# Teaching thermodynamics: The challenge*

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*Abstract*: I consider the challenges of sharing thermodynamic concepts with both the general public and with students, whom I regard mostly as students of chemistry. I deal with the following challenges: (1) The order of presentation: what are the issues relating to presenting thermodynamics before or after quantum theory? (2) What should we identify as the foundations of our subject? (3) How do we convey to the general public (and the starting student) the insights that we get from the Second Law? (4) How do we bridge the gap from the qualitative to the quantitative? (5) Does visualization of calculations and concepts always help or can it make matters more complicated? (6) How do we make the transition to discussions in terms of Helmholtz and Gibbs energies, and start doing chemically useful calculations? (7) How do we keep track of the seemingly overwhelmingly large number of equations that a systematic treatment of thermodynamics inevitably generates? (8) How should we introduce statistical thermodynamics and enrich our understanding of classical thermodynamics? (9) How do we extend calculations to show the fascinating and broad scope of elementary thermodynamics?

*Keywords*: classical thermodynamics; education; statistical thermodynamics; teaching; thermodynamics.

In the course of this paper I shall address a variety of questions relating to the presentation of thermodynamics to two types of audience: chemistry undergraduates and the general public. The original presentation on which this article is based emphasized the role of graphical representation and used numerous images; this article is a verbal summary of that presentation.

## THE ORDER

There are arguments for presenting thermodynamics before quantum theory and vice versa. To the purist, it is intellectually satisfying to see that relations between phenomena can be established without appealing to models of internal constitution. That suggests that thermodynamics should be presented first. On the other hand, it is undeniable that the subject is greatly enriched by its interpretation in terms of atoms and molecules, and that the modern student would expect that to be the mode of delivery. The danger is that thermodynamics then does not appear to be immediately applicable without going through the business of calculating partition functions, which can be done only for idealized systems. The best approach would seem to be the obvious compromise, to blend in a molecular interpretation to enrich the classical presentation.

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## THE BASIC CONCEPTS

It is vitally important to establish the molecular basis of work and heat, with both being modes of transfer of energy, work making use of uniform motion of atoms in the surroundings and heat making use of disorderly motion. With these concepts established, the Second Law becomes much simpler to understand and employ, as we shall see. I think it also very helpful to show that the transfer of energy as heat can be measured mechanically by comparing the work that must be done to achieve the same change of state in a diabatic and an adiabatic system. Although a practicing thermodynamicist might regard the thermometer as the fundamental instrument of thermodynamics, to a theoretician that is not the case: the fundamental concept is the weight (a mass in a gravitational field). A falling or rising weight can be used to measure work; through work in systems with different types of thermal boundary, heat; and through Carnot's and Kelvin's arguments, temperature too.

I think it important to show our students the interconnectedness of scientific concepts, and in particular to show that the First Law has very deep roots. The question it raises is why energy is conserved. The answer is found in Noether's theorem, that with every conservation law there is associated an underlying symmetry. In the case of the conservation of energy, the underlying symmetry is the uniformity of time: energy is conserved because time is uniform. If time were to be nonuniform, then energy would not be conserved.

The First Law also raises the question of the total energy of the universe, and correspondingly the total quantity of energy that had to be provided at the inception of the universe, for that quantity is still with us today and until, we presume, the end of time. Cosmological arguments are very problematical in thermodynamics, and are certainly not resolved by cosmology. But there are pointers that let us make an estimate of the total energy of the universe. We start by adding together the masses of all the galaxies, and then use $E = mc^2$ to convert that measure of mass to the energy it represents. Clearly, the energy so measured is huge. However, because the galaxies interact gravitationally and this interaction is attractive, there is a lowering of energy. It seems highly likely that this gravitational contribution, once one allows for the presence of gravitationally active dark matter, cancels the energy calculated by assessing mass, and that the total energy present in the universe is exactly zero! That certainly simplifies the task of accounting for the events that took place at the creation, and incidentally raises questions about what thermodynamicists are studying!

## PRESENTATIONS TO THE GENERAL PUBLIC

I regard the Second Law as the great liberator of the human spirit, as it shows the root of all change. That being so, I think it absolutely essential that we share the insight it gives with the general public. In general, I think it vital that scientists share their insights into the natural world, for a rational understanding deepens delight. There is nothing easier to share than the Second Law, for the essence is simple: matter and energy tend to spread in disorder. Precisely what we mean by disorder raises all sorts of subtle questions, but they should not be allowed to obscure the central core idea. Then it is essential to show that dispersal in disorder can be constructive and that decay in one region may drive the emergence of structure elsewhere: that structure may be mechanical, chemical, or even mental [1].

## RENDERING IT QUANTITATIVE

There comes a stage, of course, when we cannot avoid expressing all these concepts quantitatively. The key equation of classical thermodynamics is the Clausius expression, $dS = dq_{rev}/T$. Students commonly have a problem with "internalizing" this expression in the sense of seeing that it is intuitively plausible as a basis for the discussion, interpretation, and calculation of entropy changes. I find the analogy with sneezing that I have introduced elsewhere helpful [1]: the analogue of a transfer of energy as heat is a sneeze; the analogue of a high-temperature environment is a busy street and a sneeze causes little ad-

ditional disorder; the analogue of a low-temperature environment is a quiet library where the same sneeze causes a lot of additional disorder.

With the Clausius expression established, we can turn to heat engines and the phenomenological statements of the Second Law; here I find some uniform illustrations very helpful for keeping track of the flow of energy in its various forms. I like to start with the Kelvin and Clausius statements of the Second Law, and then go on to show how the Clausius definition summarizes them both. That is an important moment in thermodynamics. The same type of illustration can also be used to establish the logical equivalence of the two phenomenological statements and then to show how to evaluate the thermodynamic efficiency of an engine and the coefficient of performance of a refrigerator. The former lets us, following Kelvin, establish a measure of temperature. I remarked earlier that temperature can in principle be measured by measuring the fall of a weight: this is the justification, for the work done by an engine can be measured in that way, so in principle can the heat absorbed from the hot reservoir (as I remarked earlier), it follows that the efficiency can be measured solely by observing the motion of the weight, and therefore so can the thermodynamic temperature too.

## THE ROLE OF VISUALIZATION

I think that visualization is a hugely important component of the education of a chemist, not only because many chemists are visual learners and thinkers but also because it is a very useful way of assessing whether one really understands what is going on. That is, the attempt to render an expression or derivation in visual terms is a way of establishing whether one really understands it. As I have already remarked, in the course of this presentation I made extensive use of visual images. However, there are times when visualization can actually seem to make a derivation harder! I have to admit that I have found it very difficult to find a helpful visualization of the development of the Clausius–Clapeyron equation. In such cases, I would recommend that the instructor still try to find a visualization, for the process really strengthens one's own comprehension of what is going on, but not share it with the students!

## CONCEPTUAL ROAD MAPS

Thermodynamics is, with good reason, regarded as a forest of equations. One way to help is to construct a "road map" showing how to migrate from one equation to another. A road map is not quite the same as a concept map, which is a network of links between concepts. A road map is a network of equations and advice about how to migrate between equations by making approximations, imposing constraints, or importing other relations. Road maps can be constructed for all the areas of physical chemistry, and can be very helpful to students lost in the forest [2].

## STATISTICAL THERMODYNAMICS

Perhaps no other region of physical chemistry presents more problems to instructors than statistical thermodynamics. The problem is basically the density of mathematics and the intricacy of the calculations. First, I think it essential to identify the two principal expressions that just about everything else springs from: the Boltzmann distribution and the expression for the partition function. The former is of crucial importance for the whole of chemistry and the latter is the focus of all calculations in statistical thermodynamics, the analogue of the wavefunction for quantum mechanics. I think it is possible to generate an intuitive understanding of the partition function by exploring in detail the statistical thermodynamics of a two-level system, then enlarging its scope to an infinite array by considering the harmonic oscillator, then adding in degeneracy by dealing with the linear rotor. It is, of course, hugely important intellectually to see how the Boltzmann distribution emerges, like so much in science, from

a random (but constrained, depending on the type of ensemble) distribution of molecules over the available states of the system. I like to see how apparent order emerges from complete freedom!

Statistical thermodynamics is a crucial part of the education of a chemist, for it provides the link between the properties of individual molecules and the bulk materials that they form. It also illuminates what is meant by disorder and how distribution over available states results in chemical properties, including equilibrium constants. A road map of equations is of great assistance here, as one can be led carefully from the partition function to is application.

## EXTENDING THE RANGE

One system that I like to discuss, for it brings together so many of the concepts of classical and statistical thermodynamics, not to mention quantum mechanics, and has profound implications for the environment, is the electromagnetic field. It is an excellent exercise in the application of relations that, starting from the Planck distribution for the spectral density of black-body radiation one can arrive at expressions for the energy density, entropy density, and Helmholtz energy density of radiation at a thermodynamic temperature $T$, and then from them establish expressions for the radiation pressure and hence the Gibbs energy density of the field (which turns out to be 0). Such a calculation raises all manner of questions which really test one's comprehension of thermodynamics, such as why the radiation field is so potent despite its Gibbs energy being zero, and one can explore not just the energy balance of the Earth but its entropy balance too, and see how low entropy solar radiation can drive the machinery of the biosphere. For pedagogical reference, the relevant equations are collected in the Supplementary Information.

## CONCLUSION

I have sought to identify the central problems of teaching thermodynamics to chemists, and on the way have made suggestions about how to share our insights with the general public. I consider visualization a crucial tool in sharing information and guiding the way we teach the subject. Molecular interpretations greatly enrich the subject and help to modernize its presentation.

## SUPPLEMENTARY INFORMATION

Supplementary Information is available online (doi:10.1351/PAC-CON-10-08-17).

## REFERENCES

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