

letters

Thermodynamics for Undergraduates

To The Editor:

There have appeared in THIS JOURNAL many instructive and readable articles on thermodynamics for undergraduates in recent years. I believe that the following three comments and addenda might be of general interest.

The first comment concerns the statement that the work done by a system is a maximum for a reversible path, for which S. D. Christian has emphasized the important *caveat* that the statement applies to isothermal changes of state only [J. CHEM. EDUC., 42,

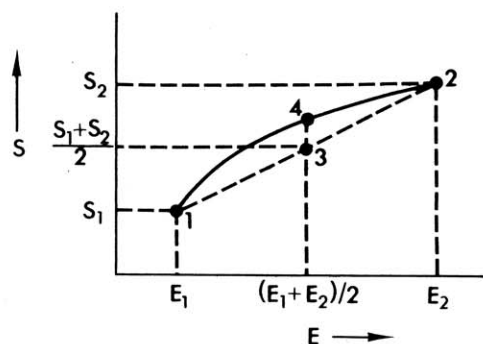
547 (1965)]. Indeed, as Professor Christian demonstrates, the statement is not true in many situations that are not isothermal. However, there are other situations in which the statement does apply, even though the temperature is not necessarily constant. I argue as follows. By manipulation of $dE = dQ - dW$ and $dS = dQ_{rev}/T > dQ_{irrev}/T$ we obtain

$$dW_{rev} = (dQ_{rev} - dE) > (dQ_{irrev} - dE) = dW_{irrev}$$

Hence for a given infinitesimal change in state (fixing dE) the work done by the system along a reversible path is larger than along an irreversible path. It follows by integration that $W_{rev} > W_{irrev}$ when the reversible and irreversible paths compared go through the same sequence of infinitesimally close states. There is no restriction on the temperature. An example is the expansion of a gas with and without friction, in which the temperature need not stay constant, but where the comparison must be between paths that go

through the same sequence of states, so that for each infinitesimal step $dQ_{rev} > dQ_{irrev}$ and also $dW_{rev} > dW_{irrev}$. In the irreversible expansion the temperature increases in some parts of the surroundings because of the friction, and the work the system performs is less than when friction is absent. The presence of friction has, however, no bearing on the sequence of changes of state in the system. For the reversible expansion we may choose to simulate temperature increases in the surroundings equal to those formerly caused by the friction, e.g., by suitable heat transfers from other parts of the surroundings. While useful for calculating the entropy generated in the surroundings by the friction, such simulation is irrelevant to the events in the system and does not change the work the system performs reversibly.

The second comment relates to the illuminating paper on the second law by H. A. Bent [J. CHEM. EDUC., **47**, 337 (1970)], which contains among other nuggets a brief discussion of the fact that $(\partial^2 S / \partial E^2)_{V,M} < 0$. Professor Bent starts by considering that $C_V > 0$, from which $(\partial^2 S / \partial E^2)_{V,M} = -1/(C_V T^2) < 0$. A recent book by Friedrich Hund (of Hund's rules fame) ["Grundbegriffe der Physik," Biographisches Institut, Mannheim, 1969, p. 130] contains an argument that shows that $(\partial^2 S / \partial E^2)_{V,M} < 0$ on the basis of the first and second law, an argument that should receive wide attention, because it is admirably simple and well-suited to demonstrate the power of thermodynamics at a level accessible to undergraduates. Hund considers two identical, constant-volume, closed systems, labeled 1 and 2. At the start the energies of the systems are, respectively, E_1 and E_2 , and the entropies S_1 and S_2 . We now allow thermal interaction and energy is interchanged until equilibrium is established. Both systems then have the same energy, $(E_1 + E_2)/2$. The entropy of the combined system is, however, larger than $S_1 + S_2$, because of the irreversible nature of the change, and the entropy of each of the identical systems in the final state is larger than $(S_1 + S_2)/2$. If we plot the entropy of either system against its energy, the curve must look as shown in the figure, the choice of initial and final states being arbitrary. Points 1 and



Entropy versus energy for a constant-volume, closed system.

2 show states of low and high energy and entropy, respectively, while point 4 shows the state of energy $(E_1 + E_2)/2$ (point 4) for which the entropy is larger than $(S_1 + S_2)/2$ (point 3). The curve bulges upward so that the second derivative of S must be negative, $(\partial^2 S / \partial E^2)_{V,M} < 0$. It then follows that $C_V > 0$.

Finally, I wish to submit a strong plea regarding the term "heat," which is often used (1) with a general meaning to denote a "form of energy" and (2) a more restricted meaning to designate a "form of energy transfer," placing heat in parallel with work. The first usage is the older of the two, but its definition requires statistical and molecular concepts (see below), while the second usage is the only one that can be defined by macroscopic criteria alone. Intermixing of the two usages is highly confusing, especially in any thermodynamic discussion. Nevertheless, usage (1) is often found, even in texts of thermodynamics. A notable exception is the very carefully written and most instructive text by H. A. Bent "The Second Law" [Oxford University Press, 1965], where the words "thermal energy" are used to replace the meaning (1) of "heat," and the same practice is followed in a few other texts. I would define "thermal energy" as the kinetic and potential energy associated with the random motions (e.g., translations, vibrations, rotations) of atoms and molecules. If the term "thermal energy" is to be used precisely, this energy must be distributed over the quantum states of the system according to the Boltzmann factor. The system must therefore be at thermal equilibrium and associated with a temperature, which indeed is an indicator of the "intensity" of the thermal energy.

Energy distributions that cannot be described in terms of the Boltzmann factor are not at thermal equilibrium and the concept of temperature has no meaning for such systems. The term "thermal energy" is no longer a precise concept. Some of the energy that is distributed over the different quantum states of the system can now be converted into macroscopic work, until a distribution consistent with a definite temperature has been reached.

The internal energy of a system at thermal equilibrium may, but need not, consist entirely of thermal energy. A wound spring contains potential energy besides, and a mixture of hydrogen and oxygen at room temperature contains a great deal of what we may loosely call chemical energy in addition to thermal energy. However, such apportionment of internal energy into thermal energy and various kinds of potential energy cannot be made by thermodynamic arguments. "Thermal energy" is not a thermodynamic concept, because it implies a distribution of energies among molecules or other microscopic entities.

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Cooperation between Graduate Institutions and 4-Year Colleges

To the Editor:

In response to the *Provocative Opinion* expressed by Dr. J. I. Ihrig [THIS JOURNAL, **47**, 69 (1971)] in which he proposes a program of training and research collaborations between four-year colleges and graduate institu-

tions, such a program is already in progress, centered at the Department of Chemistry of the University of Wisconsin-Milwaukee. It is a pilot program of two years' duration and receives support both from the National Science Foundation and UWM. A paper describing the Program was delivered by the undersigned before the Division of Chemical Education at the September, 1970 ACS National Meeting in Chicago. Copies of that paper are available on request. An evaluation of the pilot project is being conducted.

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An Abbreviation for the Word Mole

To the Editor:

Given the importance of the word "mole" and the frequency of its use, it is surprising that an abbreviation or symbol for the word has not been adopted by chemists. Perhaps the reason is that one cannot use *m* (meter), *M* (molarity), lower case "oh" (too easily confused with a zero), lower case "ell" (too easily confused with a one), script "ell" (often used for liter) and *e* (electron). May I suggest the symbol ϕ , lower case "oh" with a slash through it, the superposition of the two middle letters of the word. In typing and printing a lower case phi, ϕ , resembles ϕ and works nicely. I have tried these symbols on my freshmen, and they took to them immediately. We are relieved of the need to write out an admittedly short but very frequently used word. The extensions to $m\phi$ or $m\varphi$ (millimole) and $\mu\phi$ or $\mu\varphi$ (micromole) are also very useful.

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Carbonium Nomenclature

To the Editor:

In the February 1971 issue (p. A105) Dean L. Sinclair suggests dropping the terms carbonium ion and carbanion in favor of cation and anion. He states: "In addition to the hoary misuseage (*sic*) of "tert-butyl carbonium ion" when what is really meant is trimethyl carbonium ion, or perhaps more

explicitly, *tert*-butyl cation, a misuseage (*sic*) which appears...". Although cation and anion are good words, there is nothing bad about carbonium ion and carbanion if properly used.

The two-word expression "triphenylmethyl radical" dates from the time of Gomberg's discovery about 1900. Some years later, when it became evident that names were required for the ionic species related to this radical, the words carbonium ion and carbanion came into being; e.g., triphenylmethyl carbonium ion. It is important to note that carbonium and carbanion were separate words, the same as "radical." They were not suffixes.

For many years no ambiguity arose in using these terms. Then someone must have thought that because of the "carb" in carbonium and carbanion that carbinol-type names should have been used. Names of this type employ carbinol as a suffix rather than as a separate word; e.g., triphenylcarbinol (not triphenyl carbinol). Thus it must have been reasoned that Ph_3C^+ should be "triphenylcarbonium ion," letting the suffix -carbonium represent one of the 19 carbons. And, similarly, Me_3C^+ should be changed from *tert*-butyl carbonium ion (3 words) to "trimethylcarbonium ion" (2 words). Unfortunately, some chemists pay little attention to spaces or suffixes and, in their hands, "trimethylcarbonium" (one word) became "trimethyl carbonium" (two words). This is really unfortunate because whereas "*tert*-butyl carbonium" is quite correct "trimethyl carbonium" is quite incorrect. Sinclair seems not to have recognized this point. Unfortunate also, even for the one-word name "trimethylcarbonium," is the fact that this name differs from the name of the corresponding radical. There is an obvious advantage to an identical first name for the three structures R_3C^+ , R_3C^\cdot , and R_3C^- .

Carbonium as a separate word in chemistry can be meaningful. With it, one can say: "An alkene results by detachment of a proton from a carbonium ion." One could not substitute "cation" in this sentence for "carbonium ion" because cation is too broad. It includes not only carbonium but also ammonium, thiuronium, sodium, oxonium, pyridinium, etc. In other words, carbonium is a synonym of cation but with a more restricted meaning.

In view of the fact that IUPAC has withdrawn support from "carbinol" in organic nomenclature it would seem that chemists should hedge against using terms related to it. Thus, both *tert*-butyl cation and *tert*-butyl carbonium ion have a good background of precedent but "trimethylcarbonium ion" should be abandoned and "trimethyl carbonium ion" should never have been used.

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