

Thomson's Dilemma

Unsuccessful thermodynamic treatment of heat conduction and resistance heating led William Thomson, later Lord Kelvin, to neglect these irreversible processes and still get satisfactory results for thermoelectric phenomena.

by Bernard S. Finn

APPLICATION of the second law of thermodynamics in its classical form requires that the heat of each process be convertible into work; that is, each process must be reversible. Since no real system meets this criterion, analysis is then made in terms of some imaginary limiting case in which the parameters have been adjusted to make the irreversible effects negligible. It is sometimes impossible, however, to imagine a limit in which the irreversible processes can be disregarded. This problem was first faced by William Thomson (later Lord Kelvin) in his thermoelectric researches. His dilemma was this: Even if he did ignore the irreversible processes, he found he could still apply the second law with what seemed to be very satisfactory results. This dilemma was sufficiently interesting to excite some of the best theoretical and experimental minds over the century that was to follow Thomson's work.

Forerunners

The prelude to Thomson's studies came in two independent developments. One had its origins in a series of four lectures, between August 1821

and February 1822, in which Thomas J. Seebeck described his experiments to the Berlin Academy. He found that heating one junction of two metals in a closed circuit could cause the magnetic deflection of a compass needle.¹ Others were quick to suggest that this "thermoelectric" effect was caused by electric currents set up in the loop. Seebeck also noticed that in some instances when the junction was hot enough, a reversal of the effect was produced.² James Cumming and Antoine C. Becquerel later reported the same reversal phenomenon, independently and in more detail.^{3,4} No satisfactory explanation was provided for this surprising result, largely because the basic Seebeck effect itself eluded interpretation. Indeed knowledge of reversal was lost for practical purposes for a quarter of a century. Meanwhile, Jean C. A. Peltier discovered the inverse of the Seebeck effect in 1834 (that current through a junction could produce or absorb heat).⁵

The second preliminary development came through the researches of French engineer Sadi Carnot, published in 1824.⁶ Carnot showed that the most efficient heat engine is one in which all of the heat available from each process of its operational cycle is converted into work—that is, one in which each process is reversible, since work is easily converted into heat. In any other engine the amount of available heat must decrease, or as Rudolf Clausius would put it, the entropy must increase. This statement, made in various forms, subsequently became known as the second law of thermodynamics. It can be stated as an equal-

ity (for reversible systems) or as an inequality (for irreversible systems).

Carnot further demonstrated that the amount of heat available from a heat engine is proportional to the difference between temperatures at the two ends of the chain of processes, multiplied by a function that depends on the specific heat of air (because temperature was defined in terms of an air thermometer). It was later assumed, notably by Julius R. Mayer and Clausius,^{7,8} that the inverse of Carnot's function was a linear function of the ordinary temperature scale.

James P. Joule and Thomson proved that this was very nearly true in a series of exacting experiments in 1854 that laid the basis for a definition of absolute temperature.⁹

A curious anomaly

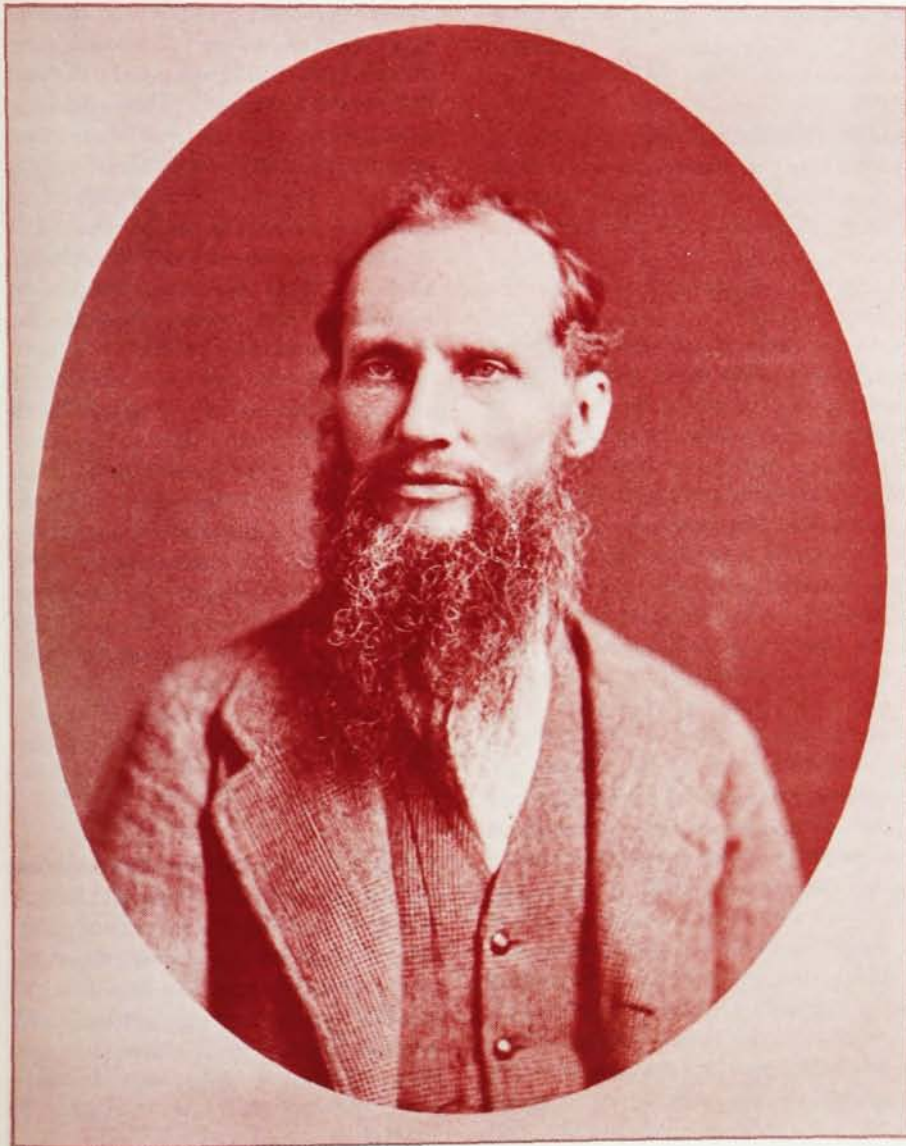
Thomson rescued Carnot's 1824 treatise from near obscurity in 1848. And in 1851 he resurrected Becquerel's peculiar thermoelectric reversal results of 1826. Joining them together gave a curious anomaly.¹⁰

Consider, with Thomson, a circuit of two metals with junctions at temperatures T and T_0 , differing by the small amount ΔT . This temperature difference produces a small voltage difference ϕ and a current i . By the conservation of energy, the rate at which work is done in the circuit ϕi divided by the mechanical equivalent of heat J must equal the rate at which heat is produced: from resistance heating $i^2 R$ and from the difference between the Peltier rates for heat given off at one junction and absorbed at the other $i\Delta\pi$ [or $i(d\pi/dT)\Delta T$]

The author received his PhD in the history of science from Wisconsin in 1963. He is curator in the division of electricity at the Smithsonian, and is managing editor of *Isis*, journal of the History of Science Society.



WILLIAM THOMSON (1824–1907): professor of natural philosophy in Glasgow until 1899, director of the Atlantic Telegraph Company, 1856, knighted in 1866, made a baron in 1892, buried in Westminster Abbey.



where π is the Peltier coefficient. Therefore

$$\frac{\phi i}{J} = i \frac{d\pi}{dT} \Delta T + \frac{i^2 R}{J}$$

At the same time, by Carnot's principle,

$$\phi = \mu \pi \Delta T$$

where μ is Carnot's function.

Thomson noted that the resistance-heating term was negligible for small currents; therefore the two equations could be combined to give

$$\phi = \mu \pi_0 \Delta T \exp \frac{1}{J} \int_0^T \mu dT$$

where π_0 is the Peltier coefficient (for the metals) at temperature T_0 . From data available Thomson was able to calculate values of μ ; these indicated that for a given temperature difference ΔT , ϕ should have increased slightly as the mean temperature was raised. Or, if Mayer's hypothesis was true, ϕ should have remained constant. This was clearly at odds with Becquerel's experiments; therefore Thomson concluded:

This result being at variance with known facts, the hypothesis on which it is founded must be false; and the author arrives at the remarkable conclusion that *an electric current produces different thermal effects, according as it passes from hot to cold or from cold to hot, in the same metal.*¹¹

Thomson went on to obtain this same remarkable conclusion from a consideration of the first law alone. In an ordinary thermoelectric circuit

heat is absorbed at the hot junction and emitted at the cold junction; heat is also emitted along the wire through resistance effects. But at the reversal temperature, where the two materials become thermoelectrically neutral, there is no longer an absorption of heat at the hot junction, seemingly causing a violation of the law of conservation of energy. This being unthinkable to Thomson, "*there must be a quantity of heat absorbed on the whole in the rest of the circuit.*"¹² In other words, there must be a net "convection of heat" against the temperature gradient produced by the electric current; in effect, electricity has a "specific heat."

Experimental evidence

There followed five years of intensive effort when Thomson searched for more direct experimental evidence of the predicted effect. Preliminary results appeared in 1854;¹³ conclusive evidence was presented in a notable experimental paper as the Bakerian Lecture of 1856.¹⁴ He concentrated initially on a circuit of iron and copper, from which the reversal evidence indicated that either positive electricity convected more heat in iron than in copper, or both. He confessed himself biased in favor of the first assumption and definitely against the third.

In a series of unsuccessful experiments he passed current through bars of various shapes, cooled at the two ends and heated in the middle, with thermometers monitoring the temperatures of the two sides. On 28 Oct. 1853 he obtained his first positive results with copper. Small temperature differences measured between the two sides indicated a "convection of heat in the nominal direction of the current." The data were, in fact, virtually inconclusive and no doubt his bias influenced such a quick judgement.

Three weeks later he obtained more definite data indicating that heat was convected in the direction of negative current in iron. At this point he decided that he should question his earlier results because:

I did not venture to draw from them so seemingly improbable a conclusion, as that the convection effects in copper and iron should be in contrary directions.¹⁵

But by March of 1854 more careful experimentation convinced him that this was exactly the conclusion that would have to be drawn.

Further experiments were performed comparing iron and copper with other metals. As a result he was able to list 13 metals in order of the relative size of their convective (Thomson) effects. It should be noted, however, that these were qualitative measurements and that he apparently made no attempt to obtain quantitative results.

Theoretical treatment

Treating the complete thermoelectric system theoretically, Thomson included the convective effect as a reversible process. But he now saw also that there were two irreversible processes at work: resistance heating and heat conduction along the wires. Unfortunately these could not be made negligible simultaneously; he neglected them anyway. The result was given in his 1851 paper in terms of Carnot's function.¹⁶ But in 1854 he had the Joule-Thomson experimental results, and what would become known as Thomson's equation was derived

$$\frac{dE}{dT} = J \frac{\pi}{T}$$

(E is the Seebeck voltage).¹⁸ Thomson made no attempt to check this experimentally, though he wrote "it would be extremely important to test ... [it] ... and so confirm or correct the only doubtful part of the theory."¹⁷

From the beginning he had been well aware of what this doubtful part was. In 1851 he wrote:

There is a degree of uncertainty in the present application of this [Carnot's] principle, on account of the conduction of heat that must necessarily go on from the hotter to the colder parts of the circuit, an agency which is not reversed when the direction of the current is changed. As it cannot be shown that the thermal effect of this agency is infinitely small, compared as with that of the electric current, unless γ [the current] be so large that the term $B\gamma^2$ [resistance heating], expressing the thermal effect of another irreversible agency, cannot be neglected, the conditions required for the application of Carnot's and

Clausius's principle cannot be fulfilled: The author therefore feels that at present this part of the theory requires experimental verification.¹⁹

This important question would be raised again whenever, in descriptions, systems include some energy flow in addition to heat flow. If there were irreversible phenomena associated with the two processes and if they could not be simultaneously made vanishingly small, was it fair to neglect them?

Boltzmann's contribution

Such concern was not, however, a major contemporary problem. There was a gap of about 30 years before anyone else attempted to attack the thermodynamics of thermoelectricity. This surprising lack of interest is matched in other fields—like chemistry—where the application of thermodynamics waited for additional theoretical work by Hermann L. F. von Helmholtz, J. Willard Gibbs and Ludwig Boltzmann. A few derivations were then published (notably by Hendrik A. Lorentz and Pierre Duhem^{20,21}) which included the basic Thomson assumption of separability. Then, in 1889, Boltzmann published an analysis that seemed to settle the matter once and for all.²²

Boltzmann started from thermodynamic expressions that included Peltier and Thomson effects, resistance heating and heat conduction. The last two are irreversible effects which, as Thomson had insisted, cannot simultaneously be reduced to zero. Therefore the second law does not hold. However, using the inequality form of the law, Boltzmann was able to arrive at the expression

$$\epsilon^2 T + [(\beta - b)\tau - eT] \epsilon + (b - \beta)\tau e + R\rho\tau^2 \geq 0$$

β and b are functions of T , related to Peltier and Thomson heat production in the two metals; R is the total resistance, τ is a small temperature increment, and ρ is defined as $fg/l + \phi\gamma/\lambda$. g and γ are heat conductivities; l and λ are lengths; f and ϕ are cross sections. Letting k and κ stand for electrical conductivities, he was able to show that

$$T \frac{dE}{dT} - J\pi \leq 2\sqrt{\frac{gT}{k}} + 2\sqrt{\frac{\gamma T}{k}}$$

If the heat conductivities were zero, Thomson's equation would hold. Such is never the case; in fact g is always large enough so that the above inequality represents no real limitation. As Percy W. Bridgman noted in 1919, "in nearly every case known"

$$2\sqrt{\frac{gT}{k}} + 2\sqrt{\frac{\gamma T}{k}}$$

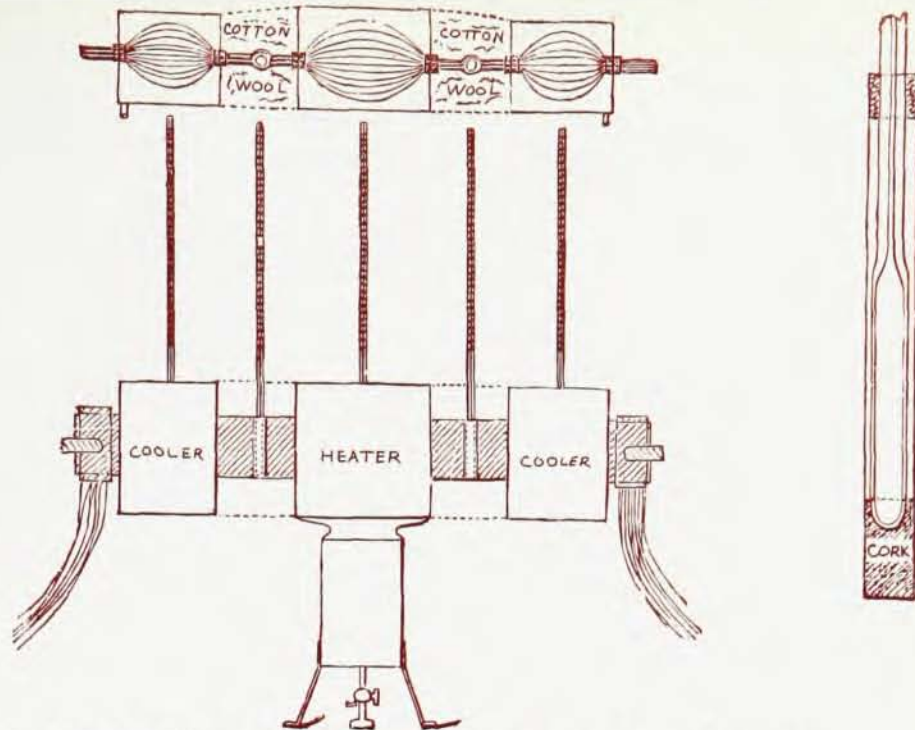
is greater than TdE/dT alone, and thus the inequalities must always hold since π always has the same sign as TdE/dT .²³

Boltzmann's results have been often cited as proof that Thomson's method cannot be justified by classical thermodynamics. A technique has been overlooked, however, which demonstrated that one might legitimately consider the various reversible processes and the two irreversible processes at the same time to yield an equation, not just an inequality. This was apparently first done by Max Planck in 1889, and shortly after by Henri Poincaré.^{24,25} In each case the irreversible changes due to resistance heating and heat conduction were considered and the inequality form of the second law was applied. A maximum condition could be produced by allowing the current to approach zero; therefore the derivative of the expression with respect to current would equal zero at zero current. When this operation was performed, the Thomson equation resulted. The Planck-Poincaré derivations are unsatisfactory in their treatments of heat conduction. But the method can be applied directly to Boltzmann's more complete analysis, with the following results:

Consider the first of Boltzmann's inequalities cited above, rewriting it as follows:

$$(\epsilon - e)[\epsilon T + (\beta - b)\tau] + R\rho\tau^2 \geq 0$$

If we allow ϵ to change so that it passes through the value of e , the first term changes sign, which means that the left-hand side of the inequality must pass through a maximum or minimum. Therefore the derivative with respect to ϵ of the left hand side of the inequality must equal 0 at $\epsilon = e$, or $eT + (\beta - b)\tau = 0$. This has obviously eliminated the heat conduction



THOMSON-EFFECT APPARATUS, 1853. The sample conductor is formed from sheets that are spread out to improve cooling and heating. This technique was used for the first copper and iron measurements.

term, and following through the rest of Boltzmann's analysis leads to Thomson's equation.

The derivations of Planck and Poincaré never entered the general literature on thermoelectricity (they were unmentioned in Bridgman's historical summary cited above) and certainly the method was never applied to Boltzmann's treatment. In part this omission may have been because there has never been any real concern over Thomson's inability to eliminate both irreversible processes in his derivation. Assuming all processes had been identified, it was plausible to treat heat conduction as part of a separate entropy system without demanding such rigor.

A new idea

On the other hand, it was also becoming apparent that perhaps all processes had not been named—and if the electric current were carrying heat, the heat flow might also be carrying an electric current.

In 1874, Friedrich W. Kohlrausch published the first suggestion of this further interaction,²⁶ though he gave credit for the idea to physiologist Ludimar Hermann; he had assisted Hermann in Zürich three years earlier in a series of conduction experiments.

The coordinate hypotheses that a current of electricity will "carry along" a current of heat and that a current of heat will "carry along" a current of electricity were the fundamental precepts of Kohlrausch's "Mitführungstheorie." In addition he assumed that the coefficients of interaction are linear and that for a given material they are in a fixed ratio, the constant of proportionality being the same for all materials.

Within a year Wilhelm Weber used the Mitführungstheorie to weave together his own particulate electrical theory and the kinetic theory of heat.²⁷ A moving stream of electrical particles would necessarily involve a translation of their kinetic energy; on the other hand, a temperature difference across a material would produce an imbalance in the kinetic energies of the constituent parts and any electrical particles free to move would do so in such a way as to produce a net electric current.

Such an approach provided a reasonable explanation for the Seebeck, Peltier and Thomson effects and it was much referred to in subsequent years, especially in Germany where the particle theory of electricity was popular. In 1898 Eduard Riecke, a former student of Weber's and his successor as

professor of physics at Göttingen, described an elaborate electron Mitführungstheorie from which the linear relationship between the interaction constants was derived.²⁸

Riecke assumed that there were both positive and negative particles free to flow in a conductor with velocity proportional to the square root of the absolute temperature. He allowed the number of particles available and their mean free path to be, in part, linearly dependent on the temperature. He was then able to calculate expressions for the Mitführungs constants: η for the heat flow produced in an electrical gradient, and ω for the electrical current produced in a thermal gradient. Since we are not primarily concerned with the development of electron theories I shall simply note that by assuming the temperature variation of the various parameters to be small and by adjusting a factor in the equation for the number of particles, Riecke obtained the relationship:

$$\frac{\omega}{\eta} = \frac{\gamma J}{\kappa T}$$

(γ is the electrical conductivity and κ is the heat conductivity). If we accept the validity of the Wiedemann-Franz-Lorenz law, $\gamma/\kappa T$ is constant; hence ω is constant, which was the Kohlrausch assumption.

Fundamental principle

Therefore, by the 1890's the notion of interacting electrical and thermal currents was well established, at least in Germany. But none of the physicists mentioned attempted to incorporate it as a fundamental principle in the thermodynamic derivation of Thomson's equation. This step was taken by a young graduate of Berlin, teaching at Leipzig, named Otto Wiedeburg.²⁹ His method of attack was in many respects identical to the familiar one Lars Onsager would take a third of a century later. Systems were analyzed in terms of quantities M and intensities J . The flow of a quantity was dependent on *all* of the intensities, and the coefficients were assumed to be linear. For thermal processes the quantity was entropy S (a major difference from Onsager who uses heat energy), and the intensity was temperature θ . Therefore, for a system

with a temperature difference as well as some other intensity gradient, he could write the following equations, where c and g are material constants and where only reversible processes are considered

$$dS = c_\theta d\theta - g_{\theta,M} dM$$

$$dM = c_J dJ - g_{J,S} dS$$

But, he noted, the energy equation for the system is

$$dE = JdM + \theta dS$$

Therefore, by Maxwell's thermodynamic relation

$$\frac{\partial J}{\partial S} = \frac{\partial \theta}{\partial M}$$

Applying this to the two equations for dS and dM gives directly

$$\frac{g_{\theta,M}}{c_\theta} = \frac{g_{J,S}}{c_J}$$

which is the equivalence of the interaction coefficients.

To extend his treatment into the range of irreversible phenomena, Wiedeburg added three terms to his energy equation: one proportional to the square of the entropy current, another proportional to the square of the other current (electrical in the thermoelectric case) and a third proportional to the product of the two currents. Applying this addition to the thermoelectric situation and assuming that the interaction coefficients were equal, Wiedeburg was able to derive Thomson's equation.

Surprisingly, nothing of Wiedeburg's approach to thermodynamics seems to have penetrated the literature of the subject, even to the point of being commented upon. In part this omission may be because Wiedeburg died soon after the above papers were written, at the age of 34. More fundamentally, it is probably owing to the novelty of the approach that did not offer any particular advantages, at the time, over the older and simpler method. The assumption of equal interaction coefficients, for instance, would have seemed no more plausible than the validity of Thomson's separation of effects. It is to be noted that a similar lack of enthusiasm greeted Onsager's work.

Onsager, a Norwegian who emigrated to the United States in 1928, approached the problem as a chemist.

In the landmark papers that he published in 1931, he analyzed steady-state systems in terms of forces X and corresponding currents J assuming the coefficients relating them to be linear.³⁰ Allowing for interactions to take place, the Onsager equations look like this

$$J_1 = L_{11}X_1 + L_{12}X_2 + L_{13}X_3 + \dots$$

$$J_2 = L_{21}X_1 + L_{22}X_2 + L_{23}X_3 + \dots$$

$$J_3 = L_{31}X_1 + L_{32}X_2 + L_{33}X_3 + \dots$$

(L_{ij} represents the conductivity coefficients for J_i under the influence of force X_j).

Basic to Onsager's initial treatment was the principle of microscopic reversibility: that under conditions of equilibrium there is equal probability of two molecular processes taking place if one is the reverse of the other. He drew an analogy from chemistry where a detailed balance is assumed when there is more than one reaction. Thus if a system can exist in the three conditions at equilibrium A, B, C, thermodynamics does not disallow



but the principle of microscopic reversibility would prefer that this be the case:



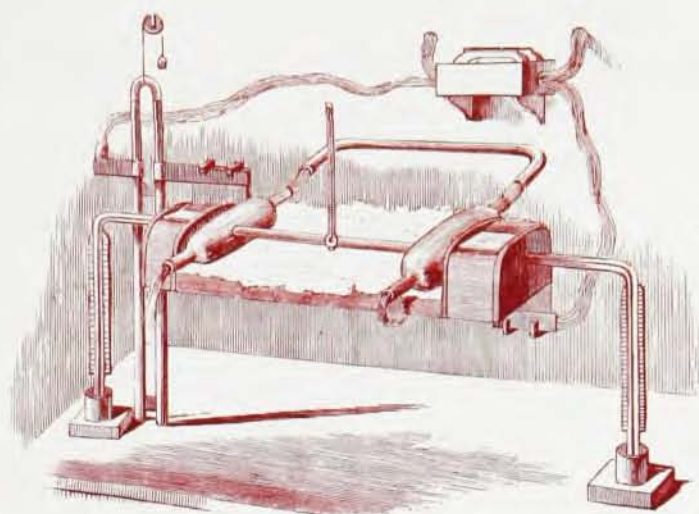
In the system of forces and currents considered by Onsager the application of this principle leads to the conclusion that L_{ij} must equal L_{ji} . Onsager then supported this analogy in his second paper by considerations based on statistical mechanics. When Onsager's assumptions were applied to thermoelectricity, one of the results was Thomson's equation.

What has it meant?

Thermoelectricity has played a fundamental role in the history of thermodynamics. In the 1850's it hovered over the birth of the new science much as a midwife, providing both Thomson and Clausius with a suitable agent for testing the power of the new approach. At the same time it suggested to Thomson that there were certain fundamental difficulties with the applica-

tion of Carnot's law; and these difficulties would be probed time and time again over the next several decades, almost always in terms of their thermoelectric problem.

It is often understood that Onsager provided the solution to the Thomson problem. But this is not strictly true.³¹ The two men made different assumptions about the nature of the processes taking place. Out of a thermodynamic necessity Thomson had to assume that there was an interaction whereby an electric potential could produce a convection of heat; and he was later able to prove its existence experimentally. His concern was over the irreversible processes represented by heat conduction and resistance heating, which he could not successfully treat thermodynamically; he therefore had to assume that they could be neglected as unimportant. Planck and Poincaré later presented a method for including these phenomena in a thermodynamic treatment, and it is they who really resolved Thomson's dilemma. (More recently the same goal has been sought in slightly different fashion by Bridgman³² and Richard C. Tolman and P. C. Fine.³³)



THOMSON-EFFECT APPARATUS, 1855.

Onsager's point of origin was quite different. He assumed that as a matter of course there might be interactions between all potential differences and flows in a system. On the basis of microscopic considerations (chemical equilibrium and statistical mechanics) he was then led to the conclusion that the reciprocal interaction coefficients should be equal. It turned out that this led to Thomson's equation.

It is interesting to note the interplay between macroscopic and microscopic thought throughout this development.

Through an intuition of microscopic effects Thomson separated out those processes that he wished to disregard in his macroscopic-thermodynamic-treatment. But a prime result of this macroscopic theory was the prediction of the Thomson effect, which became a fundamental building block of the electron theories of Weber and others. This rapid development of such approaches toward the end of the century focused attention on the possibility of interaction coefficients of Wiedeburg and Onsager.

References

1. T. J. Seebeck, *Abhandl. deut. Akad. Wiss. Berlin*, p. 265 (1822-23); *Ann. Physik* **6**, 1, 133, 253 (1826); *Ostwald Klassiker* **70**, Leipzig (1895).
2. *Ibid.*, (Abhandlungen) pp. 316, 353.
3. J. Cumming, *Thomson's Annals of Philosophy* **6**, 321 (1823).
4. A. C. Becquerel, *Ann. Chim. Phys.* **31**, 371 (1826).
5. J. C. A. Peltier, *Ann. Chim. Phys.* **56**, 371 (1834); *L'Institut* **2**, 133, 265 (1845).
6. S. Carnot, *Reflexions sur la Puissance Motrice du Feu*, Paris (1824); English translation (E. Mendoza, ed.) Dover, New York (1960).
7. J. R. Mayer, *Annalen der Chemie und Pharmacie* **42**, 233 (1842); *Phil. Mag.* **24**, 371 (1862).
8. R. Clausius, *Ann. Physik* **79**, 368, 500 (1850); *Phil. Mag.* **2**, 1, 102 (1851); *Ann. Chim. Phys.* **35**, 482 (1852); *Op cit ref. 6*.
9. J. P. Joule, W. Thomson, *Proc. Roy. Soc. 7*, 127 (1855); *Phil. Trans. Roy. Soc.* **144**, 321 (1854); *Ann. Chim. Phys.* **65**, 244 (1862); W. Thomson, *Mathematical and Physical Papers I*, Cambridge (1882), p. 357, 433.
10. W. Thomson, *Proc. Roy. Soc. Edin.* **3**, 91 (1857); *Phil. Mag.* **3**, 529 (1852); *Mathematical and Physical Papers I*, Cambridge (1882), p. 316.
11. W. Thomson, *Mathematical and Physical Papers I*, Cambridge (1882), p. 319.
12. *Ibid.*, p. 321.
13. W. Thomson, *Proc. Roy. Soc.* **7**, 49 (1855); *Phil. Mag.* **8**, 62 (1854); *Op cit ref. 11*, p. 460.
14. W. Thomson, *Proc. Roy. Soc.* **8**, 50 (1856-67); *Phil. Trans. Roy. Soc.* **146**, 649 (1856); *Phil. Mag.* **12**, 393 (1856); *Ann. Chim. Phys.* **54**, 105 (1858); *Mathematical and Physical Papers II*, Cambridge (1884), p. 189, 396.
15. W. Thomson, *Mathematical and Physical Papers II*, Cambridge (1884), p. 219.
16. *Op cit ref. 10*.
17. W. Thomson, *Proc. Roy. Soc. Edin.* **3**, 255, (1857); *Trans. Roy. Soc. Edin.* **21**, 123, (1857); *Phil. Mag.* **11**, 214, 281, 433, (1856); *Op cit ref. 11*, p. 232, 324.
18. *Op cit ref. 11*, p. 250.
19. *Ibid.*, p. 318.
20. H. A. Lorentz, *Verslagen en Mededeelingen der Koninklijke Akademie van Wetenschappen* **1**, 327 (1885); *Arch Néerl.* **20**, 129 (1886).
21. P. Duhem, *Ann. Chim. Phys.* **12**, 433 (1887).
22. L. Boltzmann, *Sitzber. Wien. Math. Natur. kl. Wien. Abt. II* **96**, 1258 (1888).
23. P. W. Bridgman, *Phys. Rev.* **14**, 315 (1919).
24. M. Planck, *Ann. Physik* **272**, 627, 936 (1889).
25. H. Poincaré, *Thermodynamique*, Paris (1892), p. 356.
26. F. W. Kohlrausch, *Nachr. Ges. Wiss. Göttingen*, p. 65 (1874); *Ann. Physik* **156**, 601 (1875).
27. W. Weber, *Ann. Physik* **156**, 43 (1875).
28. C. V. E. Riecke, *Nach. Ges. Wiss. Göttingen*, p. 48, 137 (1898); *Ann. Physik* **66**, 353, 545, 1199 (1898).
29. O. Wiedeburg, *Ann. Physik* **61**, 705 (1897); **62**, 652 (1897); *Ann. Physik* **1**, 758 (1900).
30. L. Onsager, *Phys. Rev.* **37**, 405 (1931); **38**, 2256 (1931).
31. J. C. M. Li, *J. Chem. Phys.* **29**, 747 (1958).
32. P. W. Bridgman, *Phys. Rev.* **58**, 845 (1940); *The Nature of Thermodynamics*, Cambridge (1941), p. 136.
33. R. C. Tolman, P. C. Fine, *Rev. Mod. Phys.* **20**, 51 (1948). □