Soap Suds Science-What Gibbs?
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CHEMICAL REACTION BY STEVE HERMAN

Soap Suds Science–What Gibbs?

The Gibbs Free Energy formula maps out how thermodynamically instable emulsions can be kinetically stable enough to put great products on a shelf.

> "...classical thermodynamics...is the only physical theory of universal content which...within the framework of applicability of its basic concepts will never be overthrown."
> - Albert Einstein

Most of us in R&D know that emulsions are thermodynamically unstable. We add emulsifiers to lower the surface tension and add mechanical energy through mixing to get something that is stable enough for practical use. But this leads a thoughtful person to a few obvious questions:—what is thermodynamics, and why is it important? Taking one step further, who is Gibbs and what is his free energy equation?

The identity question is easy. J. Willard Gibbs (1839-1903) was the first person to be awarded a PhD in science from an American university, granted by Yale in 1863. He published his first papers on thermodynamics in 1873, putting that science on firm footing. Gibbs later produced critical contributions to the vector theory and electrodynamics. He is unquestionably one of our greatest native-born scientists. He has several equations named for him, the Gibbs Free Energy Equation being perhaps the most famous.

SIMPLE MATH

A page of thermodynamics looks much like a calculus exam, but it maps out the crucial role heat and energy play in the formulation of emulsions. Since most people run and hide at the first mention of calculus or thermodynamics, you are urged to read on and become one of the technical elite.

Calculus is the mathematics of change. There are two flavors of calculus: differential and integral. Derivatives provide the rate of change of a function, and integrals yield the area under a curve. Figure 1 provides all you may ever need to know about advanced mathematics. The change in x is denoted Δx, which happens while y is changing by Δy. Calculus is founded on limit theory, and curves are accurately analyzed when units like Δx and Δy approach zero.

Thus Δx becomes dx when Δx becomes very, very small. Basic derivatives use the notation dx/dy, which turn into the squiggly letters of partial derivatives $\partial x/\partial y$ when there is more than one variable.

The elongated "s" is used for integrals:

Figure 1A

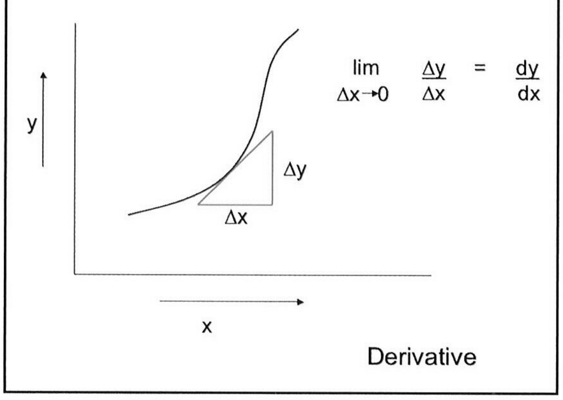


Figure 1B

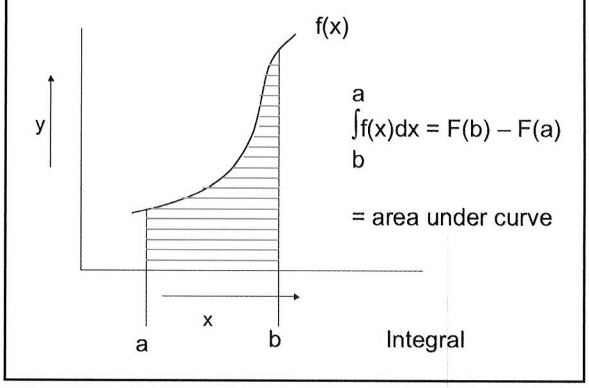
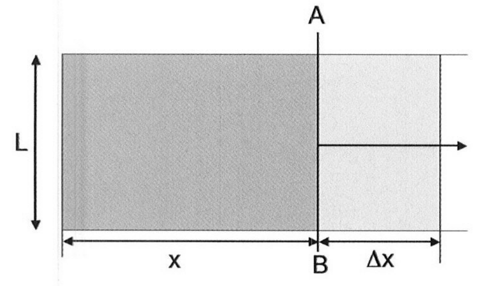
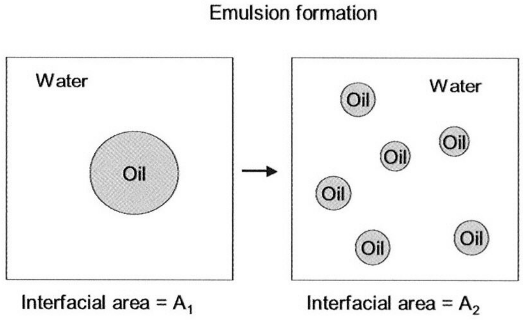


Figure 2



Expansion of a soap film

Figure 3



$$\int_a^b f(x)dx = F(b)-F(a).$$

Now that we understand calculus, thermodynamics should be a breeze. There are two fundamental laws, both of which are so easy that it is amazing how much derives from them. The First Law is the conservation of energy—energy cannot be created or destroyed. The Second Law states that processes occur in the direction of increasing disorder. It can be compared to house cleaning; there is one way for the house to look perfectly clean, and an infinite number of ways for it to be messy. It is a universal law of nature that houses tend toward messy.

Every science has a special vocabulary, and thermodynamics has a few special words. Enthalpy is heat energy, and entropy is a measure of disorder. Spontaneous reactions go downhill in energy.

We are now ready for the Gibbs Free Energy Equation:

$$G = H - TS$$

Here G is the free energy of the substance, H is the enthalpy, S is entropy and T is the temperature in degrees Kelvin (which means we start measuring at absolute zero).

The following equation expresses a change at constant temperature:

$$\Delta G = \Delta H - T\Delta S$$

We now know calculus and thermodynamics!

FILM'S FREE ENERGY FLOW

On to personal care, let us examine a film of surfactant and apply our new knowledge. Figure 2 shows a soap film on a frame with one side, connecting A and B, free to move in the direction of the arrow. If the side is moved outward at constant temperature, the work done is the product of the film tension σ and the increase in area of the film.

The energy to increase the film from zero area to A is:

$$F = \text{free energy} = \int_0^A \sigma dA = \sigma A$$

This is assuming the concentration of surfactant is large.

In English, this means that the free energy of the film is proportional to the area if the surfactant concentration is constant. Since energy tends to minimize itself, the consequence is that soap films automatically assume a shape providing a minimum area.

SOAP FILM

Soap film is as simple a case as thermodynamics gets in personal care. The next step is lipid-water systems—monolayers, bilayers, micelles and so on. Emulsions are mixtures of two phases that are not soluble in each other, and the creation of emulsions is characterized by increased surface area, as we see in Figure 3.

When the oil and water are completely separate, the interfacial area is A1. After emulsification and mixing, the area is increased to A2. The energy amount (enthalpy) is ΔA , where ΔA is the change in area and γ is the interfacial tension.

Back to Gibbs:

$$\Delta G = \Delta A - T\Delta S$$

Absorption of a surfactant lowers the surface tension γ so the energy required for emulsification is reduced. Since ΔG is greater than zero, the process of emulsification is not spontaneous and can result in a product that is kinetically stable, but thermodynamically instable. Kinetic stability means that emulsion systems are not in equilibrium. Since emulsification requires kinetic energy, dirty dishes do not spontaneously clean themselves in soapy water.

The presence of calculus at every turn makes the literature look forbidding, but one must stick a toe in its water a little to approach the theoretical heart of our formulations. Emulsifiers, mixers and informed formulations are our tools to fight thermodynamic instability. It is a fight where we can never win absolutely, but a partial victory can be enough to put great products on the shelf. ■ **GCI**

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