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[1] J. Barnóthy and M. Forró, Phys. Rev. 55, 870 (1939).
[2] See Fig. 2 of the cited article.

The Second Law of Thermodynamics and Irreversible Processes

The two papers by Eckart in the *Physical Review* for August first permit a simple interpretation which amounts to an extension of the second law.

The conventional statement of the second law, when applied to irreversible processes, is that the entropy of an isolated system increases whenever an irreversible process occurs within it. No attempt is made to evaluate how much the increase of entropy may be under such circumstances, and in fact the precise evaluation of irreversible increases of entropy has always been considered to be beyond the power of methods thermodynamic in spirit, and to be rather the proper subject of statistical mechanics or kinetic theory. This accepted impotence of thermodynamics has always struck me as a surprising thing. It would seem that thermodynamics ought to be able to handle any system that is causally determined from the macroscopic point of view, that is, any system which can be adequately described in terms of operations with macroscopic instruments. This means that whenever the readings of the macroscopic instruments are repeated the future behavior of the system as measured with those same instruments repeats. The readings of the macroscopic instruments should then become the parameters for a complete treatment, thermodynamic in an extended even if not in the classical sense. Of course there are many processes which are so complicated that they cannot be adequately described in terms of a number of macroscopic variables small enough to be manageable, as in the efflux of a jet of gas from a nozzle, and it is not to be expected that systems in which apparent irreversibility thus arises from intractable complication will be completely amenable to any treatment. But there are many systems in which irreversible processes occur which are completely describable in terms of a few macroscopic parameters, and such systems should be amenable to an exact treatment, including an exact evaluation of the increase of entropy. Examples of such completely describable irreversible processes are: conduction of heat down a temperature gradient, development of Joulean heat when an electrical current flows against resistance; development of frictional heat when one solid rubs on another or in the interior of a viscous liquid; and when there is diffusion down a concentration gradient.

Sometime ago I proposed that a plausible extension of the second law to such completely defined irreversible processes was to postulate that whenever such a process occurs a corresponding characteristic increase of entropy occurs. Thus when an electric current i flows against a resistance r at absolute temperature θ there is an increase of entropy per unit time of $i^2 r/\theta$, and when the amount of heat Q drops by conduction through a temperature range $\Delta\theta$ there is a similar increase of entropy of $Q\Delta\theta/\theta^2$. I applied the equations to thermoelectric phenomena, and showed how the equations of Kelvin could be derived without illegitimately neglecting the irreversible aspects of the phenomena, as had been necessary in all previous treatments. In my book, *The Thermodynamics of Electrical Phenomena in Metals*, several other applications were given, particularly to deducing a relation between the Nernst and the Ettingshausen coefficients. I have also discussed the matter in a forthcoming book on the foundations of thermodynamics.

It is the purpose of this note to point out that Professor Eckart's equations can be written exactly in accord with this postulate of the extended second law. In general one must have: (increase of entropy in the region within a closed surface) plus (entropy which has flowed out of the region across the surface) equals (entropy generated by irreversible processes within the surface). The last term (entropy generated by irreversible processes within the surface) should be capable of precise formulation when the irreversible processes are well defined. Such is the fact in the cases considered by Professor Eckart. In his first paper the irreversible processes are thermal conduction and viscous motion of a fluid. His Eq. (15) on page 269 is:

$$(d/dt)\int\int\int_S m\eta \, d\tau + \int\int_S (1/\theta)\mathbf{q}\cdot d\sigma$$
$$= \int\int\int_S \{[k(\nabla\theta)^2]/\theta^2 + [(\mathfrak{p}\cdot\nabla)\cdot\mathbf{V}]/\theta\} d\tau.$$

In this equation the first term on the left is recognizably the increase in unit time of the entropy of the material within the surface S, the second term is the outward flow of entropy across the surface, the first term in the integrand on the right is the rate of increase of entropy due to irreversible thermal conduction within the region and the second is the increase of entropy due to frictional generation of heat in the viscously moving liquid. The latter is obviously the general expression for the characteristic rate of entropy increase in a moving liquid, and the first is the same as the expression I had already used, $Q\Delta\theta/\theta^2$. In Professor Eckart's second paper, Eq. (26) on page 272 contains the additional terms for the characteristic increase of entropy when there is diffusion in general. Professor Eckart has pointed out to me in correspondence that the expression for the increase of entropy due to diffusion is not separable into the sum of a term due to diffusion down a concentration gradient and another due to diffusion down a temperature gradient, but the two diffusion effects are cross connected. This suggests the necessity for detailed working out of the entropy increases, which is what Professor Eckart has essentially done, and by methods entirely macroscopic. That it can be done, constitutes the justification for the proposed extended formulation of the second law.

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