity of the gas in equilibrium with it. There are commercial instruments to do this. Practical applications of water activity abound and are widely discussed. **FT**

***J. Peter Clark**, Contributing Editor,*
Consultant to the Process Industries,
Oak Park, Ill.
• jpc3@att.net

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