

DISCUSSION ON THE LAWS OF THERMODYNAMICS

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The discussion was in two parts: in the first, four provocative statements which had been submitted in advance were defended by their proposers, whilst the second was a discussion of the axiomatic foundations of thermodynamics. These foundations were a recurring theme at the conference and their place in the teaching of the subject was taken up again in the third discussion session.

In the first of the four provocations it was contended by T. Bidard (Paris) that Carnot's cycle is inadequate for the discussion of processes at high temperatures in which chemical reactions replace an external source as the origin of the heat supplied to the system¹. E. J. Le Fevre (London) agreed that this was so, but was no cause for surprise. He distinguished three types of device of interest to engineers. In the first, we put in heat, extract shaft work, and take out heat; in the second, we put in material, extract shaft work, and take out material; in the third, we put in reactive material, extract shaft work and, maybe, heat, and take out the products of the reactions. The Carnot cycle is relevant to the discussion of efficiency of the first, the concept of isentropic efficiency to the second, and that of availability to the third. He was supported by J. Kestin (Providence, USA) who said that the first of the three devices is only an artificially separated part of the third, which is all that engineers are ultimately interested in.

The second statement was made by A. J. Brainard (Pennsylvania, USA) who observed that the principle of maximum entropy does not apply to compound systems subject to internal constraints². He postulated a closed adiabatic cylinder containing two samples of gas at different pressures and temperatures separated by an adiabatic piston³. Initially the piston is held in position by a peg, and when this is removed the piston oscillates. Dissipative processes in the gases bring it to rest in a position in which the two pressures are equal. The final state of the system cannot be calculated by the methods of classical thermodynamics, although the pressure alone can be so calculated if the gases are perfect and have heat capacities independent of temperature. He showed, however, that ΔS is not a maximum (which would require a diathermal piston), nor is it as large as could be conceived with an adiabatic piston since such a value of ΔS requires that there is zero change of entropy on one side of the piston.

The results were not disputed. R. L. Scott (California, USA) said that Brainard's weaker conclusion was certainly no occasion for surprise, namely that the ΔS was not as large as that found with a different constraint, namely a diathermal piston. The final state is one of maximum entropy in the sense

that, once it has been achieved, a small arbitrary displacement of the piston causes S to increase. Kestin said that since a complicated flow pattern of gas develops during the approach to the final state the system is not describable within the implied assumption of uniform states, and so it is not surprising that the process cannot be described by the laws of classical thermodynamics alone.

As a postscript to this discussion Le Fevre said that Planck's views on the principle of maximum entropy were often misunderstood because of a fault in Ogg's translation. A correct version of Planck's text⁴ reads

The second law of thermodynamics thus says that in nature there exists, for every material system, a property such that for all changes in which the system alone participates, this property either remains constant (reversible processes) or increases (irreversible processes).

Ogg's version⁵ omits the words 'in which the system alone participates'.

In the third statement, C. Mascré (Paris) said that Lindemann's treatment of melting is not reconcilable with the zeroth law. He discussed a melting solid by means of the extensive function $S(U, V)$ and suggested that a common tangent to the solid and liquid branches in a plane of fixed V might have a slope $(\partial S/\partial U)_V$ different from the reciprocal of the absolute temperature of one of the phases if this phase has no metastable states. This contention was not accepted by L. Tisza (Massachusetts, USA), the reporter, and several others who maintained that the proper construction of Gibbs's primitive surface $S(U, V)$ is not a tangent in a plane of fixed V but a rolling tangent-plane. The discussion was brought to a close by the chairman's observation that if Lindemann's treatment of melting was irreconcilable with the zeroth law, then it was so much the worse for Lindemann's theory.

The final provocation was that of J. K. Tyldesley (Glasgow) who suggested that if the particles discussed in statistical thermodynamics were not molecules of fixed mass but were entities of variable mass then the techniques of that subject could, perhaps, be extended to discuss turbulent flow. He was supported by E. Ascher (Geneva), whilst Le Fevre thought that Burgers had already explored this extension forty years ago.

The second part of the discussion, on the proper role of axioms, was opened by M. W. Zemansky (New York), whose complaint was that those who put thermodynamics entirely on an axiomatic basis never made it clear where the physics came in. An experimentalist, when trying to explain his results in terms of a theory, is expected to make clear his mathematical assumptions, and will be rightly criticized if, say, his argument depends on a function being continuously differentiable and if he fails to make this clear. There is a reciprocal obligation on the part of the axiomatizers to say clearly where 'nature' enters into their system. Thus Landsberg's paper made no mention of work, which seemed to be anathema to him. The place of work and heat in the subject should be made clear, not concealed in this way. The chairman added that P. T. Landsberg (Cardiff) had used the word adiabatic repeatedly, and so had assumed implicitly the existence of what he called the (-1) th law, namely, that there are systems such that they can be changed only by doing work on them.

Landsberg protested that he was not himself an axiomatizer, he had

attempted only to review this approach to the subject. He admitted that axiomatics rarely yielded new science [a point later questioned by L. L. Whyte (London)], but said that nevertheless the search for axiomatic foundations was defensible. He cited Euclidean geometry as a case in point, for here the mathematics and the physics had been so mixed that the very possibility of non-Euclidean geometries had not been suspected until the nineteenth century. Similarly in thermodynamics the mathematics and physics are usually mixed in happy confusion, and it is very proper that some people should try to find the abstract mathematics that lies behind the subject as we know it.

He was supported by W. J. Hornix (Nijmegen, Netherlands) who pointed out that many have tried to reduce thermodynamics to mechanics, but have failed because the concept of heat defies such reduction. An axiomatic approach has made clear the reason for this by showing that an adiabatic process is necessarily a truly primitive term in thermodynamics; it cannot be derived from mechanics.

Tisza argued that all theories are axiomatic in some degree. We put in our axioms, we work on them, and we take out our theory. The real test of the worth of what we have done is the value of what we have added by this operation. [Had the reporter not been so busy scribbling, he would have said here that it has been generally accepted since the days of Kant that the conclusions of any formally valid argument are contained already in its premisses⁶. It follows that from a set of axioms we cannot extract a theory of greater content; we can only reveal what is already there, although this revelation can, of course, have greater value to us than the raw axioms.]

A. Katz (Rehovoth, Israel) regretted that the word adiabatic was being confined in this discussion to its thermodynamic use. He said that it had a closely related use in quantum mechanics. In a system in which the Hamiltonian is changing slowly the process is mechanically adiabatic if the system remains at all times in an eigenstate of the changing Hamiltonian. Such a process is also thermodynamically adiabatic. T. H. K. Barron (Bristol) objected to this conflation of the two ideas, and cited the case of a system of phonons whose dimensions could be changed. In a thermodynamically adiabatic process the occupation numbers change, whilst in a mechanically adiabatic process they do not.

A final diversion was introduced by Kestin who questioned whether the discussion of the thermodynamics of 'materials with memory' was a useful innovation. He said that the 'memory' of materials was not a property, but a state resulting from past actions on them. Every material, natural or artificial, is properly described by the thermodynamics of irreversible processes in terms of the concept of a local state specified by the appropriate internal variables. I. Müller (Templergraben) disagreed. He found the concept of memory to be useful in just the same way as the Navier-Stokes equations are useful as constitutive equations. They are not obeyed exactly but they are a useful idealization of the behaviour of real fluids. B. D. Coleman (Pennsylvania) closed the discussion by saying that it was his experience that materials such as molten polymers did not fit into Kestin's scheme; they were not describable by a finite (or even by a discrete) set of internal variables.

DISCUSSION REPORTS

REFERENCES

- ¹ R. Bidard, *Entropie*, No. 15, 13 (1967).
- ² H. B. Callen, *Thermodynamics*, pp 23 and 321. Wiley: New York (1960).
- ³ A. J. Brainard, *Nuovo Cimento*, **62B**, 88 (1969); *Chemical Engineering Education*, in press.
- ⁴ M. Planck, *Vorlesungen über Thermodynamik*, 10th ed., p 87. de Gruyter: Berlin (1954).
- ⁵ M. Planck, *Treatise on Thermodynamics*, translated by A. Ogg, p 88. Dover Publications: New York (n.d.).
- ⁶ F. P. Ramsey, *The Foundations of Mathematics*, p 185–188. Kegan Paul: London (1931).