## Clausius, Rudolf | Encyclopedia.com

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(b. Köslin, Prussia [now Koszalin, Poland], 2 January 1822; d. Bonn, Germany, 24 August 1888),

physics.

After receiving his early education at a small private school that his father had established and was serving as pastor and principal, Clausius continued his studies at the Stettin Gymnasium before entering the University of Berlin in 1840. Although strongly attracted by <u>Leopold von Ranke</u>'s lectures in history, he settled on a career in mathematics and physics, completing his doctor of philosophy degree at Halle in 1847.

His famous paper on the theory of heat (1850) led to his first major teaching position at the Royal Artillery and Engineering School in Berlin; his ensuing publications resulted in an invitaion to be protssor of mathematical physics at the new Polytechnicum in Zurich in 1855. In Zurich he joined a faculty which would soon number among its younger members Richard Dedekind in mathematics, Gustav Zeuner in mechanics, and Franz Reuleaux in machine design; Albert Mousson taught experimental physics and became Clausius' lifelong friend. During Clausius' years at Zurich, he enjoyed frequent visits with John Tyndall, whom he had first met in 1851 as a fellow member of the circle of students gathered about Gustav Magnus in Berlin.

In 1867 Clausius accepted a professorship at the University of Würzburg. (He expressed regrets at leaving Zurich but longed to return to Germany.) He moved on to Bonn two years later, remaining there for the rest of his life and serving as rector of the university during his final years. Clausius received many scientific honors; he was elected an honorary member of numerous scientific societies and received many awards, of which the most notable was the Copley Medal of the Royal Society in 1879.

Clausius' major contributions to physics seem to have come predominantly during the years prior to his going to Bonn, and two events may have hampered his later life as a scholar. He was wounded in 1870 while leading a student ambulance corps in the France-Prussian War and suffered continuing pain from that injury. More tagically, he had to assume sole responsability for the care of his family in 1875, when his wife died while giving birth to their sixth child; he did not remarry until 1886, shortly before the close of his career.

The significant beginning of that career, of course, dates from 1850, when Clausius established the foundations for modern thermodynamics in his first great paper on the theory of heat, "Ueber die bewegende Kraft der Warme," but several earlier papers are of interest as a revealing prelude to that major work. In one paper, dealing mainly with the problem of reflected light in the sky, Clausius' distinctive approach to many physical questions was already apparent: an excellent grasp of the fundamental facts and equations relevant to the phenomena, a microscopic model to account for them, and an attempt to correlate the two with mathematics. For example, Clausius imagined that the blue color of the sky arose from the preferential reflection of blue light from thin films of water. He postulated, therefore, the existence of water bubbles in the earth's atmosphere and investigated mathematically the requisite conditions of number, size, and thickness. Expressing a similar type of approach in another early paper, Clausius proposed that changes in molecular arrangement might explain certain anomalies encountered in the experimental study of elastic solids. In fact, that paper may mark the beginning of the line of thought which led to his rejection, in 1850, of the caloric theory in favor of the new principle of the equivalence of work and heat, for in his consideration of the possible microscopic explanations of these anomalies he criticized several proposals that were based on the concepts of free and bound molecular heats, concepts fundamental to the prevailing view.

Two ideas were central to the caloric theory: (1) the total heat in the universe is conserved and (2)the heat present in any substance is a function of the state of that substance. In thermodynamics the state of a simple homogeneous substance is defined by any two of the three variables, pressure, volume, and temperature; and any property that is similarly determined, and thus called a function of state, is subject to a certain well-developed mathematical treatment. It was therefore the second assumption—that the heat present in a substance is a function of the state of that substance—which transformed the caloric theory from a vague supposition about an imponderable fluid to a sophisticated mathematical system in which permanently valid relations could be derived. For example, Poisson was able to establish the correct pressure and volume relation for the adiabatic expansion of gases, and Clapeyron, the variation of vapor pressure with temperature.

The caloric theory further provided a conceptual framework for explaining the behavior of gases and vapors in terms of a distinction between free and latent states of heat. Free heat could be sensed and measured by a thermometer; <u>latent heat</u>, however, because it was intimately bound to the molecules, could not. Therefore, the temperature of a gas rose when it was compressed because part of the bound <u>latent heat</u> apparently was squeezed free. Clausius not only denied the fundamental

assumptions of the caloric theory but also provided a new mechanical explanation for the traditional concepts of free and latent heat.

The denial was based, of course, on what has become the first law of thermodynamics—that whenever work is produced by heat, a quantity of heat equivalent to that amount of work is consumed—a premise that Clausius believed had been firmly established by Joule's experiments. The total heat in the universe, therefore, could not be conserved; and the usual concept of heat in a substance, representing the total heat added to that substance, could no longer be considered a function of state. In Clausius' reinterpratation, the only kind of heat that could have any real existence in a substance was the free heat; and free heat was understood as the *vis viva* (kinetic energy) of the fundamental particles of matter and the determiner of temperature. Latent heat, in contrast, was heat that no longer existed, having been destroyed by conversion into work—internal work against intermolecular forces and external work against the surrounding pressure. Clausiusus made an important distinction between these two forms of work: The internal work, being determined by molecular configuration, is a state function, subject solely to the initial and final conditions of change; the external work, however, depends on the conditions under which the change occurs.

In 1850 Clausius did not give mathematical expression to these interpretive ideas of heat in a body and internal work but rather simply illustrated them with an explanation of the vaporization of water; they did, however, form the conceptual framework for his theory of heat. Even in the final edition of *Die mechaniche Wärmetheorie*, which appeared in 1887, he still introduced the first law of thermodynamics as

$$dQ = dH + dJ + dW,$$

where the increment of heat dQ added to a body is equal to the sum of the changes in the heat in the body dH, the internal work, dJ, and the external work dW. Only after confessing ignorance of the exact expression for the internal work dJ did Clausius introduce the classic thermodynamic expression

$$dQ = dU + dW$$
,

in which U was simply the energy in the body, without any attempt to differentiate that energy into molecular forms. The function U played a very important role in the new mechanical theory of heat, and it was Clausius who introduced this new state property into thermodynamic thought, another major contribution of his 1850 paper.

Clausius' manner of establishing the function U as a state property of a substance reveals another distinguishing characteristic of his thought. In his approach to the theory of heat, general concepts should not be dependent upon particular molecular models because those very concepts form the structure within which models must operate. Hence, although Clausius could have introduced the function U simply as the sum of H and U (as he did later in his developed theory), he chose to assure complete generality for his original derivation in 1850 by employing an extremely tedious analysis of an infinitesimal Carnot cycle. It was just such an approach, independent of moleular as sumptions, that became normative in thermodynamic thought.

For example, when Kelvin developed his dynamical theory of heat in 1851, he did not explain the function U in terms of molecular energy states. He simply argued that since Q and W must be equal whenever a substance undergoes a full cycle of changes, a consequence of the theorem of the equivalence of work and heat, and since every function that is characteristic of a substance shows no net change in a cycle, Q-W must represent some new function of the substance. Thus, he approached the question purely on the macroscopic level and coined the name "intrinsic energy" for U, since it represented the total mechanical work that might be theoretically obtained from the substance.

Clausius, of course, had discovered the function U a year earlier than Kelvin, but he had never given it a name. The reason is clear: The heat in body H and the internal work J were his fundamental concepts. For example, in order to simplify the function U for gases and to derive Poisson's equation for the adiabatic behavior of gases, he argued that intermolecular forces are negligible in gases because of the relative uniformity of their pressure, volume, and temperature relations. He was able, therefore, to reduce the function U to the heat absorbed at constant volume and demonstrated that this heat could only depend on the temperature. Such a simplification of the function U normally requires the use of the second law of thermodynamics, but Clausius originally proposed the idea solely on the basis of the first law and his molecular model for heat and internal work. That model for heat perhaps also provided the rationale for his brilliant revision of the traditional Carnot argument in thermodynamics, a revision that made it possible to incorporate the most significant results of the caloric theory within the new theoretical structure.

It was the idea of a universal function of temperature, introduced by Carnot but fully developed only by Clapeyron, that had proved the genius of the caloric theory. The idea depended on Carnot's theorem that all ideal engines must produce equal amounts of work with equal amounts of heat when operating between the same temperatures, whatever the substance being employed. The proof was an indirect one—that is, denying the premise would lead to a contradiction of the traditional mechanical principle that work cannot be created from nothing. In the mechanical theory of heat, however, there would no longer be a contradiction of that principle, since any work produced must be accompanied by the disappearance of an equal quantity of heat. Some other principle would have to be contradicted. Clausius rearranged the traditional argument so that any denial of the premise would require that heat be transferred from a colder to a warmer body, a conclusion which Clausius

stated would be an obvious deviation from the normal behavior of heat. Clausius was therefore able to derive Clapeyron's equation for the universal temperature function C and to continue Clapeyron's fruitful handling of vapor-liquid equilibrium. Using his assumption that internal forces are absent in gases, he established the relation.

$$C = A(a + t)$$
,

where A is the mechanical equivalent of heat and a the coefficient of expansion for gases. Clausius did not introduce the symbol T for this universal function of temperature (a + t) until his second important paper, "Ueber eine veranderte Form des zweiten Hauptsatzes der mechanischen Wärmetheorie," in which he developed the concept of entropy.

Clausius did not propose the name "entropy" at this time, calling the new theorem simply the principle of the equivalence of transformations. This accorded well with the unique engine cycle that he had conceived to establish the theorem, a cycle portraying two important types of transformation: a conversion of heat into work at one temperature and a transfer of heat from a higher to lower temperature. The two transformations were called equivalent because they could replace one another. For example, suppose that the transfer of heat had occurred. By operating the cycle in reverse, Clausius argued, the heat could be restored to its original temperature and there would be a conversion of work into heat. Clausius, by assigning positive transformation values to these processes and equal negative values to their opposites, established by his modified Carnot argument that the transformation values could only be universal functions of heat and temperature, Qf(t) and  $Q_1F(t_1, t_2)$ .

Clausius still had to establish the nature of the function  $F(t_1,t_2)$ . By combining several cycles, he demonstrated that the transformation value for a flow of heat could be reduced to the same form as a conversion of heat into work, namely,

$$Q_1F(t_1, t_2) = -Q_1f(t_1) + Q_1f(t_2),$$

so that every exchange of heat could be treated identically. The sum of transformation values for his cycle therefore, was simply the sum of Qf(t) at all temperatures; and, since the cycle consisted of a transformation plus the inverse of its equivalent,

$$\sum Qf(t) = 0$$
.

Extending the relation to any reversible cycle, Clausius created a new function of state,

$$\int dQ/T = 0$$
.

The complexity of this derivation should appear strange to a modern mind, for we see no essential difference between the heats occurring at t,  $t_1$ , and  $t_2$  in Clausius' original cycle and wonder why he differentiated them. The occurrence of  $Q_1$  at both  $t_1$  and  $t_2$  should not necessitate treating those heats as any more functionally related than the heat at t. Undoubtedly, Clausius was still under the influence of the caloric theory, in which the work accomplished by an engine cycle was supposedly caused by the fall of heat. His derivation of the new function of state,  $\int dQ/T$ , put this remaining idea at an end.

Actually, his proposed new function was not unique with Clausius, for Rankine had introduced a similar function; and suggestions of such a relation also appeared in Kelvin's thought. Clausius made his distinct in Kelvin's thought. Clausius made his distinct contribution by considering the case of irreversible processes. He concluded that since a negative transformation value would correspond to a flow of heat from a lower temperature to a higher temperature, contrary to the normal behavior of heat, the sum of transformation values in any cycle could only be zero (reversible) or positive (irreversible). He later capsuled this idea in his famous couplet for the two laws of thermodynamics: "Die Energie der Welt ist constant; die Entropie strebt einen Maximum zu."

Clausius often called upon this theorem of transformation values when challenged to defend the principle on which it was based, that heat cannot of itself (von selbst) go from a cold body to a hot bosy. For example, when Gustav Hirn proposed an intriguing thought experiment in which a gas would be heated beyond 100½C. by using a source of heat at 100½, Clausius showed that the net transformation value for the process would nonetheless be positive and therefore would not contradict his fundamental principle. The most rabid and persistent critic of that principle was the controversial Peter Guthrie Tait of Edinburgh.

Their clash was perhaps inevitable. Both were chauvinistic; both were involved in the Tait-Tyndall dispute over the relative priority claims of Joule and Julius Mayer to the discovery of equivalence of work and heat. Clausius, having innocently become involved by sending Tyndall, prior to the controversy, the complete set of Mayer's publications (at Tyndall's request), did not remain neutral. He affirmed Mayer's priority and claimed that Mayer had thus secured for Geremant a national priority as well <sup>5</sup>

This was not the first occasion on which Clausius championed German achievements against apparent British infringements. For example, in 1856 he criticized William Thomson for quoting an earlier letter from Joule containing Joule's suggestion that Carnot's function C might be the absolute gas temperature. Clausius reminded the English that a German, Karl Holtzmann, had been the first to establish that relationship in 1845 and then proceed to recount his own more recent contributions as well.

In 1872, how-ever, when Clausius began his bitter controversy with Tait by claiming that the British seemed intent on claiming more than their rightful share of the theory of heat, <sup>7</sup> he was arguing for recognition of his rights alone.

Their first exchanges appeared in the *Philosophical Magazine* but the continuing argument entered the prefaces and appendices of the various editions of their books. Clausius appears to have rebutted every denial of his axiom that Tait could muster. For example, Tait finally argued, perhaps in some desperation, that Maxwell's demon could contradict Clausius' principle by separating the faster molecules from the slower molecules. The German replied that his principle concerned what heat *von selbst* might do-and not with the help of demons.

The immediate occasion for Clausius' comments in 1872 on the British approach to the theory of heat was the appearance of Mazwell's *Theory of heat* in which the word "entropy" following Tait, was associated with the available energy in a system. This was directly contrary to Clausius' own interpretation of his concept, and Maxwell responded by making certain revisions in his treatment. Maxwell had been more knowledging his debt for certain fundametal ideas in the kinetic theory of gases, he hailed Clausius as the founder of a new science.

Clausius' first venture into the kinetic theory was "Ueber die Art der Bewegung, welche wir Warmenennen," and his image of molecular motion went far beyond the "billiard ball" model of such previous writers as Kronig. He ascribed rotatory and vibratory, as well as translational, motion to the molecules, a complexity that led to an important conclusion. The conservation of translational kinetic energy in collision could no longer be assumed, because collisions might cause transformations of one form of motion into another. Quite obviously, Clausius argued, the idea of a constant equal velocity for all molecules must be untenable. By supposing that translational velocities would vary among the molecules, Clausius offered an explanation for the evaporation of a liquid. Since only molecules with higher than average velocities possess sufficient kinetic energy to escape the attractive forces of the liquid temperature.

In his discussion of the complexity of molecular motions, Clausius did not merely suggest that motions other than translational were a possibility; he demonstrated that such motions must exist by showing that transwlational motion alone could not account for all of the heat present in a gas. He began, of course, by deriving the fundamental equation in the kinetic theory of gases,

$$3/2, pv = nmu^2/2,$$

which related the pressure p the volume v the number of molecules n their mass m and the average velocity u. The total translational kinetic energy K therefore was  $3/2 \cdot pv$ . The total heat H however, corresponding to the heat added at constant volume to an ideal gas (intermolecular forces being negligible), was [c/(c'-c)]pv where c was the heat capacity at constant pressure, the ratio of translational energy to total heat was therefore

$$K/H = 3/2(c'/c-1);$$

and since the <u>specific heat</u> ratio was known to be about 1.42 for simple gases, the translational energy *K* could be only a fraction of the heat. Other motions, Clausius maintained, must therefore exist in the molecular realm. Thus he established the first significant tie between thermodynamics and the kinetic theory of gases.

This 1857 paper also marked another important beginning in physical theory, for it presented the first physical argument in support of Avogadro's hypothesis that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. Clausius argued that if it were assumed that all types of molecules possess the same translational energy at equal temperatures, then, since all gases have the same relationship between pressure, volume, and temperature and pressure, volume and temperature, they would necessarily contain equal numbers of molecules in equal volumes at the same temperature and pressure. Avogadro's hypothesis, therefore, found support in the mechanical theory of heat, independently of the usual chemical arguments.

When, however, Clausius began to treat the chemical evidence in order to argue the case for diatomic molecules, it is surprising to learn that he apparently thought he was the first to make that suggestion. For example, he italicized his statement of Avogadro's hypothesis as though it were completely new and, in a note later appended to the paper, admitted that it was only upon reading comments by Verdet and Marignac that he learned of similar views advanced earlier by Dumas, Laurent, and Gerhardt. Still later he wished to claim, in a note added in 1866 to his paper on ozone, that he was the first to state unequivocally that the oxygen molecule was diatomic, arguing that Gerhardt sometimes wrote his formula 0<sup>3</sup>0 and sometimes 00. Fortunately, no such priority concerns ever colored his second important paper on kinetic theory. "Über die mittlere Lange der Wege," for there he developed the idea of the mean length of path of a moving molecule, an idea no one else could claim.

The occasion for Clausius' investigation of the progress of molecular collisions was the objection raised against the kinetic theory of gases by Buys Ballot: that if molecules actually possessed the velocities ascribed to them, the diffusion of gases should occur practically instantaneously. Clausius replied that the apparent discrepancy could be explained by assuming that collisions occur so frequently among the molecules that their forward progress is continually interruped.

In order to analyze the process, Clausius adopted a simplified model for his admittedly complicated molecule. He assumed that whatever the actual patterns of intermolecular forces, one could suppose that there is some average distance between the centers of molecules which would represent a general boundary between attractive and repulsive forces. If two molecules were to approach each other within that boundary, repulsion would generally occur. Thus the very complex problem of intermolecular action was reduced to a "billiard ball" model.

In order to derive an expression for the average path of a molecule between collisions, Clausius imagined only one moving molecule, with the remainder fixed in an essentially lattice framework, and set the probability of a collision proportional to the fraction of area cut off by the repulsive spheres of action. He found that for this hypothetical case, the mean length of path would be  $\lambda 3/\varrho 2$ , where is the average distance between the stationary molecules in the lattice framework and  $\varrho$  is the radius of the repulsive collision sphere about each molecule. It was only when Clausius considered the true case of all molecules in motion that he came upon an apparently significant relationship. Thus, after stating (without giving the detailed proof) that the true mean length of path would be reduced by a factor of 3/4 because the relative velocity is 4/3 the actual average velocity, Clausius found the surprising consequence that

where *l* is the mean free path. it appeared, therefore, that a neat relationship existed, the radio between the mean length of path and the radius of the collision sphere being equal to the ratio of the average space between molecules and the volume of the collision sphere for each molecule. Perhaps Clausius found this unexpected result to be a guarantee of the validity of his approach, for he rather abruptly challenged Maxwell for proposing a change in 1860 and completely failed to grasp, the significance of the new direction in Maxwell's reasoning.

The controversy concerned Maxwell's first brilliant paper on the kinetic theory of gases, in which he proposed his famous law for the distribution of velocities among colliding spherical molecules. By using this new distribution function, Maxwell was able to establish that the mean relative velocity between molecules would be larger than their average velocity by a factor of Clausius, apparently considering this an affront to his own claims, sent a very curt note to the *Philosophical Magazine* in which he detailed how he had derived 4/3, thus ignoring completely that Maxwell had adopted a wholly new approach. Maxwell never replied publicly; but he did note somewhat ironically to Tait, in recounting the history of the question, "Clausius supposing Maxwell's knowledge of the integral calculus is imperfect writes to Phil Mag showing how to do the integration on the assumption U = const." For some strange reason, Clausius never did adopt Maxwell's distribution function and continued to operate with a uniform velocity.

Clausius later gave more careful scrutiny to Maxwell's arguments and found an error that Maxwell was to admit as far more serious. <sup>12</sup> In his initial approach to the conduction of heat in gases, Maxwell drew a brilliant analogy between diffusion (a transfer of mass) and conduction (a transfer of kinetic energy), thereby making it possible to use the form of his diffusion equation to represent conduction, simply replacing the mass of a molecule with its kinetic energy. Clausius criticized this adoption of the diffusion equation, because, given the assumptions, mass transfer would accompany the heat conduction and the process would not be one of energy transfer alone. He then offered a revised theory of conduction that was more painstaking than brilliant, its only net result being replacement of a factor of 1/2 with 5/12. No further significant contributions to kinetic theory came from Clausius' pen, as he turned his thought to understanding the second law of thermodynamics.

Clausius began that search for understanding in 1862 by introducing the concept of disgregation, a concept that, he said, was based on an idea he had long held: that the force of heat for performing mechanical work (both internal and external together) was proportional to the absolute temperature. Clausius had never stated this idea explicitly before, although he had argued in 1853, by adopting an analogy between a reversible steam engine and a thermocouple, that the potential difference at a thermocouple junction should be proportional to the absolute temperature. In any event, he now wished to assert that the work which can be done by heat in any change of the arrangement of a body is proportional to the absolute temperature multiplied by a function of molecular arrangement, the disgregation Z. Given this assumption and his postulate that the heat in a body H was only a function of temperature, he was able (1) to prove his theorem of the equivalence of transformations and (2) to separate the equivalence function (entropy) into a temperature-dependent term and a configurational-dependent term,

$$dQ/T = dH/T + dZ$$
.

The mathematical expression itself was not new, Rankine having established an identical relation several years before. Clausius, however, gave a more concrete meaning to the terms involved by relating Z directly to the configuration of the particles. He seemed to be trying to handle entropy in the same way he had conceptualized the function U, breaking it into temperature-dependent and configurational-dependent terms. Some years were to pass, however, before he was able to derive an equation in pure mechanics that bore some correspondence to his idea.

His first venture led to the virial equation (1870). The derivation followed simply from a well-known equation of classical mechanics,

$$m/2(dx/dt)^2 = 1/2Xx + m/4 d^2(x^2)/dt^2$$
,

where the force X and the motions of particles are only in the x direction. Clausius eliminated the second term by taking the time average over an extended interval,

and observing that in the theory of heat, neither position nor velocity could ever increase indefinitely, so that the last term becomes negligible as the time interval approaches infinity. The virial for a large number of points in three-dimensional space became

an equation which since Van der Waals has become fundamental for deriving equations of state for real gases. Clausius, however, never extended his equation in any direction; to him the virial was but one possible expression of his idea that the force of heat—that is, the translational kinetic energy of the molecules—was proportional to the absolute temperature. He soon proach that provided a more promising mechanical analogue for disgregation. 15

Adopting a model in which moving mass points traverse certain periodic closed paths under internal and external forces defined by a function U (the potential energy function), Clausius analyzed the case in which an increment of kinetic energy is given to a particle and found that the variation in path would be governed by the relationship

in which  $\Delta$  represents the amount of variation in the quantities indicated, h is the average kinetic energy of the particle (absolute temperature), and i the period of its cyclical motion. Since the change in potential energy U traditionally represented work, the change in disgregation, by analogy, should be related to  $\Delta \log(hi^2)$ . If, Clausius suggested one further assumed that the particle moved with constant speed, then the variation in disgregation would be proportional to the variation in the logarithm of the path length, an intimation, therefore, of some correlation with molecular configuration. No sooner did Clausius present this successful interpretation of disgregation than a young Austrian physicist, <u>Ludwig Boltzmann</u>, disclosed that he had published essentially the same reduction of the second law in 1866.

Clausius, however, challenged Boltzmann's claim to priority, arguing that he had taken account of a complication which, he felt, Boltzmann had ignored: that the potential energy function U was itself subject to change during the variation, and that the variation of the potential energy function U could therefore be equated with the work done only if that additional factor were proved to be negligible. In traditional mechanics this problem did not arise because the external forces were always assumed to be constant and fixed in space. In the theory of heat, however, either pressure or volume is bound to vary and thus to change either the intensity or the location of the external forces. Clausius claimed that he had taken this complication into account but that Boltzmann had not.  $\frac{16}{2}$ 

Clausius now devoted several years to the elaboration of what he thought represented a new and unique contribution to theoretical mechanics, his idea of a variation in the force function itself. He ignored the new directions in Boltzmann's thought and, surprisingly, never once sought to find a mechanical explanation for the irreversible increase of entropy. In fact, in his final attempt, he even adopted a model in which he reduced the admittedly disordered collisions of molecules to a case of noncolliding mass points in ordered motion. Clausius made no further attempt to probe for a molecular interpretation of the second law, and his last significant contribution to the theory was a proposal for an amended version of Van der Waal's equation of state. His arguments, however, showed little relation to any molecular model; and his final equation represented the outcome of a rather methodical search for an improved empirical correlation of the data for carbon dioxide. 18

Clausius' major effort in mathematical physics after 1875 involved his quest for an adequate electrodynamic theory. He spelled out the fundamental tenets to his approach in 1875: (1)Weber's law was incorrect for the case where only one kind of electricity is assumed to move, since the equation entails that a current exert a force on a charge at rest; (2) a revision would be possible if one assumed that the electrodynamic action occurred via an intervening medium, for then electric particles that are not moving relative to each other (moving at equal velocities) could still exert forces on one another by virtue of their absolute motion in the medium; (3)forces should not be restricted to the line joining two charges. In 1876 Clausius simplified the equation he had previously proposed by subjecting it to the condition of the conservation of energy. In doing so, however, he ignored the possibility that energy changes might occur in the intervening medium.

His most elaborate treatment appeared in 1877,<sup>21</sup> and he there included Riemann's equation within the indictment he had earlier aimed at Weber's. Actually, Clausius framed an equation that showed marked similarities to Riemann's except that his noncentral forces were parallel and proportional to the absolute velocities and accelerations, rather than the relative values.<sup>22</sup> Clausius quite obviously had not tailored this theory to fit any explicit model for a single type of electricity in motion. In fact, he indicated in 1877 that his equation was not restricted to the case of a single mobile electricity but would be valid also for two electricities, whether equal or unequal in strength. His thought on electrodynamics was ruled by the earlier tradition plus two principles, the conservation of energy and simplicity, and simplicity played an important role. Thus, in his 1877 derivation, after obtaining a very general form for the equation by applying the conservation of energy as a condition, he introduced a simplifying constant and then set that constant equal to zero to obtain the desired form. He justified the choice by saying that the final equation was "in einfachster and daher wahrscheinlichster Form" ("in the simplest and therefore most probable form").

Not many scientists followed Clausius' lead, and a number of penetrating criticisms arose. One argument, ironically enough, posed the difficulty that Clausius' equation would also entail a force on a charge at rest on the earth, since the earth is moving in space. Clausius replied that the absolute velocity in his equation was relative to the surrounding medium and not to space, so that if the medium were to move with the earth, then the earth itself would be the referent for absolute motion and no such supposed force should occur. In one of those strange quirks of history, H. A. Lorentz, for whom the ether was absolutely at rest, adopted Clausius' electro-dynamic equation for deriving the force on an electron moving in that supposedly immovable ether. Perhaps Lorentz was aware that Emil Budde had answered the objection to Clausius' equation without supposing any

convection of the ether. Budde had argued that the movement of the earth in the ether would cause separations within the electricity and that those separations would cause electrostatic forces ones, thus eliminating the supposed force due to the motion of the earth. 25

Wiedemann brought Budde's argument to Clausius' attention in 1880, at the very time Clausius was penning his own reply. Clausius granted in a footnote that Budde's answer would suffice but nonetheless chose to offer his conjecture of ether convection. Clausius' ignoring of a valid quantitative answer in favor of his own speculative generality is significant, for we find a similiar indifference to ideas being expressed in thermodynamics. Clausius' great legacy to physics is entropy, and yet we find no indication of interest in Josiah Gibbs's work on <a href="https://chemical.equilibrium">chemical.equilibrium</a> or Boltzmann's views on thermodynamics and probability, both of which were utterly dependent on his idea. It is strange that he himself showed no inclination to seek a molecular understanding of irreversible entropy or to find further applications of the idea; it is stranger yet, and even tragic, that he expressed no concern for the work of his contemporaries who were accomplishing those very tasks.

## **NOTES**

- 1. "Ueber die bewegende Kraft der Warme and die Gesetze welche sich daraus für die Warmelehre selbst ableiten lassen," in Annalen der Physik, **79** (1850), 368–397, 500–524.
- 2. Ibid., 93 (1854), 481–506.
- 3. "Ueber verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Warmetheorie," *ibid*, **125** (1865), 353–400. Clausius chose the name "entropy" from the Greek word for transformation.
- 4.*Ibid*, p, 400.
- 5. "Rescension der Mayer'schen Schriften." in Literarisches Zentralblatt für Deutschland (Leipzig, 1868), pp. 832–834.
- 6. "On the Discovery of the True Form of Carnot's Function," in *Philosophical Magazine*, 11 (1856), 388–390.
- 7. "A Contribution to the History of the Mechanical Theory of Heat," ibid., **43** (1872), 106–115, See also the preface to the 2nd ed. of Tait's *Sketch of Thermodynamics* (1877) and the section entitled "Tendenz des Buches *Sketch of Thermodynamics* von Tait," in Clausius' *Die mechanische Wärmetheorie*, 2nd ed., II (Brunswick, 1879), 324–330.
- 8. Annalen der Physik, **100** (1857), 497–507.
- 9. "Ueber die mittlere Länge der Wege, welche bei der Molecularbewegung gasürmiger Körper von den einzelnen Moleculen zuruckgelegt werden," ibid., **105** (1858), 239–258.
- 10. "On the Dynamical Theory of Gases," **19** (1860), 434–436.
- 11. Maxwell-Tait correspondence, <u>Cambridge University</u> Library.
- 12. "Ueber die Wärmeleitung gasfürmiger Körper," in Annalen der Physik, 115 (1862), 1–56.
- 13. "Ueber die Anwendung des Satzes von der Aequivalenz der Verwandlungen auf die innere Arbeit," *ibid.*, **116** (1862), 73–112.
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The best original source for studying the development of Clausius' early ideas is the 1st edition of his *Die mechanische Warmetheorie*, 2 vols. (Brunswick, 1865–1867), a compilation of his original papers in thermodynamics, kinetic theory, and electricity, with additional dated comments. The Royal Society's *Catalogue of Scientific Papers* gives an exhaustive listing of his published papers and cites numerous obituaries, I, 945–947; VII, 400–401; IX, 533–534; and XIV, 259–260. Poggendorff also lists his major papers and books, I, cols. 454–455; III, 281–282; and IV, 258.

There is no biography of Clausius other than the short sketch in *Allgemeine deutsche Biographie*, LV, 720–729, but a recent article by Grete Ronge, "Die Zuricher Jahre des Physikers Rudolf Clausius" in *Gesnerus*, **12** (1955), 73–108, includes some new information about his personal life. J. W. Gibbs's evaluation of Clausius' scientific work shows particular excellence-"Rudolf Julius Emmanuel Clausius," in *Proceedings of the American Academy of Arts and Sciences*, n. s. **16** (1889) 458–465-and Francois Folie's comments on Clausius and his family" R. Clausius. Sa vie, ses travaux et leur portee metaphysique," in *Revue des questions scientifigues*, **27** (1890), 419–487-are of great value, since we know so little about him apart from his scientific writings.

There is no extensive secondary literature on Clausius himself, but helpful treatments of his ideas appear in most general histories of physics and especially in those on the kinetic theory and thermodynamics. Ferdinand Rosenberger devoted considerable space to Clausius in his *Die Geschichte der Physik*, vol. III (Brunswick, 1890), and Charles Brunold reviewed Clausius' concept of entropy in his L' entropie (Paris, 1930), pp. 58–105. G. H. Bryan offered a very positive appraisal of Clausius' contribution to mechanical interpretations of the second law of thermodynamics in his article, "Researches Relating to the Connection of the Second Law with Dynamical Principles," in Report of the *British Association for the Advancement of Science* [Cardiff, 1891] (London, 1892).

More recently, Stephen Brush has evaluated Clausius' work in the kinetic theory of gases in two articles: "The Development of the Kinetic Theory of Gases. III. Clausius," in *Annals of Science*, **14** (1958), 185–196; and "Foundations of Statistical Mechanics, 1845–1915," in *Archive for History of Exact Sciences*, **4** (1967). 145–183. Martin J. Klein has given a perceptive and sensitive appraisal of Gibbs's views on Clausius in "Gibbs on Clausius," in *Historical Studies in the Physical Sciences*, **1** (1969), 127–149. For my views on Rankine and Clausius, see "Atomism and Thermodynamics," in *Isis*, **58** (1967), 293–303; and, for a further discussion on Boltzmann and Clausius, "Probability and Thermodynamics," *ibid***60** (1969), 318–330, In my forthcoming article, "Entropy and Dissipation," due to appear in *Historical Studies in the Physical Sciences*, **2**, **1** discuss at length the relations between Clausius and the Bristish thermodynamic tradition of Thomson, Maxwell, and Tait.

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