

Heat-Fall and Entropy

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Judging from modern textbooks in physical chemistry, today's chemistry undergraduate is expected to learn almost as much physical chemistry as a student twenty years ago learned in his undergraduate course and first-year graduate courses together. My own observations suggest that today's student has a shakier grasp of basic physical chemistry as a result of this heavier undergraduate dose. I also suspect that this insecurity is discouraging students who go on to graduate school from choosing physical chemistry as a career.

Not only is the material now presented greater in scope, but also it is more highly mathematical and the presentation is often rather formal. I believe that there is significant room for improvement in the mode of presentation and that this improvement should take the form of simple physical models or statements to accompany formal or mathematical concepts.

In this paper I would like to present one example of this kind of approach. The subject is heat-fall and entropy. Compared to the quantities heat and work, entropy seems a physically unintuitive concept. Many modern texts insert at least a brief section, when entropy is first introduced, to relate it to the degree of probability or the amount of disorder. But this is not entirely satisfactory. In the first place, entropy was defined years before the probabilistic aspect was recognized. In the second place, the probabilistic explanation is much more intuitively useful for a process like the expansion of a gas than it is for the heating of a kilogram of copper from 90°C to 91°C. But entropy is usually introduced in connection with precisely such temperature changes.

Just before introducing entropy, most books describe the efficiency of reversible heat engines. They prove that the efficiency is given by

$$\frac{\text{Max work}}{\text{Heat removed from } T_h} = \frac{T_h - T_c}{T_h} \quad (1)$$

where T is in Kelvins. Most books leave it at that. If you give a closed-book quiz on this subject, a significant fraction of the students will make an error in recalling the formula . . . usually putting T_c into the denominator. For many students, eqn. (1) remains simply a plug-in formula to be memorized (temporarily) and used on tests. But this formula has a very simple physical meaning—one which, once seen, is hard to forget. In words, eqn. (1) states that

The maximum fraction of heat energy that can be turned into work is the same as the fraction of the distance to absolute zero that the (remaining) heat falls.

A numerical example quickly nails this down: What fraction of the heat energy removed from a hot reservoir at 1000 K and dumped at 500 K can be converted to work? ans. 50%. How about 1000 K to 300 K? 70%. How about 1000 K to 900 K? 10%. (see fig.)

These simple numbers make the relation obvious. Yet how many books omit such a verbal statement and then provide an example between, say, 373 K and 273 K, thereby obscuring the relation?

Once this simple heat-fall picture is recognized, other aspects of thermodynamics become much more readily grasped. One of these is the thermodynamic temperature scale. The

thermodynamic absolute zero is simply seen as the temperature to which heat must fall in order for all of it to be converted into work (treated as a limiting process). Formula (1) will not give 100% unless T_c equals zero. Any other choice of the zero of temperature would require a more cumbersome formula.

Entropy can also be discussed within this context. If some heat energy $|q|$ is withdrawn at T_h and partly deposited via a reversible heat engine at T_c , the maximum work done is

$$w = |q| \frac{T_h - T_c}{T_h} = |q| - \frac{|q|T_c}{T_h}$$

So $|q|T_c/T_h$ is the part of the heat energy which is *unavailable* for work, even under the best circumstances. The entropy change for the hot reservoir is $-|q|/T_h = \Delta S_h$. Hence, the unavailable energy is $-T_c \Delta S_h$. In words, then, the entropy change caused by removal of heat energy from a hot reservoir contains information about the amount of heat energy which will be unavailable for work under the best (i.e., reversible) circumstances. But the actual *amount* of unavailable energy cannot be known unless we know the temperature of the cold reservoir. Thus, it is $-T_c \Delta S_h$ which measures the unavailable energy. This is equal to $T_c \Delta S_c$ since the entropy changes at the two reservoirs must have equal but opposite values in a reversible process.

The above discussion, which stems naturally from the heat-fall idea, makes clear the meaning of one dictionary definition of entropy: "A mathematical factor which is a measure of the unavailable energy in a thermodynamic system."¹ (I suspect that, after studying the discussion of entropy in many modern texts, students would not know what to make of such a definition.)

The heat-fall picture makes it obvious, for constant T_c , that heat released from higher temperatures can do more work. This is handled by the entropy factor, $|q|/T_h = \Delta S$, which (multiplied by T_c) measures the *unavailable* energy and which becomes smaller as T_h increases. *Heat stored at higher temperatures has a greater capacity for work (T_c constant).* The heat-fall picture also makes it clear that the lower the value of T_c , the more work can be extracted (T_h being equal). Here ΔS is constant, but $T_c \Delta S$ becomes smaller in magnitude at T_c decreases.

The thematic approach outlined above is not intended to substitute for the rigorous, carefully defined, step-by-step development characteristic of thermodynamics. Rather, it is meant to provide a larger framework, within which the development of thermodynamics may be seen to have some physically intuitive qualities. I believe students desire and need such insights, especially with a subject like thermodynamics, which must be studied many times before one feels comfortable with it. Most modern physical chemistry texts provide the detailed development. I find the above ideas to be a useful way to provide a sense of direction in my lectures.

If T_c is $1/3$ of the distance from T_h to zero, then $1/3$ of the heat extracted from T_h can be converted to useful work, the remaining $2/3$ of the heat being released at T_c .



¹ "Webster's New Collegiate Dictionary," G. & C. Merriam Co., Springfield, MA, 1950.