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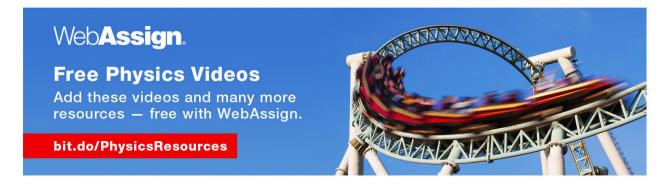Independence of the First and Second Laws of Thermodynamics
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Some comments on the "axiomatic" formulation of the first law of thermodynamics

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In the "conventional" approach to the first law of thermodynamics the state function E, the internal energy of a system, is introduced by means of

$$E_2 - E_1 \equiv \Delta E = Q - W. \tag{1}$$

Historically this formulation is tied up with the realization that mechanical energy and heat are equivalent to each other and interconvertible. Since the beginning of this century, however, attempts have been made to define thermal concepts entirely in mechanical terms. This led Carathéodory to the alternative,

$$E_2 - E_1 \equiv \Delta E = -W_{\text{adiabatic}}, \tag{2}$$

frequently referred to as the (Carathéodory) "axiomatic" formulation.[1] Once the existence of the state function E has been established through the implications of Eq. (2), one may define Q for a nonadiabatic path between the same points, 1 and 2, through the relation:

$$Q = W - W_{\text{adiabatic}}.$$

As Born, one of the early and active proponents of this "axiomatic" approach, pointed out[2]: "This procedure presupposes that mechanical work is measurable however it is applied; $\cdots$ *even for the most violent reactions*" (the italics are the author's). He admits that this may be difficult in practice, and suggests that we should restrict ourselves, whenever possible, to (adiabatic) *reversible* processes. An excellent discussion of the difficulties, in obtaining W for irreversible changes, has been given by Kivelson and Oppenheim.[3] Among other things they show that, in the irreversible compression and expansion of gases, dW cannot always be expressed in the form $P_{\text{ext}} dV$, as one is usually led to believe, and that in some cases W cannot be calculated at all without recourse to hydrodynamics. Now, at first sight, it appears that *any* problems regarding the evaluation of W have to affect *both* formulations (1) and (2) to the same extent. It will be shown below, however, that in many instances there is a real difference in this context, which favors the "conventional" treatment.

Another crucial point associated with the "axiomatic" approach is the necessity to define an adiabatic process without using the notion of heat. Leaving aside the few cases where this problem is simply swept under the rug, the usual approach here is to distinguish first between *adiabatic* and *diathermic walls*. Assuming, for simplicity, that both are impermeable to matter, the former are characterized by the property that they can transmit a disturbance only by mechanical means. Such a definition (several variations are found) is operational only in what Bridgman has called a "paper-and-pencil-sense."[4] Surely, in practice, one would ascertain whether a partition is adiabatic or not by checking if heat can flow across it, but this does not bother the true axiomaticists.

The most serious difficulty is disregarded altogether by all but a very few authors. To quote Münster[5]: "A somewhat unsatisfactory aspect of Carathéodory's theory is that $\cdots$ it is not always possible to reach any state 2 from any other state 1 by means of an adiabatic process." This point was also made by Zemansky, through the fourth edition of his well-known textbook,[6(a)] but in the fifth edition the issue was dropped entirely.[6(b)] Ironically, the relevant observation is known as the "Carathéodory Principle" (of "Adiabatic Inaccessibility"). It can be looked upon as an independent fundamental fact of experience[1,2] or, as shown by Crawford and Oppenheim,[7] as a consequence of the better known Clausius or Kelvin-Planck principles, all of which can serve as the basis for the "derivation" of the *second* law of thermodynamics.[8] This adiabatic inaccessibility, for every initial state, involves an infinite number of points (albeit located in a restricted region), and for all transitions concerned the definition (2), for ΔE, would be strictly inoperative. Münster "resolves" (?) the dilemma by observing that $\cdots$ "For such cases, it is, however, always possible to realize the *reverse* of the desired process adiabatically." He implies, as Zemansky stated explicitly,[6(a)] that ΔE can now be obtained as $W_{\text{adiabatic}; 2 \to 1}$, rather than $-W_{\text{adiabatic}; 1 \to 2}$. This "solution" of the problem at hand must be critized for two different reasons. In the first place, *these* reverse processes are *of necessity irreversible*,[9] creating possible difficulties in the evaluation of W, as discussed above. Note that here the "conventional" formulation (1) gives us much more flexibility: Since it does not tie us down to an *adiabatic* change, it is quite likely that some convenient reversible path(s) between such states 1 and 2 may be found. Secondly, it appears that, in equating ΔE with $W_{\text{adiabatic}; 2 \to 1}$, one is in effect already using a property of a state function, namely $\Delta E_{1 \to 2} = -\Delta E_{2 \to 1}$, while the first law is to *establish* this characteristic of the internal energy.

It is undeniable that the "axiomatic" approach has its appeals and the "traditional" one its drawbacks. Among the latter the necessity to define Q prior to the enunciation of the first law stands out. It is well known that this can be achieved in more than one way; the oldest procedure introduces temperature followed by (quantity of) heat. "Independent" heat measurements through the effect of a phase transition (ice calorimeter), or an electric current passed through a resistor, offer viable alternatives. The author feels that in this context the possibility of defining temperature, heat capacity, and (quantity of) heat *in that order*[10,11] deserves more attention than it has been given to date. No doubt, the presentation of the laws of thermodynamics will continue to involve strong personal preferences, and thus will remain controversial. At this stage, any contention that Carathéodory and his followers have provided us here[8] with an airtight and crystal clear alternative, which should compel all of us to discard a hopelessly clumsy heritage from the nineteenth century, seems premature, to say the least.

In assessing how the issues raised affect the teaching of (phenomenological) thermodynamics, we should distinguish between introductory and advanced courses. With regard to the latter, the author feels that graduate students should be made aware of both the conventional and the axiomatic approach, not only in the formulation of the first law, but also in the development of the second one. In this context a critical discussion, as presented above, has proven to be most à propos. When it comes to the instruction of undergraduates, the situation is much more complicated. It will come as no great surprise to the readers of this note, that here the author would prefer to confine himself to the conventional approach. This is made increasingly difficult because more and more, otherwise quite suitable, textbooks will give the axiomatic treatment of the *first* law, either exclusively or as an alternative. But in many of these monographs this is followed up by the traditional Carnot-Clausius "derivation" of the *second* law, presumably because the corresponding Carathéodory treatment presents too many mathematical difficulties for students at this level. In such "hybrid presentations" the principle of "Adiabatic Inaccessibility" need not be emphasized and its inconsistency with the definition of ΔE by means of statement (2) is not explicitly apparent. At this stage of learning thermodynamics for the first time, the student is usually sufficiently bewildered to accept formulation (2) if illustrated by some simple examples, which are carefully confined to reversible changes. The more inquisitive ones are frequently baffled by the requirement of defining adiabatic processes without the use of the notion of heat, as discussed earlier in this paper.

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[1] C. Carathéodory, Math. Ann. **67**, 355(1909). For a recent English translation, see J. Kestin, *The Second Law of Thermodynamics* (Dowden, Hutchinson & Ross, Stroudsburg, Pa., 1976), p. 229.

[2] M. Born, *Natural Philosophy of Cause and Chance* (Dover, New York, 1964.), p. 37.

[3] D. Kivelson and I. Oppenheim, J. Chem. Educ. **43**, 233, (1966).

[4] P. W. Bridgman, *The Nature of Some of Our Physical Concepts* (Philosophical Library, New York, 1952), p. 8.

[5] A. Münster (transl. E. S. Halberstadt), *Chemical Thermodynamics* (Wiley-Interscience, New York, 1970), p. 23.

[6] (a) M. W. Zemansky, *Heat and Thermodynamics*, 4th ed. (McGraw-Hill, New York, 1957), p. 60; (b) *ibid.* 5th ed. (1968), p. 76.

[7] B. Crawford Jr. and I. Oppenheim, J. Chem. Phys. **34**, 1621 (1961).

[8] In the present note, the author is not taking any position on the relative merits of the alternative "derivations" and formulations of the *second* law.

[9] For those unfamiliar with this statement we refer, for example, to the discussion in Ref. 7.

[10] See, e.g., P. S. Epstein, *Textbook of Thermodynamics* (Wiley, New York, 1937), p. 25.

[11] A particularly elegant version of this approach was given by G. E. Uhlenbeck in his summer 1967 lectures at the University of Colorado. He suggests that it can be traced back to Joseph Black's *Lectures on the Elements of Chemistry* (1803).

On momentum operators[a]

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The momentum operator P_{q_i} of quantum mechanics in Cartesian coordinate systems is given by

$$P_{q_i} = -i\hbar \frac{\partial}{\partial q_i},$$

where q_i is x, y, or z. Podolsky[1] pointed out that this prescription cannot be followed for non-Cartesian coordinates. DeWitt[2] showed that the right momentum operator in non-Cartesian coordinates is given by

$$P_{q_k} = -i\hbar \left(\frac{\partial}{\partial q_k} + \frac{1}{2} \begin{Bmatrix} j \\ jk \end{Bmatrix} \right), \tag{1}$$

where the term in the curly bracket on the right-hand side is Christoffel's symbol of the second kind. Gruber[3] has recently studied the problem and claims that the correct momentum operator is the Hermitian part of

$$P_{q_k} = -i\hbar \frac{\partial}{\partial q_k}.$$

This Hermitian part is given by

$$P_{q_k}^H = i\hbar \left(\frac{\partial}{\partial q_k} + \frac{1}{2g} \frac{\partial g}{\partial q_k} \right); \tag{2}$$

g is the Jacobian of the transformation (x, y, z) to (q_1, q_2, q_3).

In this paper we want to show that the representations of DeWitt and Gruber are equivalent.

To prove our assertion, all we have to show is that

$$\begin{Bmatrix} j \\ jk \end{Bmatrix} = \frac{1}{g} \frac{\partial g}{\partial q_k}. \tag{3}$$

Brillouin[4] has shown that

$$\frac{1}{g} \frac{\partial g}{\partial q_1} = \frac{1}{2} g^{jk} \frac{\partial g_{jk}}{\partial q_i}. \tag{4}$$

Now if we denote by $[sp, \gamma]$ the Christoffel symbol of the first kind, it is straightforward to see that